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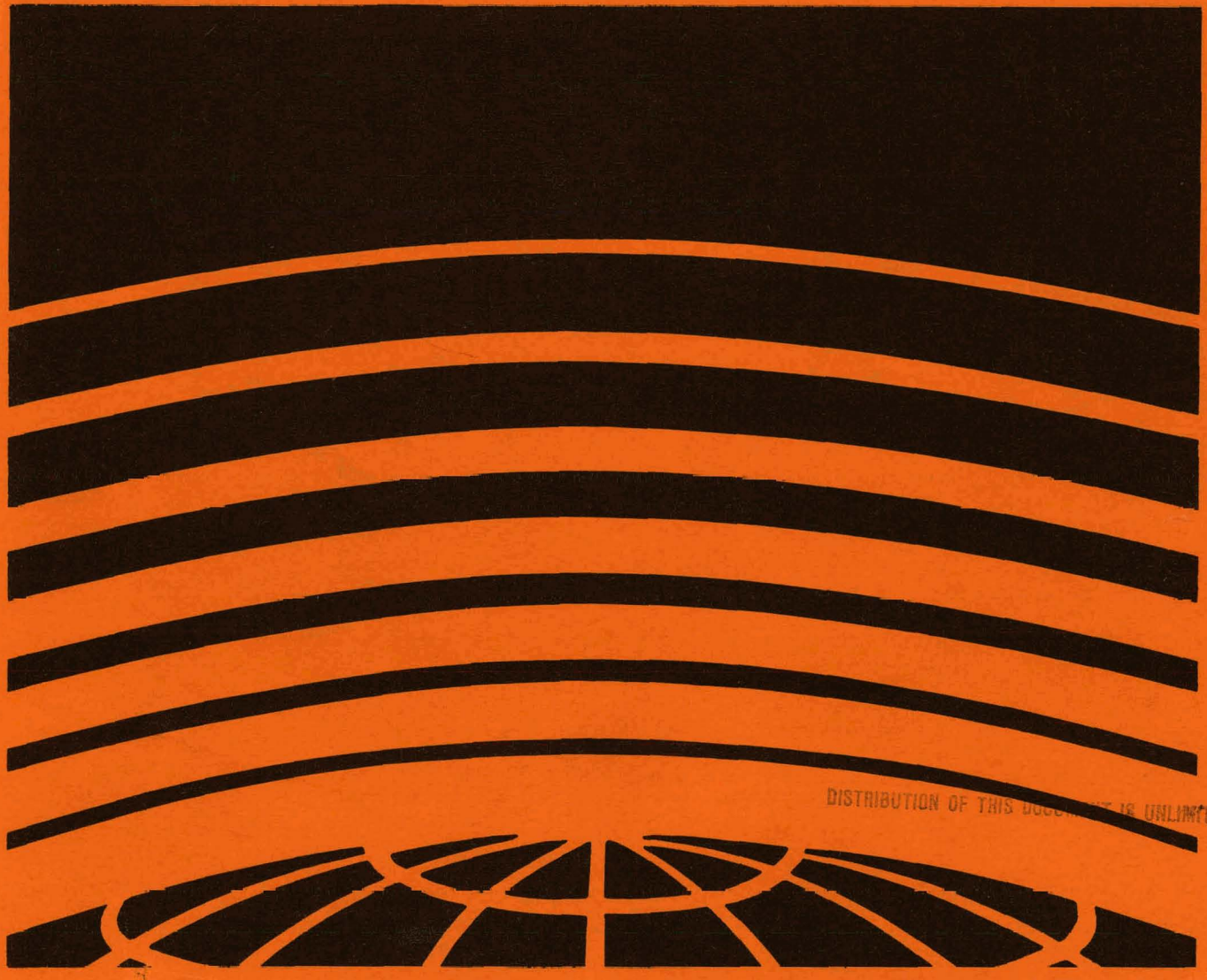
June 1980

Second U. S. Department of Energy Environmental Control Symposium

Reston, Virginia, March 17-19, 1980

PROCEEDINGS

Volume 1 of 2. Fossil Energy



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Proceedings of the Second U. S. Department of Energy Environmental Control Symposium

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FOREWORD

These proceedings document the presentations given at the Second Environmental Control Symposium sponsored by the Department of Energy (DOE). Although the symposium was organized under the auspices of the Environmental Control Technology Division, Assistant Secretary for Environment, Symposium presentations highlighted environmental control activities which span the entire Department of Energy.

The plenary topic, "How the National Energy Plan and Environmental Goals Drive DOE Environmental Control Activities," reflects the Department of Energy's goal and commitment to the support and development of energy systems that are environmentally acceptable. This commitment is, in part, shown by the extensive support of environmental control activities within the total DOE program: about $421 million in FY1979*, with a similar amount expected for FY1980.

The objectives of the Environmental Control Symposium were: (a) to emphasize that, concurrently with development of energy technologies, DOE is deeply concerned with corollary measures required to mitigate potential impacts on the environment from existing and new energy systems; and (b) to provide a forum for dissemination of information and achievements of DOE activities in environmental control. For this reason, the Symposium presentations focused on DOE-supported activities related to research, development, and demonstration of processes, procedures, and strategies to eliminate or reduce undesirable environmental impacts of energy technologies. Rather than simply identifying potential problem areas, the presentations were intended to emphasize results of ongoing efforts. Symposium topics included discussions of (a) simple "add-on" control methods for application to conventional and possibly emerging power systems; (b) in-process modifications to energy production techniques to control environmental impacts; (c) alternative energy systems; (d) environmental control aspects of energy transmission, transportation, and storage; and (e) alternative energy and environmental control strategies.

Owing to the varied topics covered in the Symposium and the total length of the papers presented, these proceedings have been arranged into two volumes, whose contents correspond to selected areas of interest. The arrangement is as follows:

Volume 1 - Fossil Energy

Session 2 -- Conventional Coal Utilization. I. -- Coal Preparation
Session 3 -- Oil Shale
Session 5 -- Conventional Coal Utilization. II. -- Combustion
Session 8 -- Advanced Coal Utilization (FBC/MHD, OCGT, Fuel Cells)
Session 11 -- Coal Conversion. I -- Gasification
Session 13 -- Fossil Resource Extraction
Session 15 -- Coal Conversion. II -- Liquids

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* *Environmental Control Technology Activities of the Department of Energy in FY1979*, U.S. Department of Energy, Assistant Secretary for Environment, Division of Environmental Control Technology (In press)

Volume 2 -- Nuclear Energy, Conservation, and Solar Energy

Session 1 -- Environmental Control Aspects of Nuclear Energy Use and Development
Session 4 -- Nuclear Waste Management.I
Session 6 -- Renewable Energy Sources.I
Session 7 -- Nuclear Waste Management.II
Session 9 -- Renewable Energy Sources. II
Session 10 -- Materials Transportation and Control
Session 12 -- Transportation and Building Conservation (Fuel Economy, Gasohol, Building Standards, Industry)
Session 14 -- Geothermal Storage and Power Transmission Systems

The Department of Energy believes that this Symposium and subsequent symposia being planned provide forums for enhanced exchange of information between the Department and the public on the Department's progress toward the goal of ensuring that the Nation's energy demands can be met in an environmentally acceptable manner.

PLENARY SESSION

How the National Energy Plan and Environmental Goals Drive DOE Environmental Control Activities.

Chairperson and Keynote Speaker:	Ruth Clusen, Assistant Secretary for Environment, U.S. Department of Energy.
Plenary Speakers:	Emelia L. Govan, Special Assistant to the Assistant Secretary for Fossil Energy, U.S. Department of Energy.
	Dr. Steven A. Reznek, Deputy Assistant Administrator for Environmental Engineering and Technology, U.S. Environmental Protection Agency.
	John W. Crawford, Jr., Deputy Assistant Secretary for Nuclear Energy, U.S. Department of Energy.
	Thomas Stelson, Assistant Secretary for Conservation and Solar Energy, U.S. Department of Energy.

CHAIRMEN AND CO-CHAIRMEN OF TECHNICAL SESSIONS

Session No.	Chairman	Co-Chairman
	Fossil Energy	
2	A. Dietz	Charles Grua
3	A. Hartstein	R. Franklin
5	M. Shapiro	M. Gottlieb
8	S. Freedman	F. Witmer
11	L. Miller	H. Jones
13	A. Sikri	J. Pell
15	J. Batchelor	M. Singer
	Nuclear Energy	
1	G. Sherwood	J. Maher
4	W. Mott	J. Counts
7	G. Oertel	C. Heath
	Conservation and Solar Energy	
6	R. Loose	R. Blaunstein
9	G.D. Allessio	R. Loose
10	J. Cece	J. Sisler
12	D. Maxfield	D. Walter
14	D. Moses	R. Loose

KEYNOTE ADDRESS

Ruth Clusen
Assistant Secretary for Environment
U.S. Department of Energy

I am very much please and honored as to be appearing before you today at this Second Department of Energy Environmental Control Symposium. I believe the very fact that you and I find ourselves at a second symposium on this subject tells us two things: First, our presence here means that we continue to face an energy crisis--our nation's energy problems are not yet solved, nor have they gone away by themselves. Second, our ongoing concern for environmental-control technologies shows that we remain committed to a policy of safeguarding our people's health and the world we live in from harm while developing our energy resources. The energy crisis is real, and so is our determination to resolve that crisis without sacrificing the environment. It is not just energy we are seeking; we must have energy we can live with.

Events on the international scene this past year--particularly, I think, events in the Middle East--have underscored the dangers of relying on other countries to supply our energy needs. In his State of the Union address, the President affirmed our determination to make ourselves self-sufficient in energy production, independent of the shifts, the caprices, and the sudden collapses of foreign suppliers.

We cannot permit our environmental goals to hamper needlessly our efforts to meet the energy needs of the United States and to achieve a genuine energy independence. Neither, however, do we dare--operating out of a crisis mentality--abandon those goals and despoil the nation's resources for ourselves and our descendants. An ancient leader, quoted by Tacitus, made this charge of the great civilization of his day: "Where they make a desert, they call it peace." It is our goal that future generations will not be able to say of us that we made the Earth a wasteland and called it prosperity.

The United States government faces the task of ensuring an adequate and reliable energy supply as required for the good of the country and for its security. In this task, as I am sure you all know, the Department of Energy is responsible for research, development, and demonstration in the realm of existing and emerging energy technologies. Those of us in DOE recognize that we also bear the responsibility for striking a balance between the development of technologies and the meeting of environmental requirements essential to the protection and enhancement of the nation's health, safety, and general welfare.

One measure of the Department's concern for environmental protection is the amount we spend on that effort. DOE funds allocated to environmental-control activities increased, in fiscal 1979, by almost one hundred million dollars over the previous year's funding level for these activities, to a total exceeding four hundred million dollars. Fossil-fuel and nuclear energy technologies accounted for about 90% of that total.

Fossil fuels are a vitally important energy source. Here in the United States we have enormous reserves of coal and oil shale--enough, if we were indifferent to the environmental degradation that would surely result, to meet our energy needs for centuries without the development of any new technologies. But we are not indifferent to the destruction of the environment, and we will not adopt any such bankrupt policy for the utilization of our fossil-fuel reserves.

In our efforts to develop these abundant natural resources, we are facing two major difficulties. The first one is an economic problem, and the second is tied to the need to safeguard the environment.

Let us consider the economic problem in connection with oil shale. One of the major reasons that we do not have a massive oil-shale industry in this country is that it has not become economically attractive, despite past predictions that it would do so. We have what you might call a receding break-even point, where by "break-even point" I mean that point in the effort at which your costs equal your expected gains. Here at DOE we have found that this break-even point behaves much like the proverbial desert mirage--we keep reaching the place where we last saw it, only to find that it has gone glimmering off to the horizon again. Several years ago, we had an analysis of the oil-shale market performed that showed it would be economical to build shale-oil production plants when the price of imported oil reached $20.00 per barrel. More recently, a similar analysis indicated that the price of imported oil must hit $40.00 per barrel before we can afford to build those plants. In other areas, too, as we approach the points where studies have shown that the development of new energy technologies would be economically attractive, we find that these points have slipped ahead of us and that we must wait for energy prices to spiral even higher.

Under Secretary Deutch has developed a formalized procedure that should help eliminate some of this running to stay in place. A small group in the comptroller's office will have the responsibility for providing the Department with much better economic forecasts than has been the case in the past. The accurate prediction of what will or will not be feasible economically has become essential, because in the near future we must proceed with the construction of the major oil-shale, coal-liquefaction, and coal-gasification plants that the United States desperately needs. This task has been mandated to DOE by the President and the Congress, and we will do everything in our power to carry out that mandate.

I said earlier that we face a twofold problem in putting our fossil-fuel reserves to the best use. While it is not DOE's intent to spend the taxpayers' money on technologies that are economically unsound, neither do we propose to spend time and money on developing an energy technology only to find that we have, in terms of the environment, created a bigger problem than the one we solved. We need to learn a great deal more than we know now about the environmental impacts associated with the major construction projects I have mentioned. For example, we find that the possibility of carcinogens being produced in processes for the generation of synthetic fuels is very real and, indeed, highly probable. We are evaluating the byproducts of processes now under development, and we are working on the control technologies

necessary for dealing with such byproducts as may prove hazardous.

Nuclear energy is another important energy resource. But the successful development of nuclear power poses some very challenging problems, and at this time its future as an energy option is uncertain. What is certain is that the solutions to these problems are not likely to come to us from a handful of experts meeting behind closed doors. Neither shall we find the answers we need by forming into hostile camps of "pro-nuclear" and "anti-nuclear" believers and waving our placards at each other in the streets.

In the main, both the proponents and the critics of nuclear power agree that this technology faces three major difficulties: (1) the problem of ensuring reactor safety, (2) the need for safe disposal of radioactive wastes, and (3) the successful prevention of proliferation of radioactive materials. Our government has been concerned about nuclear-plant reliability and safety since the early days of the Atomic Energy Commission; the Nuclear Regulatory Commission now bears primary responsibility in this area, but some of us here in DOE have also had a hand in reactor-safety efforts. As for the radioactive-waste problem, DOE is committed to the development of safe, long-term methods for the storage of nuclear waste materials. The question of waste disposal, as you know, is intimately connected with the debate over reprocessing of nuclear fuel and the nonproliferation of nuclear materials. Much time and effort are going to be required to adequately resolve these tangled problems, and the public must take part in making the decisions. Those of us in government and in the energy industry share a responsibility to interact closely with the American people to help them decide wisely how we can best take advantage of the nuclear-energy option.

As you know, DOE's environmental-control activities include many more approaches than just the fossil-fuel and nuclear energy technologies. For the near term, conservation is probably the most important of these other energy efforts. The potential gains in usable energy achievable in the United States through conservation alone are equal to the energy we get from all of our imported oil.

At first glance, it may not be obvious that any technologies--especially environmental-control technologies--are of importance in conservation efforts. That is because, for many of us, "conservation" means something negative--not using what you have used in the past. But there is a positive side to conservation, and that is the using of what you never have used before. For example, the typical American citizen generates approximately four pounds of urban, or municipal, waste each day. On the one hand, this waste is an environmental contaminant to be disposed of. But it is also, on the other hand, a potential source of energy. The technology for converting municipal waste, as well as sewage sludge, to usable energy has long been practiced in Europe. Both technological and institutional barriers have stood in the way of our implementing this technology in the United States, but DOE is making every effort to develop this potential energy source. Using the garbage we produce every day for fuel would not only furnish needed energy--it would also get rid of the garbage.

Energy conservation is advantageous in helping us to maintain a clean and healthy environment as well as in lessening our country's dependence upon foreign oil. Clearly, if we can use energy in our homes and in factories more efficiently, then less energy consumption--say, in the form of combustion of fossil fuels--is required, and over-all reductions in pollutant levels will result. The Department is promoting conservation and the technologies associated with it, not only through research and development efforts, but also through positive regulatory actions that will make implementation more attractive. A prime example of this regulatory encouragement is the availability of energy credits, in the form of income-tax deductions, to encourage the American public to conserve energy in their homes, an area in which immediate and noticeable gains are possible.

Another technology that is significant for the near term is solar-energy utilization. In many parts of the country, solar hot-water and passive-energy systems are economically competitive, on a life-cycle basis, with conventional energy systems right now. The main problem the Department faces in connection with these technologies, which are under DOE environmental review, is to encourage their rapid, widespread use in today's society. Much of the DOE Conservation and Solar Applications program is focused upon the timely commercialization of these technologies and applications, so that we can substitute renewable resources for fossil fuels where this is economically feasible.

Farther down the line are such promising technologies as nuclear fusion. We have reason to believe that our investment in fusion power will pay large dividends in the future. The reaping of those dividends is confidently expected, but it is not imminent. With this technology, as with many of the other alternative energy sources, we may find ourselves in the 21st century before its benefits are fully realized.

If we are to ensure that the energy systems we deploy in the United States will give us energy we can live with, we must make sure that environmental soundness is built into every technology we develop right from the start. Our Office of the Environment in the Department of Energy is an integral part of DOE's energy-technology development processes. This office will be brought into every energy research, development, and demonstration project as active partners from the beginning. We will provide environmental expertise, identify potential environmental problems in new energy-technology efforts, and serve as an internal environmental guardian. In this way, we can ensure that environmental-control considerations will be taken into account from the very first day and will be inherent parts of the processes we develop.

Finally, I would like to say that the energy problems we face and the tasks that we share are important ones. The problems must be solved, the work must be done. The energy needs of the nation will drive our research and development efforts, and we will produce efficient, affordable, and environmentally acceptable energy technologies. The Department of Energy

is actively engaged in the development of those technologies, and we are alert to their environmental impacts. I believe you will find that this conference confirms the Department's dedication to the principle that any energy technologies we develop must be environmentally safe.

Thank you. I hope you will all find your participation in this conference both pleasant and profitable.

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SESSION 2
CONVENTIONAL COAL UTILIZATION
I – COAL PREPARATION

Chairman: A. Dietz
Co-Chairman: Charles Grua

EFFECT OF COAL CLEANING ON FUGITIVE ELEMENTS: SECOND PROGRESS REPORT

Charles T. Ford
Bituminous Coal Research, Inc.

INTRODUCTION

Within the past few years, several trace elements--specifically arsenic, cadmium, lead, mercury, and selenium--have been pointed to with increasing frequency as potential environmental problems. The coal industry has been indicated as a major contributor to the levels found in the environment, and responded by establishing in 1971 a research program at Bituminous Coal Research, Inc., for obtaining valid information concerning potential trace element problems as they relate to coal. This program is designed to define the nature of the trace element problem as it relates to coal mining, preparation, and utilization.

One means of controlling trace element emissions is to remove these trace constituents prior to combustion. It was suggested that those trace elements associated with the ash could be removed during the coal preparation process.

In a previous limited study (Ford, Care, and Bosshart, 1976), BCR demonstrated coal cleaning to be a possible technology for controlling many of the potentially harmful constituents of coal. Based on those promising results, a more extensive coal cleaning scheme was designed specifically to evaluate the effect of such cleaning on trace or fugitive elements, those constituents of coal which have the potential to be released and cause environmental problems. This paper describes progress in cleaning, analyzing the samples resulting from the cleaning, and evaluating the data from 20 coals studied during the project. A preliminary progress report on this project was presented at the last DOE Environmental Control Symposium. (Ford, Boyer, 1978)

The work was originally funded jointly by the U.S. Bureau of Mines, the U.S. Energy Research and Development Administration (ERDA), and BCR. The project is currently funded by the U.S. Department of Energy (DOE) and BCR.

The overall objectives of the project are: (a) to prepare a comprehensive state-of-the-art report on the effect of coal mining, preparation, transportation, and utilization on the trace elements found in coal; (b) to determine the effect of coal cleaning on fugitive elements; and (c) to provide a description of accurate analytical methods that can be used by coal industry and commercial laboratories for determining the concentration of selected trace elements in a variety of coals. The portion of the study described here involves only the effect of coal cleaning on fugitive elements.

The objectives of this portion of the study were approached as follows:

The effect of coal cleaning on fugitive elements was evaluated by exhaustively studying samples of run-of-mine (ROM) coal obtained from various geographical locations throughout the United States. All ROM samples were subjected to controlled coal cleaning at the BCR laboratories. Each coal was crushed; the coarser fractions were subjected to heavy media separations, and the fine fraction was hydraulically classified. This cleaning is representative of that which presently exists in the industry.

Some of the coals were subjected to additional, more extensive, processing and evaluation. Representative samples of these were crushed, screened, and the resulting narrow particle size fractions were hydraulically classified.

Each sample produced by the coal-cleaning task was characterized by general chemical and trace and major element analysis, as well as petrographic analysis where appropriate. Those elements chosen for study include the trace elements antimony, arsenic, beryllium, cadmium, chromium, cobalt, copper, fluorine, lead, manganese, mercury, nickel, selenium, vanadium, and zinc, the major elements in coal ash including silicon, aluminum, iron, calcium, magnesium, titanium, sodium, potassium, and phosphorus, and the more prevalent constituents such as sulfur.

EXPERIMENTAL PROCEDURE

Approximately 450 kg (1,000 lb) of run-of-mine (ROM) coal was collected at each of 20 mine sites. The coals were representative of the seam or seams being mined at that site and were selected on the basis of present and near-future utilization. They were numbered 1R through 20R (R for run-of-mine) and are listed by seam in Table 1. Figure 1 is a map showing the locations of the 20 mines sampled during this project. From Table 2, showing the geologic age relationships of the coals, it can be seen that the 20 coals represent very young (Paleocene) to very old (lower Pottsville) coals.

Two basic controlled cleaning procedures were utilized at BCR for the 20 coals. One of these, designated Procedure A and diagrammed in Figure 2, simulates coal cleaning techniques currently being utilized by the coal industry. This procedure involves basic crushing and screening to reduce the coal to three fractions: (a) 31.8 x 6.35 mm (1-1/4 x 1/4 inch), (b) 6.35 mm (1/4 inch) x 30 mesh, and (c) 30 mesh x 0. The 31.8 x 6.35-mm (1-1/4 x 1/4-inch) fractions and the 6.35-mm (1/4-inch) x 30-mesh fractions were then cleaned by heavy media gravity separations utilizing magnetite and the BCR double-cone heavy-media device. Three separating gravities (usually 1.35, 1.55, and 1.80) were used, producing four gravity fractions for each of the coarse-size fractions.

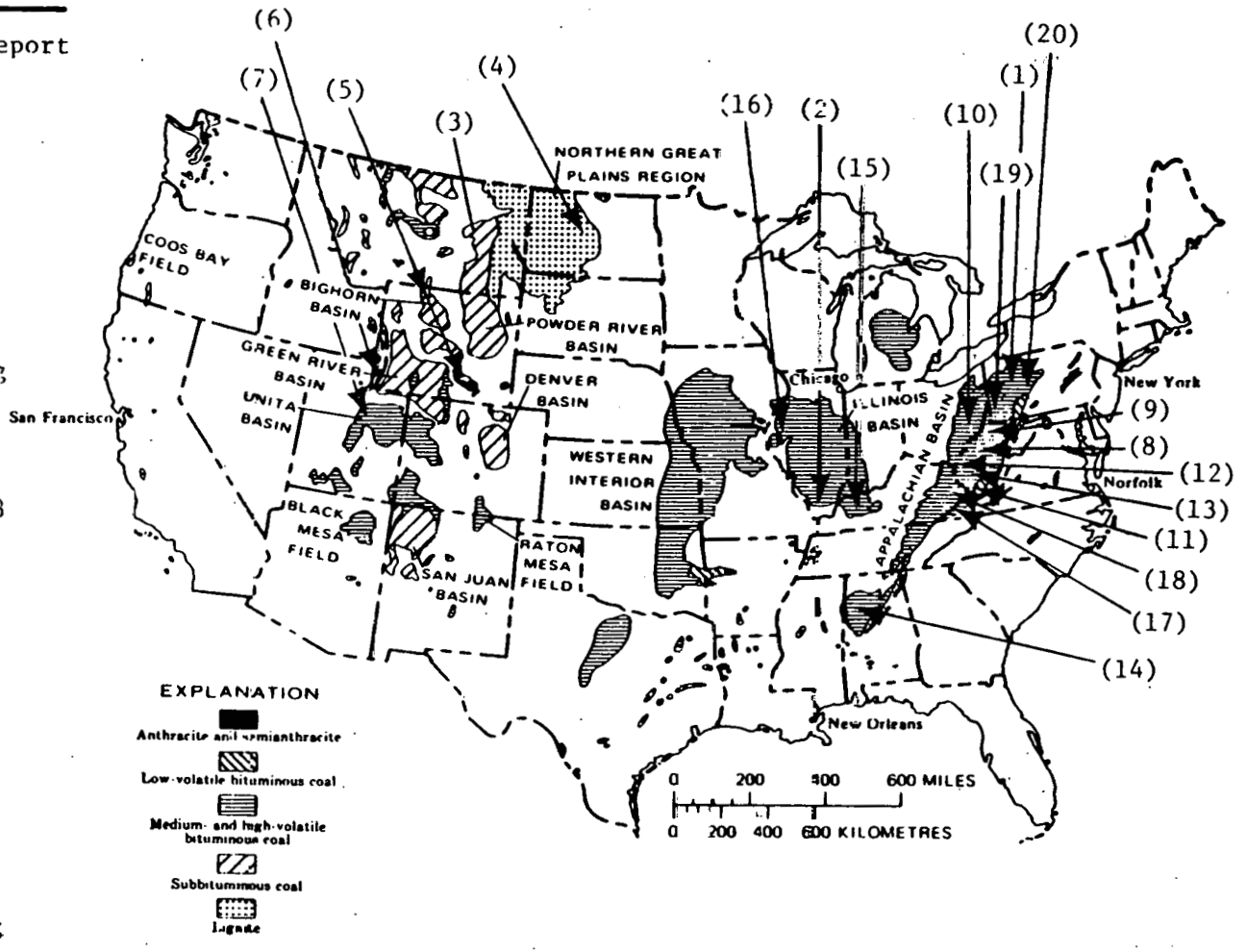
The minus 30-mesh fraction was cleaned by utilizing a hydraulic classifier after removal of the minus 270-mesh fines. Four fractions were produced from this cleaning: a low-velocity overflow, a medium-velocity overflow, a high-velocity overflow, and a sink fraction. As with the heavy media separations, efforts were made to maintain consistent flows for each

TABLE 1. COALS USED IN BCR FUGITIVE ELEMENT STUDY

Sample Number	Location County, State	Seam
1R	Indiana, PA	Upper/Lower Freeport
2R	Franklin, IL	Illinois No. 6
3R	Rosebud, MT	Rosebud
4R	Mercer, ND	Beulah-Zap
5R	Carbon, WY	Hannah No. 60
6R	Lincoln, WY	Adaville No. 1
7R	Carbon, UT	Castle Gate D
8R	Nicholas, WV	Lower Kittaning
9R	Harrison, WV	Pittsburgh
10R	Noble, OH	Meigs Creek
11R	McDowell, WV	Pocahontas No. 3
12R	Logan, WV	Stockton
13R	Raleigh, WV	Sewell
14R	Walker, AL	Mary Lee
15R	Muhlenburg, KY	Kentucky No. 9
16R	Fulton, IL	Illinois No. 5
17R	Wise, VA	Imboden
18R	Knott, KY	Upper Elkhorn No. 3
19R	Washington, PA	Pittsburgh
20R	Cambria, PA	Lower Kittaning

Coal Seams

1. Upper/Lower Freeport
2. Illinois No. 6
3. Rosebud
4. Beulah-Zap
5. Hannah no. 60
6. Adaville No. 1
7. Castle Gate D
8. Lower Kittanning
9. Pittsburgh
10. Meigs Creek
11. Pocahontas No. 3
12. Stockton
13. Sewell
14. Mary Lee
15. Kentucky No. 9
16. Illinois No. 5
17. Imboden
18. Elkhorn No. 3
19. Pittsburgh
20. Lower Kittanning



BCR 6082G50

Figure 1. Coal Fields of the Conterminous United States Showing Coal Sample Locations

TABLE 2. STRATIGRAPHIC OCCURRENCE OF COALS

		Rocky Mountain	Northern Great Plains	Illinois Basin	Appalachian Basin
PALEOCENE		(5R) Hannah #60 Series	(4R) Beulah-Zap (3R) Rosebud		
CRETACEOUS		(6R) Adaville #1 (7R) Castle Gate D			
PENNSYLVANIAN	MONONGAHELA				(10R) Meigs Creek (9R)&(19R) Pittsburgh
	ALLEGHENY			(2R) Illinois #5 (16R) (15R) Illinois #5/Kentucky #9	(1R) L. Freeport (8R)&(20R) L. Kittanning
	POTTSVILLE				(12R) Stockton (18R) Up. Elkhorn #3 (17R) Imboden (13R) (14R) Sewell/ Mary Lee (11R) Pocahontas #3

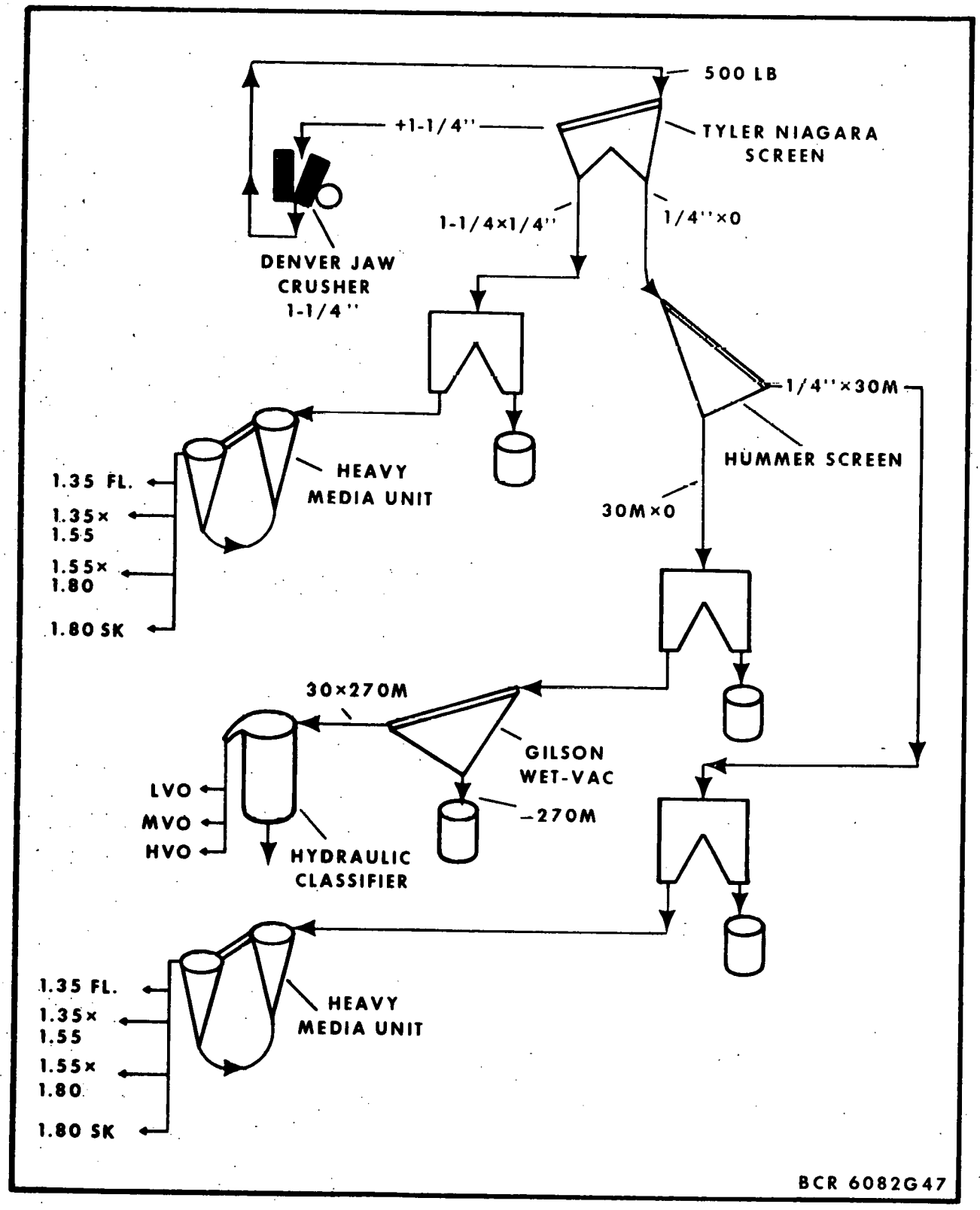


Figure 2. Preparation Flow Schematic, Procedure A.

of the fractions, but these flows sometimes had to be altered to obtain sufficient amounts in each fraction for analysis and evaluation.

The second basic procedure, designated Procedure B and diagrammed in Figure 3, was utilized to simulate an "optimum" coal cleaning process. This procedure was designed to yield relatively pure fractions of each type of material--coal, shale, and pyrite--in order to make better judgments on trace-element associations than could be made with Procedure A. Basically, the 31.8-mm (1-1/4-inch) x 0 ROM coal was reduced by screening to a series of nine fine coal fractions sized from 30 mesh to minus 270 mesh. All but the minus 270-mesh fractions were subjected to hydraulic classification to produce an ultra-clean coal fraction, a clean coal fraction, a shale fraction, and a pyrite fraction for each of the size fractions.

The effect of cleaning on each of the coals was determined by analyzing the coals and evaluating the results. General chemical determinations were made as well as petrographic and trace determinations. The techniques and apparatus for the analyses are described in a separate final report for this project.

Material balances were calculated for each of the individual cleaning operations and the percent of each constituent removed was summarized by group and by constituent. The material balances also included a differential value between composite and feed by which judgments could be made on the cleaning and analyses. Linear correlation coefficients and F-test ratios were also calculated to demonstrate the relationships between each constituent and every other constituent.

RESULTS AND DISCUSSION

Twenty coals were cleaned by cleaning Procedure A to evaluate the effect of the cleaning on both the major and trace constituents of coal. Eight of the 20 coals were subjected to additional cleaning using cleaning Procedure B. The objective was to obtain relatively pure fractions of coal, shale, and pyrite with which to evaluate the elemental associations. Generally, the results of the analyses and the agreement obtained in the great majority of material balances indicated that the cleaning strategies employed were particularly effective and the separations needed to attain the objectives of the project were achieved. In about 95 percent of the more than 5,000 individual material balances for this study, the calculated difference between composite and feed values was less than 25 percent. This figure was quite satisfactory, particularly for trace element analysis.

The concentrations of each constituent were calculated in the cleaned coal obtained by each of the individual cleaning operations. For Procedure A, this involved heavy media cleaning of the coarser fractions and hydraulic classification of the fines. The cleaning level selected for all of the evaluations reported assumed the first two fractions--the lighter gravity

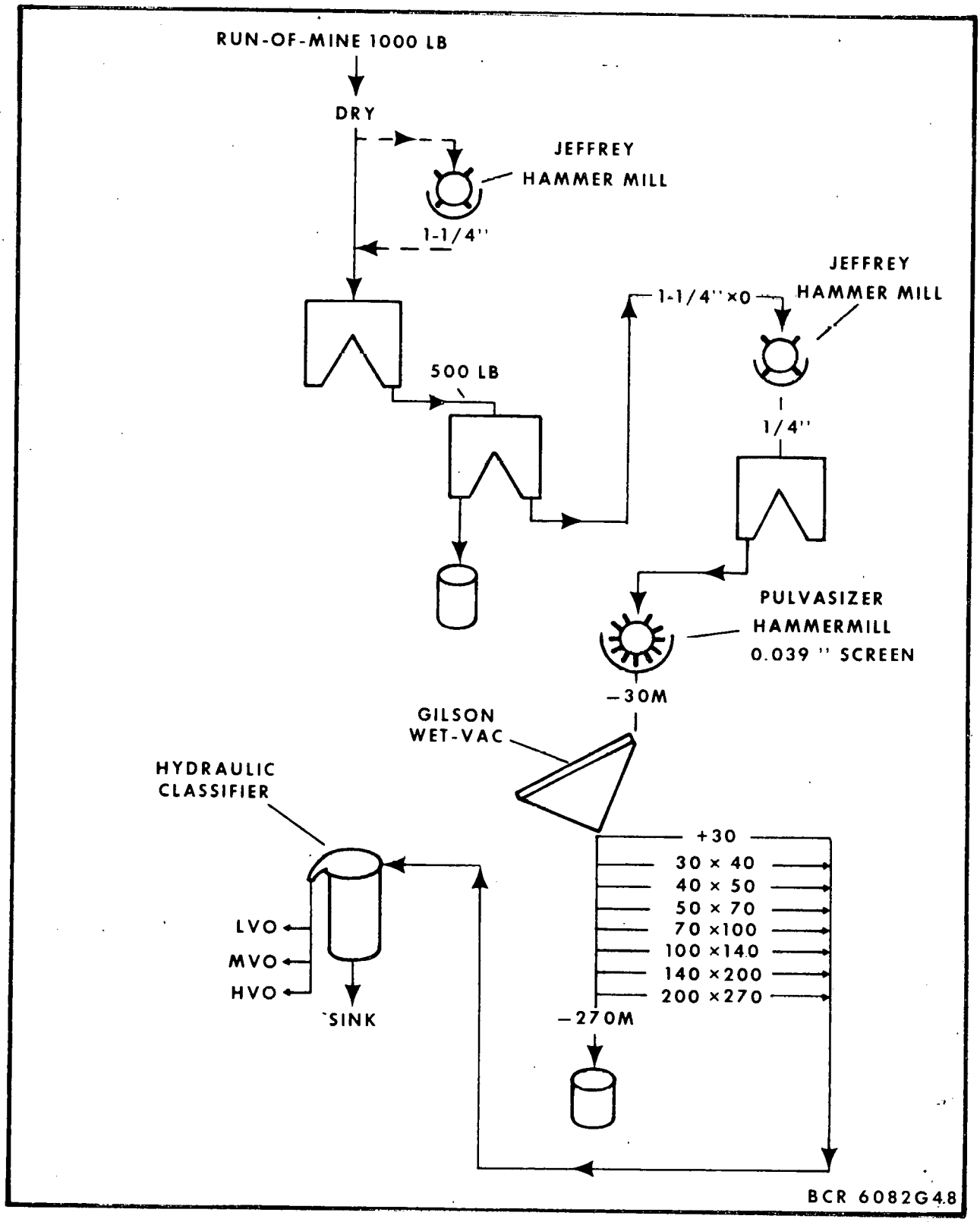


Figure 3. Preparation Flow Schematic, Procedure B.

materials from the heavy media separations and the two lower velocity materials from the hydraulic classifier--as the cleaned coal. Other levels of cleaning could have been evaluated, but this was not done for this presentation.

In addition, concentrations were calculated in the combined clean coal fractions obtained from Procedure A. From these, the corresponding percent removed of each constituent was also obtained and presented in Table 3 for each of the 20 coals. The petrographic constituents are not included since their removal was obviously not the objective of this study.

The negative percentages in this table indicate an increase in the level of that particular constituent, as was anticipated, for example, for organic sulfur. The actual product yield and Btu recoveries for these 20 coals are presented in Table 4.

From the data in Tables 3 and 4, an evaluation can be made of the effectiveness of cleaning these coals and the differences by coal and by constituent. From a conventional coal cleaning viewpoint, the Btu recovery was quite good for most of the coals with an average recovery of 94 percent. The lowest recovery, 82 percent, was experienced with coal 13R which had the highest ash content (50.6 percent) of all of the 20 run-of-mine coals.

The product yield was also quite good for the majority of the coals. The exceptions were coals 8R, 12R, 13R, 19R, and 20R, which also had the highest ash contents of the 20 run-of-mine coals.

The averages of the percent removed of all of the constituents listed in Table 3 are displayed in Table 5. Additionally, the averages of twelve coals--1R, 8R, 9R, 10R, 11R, 12R, 13R, 14R, 17R, 18R, 19R, and 20R--from the Eastern United States, the averages of three coals--2R, 15R, and 16R--from the Midwestern United States, and the averages of five coals--3R, 4R, 5R, 6R and 7R--from the Western United States are also displayed in this table. The same data are presented in a different manner in Table 6. The constituents are grouped by the level of each removed for all 20 coals and for each region.

Some trends are evident by the groupings in Table 6. Ash, arsenic, cadmium, chromium, fluorine, lead, manganese, zinc, silicon, aluminum, iron, calcium, magnesium, titanium, sodium, potassium, and phosphorus were removed effectively; pyritic sulfur, cobalt, copper, mercury, and selenium were removed less effectively. The more effective cleaning of the Eastern and Midwestern coals can be seen as well as the different responses to cleaning of the coals from these two regions. The differences are subtle except for cobalt and vanadium. Cobalt removal was very effective with the Midwestern coals, even though the levels were relatively low compared to the Eastern coals.

Perhaps more surprising was the effective removal of vanadium from the Eastern coals in view of the reported association of vanadium with the organic portion of the coal. This organic association could still be

TABLE 3. COMPARISON OF EFFECT OF CLEANING BY PROCEDURE A
(Percent Removed)

	Coal Number																			
	1R	2R	3R	4R	5R	6R	7R	8R	9R	10R	11R	12R	13R	14R	15R	16R	17R	18R	19R	20R
Ash	64	48	38	30	12	7	46	75	58	26	77	74	83	57	61	57	73	84	76	78
Total Sulfur	47	39	48	40	8	6	-1	-22	32	8	-21	-33	14	-13	21	21	-6	0	-9	55
Chlorine	-38*	-5	0	86	-29	71	-10	-13	-13	-20	-	-	-70	-	-6	-	-	49	-	-
Pyritic Sulfur	62	45	54	42	-18	15	15	1	45	14	28	-5	47	4	35	27	17	11	4	69
Organic Sulfur	-18	-7	3	6	24	-24	-16	-42	-13	-11	-32	-57	-101	-37	-34	-18	-15	-22	-40	-25
Antimony	17	-33	52	23	32	20	48	-10	64	20	-3	-9	-	-	-	-	-	-	-	-
Arsenic	76	44	73	57	23	40	44	40	63	42	45	71	57	65	45	65	63	49	60	84
Beryllium	25	17	4	0	13	-37	14	23	36	11	27	17	39	26	27	5	29	-2	37	25
Cadmium	23	61	30	20	-32	50	57	25	27	14	44	50	68	36	62	84	19	37	42	44
Chromium	44	27	35	19	-38	33	37	55	47	15	69	62	82	40	55	45	59	76	58	62
Cobalt	-	-	-	-	-	-	-	-	-	-	13	-17	68	15	60	59	28	34	58	67
Copper	47	35	19	20	-2	7	14	25	47	11	35	32	44	36	59	41	42	23	67	77
Fluorine	44	51	25	13	1	-1	27	74	59	28	82	68	80	38	59	53	70	73	64	69
Lead	71	53	35	33	14	48	37	43	66	19	57	54	78	45	60	62	54	62	66	85
Manganese	80	62	8	37	17	-1	59	79	53	34	78	88	93	51	81	64	89	76	80	79
Mercury	61	1	43	14	20	2	34	29	32	27	24	33	47	40	26	-1	15	39	13	41
Nickel	37	18	-8	-4	-14	29	27	33	53	17	28	23	70	23	65	48	35	28	38	24
Selenium	55	16	48	32	13	30	0	17	37	28	13	4	32	34	20	29	24	17	43	67
Vanadium	42	10	14	-1	-8	-11	24	48	42	12	63	54	63	51	29	41	58	67	47	60
Zinc	59	42	57	26	-126	41	54	50	59	22	76	66	78	51	61	83	77	77	62	58
Silicon	67	43	42	51	7	-5	50	76	64	26	81	75	90	58	61	56	76	88	80	82
Aluminum	59	40	28	29	-1	8	35	69	50	24	73	68	87	53	60	52	66	84	77	73
Iron	69	60	76	54	6	46	27	58	52	26	56	75	74	49	56	58	75	68	41	73
Calcium	37	63	-5	11	28	-10	23	45	56	25	48	72	67	41	58	57	52	41	75	30
Magnesium	72	48	4	8	3	-2	27	78	53	35	78	82	92	59	82	70	83	88	82	85

*Negative values indicate enrichment rather than removal.

TABLE 3. COMPARISON OF EFFECT OF CLEANING BY PROCEDURE A
(Percent Removed)
(Continued)

	Coal Number																		
	1R	2R	3R	4R	5R	6R	7R	8R	9R	10R	11R	12R	13R	14R	15R	16R	17R	18R	19R	20R
Titanium	53	40	39	32	-6*	-5	35	69	54	27	72	70	88	51	54	48	62	82	76	73
Sodium	52	35	12	4	10	0	27	61	33	26	70	78	77	60	75	63	78	79	80	76
Potassium	73	49	60	48	22	9	86	87	75	32	92	83	92	63	76	61	84	93	81	88
Phosphorus	13	84	7	22	5	18	1	48	69	48	76	68	69	4	91	88	64	76	59	77

*Negative values indicate enrichment rather than removal.

TABLE 4. PRODUCT YIELD AND CALORIFIC VALUE RECOVERY FOR EACH OF THE TWENTY COALS CLEANED BY PROCEDURE A

Coal	Product Yield, percent	Btu Recovery, percent
1R	80	97
2R	90	99
3R	87	94
4R	92	96
5R	97	99
6R	99	99
7R	90	97
8R	62	90
9R	89	100
10R	86	91
11R	71	93
12R	50	79
13R	40	82
14R	72	92
15R	83	99
16R	86	100
17R	74	92
18R	78	99
19R	64	88
20R	62	88
Average	78	94

TABLE 5. COMPARISON BY REGION OF EFFECT OF CLEANING BY PROCEDURE A.
(Percent Removed of Each Constituent)

		Average, 20 Coals	Average, East*	Average, Midwest**	Average, West+
Product Reject		22	31	14	7
Calorific Value		-26	-37	-16	-4
Ash		56	69	55	27
Total Sulfur		12	4	27	20
Chlorine		-7	-34	-6	24
Pyritic Sulfur		26	25	36	22
Organic Sulfur		-24	-34	-20	-1
Antimony	Trace Elements	18	13	-33	35
Arsenic		55	60	51	47
Beryllium		17	24	16	-1
Cadmium		38	36	69	25
Chromium		44	56	42	17
Cobalt		39	33	60	--
Copper		34	41	45	12
Fluorine		49	62	54	13
Lead		52	58	58	33
Manganese		61	74	69	24
Mercury		27	33	9	23
Nickel		29	34	44	6
Selenium		28	31	22	25
Vanadium		35	51	27	4
Zinc		49	61	62	10
Silicon	Major Elements	58	72	53	29
Aluminum		52	65	51	20
Iron		55	60	58	42
Calcium		41	49	59	9
Magnesium		56	74	67	8
Titanium		51	65	47	19
Sodium		50	64	58	11
Potassium		68	79	62	45
Phosphorus		49	56	88	11

*East: Coals 1R, 8R, 9R, 10R, 11R, 12R, 13R, 14R, 17R, 18R, 19R, 20R
**Midwest: Coals 2R, 15R, 16R
+West: Coals 3R, 4R, 5R, 6R, 7R

TABLE 6. EFFECTIVENESS OF CLEANING BY PROCEDURE A

	Level of Each Constituent Removed		
	>50 percent	35-49 percent	20-34 percent
Average 20 Coals	Ash, As, Pb, Mn, Si, Al, Fe, Mg, Ti, Na, K	Cd, Cr, Co, F, V, Zn, Ca, P	S_{pyr}, Cu, Hg, Ni, Se
Average East*	Ash, As, Cr, F, Pb, Mn, V, Zn, Si, Al, Fe, Mg, Ti, Na, K, P	Cd, Cu, Ca	S_{pyr}, Be, Co, Hg, Ni, Se
Average Midwest**	Ash, As, Cd, Co, F, Pb, Mn, Zn, Si, Al, Fe, Ca, Mg, Na, K, P	S_{pyr}, As, Cr, Cu, Ni, Ti	S_T, Se, V
Average West+		Sb, Fe, K	Ash, S_T, S_{pyr}, Cl, Cd, Pb, Mn, Hg, Se, Si, Al

*East: Coals 1R, 8R, 9R, 10R, 11R, 12R, 13R, 14R, 17R, 18R, 19R, 20R
**Midwest: Coals 2R, 15R, 16R
+West: Coals 3R, 4R, 5R, 6R, 7R

possible with vanadium and the Midwestern coals, where its removal was less effective.

With few exceptions, the Eastern and Midwestern coals were cleaned much more effectively than the Western coals. No constituents were removed from the Western coals at the 50 percent or greater level and only three, antimony, iron, and potassium, at the 35 percent or greater level. Chlorine appeared to be removed from the Western coals but was concentrated in the Eastern and Midwestern coals.

As expected, trace and major element control was more effective in some coals than in others. The magnitude of the difference was, perhaps, not expected. The averages by coal of the 15 trace elements removed by cleaning Procedure A are presented in Table 7. The 15 are those which appear in Table 5 and elsewhere from "antimony" up to and including "zinc." The average of these same 15 grouped by region is presented in Table 8. Similarly, the data for nine major elements in coal ash are presented by coal in Table 9 and by region in Table 10. From these data, it is obvious that the effectiveness of removal of most of these elements from the Eastern and Midwestern coals is significantly greater than from the Western coals. However, it must be pointed out that there were also greater concentrations of impurities in the Eastern and Midwestern coals than in the Western coals, as can be seen from the data in Table 11.

Great differences in response to cleaning were exhibited by each coal. To compare each coal on some common basis, what was needed was a calculated expression relating the trace element concentrations to calorific value of each coal, similar to the familiar "pounds of sulfur per million Btu's." This expression has been calculated for sulfur in pounds per million Btu's and for each of the trace and major elements, and expressed as grams of each element per million Btu's. These values are presented in Table 12 for the feed coals and in Table 13 for the cleaned coals. The data, as expressed in this manner, provide a very real basis for comparing the trace element concentrations in each coal on a common ground, the heating value.

These studies with 20 coals, as well as previous limited rough cleaning studies at BCR with eight coals, have confirmed that removal of some potentially harmful trace elements can be effected by coal cleaning. The studies thus far revealed differing responses to the various cleaning processes. Generalizations and specific conclusions concerning the effect of cleaning on fugitive elements will be explored further in the final report which was in progress when this paper was prepared. Extensive evaluations of elemental associations are also included in the final report.

One portion of the final report will contain a description of the analytical procedures used in the study. These procedures could be used by coal industry and other laboratories for determining the concentrations of selected trace elements in a variety of coals.

TABLE 7. AVERAGE, BY COAL, OF PERCENT OF FIFTEEN TRACE ELEMENTS REMOVED BY CLEANING PROCEDURE A

Coal	Percent Removed
1R	49
2R	29
3R	31
4R	21
5R	-6
6R	18
7R	34
8R	38
9R	49
10R	21
11R	43
12R	40
13R	64
14R	40
15R	51
16R	48
17R	47
18R	47
19R	53
20R	60

TABLE 8. AVERAGE, BY GEOGRAPHICAL REGION, OF PERCENT OF FIFTEEN TRACE ELEMENTS REMOVED BY CLEANING PROCEDURE A

Region	Percent Removed
East*	44
Midwest**	40
West+	20

*East: Coals 1R, 8R, 9R, 10R, 11R, 12R, 13R, 14R, 17R, 18R, 19R, 20R
**Midwest: Coals 2R, 15R, 16R
+West: Coals 3R, 4R, 5R, 6R, 7R

TABLE 9. AVERAGE, BY COAL, OF PERCENT OF NINE MAJOR ELEMENTS IN ASH REMOVED BY CLEANING PROCEDURE A

Coal	Percent Removed
1R	55
2R	51
3R	29
4R	29
5R	8
6R	7
7R	35
8R	66
9R	56
10R	30
11R	72
12R	75
13R	82
14R	49
15R	68
16R	61
17R	71
18R	78
19R	72
20R	73

TABLE 10. AVERAGE, BY GEOGRAPHICAL REGION, OF PERCENT OF NINE MAJOR ELEMENTS IN ASH REMOVED BY CLEANING PROCEDURE A

Region	Percent Removed
East*	65
Midwest**	60
West+	22

*East: Coals 1R, 8R, 9R, 10R, 11R, 12R, 13R, 14R, 17R, 18R, 19R, 20R
**Midwest: Coals 2R, 15R, 16R
+West: Coals 3R, 4R, 5R, 6R, 7R

TABLE 11. COMPARISON OF INITIAL CONCENTRATIONS OF IMPURITIES IN COALS BY GEOGRAPHICAL REGION

	Average, 20 Coals	Average, East*	Average, Midwest**	Average, West+
Ash, percent	23.0	29.1	20.3	10.2
Total Sulfur, percent	1.79	1.77	3.54	0.78
Chlorine, percent	0.07	0.07	0.14	0.04
Pyritic Sulfur, percent	1.28	1.23	2.72	0.56
Organic Sulfur, percent	0.46	0.52	0.68	0.18
Antimony, ppm	1.01	0.91	1.73	0.83
Arsenic, ppm	12.1	15.7	9.95	4.70
Beryllium, ppm	1.90	2.49	1.75	0.54
Cadmium, ppm	0.57	0.10	3.31	0.06
Chromium, ppm	29.6	39.8	25.4	7.61
Cobalt, ppm	6.27	8.59	5.12	1.40
Copper, ppm	18.1	24.1	11.2	7.75
Fluorine, ppm	146	186	132	58.3
Lead, ppm	13.7	14.3	27.3	4.03
Manganese, ppm	67.3	62.8	137	36.5
Mercury, ppb	188	234	173	85.6
Nickel, ppm	18.4	23.9	18.7	4.84
Selenium, ppm	2.82	3.67	2.45	1.02
Uranium, ppm	1.78	2.02	1.99	1.07
Vanadium, ppm	44.4	57.8	48.3	10.0
Zinc, ppm	57.8	33.2	238	9.20
Silicon, ppm	61,300	80,200	51,000	22,200
Aluminum, ppm	29,300	40,400	19,100	8,680
Iron, ppm	14,400	15,800	24,600	4,930
Calcium, ppm	5,750	2,690	8,240	11,600
Magnesium, ppm	2,300	2,330	1,640	2,610
Titanium, ppm	1,520	2,050	1,070	532
Sodium, ppm	976	741	990	1,530
Potassium, ppm	5,340	7,640	4,000	641
Phosphorus, ppm	200	203	211	185

*East: Coals 1R, 8R, 9R, 10R, 11R, 12R, 13R, 14R, 17R, 18R, 19R, 20R
**Midwest: Coals 2R, 15R, 16R
+West: Coals 3R, 4R, 5R, 6R, 7R

TABLE 12. GRAMS OF TRACE AND MAJOR CONSTITUENTS PER MILLION BTU'S IN CLEANED COAL

Constituent	Coal Number 1R	2R	3R	4R	5R	6R	7R	8R	9R	10R
Total Sulfur*	0.87	1.27	0.52	0.49	0.47	0.46	0.45	0.69	2.00	3.62
Antimony	0.029	0.018	0.033	0.018	0.018	0.009	0.014	0.046	0.005	0.010
Arsenic	0.310	0.215	0.088	0.183	0.044	0.023	0.038	0.182	0.171	0.097
Beryllium	0.044	0.031	0.032	0.029	0.005	0.005	0.027	0.067	0.020	0.053
Cadmium	0.002	0.006	0.003	0.002	0.002	0.000	0.001	0.002	0.002	0.003
Chromium	0.537	0.533	0.203	0.173	0.253	0.148	0.298	0.651	0.319	0.792
Cobalt	-	-	-	-	-	-	-	-	-	-
Copper	0.373	0.249	0.407	0.231	0.258	0.086	0.282	0.691	0.183	0.386
Fluorine	2.07	1.93	1.82	1.14	2.68	0.572	2.77	1.61	1.68	3.32
Lead	0.145	0.356	0.318	0.052	0.060	0.011	0.066	0.287	0.089	0.189
Manganese	0.314	0.488	2.31	0.871	1.41	0.876	0.225	0.463	0.634	0.747
Mercury	0.008	0.005	0.003	0.004	0.002	0.002	0.001	0.005	0.005	0.006
Nickel	0.421	0.522	0.206	0.197	0.134	0.111	0.179	0.535	0.236	0.520
Selenium	0.090	0.053	0.032	0.027	0.018	0.016	0.046	0.145	0.023	0.125
Vanadium	0.833	0.813	0.461	0.450	0.317	0.095	0.398	1.13	0.411	1.16
Zinc	0.469	1.84	0.214	0.107	0.385	0.397	0.102	0.608	0.234	0.494
Silicon	611	740	891	295	399	229	668	780	401	1190
Aluminum	405	367	557	191	158	86.1	224	489	256	650
Iron	212	267	79.5	148	152	13.9	84.5	144	440	624
Calcium	42.1	39.4	275	590	617	181	227	76.3	91.9	50.2
Magnesium	12.2	15.6	116	154	76.6	45.0	63.7	22.9	17.5	31.1
Titanium	25.5	21.0	25.7	10.3	12.9	5.25	16.7	29.6	14.6	34.3
Sodium	6.91	27.6	8.33	262	13.1	2.77	8.31	9.09	14.9	12.2
Potassium	47.3	52.2	16.9	12.3	5.24	1.20	6.40	41.3	22.1	71.7
Phosphorus	7.27	0.879	3.04	4.50	13.4	0.851	10.4	2.64	4.01	1.73

*Pounds per million Btu's

TABLE 12. GRAMS OF TRACE AND MAJOR CONSTITUENTS PER MILLION BTU'S IN CLEANED COAL (Continued)

Constituent	Coal Number 11R	12R	13R	14R	15R	16R	17R	18R	19R	20R
Total Sulfur*	0.37	0.71	0.65	0.76	2.35	2.43	0.52	0.80	1.16	0.84
Antimony	0.020	0.026	-	-	-	-	-	-	-	-
Arsenic	0.058	0.081	0.284	0.298	0.199	0.104	0.069	0.203	0.214	0.141
Beryllium	0.061	0.114	0.053	0.065	0.044	0.081	0.051	0.122	0.046	0.058
Cadmium	0.002	0.002	0.001	0.002	0.034	0.033	0.002	0.001	0.003	0.001
Chromium	0.307	0.772	0.411	0.928	0.501	0.436	0.405	0.218	0.623	0.573
Cobalt	0.249	0.290	0.124	0.405	0.068	0.064	0.165	0.149	0.147	0.086
Copper	0.521	0.850	0.579	0.682	0.181	0.203	0.341	0.457	0.249	0.223
Fluorine	0.919	3.16	1.71	3.95	2.01	2.31	1.89	1.82	2.62	1.33
Lead	0.181	0.324	0.130	0.246	0.121	0.584	0.144	0.133	0.168	0.115
Manganese	0.376	0.160	0.361	0.755	1.03	2.78	0.236	0.652	0.347	0.270
Mercury	0.002	0.004	0.002	0.005	0.006	0.004	0.003	0.003	0.005	0.007
Nickel	0.432	0.748	0.383	0.720	0.277	0.270	0.367	0.359	0.524	0.798
Selenium	0.072	0.196	0.035	0.056	0.109	0.038	0.097	0.091	0.056	0.036
Vanadium	0.506	1.38	0.983	1.41	2.15	0.624	0.645	0.479	1.08	0.891
Zinc	0.199	0.570	0.417	0.492	1.14	3.23	0.201	0.182	0.426	0.514
Silicon	463	1000	435	1080	702	965	449	238	583	545
Aluminum	302	669	299	734	288	316	373	152	323	330
Iron	124	64.5	188	196	450	362	76.8	146	238	168
Calcium	38.5	15.4	20.5	58.9	112	209	16.6	34.0	36.7	30.4
Magnesium	14.2	18.5	12.7	35.3	12.3	21.5	13.5	10.6	10.9	5.76
Titanium	18.4	32.0	12.2	40.2	17.3	20.1	18.6	6.96	15.7	18.5
Sodium	7.40	5.50	9.11	14.4	5.42	14.5	5.03	4.57	6.06	3.27
Potassium	20.0	77.2	34.2	86.5	40.2	57.1	43.0	17.8	35.7	24.3
Phosphorus	0.672	1.48	1.78	10.3	0.716	1.05	1.57	0.539	5.93	1.22

*Pounds per million Btu's

TABLE 13. GRAMS OF TRACE AND MAJOR CONSTITUENTS PER MILLION BTU'S IN FEED COAL

Constituent	Coal Number 1R	2R	3R	4R	5R	6R	7R	8R	9R	10R
Total Sulfur*	1.98	2.29	1.07	0.84	0.52	0.49	0.49	0.83	3.33	4.19
Antimony	0.042	0.015	0.073	0.024	0.027	0.011	0.029	0.061	0.017	0.013
Arsenic	1.57	0.419	0.352	0.447	0.058	0.038	0.074	0.445	0.514	0.177
Beryllium	0.072	0.042	0.036	0.030	0.006	0.004	0.033	0.128	0.036	0.064
Cadmium	0.003	0.018	0.005	0.003	0.002	0.001	0.002	0.004	0.003	0.003
Chromium	1.16	0.804	0.339	0.222	0.186	0.222	0.506	2.10	0.674	0.990
Cobalt	-	-	-	-	-	-	-	-	-	-
Copper	0.861	0.419	0.545	0.300	0.255	0.093	0.351	1.35	0.394	0.459
Fluorine	4.48	4.31	2.63	1.38	2.75	0.565	4.07	9.04	4.59	4.91
Lead	0.600	0.831	0.528	0.080	0.071	0.022	0.114	0.735	0.297	0.249
Manganese	1.95	1.40	2.69	1.44	1.73	0.866	0.584	3.20	1.52	1.20
Mercury	0.026	0.006	0.006	0.005	0.002	0.002	0.002	0.010	0.009	0.009
Nickel	0.814	0.701	0.206	0.198	0.119	0.157	0.266	1.17	0.569	0.665
Selenium	0.242	0.070	0.066	0.041	0.021	0.023	0.049	0.255	0.041	0.184
Vanadium	1.73	0.999	0.578	0.464	0.296	0.086	0.561	3.17	0.791	1.40
Zinc	1.38	3.50	0.528	0.150	0.173	0.673	0.241	1.76	0.649	0.673
Silicon	2250	1440	1640	623	436	219	1450	4800	1260	1710
Aluminum	1200	675	834	278	159	94.1	371	2320	580	911
Iron	822	728	353	337	164	25.8	124	503	1040	899
Calcium	81.4	119	280	692	872	165	316	204	237	71.3
Magnesium	53.0	33.2	130	174	80.1	44.0	94.3	155	41.6	50.7
Titanium	65.1	38.5	45.0	15.9	12.3	5.01	27.5	140	36.1	49.9
Sodium	17.5	46.9	10.2	285	14.7	2.78	12.3	34.1	24.9	17.7
Potassium	213	114	45.8	24.7	6.82	1.32	48.1	453	97.7	112
Phosphorus	10.1	6.10	3.51	6.02	14.4	1.04	11.3	7.35	14.5	3.53

*Pounds per million Btu's

TABLE 13. GRAMS OF TRACE AND MAJOR CONSTITUENTS PER MILLION BTU'S IN FEED COAL (Continued)

Constituents	Coal Number									
	11R	12R	13R	14R	15R	16R	17R	18R	19R	20R
Total Sulfur*	0.41	0.84	1.57	0.86	3.54	3.66	0.60	1.02	1.45	2.65
Antimony	0.026	0.038	0.056	0.076	0.153	0.044	0.030	0.032	0.054	0.048
Arsenic	0.138	0.432	1.37	1.07	0.430	0.348	0.227	0.501	0.738	1.25
Beryllium	0.111	0.219	0.179	0.113	0.071	0.101	0.087	0.152	0.099	0.109
Cadmium	0.005	0.007	0.009	0.004	0.106	0.288	0.003	0.002	0.007	0.003
Chromium	1.29	3.19	4.70	1.97	1.32	0.943	1.23	1.15	2.02	2.12
Cobalt	0.374	0.390	0.795	0.610	0.201	0.185	0.283	0.287	0.474	0.374
Copper	1.05	1.97	2.15	1.35	0.520	0.406	0.716	0.754	1.03	1.35
Fluorine	6.67	15.6	17.6	8.04	5.89	5.81	7.66	8.50	9.85	5.99
Lead	0.550	1.10	1.26	0.570	0.356	2.15	0.380	0.441	0.671	1.10
Manganese	2.23	2.08	10.5	2.417	6.41	9.09	2.75	3.44	2.42	1.84
Mercury	0.004	0.010	0.009	0.010	0.010	0.005	0.004	0.006	0.008	0.016
Nickel	0.792	1.53	2.63	1.20	0.942	0.614	0.692	0.637	1.16	1.48
Selenium	0.108	0.321	0.105	0.110	0.163	0.053	0.158	0.140	0.135	0.152
Vanadium	1.82	4.70	5.50	3.65	3.61	1.26	1.89	1.85	2.75	3.12
Zinc	1.08	2.62	3.96	1.28	3.44	22.6	1.07	0.986	1.52	1.74
Silicon	3260	6410	9310	3300	2150	2620	2290	2530	4070	4210
Aluminum	1460	3310	4970	1990	848	783	1350	1230	1890	1740
Iron	373	401	1510	495	1220	1040	373	573	555	863
Calcium	96.6	86.2	129	127	317	581	42.8	72.6	199	61.6
Magnesium	85.3	165	316	111	81.2	85.8	100	109	85.0	52.8
Titanium	84.9	170	206	106	44.7	46.3	61.1	48.1	90.4	95.5
Sodium	32.0	39.8	82.1	45.9	25.6	46.7	28.0	27.2	41.3	19.5
Potassium	340	722	905	302	199	173	325	300	262	283
Phosphorus	3.66	7.33	12.0	13.7	9.17	10.4	5.29	2.89	19.8	7.35

*Pounds per million Btu's

A proposal for continuation of this work was submitted to the U.S. Department of Energy. The continuation will involve field evaluations of operating cleaning plants to compare the response of trace and major elements to coal cleaning, as actually practiced, to the controlled cleaning procedures used in the laboratory. These field evaluations have already been initiated through a modification of the present contract.

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ENVIRONMENTAL CONTROL TECHNOLOGY RESEARCH IN HIGH SULFUR COAL PREPARATION WASTE DRAINAGES

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ABSTRACT

We have performed laboratory experiments to investigate the efficacy of several control options for treating coal wastes at the preparation plant, during or after disposal. Our research revealed that calcining is one of the more effective and permanent means of treating high-sulfur coal wastes before disposal to decrease, quite dramatically, the release of environmentally undesirable pollutants into the drainages from disposal sites. Pretreatment of the waste by slurrying with lime/limestone mixtures, although still in the research stage, promises effective control of trace element releases and good economy. Another potential control method is codisposal of coal wastes with lime or limestone to neutralize the acid drainage and retain soluble aqueous contaminants within the waste site. Other experiments have examined the feasibility of using natural materials, such as clays, soils, and alkaline combustion products to attenuate through alkaline neutralization, sorbent, or ion exchange action, concentrations of trace elements of environmental concern ion the waste pile effluents. We have also investigated the potential of contaminated effluent treatment using alkaline neutralization, ion exchange, and reverse osmosis. These results are discussed briefly. The various tradeoffs for these control options are considered in terms of contaminant reduction, complexity, permanency, and relative economics.

INTRODUCTION

The mineral wastes from coal preparation and coal mine development constitute a major environmental problem in the United States.[1,2] More than 3 billion tons of these materials have accumulated thus far and are increasing yearly at the rate of more than 100 million tons. In an effort to produce cleaner coals and also to upgrade their environmental acceptability, the level of waste production is expected to increase markedly with increased use of coal, in the near future. In addition to being large volume wastes, these coal preparation discards present problems of serious environmental concern. Of the

nearly 5000 coal waste dumps, half pose some type of health, environmental, or safety problem. One of the growing environmental concerns is the effect that trace metals in the waste dump drainages will have as they collect in the surrounding streams and soils. In acknowledging this latter concern, the Department of Energy (DOE) and the Environmental Protection Agency (EPA) have jointly sponsored, since 1975, research at the Los Alamos Scientific Laboratory (LASL) to evaluate the trace element problem and to determine and recommend corrective measures.

The overall objectives of the LASL research program are to assess the problem of trace element contamination in coal waste drainages and to identify suitable control technologies. More specifically these are to

- assess the nature and magnitude of trace elements in the effluents from coal preparation wastes,
- identify the chemistry of the trace constituents of environmental concern,
- identify and experimentally verify effective environmental strategies to control the release of hazardous constituents, and
- analyze the tradeoffs associated with the different control technologies and recommend control measures or necessary research development and demonstration (RD&D) programs.

We have, in past publications,[1-5] described the results of our assessment of the nature and the magnitude of the water contamination resulting from the leaching of these coal wastes. We have also identified nine elements (aluminum, cadmium, cobalt, copper, fluorine, iron manganese, nickel and zinc) as existing in the refuse leachates in concentrations sufficiently high to be of concern. The severity of the environmental hazard associated with these trace elements was quantified using EPA's Multimedia Environmental Goals/Minimum Acute Toxicity Effluent (MEG/MATE) system.[6]

In this paper we will concentrate on the description of the research performed to identify and to verify experimentally effective environmental control technologies to control the release of these environmentally undesirable trace elements and to analyze the technologic and economic trade-offs that must be considered in recommending further research and/or RD and D programs.

Control strategies for effective and environmentally acceptable disposal of coal preparation wastes fall into three logical categories.

I. Alter the waste structure to produce an environmentally acceptable waste.

II. Dispose the waste in a manner that will produce an environmentally acceptable drainage.

III. Collect and treat the contaminated drainage from disposed, but untreated waste.

Category I eliminates the source of the problem by immobilizing or removing the potential pollutants from the waste. The second category could be implemented by retaining the pollutants in the dump, providing back-up safeguards (if necessary), and monitoring the dump to insure environmentally acceptable containment. A properly devised and monitored disposal scheme in Category II could provide for an orderly release of environmentally acceptable levels of pollutants. This category also recognizes that an acceptable, environmental control can be found without the need to destroy or alter the waste itself. In Category III, one could isolate the dump, let it generate pollutants as it would, collect the contaminated drainage, and remove the pollutants from the drainage before releasing the water into the local waterways. This strategy is the least desirable from an environmental viewpoint because it is nearly impossible, with such large volumes of wastes and extensive drainage areas, to insure that the pollutants will not inadvertently escape into the environment in unacceptable quantities. All three control strategies, when viewed in terms of the tradeoffs among their economic impact, technical complexity, and overall effectiveness, have good and bad features and no single strategy is obviously more promising than the other two.

ENVIRONMENTAL CONTROL TECHNOLOGY: EXPERIMENTAL DESCRIPTION AND DISCUSSION

I. Producing an Environmentally Acceptable Waste

The possibility that the release of toxic trace elements into the environment can be controlled by pretreatment of coal preparation wastes has been investigated experimentally. One approach that we have considered is calcining (high-temperature heat treatment of these materials to remove volatile, acid-forming constituents and to chemically immobilize potentially toxic trace elements in the refuse matrix. In these researches, we have studied the changes in both the chemical and physical characteristics of the refuse and trace element mobilities that result from the heat treatment. Our research has revealed that refuse calcining is technically one of the more effective and probably permanent

means of treating high-sulfur coal wastes to completely eliminate releases of acidic or contaminated drainage from refuse disposal sites.

Our initial set of calcining experiments was performed using high-sulfur coal preparation wastes from an Illinois Basin coal cleaning plant to determine the effects of heat treatment on the elemental composition of this type of refuse material. The sample was prepared by crushing the refuse to -3/8 in. and calcining it in a quartz tube at 800 to 850°C in air for 6 h. The calcined material, which had partially agglomerated, was ground to -20 mesh for subsequent studies. The analysis of the chemical and trace element composition of the calcined refuse sample showed a marked decrease in the concentration of the volatile components in the refuse. Of particular interest was the loss of sulfur that occurred as a result of the calcining. From an original concentration of 13.4 wt% sulfur in the noncalcined sample, the described sample treatment yielded a product that contained only 0.7 wt% sulfur. Other volatile components whose concentrations were decreased by the calcining were bromine, lead, and cadmium. The complete elemental analyses for the calcined refuse samples and the percent retention upon calcination appear in Table I.

Calcining and leaching experiments were conducted to determine optimal heat-treatment conditions necessary to immobilize the potentially toxic trace elements in the refuse matrix. These experiments were performed using high-sulfur coal preparation waste from Illinois Basin Plant C. The waste was ground to -20 mesh and calcined in air at 600, 800, 1000, and 1200°C for 2 h.

The effect of refuse calcining treatments on the mineral composition of the refuse is illustrated in Table II, where the changes in refuse mineralogy that occurred at various temperatures are delineated. The two most environmentally active species, pyrite (marcasite) and calcite, have been transformed to high-temperature phases by 600°C. By 1000°C, even the clay minerals have been converted to structurally indefinable aluminosilicates, and the samples have become fused or sintered at particle surfaces. The x-ray diffraction analyses reported in Table II support the concept that the mineralogical transformations thought to occur in the coal wastes have been effected by heat treatment in the range of 800 to 1000°C.

Studies of the trace element leachabilities of the calcined refuse samples have been conducted in the laboratory. The effects of calcining temperature on leachate pH and total dissolved solids (TDS) content are seen in Table III Calcining to 600°C and higher results in leachates with higher pH values.

TABLE I

EFFECT OF CALCINING ON TRACE ELEMENT RETENTION FROM PLANT B COAL REFUSE

Element	Level[a]	Retention (%)[b]	Element	Level[a]	Retention (%)[b]
Na	1 140	90	Zn	300	120
Mg	4 900	120	Ga	29	-
Al	115 000	120	As	110	70
SiO_2	168 000	80	Br	<0.1	<5
P	560	-	Mo	35	40
S	11 400	5	Cd	0.29	40
Cl	<100	-	Cs	9	80
K	24 500	140	La	60	100
Ca	1 900	110	Ce	130	110
Sc	20	100	Eu	2	100
Ti	5 490	100	Yb	5	100
V	120	90	Lu	0.6	90
Cr	100	100	Hf	5	100
Mn	190	80	Ta	1.7	120
Fe	190 000	110	Pb	12	20
Co	70	140	Th	15	100
Ni	110	100	U	6	140
Cu	73	130			

[a] Experimentally determined concentration before calcining, in parts per million.
[b] Error approximately ± 30% of value.

TABLE II

PRESENCE OF COAL REFUSE MINERALS AT VARIOUS CALCINING TEMPERATURES

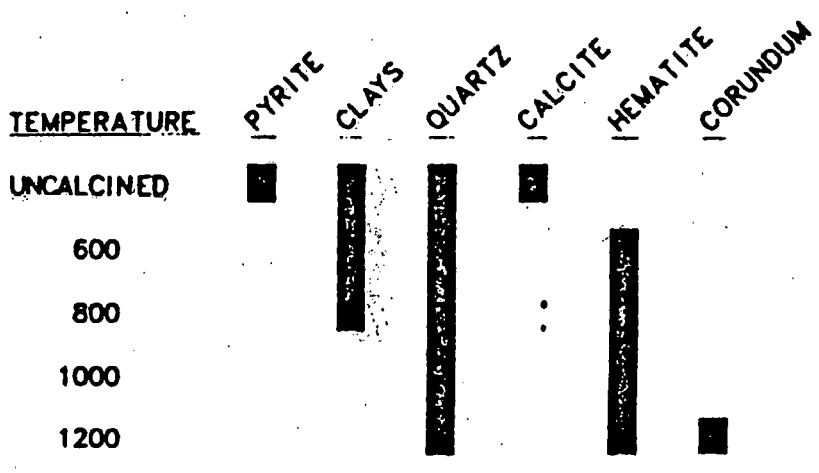


TABLE III

EFFECT OF CALCINING TEMPERATURE ON THE LEACHABILITY OF A HIGH-SULFUR COAL REFUSE MATERIAL[a]

Calcining Temp (°C)	Sample Wt Loss (%)	Leachate pH	Leachate TDS (Wt %)
Uncalcined	-	2.9	1.4
600	23	5.9	0.2
800	23	6.2	0.3
1000	23	8.0	0.2
1200	23	8.0	-

[a] 20-g samples of crushed refuse/100 mℓ H_2O/48 h.

This is a consequence of the conversion of the acid-forming mineral species, pyrite and marcasite, to more stable oxide forms and the driving off of the sulfur. Calcining of the refuse also significantly reduced the general leachability of the material as evidenced by the reduced TDS values of the leachates.

The success of calcining at reducing trace element releases during refuse leaching is illustrated by Table IV which lists trace element data from a comparison leaching test of calcined and uncalcined refuse samples. The refuse samples referred to in the table had been subjected to static leaching for 48 h. It is seen that the concentrations of the group of toxic elements listed are reduced in the leachates from the calcined refuse by as much as two orders of magnitude over the concentration in the uncalcined refuse leachates and none of the trace elements of environmental concern are extant in the leachates in concentrations in excess of the MEG/MATE values. Calcining appears to produce an innocuous waste.

Our current research has revealed another most promising control for the high-sulfur coal preparation wastes. We have found that pretreatment by grinding the waste, slurrying it with 0.35% lime and 1% ground limestone produces a neutral and durable waste that, when exposed to simulated weathering and leaching conditions, is environmentally acceptable in terms of low trace element concentrations and prevention of acid formation in the leachates. The experiments to test this concept of producing a non-contaminating waste by treatment prior to disposal have been scaled up to simulate environmental leaching, under

TABLE IV

TRACE ELEMENT LEACHABILITY OF A HIGH-SULFUR COAL REFUSE SAMPLE CALCINED AT 1000°C[a]

Element	Uncalcined Refuse (ppm)	Calcined Refuse (ppm)
Al	100	0.4
Fe	600	<0.03
Mn	5.8	0.03
Co	2.8	<0.01
Ni	4.8	0.01
Cu	0.10	0.01
Zn	2.8	0.05
Cd[b]	68[b]	0.3[b]
pH	2.9	8.0
TDS (%)	1.4	0.2

[a] 50-g samples of crushed refuse/200 mℓ H_2O/48 h.
[b] In parts per billion.

rainfall conditions similar to those in the Illinois Basin, and are being carried out as this is being written. The preliminary results that are available show the change (or lack thereof) of pH and of iron content in the waste pile effluents as a function of time (i.e. this is related to leachate volume since there is a "rain" of 3/4 inch every week on the experiment). These results are presented in Tables V and VI where it can be seen that the effluent from the lime/limestone slurried waste is effectively neutral and contains little iron, and so far, has remained constant with time. Results of waste slurried with lime are included for comparison. One of the most interesting aspects of the lime/limestone slurry control technology is that our economic analysis[7] shows this treatment to be competitive with alkaline neutralization - one of the least expensive ECT options for treatment of high sulfur coal waste drainages.[7]

II. Waste Disposal to Produce an Environmentally Acceptable Effluent

Several methods have been considered as treatments during the waste disposal to prevent the release of trace contaminants as the waste dump is leached by rainfall, surface or ground water. Codisposing the waste with neutralizing

TABLE V

ACIDITY OF WASTE PILE EFFLUENT

(pH)

TIME	LIME (%)			LIME + LIMESTONE (%)
(WEEKS)	0.33	1.1	3.3	0.35 + 1
0	6.5	11.0	12.1	7.6
3	2,5	2.5	11.7	7.4
6	2.2	4.2	11.5	7.3
9	2.0	3.0	9.6	7.5

agents or sorbents and sealing the surfaces of the waste particles have been investigated experimentally. Small particle limestone, lime, certain types of clays and soils, and industrial wastes, such as fly ash and alkaline sludges, have all shown promise as neutralizing agents when codisposed with highly acidic coal wastes in our laboratory testing. The most interesting results from these experiments included the lime codisposal and the use of sorbents or attenuating agents. This discussion will concentrate on these two groups of experiments.

Our efforts involving the additions of powdered lime to high-sulfur refuse materials to control leachate pH and trace element content proved to be very fruitful. For these experiments, powdered lime in varying amounts (3 to 50 g) was slurried in 150 mℓ of distilled water with 530 g of -3/8-in., high-sulfur coal refuse from Illinois Basin Plant B. The resultant mixture was subsequently dried in air at 50°C and recrushed to -3/8-in. particles. Four different lime concentrations were used, 0.5, 1.5, 3, and 10 weight percent. Column leaching experiments were conducted with about 500 g of each of the samples to determine

TABLE VI

TOTAL IRON IN WASTE PILE EFFLUENT

(PPM)

TIME	LIME (%)			LIME + LIMESTONE (%)
(WEEKS)	0.33	1.1	3.3	0.35 + 1
0	--	--	--	--
3	1600	1.4	0.3	< 0.01
6	10000	0.8	< 0.01	< 0.01
9	13000	3.9	0.1-0.3	0.01

the effects of the lime additions. The refuse mixtures were packed into pyrex columns 40 cm long by 5 cm in diameter and subsequently leached with distilled water at a flow rate of 0.5 mℓ/min until more than 4 ℓ of water had been passed through the refuse beds. Leachate flow was interrupted once during the experiment at the 4.2-ℓ point, and dry air was passed through the column for 2 wk to test the acid-regeneration potential of the refuse/lime mixtures.

The mixture containing 3 wt% lime was especially interesting because a leachate pH of 7 was maintained for nearly the entire duration of the continuous part of the leaching experiment (until 4.2 ℓ had been passed through the column). The TDS values for this refuse/lime combination were also very respectable (ranging downward from about 0.6 wt%), especially considering that the dissolution of the lime itself adds substantially to the dissolved solids content of the solution. By the end of the continuous part of the leaching experiment, concentrations of troublesome trace elements, especially iron and manganese, had been reduced to environmentally acceptable levels. Regeneration of this refuse/lime mixture with air did tend to lower the leachate pH and to elevate the trace element concentrations. However, we did not continue the study long enough after the regeneration point to determine subsequent behavior. These data are shown in Table VII.

TABLE VII

ANALYSES FOR DYNAMIC LEACHING STUDIES OF LIME/REFUSE MIXTURES
(3 wt% Lime)

Sample No.[a]	1	3	5	7	12	16	18	20
Vol(ℓ)	0.042	0.168	0.336	1.125	2.076	4.233[b]	4.562	4.830
pH	6.6	6.3	6.5	6.8	7.4	7.9	2.8	3.0
TDS(%)	0.54	0.48	0.37	0.27	0.24	0.15	0.73	0.45
F	0.15	0.15	<0.15	<0.15	<0.15	<0.15	4.8	1.6
Na	7.9	6.4	3.4	1.5	1.1	1.0	4.9	2.0
Al	0.7	<0.6	<0.6	<0.6	<0.6	<0.6	180	54
K	8.9	12.4	6.1	5.3	3.5	3.0	7.9	8.2
Ca	890	870	780	700	620	380	550	540
Cr (μg/ℓ)	<1	<1	23	3	2	<1	19	6
Mn	3	2	2	1	0.6	0.3	12	5
Fe	120	120	69	14	7	3	700	300
Co	0.7	0.6	0.4	0.2	0.2	<0.07	8	3
Ni	1	0.9	0.7	0.3	0.2	0.1	12	4
Cu	0.04	0.04	0.04	0.03	0.02	0.02	0.9	0.2
Zn	0.5	0.4	0.2	0.1	0.08	0.07	14	5
Cd (μg/ℓ)	5.4	4.0	2.0	0.6	0.4	0.6	100	32

[a] Concentrations in μg/mℓ unless noted otherwise.
[b] Water flow was stopped at this point, air was passed through the column for 2 wk, then water flow was resumed.

The codisposal of alkaline agents, such as lime, with acidic coal refuse materials does appear to be an attractive option for controlling trace element contamination of disposal area drainages. The technique is only moderately costly and appears to be a highly effective means of preventing the release of a contaminated drainage from coal refuse dumps. The technology for mixing alkaline agents with coal refuse materials should be relatively simple and is immediately effective.

The codisposal of attenuating agents or sorbents, other than lime or limestone, with acidic coal refuse materials also has great potential for reducing or abating trace element contamination of disposal site drainage. Many natural materials, such as certain types of clays and soils, and many industrial wastes, such as fly ash or alkaline sludges, may have considerable capacity to attenuate contaminated refuse drainage, and often these materials are available in large and accessible quantities near refuse disposal sites. Our research was directed at assessing the potential of various attenuating agents for reducing the trace element and acid compositions of coal refuse leachates and thus at revealing the possible effectiveness of this class of agents as refuse dump additives.

Our initial investigation into this area included a series of natural and man-made materials collected from various parts of the country. In one set of experiments, acidic coal refuse leachates were equilibrated with eleven solid sorbent materials to evaluate their trace element attenuation capacities. The solids used were

- $CaCO_3$ (standard)
- Acid mine drainage treatment sludge
- Bottom ash from a western power plant
- Precipitator ash (fly ash)
- Bottom slag from a midwestern plant
- SO_2 scrubber sludge from a midwestern plant
- Alabama soil
- Illite clay
- Montmorillonite clay
- Kaolinite clay
- Sea sand (two replicates).

The experimental procedure consisted of shaking the solid with the coal refuse leachate for 15 h, measuring the pH, and analyzing the filtrate for trace elements. Companion experiments in which the solids were shaken with distilled water were carried out to evaluate the alkalinity of the sorbent and to determine its water soluble components. The pH values of the filtrates from the solid attenuating materials previously mixed with distilled water ranged from 5.8 (sea sand) to 11.2 (precipitator ash). The pH values of the filtrates from the refuse leachate/solid mixture ranged from 2.8 (sea sand) to 9.6 (precipitator ash). As a general rule, the higher the pH, the lower the trace element concentrations. Total dissolved solids are not included in these discussions because after equilibration, the soluble matter of some sorbent materials artifically elevated the TDS values in the leachates.

The results of these experiments are discussed with reference to Tables VIII and IX. Table VIII has essentially all the data pertinent to the experiments, including the liquid/solid ratios, the measured pH values, and the trace element concentrations. In general, Table VIII is self explanatory and points out the potential benefits of using some of the coal combustion by-products and naturally occurring clays as a treatment for coal refuse drainages, even where the acid content of the drainage is quite high. Table IX lists in a more qualitative manner, the performance of the various sorbents with regard to leachate pH elevation and attenuation of the 13 trace elements that we have identified as being of greatest environmental concern in the Illinois Basin coal refuse effluents. We have isolated different sections in Table IX to draw attention to some of the salient features. For example, because the solubilities of Fe^{+3} and Al^{+3} are highly dependent on pH in acidic solutions, those sorbents that are most effective in elevating the pH are also most effective in decreasing the concentrations of Fe^{+3} and Al^{+3}. The results listed in Table IX are quite striking and demonstrate clearly that 7 of the 11 sorbents tested are effective in controlling the key leachate parameters. Cost analyses of various codisposal options, including lime and fly ash with and without limestone modification are favorable for several options.

Many alkaline soils do have a significant capacity to reduce the trace element and acid contents of refuse drainages. This attenuating capacity appears to function mainly on the strengths of these soils in controlling leachate acidity. The additional question concerning whether the cation-exchange capacity of each soil type has any major bearing on the capacity of the soil to

TABLE VIII

RESULTS OF EXPERIMENTS USING ELEVEN SORBENTS FOR pH CONTROL AND TRACE ELEMENT ATTENUATION FOR AN ILLINOIS BASIN HIGH-SULFUR COAL REFUSE LEACHATE

Sample	Sorbent	Liquid	Liquid/Sol Ratio	pH	Element Levels Removed												
					P PPM	Na PPM	Al PPM	K PPM	Ca PPM	Cr PPB	Mn PPM	Fe PPM	Co PPM	Ni PPM	Cu PPM	Zn PPM	Cd PPB
0		Leachate		2.64	2.0	108	10	12	275	22	4.0	105	1.9	2.6	0.055	1.02	6.0
0		H_2O			<0.1		<0.5			<1	<0.02	<0.05	<0.05	<0.03	<0.02	<0.01	<0.1
1	AMD Treatment	Leachate	4	7.63	0.2	82	<0.2	11	600	1.0	0.11	0.2	<0.1	<0.05	<0.01	0.04	8
2	Sludge	H_2O	4	7.67	0.2	5	0.6	2.3	590	5.3	0.05	0.2	<0.1	<0.05	<0.01	0.04	1
3	Bottom Ash	Leachate	3	8.08	1.5	150	<0.2	12.2	520	1.1	3.40	0.2	0.4	0.63	0.05	0.07	1.3
4		H_2O	3	8.59	0.7	35	<0.2	1.8	54	1.5	0.05	0.1	<0.1	<0.05	0.01	0.01	0.2
5	Precipitator Ash	Leachate	3	9.63	1.6	163	0.6	11.2	550	73	0.04	0.2	0.1	<0.05	0.01	0.02	0.1
6		H_2O	3	11.23	1.1	49	2	2.6	65	90	0.04	<0.1	<0.1	<0.05	0.01	<0.005	0.1
7	Illite	Leachate	3	8.08	1.5	145	0.6	50	450	1.6	0.25	0.3	0.1	0.07	<0.01	0.35	0.3
8		H_2O	3	7.84	1.6	22	<0.5	18	34	5.0	0.02	<0.1	<0.1	<0.05	<0.01	0.01	1.5
9	Montmorillonite	Leachate	9	7.95	0.4	770	7	17	110	4.4	0.67	1.4	0.2	0.22	0.03	0.19	2.3
10		H_2O	9	8.46	0.2		21		2	3	<0.1	1	<0.3	<0.3	<0.07	<0.05	<0.4
11	Kaolinite	Leachate	3	4.29	2.6	106	13.5	18	290	3.6	40.1	6.4	1.5	2.47	0.27	18.4	20
12		H_2O	3	6.03	0.3	6	0.4	1.6	<2.5	1.1	0.01	<0.1	<0.1	0.02	0.01	<0.005	0.2
13	Alabama Soil	Leachate	3	4.01	2.3	90	10	4.6	220	1.4	17.1	9.6	1.3	1.02	0.06	0.50	8
14		H_2O	3	6.30	0.2	5	<0.2	0.7	<2.5	<1	0.04	<0.1	<0.1	<0.05	0.01	0.01	1
15	$CaCO_3$	Leachate	3	8.03	0.16	102	<0.2	16	160	29	0.01	<0.1	0.1	0.12	0.02	0.01	0.5
16		H_2O	3	9.14	0.45	11	<0.2	4.9	4	163	<0.01	<0.1	<0.1	<0.05	0.02	<0.005	0.3
17	Bottom Slag	Leachate	3	4.23	0.9	102	2	15	330	<1	3.78	108	1.6	3.34	0.04	1.30	51
18		H_2O	3	7.63	0.2	2.5	0.5	1.5	16	<1	<0.01	0.35	<0.1	<0.05	0.01	0.01	0.4
19	SO_2 Scrubber	Leachate	3	7.34	4.0	125	<0.2	46	760	2.8	2.20	<0.1	0.7	0.80	0.02	0.60	26
20	Sludge	H_2O	3	8.35	4.2	25	<0.2	31	410	8.4	0.05	<0.1	<0.1	<0.05	0.01	0.02	3.0
21	Sea Sand	Leachate	3	2.60	1.8	95	11	12	250	29	3.52	120	1.7	2.2	0.13	0.98	9.0
22		H_2O	3	5.88	0.2	<1	<0.2	0.2	<2.5	<1	0.01	<0.1	<0.1	<0.05	0.01	<0.005	0.3
23	Sea Sand	Leachate	3	2.81	1.5	95	11	11	250	21	3.40	113	1.6	2.10	0.13	0.97	7
24		H_2O	3	5.83	0.17	<1	<0.2	0.4	<0.5	2.5	<0.01	<0.1	<0.1	<0.05	<0.01	<0.005	0.8

TABLE IX

COMPARISON OF CAPABILITIES OF ELEVEN SORBENTS TO ELEVATE pH AND TO ATTENUATE THIRTEEN TRACE ELEMENTS IN ILLINOIS BASIN COAL REFUSE LEACHATES[a]

Sorbent	pH	Fe	Al	Ni	Mn	Zn	Co	Cr	Cu	F	Cd	Na	K	Ca
$CaCO_3$	EEE	EEE	EEE	GG	EEE	EEE	GG	P	FF	GG	GG	P	P	P
AMD Treatment Sludge	EEE	EEE	EEE	EEE	GG	GG	GG	GG	GG	GG	P	P	P	o
Illite	EEE	EEE	GG	GG	GG	FF	GG	GG	GG	P	GG	P	o	o
Precipitator Ash	EEE	EEE	GG	GG	EEE	GG	GG	o	FF	P	GG	P	P	o
Montmorillonite	EEE	EEE	FF	GG	GG	GG	GG	GG	FF	GG	FF	o	P	FF
Bottom Ash	EEE	EEE	EEE	FF	P	GG	FF	GG	P	P	FF	P	P	o
SO_2 Scrubber Sludge	EEE	EEE	EEE	FF	P	P	P	FF	FF	o	o	P	o	o
Alabama Soil	FF	GG	P	P	o	P	P	GG	P	P	P	P	P	P
Bottom Slag	FF	P	FF	P	P	P	P	GG	P	P	o	P	P	P
Kaolinite	FF	GG	P	P	o	o	P	FF	o	P	o	P	P	P
Sea Sand	P	P	P	P	P	P	P	P	o	P	P	P	P	P

[a] EEE = > 100x Reduction
GG = 10 to 100x Reduction
FF = 3 to 10x Reduction
P = 0.5 to 3x Reduction
o = > 2x Increase

attenuate leachate contamination is somewhat more difficult to answer based on the data that we have obtained thus far. It is significant, however, that even those soils with essentially no acid-neutralizing capacity do attenuate many of the leachate contaminants somewhat. This observation lends credence to the postulate that both the alkalinity and ion-exchange capacity are important in determining the contaminant-attenuating properties of soils.

III. Treatment of the Contaminated Drainage

Our attention in this area has been given to pollution abatement techniques that have proved effective in treating acidic waste waters with compositions similar to coal refuse drainage. These techniques include alkaline neutralization, ion exchange and reverse osmosis. We also studied the effectiveness of using a variety of sorbents, such as clays, soils, and solid coal combustion by-products, on high-sulfur coal refuse leachates. In these studies we continued to give greatest emphasis to the control of the trace elements that we have identified in our previous studies as being of greatest concern in the drainages from Illinois Basin coal refuse.

All the drainage treatments were effective in reducing the concentrations of trace elements of environmental concern to acceptable levels. The results of these experiments and their ECT potentials are compared in Table X.

TABLE X

MATRIX GRID SUMMARY OF ENVIRONMENTAL CONTROL OPTIONS FOR CONTAMINATED COAL REFUSE DRAINAGE

Parameter	Alkaline Neutralization	Reverse Osmosis	Ion Exchange
Cost	low	moderate	moderate
Effectiveness	good	good	good
Process complexity	moderate	high	high
Treatment duration	very long	very long	very long
Permanency	poor	poor	poor
Likely RCRA Classification	hazardous	hazardous	hazardous

SUMMARY

Making a selection from among the various control options is by no means a straigh forward matter. The applicability of any of the control strategies must be evaluated in terms of the pertinent tradeoffs. For example, coal refuse calcining has excellent potential for preventing the release of trace elements from coal refuse piles and is a one-time treatment, but it is expensive. The slurry lime/limestone pretreatment appears to have great potential, and its economics are very attractive; however, the data proving the viability of the method over long time periods are just now bieng generated. Alkaline neutralization, is also low in cost. However, all the effluent from a given dump will have to be treated, and when the acid-regeneration capability of the high-sulfur waste is considered, the acid effluent from a given refuse pile might have to be treated for upwards of a hundred years. Taking several of the more important factors into consideration, we have generated a comparison of several of the control options in the form of the following grid. The options seem to be choices based primarily on economics and commitment to responsibility.

COMPARISON OF ENVIRONMENTAL CONTROL OPTIONS

Parameter	Calcining	Lime/Limestone	Codisposal	Alkaline neutralization
Cost	High	Low	Moderate	Low
Effectiveness	Good	Good	Good	Good
Complexity	High	Moderate	Moderate	Moderate
Treatment duration	Short	Short	Short	Long
Permanency	Good	Uncertain	Uncertain	Poor

In summary, our past laboratory studies that have examined in detail the sources of trace elements in coal waste drainages, the mechanisms of their release, and their fate upon weathering and leaching have allowed us to understand the problem sufficiently well to address the key environmental control technology issu effectively. A substantial portion of our efforts are now directed at identifying the most promising control options, demonstrating more clearly their utility, and analyzing their advantages and disadvantages.

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RECONNAISSANCE AND PROCESSING OF IMPOUNDED COAL WASTES IN ALABAMA

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The Mineral Resources Institute of The University of Alabama is conducting a study under a grant from the Department of Energy to sample, test and analyze fine coal impoundments in Alabama to determine the quantity of coal in place, and the quantity, and quality of recoverable coal in each impoundment.

The current washer waste from twenty-three coal preparation plants have been sampled to determine the quantity of waste and the amount of recoverable coal based on washability tests. The data indicate that about 1,725,000 tons of fine-size waste is being discarded each year, of which about 575,000 tons are recoverable as a clean coal product containing 6.4 percent ash, 13,850 BTU/lb., and 0.79 percent total sulfur.

Investigations are underway to survey the surface area and profile of the different waste impoundments. Twenty-four impoundments ranging in size from 1 to 34 acres in surface area have been surveyed. The largest impoundment is estimated to contain 2 million tons of fines, according to company records.

A drill sampling technique has been developed for obtaining representative samples from impoundments to insure true samples of waste fine coal at all depths to the bottom of the impoundments. A test tank was built that contained several layers of known amounts of coal, shale, and clay. Holes were drilled in the test tank, and drill samples taken for each four feet of depth in the tank. The drill hole samples checked within $\pm$ 10 percent of the analysis of the known material placed in the tank.

Drilling and sampling operations have been completed on waste fine impoundments in three areas. The impoundments were in the tonnage range of 200,000 to 500,000.

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RECONNAISSANCE AND PROCESSING OF IMPOUNDED COAL WASTES IN ALABAMA

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INTRODUCTION

Coal mining is the largest mining industry in Alabama. Production from Alabama mines in 1978 was about 18.5 million tons (down from 22.5 million tons in 1977).[1] Present projections forecast a steady increase in production, with tonnages almost doubling by 1985.[3] Approximately 13 million tons of coal were produced by strip mining methods in 1978, and about 5.5 million tons were produced by underground mining during the same period. Surface mining is expected to continue at about 14 million tons per year, but by 1985 underground coal mining is expected to increase to about 25 million tons.[2]

About 14 million tons per year of surface and underground mined coal are subjected to some means of washing and cleaning. The methods used are screening accompanied by heavy media separation, jigging, tabling, spiralling, and flotation. Some of the simpler approaches employ screening and jigging, or tabling. Except where flotation is used, the screen undersize fraction (finer than 0.25 inch in many instances) is rejected, with the result that 10 to 15 percent of the coal is lost. Thus, in the State of Alabama about 2 million tons of fine-size material are wasted annually in the fines which are impounded from treatment of coal.

The fine-size waste, currently being impounded, creates a number of environmental problems, including stream pollution by acid water drainage from the ponds. Reclamation of the fine-size waste would eliminate many of the environmental problems, and result in the conservation and development of additional natural resources in Alabama.

This investigation is part of a coal research program conducted by the Mineral Resources Institute and State Mine Experiment Station of The University of Alabama to investigate the feasibility of recovering fine-size coal from impounded coal wastes in Alabama.

PROGRAM PLAN

This investigation is being funded by the Department of Energy. The purpose of the study is to sample, test and analyze coal impoundments in Alabama to determine the quantity of coal in place, and the quantity, and quality of recoverable coal in each impoundment. The sampling and testing procedures being developed are expected to be applicable to the impoundments located in other coal producing states. A second objective of the work is to sample the washery wastes currently discharging into the impoundments, and to determine the quantity and quality of coal recoverable.

The program for drilling and sampling the waste coal impoundments involves the following phases:

1. Survey to determine the surface area and profile of each waste impoundment.
2. The impounded area is drilled on nominal 150 foot centers to the bottom of the pond.
3. Drill samples are taken in increments of each 10 feet of depth.
4. Bulk density samples are taken on each drill hole.
5. The individual drill samples are separated by heavy liquids at 1.40 and 1.60 specific gravity. The various heavy liquid fractions are analyzed for ash, BTU/lb., and total sulfur.
6. Upon completion of the drilling of each impounded area, a composite sample is made of all the drill holes. This sample is wet screened at 20, 40, 60, 100, and 200 mesh. Each screen fraction is separated in heavy liquids at 1.40 and 1.60 specific gravities. The minus 200 mesh fraction is also separated at 2.0 specific gravity. Each specific gravity fraction is analyzed for ash, BTU/lb., pyritic sulfur, and total sulfur.
7. A composite sample of all the drill holes is analyzed for proximate analysis, ultimate analysis, BTU/lb., pyritic sulfur and total sulfer, free swelling index, fusibility of ash, hardgrove grindability index, major elements in ash, and trace elements in ash.
8. The total tonnage and quality of recoverable coal is determined.

The final report on the project will contain the following data for each waste coal impoundment area:

1. Plan view of impoundment areas with drill hole locations.
2. Cross sections of impoundment areas.
3. Drill hole log.
4. Sink-float and chemical analysis of drill holes in increments of each 10 feet of depth.

5. Screen analysis and heavy liquid separation at various specific gravities of composite sample of each waste impoundment area. Chemical analysis of each specific gravity fraction.
6. A detailed analysis of each composite sample giving the complete physical and chemical properties.
7. A calculation of total tonnage and recoverable coal from each waste impoundment area.

SAMPLING AND EVALUATION OF CURRENT FINE-SIZE WASTE FROM PREPARATION PLANTS

Samples of fine-size waste currently being discharged were collected from twenty-three coal preparation plants in Alabama. This program has developed data to evaluate the quantity and quality of coal currently being wasted.

The data on the current fine-size waste coal were obtained by taking timed samples of the waste at each preparation plant. Additional sampling and operational data were supplied by the various mining companies. The data assembled from sampling of the twenty-three plants indicated that 1,714,000 tons of fine-size waste containing 568,180 tons of recoverable coal of high quality, are being discarded each year.

Analysis of the current fine-size wastes indicated 20 to 64 percent ash, 3,900 to 11,320 BTU/lb., and 0.79 percent total sulfur. Results of the composite samples are shown at the bottom of Table 1.

TEST TANK TO DETERMINE DEVIATIONS IN DRILLING

The function of the test tank was to develop and verify a sampling technique for obtaining representative samples from impoundments using power drilling equipment to ensure true samples of material at all depths down to the bottom of the impoundments.

An 8' x 8' x 20' test tank was built at one of the coal mining operations. The test tank was filled with five layers of known amounts of coal, shale, and clay. The drill should recover samples from the test tank with deviations of no more than $\pm$ 10 percent of the coal placed in the tank. Four holes were drilled in the test tank, and drill samples were taken for each four feet in depth in the tank. The drill samples were wet screened on 200 mesh and the screen fractions sink-floated at 1.40 and 1.60 specific gravities. The drill hole samples were composited and analyzed. A comparison of the material placed in the tank and the composite analysis of the drill hole samples is shown in Table 2. The drill hole samples checked very closely with the

Table 1 - Analysis of Current Fine-Size Waste from Alabama Coal Preparation Plants

Coal Seam	Total Fine-Size Waste				Recoverable Coal			
		Analysis, Percent				Analysis, Percent[1]		
	Annual Tonnage	Ash	Btu/lb.	Total Sulfur	Annual Tonnage	Ash	Btu/lb.	Total Sulfur
American (1)	88,000	59.7	4,964	0.59	8,480	6.6	13,820	1.10
American (2)	115,000	27.9	10,182	0.87	56,200	7.4	13,780	1.22
American, Pratt and Nickel Plant	84,000	37.8	8,749	1.11	37,300	7.4	13,720	1.50
Blue Creek (1)	29,000	40.5	7,975	0.94	10,600	5.1	13,980	0.86
Blue Creek (2)	32,000	28.7	9,620	1.01	18,500	7.2	13,720	0.74
Blue Creek (3)	98,000	42.5	6,569	0.73	38,500	9.2	13,520	0.80
Blue Creek (4)	97,000	56.7	5,261	0.45	22,700	11.4	13,694	0.63
Black Creek (1)	24,000	25.9	10,480	0.52	14,200	5.1	13,920	0.49
Black Creek (2)	68,000	41.7	7,523	0.67	29,200	3.6	14,350	0.68
Black Creek (3)	47,000	59.5	4,645	0.90	10,100	4.3	13,950	1.00
Black Creek (4)	90,000	31.8	7,502	0.87	33,700	3.8	13,936	0.61
Black Creek (5)	21,000	24.1	9,525	0.66	10,300	2.8	14,620	0.72
Carter, Brookwood	192,000	26.2	10,835	0.78	85,000	4.2	14,210	0.77
Mary Lee (1)	51,000	59.1	4,724	0.47	8,100	8.9	13,367	0.65
Mary Lee (2)	125,000	62.3	4,375	0.34	7,400	7.1	13,795	0.60
Mary Lee (3)	87,000	42.3	7,604	0.53	26,000	8.2	13,450	0.72
Mary Lee (4)	155,000	52.3	5,883	0.60	33,900	7.1	13,760	1.06
Mary Lee (5)	27,000	38.6	7,981	0.71	15,700	10.5	12,556	0.80
Mary Lee (6)	29,000	20.3	11,321	0.88	21,500	8.5	13,432	0.91
Pratt (1)	105,000	64.1	3,895	0.72	13,300	5.8	13,407	1.20
Pratt (2)	98,000	40.0	8,250	0.92	45,500	5.5	14,490	0.90
Rosa	32,000	40.8	8,232	0.85	10,700	4.2	14,310	0.75
Woodstock	20,000	55.2	5,593	1.32	11,300	9.7	13,100	0.91
Composite Analysis	1,714,000	43.9	7,050	0.72	528,180	6.4	13,850	0.79

[1]Float at 1.60 specific gravity.
[2]Numbers in parenthesis indicate samples from the same coal seam taken at different preparation plants.

Table 2 - Analysis of Fine-Size Waste Coal in Test Tank

Samples	Analysis of samples placed in test tank				Analysis of composite drill samples in test tank			
	Direct Percent		Cumulative Percent		Direct Percent		Cumulative Percent	
	Weight	Ash	Weight	Ash	Weight	Ash	Weight	Ash
First Layer 0-4 ft.								
Plus 200 mesh								
Float 1.40 sp. gr.	17.8	4.8	17.8	4.8	18.3	5.1	18.3	5.1
Float 1.60 sp. gr.	4.4	23.7	22.2	6.4	4.2	24.4	22.5	8.0
Sink 1.60 sp. gr.	20.9	70.9	43.1	37.8	21.2	72.9	43.7	39.8
Composite plus 200 mesh			43.1	37.8			43.7	39.8
Minus 200 mesh								
Float 1.40 sp. gr.	0.0	--	--	--	0.0	--	--	--
Float 1.60 sp. gr.	0.0	--	--	--	0.0	--	--	--
Sink 1.60 sp. gr.	56.9	44.8	56.9	44.8	56.3	41.9	56.3	41.8
Composite minus 200 mesh			56.9	44.8			56.3	41.8
Composite Feed			100.0	41.8			100.0	41.0
Second Layer 4-8 ft.								
Plus 200 mesh								
Float 1.40 sp. gr.	25.3	4.6	25.3	4.6	24.3	4.7	24.3	4.7
Float 1.60 sp. gr.	4.4	20.7	29.7	7.0	4.3	22.1	28.6	7.3
Sink 1.60 sp. gr.	5.2	74.6	34.9	17.1	5.5	75.3	34.1	18.3
Composite plus 200 mesh			34.7	17.1			34.1	18.3
Minus 200 mesh								
Float 1.40 sp. gr.	0.0	--	--	--	0.0	--	--	--
Float 1.60 sp. gr.	12.9	27.0	12.9	27.0	12.2	26.3	12.2	26.3
Sink 1.60 sp. gr.	52.2	35.4	65.1	33.7	53.7	36.2	65.9	34.3
Composite minus 200 mesh			65.1	33.7			65.9	34.3
Composite Feed			100.0	27.9			100.0	28.8
Third Layer 8-12 ft.								
Plus 200 mesh								
Float 1.40 sp. gr.	19.2	5.8	19.2	5.8	18.6	5.6	18.6	5.6
Float 1.60 sp. gr.	6.7	23.4	25.9	10.3	7.0	23.6	25.6	11.4
Sink 1.60 sp. gr.	34.3	79.5	60.2	49.7	33.4	78.1	59.0	48.7
Composite plus 200 mesh			60.2	49.7			59.0	48.7
Minus 200 mesh								
Float 1.40 sp. gr.	0.0	--	--	--	0.0	--	--	--
Float 1.60 sp. gr.	8.9	20.1	8.9	20.1	8.6	21.4	8.6	21.4
Sink 1.60 sp. gr.	30.9	79.5	39.8	66.2	32.4	74.6	41.0	63.4
Composite minus 200 mesh			39.8	66.2			41.0	63.4
Composite Feed			100.0	56.3			100.0	54.8
Fourth Layer 12-16 ft.								
Plus 200 mesh								
Float 1.40 sp. gr.	19.3	4.4	19.3	4.4	20.1	4.6	20.1	4.6
Float 1.60 sp. gr.	4.9	20.4	24.2	7.6	4.6	22.4	24.7	7.8
Sink 1.60 sp. gr.	20.6	79.8	44.8	40.8	18.2	78.5	42.9	38.0
Composite plus 200 mesh			44.8	40.8			42.9	38.0
Minus 200 mesh								
Float 1.40 sp. gr.	0.0	--	--	--	--	--	--	--
Float 1.60 sp. gr.	13.8	13.5	13.8	13.5	13.5	13.7	12.7	13.7
Sink 1.60 sp. gr.	41.4	36.4	55.2	30.7	30.7	35.9	57.1	30.9
Composite minus 200 mesh			55.2	30.7	30.7		57.1	30.9
Composite Feed			100.0	35.2	35.2		100.0	33.9
Fifth Layer 16-20 ft.								
Plus 200 mesh								
Float 1.40 sp. gr.	18.5	5.0	18.5	5.0	17.7	5.1	17.7	5.1
Float 1.60 sp. gr.	5.7	20.3	24.2	8.6	5.4	20.6	23.1	8.7
Sink 1.60 sp. gr.	27.5	78.6	51.7	45.8	27.1	77.8	50.2	46.0
Composite plus 200 mesh			51.7	45.8			50.2	46.0
Minus 200 mesh								
Float 1.40 sp. gr.	0.0	--	--	--	0.0	--	--	--
Float 1.60 sp. gr.	12.1	37.0	12.1	37.0	11.5	38.5	11.5	38.5
Sink 1.60 sp. gr.	36.2	39.5	48.3	38.9	38.3	39.8	49.8	39.5
Composite minus 200 mesh			48.3	38.9			49.8	39.5
Composite Feed			100.0	42.5			100.0	42.7

analysis of the known material placed in the tank. With very few exceptions the analyses checked within ± 10 percent.

FIELD DRILLING OPERATIONS

The drill rig used in the exploratory program is a Simco Model 4000 TR-1 hydraulically operated, cat mounted rig with 1 1/2 pounds per square inch ground pressure. It is equipped with a wire line hoist assembly for handling drill rod and sampling tools and a cat head used for operation of 140 pound hammer to advance the AW drill rod and sampler assembly. The drill rig is shown in figures 1a and 1b. Hollow augers are used to advance the drill hole as sampling proceeds. The augers are in 5 foot lengths and have an inside diameter of 2 1/4 inches which accommodates sampling tools and drill rod and has an outside diameter of 5 inches. The cutting head has an outside diameter of 6 inches. The hole is started by advancing the appropriate sampler approximately 2 feet using the AW rod and 140 pound hammer. One section of the hollow auger is then advanced 2 feet in the hole and the sampler is again driven 2 feet in advance of the auger. As the hole advances additional sections of auger are added and sampling continues until the original ground surface is encountered at the bottom of the hole.

Two types of sampling tools are used. The split tube sampler is used in firmly packed material while the plunger type sampling tube is used in soft slushy material. The split tube sampler is designed for taking samples at the bottom of a cleaned bore hole by the drive weight method. The split section 24 inches long, is held together with a ball check head section and a hardened steel drive shoe. The ball check feature in the head prevents samples from being washed out of sampler upon withdrawal from the hole and the head has a standard thread for attachment to the AW drill rod. Details of the split tube sampler are shown in Figure 2. The plunger type sampler features a stationary piston, that is, the piston remains stationary as the outer tube of the sampler is pushed ahead into the fine wet silt. The piston creates a suction on the sample assisting it into the sample tube. The sampler features a vacuum release and cone clamp assembly that prevents the piston from pushing out the sample upon recovery. After extraction from the hole the cone clamp assembly is then released by loosening the piston rod and the sample is extruded into an air tight sample bag by advancing the piston rod. Details of the plunger type sampler are shown in Figure 3.

Investigations now are underway to survey the surface area and profile of the different waste impoundments. Twenty-four impoundments ranging in size from 1 to 34 acres in surface area have been surveyed. The largest impoundment is estimated to contain over 2 million tons of fines, according to company records.

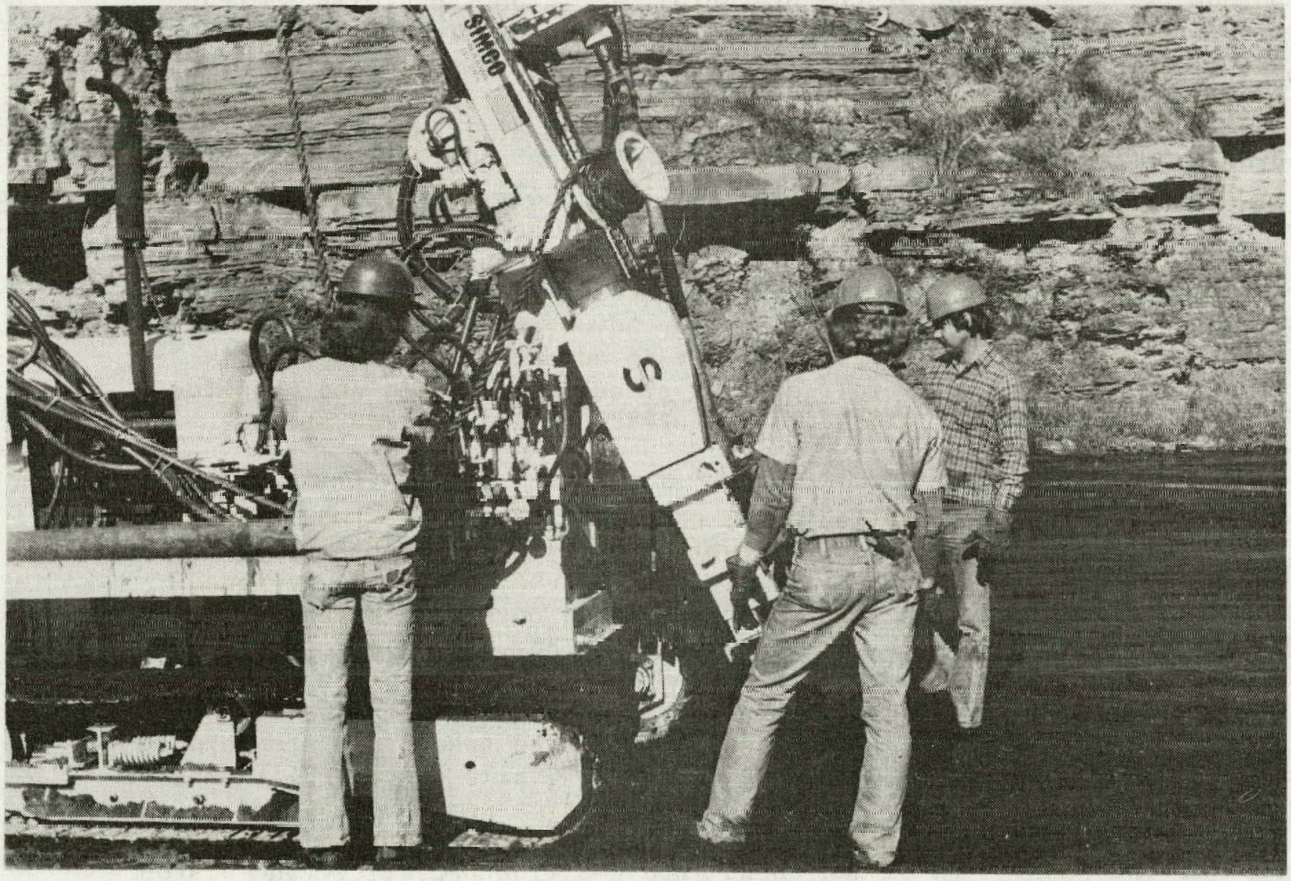


Figure 1a - Hydraulically operated drill rig in operation at waste fine coal impoundment area.

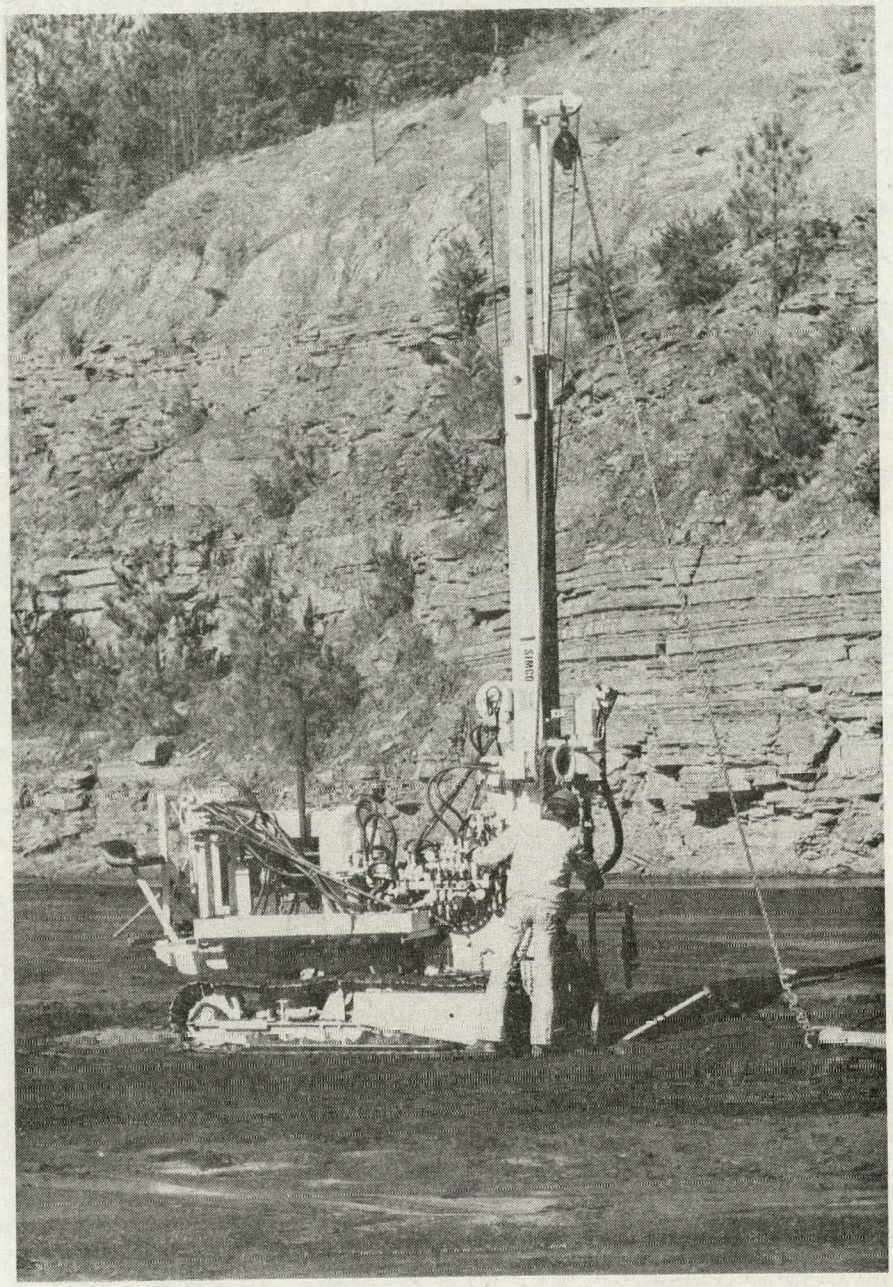


Figure 1b - Hydraulically operated drill rig in operation at waste fine coal impoundment area.

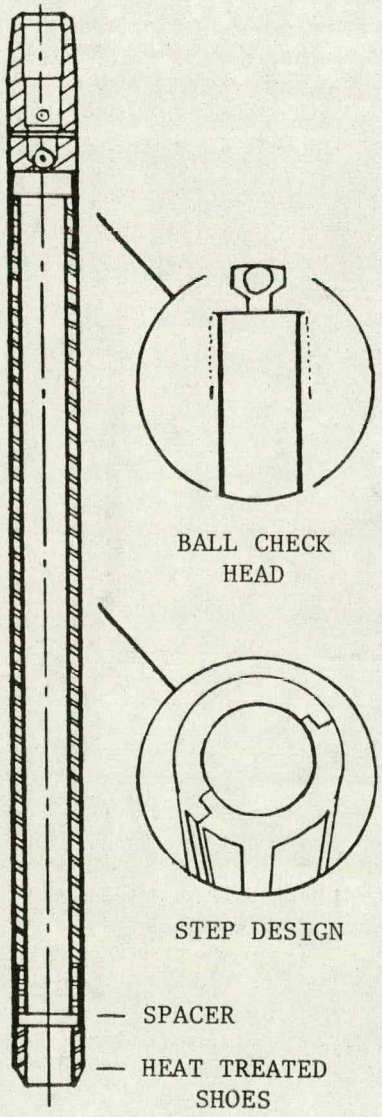


Figure 2 - Split Tube Sampler

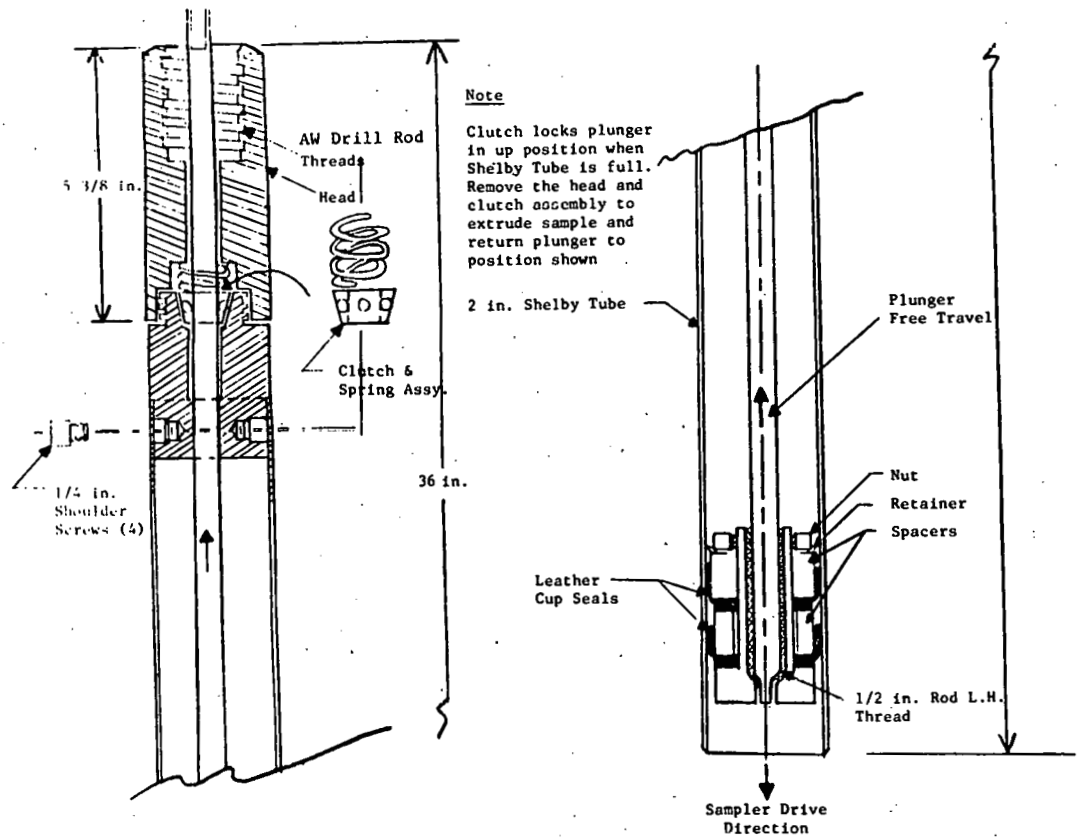


Figure 3 - Plunger Type Sampler

During the past three months the drill rig was in operation drilling the waste fines at three different mining operations. The areas that were drilled included the following coal seams: Mary Lee, Woodstock and Thompson, and American, Pratt and Nickel Plate. The waste fine coal impoundments were in the tonnage range of 200,000 to 500,000.

Heavy liquid analysis of the composite drill sample of the Woodstock-Thompson seams waste impoundment indicates that over 40 percent of the total weight is recoverable in a clean coal product analyzing 6.4 percent ash, 0.65 percent total sulfur, and 13,705 BTU/lb. at 1.60 specific gravity. Detailed results of analysis of the composite sample are shown in tables 3 and 4. The raw tonnage, estimated at 235,000 tons, was derived from drill hole locations and bulk density samples of each drill hole. The tonnage of recoverable clean coal from the impoundment is about 95,000 tons.

CONCLUSIONS

The data assembled from sampling of the various coal preparation plants in Alabama indicate that about 1,714,000 tons of fine-size waste are being discarded each year in Alabama, containing over 528,000 tons of recoverable coal. Clean coal products containing as little as 3 percent to as much as 11 percent ash can be obtained by heavy liquid separation. Fine coal which had been wasted in the past can readily be recovered as a clean commercial grade product by the use of gravity separation.

A drilling technique has been developed for obtaining representative samples from impoundments to insure true samples of waste fine coal at all depths to the bottom of the impoundments. Drilling and sampling have been completed on waste fine impoundments in three areas.

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1. Alabama Department of Public Relations, Division of Safety and Inspection, Annual Statistical Report, Fiscal Year 1977-1978, 68 pp.

2. Hunter, Thomas W., Effects of Air Quality Requirements on Coal Supply, Bureau of Mines, Mineral Industry Surveys, 1977, pp. 13-18.

3. Ward, Willard, E., II, and Francis E. Evans, Jr., Coal-Its Importance to Alabama. Geological Survey of Alabama, Information Series 53, 1975, 26 pp.

Table 3 - Analysis of Composite Drill Sample from the Woodstock, Thompson Seams Waste Coal Impoundment

Screen Size Mesh	Direct, Percent					Cumulative, Percent				
	Weight	Ash	BTU/lb.	Pyritic Sulfur	Total Sulfur	Weight	Ash	BTU/lb.	Pyritic Sulfur	Total Sulfur
Plus 20 mesh										
Float 1.40 sp. gr.	14.1	3.4	14,383	0.00	0.63	14.1	3.4	14,383	0.00	0.63
Float 1.60 sp. gr.	1.1	23.1	10,935	0.30	1.54	15.2	4.8	14,134	0.01	0.71
Sink 1.60 sp. gr.	4.5	78.8	1,386	0.95	1.38	19.7	21.7	11,221	0.22	0.86
Composite plus 20 mesh	19.7					19.7	21.7	11,221	0.22	0.86
Plus 40 mesh										
Float 1.40 sp. gr.	5.9	3.4	14,339	0.09	0.58	25.6	17.5	11,940	0.19	0.80
Float 1.56 sp. gr.	0.8	22.7	10,992	0.55	0.98	26.4	17.6	11,911	0.30	0.80
Sink 1.60 sp. gr.	3.9	75.5	1,992	1.54	1.58	30.3	25.1	10,634	0.37	0.90
Composite plus 40 mesh	10.6					30.3	25.1	10,634	0.37	0.90
Plus 60 mesh										
Float 1.40 sp. gr.	5.7	3.5	14,037	0.11	0.61	36.0	21.6	11,173	0.33	0.85
Float 1.60 sp. gr.	0.7	25.8	10,403	0.52	1.06	36.7	21.7	11,158	0.33	0.85
Sink 1.60 sp. gr.	4.9	63.8	4,617	1.02	1.45	41.6	26.7	10,383	0.41	0.92
Composite plus 60 mesh	11.3					41.6	26.7	10,383	0.41	0.92
Plus 100 mesh										
Float 1.40 sp. gr.	4.4	3.4	13,894	0.18	0.62	46.0	24.4	10,723	0.39	0.78
Float 1.60 sp. gr.	0.6	32.0	9,463	0.49	0.82	46.6	24.6	10,707	0.39	0.78
Sink 1.60 sp. gr.	3.8	58.4	5,884	0.63	1.20	50.4	27.1	10,541	0.41	0.81
Composite plus 100 mesh	8.8					50.4	27.1	10,541	0.41	0.81
Plus 200 mesh										
Float 1.40 sp. gr.	5.8	4.5	13,742	0.10	0.57	56.2	24.8	10,694	0.37	0.78
Float 1.60 sp. gr.	1.6	32.5	9,868	0.16	0.67	57.8	25.0	10,671	0.37	0.78
Sink 1.60 sp. gr.	4.5	54.7	5,637	1.11	1.55	62.3	27.1	10,307	0.42	0.83
Composite plus 200 mesh	11.9					62.3	27.1	10,307	0.42	0.83
Minus 200 mesh										
Float 1.40 sp. gr.	0.0	----	------	----	----	----	----	------	----	----
Float 1.60 sp. gr.	0.0	----	------	----	----	----	----	------	----	----
Sink 1.60 sp. gr.	37.7	56.5	5,637	0.74	0.89	37.7	56.5	5,608	0.74	0.89
Composite minus 200 mesh	37.7					37.7	56.5	5,608	0.74	0.89
Composite Feed	100.0					100.0	38.2	8,535	0.54	0.90

Table 4 - Analysis of Composite Drill Sample from Woodstock-Thompson Seams at Various Specific Gravities

Product	Direct, Percent					Cumulative, Percent				
	Weight	Ash	Btu/lb.	Pyritic Sulfur	Total Sulfur	Weight	Ash	Btu/lb.	Pyritic Sulfur	Total Sulfur
Composite Float 1.40 sp. gr.	35.9	3.6	14,257	0.06	0.60	35.9	3.6	14,157	0.06	0.60
Composite Float 1.60 sp. gr.	4.8	27.6	10,326	0.35	0.98	40.7	6.4	13,793	0.09	0.65
Composite Float 2.0 sp. gr.	22.4	35.8	8,975	0.43	1.04	63.1	16.8	12,082	0.21	0.78
Composite Sink 2.0 sp. gr.	36.9	74.8	2,450	1.12	1.24	100.0	38.2	8,530	0.54	0.90
Composite Feed	100.0					100.0	38.2	8,530	0.54	0.90

COAL DESULFURIZATION: APPLICATION OF BASIC RESEARCH IN SULFUR CHEMISTRY TO PROCESS RESEARCH AND DEVELOPMENT

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One of the main problems arising from the more extensive utilization of coal is that it contains sulfur in concentrations ranging from 0.2 to 10 weight per cent.[1] Because of the impact of SO_2 on the environment, a large percentage of coals will require pre- or post-combustion desulfurization treatments, and a substantial portion of the coal preparation effort at the Ames Laboratory is in the development of desulfurization technology. The ultimate objective of this effort is to discover a highly efficient, low cost process for desulfurizing large quantities of coal.

There are basically three kinds of desulfurization techniques: physical methods such as crushing and gravity separation; physico-chemical treatments such as chemical comminution and froth flotation; and chemical processes such as oxidative leaching. This paper will focus on the contributions of Ames Laboratory to the development of the latter techniques. In particular, a description of the Organosulfur Studies underway at the Ames Laboratory will be used as a vehicle for elucidating the role of the chemist in coal desulfurization research and development.

The organosulfur project can be viewed as consisting of four closely interrelated research areas:

1. Determination of the forms and concentrations of sulfur in coal, especially organic sulfur including the organosulfur functional group distribution (FGD);
2. Evaluation of the effectiveness of oxydesulfurization process, i.e. determining the fate of organic sulfur during processing;
3. Improvement of processes which are currently in use by adding catalysts, modifying reaction conditions, and/or using new techniques such as sonication;
4. Investigation of new organosulfur chemistry to gain more information about the organosulfur FGD or to develop new desulfurization processes.

Sulfur is present in coal in three forms: elemental, inorganic (pyritic and sulfatic), and organic. Although there are a number of physical and physico-chemical beneficiation processes for removing some forms of sulfur from coal, there are two types of sulfur that cannot be removed by these procedures. One of these is microfine pyrite crystals which are randomly distributed and encapsulated in the coal matrix[2] and are not amenable to removal by conventional physical methods. The other type, organic sulfur, is present in concentrations ranging from 0.5 to 4.0 weight per cent and usually comprises from 20 to 70 per cent of the total sulfur in coal.[3] These latter sulfur atoms are chemically bound to carbon and thus are an integral part of the organic coal matrix. As a consequence, organic sulfur is extremely difficult to remove; and highly selective chemical reagents will be required to remove this form of sulfur without chemically and thermally degrading the coal. Because organic

sulfur is usually much less reactive than pyritic sulfur, chemical desulfurization procedures which were originally developed to remove pyritic sulfur have been minimally effective in removing organic sulfur.

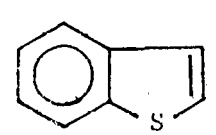
One of the major limitations in evaluating the effectiveness of coal desulfurization processes is the lack of accurate analytical methods for determining sulfur in coal. The greatest difficulty is encountered in the qualitative and quantitative analysis of organic sulfur. At two standard deviations (95% confidence level), the precision of analysis of organic sulfur by the ASTM method was found to be ±25%.[4] It is likely that the sample to sample accuracy is ±40%. Consequently it is extemely difficult to evaluate the effectiveness of a desulfurization technique by analyzing the organic sulfur content of a coal before and after processing.

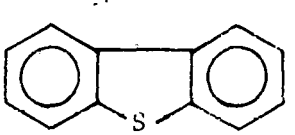
Methodology for the qualitative analysis of organic sulfur in coal is just as crude. Even though some progress has been made in determining the nature of organosulfur components in coal, there is still very little information detailing the identity of even the functional group distribution of these sulfur moities.[5] Specific organosulfur compounds such as methyl thiophenes and dibenzothiophenes have been isolated by vacuum distillation (or pyrolysis) of a high volatile bituminous coal at 150°C.[6] However, these materials were identified as an incidental consequence of investigating other types of compounds in coal. Efforts have also been made to delineate the organosulfur functional group distribution through chemical and physical properties although the bases for these studies were generally obscure. The best of these methods,[7] which is based on the reactions of sulfides and mercaptans with methyl iodide, was developed in 1936. Furthermore, nitrogen bases, which are also present in coal, will interfere with this analysis for organic sulfur forms.

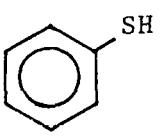
EVALUATION OF THE AMES PROCESS

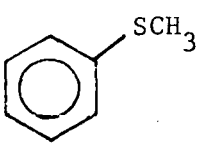
When this project was initiated, there was an urgent need for an evaluation of the effectiveness of oxydesulfurization processes in removing organic sulfur from coal. Therefore during the initial phases of this investigation, it was assumed that a definitive knowledge of the organosulfur functional group distribution was not a prerequisite for investigating the viability of a chemical desulfurization procedure. In these initial evaluations, valuable information was obtained by determining the effect of the Ames Process on a representative series of organosulfur compounds.

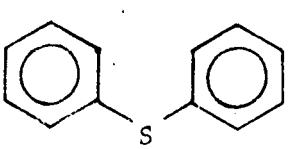
The following organosulfur compounds have been subjected to Ames Process conditions (150°C, 200 psi O_2, 0.2M aqueous Na_2CO_3, 1 hour) either by themselves

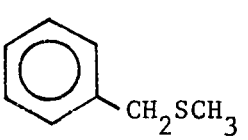


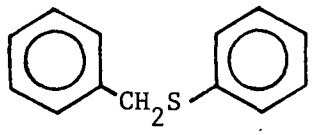










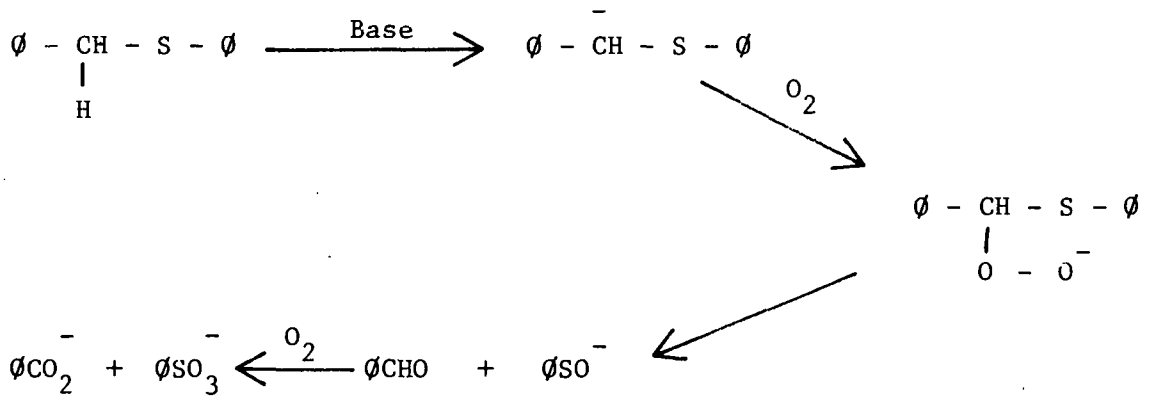


$(n\text{-}C_8H_{17})_2S$

or in the presence of coal. To provide a basis for comparison of the results, the model sulfur compounds which were processed in the presence of coal were also processed with coal under a nitrogen atmosphere, i. e. no oxygen present. The results of these experiments are summarized in Tables I and II.

From the results in Table I and II, it is clear that, of the model compounds that were studied, only thiophenol and compounds containing a benzylic sulfide linkage reacted. Thiophenol was converted to phenyl disulfide which was resistant to further oxidation. Benzyl phenyl sulfide was oxidized and cleaved to give benzaldehyde, benzoic acid and benzenesulfonic acid; benzyl methyl sulfide gave similar results. The other model compounds were unreactive under the Ames Process conditions either by themselves or in the presence of coal. Even in the presence of coal, more than 70% of the non-benzylic sulfides was recovered. The reduced recoveries of all compounds in the presence of coal (see Table I) were attributed to adsorption of the organosulfur material by the microporous structure of coal and the mechanical loss associated with working up the reaction mixture. This hypothesis was confirmed by the correspondingly low recoveries of starting sulfides from reactions run in the presence of coal under nitrogen atmosphere--an inert atmosphere. Furthermore, no oxidation products were detected in the reaction mixtures. Clearly, of the compounds investigated thus far, only benzyl sulfides and thiophenol reacted under Ames Process conditions; and the two benzyl sulfides were the only compounds in which carbon sulfur bond cleavage occurred.

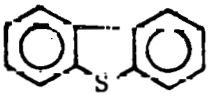
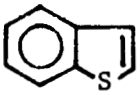
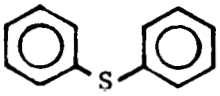
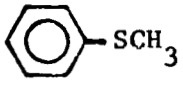
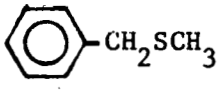
The base-catalyzed reaction of benzylic sulfides with molecular oxygen has been studied under a variety of conditions. Wallace *et. al.*[8] reported that the oxidation of benzyl phenyl sulfide at 80°C with oxygen in the presence of potassium *t*-butoxide afforded benzoic acid. These authors proposed the following reaction scheme to explain the product:



We believe that similar reactions are occurring under Ames Process conditions.

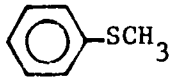
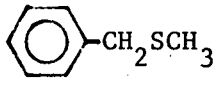
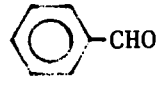
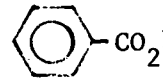
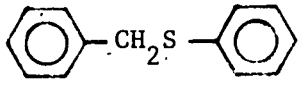
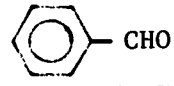
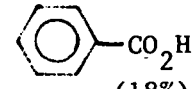
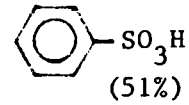
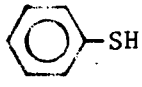
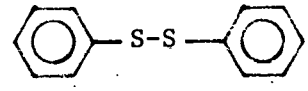
Conceptually, oxydesulfurization has been described[9] as a two-step process which can be represented by the following chemical equations: selective

TABLE I. EFFECT OF AMES PROCESS[a] ON MODEL ORGANOSULFUR COMPOUNDS

COMPOUND	RECOVERED YIELD (%) OF STARTING SULFIDE		
	Model Cmpd. Only	Lovilia Coal Added N_2	Lovilia Coal Added O_2
	96	83	76
	87	--	--
	98	76	74
	89	--	--
$(n\text{-}C_8H_{18})_2S$	90	--	82
	36	75	13

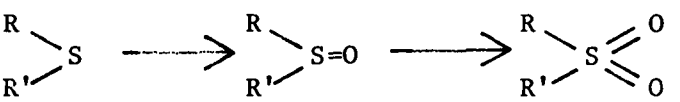
[a]Process Conditions: 150°C, 200 psig O_2, 0.2M aq. Na_2CO_3, 1 hour.

TABLE II. EFFECT OF AMES PROCESS[a] ON MODEL ORGANOSULFUR COMPOUNDS

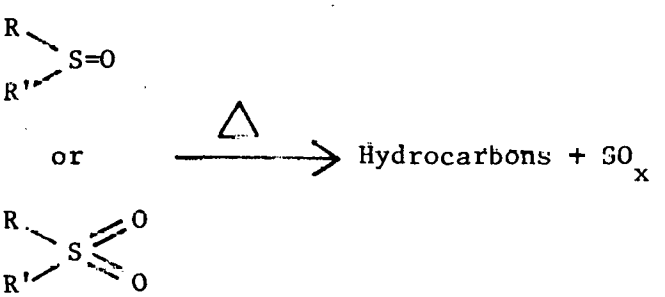
COMPOUND	RECOVERED YIELD (%) OF STARTING SULFIDE	PRODUCT (% YIELD)
	89%	None Detected
	36%	 (23%)  (34%) CH_3SO_3H
	29%	 (31%)  (18%)  (51%)
	0%	 (70%)

[a]Process Conditions: 150°C, 200 psig O_2, 0.2M aq. Na_2CO_3, 1 hour.

Step 1.

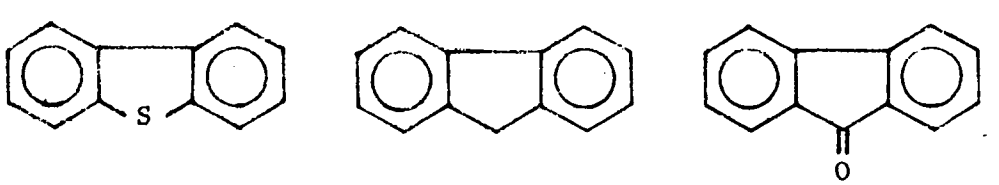


Step 2.



oxidation of the sulfur to sulfoxides and sulfones with the latter as the most likely product; and thermal decomposition of the oxidation products, preferably under basic conditions. In this formulation, the overall reaction is initiated by oxidation of the sulfur and, in fact, is made possible by this oxidation which results in polarization and weakening of the carbon to sulfur bonds.[9]

We have found no evidence to support this formulation of the Ames Process; oxidation of the sulfur was detected only in thiophenol and in the benzyl sulfides. In the first case, oxidation of mercaptans to disulfides is a well known, facile reaction which occurs under conditions such as the Ames Process. No further oxidation of the disulfide was detected. In the latter case, carbon-sulfur bond cleavage was apparently initiated by oxidative attack at the benzylic carbon-hydrogen bond instead of at sulfur. This theory is supported by more recent experiments in which mixtures of dibenzothiophene (DBT), and fluorene, 2, were subjected to Ames Process conditions. Although DBT was recovered unchanged (86% recovery) only 45% of the fluorene was recovered; 27% of the fluorene had been oxidized to fluorenone, 3.



1 2 3

The substantial impact of this discovery is apparent when one considers the hypothetical bituminous coal structure shown in Figure 1. Of the four sulfur atoms present in this "molecule," only one of them is attached to a

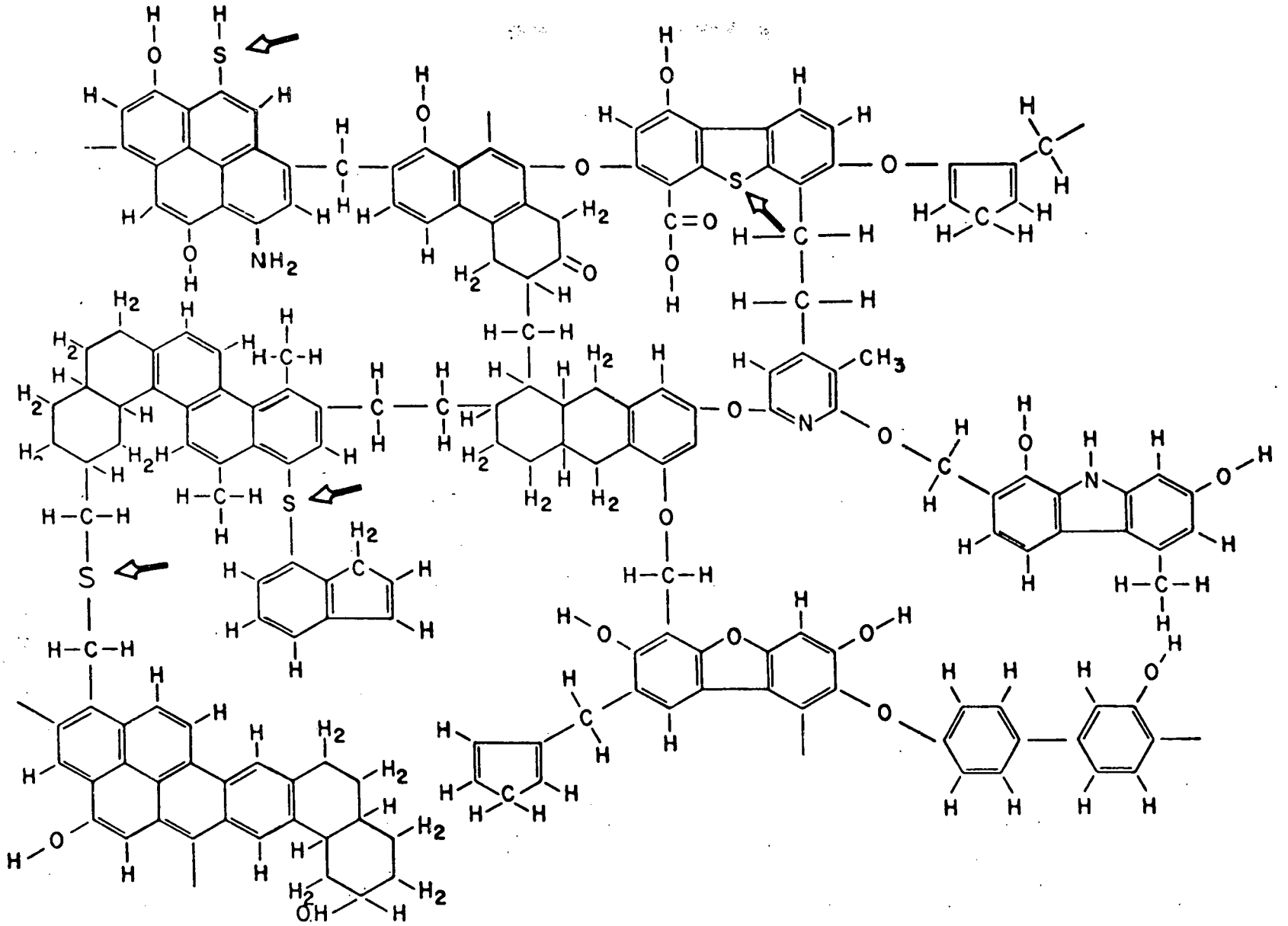
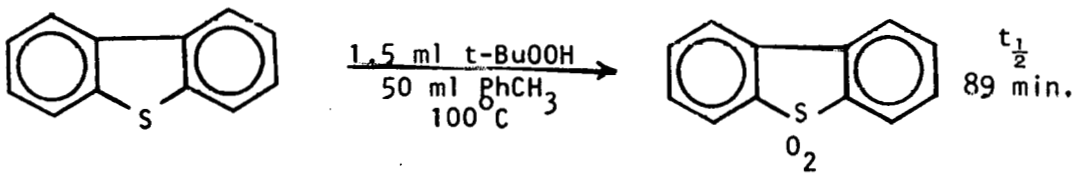


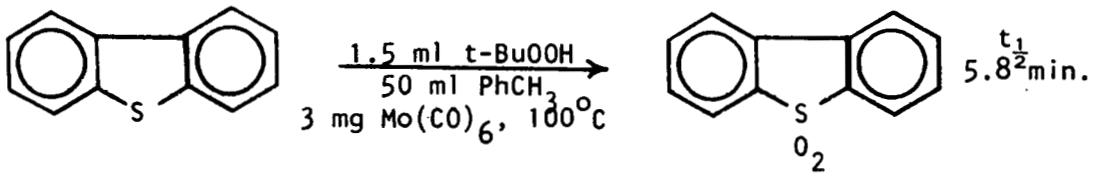
Figure 1. Schematic representation of structural groups and connecting bridges in bituminous coal.

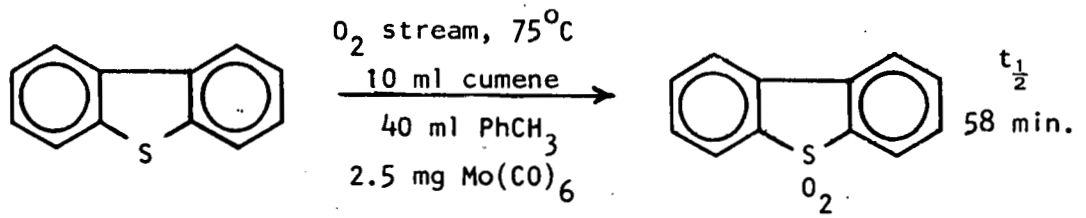
benzylic carbon and, thus, could be removed by the Ames Process. On the other hand, there are more than twenty benzylic positions in this structure which could be susceptible to oxidation. Oxidation of all of these benzylic carbon-hydrogen bonds could result in a significant loss of heating value.

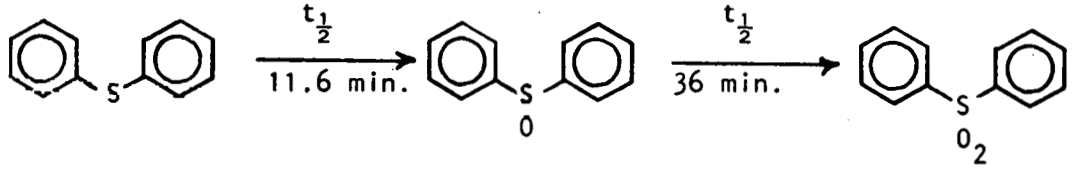
OXIDATION OF ORGANOSULFUR COMPOUNDS UNDER MODIFIED AMES PROCESS CONDITIONS

Another of our primary objectives has been to develop reaction conditions for the efficient conversion of organic sulfides to the oxidized products (Step 1 of the Ames Process) using moderate temperatures and pressures. Our initial experiments were conducted in toluene rather than water. Under these conditions our reaction mixtures were homogeneous, and the results were reproducible. Thus far, we have been able to efficiently oxidize dibenzothiophene, phenyl sulfide, and phenyl disulfide under the following conditions:

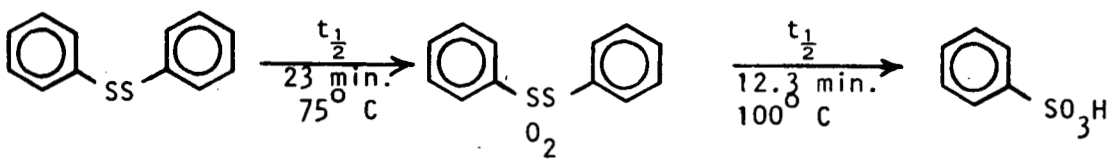
1. 

2. 

3. 

4. 

Reaction Conditions: 3.1 ml t-BuOOH, 50 ml $PhCH_3$, 6 mg $Mo(CO)_6$, 75°C

5. 

Reaction Conditions: 13 ml t-BuOOH, 50 ml $PhCH_3$, 12 mg $Mo(CO)_6$

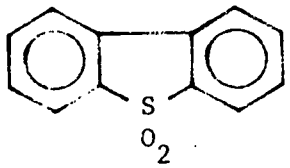
On the basis of our experiments, and from results reported in the literature, we have reached the following conclusions:

1. Organic sulfides can be effectively oxidized to sulfones using alkyl hydroperoxides in organic solvents.
2. In the absence of added hydroperoxide, these same sulfides can be oxidized just as effectively by bubbling a stream of oxygen through the organic solvent provided a substance such as cumene or tetralin is present. These substances are known to readily form hydroperoxides in the presence of oxygen, and thus they provide a method for the in situ generation of hydroperoxides.
3. The rates of both the molecular oxygen and hydroperoxide oxidations can be increased by a factor of 10 to 15 by the addition of $Mo(CO)_6$.
4. $Mo(CO)_6$ and $ZrCl_4$ are effective oxidation catalysts in non-aqueous media but we have been unable to specifically oxidize organic sulfur under aqueous conditions.

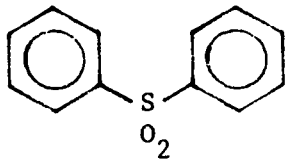
Thus, it appears that extensive molecular oxidation of the organic sulfur in coal to sulfones and sulfonic acids can be accomplished under mild conditions, but only in non-aqueous media. Under these conditions, the reaction would probably be catalyzed by $Mo(CO)_6$.

REACTIONS OF SULFONES

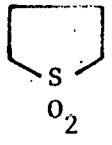
Simultaneously, we have been probing reactions of sulfones under conditions similar to those of the Ames Process in order to discover a desulfonylation method (Step 2 of the Ames Process). As expected, sulfones were completely inert under Ames Process conditions. In fact, absolutely no desulfonylation was detected for the following compounds when subjected to any of the conditions listed below.



4



5

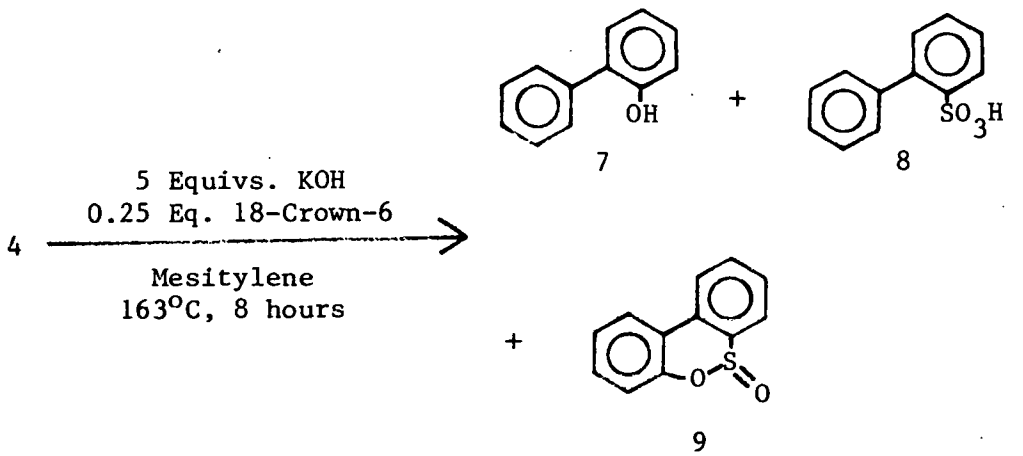


6

Conditions

1. 0.2M Na_2CO_3 in 80% v/v EG:H_2O, 130°C, 20 hours.
2. 0.2M NaOH (or KOH) in EG, 190°C, 20 hours.
3. 0.4M NaOH in H_2O, 225°C, 20 hours.

However, when sulfone 4 was reacted with five equivalents of potassium hydroxide in refluxing mesitylene, the sulfone disappeared after 20 hours. By adding 0.25 equivalents of 18-Crown-6 ether (a phase transfer reagent for solubilizing potassium hydroxide), the reaction time was reduced to eight hours; and three products were identified as indicated by the following equation:



Compounds 7 and 8 have been previously reported as products from the reaction of 4 with potassium hydroxide at much higher temperatures.[8] The sultine, 9, has not been previously reported and represents a potential breakthrough in our desulfonylation studies. We have isolated 9 in yields as high as 26 per cent; and it does not appear to be a precursor to the phenol or the sulfonic acid. The sultine is far more reactive than the sulfone, 4, and, on this basis, would desulfurize more readily in this form.

CONCLUSIONS

Studies of the basic chemistry of organic sulfur compounds under process conditions is a valuable tool for process evaluation and improvement. Our studies show that the alkaline leaching of coal under air pressure readily removes pyritic sulfur, but is likely to affect only one particular functional type of organic sulfur compounds. Moreover, conditions severe enough to oxidize additional classes of organic sulfur compounds will likely oxidize the carbon-hydrogen structure of coal and significantly decrease heating value.

New chemistry on each of the two steps of oxydesulfurization, (1) oxidation and (2) desulfonylation, has been found. Catalytic formation of organic hydroperoxides under process condition gives a new oxidant which allows organic sulfur to be oxidized selectively. By use of phase-transfer reagents, the reaction of dibenzothiophene sulfone with potassium hydroxide can be accomplished at temperatures lower than those observed by previous workers. A new intermediate product was discovered. Exploitation of its chemistry may allow the development of milder conditions for dibenzothiophene desulfurization.

Basic studies of the chemistry of other desulfurization methods should be equally successful. Each advance in fundamental knowledge of the chemistry of underlying processes will allow the systematic development of improved methods.

ACKNOWLEDGEMENTS

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CHEMICAL COAL CLEANING

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U. S. Department of Energy, Pittsburgh Energy Technology Center

Paper not submitted for publication in Proceedings.

SULFUR AND ASH REDUCTION IN COAL BY MAGNETIC SEPARATION*

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I want to discuss magnetic preparation of dry crushed coal in the context of its potential role as one of the unit operations in the overall coal preparation process. Therefore, I will first discuss physical coal preparation in general.

The Bureau of Mines *Report of Investigation 8118*[1] presents rather comprehensive washability data for 455 channel samples of coals of the United States. I will use here their averages of 227 samples from the Northern Appalachian region. The averages for the total U.S. samples are quite similar.

Figure 1 displays ash reduction as a function of the specific gravity of separation and the top size of the sample being separated. The yield or Btu recovery is not displayed here but can be determined from the detailed washability data. These two sources show that at least half of the ash can be removed from these coals with a Btu recovery in excess of 90%. These channel samples averaged 15.1% ash. Thus, physical preparation of the some 500×10^6 tons of coal burned by utilities this year could reduce by 40×10^6 tons the amount of ash shipped, pulverized, blown through a boiler, removed by precipitators, and pumped to ash pits. This 40×10^6 tons is a conservative estimate because run-of-mine coal typically contains 3 to 10% more ash than channel samples.

Figure 2 displays the sulfur reduction in terms of pounds of SO_2 generated per million Btu as a function of specific gravity of separation and top size of the sample being separated. Again, we see that physical preparation can remove an average of about 45% of the SO_2 with a Btu recovery in excess of 90%. This sulfur reduction would make only a small percentage of these coals into compliance fuels. However, since these coals average 4.8 lb of SO_2 per 10^6 Btu, physical preparation of the some 500×10^6 tons of coal burned by utilities this year could reduce the SO_2 created by 13×10^6 tons. This in turn could reduce by at least 30×10^6 tons per year the limestone to be mined, transported, crushed, slurried, and fed to scrubbers. It could also reduce by at least 36×10^6 dry tons per year the scrubber waste for disposal (Table 1).

Figure 3 illustrates one deep beneficiation method that can achieve these reductions and recoveries. A separation of the coarse coal (1-1/2-in. top size) will yield an average coarse coal product containing about 50% of the Btu with the ash reduced about 70% and the sulfur reduced about 50%. A second

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*Research sponsored jointly by the Division of Fossil Fuel Extraction, U.S. Department of Energy and the Tennessee Valley Authority, Division of Energy Demonstration and Technology, under contract W-7405-eng-26 with the Union Carbide Corporation.

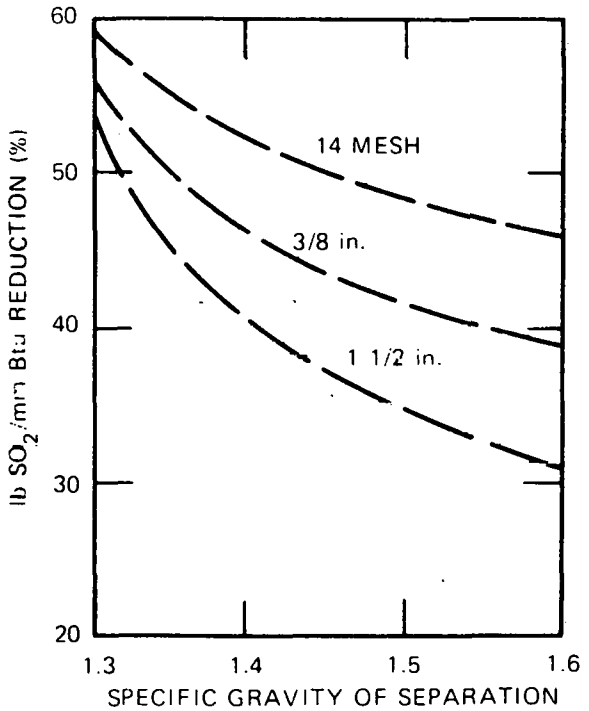


Fig. 1.

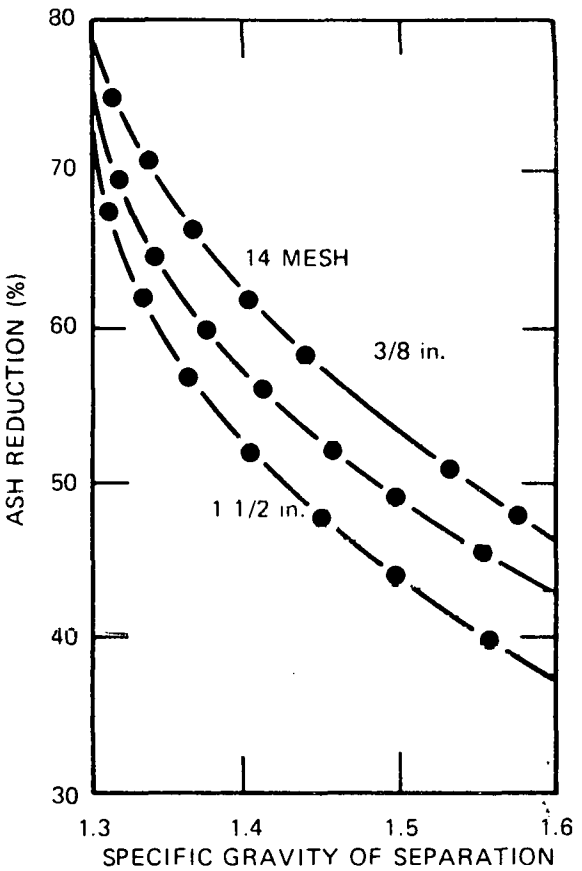


Fig. 2.

NORTHERN APPALACHIAN REGION (227 SAMPLES)

THE EFFECT OF CRUSHING TO 1-1/2-in., 3/8-in., AND 14-MESH TOP SIZE ON THE REDUCTION OF ASH, PYRITIC SULFUR, TOTAL SULFUR, AND POUNDS SO_2 EMISSION PER MILLION Btu AT VARIOUS SPECIFIC GRAVITIES OF SEPARATION FOR THE NORTHERN APPALACHIAN REGION COALS.

THE AVERAGE RAW COAL OF THE REGION CONTAINED 15.1% ASH AND WOULD PRODUCE 4.8 lb $SO_2/10^6$ Btu FIRED AT THE POWER PLANT.

separation at a specific gravity of 1.6 will yield a middlings containing most of the remaining Btu and a coarse refuse containing about 6% of the Btu, 40% of the ash, and 30% of the sulfur. The middlings are then crushed to 14 mesh and separated at a specific gravity of 1.6. The coarse and fine product combined will yield over 90% of the Btu with an ash reduction of 50% and a sulfur reduction of 45%. Thus, deep beneficiation usually requires some fraction of the coal to be crushed and prepared as fine coal, and magnetic preparation of dry fine coal is being developed as an alternative to existing wet fine coal processes.

There is adequate evidence[2-4] to convince me that physical preparation of steam coal is economic in the hard engineering power production costs of transportation, maintenance, availability, and capacity as well as being an

Table 1. Reduction of power plant wastes achievable by physical preparation of steam coal[a]

Reduction	Amount of reduction
Ash generation, tons per year	40×10^6
SO_2 generation, tons per year	13×10^6
Limestone consumption, tons per year	30×10^6
Scrubber waste (dry weight), tons per year	36×10^6
Pulverizer maintenance cost, dollars per year	20×10^6

[a]Assumptions:

- 500×10^6 tons of steam coal burned per year,
- U.S. average analysis of raw coal ash and sulfur,
- U.S. average washability of raw coal,
- Stack gas scrubbing with limestone at 1.4 stoichiometric,
- Average pulverizer maintenance cost of $0.50/ton.

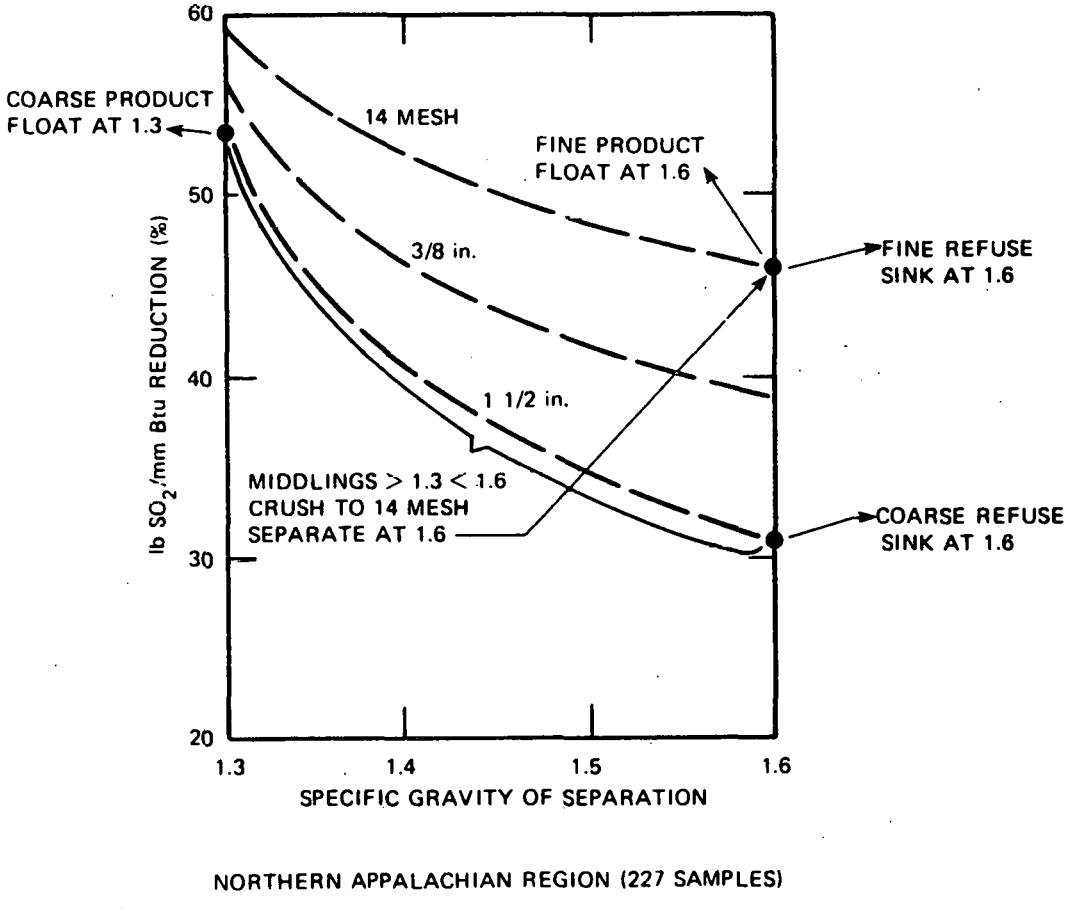


Fig. 3. A deep beneficiation technique, yielding a mix of coarse coal and fine coal product.

economic tactic in the emission control strategy. Furthermore, it is my opinion that, considering the associated costs throughout the coal production and use system, dry preparation of fine coal will be more economic than wet preparation. In this context we are pursuing the development and commercialization of both high-gradient magnetic separation and open-gradient magnetic separation.

High-gradient magnetic separation of coal depends on the fact that the iron pyrite and much of the other inorganic contaminants in coal are weakly paramagnetic; that is, they are weakly attracted into a magnetic field. A batch, high-gradient magnetic separator (HGMS) can consist of a solenoid with its core cavity filled with a filamentary or expanded metal mesh, as shown schematically in Fig. 4. A typical mesh is shown in Fig. 5. Each wire or element of the mesh becomes a small magnet with a high field gradient that attracts and traps weakly magnetic particles. The assembly behaves as a magnetic filter. If crushed coal is fed into such a device as shown in Fig. 6, the clean coal will pass through, and much of the inorganic material will be trapped. When the magnet is turned off, the inorganics will fall out as in Fig. 7. Such batch devices are adequate for laboratory testing, but a continuous machine is more suitable for separation at production rates. A continuous carousel type machine is shown schematically in Fig. 8. In these machines the mesh passes continuously through the magnetized cavity so that the product coal can pass directly through, while the trapped inorganics are carried out of the field and released separately. Such machines are commercially produced for the minerals industry with capacities of up to several hundred tons of feed per hour.

We have performed a large number of batch separation tests[5] on several coals to determine the appropriate values for each of the many parameters controlling the process. Although it is unlikely that we have yet optimized all of the parameters, we are now able to repeatedly obtain good separations on the coals and size fractions tested. The separations of a −100 +200 mesh fraction of a Western Kentucky seam No. 9 coal are shown in Fig. 9. The sulfur remaining in the product is plotted against the Btu recovery along with a plot of gravimetric separation of the same coal and size fraction at specific gravities of 1.3, 1.4, 1.5, 1.6, and 1.7 for comparison. The close similarity of the data argues that the HGMS is about as effective as the gravimetric process and can remove essentially all of the liberated pyrite at a Btu recovery of about 95%. The ash data for these same separations are displayed in Fig. 10 and show that while the HGMS was not quite as effective in these tests as the gravimetric separator, it did remove over half the ash. It is likely that some of the inorganics are not sufficiently magnetic to be trapped, and it is also possible that we have not yet tested the best possible set of conditions. A similar series of tests with a Pennsylvania Lower Freeport Coal also achieved sulfur reductions equaling and ash reductions approaching those of the gravimetric process.

Using the design information developed in that series of batch tests the continuous separation machine has been set up as shown in Fig. 11 to test continuous separation at a 1-ton/h feed rate. The Tennessee Valley Authority (TVA) and Pennsylvania Power and Light, who are participating with the Department of Energy (DOE) in this program, have supplied 25 tons of Kentucky No. 9 and Lower Kittaning steam coals, respectively, for testing. These coals have

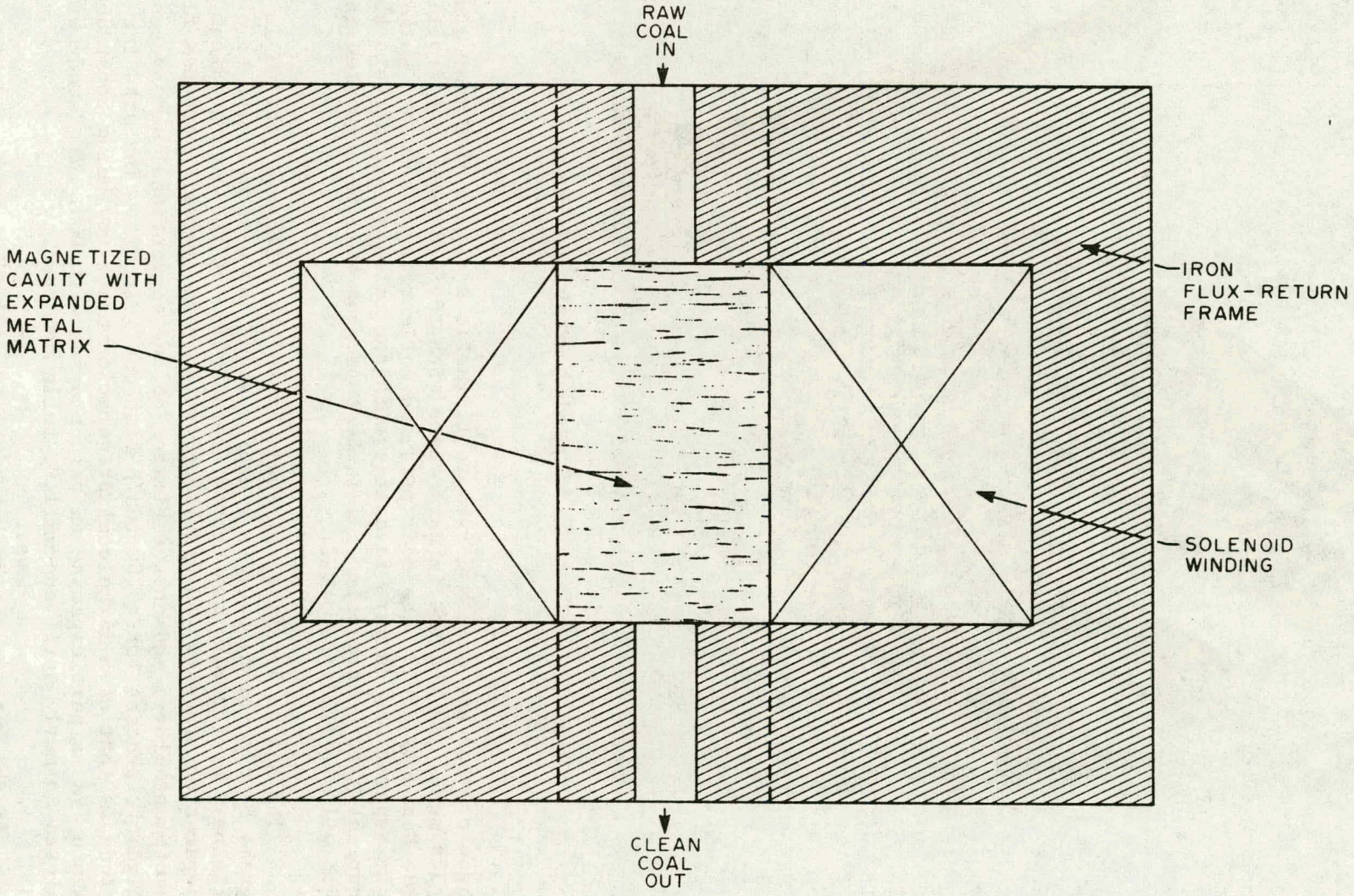


Fig. 4. High-gradient magnetic separator.

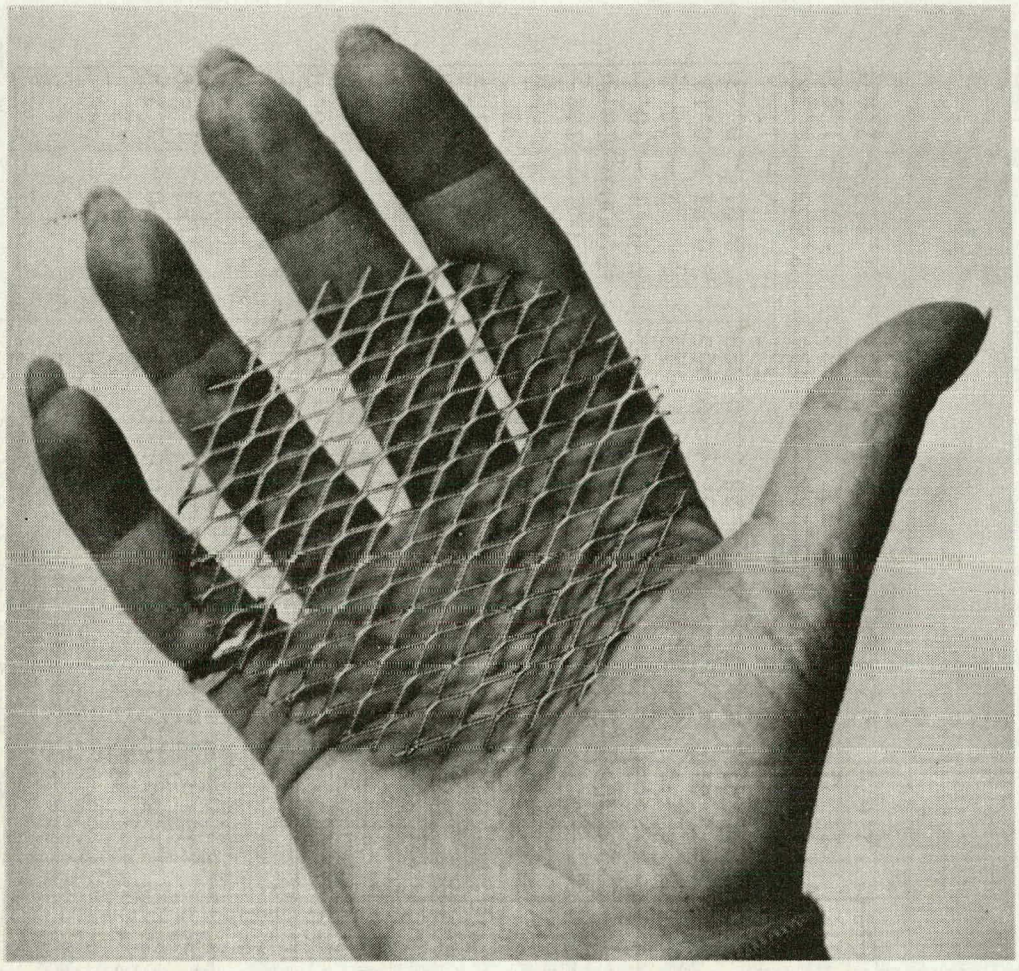


Fig. 5. Expanded metal mesh disk.

been crushed and screened into test fractions of −28 +100 mesh and −100 +325 mesh. In the preliminary tests with the −28 +100 mesh fraction of the Kentucky No. 9, the coal feed and collection systems are working well, and the separations compare favorably with the batch solenoid tests being run concurrently for correlation. This test program will be completed in early April and will be fully reported.

The design information developed in the batch and continuous test programs is also being used in a design study and cost estimate to obtain a preliminary engineering and economic evaluation of the high-gradient magnetic separation process. An architect-engineer is preparing process flow sheets, equipment lists, and cost estimates of the conventional wet processes and the magnetic process for a 200-ton/h fine coal circuit. The site for the design study is that of a large coal preparation plant now being constructed by TVA. Again TVA is participating in this program with DOE. The study will be completed in early April and will be fully reported.

If the outcome of the 1-ton/h tests and the engineering-economic evaluations are favorable, a 10- to 20-ton/h demonstration plant will be constructed

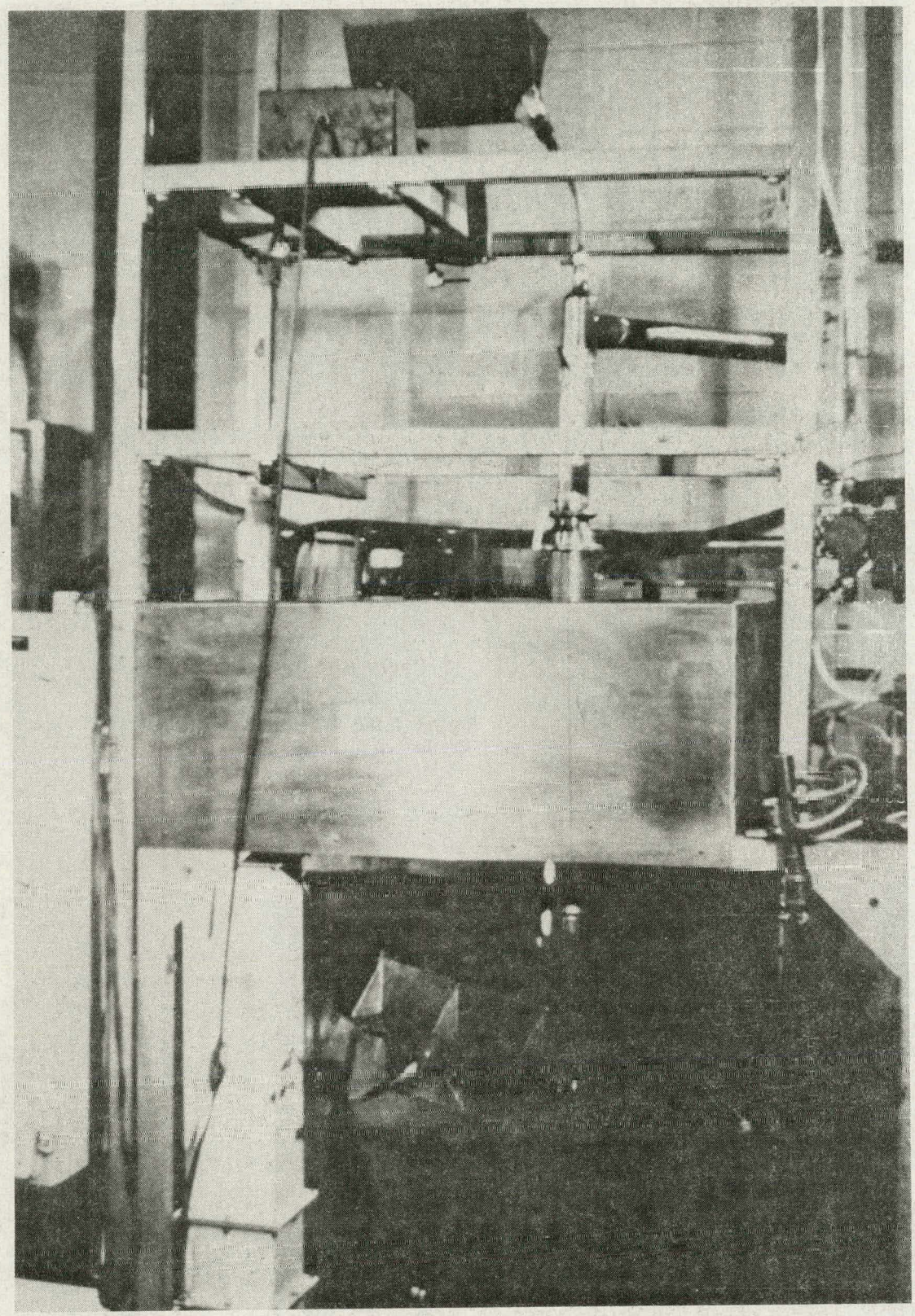


Fig. 6. HGMS test setup.

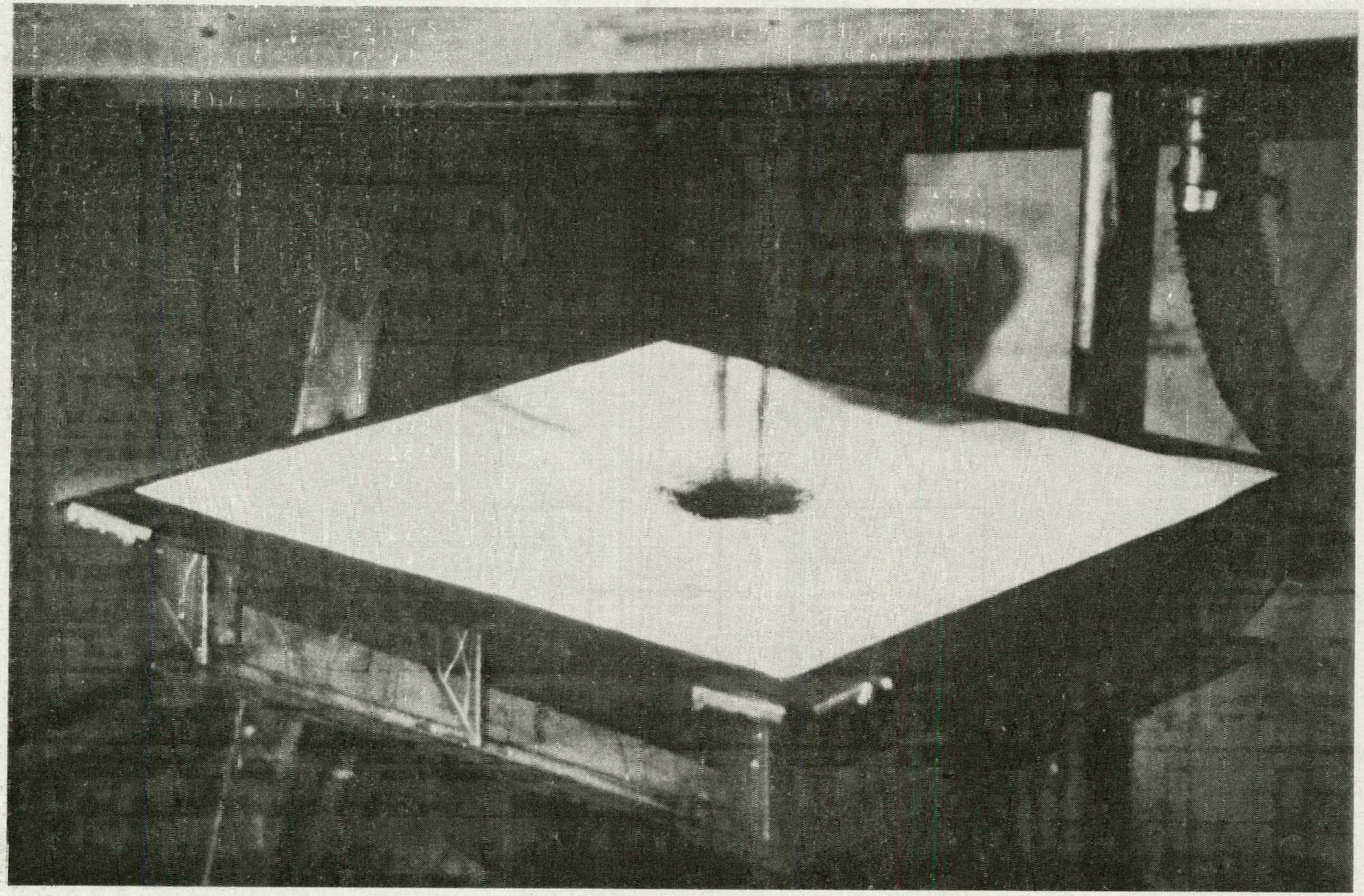


Fig. 7. Release of inorganics.

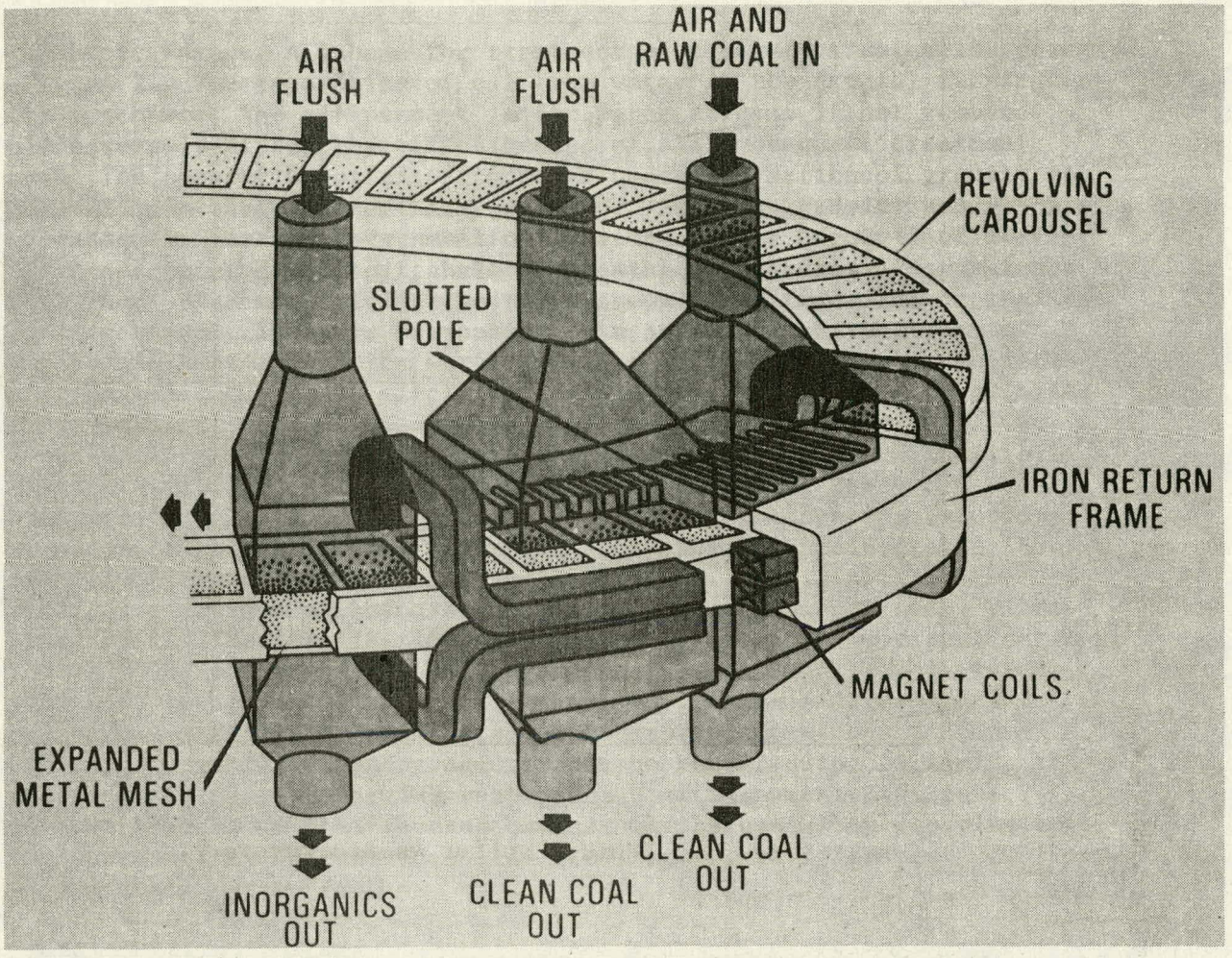


Fig. 8. Continuous separation in a carousel magnetic separator.

and operated in a utility or industrial environment with the participation of utilities and industries.

Open-gradient magnetic separation is able to use not only the force attracting the inorganic or mineral particles into the magnetic field, as in the HGMS, but also the force repelling the organic or coal particles out of the field. The forces are about equal in magnitude but are opposite in sign. If a stream of crushed coal falls through a cavity having a properly shaped magnetic field, the clean coal particles will be deflected to decreasing field, and the mineral particles will be deflected to increasing field, spreading the stream into a spectrum. If that spectrum is split at the proper point, then the bulk of the pyrite and ash can be conducted off in one stream and the bulk of the clean coal in the other. Since particles are not trapped in a magnetized mesh, the process is one of simple continuous flow with no moving machinery required. A means to accomplish this separation on a laboratory scale is illustrated schematically in Fig. 12. We have demonstrated[6] separations in such a device equaling in yield and quality the gravimetric separations of identical samples. Since open-gradient separation is possible at this time only in small laboratory machines, it must be considered only as a

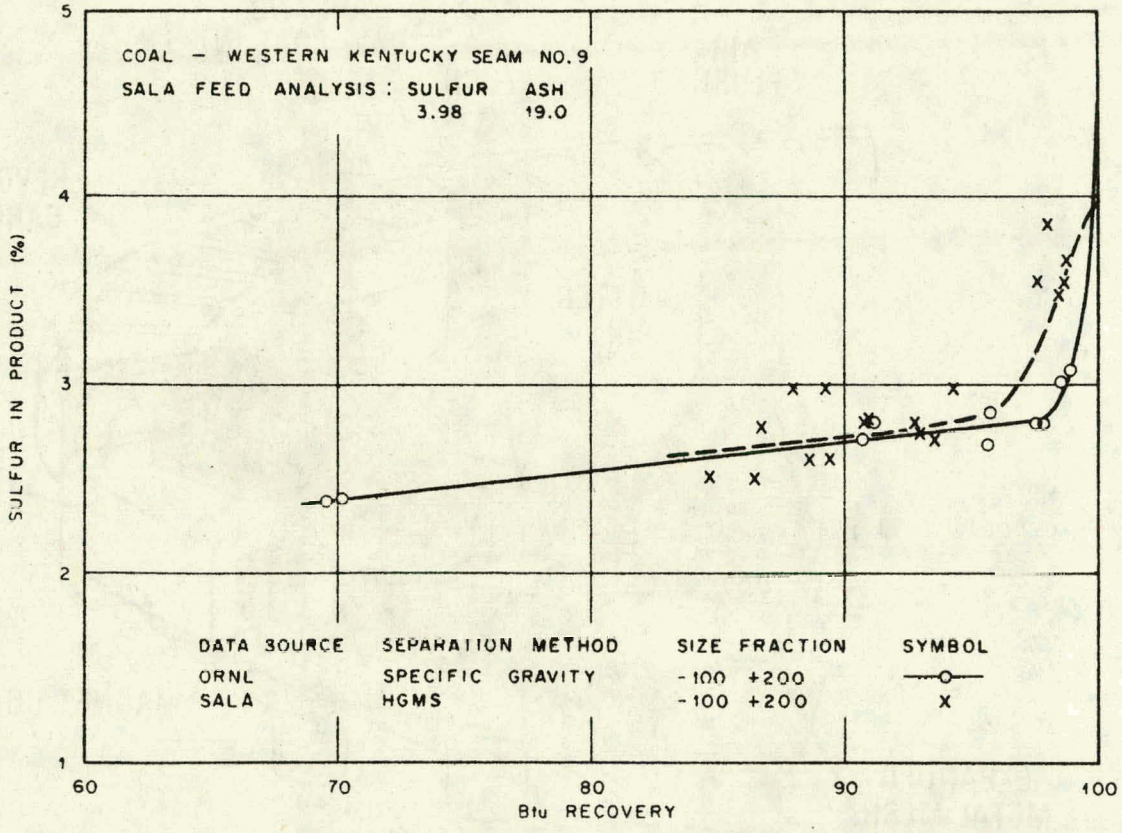


Fig. 9. Product sulfur vs Btu recovery.

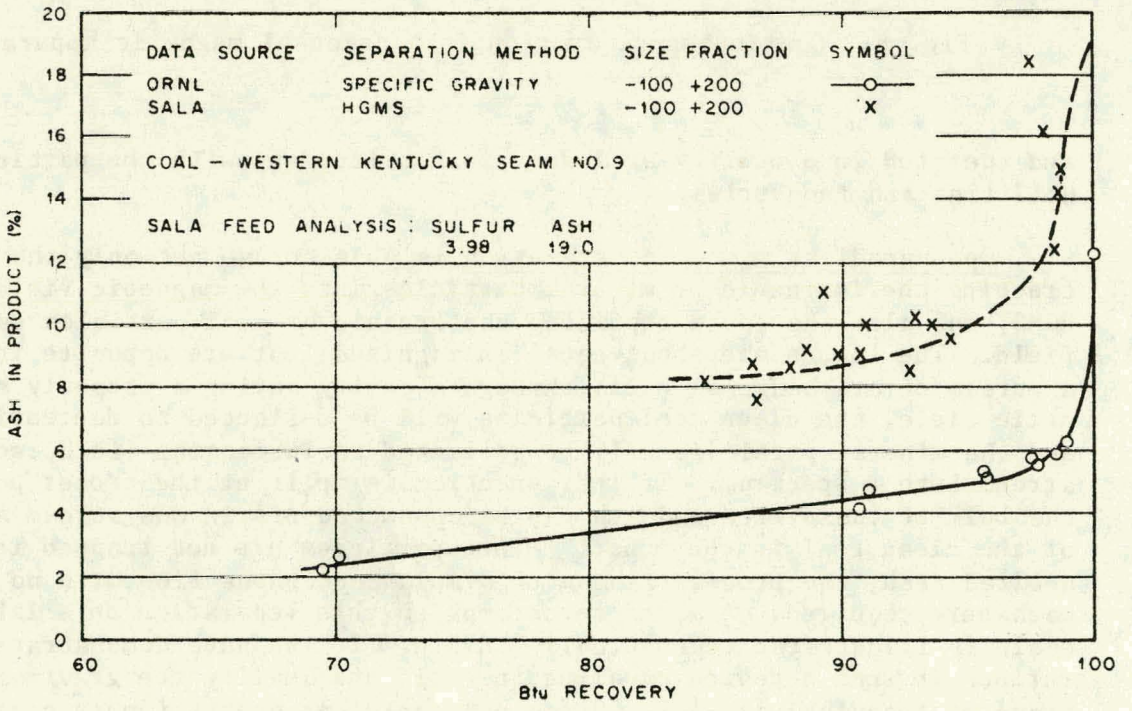


Fig. 10. Product ash vs Btu recovery.

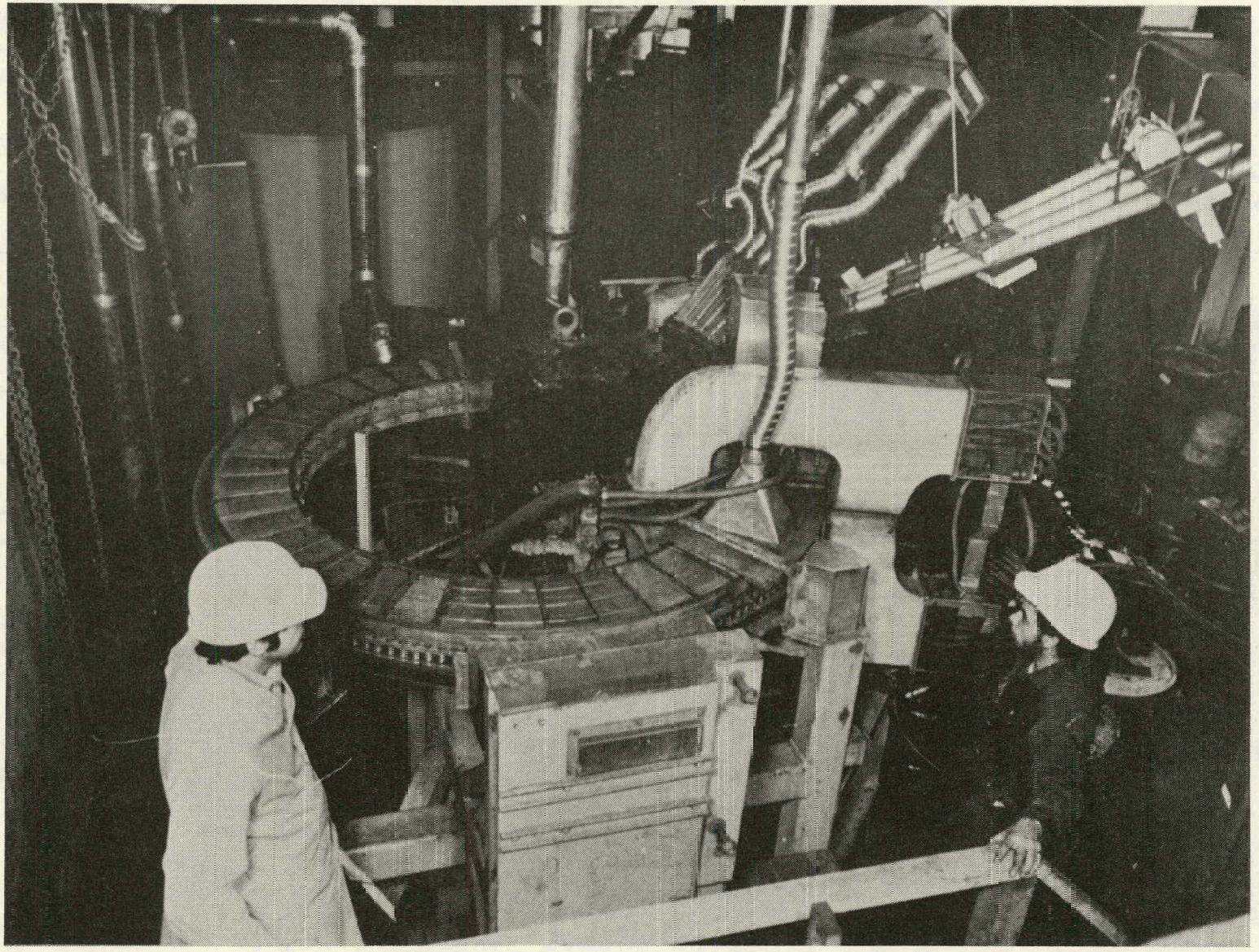


Fig. 11. Continuous separation experimental arrangement.

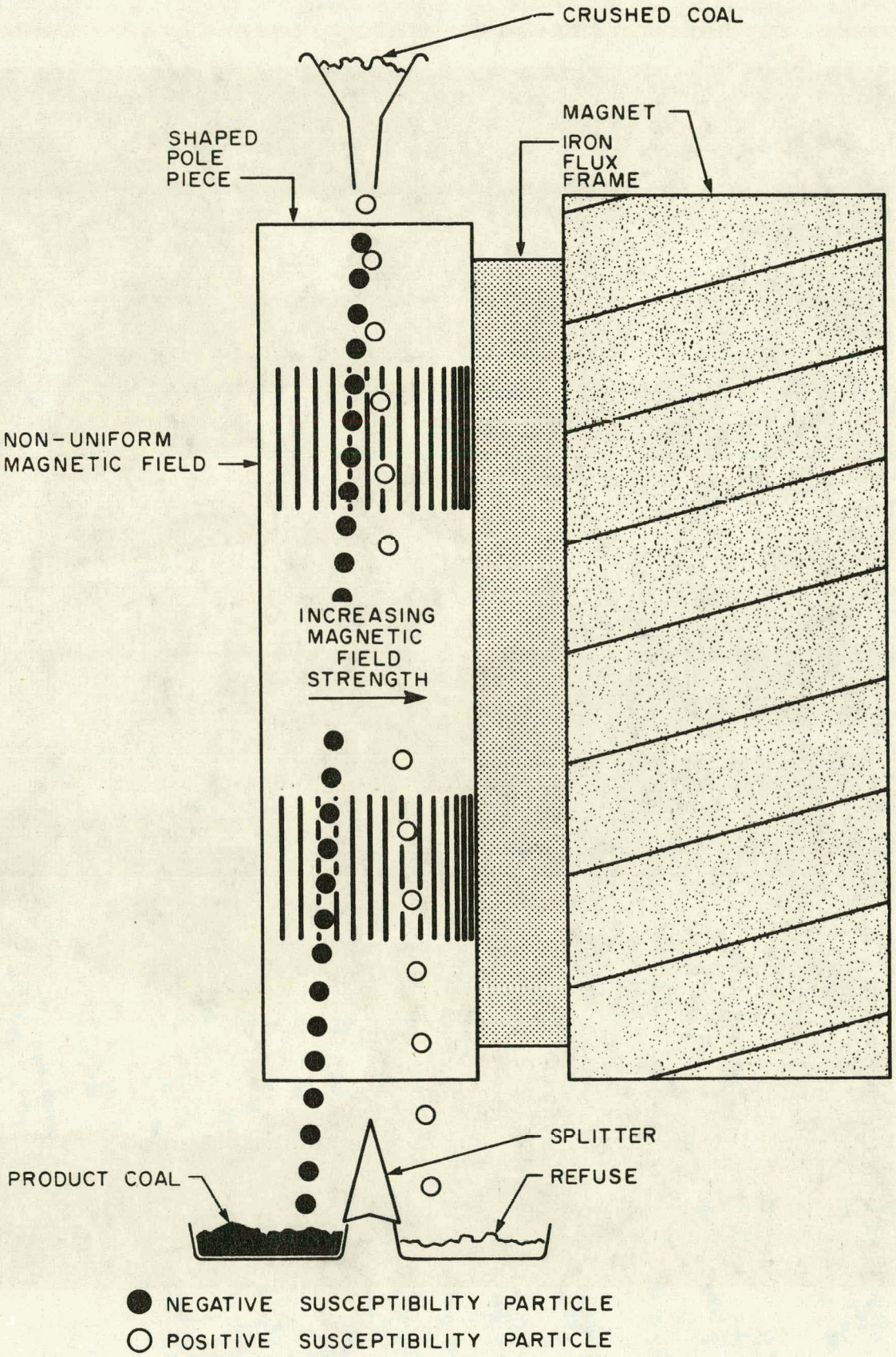


Fig. 12. Schematic of open-gradient separator.

laboratory process useful for assaying the magnetic separability of coals. However, we have measured the parameters controlling this process, have constructed therefrom a mathematical model, and are able to predict the forces and separations achievable by magnets of various configurations and sizes. It now appears possible to design and build a magnet capable of accomplishing free-fall, open-gradient separation of coal at rates of many tons per hour. Since this process offers the potential of being simpler, cheaper, and more selective than the HGMS, we are now experimentally corroborating the calculations and will attempt to develop it as a commercial process.

The magnetic-preparation-of-coal program reflects the position that the deep physical preparation of steam coal is both economic and viable in the environmental control strategy and that dry preparation of fine coal is economic as compared with wet processes. The program has demonstrated the technical feasibility of two magnetic processes, has demonstrated one process at a pilot plant scale of 1 ton/h and is continuing to develop one or both processes to commercial viability.

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THE DEPARTMENT OF ENERGY OIL SHALE PROGRAM

A. Hartstein and R. Franklin
U.S. Department of Energy

Paper not submitted for publication in Proceedings.

SESSION 3
OIL SHALE

Chairman: A. Hartstein
Co-Chairman: R. Franklin

THE OIL SHALE TASK FORCE: PAST, PRESENT, AND FUTURE

Dr. Willard R. Chappell
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1. INTRODUCTION

The Oil Shale Task Force was formed in response to a letter from Governor Lamm to Secretary Schlesinger on May 8, 1978. The Governor asked the Department of Energy "to assist Colorado by working with us in developing additional research and analyses of current and future efforts". The Department created the Task Force, initially termed the DOE/EV Modified In Situ Task Force, to plan, implement, and coordinate a comprehensive, integrated research program on the environmental and health impacts of Modified In Situ (MIS) processes. More recently, the charge to the Task Force has been broadened to cover surface processes as well as in situ processes. In terms of the Oil Shale R.D. and D. Program Management Plan[1], the Task Force plays the role of coordinating the work being done in the Environmental Activity within the subactivity on Data Base Development.

The Task Force consists of scientists from the various National Laboratories, Universities, the Laramie Energy Technology Center, and two individuals who play a key role in linking to outside groups. The membership of the Task Force is shown in Table 1. As chairman, I have formed an Advisory Group to facilitate communication with outside groups. The Group has a broad representation involving people from both the private and public sectors, as can be seen from Table 2.

2. THE PAST

The basic approach taken was to develop a generic research plan that addressed the issues shared by all MIS processes. This plan is supplemented by appendices for different processes and sites. Such a plan was developed for the Occidental operation in Logan Wash. The site-specific plan then became the implementation plan.

In February, 1979, the Task Force was provided with samples of a spent shale core that was obtained from Retort 3E at Logan Wash. Data pertinent to the spent shale core samples is given in Table 3. Figure 1 illustrates Fischer Assay data and mineralogic characterization of the spent shale samples. In March, 1979, a team from PNL, EML, and LASL extensively sampled groundwater from monitoring wells and sumps as well as effluents and products from Retort 6 at Logan Wash while retorting was in progress. Standard sampling protocols were used. Table 4 describes preservation techniques employed on the samples obtained.

These materials were then distributed to the Task Force. Rather extensive chemical and physical characterization have been performed. In addition, leaching studies and bioassays have and are being carried out.

A progress report[2] was recently prepared which gives a detailed description of the results obtained between March and July of 1979. The Task Force convened a workshop in July of 1979 where all of the scientists who had been working on the OXY samples were brought together to discuss the results. These discussions resulted in fruitful and vigorous debate over the meaning, validity and significance of the data. The result of the workshop was the first draft of the report just mentioned.

TABLE I

The Oil Shale Task Force Members

Willard R. Chappell, Chairman
University of Colorado at Denver
Denver, Colorado

David Farrier
Laramie Energy Technology Center
Department of Energy
Laramie, Wyoming

Phyllis Fox
Lawrence Berkeley Laboratory
Berkeley, California

Jon Fruchter
Darryl Hessel
Richard Pelroy
Ray Wildung
Batelle-Pacific Northwest Laboratories
Richland, Washington

Walter Hecox*
State of Colorado
Department of Natural Resources
Denver, Colorado

L.M. Holland
Marvin Tillery
George Voelz
Paul Wagner
Los Alamos Scientific Laboratory
Los Alamos, New Mexico

Richard Ragaini
Hector Timourian
Lawrence Livermore Laboratory
Livermore, California

Robert Siek
Council of Energy Resource Tribes

DOE Liaisons:

Ralph Franklin
Office of Environment
Washington, D.C.

Arnold Harak
Laramie Energy Technology Center
Laramie, Wyoming

Arthur Hartstein
Office of Fossil Energy
Washington, D.C.

Jack O'Brien
Lakewood, Colorado

Technical Staff

John Lanning
University of Colorado at Denver
Denver, Colorado

Carol Nieuwenhuis
University of Colorado at Denver
Denver, Colorado

* Replaced Robert Siek, December, 1979.

TABLE 2

Advisory Group Members

Merril R. Coomes	TOSCO Corporation, Los Angeles, California
Carol R. Edmonds	Colorado House of Representatives, Denver, Colorado
Rosielea Gash	Rio Blanco Oil Shale Company, Denver, Colorado
Bobby J. Gunther	U.S. Public Health Service, Denver, Colorado
John Hutchins	Energy Development Consultants, Inc., Golden, Colorado
Glen A. Miller	U.S. Geological Survey, Grand Junction, Colorado
Rafael Moure	Oil, Chemical & Atomic Worker Int'l. Union, Denver, Co.
Paula Phillips	Environmental Defense Fund, Denver, Colorado
Martin Robbins	Colorado Energy Research Institute, Golden, Colorado
Allen Sass	Occidental Oil Shale, Inc., Bakersfield, California
Terry Thoem	Office of Energy, Denver, Colorado
Anne V. Vickery	Colorado Mountain Club, Boulder, Colorado

TABLE 3

Designation and Distribution for Occidental Room 3E
Retorted Shale Core Samples

Core Sample Number	Depth (ft. from ground surface)	Total Sample Weight (g)	CU Sample (g)	LASL Sample (g)	PNL Sample (g)
1	442-445	54.2	25	10	10
2	454-457	54.2		20	20
3	457-460	51.8	25	10	10
4	460-463	57.3	25	10	10
5	463-466	52.7		10	20
6	468-469	58.0		20	20
7	469-470.5	54.3		20	20
8	470-475	55.4		20	20
9	475-477	55.8		20	20
10	475.5-477.5	52.6		20	20
11	477-480	55.3		20	20
12	480.5-481.5	50.3		20	20
13	481.5-485.5	52.2		20	10
14	484-485	50.6	25	10	10
15	483.5-485.5	49.8	20	10	10
16	485.5-500.5	52.8		20	20
17	500-506	50.2	20		10
18	506-515	54.5	25		10

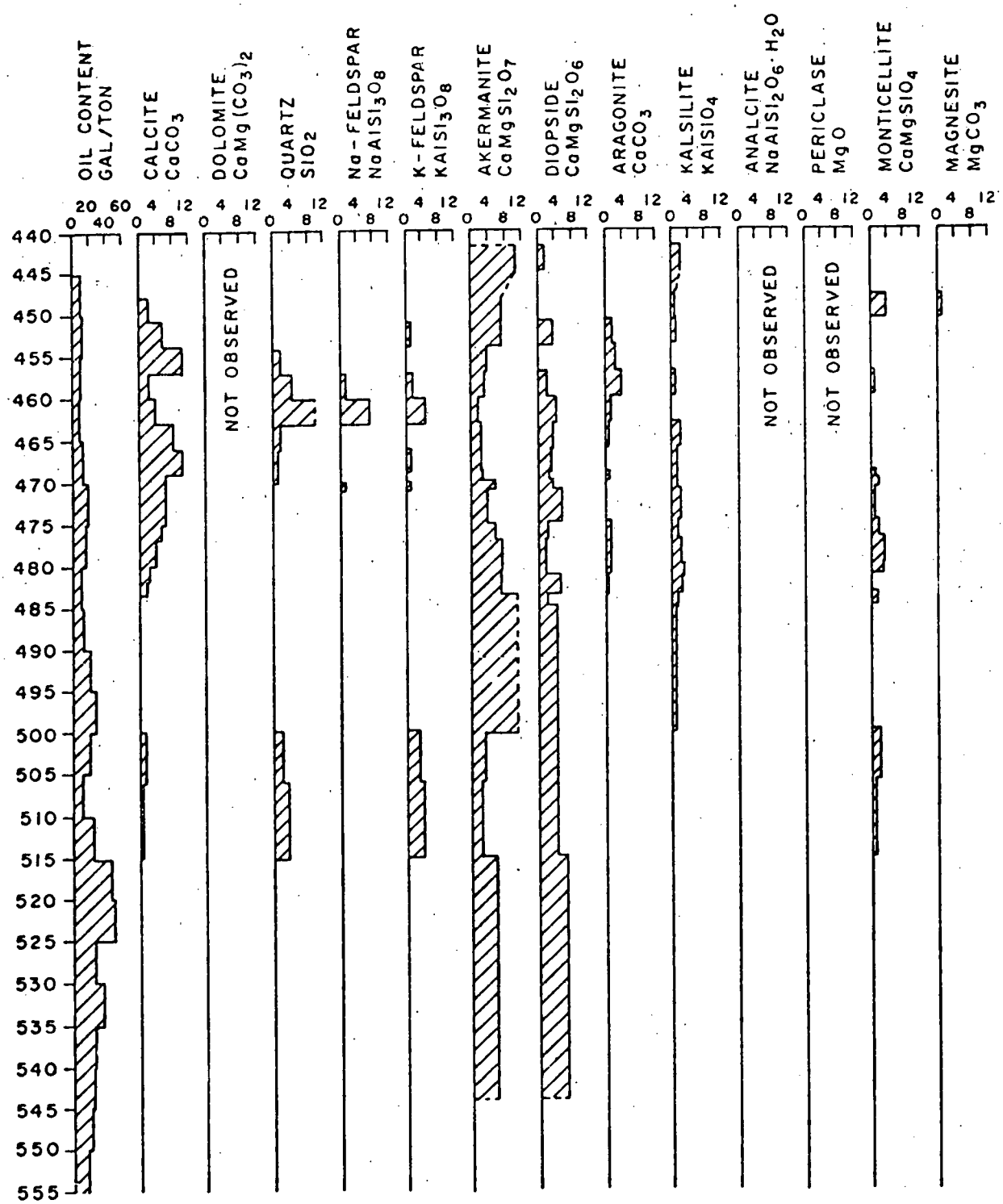


Figure 1. XRD peak heights (in inches) of minerals found in the spent shale cores, from the top to the bottom of retorted chamber, Room 3E, Logan Wash site, Colorado.

TABLE 4

Preservation of Ground and Effluent Samples at Logan Wash

Samples collected in polyethylene bottles--filtered samples filtered through 0.4 μ Nucleopore filters. Each sample was divided into seven subsamples treated as follows:

1. Filtered -- untreated, refrigerated
2. Filtered plus 5 mℓ Ultrex nitric acid
3. Filtered -- untreated
4. Unfiltered plus 5 mℓ concentrated sulfuric acid
5. Unfiltered plus 1 g copper sulfate plus 6 mℓ concentrated phosphoric acid
6. Unfiltered -- untreated
7. Unfiltered plus 5 mℓ Ultrex nitric acid

That draft was then distributed to the Task Force and the Advisory Group for comments that were incorporated in subsequent drafts.

The report is divided into three sections corresponding to the format of the workshop, namely: Characterization, Leaching, and Health. Many of the results obtained to data should be considered to be preliminary until verified by additional analyses. With this proviso the principal conclusions to date are:

Characterization Studies

- Liquid Samples:
  - --Those samples of Oxy oil that have been analyzed have lower concentrations of arsenic and selenium and higher concentrations of vanadium, cobalt, nickel, and zinc than other shale oils that have been analyzed.
  - --In general the shale oils that have been measured (both surface and MIS) are higher in arsenic, selenium, cobalt, and nitrogen and lower in vanadium and nickel compared to crude petroleums.
  - --Retort 6 product waters are compositionally different from product waters produced by above-ground processes.
  - --Although the concentrations of many elements and chemical species are lower in effluents from Retort 6 compared to above-ground retorts, higher water and gas production rates per barrel of oil are often involved with MIS processes and these may lead to higher total emissions per barrel of oil for some substances by the MIS process.
- Gaseous Samples:
  - --Mercury has been detected in all gas samples which have been analyzed to date.
  - --Very little arsenic in any form is present in these samples.
- Solid Samples:
  - --The core samples from Retort 3E show considerably greater compositional variation than found in shale samples from above-ground and simulated in situ retorts.
  - --Boron, fluoride, arsenic, sulfur, and molybdenum generally increase with depth. Other elements fluctuate more or less randomly with depth.
  - --All core samples measured showed residual mercury concentrations as opposed to spent shales obtained from simulated in situ retorts.
  - --Oxy spent shales are generally higher in boron and calcium and lower in sodium and molybdenum that other spent shales studied to date.

Leaching Studies

- Although the Retort 3E shale was exposed to high retorting temperatures, a water soluble fraction exists and is rapidly leached from the retorted shale under laboratory conditions.
- Leachate concentrations of aluminum, arsenic, boron, fluoride, molybdenum,

selenium, and vandium are sufficiently high to warrant further investigation to determine whether they are of environmental concern.

- Retort 3E can be divided into a small number of zones or divisions which give similar leachates. This implies that retorting conditions (e.g., temperature) and/or the character of the initial raw shale may play a significant role in determining the character of the leachate. If so, the environmental impact could be lessened by using appropriate retorting conditions.

Health Studies

- The Oxy crude shale oil from Retort 6 at Logan Wash and several associated by-products (product water, boiler blowdown, etc.) were found to possess either a very low order mutagenic activity or no activity at all.
- Early results from the inhalation studies using raw shale dust from another location have failed to demonstrate a carcinogenic effect following sixteen months of exposure at dust concentrations well above the anticipated industrial exposures.
- Industrial hygiene sampling of the mine atmosphere at Logan Wash revealed no significant dust levels above standards for nuisance dusts having relatively high silica content.
- Two different types of particles were detected in the mine atmosphere. One type, a solid compact particle, was found to possess a higher silica content than the other type, a porous particle, which possesses a higher calcium content than the first type.

These results need to be verified by additional analyses and bioassays. In addition, two new cores of Retort 3E have recently been obtained in a jointly funded program with OXY. These cores will give access to more samples than were previously available.

From the point of view of environmental control, there are a few significant findings. One is the existence of mercury concentrations in the off gas from Retort 6 in the range of 10-25 ug Hg/m^3. This result gives support to earlier work by Fox[3] on simulated *in situ* retorts indicating a potential need for Hg removal from off gases. Another result of some importance is that there are significant levels of some contaminants in the leachate. This result relates to the hypothesis by Smith[4] that the high temperature reactions in *in situ* retorting would lead to the creation of chemically inert igneous and/or metamorphic minerals. At present, the initial work on the OXY core samples indicates that a water soluble fraction does exist. However, on the positive side, the majority of the dissolved salts are rinsed out of the MIS retorted shale faster than is the case of surface-retorted shales.

As previously mentioned, the core can be divided into a small number of zones which give similar leachates indicating that retorting conditions may play an important role. If this is true, and if we gain an understanding of the physical and chemical mechanisms involved then we increase the likelihood that appropriate retorting conditions could be used as a control.

The biological results are positive. If verified by additional work on the Logan Wash samples and samples from other sites, they would lessen some of the concern about worker exposure relative to the surface processes.

3. THE PRESENT

Present activities of the Oil Shale Task Force are concentrated in two major areas. Work is being completed on the samples obtained from Retort 6 while study of the two new spent shale cores is being initiated. This work will lead to a picture of the temporal variations in the data. In addition, the greater quantities of material available from the new cores will allow us to conduct studies which were not possible with the previous samples. One such area involves looking at thin sections of retorted shale in order to better understand mineralogical changes which occur during retorting and how these relate to retorting parometers.

The Task Force is also engaged in a planning effort aimed at carrying out research at the C-a Lease Tract in cooperation with the Rio Blanco Oil Shale Company. Plans are being made to carry out intensive sampling before and after rubblization and before and after ignition (which is estimated to occur in May, 1980). Moreover, the Task Force is planning to cooperate in a joint study of the leaching of raw shale piles that will be carried out in cooperation with Rio Blanco, the Area Oil Shale Supervisor's Office, and E.P.A. These efforts are a part of the detailed plans developed for the R.D. & D. Plan.

4. THE FUTURE

The future research activities will consist of the implementation of the R.D. & D. Plan. This will involve work at the various Program Opportunity Notice's simulated retorts such as those at Lawrence Livermore Laboratories and Laramie Energy Technology Center, and other facilities and sites as is necessary to achieve the objectives of the R.D. & D. Plan.

Two future activities involve an effort to share the results of the work of the Department of Energy and the Task Force with broader audiences. The Task Force will be conducting a public meeting in April in order to describe D.O.E.'s oil shale environmental research activities (as opposed to plans) the Task Force will sponsor a major symposium on the environmental effects of oil shale development. The principal focus of the symposium will be a series of "state-of-the-art" papers which review each of the major areas (e.g. land reclamation) in detail and describe progress in terms of understanding the issues and solving the problems.

5. SUMMARY

The Oil Shale Task Force is a mechanism for coordinating the environmental research being performed by various groups as part of the Data Base Subactivity of the Environmental Activity of the R.D. & D. Plan. The Task Force approach has proven useful as a means of facilitating communication between researchers and with the user groups such as state regulatory agencies, industry and environmental groups. A considerable amount of data has been obtained leading to some important conclusions regarding the MIS process. Additional activities are underway and will be the subject of future reports.

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OIL SHALE HEALTH AND ENVIRONMENTAL RESEARCH*

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INTRODUCTION

The orderly development of alternative energy resources requires an understanding of all of the associated costs. The impact on health and environment is one of the more important considerations because of the limitations that may be imposed if significant adverse effects result or cannot be mitigated. As far as possible, control requirements should be determined prior to large scale utilization in order to minimize the necessity for retrofitting and to avoid later discovery of health problems and the attendant need for compensation.

Several distinct technologies will be utilized to recover shale oil from the Green River formation (1). Each approach offers distinct and, in some cases, unique occupational health considerations requiring site and technology-specific biological/toxicological experimentation. The United States Department of Energy, through the Oil Shale Task Force established by the Assistant Secretary for Environment, is conducting occupational health and toxicological studies in conjunction with the development of the various technologies.

Industrial Hygiene Studies

Most recovery processes currently under consideration will require underground mining and processes involving surface retorting also require crushing to aid transport of the shale and to provide consistant processing results. Samples have been collected during mining operations at various locations in an effort to characterize potential occupational exposures.

Dust exposure is frequently encountered in mining operations. Two sampling methods are routinely used to determine the concentration of airborne dust and standards are expressed in terms of these sampling methods. Total airborne dust is determined by drawing the sample through a high efficiency filter, collecting all particles carried by the air flow. Dusts encountered in most mining operations are classified as mineral dust and the threshold limit value (TLV) is stated as

$$\frac{30\ \text{mg/m}^3}{\%\ \text{quartz} + 3}$$

for total airborne dust. The % quartz is determined from the airborne dust samples. The term respirable dust sample refers to the fraction of particles in the total sample having a high probability of penetrating to

*This work was supported by the U. S. Department of Energy.

the gas exchange regions of the lung. Several criteria are currently used to define respirable, however, for most industrial hygiene sampling the criteria of the American Conference of Governmental Industrial Hygienists are used. This approach uses a preselector to remove a fraction of the particles according to aerodynamic diameter** and the material penetrating the preselector is classified as respirable. The penetration characteristics of the preselector are given in Table I. (2)

TABLE I

Aerodynamic Diameter (μm)	% Passing Size Selector
≤ 2.0	90
2.5	75
3.5	50
5.0	25
≥ 10.0	0

The threshold limit value for respirable dust (2) is stated as

$$\frac{10 \text{ mg/m}^3}{\% \text{ quartz} + 2}.$$

Certain mineral dusts, known to be more toxic, have lower TLV values than those derived from standard formulas (i.e., asbestos, coal mine dust). (2)

Mine air samples of both total and respirable dusts were collected in two oil shale mines. Quartz content in airborne dust samples was not measured in all cases and where quartz content in airborne dust was measured all values were less than 10%. Quartz content of oil shale rock from different areas of the Piceance basin has been measured and a variety of values have been reported. (3) A value of about 15% represents a reasonable estimate of the average and would be consistent with the lower value observed for airborne mine dust which also contains dust particles from sources other than oil shale rock. The dust concentrations measured in two mines are listed in Table II. (3-4) The dust levels measured in active working areas were frequently above the TLV in the Anvil Points mine. These levels did not represent overexposure of any workers since the TLV values are time-weighted values for an 8 hour work shift. In the Anvil Points mine all workers performed several tasks and were not involved in any operation for extended periods. (5) However, these measurement do indicate that dust exposure is a potential problem and dust suppression will undoubtedly be required during mining operations.

**Diameter of a unit density sphere having the same terminal settling velocity as the particle of interest.

Particle size was measured by Andersen eight stage cascade impactors. In the Anvil Points mine the mass median aerodynamic diameter (mmad) was found to be 2.2 μm with a geometric standard deviation (σ_g) of 3.5 during mucking and loading. In the Logans Wash facility the mmad ranged from 1.5 to 3.7 μm with a σ_g of 2.6 to 4.3.

The Anvil Points mine was sampled for a variety of gases during normal operation and after blasting with conventional explosive agents (ammonium nitrate and fuel oil). These sampling results are shown in Table III. Attempts were made to collect formaldehyde samples in the mine at Logan's Wash as a possible indication of diesel exhaust, however no detectable aldehydes were found on any of the 25 samples. The mining aspects of shale oil recovery will be similar for many recovery technologies but processing procedures following mining will be technology specific and may result in

TABLE II

Dust Concentrations Measured in Mining Areas (mg/m^3)

Mine Operation	Total Dust* Range	Total Dust* Average	Respirable Dust† Range	Respirable Dust† Average
Anvil Points Drilling	6.5-31.5	14.7	3.7-14.6	9.8
Anvil Points Loading	6.6-7.0	6.8		
Anvil Points Mucking		14.1		
Anvil Points Roof Bolting		12.6		
Anvil Points General Mine	3.8-14.6	9.2	0-0.28	0.14
Logan Wash General Mine	0.32-0.82	0.50	0.05-0.48	0.23
Logan Wash Haulage Way				1.17

*TLV assuming 15% quartz = 1.67 mg/m^3
*TLV assuming 5% quartz = 3.75 mg/m^3
†TLV assuming 15% quarts = 0.59 mg/m^3
†TLV assuming 5% quartz = 1.43 mg/m^3

significantly different occupational health exposures. Most above ground retorting methods require crushing and grading shale.

We have collected samples around one crushing operation but the equipment used was not representative of a mature industry so the data is not presented.

Sampling has been conducted during operation of the Paraho above ground retort at Anvil Points. This is a gas combustion retort employing a vertical kiln, through which coarsely crushed shale moves downward and the gas and vapors flow upward. The retort may be operated in a direct or

indirect heating mode to decompose the kerogen into a recoverable vapor and gas. The retort was operated in the direct mode during the sampling period. The results of dust sampling around the retort are given in Table IV. Dust concentrations around the retort were high due to the raw shale conveyor discharge, degradation of the top rotary seal and the hot shale discharge at the bottom of the retort. While these dust levels indicate a need for dust suppression, personal sampling devices on the retort operator indicated no overexposure.

Gas and vapor concentrations were measured around the retort using detector tubes and the results are shown in Table V. Carbon monoxide and hydrocarbon concentrations were significant around the upper portion of the retort. The hydrocarbon gases may include polynuclear aromatic

TABLE III

Gas Measurements--Anvil Points Mine

	Normal Conditions	After Blasting
CO	< 20 ppm	up to 100 ppm
CO_2	trace	≈ 0.12%
HCN	trace	trace
NH_3	trace	3-6 ppm
HCHO	trace	trace
SO_2	trace	trace
H_2S	trace	
NO	< detectable	20 ppm
NO_2	< detectable	20 ppm
O_2	20.8%	20.8%
Total Hydrocarbons	0 to 16 ppm	up to 120 ppm

hydrocarbons and some nitrogen compounds, which would represent an exposure to potentially carcinogenic materials. Charcoal-absorber gas badges worn by the retort operator and by workers in the retort area collected no measurable organic matter. Further studies are needed to evaluate the potential presence of polynuclear aromatic and nitrogen compounds in these areas.

During the operation of the retort, there was a strong odor of nitrogen bases present downwind. Nitrogen bases are nitrogen compounds

which can be extracted from an oil mixture by means of strong mineral acids and consist of homologues of pyridine, pyrole, quinoline, acridine, and similar heterocyclic nitrogen compounds. Little is known of the toxicity of these materials although they are somewhat irritating to the respiratory system. No occupational health standards have been established and air samples were not collected for these materials.

A variety of above ground retorting techniques have been developed and many of the control requirements to provide acceptable working environments will be similar for all systems. However, the wide range of retorting conditions that are encountered in the different systems and that may be varied in single systems may result in unique requirements for control equipment. Some of these systems have been throughly characterized with respect to potential emissions and occupational health exposures. Several technologies remain to be characterized.

TABLE IV

Dust Concentrations in the Retort Area

Operation	No. of Samples	Concentration (mg/m^3) Total Dust Max.	Total Dust Avg.	Resp. Dust Max.	Resp. Dust Avg.	Particle Size mmad[b]	Particle Size σ_g[c]
Top Seal	7	90.8	41.5	15.6	8.7	3.9	3.6
Bottom Seal	6	54.0	17.3	4.5	1.8	7.3	2.7
Retort, Ground Level	2	12.0	0.8	4.4	2.5	7.0	2.7
Middle Distributor	4	28.6	14.6	4.2	1.5		
Bottom Distributor	1	----	59.2	----	----		
Bottom Conveyor	1	----	7.4	----	ND[a]		
Outside Landings	4	2.7	1.3	1.8	0.8		
At Thermal Oxidizer	1	----	1.1	----	0.9		
Retort Operator (Personal Sample)	1	----	1.7	----	0.4		

[a] No detectable dust in the single sample collected

[b] Mass median aerodynamic diameter

[c] Geometric standard deviation

Modified *in situ* methods where some fraction of the shale is mined out to provide the permeability needed for retorting are also being investigated. These techniques may result in unique occupational health situations. Full scale operations will result in extensive underground mines in which retorts are in the formation phase, are burning with underground circulation of combustion gases and recovery products, are in the cooling phase or are being abandoned. To date modified *in situ* operations have been carried out with a phased approach with only limited periods where all phases of the operation were underway simultaneously. Some sampling has been conducted but more information will be required before the potential occupational health problems associated with the modified *in situ* technologies are all characterized. Large numbers of samples have been and will continue to be collected from *in situ* processing for toxicology testing.

TABLE V

Gas and Vapor Concentrations in the Retort Area

Location	Total Hydrocarbon	Contaminant Concentrations in ppm									
		CO	NO_2	NH_3	H_2S	SO_2	CS_2	HCN	HCHO	HNO_3	CO_2
Retort, Top Seal	100-400	25	N.D.[b]	N.D.	20	N.D.	----	8	2	N.D.	1000
Retort, Bottom Seal	0.7, 0.2	5	N.D.	0.1	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	----
Retort, Ground Level	100	----	----	----	----	----	----	----	----	----	----
Retort, Bottom Distributor	9.0, 3.0, 0.2	----	----	----	----	----	----	----	----	----	----
Retort, Middle Distributor	3.0, 0.2	----	----	----	----	----	----	----	----	----	----
Retort, Top Distributor	4.5, 4.0, < 25	N.D.	N.D.	N.D.	N.D.	N.D.	----	N.D.	----	N.D.	----
Retort, Off-Gas Collector	10-50	----									
Retort, Thermal Oxidizer	N.D., 0.6, < 25 ppm	200	10-15	4-6%[a]	N.D.	> 35	----	60			
Recycle Gas Blower	80-170 200-5000	20-700	N.D.	40, > 30	10-20	N.D.	5	5-15	10-15	N.D.	5000
Blower Area	----	15-25									
Retorted Shale Conveyor	----	10									
Retorted Shale Piles	N.D.	12	----	----	N.D.	N.D.	----	N.D.	----	----	----

[a]Single sample, result highly unlikely, unknown interferences, possibly amines.

[b]None detectable.

Biological Studies

Inhalation studies. Comparative inhalation studies involving two rodent species have been completed or are in progress. Exposure materials include raw shale, two kinds of spent shale and appropriate controls (Table VI). The first study utilized Syrian hamsters because they are regarded as the species of choice for investigation of chemical carcinogenesis of the lung. The exposure period covered 16 months, or about 60% of the hamster lifespan, and the dust concentrations were considerably higher than those that might be anticipated during actual oil shale recovery operations. Most of the animals in these experiments are dead and no tumors have been observed. Many animals surviving the entire exposure period exhibited mild degrees of localized fibrosis of the lung even though the Syrian hamster is not a good model for the pnuemoconiotic diseases.

The second inhalation study, which is still in progress, utilizes Fischer-344 rats which are a more appropriate animal for the study of

TABLE VI

Inhalation Studies

STUDY I

Materials	Animals	Concentration	Duration*
Raw Shale	64 Syrian Hamsters	50 mg/m^3	16 months
Spent Shale A	64 Syrian Hamsters	50 mg/m^3	16 months
Spent Shale B	64 Syrian Hamsters	50 mg/m^3	16 months
Sham Controls	64 Syrian Hamsters	-----	16 months

STUDY II

Raw Shale	64 Fischer 344 Rats	120 mg/m^3	Lifetime**
Spent Shale A	64 Fischer 344 Rats	120 mg/m^3	Lifetime
Quartz	64 Fischer 344 Rats	20 mg/m^3	Lifetime
Deposition Study (Raw Shale)	64 Fischer 344 Rats	120 mg/m^3	Serial Sacrifice
Sham Controls	64 Fischer 344 Rats	-----	-----

* 4 hrs/day

** 6 hrs/day

fibrotic and obstructive lung disease. As a part of this experiment animals are sacrificed at frequent intervals for neutron activation analysis of the deposition of inhaled materials in the lung. Results of histological examinations of the sacrificed animals indicates a more general fibrotic response than that seen in hamsters and which may lead to focal emphysema with time.

Mutagenesis and Carcinogenesis Assays. Many of the materials acquired during industrial hygiene studies of specific sites have been tested by both bacterial mutagenesis (Ames Assay) procedures and mouse "skin-painting" schemes. These approaches are particularly useful for the liquid products and by-products.

Using the Salmonella histidine-reversion test, several of the product oils and some of the so-called process waters have been assayed for mutagenic activity. (6) It is apparent from the results that the product oils and the associated process waters vary considerably in their biological activity and that the variation may be process dependent. Oil from one specific MIS retort exhibited considerably less mutagenic activity than the product oil from a specific surface retort. The mutagenic activity of the oil from surface retorting, however, was greatly diminished after hydrotreating.

The mouse skin system was used to evaluate the carcinogenic potential of two crude shale oils and two natural petroleums. Four dose levels of each test oil and two dose levels of benzo-a-pyrene (BaP) were applied to C3Hf/He mice three times per week. Groups of mice, subjected to frequent shaving, application of carrier solvent or left untreated, served as controls. Each shale oil represented a different extraction process, and the natural petroleums originated from different geographic regions.

In the group treated with shale oil from an above ground process, the first tumors were observed after 20 weeks of application, and 90% of the mice had tumors by the 58th week (mean latency = 36 weeks). The shale oil from an in situ process had a latency period to first tumor of 25 weeks, and 35% of the mice had tumors after 58 weeks of treatment (mean latency = 48 weeks). Of the natural petroleums, only one, a U.S. gulf coast oil (API Reference oil #2), caused tumors with a latency period of 35 weeks and 18% tumor incidence after 58 weeks of exposure. In all cases of positive effect, only the highest dose levels (5 mg/application) have proven to be carcinogenic. The two groups exposed to BaP differed in temporal distribution of both initial tumor latency and total tumor occurrence. While 100% of the mice in each dose group experienced tumors, the mean latency in the high dose group (10 µg/treatment) was 29 weeks compared with a 40 week mean in the low dose group (2 µg/treatment) (Table 7).

Papillomas and squamous carcinomas were the only cutaneous tumors observed in any of the experiments. For the purpose of estimating latency, no distinction was made between histological types, and many of the papillomas persisted as such until the death or sacrifice of the animal. Many of the mice in each of the positive groups exhibited multiple tumors. Tumors that appeared to be papillomas at first observation were often later accompanied by apparently contiguous squamous cell carcinomas. Some of the squamous neoplasms were associated with lung metastases.

TABLE VII

Tumor Incidence

Compound	Time to First Tumor	% Tumor Incidence at 58 Weeks
Shale Oil A	20 weeks	90
Shale Oil B	25 weeks	35
US Gulf Coast Petroleum (API #2)	35 weeks	18
Kuwait Petroleum (API #1)	0	0
Benzo(a)Pyrene (10 µg)	18 weeks	100

DISCUSSION

While there have been sporadic efforts to demonstrate certain shale oil extraction technologies in recent years, none of the techniques have been thoroughly analyzed to determine the extent of potential occupational health impacts and even those technologies that have been demonstrated cannot be regarded as typical of a scaled-up, fully mature industry. Industrial hygiene studies have served to identify operations within certain technologies where mitigating methods can and should be applied to protect the industrial populations. Judging from data developed by on-site sampling it is probable that, with the possible exception of MIS techniques, oil shale mining presents no unique problems that cannot be handled with state-of-the-art control procedures. The conditions that may exist in a mine where in situ retorts are being simultaneously prepared, burned and abandoned have not as yet been defined.

The probability of combined exposures to spent shale dusts and fugitive emissions in the form of vapors and gases added to the potential for skin exposure to product oils and other liquid effluents raises more complex questions. It has been shown by both epidemiological evidence and experimental data gathered both in the U.S. and in foreign industries that crude shale oil and some of its products carry a higher carcinogenic potential than most of the natural petroleums (7-8). Preliminary data suggest that this particular hazard may be almost self-eliminating if hydrotreating, in preparation for refining, is universally practiced.

The determination of specific hazards should be done on a technology-specific basis since it is highly probable that the biological activity of most of the products and by-products of shale oil production is process-specific.

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SPENT SHALE GROUTING OF ABANDONED IN-SITU OIL SHALE RETORTS

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1. INTRODUCTION

In vertical modified in-situ (VMIS) oil shale retorting, the resource is processed in the ground. Large chambers of rubblized oil shale are formed by mining out about 20 to 40 percent of the in-place shale and blasting the balance into the created void. The mined-out material is brought to the surface and oil is recovered from it by surface retorting. The in-place material is pyrolyzed to recover oil, leaving large numbers of abandoned retort chambers underground.

This type of oil shale processing may result in a number of environmental problems including in-situ leaching of the abandoned retorts, low resource recovery (large pillars are required to support the overburden), and subsidence. These problems may be mitigated by filling abandoned retorts with a grout prepared from spent shale produced during surface retorting of the mined shale. This would fill the void space created by mining, thus improving retort structural strength and stiffness, and reduce retort permeability to groundwater flow. If sufficient strength could be developed, it may be possible to design retorts so that the pillars could be retorted and resource recovery improved.

This paper summarizes the results of laboratory investigations to produce a grout from spent shale. Spent shale grouts may be variously produced by modifying surface retorting conditions and/or by adding chemicals such as limestone or gypsum to the spent shale. A number of processes have been proposed and investigated including heating in steam at 700°C, limestone addition to surface spent shale followed by calcining at 1000°C, and limestone addition to raw shale followed by calcining at 1400-1500°C. This paper reviews these data in the framework of required grout characteristics for effective environmental control and technical and economic feasibility.

2. RETORT ABANDONMENT ENVIRONMENTAL ISSUES

Figure 1 shows in simplified form the relative positions of the target oil shale layer, the Mahogany Zone, fractured oil shale artesian aquifers, and VMIS retorts and summarizes the resulting environmental problems--contamination of surface and ground waters by leaching of in-situ spent shales and mixing of lower and upper aquifer waters, overburden cracking and ground subsidence, and low resource recovery.

The VMIS process requires a thick, continuous, vertical section of oil shale not interrupted by significant thicknesses of barren rock (Smith, 1978). Based on commercial designs of industrial developers, it is apparent that about 300 feet of continuous vertical oil shale is required for the process to be economical. Most of the resources where necessary geologic conditions exist are in the Piceance Creek Basin of Colorado where confined aquifers penetrate the oil-bearing strata (Weeks et al., 1974). In most of this region, the Mahogany Zone, which is the target of VMIS retorting, is 100 to 200 feet thick. In order to have a sufficiently long vertical section of oil shale, the installed retorts must intersect the stratum immediately above and/or below the Mahogany Zone where water-bearing zones exist. Therefore, it will be difficult to locate VMIS retorts in completely dry zones and a geometry similar to that shown in Figure 1 will be used.

This manner of locating retorts will create the potential for water to flow from one aquifer to the other through the retorts. During development and retorting, aquifers will be dewatered. Following abandonment, groundwater will re-invade the aquifers and fill the retorts, leaching spent shale. The leached material, which includes many organic and inorganic compounds, can be transported in the aquifers and ultimately discharged into streams and springs or withdrawn from wells. Local streams which receive groundwater inflow are tributary to the Colorado River system where salinity is already of national and international concern.

If a retort penetrates one aquifer, there will be a hydraulic gradient in the horizontal direction across the retort causing horizontal flow through the retort which will transport leached material into the aquifer. If a retort penetrates more than one aquifer and the aquifers are at different heads, there will also be a vertical hydraulic gradient causing flow through the retort from one aquifer to the other. This condition could be more serious as the vertical gradient resulting from this condition could be greater than the horizontal gradient; thus the rate of flow through and leachate transport away from the retort would be greater.

The problem of aquifer and eventual surface stream pollution by leaching of vertical modified in-situ retorts in the Piceance Creek Basin has been quantified by Fox (1979). This study concluded that it could take centuries before significant groundwater degradation would occur, due to the low flow velocities in many areas of the Basin. However, the report pointed out that the potential long-term effects could be serious due to the critical issue of salinity in the Colorado River system and the slow self-purification properties of groundwater aquifers. Leachates could result in salinity increases in the Colorado River at Lees Ferry of from 0.03 to 50 mg/l (Fox, 1979). A TDS increase of 50 mg/l in the Colorado River would have a significant

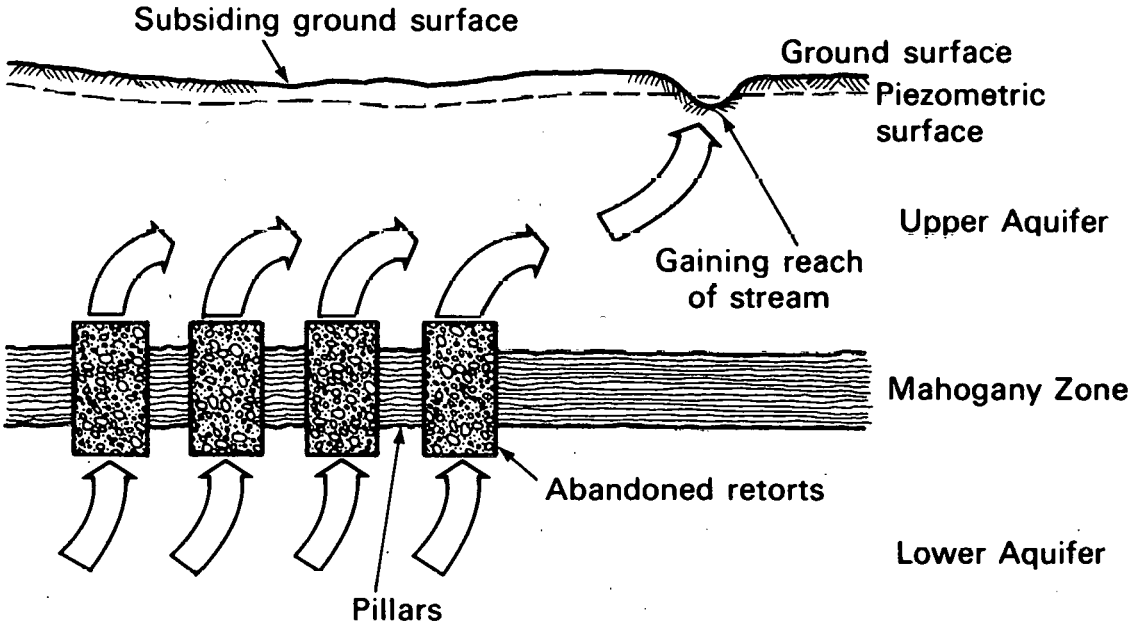


Figure 1. Schematic showing environmental issues of VMIS retort abandonment.

economic impact upon irrigated agriculture. Kleinman (1974) estimates the total economic loss due to Colorado River salinity increases to be $200,000 to $400,000 per year per mg/l (1974 dollars). Additionally, elevated concentrations of certain toxic or carcinogenic organic materials may occur in aquifers or surface streams. If these waters were used for municipal supply or stock water, local health problems might result.

In some areas of the Piceance Creek Basin, such as lease tract C-b, water quality of the lower aquifer is much worse than that of the upper aquifer. In these cases, contact between the two aquifers created by the retorts would permit degradation of the upper aquifer in the absence of leaching.

Resource recovery in VMIS retorting is poor. Oil recovery is low and 25 to 50 percent of the developed area must be left intact as pillars between retorts to support the overburden. If sufficient strength could be developed in abandoned retorts, it might be possible to design a retorting system so that pillars could be retorted and resource recovery improved.

Finally, considerable concern exists over the long-term stability of abandoned retorts. Computational techniques are inadequate to predict incidences of subsidence, and there are presently no field data available to assess this problem. (Field experiments have consisted of single, small retorts while commercial operations may use many hundreds of very large retorts.)

3. SPENT SHALE GROUTING

The three principal environmental problems associated with VMIS retorting--contamination of surface and ground waters, subsidence, and low resource recovery--may be alleviated by filling the abandoned in-situ retorts with a grout based on surface spent shale. This grout would fill some of the voids, reducing the permeability of the retorts and provide for protection against subsidence by increasing retort stiffness and strength. If adequate strength could be developed in the retorted mass, it may be feasible to retort some of the pillars, thus improving resource recovery.

A cheap material, such as spent shale, would have to be used as the basis of such a grout because 9 to 13 ft^3 of voids must be filled for each barrel of oil recovered. Thus, conventional grouting materials are too costly for this application (Fox et al., 1978). The feasibility of this proposal depends on the properties of spent shale and the criteria required for the grout.

SPENT SHALE

Oil shale, which is a low-grade fossil fuel, produces about 1.4 tons of solid waste, referred to as spent shale, for each barrel of oil produced. This material typically contains 0.1 to 4 percent residual carbon, has little strength, and is easily crushed to a fine powder. The major elements in spent shales (greater than 1 percent by weight) are iron, calcium, magnesium,

potassium, silicon, aluminum, oxygen, and sodium. The major mineral phases depend upon the retorting conditions and may include carbonates for low retorting temperatures and silicates for higher temperatures.

The feasibility and methods of forming an adequate cementitious grout from spent shale depend on the chemical reactions that occur during surface retorting. Production of cementitious properties depends principally on the absence of char and the formation of calcium silicate compounds such as tricalcium silicate ($3CaO \cdot SiO_2$) and dicalcium silicate ($2CaO \cdot SiO_2$), which are the major active compounds in portland cement.

In the manufacture of portland cement, these calcium silicate compounds are formed from lime and silica produced by the decomposition of limestone and clay in reactions such as:

$$3CaO + SiO_2 \xrightarrow{\Delta} 3CaO \cdot SiO_2 \qquad (1)$$

$$2CaO + SiO_2 \xrightarrow{\Delta} 2CaO \cdot SiO_2 \qquad (2)$$

The formation of these compounds, rather than noncementitious ones such as $CaO \cdot SiO_2$, depends upon lime and silica being in near stoichiometric ratios.

Colorado oil shales contain an abundance of dolomite, quartz, and feldspar and are deficient in calcium relative to silica compared to other cement raw mixes. A number of investigations (Campbell, 1978; Campbell and Taylor, 1978; Burnham et al., 1978; Parker et al., 1978; and Heistand et al., 1978) have indicated that some free lime can be formed, char can be removed, and cementitious properties produced in spent shales.

PRODUCTION OF SPENT SHALE GROUTS

Three strategies have been proposed for manufacturing a grout from spent shale--grout production from raw shale, grout production from as-received surface spent shale, and grout production from treated surface spent shale. Each of these is summarized in Table 1 and discussed here.

Grout Production from Raw Shale

Sellers and Chapin (1959) obtained a patent on the production of portland cement from a 1.8:1 mixture of limestone and raw oil shale. The coarse-ground raw shale and limestone are ground to a powder and fired at 1400 to 1500°C to form portland cement clinker. The lime and silica content of the shale (with additional lime) are the raw materials. The high energy requirements, and hence cost, associated with this process make it economically unattractive for grouting of in-situ retorts.

Grout Production from Treated Spent Shales

A cementitious grout may also be produced from spent shale by heat treating as-received spent shale, by using admixtures such as gypsum and lime, or by changing the operating conditions of existing retorting processes, such as Lurgi or Paraho. Significant modifications in existing

Table 1. Summary of processes for developing a grout from spent shale.

	Process	Unconfined compressive strength [a]		Permeability [a]		Comments
		Sample preparation	Compressive strength, psi	Sample preparation	Permeability cm/sec	
RAW SHALE GROUT						
Sellers and Chapin, 1959	1.8:1 mixture of limestone and raw shale calcined at 1400-1500°C		(produces portland cement)			Energy intensive (no oil recovery) high cost
TREATED SPENT SHALE						
Farris, 1979	Direct-mode retorting 2 hr at 822°C	Compacted to Proctor density with 25% moisture, cured 28 days	270	ASTM D 2434	3.8×10^{-4} [b]	Requires minor modification of surface retorting technology
	Indirect-mode retorting 2.9 hr at 832°C	"	325	ASTM D 2434	3.9×10^{-4} [b]	"
Mallon, 1979	Oil recovery at 500°C in N_2, char combustion below 650°C in N_2-air mix, temperature raised to 700°C in 100% air, then 70 min in 100% steam at 700°C	Fluid grout flowed into spent shale rubble, cured 70 days	522	Fluid grout flowed into spent shale rubble, cured 28 days	4×10^{-7}	Requires development of new surface retorting technology, steam atmosphere could prematurely hydrate cement
Mehta and Persoff, 1980	1:1 mixture of Lurgi spent shale and limestone, calcined 1 hr at 1000°C, ground, 5% gypsum added	ASTM C 109, cured 28 days	3750	Not determined		Uses existing technology for both spent shale production and subsequent heat treatment
AS-RECEIVED SPENT SHALE						
Culbertson et al., 1970	TOSCO	Compacted with 20% moisture	200-500	Not reported		Economic, uses existing technology, in-situ compaction not feasible
Holtz, 1976	Paraho	Compacted at 56,000 ft-lb/ft^3 (ASTM D 1557)	up to 200	Compacted at 56,000 ft-lb/ft^3 (ASTM D 1557) tested at 200 psi	8×10^{-8}	"
Nevens et al., 1977	Lurgi	Grout with 0.75 water-solids ratio, cured 24 days at 180°F	up to 200	ASTM D 2434	10^{-5}-10^{-6}	"
Peterson et al., 1978	Indirect-heat	Compacted at 56,000 ft-lb/ft^3	104	Not reported		"

[a] Direct comparison of results is not possible because various test methods were used.

[b] Optimum retorting conditions for permeability were slightly different from optimum for strength.

processes may sacrifice oil production and result in a new, high-risk technology while modification of as-received spent shale has the advantage of using existing technology for both the retorting and subsequent heat treatment and thus, does not interfere with oil production.

Three investigations have been conducted on these types of processes. Mallon (1979) produced a low-strength grout by exploiting retorting chemistry in a bench-scale retort. Farris (1979) investigated the effects of various retorting conditions on spent shale strength, and Mehta and Persoff (1980) produced a high-strength hydraulic cement by adding limestone to Lurgi spent shale and heating the mixture at 1000°C. Each of these approaches is discussed here.

Farris (1979) operated a laboratory retort to determine retorting conditions which would maximize the strength of compacted spent shale. Direct-mode retorting for 2.0 hours at 822°C gave a strength of 270 psi. Indirect-mode retorting for 2.9 hours at 832°C gave a strength of 325 psi. The strength development was attributed to the formation of interlocking acicular crystals, thought to be hydrated calcium aluminum sulfate. These strengths were measured on samples which were compacted with 25 percent moisture to Proctor densities of 96 to 100 percent, and thus are not representative of strengths obtainable in grouted retorts.

Mallon, on the other hand, used the work of Campbell (1978) and Burnham (1978) to develop a process that would produce cementitious compounds. He retorted Anvil Points oil shale in a small laboratory electric furnace. Oil recovery, char combustion, and cement formation were carried out in separate steps. Mallon first heated the shale to 500°C in nitrogen to remove the oil by pyrolysis. The char was then completely burned off by gradually introducing air while holding the temperature below 650°C to prevent the decomposition of carbonates. The gas flow was then changed to 100 percent air for 15 minutes while the temperature was raised to 700°C and then to 100 percent steam for 70 minutes at 700°C to form cementitious compounds. The resulting clinker was pulverized and slurried and poured into spent shale to simulate grouting of in-situ rubble. The grouted rubble had a 10-week compressive strength of 522 psi and a 4-week permeability of 4×10^{-7} cm/sec.

Mehta and Persoff (1980) produced a high-strength hydraulic cement from Lurgi spent shale by heating a 1:1 mixture of limestone and spent shale for 1 hour at 1000°C. The resulting cement had a 28-day compressive strength of 3150 psi (ASTM C 109). The addition of 5 percent gypsum by weight to the cement produced a 28-day compressive strength of 3750 psi while 10 percent gypsum addition to the raw mix produced a strength of 4375 psi.

Grout Production from Untreated Surface Spent Shale

Other investigators have proposed the use of untreated spent shale to seal abandoned in-situ retorts. The developers of lease tract C-a, for example, propose to use as-received surface spent shale with additives to backfill abandoned retorts and are presently conducting an investigation of this option under U. S. Bureau of Mines funding. In this strategy, spent shale from a surface process is slurried with water, admixtures such as slurry fluidizers are added, and the slurry is pumped into the abandoned retorts. This strategy has the advantage of being cheaper than the other two strategies, but it is presently uncertain whether it can produce sufficiently low permeabilities and adequate strength and stiffness.

Nevens et al. (1977) simulated the backfilling of an abandoned VMIS retort with a slurry of Lurgi spent shale. Unconfined compressive strengths of the set slurries ranged from 5 to 200 psi. Permeability measured by ASTM D 2434 on the Lurgi spent shale decreased from initial values of 10^{-4} cm/sec to 10^{-5} to 10^{-6} cm/sec after 28 days. The temperature at which spent shale is burned to provide heat for the retorting process appeared to be important. In-situ spent shale was observed to rapidly absorb water (4 gallons per cubic foot), suggesting that slurries may be dehydrated when pumped into abandoned retorts. In a test to simulate grouting of an in-situ retort, a slurry with 164 percent by weight of water was poured into a hand-packed drum of in-situ spent shale and water was drained from the bottom. No cementation was observed and the compressive strength after 13 days of curing was only 16 psi.

Rheological measurements by Persoff (1980) showed that slurries of Lurgi spent shale fit the Casson flow model; that is, they had a finite yield stress. The yield stress increased with decreasing water-solids ratio (wsr) in the grout, and ranged from 4 dyne/cm^2 for a slurry with wsr of 1.8 to 167 dyne/cm^2 for wsr of 0.8. Slurries with wsr greater than 1.0 were considered unsuitable for grouting because the suspensions were unstable and settled leaving a clear supernatant. Addition of common cement-slurry fluidizers to slurries with wsr of 1.0 changed the flow behavior to Newtonian, i.e., the yield stress was reduced to zero. A sample simulating a grouted retort was prepared by flowing grout with wsr of 0.8 and 5 percent added portland cement into pre-wetted spent shale rubble. Permeability of this specimen was 2 x 10^{-5} cm/sec.

Several investigators studying the stabilization of surface spent shale disposal piles observed self-cementing properties of untreated spent shale. In all of these studies, strength and permeability were measured on samples which were compacted with near-optimum moisture content, and thus are not representative of strengths or permeability produced by in-situ grouting.

Culbertson et al. (1970) studied the stabilization of spent shale from a TOSCO retort. Shear strength and compressive strength of all samples increased gradually with time, suggesting a cementitious reaction. Compressive strengths in the range of 250 to 500 psi were obtained. Strength development was positively correlated with the amount of cohesive hydrates formed, as detected by differential scanning calorimetry. After 15 days of setting, no loss of strength was reported when samples were resaturated with water.

Peterson et al. (1978) studied the geotechnical properties of a fine-grained surface-retorted spent shale from an indirect-heating process to evaluate the stability of disposal piles. Unconfined compressive strengths of compacted samples increased with time, indicating some self-cementing properties. The maximum compressive strength developed was 104 psi; this required a compaction effort of 56,000 ft-lb/ft^3.

Compaction studies on spent shales from a Paraho direct-mode semiworks retort showed that unconfined compressive strengths up to 200 psi were obtained with 56,000 ft-lb/ft^3 of compactive effort at 22 percent moisture content. Spent shale was described as a low-grade cement (Holtz, 1976). Permeability of this material was measured after compactive efforts ranging from 6,200 to 56,000 ft-lb/ft^3 under stresses of 50 to 200 psi.

Observed permeabilities ranged from 8×10^{-8} cm/sec at 200 psi for maximum compactive effort, to 1.5×10^{-5} cm/sec at 50 psi for minimum compactive effort. Despite great variability reported for the material it was considered suitable for use in earth dams.

EVALUATION

The preceding section presented several methods to produce a grout from oil shale materials. These included direct conversion of raw shale, modification of operating conditions of the surface retort, additional treatment of as-received spent shale, or addition of admixtures to as-received spent shale. The relative merits of these approaches depend on a wide range of factors including grouting criteria, cost, availability of technology, and raw materials, and properties of the raw materials. There is presently inadequate information to select among the proposed methods, as additional experimental work is required to demonstrate feasibility and determine design criteria. However, it is instructive at this point to discuss potential grouting criteria and to qualitatively evaluate the various processes within this framework.

The characteristics of a grout used to seal an abandoned in-situ retort will depend on the goals of the grouting operation: alleviation of aquifer disruption, subsidence control, and/or enhanced resource recovery. The specific goals of any abandonment plan will depend on the geologic and hydrologic conditions of the specific site and societal goals regarding resource recovery. These criteria will have to be determined on a case-by-case basis. However, as a minimum, any grout used to seal an abandoned VMIS retort should have the following characteristics:

(1) The grouted area must be impermeable enough to prevent the degradation of local ground water or surface water.

(2) The grouting material must be chemically stable in the presence of saline groundwater.

(3) The grout viscosity must be low enough and the setting time long enough for the slurry to penetrate a large area.

(4) The grouted area should be able to withstand hydrostatic and overburden pressures, depending on the application. The hydrostatic pressure is due to natural head differences that exist between the aquifers surrounding the oil shale deposits in some areas and to significant dewatering during retorting.

Preliminary structural analysis of retorts indicates that with a 45 percent extraction ratio (called for in development plans), no grouted retort strength or stiffness is required; that is, the overburden and pillars are stable as designed even if left ungrouted. Increasing resource recovery beyond 45 percent requires the substitution of grouted retorts for pillars and the development of strength and stiffness in the retorts. One hundred percent extraction can be realized if the grouted retorts have a strength of about 1000 psi and a stiffness (tangent modulus at zero strain) of 500,000 psi. This modulus requirement assumes that no retorts are left ungrouted at the end of the project, and that retorts are grouted soon after they are burned. The actual temporal sequence of retorting and grouting is important.

Brown et al. (1977) estimated that an average post-grouting permeability two orders of magnitude lower than the host rock would be required to keep the incremental salt loading to Piceance Creek less than 100 mg/l per 30,000 barrel-per-day production. The value proposed was 3×10^{-6} cm/sec.

Based on these criteria and the previously reported work, it appears that grout production from as-received spent shales and various treated spent shales may achieve a sufficiently low permeability to minimize contamination of surface and ground waters. Nevens et al. (1977) measured a 28-day permeability of 3×10^{-6} cm/sec for a Lurgi spent shale produced at moderate temperatures. Lurgi spent shales produced at higher and lower temperatures had higher permeabilities. These investigators observed that the permeability decreased over time, and they hypothesized that it may be possible to obtain a permeability of 10^{-7} cm/sec, given sufficient time. Similarly, Holtz (1976) measured permeabilities as low as 8×10^{-8} cm/sec for compacted Paraho spent shales, and Mallon (1979) measured a permeability of 4×10^{-7} cm/sec for a grouted sample of spent shale.

The most important factors for control of overburden cracking and subsidence are design strength of pillars and stiffness of the grouted retorts. Presumably, if the pillars are properly designed, they will provide adequate strength. No stiffness measurements have been reported for grouts studied.

Adequate strength and stiffness of grouted retorts are required for enhanced resource recovery. A compressive strength of about 1000 psi would have to be developed in the grouted retort to permit recovery of one hundred percent of the pillars. Strengths have been measured by several methods, but in most cases the samples (low moisture content, compacted) were not representative of grout in an in-situ retort. The grout proposed by Mehta and Persoff (1980) appears the most likely to satisfy the structural requirements for increased resource recovery.

These results indicate that the goals of retort abandonment and grouting criteria must be clearly defined before a grout can be selected. If in-situ leaching and subsidence are addressed, it may be possible to control these problems by filling the abandoned retort with a slurry of as-received spent shale. A small amount of fluidizer would probably be added to reduce the viscosity. The projected cost of this option is approximately 35¢ to $1.30 per barrel of oil for retorts located on lease tracts C-a and C-b (Persoff and Fox, 1980). On the other hand, enhanced resource recovery would require a relatively high-strength cement at a considerably higher cost. Economic trade-offs must be made between leaving some resource unrecovered and obtaining improved resource recovery at a greater cost.

4. SUMMARY

Vertical modified in-situ retorting may result in in-situ leaching of abandoned retorts, overburden cracking and subsidence, and low resource recovery. These problems may be controlled by filling the abandoned retorts with a grout based on surface spent shale. A number of grouts with a range of properties have been proposed. These include production of portland cement from raw shale, development of high-strength hydraulic cement by lime addition to Lurgi spent shale, development of low-strength grout by retorting in steam at 700°C following oil recovery and char combustion, and use of as-received spent shales with various additives.

These investigations suggest that untreated spent shale may be used to control in-situ leaching and subsidence. However, if additional resource recovery is required, a higher strength grout will be required.

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CONTROL TECHNOLOGY RESEARCH DEVELOPMENTS FOR IN SITU OIL SHALE PROCESS WATERS

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ABSTRACT

Development of treatment and management techniques for the water produced during in situ oil shale retorting operations is one of the most important initial steps required towards the achievement of the ultimate goal of successful commercialization. This paper identifies the three distinct water streams produced during a retorting operation and discusses treatment schemes for each type. Significant research results obtained from the current water treatment projects of the Laramie Energy Technology Center (LETC) are presented and a summary overview of water related environmental research conducted under the leadership of LETC is provided.

INTRODUCTION

One of the primary objectives of the U.S. Department of Energy (DOE) in regard to synthetic fuels is to foster the development of a commercial oil shale industry. Compared to aboveground oil shale processing, in situ processing has several distinct advantages (1,2,10)* :

Less surface disturbance.

Less water required.

Lower capital and labor costs.

Amenable to leaner shale.

Minimizes health and safety hazards to the workers.

Reduces the socioeconomic impacts normally experienced from rapid industrial growth in rural areas.

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* Underlined numbers in parentheses refer to items in the list of references at the end of this paper.

The Division of Environmental Sciences at the Laramie Energy Technology Center (LETC) is responsible for environmental efforts associated with DOE underground coal gasification, and oil shale and tar sands recovery projects and for developing an environmental technology base to assure the environmental acceptability of these fossil fuel processing technologies. The Division works closely with regulatory agencies to insure that LETC field projects are conducted in an environmentally acceptable manner and in compliance with Federal, State and local laws, regulations, and guidelines. In addition, the Division maintains a core effort directed at mitigation of environmental effects associated with the oil shale, coal, and tar sands processing technologies. The overall strategy for conducting environmental work is based on the concept of a continuous cycle of activities involving planning, research and development, implementation of environmental controls, and review of accomplishments. The driving force for this cycle is the changing implementation opportunity which progresses in size from laboratory and pilot scale experiments through increasingly involved field activities and ultimately to full scale demonstration and commercial scale operations. Field operations offer the most realistic and advantageous opportunities for determining and resolving the potential environmental effects of fossil fuel processing. Therefore, the work is closely coordinated with project and engineering staff as well as with other agencies and laboratories in the planning and coordination of field activities so that environmental and process related objectives can be simultaneously pursued. This approach acknowledges that the attainment of commercialization goals requires parallel advances in overcoming engineering, economic, and environmental problems.

Currently, a large number of water related research projects are being sponsored by LETC. Water-related control technology research has been at a high level of activity because of the numerous concerns for surface and subsurface water impacts associated with in situ oil shale processing. A refrigerated research sample repository (RRSR) has been established at LETC (3). The purpose of the repository is to provide for controlled storage and processing of large amounts of waters significant to environmental research for fossil fuel processing. The RRSR facility consists of two adjacent buildings with a total of 11,000 sq. ft. of open floor space. The facility is thermostatically refrigerated to 36±4°F. The capacity of the RRSR is 92,000 gallons (allowing 50 percent free space for access) based on storage in 3,066 thirty-gallon drums double stacked on pallets. At present, large volume amounts of various oil shale process waters are in storage at this facility. Major efforts are continuing towards using these waters to determine their bioenvironmental impacts and to develop water treatment schemes to mitigate such impacts. This facility at LETC is believed to be the first one of its type anywhere in the country. Current water treatment projects under investigation by LETC include laboratory studies of treatment by stripping, ultrafiltration, biological oxidation, ion exchange, reverse osmosis, and carbon/resin adsorption. Preliminary experimental results indicate that stripping and reverse osmosis may be particularly suited for the treatment of water streams in a commercial scale oil shale plant (4,9,13).

During an in situ oil shale processing operation, three distinct water streams may be produced:

Gas Condensate Water. A relatively large quantity of water leaves the retort in the vapor phase with the retort gases. During gas scrubbing this water vapor is condensed and collected as a gas condensate. This gas condensate contains ammonia along with some carbon dioxide, hydrogen sulfide, and volatile organics. Inorganic salts are normally not significant in the gas condensate. A summary of water quality parameters measured for a gas condensate water is presented in Table 1.

Retort Water. This water condenses out in the retort itself and is pumped to the surface mixed with oil. This water, which will generally have leached out significant concentrations of inorganic salts as it flowed down the rubblized shale, must be separated from the oil before it can be treated. Retort water is of a quality significantly different from that of the gas condensate. A summary of water quality parameters found in a retort water is presented in Table 2.

Mine Drainage Water. The third type of water stream is the mine drainage water which may be released from aquifers at various levels in the oil shale deposits. This water must be consumed or discharged to a surface stream or reinjected into the aquifers. As with the retort water, mine drainage waters contain considerable amounts of leached inorganic salts, but are not associated with the retorting operation and so do not contain significant concentrations of dissolved gases and organics. Excess mine drainage water that is surface discharged generally will require some treatment, depending on discharge permits, but should nevertheless be regarded as a water resource and not a wastewater. A summary of water quality parameters found in a mine drainage water is presented in Table 3.

The quality and quantity of process waters produced in any oil shale retorting operation vary considerably with the type of shale and the hydrologic conditions in the area (5,6,11,12). Even in the same general location, water quality parameters may be spatially variable. Reliable chemical characterization of synfuel process waters has been difficult to obtain (7). This is due to the lack of adequate standards and limitations of many available analytical methods. Concentrations of many constituents fall outside the recommended ranges for published methods or chemical interferences produce inaccurate results. In view of these analytical problems, the results presented should be interpreted with some caution.

PROPOSED TREATMENT SCHEMES

Gas Condensate Water. In general, the gas condensate water treatment scheme would consist of oil-water separation, ammmonia stripping and recovery, followed by a polishing step such as reverse osmosis, as shown in Figure 1. The stripping step is the single most important operation in this scheme. Preliminary treatment studies have shown that more than 90 percent of chemical oxygen demand (COD) can be stripped during this step. The results of this treatment scheme are further discussed later in this paper. In a commercial-scale plant, the treated water may be used, possibly as cooling tower makeup water, within the plant (8).

TABLE 1. CHEMICAL COMPOSITION OF OXY GAS CONDENSATE WATER [a]

Parameters (mg/ℓ except where noted)	1	2	3	4	5	6	7	Average	Range
Sodium	4.7	3.0	1.3	2.0	1.2	1.1	32	6.5	1.1 - 32
Potassium	0.5	<0.1	<0.1	<0.1	<0.1	<0.1	0.9		<0.1 - 0.9
Calcium	0	Int.	Int.	Int.	Int.	Int.	Int.		
Magnesium	0.2	0.8	0.9	0.9	1	0.8	0.8	0.8	0.2 - 1
Chloride	NR	NR	320	290	590	260	280	348	260 - 590
Fluoride	0.4	0.36	0.66	0.48	0.39	0.32	0.61	0.46	0.36 - 0.66
Nitrate (NO_3-N)	NR	NR	270	280	150	130	180	202	130 - 280
Sulfate	NR	NR	37	<0.1	12	36	17	20	<0.1 - 37
Carbonate	2,200	3,700	5,300	4,800	4,500	7,900	6,300	4,960	2,200 - 7,900
Bicarbonate	21,000	22,000	13,000	20,000	20,000	14,000	17,000	18,100	13,000 - 22,000
pH (standard pH units)	8.7	9.23	9.17	9.20	9.13	9.19	9.19	9.12	8.7 - 9.23
Total Dissolved Solids	0	148	140	96	92	108	308	127	0 - 308
Conductivity (micromhos/cm)	NR	31,000	30,000	30,000	30,000	30,000	30,000	30,000	30,000 - 31,000
Hardness (as $CaCO_3$)	0.8	Int.	Int.	Int.	Int.	Int.	Int.		
Total Alkalinity (as $CaCO_3$)	NR	24,200	19,800	24,200	24,300	24,400	24,100	23,500	19,800 - 24,400
Phosphate - total	Int.	0.48	NR	NR	NR	NR	NR		
Nitrogen (NH_3)	NR	NR	2,400	2,000	1,600	1,400	1,800	1,840	1,400 - 2,400
Total Kjeldahl Nitrogen	6,900	NR	NR	NR	NR	NR	NR	6,900	6,900 - 6,900
Oil and Grease	<0.1	36	30	33	38	36	38	30	<0.1 - 38
Thiocyanate	<0.05	NR	11	12	9	10	12	9	<0.05 - 12
Tetrathionate	<0.05	NR	10	<0.1	<0.1	<0.1	<0.1		<0.05 - 10
Thiosulfate	<0.05	NR	58	128	122	112	110	88	<0.05 - 128
Chemical Oxygen Demand	NR	NR	3,000	3,200	6,500	3,800	11,000	5,500	3,000 - 11,000
Cadmium (total)	<0.01	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.01 - <0.1
Chromium (total)	<0.1	<0.1	0.16	0.19	0.12	0.14	0.16	0.14	<0.1 - 0.19
Lead (total)	<0.1	<0.1	<0.1	<0.1	<0.1	0.1	<0.1	<0.1	<0.1 - 0.1
Boron (total)	0	NR	0.7	0.8	0.5	0.9	1	0.6	0 - 1
Copper (total)	<0.01	NR	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.01 - <0.1
Iron (total)	0.0	NR	<0.1	0.2	0.2	<0.1	0.2	0.1	0 - 0.2
Manganese (total)	0.03	NR	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	0.03 - <0.1
Zinc (total)	0.03	NR	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	0.03 - <0.1
Nickel (total)	<0.01	NR	NR	NR	NR	NR	NR	<0.01	<0.01 - <0.01
Arsenic (total)	0.04	NR	Int.	Int.	Int.	Int.	Int.	0.04	0.04 - 0.04
Selenium (total)	0.02	NR	0.09	0.12	0.12	0.09	0.07	0.08	0.02 - 0.12
Mercury (total)	<0.1	NR	Int.	Int.	Int.	Int.	Int.	<0.1	<0.1 - <0.1
Aluminum (total)	<0.5	NR	0.6	<0.5	<0.5	<0.5	<0.5		<0.5 - 0.6
Cyanide (total)	0.33	NR	Int.	Int.	Int.	Int.	Int.	0.33	0.33 - 0.33
Lithium (total)	<0.01	NR	NR	NR	NR	NR	NR	<0.01	<0.01 - <0.01
Cobalt (total)	<0.04	NR	NR	NR	NR	NR	NR	<0.04	<0.04 - <0.04
Molybdenum (total)	<0.1	NR	NR	NR	NR	NR	NR	<0.1	<0.1 - <0.1
Vanadium (total)	<0.3	NR	NR	NR	NR	NR	NR	<0.3	<0.3 - <0.3
Barium (total)	NR	NR	<1	<1	<1	<1	<1	<1	<1 - <1
Total Carbon	NR	NR	5,583	5,562	5,547	5,630	5,540	5,570	5,540 - 5,630
Total Inorganic Carbon	NR	NR	4,635	4,744	4,635	4,632	4,642	4,660	4,632 - 4,744
Total Organic Carbon	NR	NR	948	818	912	998	898	915	818 - 998

Int. - Interference
NR - Not Run

[a] Analyses of 7 random samples from a field composite of pilot plant condensate produced during March 1979 from the Occidental Oil Shale, Inc. Retort 6 at Logan Wash near DeBeque, Colorado.

TABLE 2. CHEMICAL COMPOSITION OF OXY RETORT WATER [a]

Parameters (mg/ℓ except where noted)	1A	1B	2	3	4	5	Average	Range
Sodium	60	67	3,400	3,200	3,400	1,100	1,871	60 - 3,400
Potassium	0.8	0.7	98	80	92	45	52.75	0.7 - 98
Calcium	5.7	8.1	<0.1	<0.1	<0.1	4.8	3.15	<0.1 - 8.1
Magnesium	14	1.8	1.2	0.8	0.8	5.6	4	0.8 - 14
Chloride	55	60	520	430	540	25	271.67	25 - 540
Fluoride	0.32	0.43	32	39	42	23	22.8	0.32 - 42
Nitrate (NO_3-N)	120	Int.	3,200	1,500	1,100	610	1,306	120 - 3,200
Sulfate	193	213	881	1,160	1,900	1,120	911	193 - 1,900
Carbonate	210	720	2,200	2,000	2,500	1,100	1,455	210 - 2,500
Bicarbonate	4,800	7,600	6,900	5,300	4,000	3,700	5,838	3,700 - 7,600
pH (standard pH units)	8.48	9.04	9.06	9.23	9.33	9.00	9.02	8.48 - 9.33
Total Dissolved Solids	490	600	10,400	8,340	8,620	5,500	5,658	490 - 10,400
Conductivity (micromhos/cm)	12,000	12,500	14,000	13,000	14,000	11,000	12,750	11,000 - 14,000
Hardness (as $CaCO_3$)	72	28	4.9	3.3	3.3	35	24.4	3.3 - 72
Total Alkalinity (as $CaCO_3$)	4,280	7,400	9,300	7,700	7,400	4,900	6,830	4,280 - 9,300
Nitrogen (NH_3)	1,500	2,200	1,000	820	930	1,200	1,275	820 - 2,200
Oil and Grease	260	NR	260	250	240	810	364	240 - 810
Thiocyanate	3	NR	92	43	37	15	38	3 - 92
Tetrathionate	<0.1	NR	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1 - <0.1
Thiosulfate	16	NR	112	<0.1	40	21	37.8	<0.1 - 112
Chemical Oxygen Demand	12,500	2,000	2,600	18,300	14,000	14,800	10,700	2,000 - 18,300
Chromium (total)	<0.1	NR	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1 - <0.1
Boron (total)	2		17	15	17	14	13	2 - 17
Arsenic (total)	0.029		Int.	0.01	0.12	0.062	0.055	0.01 - 0.12
Selenium (total)	0.05		0.15	<0.01	0.048	0.23	0.098	0.01 - 0.23
Cyanide (total)	2.3		11	2	8.8	4.4	5.7	2 - 11
Total Dissolved Carbon	2,639		4,183	3,907	3,297	3,243	3,454	2,639 - 4,183
Dissolved Inorganic Carbon	1,427		1,571	1,231	1,102	777	1,222	777 - 1,571
Dissolved Organic Carbon	1,212		2,612	2,676	2,195	2,466	2,232	1,212 - 2,676

Int. - Interference
NR - Not Run

[a] Analyses of 5 random samples from the Occidental Oil Shale, Inc. Retort 6 at Logan Wash near DeBeque, Colorado. The samples were collected monthly from January - May 1979. Sample number 1 was split.

TABLE 3. CHEMICAL COMPOSITION OF OXY MINE DRAINAGE WATER[a]

Constituent	Concentration (mg/ℓ unless noted)	
	Upper Mine Aquifer Range	Lower Mine Aquifer Range
Bicarbonate	350 - 2100	265 - 4300
Boron	<0.16 - 11	.05 - 12
Calcium	5.4 - 52	4 - 28
Carbonate	0 - 53	0 - 360
Chloride	4.1 - 151	1 - 700
Fluoride	3.1 - 19	6.5 - 45
Magnesium	4.2 - 54	1.9 - 29
Silica	10 - 19	2 - 19
Sodium	200 - 780	143 - 2320
Sulfate	<5 - 370	<4 - 350
TDS	750 - 1800	356 - 5747
pH (units)	8.3 - 8.9	8.3 - 9.3
Phenol, µg/l	<1 - 174	
Ammonia	<1 - 1.8	17

[a] Data from the C-b Shale Oil Venture and from the Denver Research Institute.

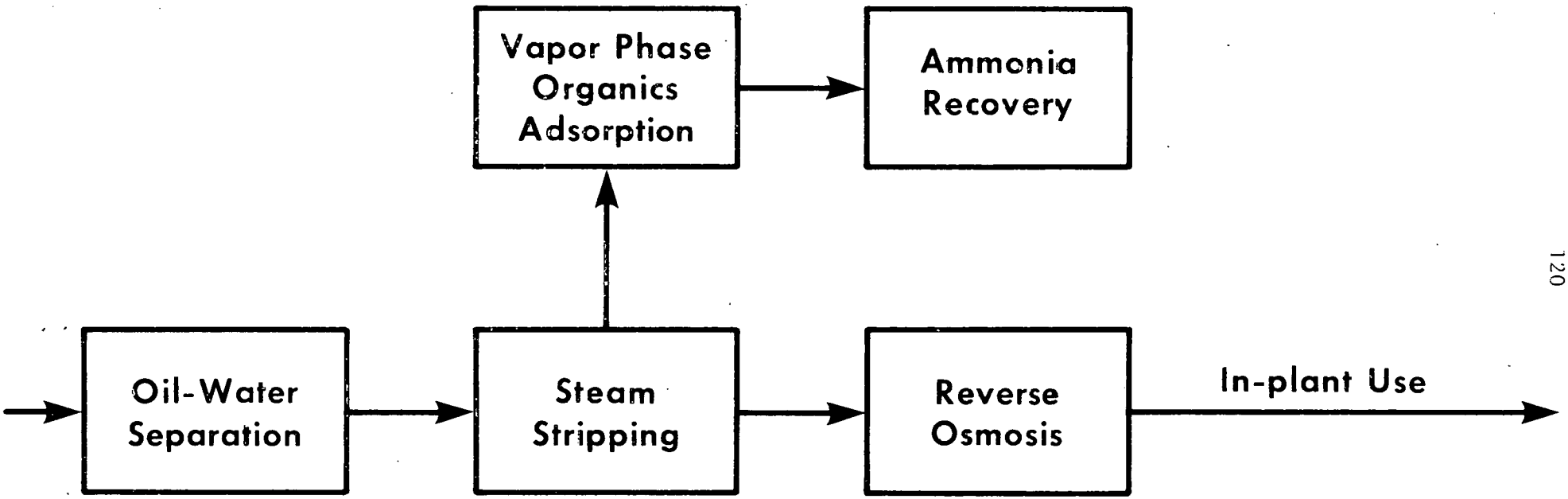


Figure 1. A scheme for treatment of gas condensate water.

Retort Water. A scheme for treatment of the retort water is presented in Figure 2. The separation of oil from water is the crucial first step in this scheme. The oil present in the water stream, if not removed, would adversely affect the effectiveness of all subsequent treatment steps. The separation of oil from water under the action of gravity is standard industrial and refinery practice. However, gravity separators are inadequate for the very small oil particles that occur in oil-water mixtures associated with oil shale processing. Centrifugal separators may be used as a means of increasing the separating force and decreasing residence times. However, equipment costs are high and this type of separator is used mainly for water-in-oil emulsions rather than oil-in-water systems. Chemical, electrical and physical methods are available to break oil/water emulsions. One physical method that may be of use for oil shale wastewaters is the "filter coalescence" of the small oil droplets to a size sufficient for gravity separation. There are several advantages of filter-coalescers, but extensive pilot testing is needed for specific systems. Ultrafiltration is another method suitable for separation of very fine oil droplets from water. Costs are higher than for filter coalescence, but a high quality product is obtained. Ultrafiltration may find application as a polishing step, or as a pretreatment to other membrane water treatment processes. Subsequent to oil-water separation, stripping of ammonia is required. Ammonia stripping is straightforward for gas condensates, but retort waters contain fixed ammonia and special design procedures may be required for stripping this fixed ammonia (9). Recent laboratory tests with several different membranes have shown that reverse osmosis may be useful in removing up to 98 percent total dissolved solids (TDS) and up to 97 percent COD from stripped retort water (4).

Mine Drainage Water. A scheme for treatment of the mine drainage water is presented in Figure 3. The flow for this water stream is very much dependent upon site conditions, and could be as high as six barrels of water per barrel of oil produced, or higher. If the final effluent is to be discharged to a stream or river, traces of boron, phenol, and ammonia present in the mine drainage water will have to be removed prior to discharge.

As discussed earlier in this paper, stripping is the single most important step in the gas condensate water treatment scheme. In a laboratory experiment, a gas condensate sample was batch stripped by boiling at atmospheric pressure for about 90 minutes (4). Both ammonia and organics (as measured by COD) were removed at approximately equal rates, as illustrated in Figure 4. If stripping were carried out at slightly elevated pressure and temperature as would occur in an industrial steam stripper, then it can be expected that close to 100 percent organics removal will be obtained. Rejections obtained with this stripped gas condensate by various reverse osmosis (RO) membranes are presented in Table 4. As seen from the table, the stripped water is of suitable quality for plant reuse. Further treatment through RO membranes produces a high quality water suitable for river discharge. Organics removal ranged from 75 to 95 percent, apparently increasing with increasing feed pH. Results of RO rejections with a sample of the LETC 10-ton simulated in situ retort water are presented in Tables 5 and 6. In spite of the high TDS in the sample, RO rejections of both organics and inorganics

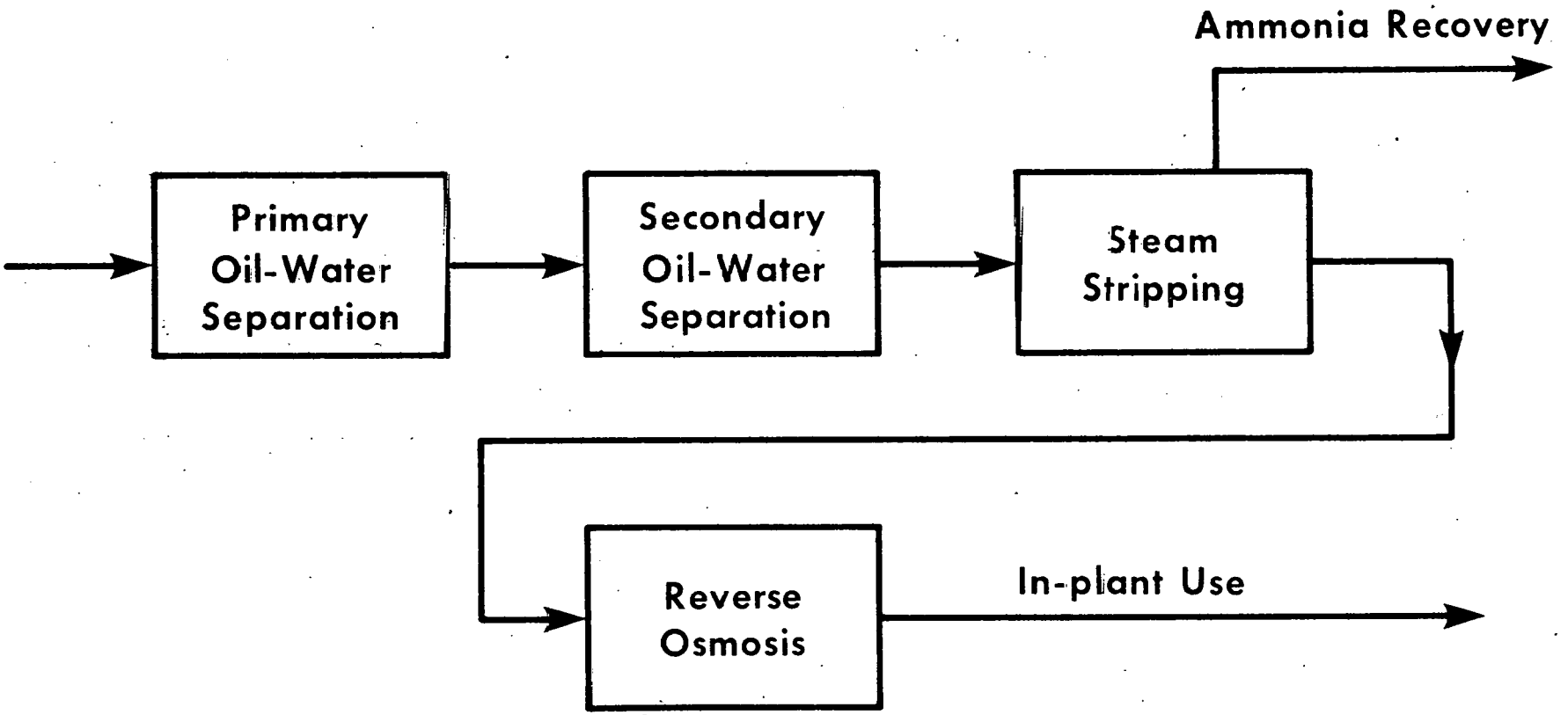


Figure 2. A scheme for treatment of retort water.

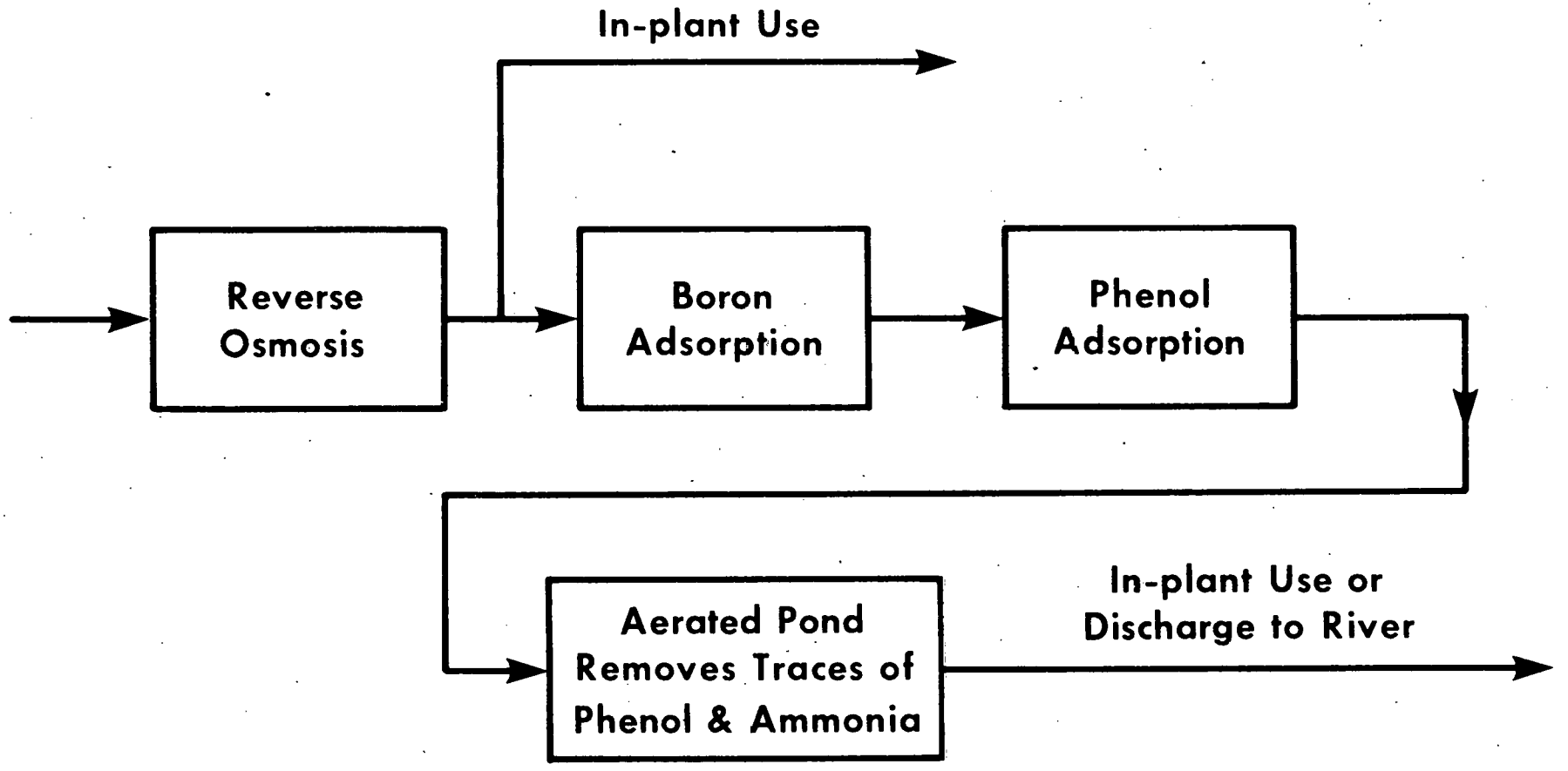


Figure 3. A scheme for treatment of mine drainage water.

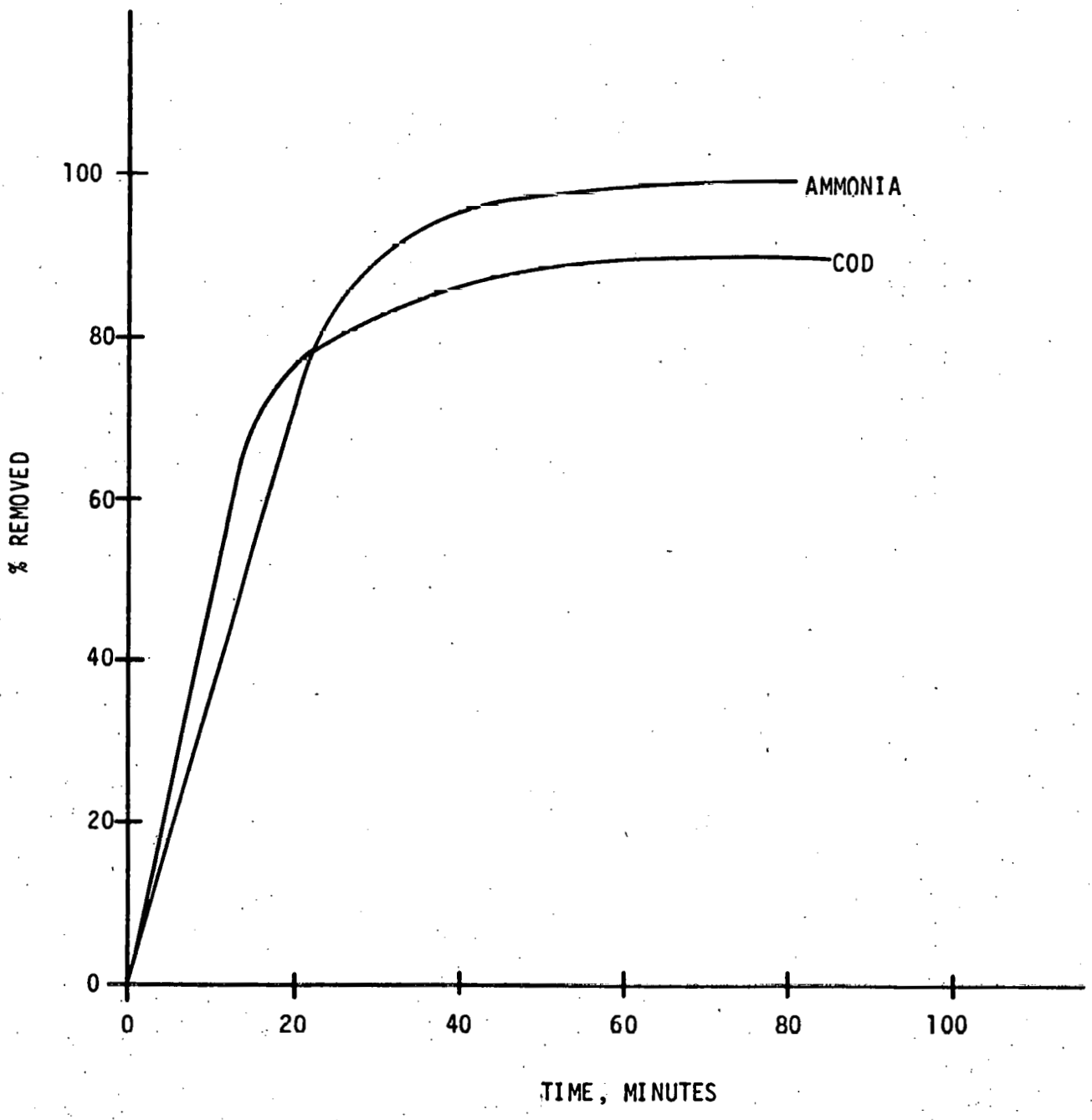


Figure 4. Ammonia and organics (COD) stripping from Oxy gas condensate.[a] Batch stripping at 100°C.

[a] Water quality parameters are presented in Table 1.

TABLE 4. REJECTIONS OBTAINED WITH STRIPPED OXY GAS CONDENSATE [a]

Constituent	Filtered Gas Condensate mg/l	Stripped Gas Condensate mg/l	% Rejections by RO Membrane			
			Osmonics Sepa 97(CA)	Osmonics Sepa 97(CA)	Membrane Systems Blend CA	Filmtec Composite
Ammonia (N)	7,600	70	93	98	90	87
Alkalinity	24,000	385	66	96	92	80
Hardness	< 2					
TDS (105°C)	270	400	90	97	87	79
COD	2,300	450	73	84	84	95
Feed pH	8.6	8.6	3.0	6.4	5.0	8.8
Product pH	8.6	8.8	4.1	7.1	5.9	9.6

%Rejection = (1 - permeate concn./avg. of feed and concentrate concn.) 100.

[a] Water quality parameters are presented in Table 1.

TABLE 5. REJECTIONS OBTAINED WITH STRIPPED LETC RETORT WATER AFTER ULTRAFILTRATION THROUGH AN AMICON UM10 MEMBRANE [a]

Constituent	Stripped Retort Water mg/l	Ultrafiltered Water mg/l	% Rejections by RO Membrane			
			Osmonics Sepa 97(CA)	Membrane Systems Blend CA	Filmtec Composite	Filmtec Composite
Ammonia(N)	440	440	89	96	42	31
Alkalinity	15,800	15,600	95			
Hardness	120		>85	>85	>85	>85
TDS (105°C)	53,000	50,100	96	98	96	98
COD	9,700	9,200	86	82	84	97
Feed pH	8.6→11	10.3	6.8	4.5	6.8	10.3
Product pH	10.3	10.3	8.4	5.3	8.7	10.2

% Rejection = (1 - permeate concn./avg. of feed and concentrate concn.) 100.

[a] This water was obtained from run S-47 of the LETC 10-ton simulated in situ retort.

TABLE 6. REJECTIONS OBTAINED WITH STRIPPED LETC RETORT WATER AFTER ULTRAFILTRATION THROUGH A SEPA-O MEMBRANE [a]

Constituent	Stripped Retort Water mg/l	Ultra-Filtered Water mg/l	% Rejections by R.O. Membrane	
			Osmonics Sepa 97(CA)	Membrane Systems Blend (CA)
Ammonia (N)	440	440	92	90
Alkalinity	15,800	15,700	99	99
Hardness	120		>85	>85
TDS(105°C)	53,000	49,000	97	98
COD	9,700	9,650	84	88
Feed pH	8.6→11	10.3	5.5	5.5
Product pH	10.3	10.3	6.0	5.7

% Rejection = (1- Permeate concn./avg. of feed and concentrate concn.) 100.

[a] This water was obtained from run S-47 of the LETC 10-ton simulated in situ retort.

were sufficiently high to produce a permeate suitable for plant reuse. Membrane fluxes were in the range of 2-7 gallons per sq. ft. per day which are 50 percent or less of the manufacturers' reported values. With time and as the concentrate concentration in the batch system increased, plugging was evident with most of the membranes tested. Reasons for the plugging might include precipitation of calcium carbonate and organic fouling. Pretreatment by ultrafiltration to remove the larger organic molecules had no effect. Experiments with another retort water sample which was highly contaminated showed that even with various pretreatments the water was still not nearly suitable for RO and plugged all membranes after only small throughputs had been accomplished. However, this latter retort water sample was not a typical sample. Experiments with mine drainage water by various RO membranes are in progress at this time. Results in the relatively short term batch tests can be misleading. The data have clearly demonstrated that RO is a candidate for the treatment of process waters, but that information on fouling and membrane life must be obtained to determine its feasibility in practice. Future tests on a flow module should provide much of these data.

SUMMARY

In situ oil shale processing on a commercial scale, if technically feasible, does have several advantages over aboveground processing. Three distinct water streams are produced during an in situ processing operation. This paper has illustrated the preferred schemes for treating these water streams. Much additional research in environmental, process, and economic areas is required. A summary overview to highlight the multifaceted research program being conducted by the U.S. Department of Energy at the Laramie Energy Technology Center to address these concerns has been presented.

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RETORTED OIL SHALE MANAGEMENT

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INTRODUCTION

A limited supply of domestic oil and natural gas in conjunction with recent world developments (e.g., OPEC production cutbacks and price increases, and political instability in the Middle East) have emphasized our nation's need to lessen our dependence on foreign energy sources. Much of America's future energy needs could be met on a short-term basis by developing our own resources including the nation's western oil shale reserves. Western oil shales of the Green River Formation contain in excess of 318 billion m^3 (2 trillion bbl) of oil in place. The known resources of high-grade shale (greater than 104 liters of oil/tonne or 25 gallons of oil/ton of oil shale) are estimated to hold 95.5 billion m^3 (600 billion bbl) of oil with at least 13 billion m^3 (80 billion bbl) recoverable by present technology (Yen 1976). This amount of oil is much more than the sum of the resources of Prudhoe Bay in Alaska and in the Continental shelf reserves on the U.S. West Coast (Slawson and Yen 1979). In fact, Hubbert (1974) has reported that the ultimate total U.S. crude oil production would probably be between 150 and 170 billion barrels. Both government and industry specialists have speculated that by the end of this century, the United States is capable of developing an oil shale industry with an output of 160,000 m^3 to 320,000 m^3 (1 million to 2 million bbl) of oil per day (Energy Development Consultants, Inc. 1979; Slawson and Yen 1979).

Interest in developing a viable oil shale industry is intensifying in both private and governmental circles. Several companies involved in the oil shale industry are in the midst of implementing recovery technologies that approach commercial scale (Colorado Energy Research Institute 1979). After extensive development testing and monitoring, several other companies have announced construction plans scheduled to commence when environmental issues are resolved and economic conditions justify the large capital investment (EPA 1979). Congress is currently considering several pieces of legislation that would encourage development of our oil shale resources. In addition, the Department of Energy is involved in a number of cost-sharing contracts with industry to look at new oil shale recovery technology.

This increased interest in oil shale development has also increased concern about environmental impacts associated with large-scale mining and processing operations. One of the major environmental problems connected with the oil shale industry is the disposal of retorted shale with minimal environmental impact. Retorted shale disposal is a significant problem because of the large volume of waste material generated and because of the chemical and physical characteristics of this waste.

Large quantities of retorted oil shale will be produced with either the development of large-scale aboveground retorts or by the use of modified *in situ* technology. With surface retorting it is estimated that a one million

barrel a day industry would require 1.4 million tons daily of raw shale that produces 30 gallons of oil per ton. During the retorting process, the mass of the shale will decrease by 12-15%, but volume may increase as much as 50% as a result of mining and crushing. A million barrel a day surface retort industry would generate approximately 180,000 acre feet of waste material per year (U.S. Department of the Interior 1973). Modified *in situ* technology requires that from 20-50% of the shale be mined out prior to rubblization and retorting (Energy Development Consultants, Inc. 1979). Industry plans call for this mined out shale to be brought above ground and eventually retorted in surface facilities. With either retorting method, part of the retorted shale may be returned under ground but over half would need to be disposed of above ground. Most of the major oil shale developers plan to dispose of the retorted shale above ground in canyon locations (Crawford et al. 1977). Disposal sites for this material may require between 200-400 ha of land per year.

The surface disposal of retorted shale may result in environmental degradation because retorted shale is subject to water and wind erosion (Fletcher and Baldwin 1973). Erosion or runoff from shale disposal sites could cause contamination of surface groundwaters by the addition of salts, sediment, organic substances, and trace elements present in the shale material. Such contamination will have an adverse effect on the quality of water for other uses in the upper Colorado Basin and add to the salt loading of the lower Colorado Basin (Crawford et al. 1977). In addition, trace elements in retorted shale may accumulate in vegetation growing on the shale to levels toxic for domestic livestock and wildlife. Air quality has been identified as one of the most significant obstacles to the development of an oil shale industry (Energy Development Consultants 1979). Therefore, control measures will be necessary on disposal sites to reduce fugitive dust emissions to a minimum.

Although the characteristics of the processed shale differ with different retorting methods and temperatures, vegetation establishment directly on the various shales is difficult because of the nature of the material. Retorted shale generally has high pH, high soluble salt content, and low amounts of plant available nitrogen and phosphorus. Plant growth may also be limited by physical problems connected with the texture and the color of the retorted shale.

Because of the above mentioned problems, long-term stabilization of the retorted shale disposal sites will be required if environmental impacts are to be minimized and the land returned to a productive use following extraction of the resource. Disposal sites will need to be reclaimed to a point where they are capable of supporting diverse and functional ecosystems. Energy flow and nutrient cycling will need to be reestablished in a community composed of a wide variety of producers, consumers, and decomposers. The reclaimed land must be aesthetically designed to blend in with the surrounding landscape.

The prospects for achieving a long-term stable ecosystem on massive retorted shale disposal sites have not been fully addressed; and, it remains one of the major problems of oil shale development (ERDA 1976). Three approaches to this problem have been put forth by industry, government, and research institutions; and, they are as follows.

1. Establishment of salt-tolerant or adapted vegetation directly on retorted shale without modification of the shale material

2. Amelioration of the retorted shale to enhance its suitability as a plant growth medium and subsequent vegetation establishment

3. Covering of the retorted shale with suitable geologic and/or soil material prior to vegetation establishment

This paper reports on the results and findings of a long-term ecosystem study directed toward providing guidelines for the reclamation of Colorado oil shale lands. The study, presently underway in the Piceance Basin of northwestern Colorado, is evaluating the effect of retorted shale properties and the method of disposal on various ecosystem components. The goal of this study is to develop specific recommendations for the reestablishment of ecosystems on land disturbed by retorted oil shale disposal.

PAST RESEARCH--PLANT GROWTH ON RETORTED SHALE

Merkel (1973) reported on a study at Parachute Creek to evaluate plant growth on various TOSCO II processed shale-soil mixtures. The results showed low plant survival on processed shale, better survival on 50/50 retorted shale-soil mixtures, and excellent survival and growth on topsoiled plots. Merkel concluded that it was not practical to seed directly into retorted shale without leaching or irrigation. Retorted shale could be revegetated without irrigation if topsoil were used to cover the shale.

Schmehl and McCaslin (1973) found in their research that TOSCO II and U.S. Bureau of Mines retorted shales were highly saline, alkaline, and low in plant available phosphorus and nitrogen. In a greenhouse study, the growth of tall wheatgrass and Russian wildrye on untreated retorted shale was extremely poor. Mixtures of up to 50% shale and 50% soil produced far less plant production than would be acceptable under field conditions. Tall wheatgrass exhibited good growth in retorted shale following leaching of 62% of the soluble salts and additions of nitrogen and phosphorus fertilizers.

Herron et al. (1979) and Berg et al. (1980) constructed plots in Parachute Creek to evaluate Union Oil Process B and decarbonized shales as plant growth media. After four growing seasons Process B shale (which had been leached, fertilized, mulched, and irrigated for plant establishment) supported comparable amounts of vegetative cover when compared with soil over shale and soil control treatments. However, the investigators recommended the use of a soil cover with Process B shale because of the higher quality of the runoff and the greater ability to establish and maintain a more diverse plant community. The decarbonized shale had severe limitations as a plant growth medium. Vegetation cover on the decarbonized shale plots was considerably less than the plots with soil over decarbonized shale. The soil control had greater vegetation cover than either the decarbonized shale to surface or the soil cover treatments. Much of the vegetation present on the decarbonized shale plots and soil over decarbonized shale was weedy annual species.

Frischknecht and Ferguson (1979) set up studies in Colorado and Utah to evaluate the effects of soil depth over TOSCO II processed shale. In Utah, after two years, seven shrub species belonging to the Chenopodiaceae family exhibited good growth on processed shale without soil covering. Irrigation increased plant survival slightly on processed shale but did not improve survival on treatments with soil over shale. Seven other shrubs and forbs demonstrated very poor survival and growth on processed shale but performed better with a 30 cm covering of soil material. In Colorado, plant vigor and growth rates were highest on plots with a soil covering. Fourwing saltbush and prostrate summer cypress, two species which showed good survival on retorted shale, doubled in height when grown on plots covered with topsoil or subsoil material. It was concluded that a topsoil covering of 30 cm or more should be used when revegetating processed shale disposal sites. The use of topsoil increased the number of adapted species and significantly reduced the need for supplemental fertilizers.

Harbert et al. (1979) in a lysimeter study at the DOE Anvil Points Facility concluded that freshly retorted shale produced by the Paraho direct-heated process was unsatisfactory as a plant growth medium. Following leaching, fertilization, mulching, and irrigation only a sparse vegetation cover was established directly on retorted shale. However, soil cover over retorted shale and soil control treatments supported adequate plant cover. Thus, Harbert et al. (1979) recommended that the shale be covered with soil to insure the establishment of an adequate vegetation cover. The use of a soil cover may also be necessary to prevent water movement through retorted shale disposal piles and subsequent contamination of ground water. If water penetration is to be avoided, the depth of soil cover will have to be sufficient to hold seasonal precipitation particularly from spring snowmelt.

According to Cook et al. (1974) topsoil should be applied evenly at a minimum depth of 15-20 cm over subsoil material so that a plant growth medium of at least 45 cm is produced. A 45 cm depth is necessary for storage of water to field capacity that is received during fall and winter. Soil moisture is necessary for plants to survive the dry summer months that frequently prevail in Colorado.

In a study by Harbert and Berg (1978) utilizing TOSCO II and USBM retorted shales it was reported that rapid stabilization with native vegetation will require highly intensive management including leaching, N and P fertilization, and irrigation for establishment. Nitrogen application will also be required for a number of years following establishment. In addition, the study also concluded that an alternative stabilization procedure would be the use of a minimum of 30 cm of soil over unleached retorted shale. This 30 cm soil cover will only be effective for lower pH processed shale in which roots of adapted species can grow into and thus utilize stored water. High pH retorted shale (Paraho direct and decarbonized) will require thicker soil coverings because of the inhibiting effect that high pH has on root development.

Reports have been made concerning the concentration and toxic effect of trace elements in vegetation grown on retorted shales. Kilkelly et al. (1978) in a trace element study on TOSCO II and USBM retorted shales found that boron might be a potential hazard to plants growing directly on these shales. It

was further noted that molybdenum was being concentrated by fourwing saltbush from USBM spent shale at levels that might be toxic to ruminants. Ward and Nagy (1977) analyzed barley grown on TOSCO II and USBM retorted shales for certain trace elements. Molybdenum and zinc were higher in the barley grown on the retorted shales than in the soil treatments.

RETORTED SHALE PLANT COMMUNITY SUCCESSION STUDY

Introduction

In 1976 the Department of Energy (then ERDA) funded an interdisciplinary research project with Colorado State University. The overall goal of the project is to formulate guidelines for the rehabilitation of Colorado oil shale lands. These rehabilitation studies focus on the reestablishment of diverse and functional ecosystems with a minimal input of scarce resources. An integrated approach is being taken in order to address key ecological components that are important in the reclamation of retorted shale.

Site Description and Methods

The site at which this study is being conducted is located in the Piceance Basin in northwestern Colorado. It is approximately 3 km southeast of Federal Oil Shale Lease Tract C-a and 15 km northwest of Federal Oil Shale Lease Tract C-b. The study site is situated on nearly level terrain at an elevation of 2,042 m.

The climate of the area is classified as arid-steppe or semiarid. Annual precipitation averages 34 cm with approximately one-half of the precipitation falling as snow during the period of December to April. Annual temperature fluctuations are extreme with summer temperatures reaching 37.5 C and winter temperatures dropping as low as -40 C. The vegetation at the site is dominated by big sagebrush with an understory of mostly western wheatgrass.

Construction of the simulated retorted shale disposal study began in June 1977 with the removal of vegetation from six rectangular panels measuring 23x109 m. Five of these panels were then excavated to specified depths according to the designated profile configuration listed below. Excavated topsoil and subsoil were stockpiled separately.

Paraho retorted shale (direct mode process) was then transported from the Anvil Points Facility west of Rifle, Colorado, to the study site. Each of the five excavated panels received 61 cm of retorted shale material. Topsoil, subsoil, and gravel material were then deposited over the retorted shale according to the experimental design. The soil-shale treatments are as follows:

1. Processed shale without any surface covering
2. 30.5 cm soil over retorted shale

3. 61 cm soil over retorted shale
4. 91.5 cm soil over retorted shale
5. 61 cm soil over 30.5 cm rock capillary barrier over retorted shale
6. Soil check with no retorted shale

The gravel in treatment No. 5 above was implemented to evaluate the effectiveness of gravel as a barrier to the capillary rise of salts from the retorted shale to the overlying soil material.

To measure important ecosystem components, a comprehensive sampling program was initiated in 1978 and 1979. The aboveground vegetation was sampled for density, cover, and biomass across all soil-shale treatments. In addition to vegetation sampling, soil and shale samples were taken from the soil-shale treatments to monitor microbial activity and chemical changes through time.

Results

As part of this integrated approach, vegetation on a simulated retorted shale disposal study has been sampled to monitor plant establishment and successional changes. Following two growing seasons there were significant differences between aboveground plant production on the various soil-shale treatments. The most significant response was the failure to establish a stand of vegetation on the retorted shale to surface treatment. The plant species seeded in the fall of 1977 were unable to become established because of the limiting plant growth characteristics of retorted shale material. Paraho retorted shale is a gravelly silt loam textured material which has a pH of 11.5 immediately following retorting and a pH of 9.6 and an electrical conductivity of approximately 7.0 on a 1:1 by weight water to shale extract after two months of weathering in the field.

Paraho retorted shale is also extremely deficient in nitrogen and phosphorus, and despite fertilization vegetation failed to establish. Our recent greenhouse studies have shown that high levels of nitrogen and phosphorus may be necessary to establish and maintain an adequate stand of vegetation directly on retorted shale. From our investigations it appears that pH, EC, SAR, and fertility status of the shale were limiting factors to plant establishment. In addition, surface temperatures of 65 C were measured during the first and second growing seasons on the retorted shale treatment. These extremely high temperatures may have been lethal to the limited number of plant species that were able to germinate and emerge.

Another problem with revegetating directly on retorted shale is the uptake and concentration by plants of potentially toxic trace elements. Plant analysis that was done on legume and shrub species seeded on the shale disposal study indicated that boron concentrations are approaching levels that may be harmful to plant growth. These plants are also accumulating molybdenum at levels that are toxic to livestock. These concentrations are evident on treatments ranging from 30-91 cm of soil over retorted shale. The concentrations are highest in the 30 cm soil treatment and decrease with increasing amounts of soil cover. Utah sweetvetch contained molybdenum levels of 26 ppm on the 30 cm soil cover treatment, 9.7 ppm on the 60 cm treatment, and 6.4 ppm

on the 91 cm soil cover treatment (Lindsay 1979). When root samples were taken on the soil-shale treatments, it was observed that roots from all plants growing in soil cover displayed normal morphology while those growing into the shale were dramatically altered. Root penetration was limited to the upper 8 cm of the retorted shale and became extremely diffuse and less vigorous.

Because of the requirements for large inputs of scarce resources and the possible environmental hazards of revegetating retorted shale directly, a more feasible and environmentally acceptable approach appears to be the covering of retorted shale with a suitable amount of soil material. The results from our study indicate at the present time that a minimum of 61 cm will be required for an adequate soil covering. The total aboveground biomass of seeded species was greatest on those treatments with 61 and 91 cm of soil over shale. Because of the restricted rooting depth and lower available moisture, the 30 cm soil covering supported less plant growth than the greater soil profile depths. It is believed that this difference will become more pronounced in subsequent years as the plant communities mature and competition for soil water becomes more acute especially in low precipitation years.

A regression analysis was used to determine the relationship between aboveground biomass production and depth of soil cover. The coefficient of determination for the regression of aboveground production on soil depth was 0.92, and the regression was significant at the .01 level of probability. This relationship between soil depth and aboveground production was consistent to a soil depth of 61 cm. The increased production on the 91 cm soil covering was not significant. However, in light of the trace element problem and as roots begin to fill the soil profile, the optimum soil depth may change.

A significant part of our integrated approach to reestablishing ecosystems associated with the aboveground disposal of retorted shale is the characterization and monitoring of microbial activity as affected by revegetation practices. Hersman and Klein (1979) investigated in a laboratory study the effects of retorted oil shale additions on the microbiological characteristics of surface soils to evaluate possible effects of mixing soil and retorted shale which might occur as part of reclamation programs in areas disturbed by oil shale disposal. Retorted Paraho (direct) shale material had varied effects on several important microbial processes and on the different major groups of soil microorganisms. With retorted shale present at up to 10% by weight no negative effects on oxygen uptake or on actinomycete and bacterial populations were noted, while significant reductions in nitrogen fixation rates, dehydrogenase activity, fungal populations, glucose mineralization, and ATP concentrations occurred. These results suggest that the more specialized functions of the soil microbial population, especially nitrogen fixation, have a greater sensitivity to retorted oil shale material.

In light of these results on microbial processes, it may be necessary to insure that little physical mixing of the surface soil and retorted oil shale occurs. To minimize upward movement of soluble fractions from the retorted shale under specific climatological conditions it may be necessary to consider the construction of capillary barriers below the surface soil cover. In addition, the surface soil depth chosen should be sufficient to allow plants to establish a functional decomposer community in the plant root zone which will not be excessively influenced by the underlying shale material.

CONCLUSIONS

Based on the results from this research it appears that the most feasible approach to surface stabilization of Paraho retorted shale is to cover the material with an adequate amount of suitable soil or geologic material. This approach offers the advantage of greater and more diverse vegetation establishment without high levels of leaching, fertilization, mulching, irrigation, and management. It also provides a growth medium that will support a diverse microbial community that is essential for a natural functioning ecosystem. The use of a soil cover will reduce the possibility of toxic element concentration in the vegetation and movement upward of harmful chemical constituents from the shale into the overlying root zone.

Under natural weathering conditions retorted shale will become a more suitable plant growth medium. Shale and shale leachate samples taken from the soil-shale profiles have shown that pH and EC decrease with time under natural weathering and soil-forming processes. However, the time period required to allow natural weathering processes to improve the plant growth characteristics of the shale is not acceptable under present environmental and legislative constraints. Therefore, it is recommended that soil covers be an integral part of future retorted shale management plans.

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SESSION 5
CONVENTIONAL COAL UTILIZATION
II – COMBUSTION

Chairman: M. Shapiro
Co-Chairman: Myron Gottlieb

The Goals of the Fossil Energy Advanced Environmental Control Technology Program

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The Advanced Environmental Control Technology (AECT) Program is a new program within DOE which began in FY 1979. The Flue Gas Cleanup Project is a vital short term part of the AECT. Its purpose is the development, improvement, and technical and economic evaluation of existing and promising new methods for removing undesirable pollutants and wastes resulting from the combustion of coal.

The project is directed toward conducting full-scale verification of equipment and systems that will reliably and economically provide solutions to environmental degradation associated with direct coal utilization. The objective is to provide technology to meet environmental regulations in the early- and mid-1980's considering reliability, costs, and energy efficiency.

Flue Gas Cleanup (FGC) addresses the removal of gaseous and particulate pollution-causing contaminants from the stack gases of combustion units. The justification for this effort is as follows:

- Conventional combustion is the most available utility-scale approach using coal in the near-term through 1990.
- FGC is required in most combustion applications (new construction) to meet EPA regulations.
- Stricter New Source Performance Standards (NSPS) are already in force for utilities, and standards are in preparation for industry.
- The Resource Conservation and Recovery Act (RCRA) may affect the use of current lime/limestone systems due to sludge disposal problems.
- Environmental standards are a moving target which must be met through improved capability of control technologies.
- Poor scrubber performance, sludge disposal problems, or high cost are court-accepted reasons for exemptions to burn oil or exemptions from oil-to-coal conversions.
- Poor scrubber availability results in plant shutdowns with subsequently increased usage of oil and gas in turbines and possible power shortages.

The primary focus in flue gas cleanup has in the past been in the areas of SO_2 and particulate (flyash) control for electic utility applications. Approximately 16,000 MW or 6% of the total coal fired power generating capacity is controlled by Flue Gas Desulfurization (FGD). This will increase to about 25% by 1986. Most of the initial applications were retrofitted, whereas by 1985 about 75% of the operational FGD systems are expected to be new unit or plant applications. The vast majority of these systems will utilize the lime and/or limestone processes.

DISTRIBUTION OF FGD SYSTEMS BY CHEMICAL PROCESS

	FGD Capacity, MW			
Process	perational	Under Construction	Planned	Total
Limestone	8,734	8,687	10,848	28,269
Lime	6,070	6,029	3,482	15,581
Lime/Limestone	20	330	330	680
Sodium carbonate	375	509	0	884
Magnesium oxide	120	0	1,326	1,446
Wellman Lord	735	180	940	1,855
Dual Alkali	0	1,102	0	1,102
Aqueous carbonate	0	400	100	500
Citrate	0	60	0	60
Total	16,054	17,297	17,026	50,377

Source: PEDCo Environmental, Inc., "Status of Flue Gas Desulfurization in the United States," March 1979.

Commendable work in the development of FGD systems was done by EPA. However, a major goal of EPA was to demonstrate that existing scrubber technology could meet or exceed existing and proposed NSPS. The near-term DOE role is to develop and demonstrate improved technology to encourage industry and the electric utilities to convert to coal by making its use environmentally and economically attractive.

AECT has prepared plans to implement the FGC project to better meet the DOE objectives. The basic philosophy is as follows:

- Lime/limestone systems predominate in the utility market and will continue to do so in the near-term.
- FGD systems for industrial applications must be improved and reduced in cost if industry is to convert to coal.
- In the future, dry scrubbing may reduce water consumption, waste disposal problems, and costs if systems now being demonstrated for low-sulfur high alkali Western coals can be adapted to high-sulfur Eastern coals.

- Wet and dry regenerable systems reduce land requirements and simplify waste disposal problems even if the by-products do not have commercial value.

- Retrofit applications should be considered for all systems improvements or new systems.

- NO_x/Particulate systems removing all contaminants in a single system or device should provide environmental, technological, and economic breakthroughs.

The Flue Gas Cleanup Program is divided into two primary areas: (1) Flue Gas Desulfurization (FGD) Systems which addresses SO_2 control through the use of scrubbers; and (2) NO_x Particulate Control which addresses the removal of NO_x, particulates, and other contaminants of flue gases in an integrated system.

Based on the philosophy outlined, anticipated budget limitations, and state of existing technology, the proposed strategy is as follows:

1. Attempt to make near-term improvements and retrofits to existing lime/limestone technology.

2. Expedite the development and demonstration of dry scrubbers, regenerable systems, and other improved methods of SO_2 control which have both industrial and utility applications, and which mitigate the problems of lime/limestone processes.

3. As rapidly as possible, develop the ultimate technology to remove all pollutants - SO_2, NO_x, particulates, trace elements, etc., in a single economically attractive process.

4. Develop crosscut technology applicable to the improvement of all systems, such as sampling, instrumentation, process controls, and waste management.

Most of the problem areas with early lime/limestone systems, are now being overcome by the normal forces of the market and competitive incentives. Vendors are now offering both cost and performance guarantees. However, in general, the installations with the best performance records have used low or medium sulfur coal. Long-term performance and maintainability with high-sulfur Eastern coals remains unproven on a large scale.

Current lime/limestone FGD units are characterized by chemical plant rather than power plant operation. Those which have operated successfully generally have required large crews. Past units typically did not adapt well to changes in coal supplies, sorbent limestone grades, or plant load variation, and are difficult to "chemically" control.

The secondary pollution issue is becoming increasingly severe. Lime/limestone FGD units essentially trade air pollution for solid waste and water polllution because of the large quantities of waste material (sludge) produced by this nonregenerable process. Lime/limestone sludge problems are particularly severe if the FGD process does not produce an easily dewatered product such as gypsum. In addition, installation of a lime/limestone FGD system which complies with the SO_2/NSPS may cause the power plant to violate the new NSPS regulations for particulate emissions, since no technology is currently available for the control of FGD scrubber-generated particulates which pass through the mist eliminator. The present cost of sludge disposal is approximately 20 percent of FGD operating costs.

Current lime/limestone FGD capital costs are approximately $56-140/KW for a typical coal-fired installation; corresponding annualized costs may be as high as 10 mills/KWH. Studies also show that total energy supplied to the boiler must be increased 3 to 7 percent depending on FGD type, coal type, and other variables. The plant size and capital costs must, therefore, be increased to maintain the desired electrical output. As a result, lime/limestone FGD systems account for almost 25 percent of the costs of new power plants.

AECT has placed its near-term emphasis on the use of high-sulfur coals in lime/limestone systems which predominate in the utility area. Existing test facilities, such as the three 10 MW units at TVA, will be utilized to a large extent. Present interest in acid rain indicates the desirability of improving the existing systems ability to capture SO_2. Major emphasis is being placed on characterizing wastes from all types of coalfired plants and in developing standardized sampling and test procedures to permit intelligent compliance with RCRA and other ground and water pollution regulations. Improved methods of waste disposal and waste management are being developed. These include the use of organic and inorganic additives and forced oxidation to produce stabilized wastes or potential by-products. This near-term lime/limestone sub-task will phase out by FY 1986.

AECT is exploring so-called "advanced" systems which may overcome the inherent problems of lime/limestone processes. These include various dry processes, dual alkali systems, and wet and dry regenerable and nonregenerable processes, some of which produce sulfur or sulfuric acid as by-products. All of these are being studied to select those for future scale-up and testing, and evaluation is planned at industry-owned pilot or prototype plants now in operation or undergoing shakedown. Industrial plants and second-generation plants will produce unique wastes and waste management problems. Solution to to these problems will be continually sought in the AECT program. Cost-shared demonstration of industrial and utility advanced scrubber technology is planned in new and, hopefully, in retrofit applications.

These technologies are expected to improve SO_2 capture, be more cost-effective than lime/limestone, reduce waste problems, and require less water and energy. However, they do not address the problems of NO_x control and

respirable particulate capture. Research is needed in thess areas and is being being performed under the AECT program. The goal is development and demonstration of a cost-effective environmentally acceptable system or "black box" capable of controlling emissions of all pollutants, including trace elements, and demonstration of acceptable systems for waste management. It is hoped that such a system can be developed for demonstration by 1986.

NO_x Particulate Control

The presence of SO_2 may cause non-desirable synergistic effects on NO_x, particulate, and trace metal removal from coal combustion. This effort extends coal flue gas technology beyond sulfur removal to control of NO_x, particulates and trace metals in anticipation of possible impacts caused by the increasingly extensive use of coal. The target is a more complete control of the total spectrum of pollutants with technology to become available in the late 1980's period.

To determine the most cost-effective route for NO_x control in coal combustion, a state-of-the-art assessment of existing methods for NO_x abatement will be carried out to weigh the relative merits of decomposition by ammonia (NH_3) injection, retrofit modification of FGD systems, and dedicated NO_x removal procedures. Dedicated NO_x cleanup can consist of decomposition methods in the flue gas or tail-end stand-alone techniques. NH_3 injection may function as such a method, and efforts in that area will focus on NO_x removal efficiency and the environmental effects of escaping NH_3. In addition, innovative concepts for tail-end NO_x control will be evaluated for retrofit capability on installations which include other cleanup systems.

Coal combustion results in the emission of large amounts of particulate matter. Particulate cleanup devices include advanced centrifuges, electrostatic precipitators, and fabric filters (baghouse filters). Primary needs are to improve filtering efficiency, especially for particles of less than two microns in size, and improving the ability to operate at higher temperature.

Developmental efforts to combine NO_x removal with FGD for SO_2 control will be evaluated. The feasibility of retrofit modifications of lime/limestone FGD scrubbers for simultaneous NO_x removal, either by additive selection or by hardware design changes, will be examined. In addition, new process concepts which effect simultaneous SO_2/NO_x removal will be tested.

Successful accomplishment of these objectives requires the close coordination and timely support of EPRI, TVA, EPA, other groups within Fossil Energy, electric utilities (full-scale power plant testing), and industry (power plants, equipment) through cost-sharing, and the use of available operational and test facilities. The end result must be the commercial acceptance of the new or improved technology. Thus, the developers of the technology must have credence with industry and the electric utilities. A large portion of AECT funds will be spent on applied contract research and development with limited back-up support from in-house laboratories.

Broad program management and development, including interface with other Government agencies, will be done by the DOE Headquarters staff. Management of individual tasks and subtasks, including most procurement actions, will be handled through Morgantown, the lead field Energy Center for this project.

In summary, the ultimate goal of DOE's coal strategy is to decrease the Nation's dependence on imported oil through a range of cost-effective uses of coal. Because close to 90 percent of the coal consumed in this country is, and will continue to be, burned directly, the primary objective of the AECT Program is to assure that stationary facilities now burning coal can continue to do so while meeting applicable environmental standards, and to make coal the preferred fuel for new industrial and utility applications.

COAL COMBUSTION CLEANUP TECHNOLOGY DEVELOPMENT

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Department of Energy

1. INTRODUCTION

Cleanup technology for conventional coal combustion is being developed under the DOE Advanced Environmental Control Technology program to meet the needs for environmentally acceptable increased use of coal. The program objective is to provide the needed technology to meet environmental regulations and constraints within a framework that considers costs, energy efficiency, and acceptability of the technology to the utility and industrial sectors. A sub-element of this total program is the Flue Gas Cleanup program area which specifically addresses the pollutants associated with gaseous emissions from coal combustion. This paper describes the objectives and implementation approach of the Flue Gas Cleanup program area.

Conventional combustion offers the most readily available means to increase coal utilization in the near term period through 1990. Cleanup technology is needed to insure acceptable environmental impact of increased coal use to meet existing standards and to anticipate future environmental standards which may require technologies with improved control capabilities.

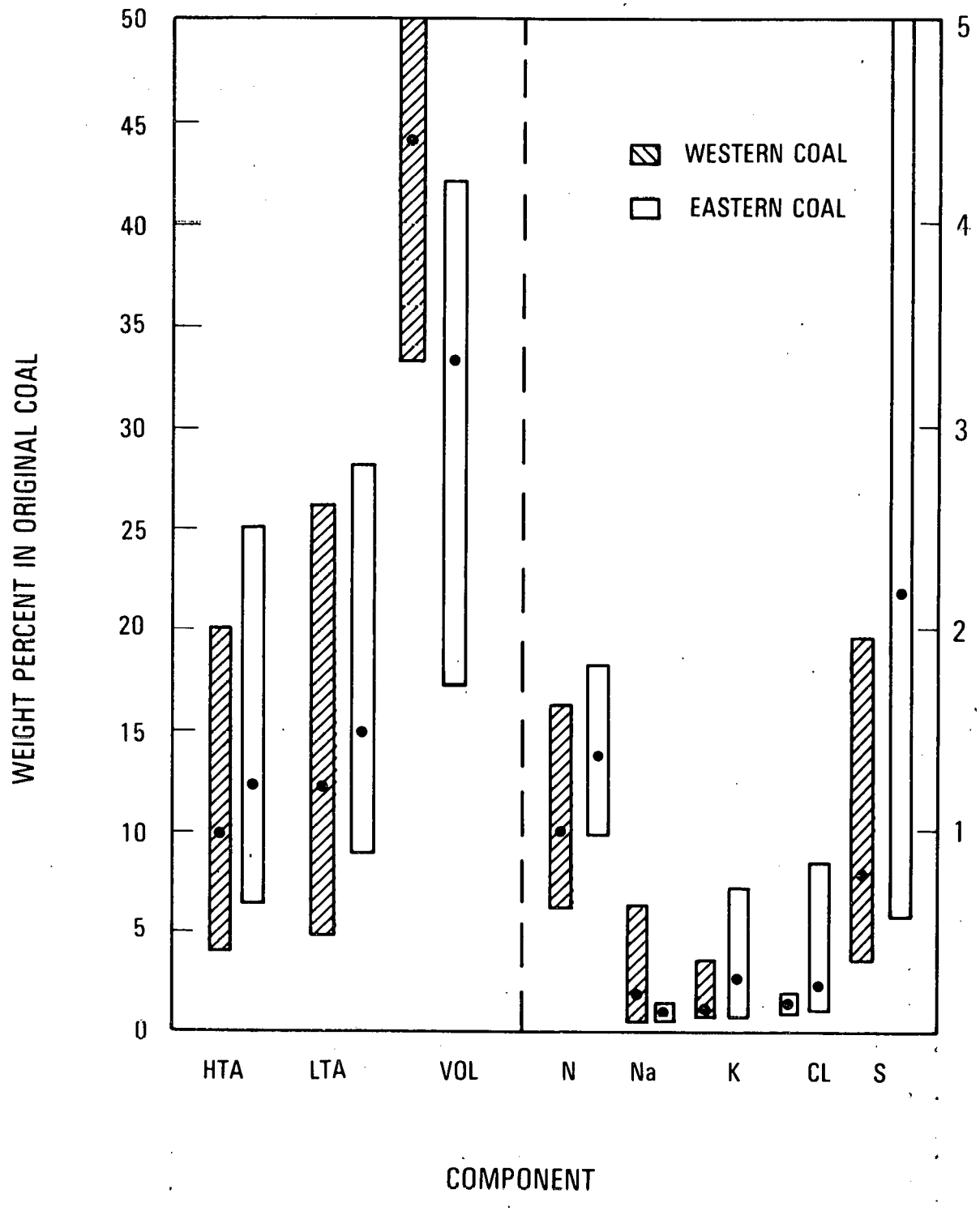
Under DOE's Fossil Energy decentralized management approach, the Morgantown Energy Technology Center has been designated as the lead center for the program implementation. Technology development needed to meet the program goals is being initiated through multiple projects with industry, national laboratories, universities, and other R&D organizations.

2. BACKGROUND

Contaminant levels in coal vary considerably with the coal rank. Within a coal rank or even a single coal seam, contaminant levels often vary substantially creating differing requirements for cleanup of flue gas from combustion. Figure 1 illustrates the variability of several important contaminants in U.S. coals. A general subdivision between western and eastern coals is indicated and average or typical contaminant levels are indicated by solid dots within the range bars.

Particulate emissions in combustion flue gas arise from high temperature ash (HTA) components in the coal. Ash levels can range from about 4 to as high as 25 percent on a weight basis. While most ash remains in the combustor, substantial levels are carried off with the flue gas requiring control. Fine ash particulates below 10 microns require more costly cleanup equipment and are of particular concern. Formation of these fine ash particles during devolatilization and char burning stages of combustion and reactions with gas phase components involves complex interrelated processes. Understanding these processes is needed to define and characterize the size distribution and chemical makeup of emitted particles.

FIGURE 1
RANGE OF CONTAMINANT CONCENTRATIONS IN BITUMINOUS, LIGNITE, AND SUB-BITUMINOUS COALS



Hydrocarbon emissions from coal combustion arise from volatiles (VOL) in coal. The volatiles make up substantial fractions of the coal. Generally, volatiles are consumed during combustion but can be an environmental concern, especially when combustion conditions are not properly maintained. Complex chemistry is involved in the formation and combustion of volatiles from coal.

Fuel bound nitrogen (N) varies from about 0.5 to 2 weight percent of the fuel. Oxidation of this nitrogen along with atmospheric nitrogen during combustion produces NO_x emissions. Two forms of the oxides, NO and NO_2 are toxic and involved in the formation of photochemical smog. Elements 'such as sodium (Na), potassium (K), and chlorine (CL) are not usually of environmental concern but are important considerations for protection of process equipment such as gas turbines and scrubbers in systems utilizing this equipment. Sulfur (S) levels vary widely with western coals generally somewhat lower in sulfur levels than eastern coals. Control of SO_2 formed during combustion of coal has received extensive attention.

Current environmental standards which directly affect coal combustion include New Source Performance Standards, State Implementation Plans, Ambient Air Quality Standards, Prevention of Significant Deterioration Regulations, and the Resource Conservation and Recovery Act. These standards and regulations set the current requirements for cleanup of various pollutants. Additionally, future regulations may require more stringent control of currently controlled contaminants and may in addition require emission control of other coal contaminants. These current and potential future regulations define the cleanup targets of the Flue Gas Cleanup program.

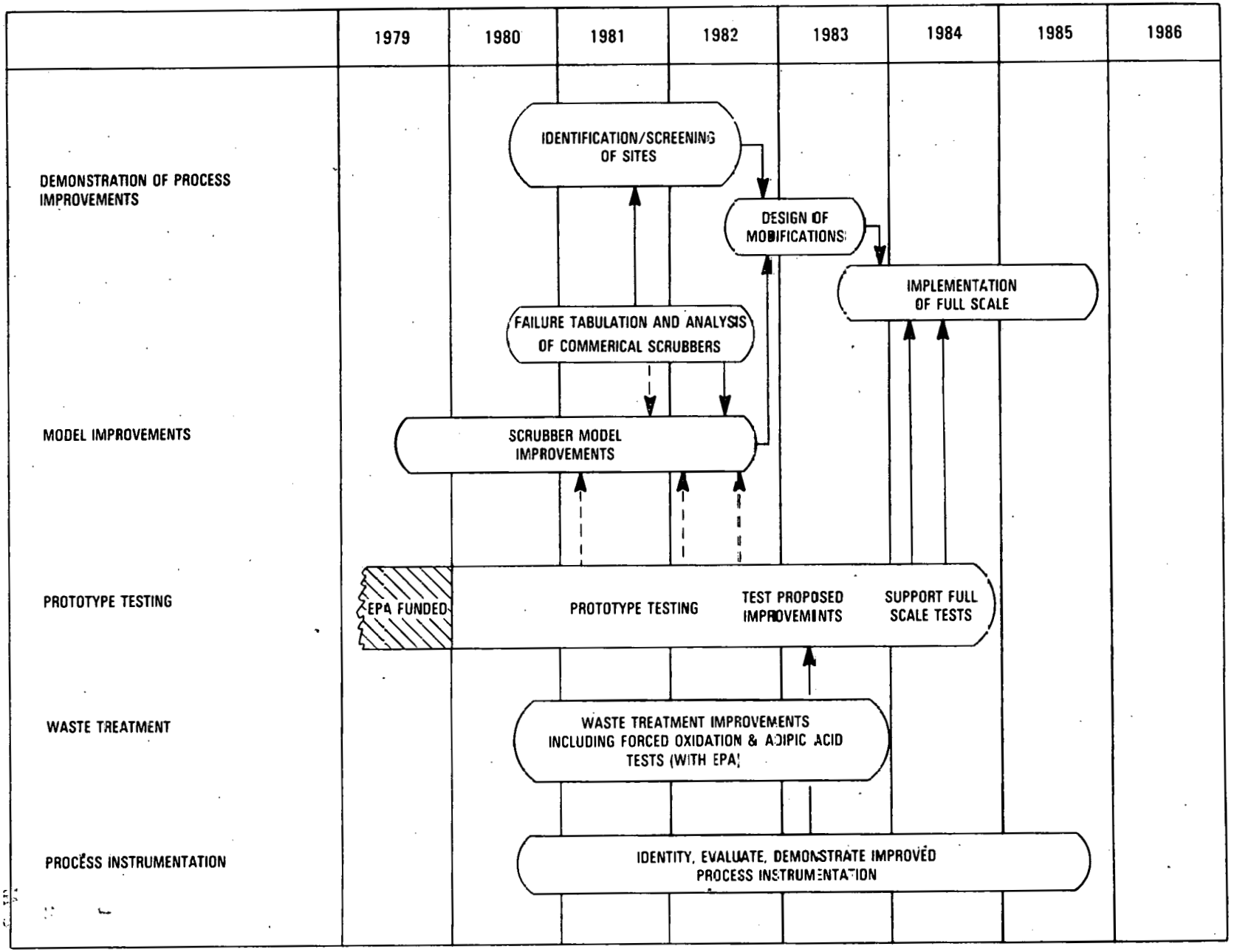
The AECT Flue Gas Cleanup program is divided into two primary areas. The first primary area is Flue Gas Desulfurization which considers as separate subareas for lime/limestone scrubbers and advanced flue gas desulfurization systems. The second primary area is NO_x/Particulate control. This area addresses technology for NO_x and particulate control and, in addition, considers hydrocarbons and trace metal contaminants. In discussing specific objectives and implementation plans, the two desulfurization subareas and the NO_x/Particulate area are considered separately below.

Lime/Limestone Scrubber Program Subarea

Lime and limestone scrubber systems are currently installed in many utility power plants to control sulfur dioxide emissions to required levels. Experience with these scrubbers has indicated a need for improvements in overall performance and a need to mitigate the associated sludge management problems. Objectives of the AECT program in this area include: (1) improvement of SO_2 capture performance, (2) improvements in sludge disposal characteristics, and (3) assuring scrubber availability, particularly with high sulfur coal and closed water loop applications. The program aims to provide demonstration and encouragement of commercial use of improvements by 1986.

Figure 2 illustrates the types of development activities and their interrelationships during the life of the project. Technology improvements are expected from R&D activities in scrubber model refinement, prototype testing on the $10MW_e$ TVA Shawnee Facility, waste management studies, and in refinement

FIGURE 2–LIME/LIMESTONE SCRUBBERS



of process instrumentation. Each of these activities consists of a number of individual projects by various organizations. Ultimately, results of these projects will be integrated into a demonstration of the improvements resulting from the R&D activities.

Advanced Flue Gas Desulfurization

Advanced flue gas desulfurization systems will be needed in a longer term to minimize the overall environmental impact of coal utilization and to reduce costs to consumers for this environmental control. While lime and limestone systems essentially trade air pollution for solid waste problem, the amount of solid waste that will result from an expanded coal economy will present more serious disposal problems. Advanced flue gas desulfurization systems include non-regenerable processes which improve the disposal characteristics of solid wastes and regenerable processes which minimize solid waste production. Advanced FGD processes vary in their stage of development from demo-ready technologies to processes which have yet to be tested on the pilot scale.

AECT activities from these technologies is aimed at ultimate demonstrations of the best of these advanced processes. Figure 3 illustrates the kinds of activities which are intended to lead to ultimate demonstrations. Both utility and industrial activities are included in this plan.

NO_x/Particulate Control

The second primary area of the Flue Gas Cleanup program considers technology development for control of nitrogen oxide emissions and combined control of nitrogen and sulfur oxides, control of fine particulates as well as total particulates, and control of hydrocarbon and trace elements. Figure 4 illustrates the major activities in these areas.

Nitrogen oxide formation and control chemistry is being studied in a number of projects along with pilot scale testing being done jointly with EPA. This work will lead to assessment of the need and options for development and demonstration of advanced NO_x control methods.

Fine particulate, hydrocarbon, and trace element emissions includes activities on instrumentation development, characterization of emerging coal combustion technologies such as fluidized-bed combustion, and development of advanced particulate control methods. Decisions on pilot and larger scale testing will be dependent on future environmental standards and regulations relating to these pollutants.

Limited activities will be carried out to evaluate and assist in potential problems of current electrostatic precipitators and baghouses in meeting total particulate emission levels.

Joint Projects

The AECT program currently has a number of cooperative projects with the Environmental Protection Agency (EPA) and with the Tennessee Valley Authority (TVA). The projects are jointly funded and administered by one of the agencies. Cooperative sponsorship allows each organization to meet its individual

FIGURE 3-ADVANCED FLUE GAS DESULFURIZATION

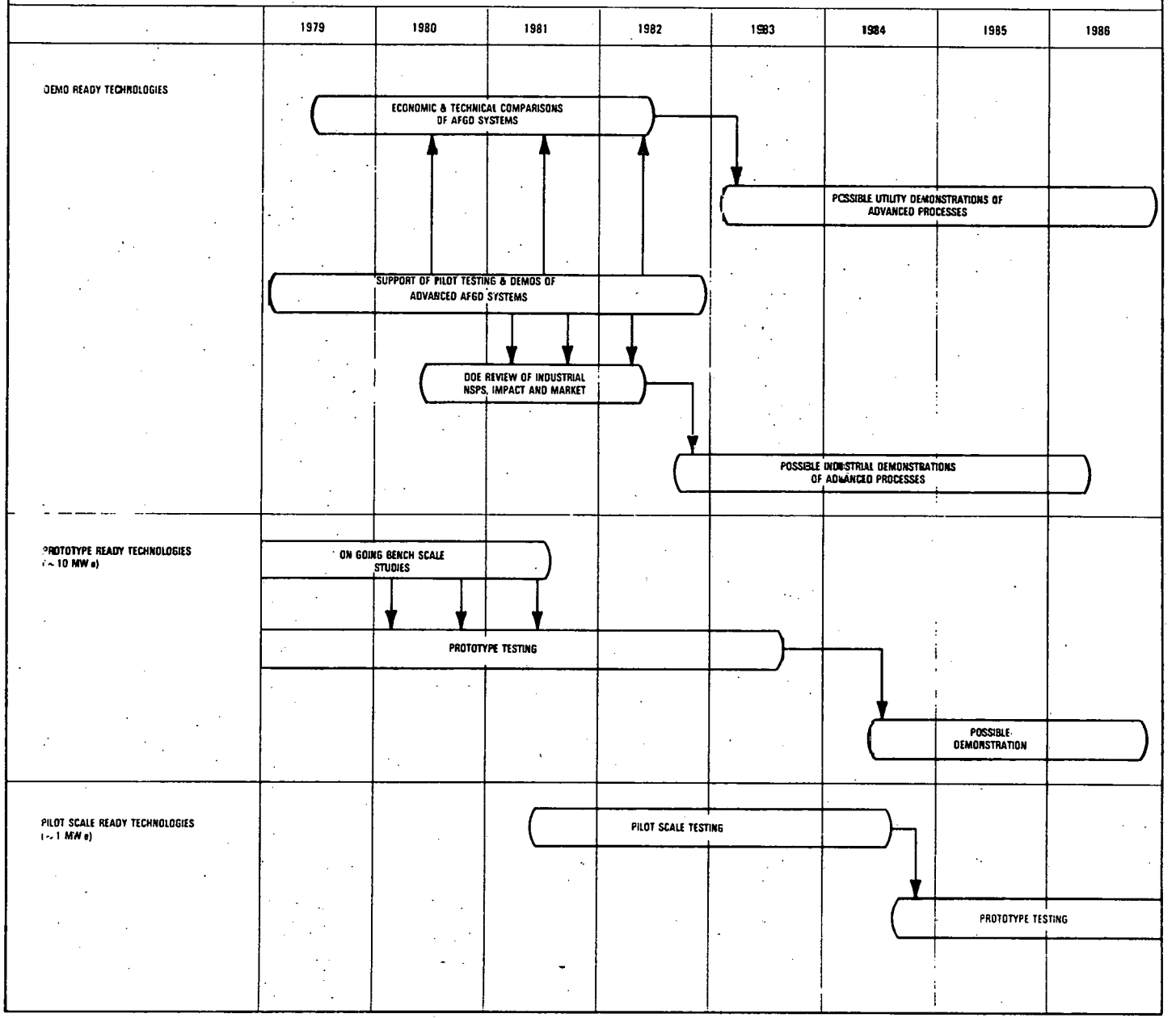
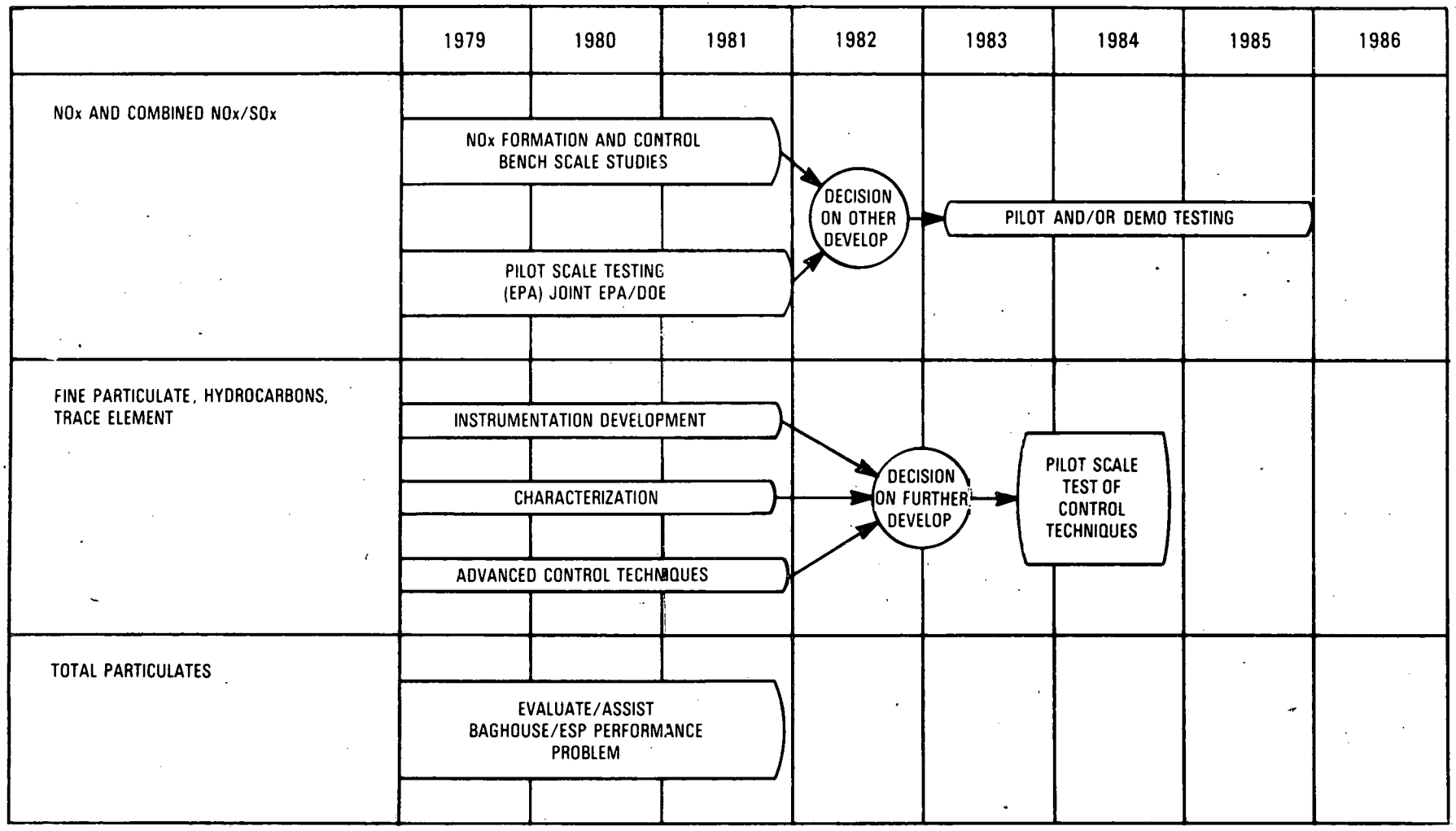


FIGURE 4-NOx AND PARTICULATE CONTROL



goals while avoiding duplication and minimize overall costs. Jointly with EPA, the AECT program is funding in fiscal year 1980 projects on dry scrubbing, a full-scale adipic acid addition demonstration, a dual alkali FGD development and demonstration program, full-scale demonstration of the Rockwell Aqueous Carbonate FGD Process, development of a high temperature and high pressure electrostatic precipitator, low NO_x burner development, testing of the Hitachi Zosen NO_x reduction process and the UOP-Shell copper oxide simultaneous NO_x and SO_x removal process, and technology transfer symposia. The Shawnee Test Facility has also been jointly funded by EPA and the AECT program in fiscal year 1980.

3. SUMMARY

A comprehensive program to address the diverse environmental issues related to expanded coal utilization is being initiated as part of the DOE Advanced Environmental Control Technology program. Project activities ranging from studies of the fundamental processes involved in pollutant formation to demonstrations of well developed control methods are being supported. The program aim is to provide the needed cleanup technology to meet environmental constraints within a framework that considers costs, energy efficiency, and acceptability of the technology to the utility and industrial sectors.

ENVIRONMENTAL CONTROL DEVELOPMENTS IN THE DIRECT COMBUSTION OF LOW-RANK COALS

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INTRODUCTION

Grand Forks Energy Technology Center (GFETC) has been designated by the Department of Energy as the lead Center for low-rank coals technology. Low-rank coals are generally considered to be coals having less than 11,500 Btu/lb (6,390 kcal/kg) heating value on a moist, mineral-matter-free basis. They comprise approximately one-half of the identified coal resources of the U.S.A., and are principally found in the Western states, with major subbituminous coal fields located in Montana, Wyoming, Colorado and New Mexico, and large lignite deposits situated in North Dakota and Texas.

The average sulfur content in these coals is only 0.7% which is an attractive feature to coal burning plants subject to the 1971 NSPS emission standard of 1.2 lb $SO_2/10^6$ Btu. Moreover, the mol ratio of alkali to sulfur (Ca/S) in these coals is often greater than unity, suggesting the use of western coal fly ash for removing sulfur dioxide from flue gas. GFETC in 1971 pioneered studies on utilizing the alkali in western coal fly ash in flue gas desulfurizing wet scrubbers.

One of the challenges facing the environmental control engineer reflects the fact that some low-rank coals have both low sulfur and low sodium contents, which causes their fly ash to possess high electrical resistivity. This has an adverse effect on the performance of an electrostatic precipitator (ESP) collecting the fly ash.

Another challenge facing the environmental engineer arises from the fact that sludges from wet scrubbers using fly ash from low-rank coals for flue gas desulfurization often have high concentrations of soluble salts, which may be leached out readily. It is possible for these salts to enter neighboring ground water, and in certain situations they could raise the concentration of salts in the ground water above the maximum levels specified in the National Interim Primary Drinking Water Regulations (NIPDWR). On the positive side, the dominant sulfur form in the scrubber liquor is sulfate, and as a result the sludge is readily dewatered and has above average settling characteristics. Moreover, the sludge has good load bearing characteristics, reflecting its residual alkalinity which imparts some pozzolanic characteristics to it.

GFETC has an on-going R&D program investigating a variety of environmental control technologies applicable to low-rank coals. One facet of the program focuses on flue gas desulfurization (FGD) in a wet scrubber using low-rank coal fly ash as the absorbent for sulfur dioxide. Another project is targeted to flue gas sulfur dioxide cleanup using dry sorbents. A third project is directed to the sampling, characterizing and control of particulate matter in flue gases emitted

during the combustion of low-rank coals. A fourth project is the characterization of the physical and chemical properties of sludges generated during wet scrubbing of flue gases with low-rank coal fly ash.

GFETC has well-designed pilot plant facilities dedicated to studying the inherent characteristics and behavior of low-rank coals and their combustion products with respect to their effect on the environment and their interaction with it. Two of the principal pieces of equipment specifically designed, constructed and currently operated for this use are a 130-scfm wet scrubber used in flue gas desulfurization studies, and a 75-lb/hr pulverized coal-fired furnace used in both dry sorbent and particulate studies. This furnace is equipped with an ESP or, alternatively, with a baghouse. In addition, a 130-scfm combustor and experimental high-temperature baghouse are being installed for continued studies on the use of dry sorbents for sulfur dioxide control in flue gas.

Besides the pilot facilities, GFETC has a well-equipped analytical department which provides services to the pilot plant effort, and also investigates new techniques and procedures applicable to the analysis of low-rank coals and their combustion products. In addition, the analytical department studies the physical and chemical phenomena underlying the combustion process and the potential chemical influence of its products on the environment.

Beyond its programs in the pilot plant and laboratory, GFETC works closely with low-rank coal fired electric utility companies in field testing new environmental control technologies and processes. This work occasionally involves sending a team of two to ten GFETC personnel to a utility power plant for two to twelve weeks to monitor a new operation or process and/or collect specific experimental data.

WET SCRUBBING

In 1971, GFETC initiated a research program that resulted in the development of technology for using high-alkali fly ash from low-rank coals to remove sulfur dioxide from flue gas in wet scrubbers. One of the salient findings of these early studies at GFETC was the fact that fly ash can be solubilized in an aqueous media, with calcium oxide availability increasing as the pH is lowered.

The pilot plant wet scrubber at GFETC consists of a 130-scfm flooded disk venturi atop an absorption tower containing conical "rain and drain" trays, as shown in Figure 1. Pressure drop across the scrubber is controlled by adjusting the height of the flood disk. The scrubber system operates in a "closed loop" mode, with scrubber liquor returned to a fly ash mix tank equipped with an overflow weir. Overflow from the mix tank flows to a settling tank where calcium sulfate precipitates and unreacted fly ash is allowed to settle. A floating overflow weir in the settling tank provides scrubbing liquid to the flooded disk. A 33-inch length of removable pipe in the discharge line from the tower is provided for use in calcium sulfate scaling experiments.

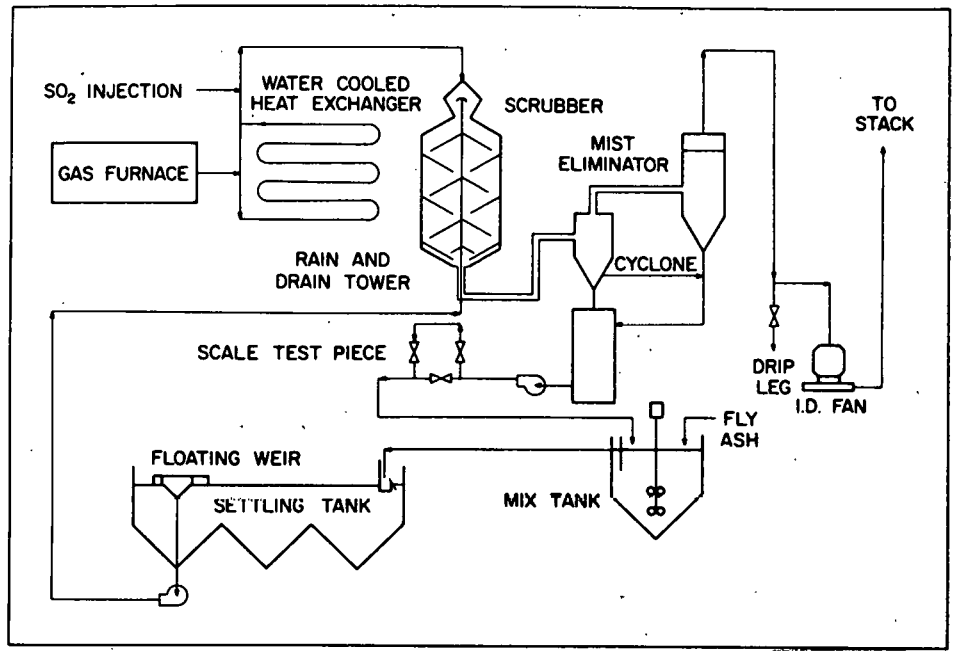


FIGURE 1. - 130-scfm pilot plant scrubber, Grand Forks Energy Technology Center.

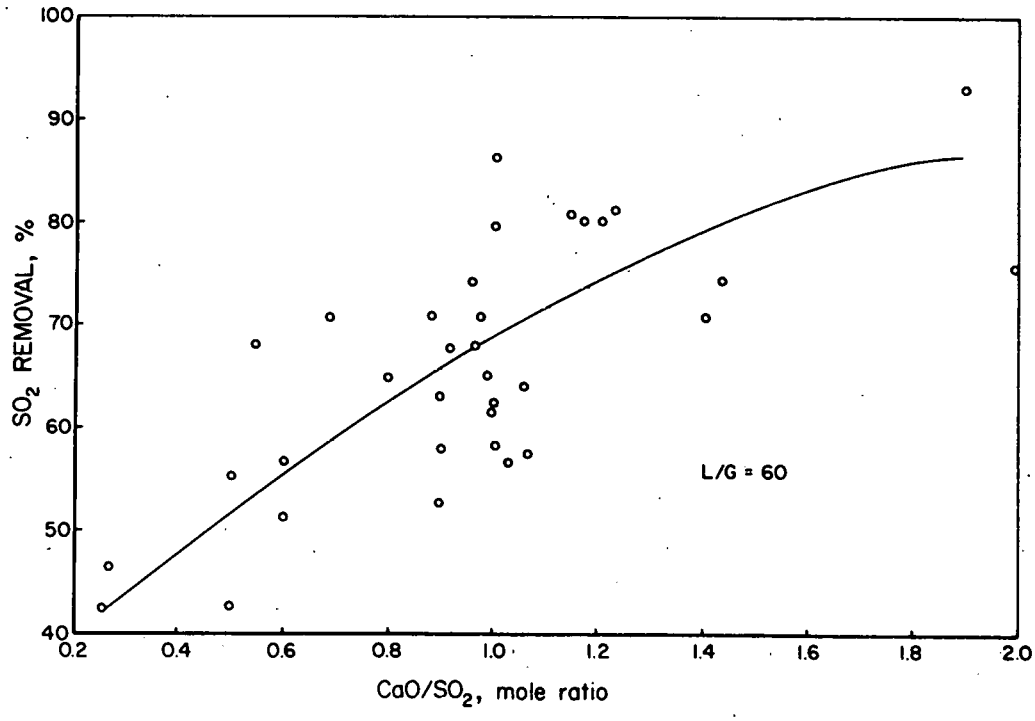


FIGURE 2. - Sulfur dioxide removal as a function of CaO/SO_2 mol ratio at L/G = 60.

The results of current studies in the pilot plant confirm earlier data (1) which indicated that percent sulfur dioxide removal increases with increasing CaO/SO_2 mol ratio (mols CaO in incoming fly ash ÷ mols SO_2 entering in flue gas). As shown in Figure 2, sulfur dioxide removal increases from about 42% at a CaO/SO_2 mol ratio of 0.26 to approximately 86% at a mol ratio of 1.9. These data are based on a constant L/G of 60, where L refers to slurry flow to the scrubber in gpm, and G refers to flue gas flow through the scrubber in acfm/1,000.

The results of these current studies also indicate the same variation of percent alkali utilization with CaO/SO_2 mol ratio as in previous work (1). The results indicate that alkali utilization drops from 100% at a CaO/SO_2 mol ratio of 0.5 to 42% at a mol ratio of 2.0, as shown in Figure 3, which is based on a constant L/G = 60.

An EPA report on the alkali scrubbing test facility at the TVA Shawnee Power Station, Paducah, Kentucky, published in 1975, indicated that calcium sulfate scaling decreased with increasing liquid-to-gas ratio in a limestone wet scrubbing system (2). A similar result was found in the Western fly ash alkali wet scrubbing system in the present study. Figure 4 shows that the scaling rate in the test pipe section in GFETC's pilot scrubber dropped from 1.7 gm/hr to almost 0.2 gm/hr as the L/G was increased from 36 to 80 gal/1,000 acf flue gas.

The significance of the information in Figures 2, 3 and 4 is the indication that power plants burning low-rank coals and utilizing fly ash wet scrubbing can meet the June, 1979 New Source Performance Standards on sulfur dioxide emissions if the Ca/S ratio in their coal exceeds a certain minimum. Low-rank coals average approximately 0.7% sulfur, with 70% removal required to meet the June 1979, New Source Performance Standards. Figure 2 indicates that this requirement can be met in a fly ash wet scrubber if the Ca/S mol ratio in the feedstock exceeds 1.1 and L/G in the scrubber is 60 or higher. It should be recognized that the sulfur content in coal is variable, which would probably necessitate use of a somewhat higher Ca/S mol ratio and/or higher L/G ratio in an actual operating situation than indicated above. In addition, it should be stressed that the information presented herein is based on a single pilot facility using a limited number of low-rank coals and a limited range of operating conditions, and results might differ in other units depending on the specific situation.

Currently, five low-rank coal-fired electric power plants are using, or are planning to use, fly ash technology for flue gas desulfurization. Approximately 3100 MW's of generating capacity are presently utilizing fly ash technology and an additional 2950 MW's of capacity in the planning or construction stages is based on the use of fly ash for SO_2 removal. Table 1 details the size and location of the current, planned and in-construction FGD plants designed to use fly ash from low-rank coals.

DRY SORBENTS

A second approach at GFETC to flue gas desulfurization is the use of dry sorbents based on sodium compounds. A sulfur dioxide removal

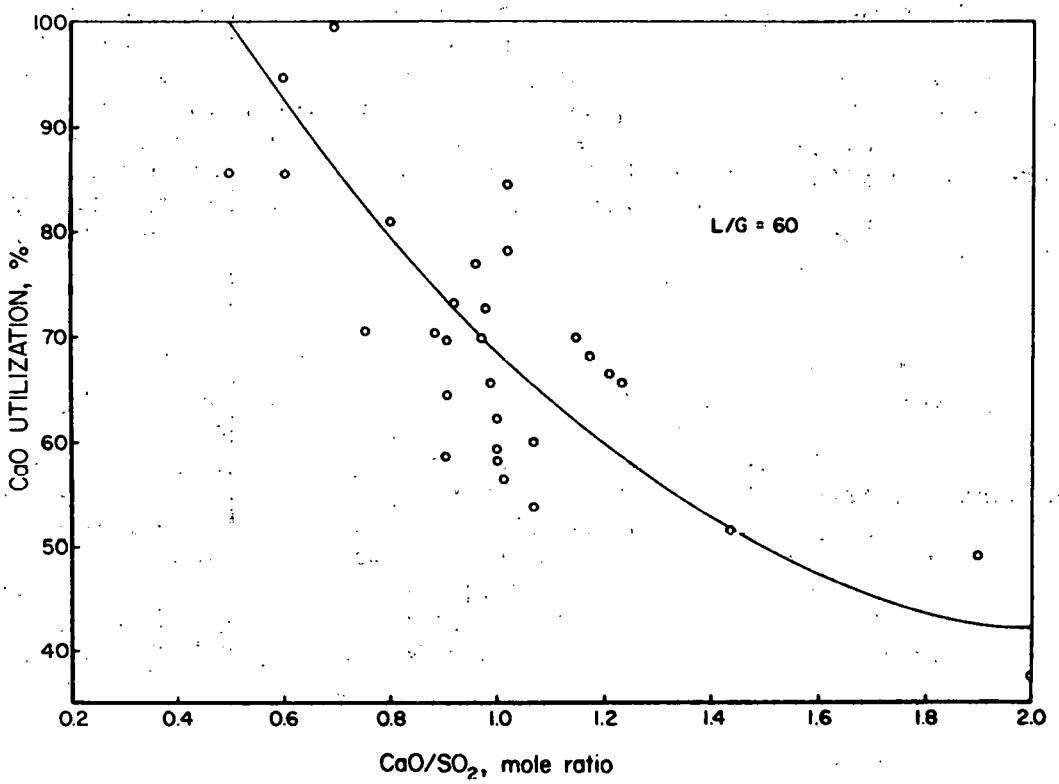


FIGURE 3. - Fly Ash CaO utilization as a function of CaO/SO_2 mole ratio, at L/G = 60.

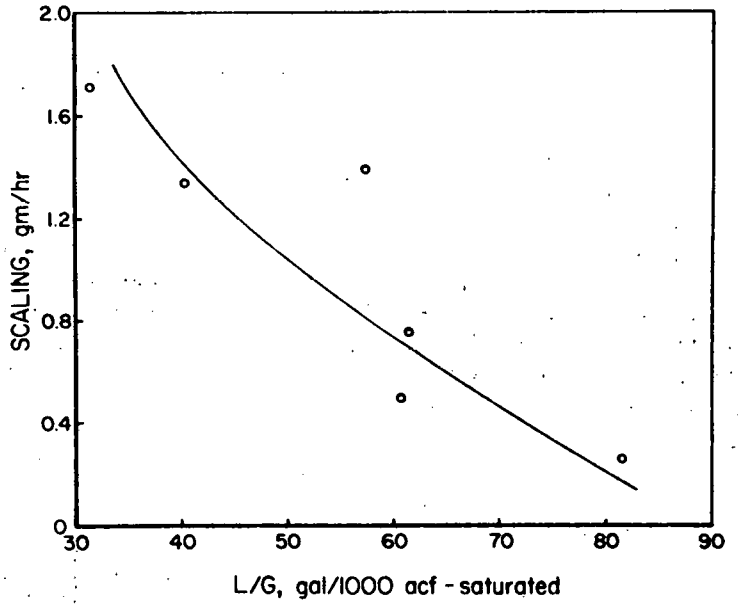


FIGURE 4. - Scaling as a function of liquid-to-gas (L/G) ratio.

TABLE 1. - FGD Wet Scrubbers Utilizing Alkaline Western Fly Ash

Utility/Station	Capacity	Status	FGD Design	Alkali Source
Northern States Power Co.				
Sherburne County	Unit 1 - 700 MW	In-Service	Venturi-marble bed	Subbituminous fly ash - limestone
	Unit 2 - 700 MW	In-Service		
Minnesota Power & Light Co.				
Clay Boswell	Unit 3 - 1 MW	Pilot Plant		
	Unit 4 - 500 MW	Under construction	Venturi-spray tower	Subbituminous fly ash - lime
	Unit 1 - 500 MW	Planned -- mid-1980's	Undetermined	
Montana Power Co.				
Colstrip	Unit 1 - 360 MW	In-service		
	Unit 2 - 360 MW	In-service	Venturi-spray tower	Subbituminous fly ash - lime
	Unit 3 - 700 MW	Planned		
	Unit 4 - 700 MW	Planned		
Square Butte Electric Coop.				
Milton R. Young	Unit 2 - 440 MW	In-service	Spray tower*	Lignite fly ash - lime
United Power Association-Cooperative Power Association				
Coal Creek	Unit 1 - 550 MW	In-Service	Spray tower*	Lignite fly ash - lime
	Unit 2 - 550 MW	Under construction		

*These units are preceded by electrostatic precipitators which renove particulate matter from the flue gas.

process which requires little or no water would be particularly attractive to coal-fired plants located in areas of scarce water supplies. Advantages envisioned for a dry FGD system versus a wet scrubber are: 1) lower capital investment, 2) simpler operation, 3) faster response to changes in sulfur dioxide concentration, 4) better operating reliability, 5) lower operating costs and 6) the waste product produced would be dry.

Pure sodium bicarbonate has been used with good success as a dry sorbent for SO_2, but cost probably precludes its acceptance on a commercial basis. Two naturally occurring high-sodium minerals that are receiving increased attention as candidates for a dry sorbent SO_2 removal system are nahcolite and trona.

Nahcolite contains about 70% sodium bicarbonate and 7% sodium carbonate, and large deposits are located in the Wyoming Green River formation and in northwestern Colorado. It is not mined commercially at present, although interest is mounting as evidenced by a recent article (3) which indicated the technical and economic feasibility of mining 1000 ton/day of nahcolite in the Piceance Basin, Colorado. The mineral is normally found admixed with oil shale and large quantities are projected to become available when oil shale operations commence on a commercial scale.

Trona contains approximately 42% sodium carbonate and 30% sodium bicarbonate, and it is currently mined in California and Wyoming for the production of soda ash. There does not appear to be much excess production capacity available at the present time. All current reserves are dedicated to soda ash production and, because of existing depletion allowance constraints, the exact price structure for alternative markets - such as sulfur dioxide control - is not well established (4).

A laboratory research project was conducted in 1978 under the auspices of GFETC to examine some of the fundamental variables governing the performance of nahcolite and trona as SO_2 dry sorbents (5). The study examined the effect of temperature, moisture and adsorbent particle size on sulfur dioxide removal from a gas stream. The results of the study indicated that nahcolite was a more effective dry sorbent for sulfur dioxide than trona, reflecting the former's greater specific surface area. The investigation also established that sorbent effectiveness increases as particle size decreases.

GFETC has been conducting a pilot plant investigation of the dry sorbent characteristics of nahcolite and trona for more than a year, using a 75-lb/hr pc-fired pilot plant combustor equipped with a baghouse. A drawing of the unit appears in Figure 5. The majority of recent test runs have been with trona, on the basis that this mineral has a greater chance than nahcolite of being commercially available for a dry sorbent SO_2 removal system in the near or intermediate future. The pilot plant tests have evaluated the effect of changes in the entering Na_2O/SO_2 mol ratio on sulfur dioxide removal and alkali utilization. In addition, the study has investigated the effect of changes in dry sorbent injection temperature on sulfur dioxide removal.

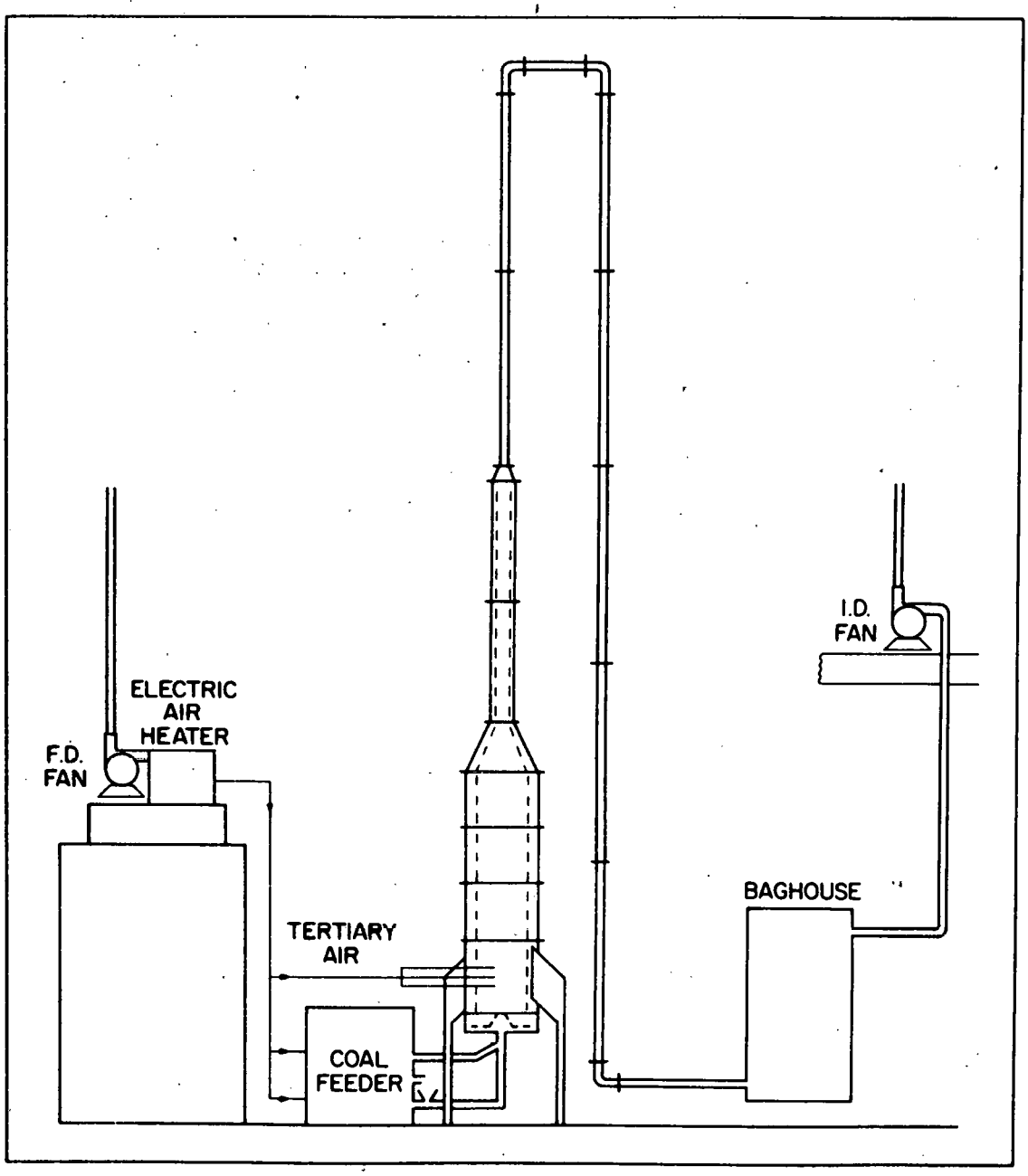


FIGURE 5. - Schematic of pilot plant combustor with baghouse.

Figure 6 shows the increase in sulfur dioxide removal with increasing Na_2O/SO_2 mol ratio, for minus 200 mesh trona. This figure indicates that sulfur dioxide removal increases from about 75% to 95% as the mol ratio of equivalent Na_2O in the entering trona to the entering SO_2 increases from 0.95 to 1.8. It should be noted that the curve in Figure 6 also approximates data for minus 100 mesh nahcolite at the same injection temperature and baghouse temperature.

The utilization of trona in removing sulfur dioxide in the pilot plant experiments was about 75% at a Na_2O/SO_2 mol ratio of 1.0, as shown in Figure 7. One of the problems faced in achieving high utilization of dry sorbent stems from the fact that the reaction product(s) between the dry sorbent and sulfur dioxide tend to remain on the surface of the dry sorbent particles and clog the particle pores, thereby hindering further reaction (5)(6). It should be noted that preliminary analysis of the pilot plant data indicates 5% to 15% of the dry sorbent reacts with nitrogen oxides (expressed as NO) in the flue gas, and therefore, overall utilization of the sorbent may be higher than the value calculated based on SO_2 removal only.

The effectiveness of trona and nahcolite for removing sulfur dioxide from flue gas is strongly dependent on temperature. In the pilot plant, sulfur dioxide removal increased from about 50% to 80% as the flue gas temperature at the injection point was raised from approximately 510°F to 700°F. It should be pointed out that a similar correlation results when sulfur dioxide removal is plotted versus baghouse temperature, reflecting the fact that injection temperature and baghouse temperature are directly related, although not on a 1:1 basis. The highest baghouse temperature reached was 490°F, which is near the upper operating limit for baghouse fabric material normally available today.

The injection rate and/or bag cleaning cycle appears to significantly influence the effectiveness of dry sorbents for removing sulfur dioxide. Injection procedures investigated in the pilot plant included: 1) injecting a single large shot of dry sorbent into the flue gas after each baghouse cleaning cycle, 2) injecting continuously at a steady rate, 3) injecting at a steady rate for 5 minutes out of every 10 minutes, and 4) injecting continuously at a rate which varied directly with exit sulfur dioxide level. A preliminary analysis of test data indicated that the last method listed resulted in the greatest sulfur dioxide removal.

FLUE GAS CLEANUP AND PARTICULATE CONTROL

GFETC was one of the early investigators to establish that high fly ash resistivity of certain low-rank coals primarily reflected low concentrations of Na_2O and SO_3 in the ash. Pioneer research at GFETC also revealed that high resistivity fly ash can be "conditioned" by adding high sodium fly ash to it. As little as 1% addition of high-sodium fly ash to a high resistivity fly ash upstream of the electrostatic precipitator (ESP) can make a significant improvement in ESP performance.

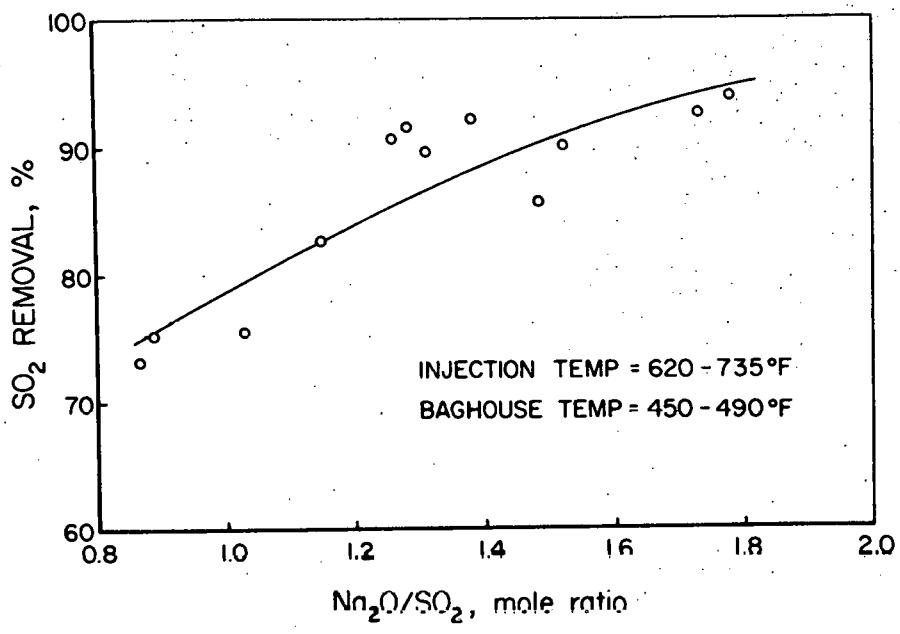


FIGURE 6. - Sulfur dioxide removal as a function of Na_2O/SO_2 mol ratio using Trona (minus 200 mesh) dry sorbent.

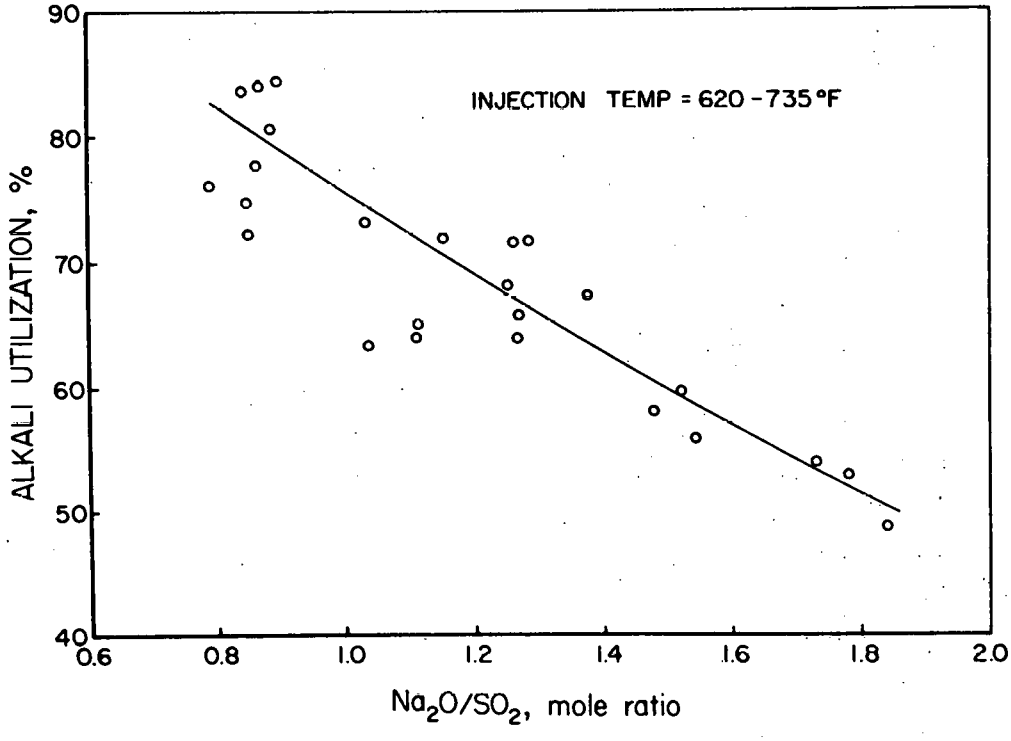


FIGURE 7. - Trona (minus 200 mesh) utilization as a function of Na_2/SO_2 mole ratio.

GFETC has a 75-lb/hr pc-fired combustor equipped with an in-situ point-to-plane resistivity measuring instrument and a pilot ESP. The ESP is a tubular unit with a nominal I.D. of 8 inches. Inside the tube is a 1/8-inch diameter stainless steel discharge electrode.

In response to requests for assistance from outside sources, GFETC recently undertook two flue gas investigations. One study involved unwashed versus washed coal, and the other dealt with the combustion products from a boiler fuel comprising a mixture of lignite and sunflower hulls.

The raw versus washed coal study concerned itself with subbituminous coal from the Loma mine in Garfield County, Colorado. The unwashed coal contained 16.1% ash which was reduced to 7.9% after washing and drying. Both the raw and cleaned coal were tested in GFETC's pilot combustor, and ESP performance and in-situ resistivities were measured for each coal. In addition, the compositions of the two fly ashes collected by the ESP were determined by chemical analysis, and the particle size distribution of each fly ash was measured using a Coulter Counter.

The results of the study indicated that the only significant difference between the two types of coal was a substantial reduction in ash content in the cleaned coal. This reduction was reflected in a similar reduction in the level of emissions from the pilot ESP, but did not appear to significantly affect fly ash particle size distribution or ESP collection efficiency which was 90%-94% for both coals. Fly ash resistivity was high for both the unwashed and washed coals, reflecting a low sodium content in both types.

Proximate and ultimate analyses for the two coals, along with coal ash analysis appear in Table 2. ESP operating data, in-situ resistivity measurements and fly ash composition data are shown in Table 3.

The second investigation was a short study conducted in cooperation with Basin Electric Power Cooperative (BEPC) to evaluate the suitability of burning sunflower hulls with lignitic coal. Two objectives of the study were to determine ESP efficiency and fly ash particle size distribution with coal/hull mixtures. The study involved a series of tests in GFETC's pilot plant combustor, plus participation in a one-week test at BEPC's 42-MW, pc-fired William J. Neal Station at Velva, North Dakota.

Sunflower hulls were determined to have a heating value of approximately 7,600 Btu/lb, and ash and moisture contents of about 7% and 8%, respectively. The potassium oxide content of the ash was variable, ranging from 12% to 28%.

The tests in GFETC's pilot unit were conducted using 100% subbituminous coal, coal with 10% sunflower hulls and pure sunflower hulls. The hulls were found to have good combustion characteristics, and there were no difficulties encountered in maintaining a stable flame, even when burning 100% hulls. The average in-situ resistivity measured for the 100% coal fly ash was 2.3×10^{11} ohm-cm compared to 6.1×10^{10} ohm-cm for 100% sunflower hulls fly ash. In-situ resistivity for the 90% coal /10% hulls mixture was indicated to be only 1.3×10^{10} ohm-cm, but this low value might simply have reflected the variable potassium content of the hulls.

Table 2. - Coal and Coal Ash Analysis
Raw and Washed Coal
Loma Mine, Colorado

Coal Sample:	Raw		Washed	
	As-Rec'd	MAF(1)	As-Rec'd	MAF(1)
Proximate Analysis, % by Wt.				
Moisture	6.2	-	6.2	-
Volatile Matter	34.7	44.7	37.7	43.8
Fixed Carbon	43.0	55.3	48.3	56.2
Ash	16.1	-	7.9	-
Ultimate Analysis, % by Wt.				
Hydrogen	5.0	5.6	5.4	5.5
Carbon	61.4	79.0	68.7	80.0
Nitrogen	1.2	1.6	1.3	1.5
Sulfur	0.6	0.7	0.5	0.6
Oxygen	15.7	13.1	16.2	12.4
Ash	16.1	-	7.9	-
Heating Value, Btu/lb	10,750	13,840	12,160	14,150
Coal Ash Analysis, % by Wt.				
SiO_2		51.5		55.1
Al_2O_3		34.2		35.5
Fe_2O_3		2.9		2.3
TiO_2		1.1		1.6
P_2O_5		0.2		0.7
CaO		4.4		2.2
MgO		1.2		0.6
Na_2O		0.5		0.5
K_2O		0.5		0.4
SO_3		0.3		1.1

(1) MAF = Moisture and ash-free.

Table 3. - Pilot Plant ESP Summary Data
Raw and Washed Coal
Loma Mine, Colorado

Coal Sample:	Raw		Washed	
ESP Operating Data				
Temperature, °F	320	470	320	470
Inlet Loading, gr/dry SCF	10.9	10.8	3.6	4.4
Measured Efficiency, pct	93.6	90.9	93.5	92.1
Emission Level, $lb/10^6$ Btu	0.51	0.66	0.17	0.23
In-Situ Resistivity				
Temperature, °F	350	590	430	590
Resistivity, ohm-cm	8.6×10^{13}	7.6×10^{11}	5.7×10^{12}	8.4×10^{11}
Fly Ash Composition, % by Wt.				
SiO_2	51.5	53.6	53.9	53.0
Al_2O_3	37.0	36.0	38.4	39.2
Fe_2O_3	2.9	2.9	2.3	2.3
TiO_2	1.0	1.0	1.5	1.4
P_2O_5	0.2	0.1	0.3	0.3
CaO	4.2	3.8	1.7	1.8
MgO	0.9	0.8	0.3	0.3
Na_2O	0.2	0.5	0.9	0.4
K_2O	0.5	0.6	0.4	0.4
SO_3	0.9	0.7	0.4	0.8
Fly Ash Particle Size, pct by Weight Smaller Than Indicated Size in Micrometers				
5.0	3.0	3.2	2.5	2.8
6.4	6.6	7.1	5.5	6.2
8.0	11.5	12.0	9.7	10.7
10.1	17.5	18.1	15.9	17.0
12.7	24.8	25.3	24.0	24.9
16.0	33.2	33.6	34.4	34.2
20.2	43.4	43.1	45.4	45.0
25.4	54.4	53.1	57.6	56.9
32.0	66.1	64.1	69.4	68.3
40.3	79.2	76.6	80.7	79.6
50.8	90.1	87.3	89.7	88.8
64.0	95.6	93.6	95.1	95.2
80.6	96.3	95.0	96.1	97.5
Mass Mean Diameter, μm	23.3	23.6	22.3	22.3

ESP collection efficiency in the pilot plant for fly ash produced from 100% hulls was only 88% at the start of the run and gradually decreased during the test. Visual observation of the ESP afterwards revealed that the wire electrode was coated with sticky ash. When a 90% coal/10% hulls mixture was burned, initial ESP collection efficiency was 97% to 99%, which was above the efficiency obtained with 100% coal and significantly higher than the 88% efficiency realized with 100% hulls. However, as the test progressed, ESP collection efficiency decreased, reaching a low of about 88% after two hours of operation. Visual inspection of the ESP at the end of the test disclosed that the electrode was again coated with sticky ash.

ESP performance during the field test at the William J. Neal Station was determined by measuring the inlet and outlet particulate loads, and also by recording the ESP operating voltage requirements. ESP efficiency appeared to be improved by the addition of the sunflower hulls to the lignite, as shown in Table 4. This improvement was confirmed by a decrease in voltage requirements which were about 15% lower in all tests with the hulls.

Table 4. - ESP Particulate Removal Efficiency

Power Load ESP Efficiency %	50%	75%
0% Hulls (Baseline)	98.3	98.0
5% Hulls	99.6	98.5
10% Hulls	99.0	Not Determined

There was no indication during the field test of a decrease in ESP collection efficiency with time, caused by a sticky-ash buildup on the electrodes. However, each test involving sunflower hulls lasted only about four hours, and the buildup may not have been observed. Additional tests, of extended duration, will have to be conducted to determine long-term ESP operational reliability.

Particulate size measurements on samples aspirated at the ESP outlet during the field test indicated an increase in particle size with increasing amounts of hulls in the lignite/hulls fuel mixture. For example, at 50% power load, the mass mean diameter of the fly ash particles increased from 40 μm to 62 μm as the percentage of hulls in the fuel mixture increased from 0% to 10%, as shown in Table 5, a similar trend existed at 75% load. Table 5 indicates a difference in particle mass mean diameter between 50% load baseline and 75% load baseline, which may be attributable to different boiler operating conditions and ESP time-temperature histories at the two load conditions considered herein.

Table 5. - Fly Ash Particle Size

Power Load Mass Mean Diameter, μm	50%	75%
0% Hulls (Baseline)	40	6
5% Hulls	48	20
10% Hulls	62	Not Determined

WASTE MANAGEMENT

Wet scrubbing in the most widely used and commercialized method employed today for desulfurizing flue gas. Through research, it has been developed into a feasible, reliable and efficient process. Although wet scrubbing has its values, it also has its problems. One of these problems is the production of a waste sludge that is saturated with potential pollutants.

Concomitant with increased coal usage in future years, there will be an increase in the amounts of flue gas desulfurization sludge produced. Study of the disposal of this waste material is important because of the possible increase in solid and liquid pollution problems associated with its production.

To date, sludge waste is frequently disposed of in mine landfill or by ponding. Efforts are being made to uncover possible uses for sludge and thereby avoid disposal. Irrespective of what method is available to remove sludge, it must be tested for its pollutant potential and treated accordingly. The migration of trace elements through soil or aqueous media must be altered or eliminated, to minimize contamination of the environment. Therefore, it is important to assess and characterize the chemical and physical properties of these wastes.

A study was recently completed of sludge material obtained during a test of a pilot wet scrubber located at Minnkota Power Cooperative's Milton R. Young Generating Station at Center, North Dakota. The 5,000-acfm pilot scrubber (equivalent to about 1.4 MW) was operated on a slip stream of flue gas collected downstream of the ESP on Center Unit #1, a 238-MW cyclone-fired boiler. Fly ash from the power plant ESP was used in the scrubber as absorbent to remove sulfur dioxide from the flue gas. During the test period from August, 1976 to March, 1977, a parametric study was conducted in which SO_2 removal efficiency was investigated as a function of liquid-to-gas (L/G) ratio, inlet SO_2 concentration, CaO to SO_2 mol ratio, and recirculated suspended solids.[2]

Sludges from ten segments of the scrubber test program were selected for characterization. Variations in scrubber operating conditions for the ten test periods are summarized in Table 6. A number of laboratory analyses were performed to physically characterize the sludges. These analyses included density, moisture, permeability, void ratio, specific surface area, and unconfined compressive strength. The results of the physical characterization study appear in Table 7.

The physical property that most significantly affects the pollution potential of a waste material is permeability, and disposal techniques such as chemical fixation are designed to minimize this physical characteristic. The permeabilities reported in Table 7 represent the maximum percolation rate through each of the sludge materials. Review of the data in Table 7 and the operating data in Table 6 indicate that sludge permeability is decreased by the addition of sodium and magnesium ions to the scrubber solution, or by operating the scrubber at low pH.

Table 6. - Operating Data from Parametric Study of Wet Scrubbing at Center, North Dakota

Test	Scfm-dry	L/G[1]	CaO/SO_2[2] Fly Ash	CaO/SO_2[2] Lime	SO_2,ppm-dry Inlet	SO_2,ppm-dry Outlet	Pct SO_2 Removal	Fly Ash CaO Utilization,%	Suspended Solids, pct	pH
1-3	3574	59.8	1.13	--	996	200	79.9	70.7	1.93	3.8
3-1	3377	61.0	0.60	--	994	372	62.5	107.8	5.50	3.5
3A-2	3580	80.8	0.82	--	990	246	75.2	91.7	5.10	4.3
3A-3	3336	81.8	0.62	0.42	1026	235	77.1	55.2	6.81	4.0
3A-4	3577	80.1	0.36	--	1800	1014	43.7	121.4	6.53	3.6
3A-7	3390	81.0	0.70	0.36	1818	400	78.0	57.9	10.65	5.2
5-4(3)	3554	20.5	0.62	--	958	360	62.4	100.0	2.58	4.0
5-14(4)	3442	40.9	0.66	--	937	334	64.4	97.6	3.20	3.8
6-4	2275	115.3	0.63	--	960	268	72.1	114.0	1.16	2.7
6-5	1764	154.0	0.59	--	1014	151	85.1	144.2	1.05	2.8

1) Gallons of recirculated slurry per 1000 acf (saturated) flue gas.
2) Mol ratio based on inlet SO_2 concentration.
(3) High sodium test (4.5% Na)
(4) High magnesium test (3.0% Mg)

Table 7. - Physical Characterization Data for Sludges from Parametric Study of Wet Scrubbing Using Center, North Dakota Fly Ash

Test	Bulk Density (gm/cm^3)	Dry Density (gm/cm^3)	%Moisture	Permeability (cm/sec)	Void Ratio	Surface Area ($meters^2/gm$)	Unconfined Compression Strength (kg/sq. ft)
1-3	1.65	2.59	37.7	3.5×10^{-5}	1.57	26.9	2.78
3-1	1.76	2.45	31.7	1.4×10^{-5}	1.14	25.3	2.54
3A-2	1.75	2.57	31.9	1.2×10^{-5}	1.20	26.9	2.62
3A-3	1.74	2.53	34.7	1.7×10^{-5}	1.34	26.9	1.56
3A-4	1.65	2.49	39.2	1.6×10^{-6}	1.60	20.1	3.20
3A-7	1.69	2.55	36.2	1.9×10^{-5}	1.45	14.7	3.25
5-4(1)	1.55	2.57	40.7	3.5×10^{-6}	1.77	25.3	2.23
5-14(2)	1.69	2.55	33.0	5.2×10^{-6}	1.26	14.7	2.34
6-4	1.67	2.54	34.2	5.2×10^{-6}	1.32	17.1	2.74
6-5	1.60	2.50	40.5	8.2×10^{-7}	1.70	23.0	Not Determined

(1) High sodium test (4.5%, Na)
(2) High magnesium test (3.0%, Mg)

Permeability coefficients for lime and limestone materials are reported to range from 10^{-4} to 10^{-5} cm/sec., typical of silty sand to sandy clay (10^{-4} cm/sec. and $5x10^{-6}$ cm/sec., respectively) (7). Values reported for the alkali ash sludge of this study are similar to those for sandy clay. All of the permeability values shown in Table 7 are within the range of values reported for lime/limestone waste (7)(8), or material slightly less permeable.

In addition to physically characterizing the sludge, column leaching tests were conducted at GFETC to determine the mobility of potential chemical pollutants in the sludge samples. These tests were designed to realistically duplicate the potential environmental impact of chemicals released from ash alkali FGD sludge.

The results of these column leaching tests have been reported elsewhere (9), and are too lengthy to include here. They may be summarized by stating that the concentration of most chemical species in the leachate decreased to 10% of the initial leachate concentration, or less, by the fifth pore volume displacement (PVD). Only four chemicals appeared in the leachate at concentration levels exceeding existing U.S. Public Health Service water standards or National Interim Public Drinking Water Regulations. The data indicated that both sulfate and iron were in violation of the standards throughout the leaching test (50 PVD's). Cadmium was in violation during the first 5 PVD's and manganese during 15 PVD's. However, the data represented only leachate quality from the sludge, and excluded consideration of ion exchange capacity by surrounding soils in an actual landfill disposal site, or site specific hydrologic characteristics. The results did demonstrate, however, that some chemical species have considerable mobility.

FUTURE PLANS

GFETC's future environmental control activities related to low-rank coals call for continuation and expansion of the programs outlined in this report. In the wet scrubber flue gas desulfurization program, an investigation will be made in the pilot plant of chemical additives to increase sulfur dioxide removal and/or fly ash utilization. Adipic acid has been reported to be beneficial in this respect in pilot plant tests at TVA's Shawnee Power Station test facility and in EPA's pilot plant at the Industrial Environmental Research Laboratory, Research Triangle Park, North Carolina (IERP-RTP) in FGD systems based on lime/limestone (10)(11)(12). Tests in GFETC's fly ash alkali wet scrubber will be made to determine if adipic acid is of equal benefit in a fly ash-based system.

The research program on dry sorbents will be expanded to higher temperatures provided a satisfactory fabric filter can be obtained that will withstand 500°F to 800°F. Studies are also planned for using dry sorbents for NO_x control, with attention first given to nahcolite and trona. In addition, laboratory experiments will be undertaken to determine the reaction kinetics of dry sorbents with sulfur dioxide and nitrogen oxide. The laboratory investigation will also study techniques to reactivate spent dry sorbent materials.

In the immediate future, the particulate control program at GFETC will emphasize fly ash sampling and characterization, particularly in the submicron range. Included in this work is a program to develop and evaluate methods of fly ash sample collection, preservation and redispersion, and methods for determining particle size distribution, and particle bulk and surface composition. Also included in this program is a study of the distribution of elements within particles (i.e., as a function of depth below the surface) and a study of element variation with particle size and morphological characteristics.

GFETC's immediate objective in the area of waste management is to obtain additional data on the physical and chemical characteristics of waste materials generated by the combustion of low-rank coals. The development of suitable techniques for providing environmentally satisfactory disposal of these waste materials will receive high priority. In addition, a field test is planned of a fly ash alkali FGD sludge disposal site to determine the leaching characteristics of the major and minor trace elements.

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FLUE GAS CLEAN-UP RESEARCH AT THE PITTSBURGH ENERGY TECHNOLOGY CENTER

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1. INTRODUCTION

Research is underway at PETC on several aspects of advanced flue gas clean-up technology. This research is reviewed briefly in this paper. Processes being investigated include dry scrubbing, a fluidized bed copper oxide process for simultaneous SO_2/NO_x removal, direct reduction of SO_2 to sulfur, absorption/steam stripping, and several aspects of the Resource Conservation and Recovery Act. Further details are available from the authors.

Dry Scrubbing

PETC began a program in dry scrubbing in fiscal year 1979. The initial effort is concentrating on injection of dry alkali sorbents into the flue gas from a coal-fired furnace with subsequent collection of spent sorbent and fly ash in a baghouse. Data are being generated for low, medium, and high sulfur coals with a variety of sorbents including sodium bicarbonate, nahcolite (a sodium bicarbonate mineral), and trona (a sodium carbonate/bicarbonate mineral).

The dry sorbent tests are being conducted in a 500 lb coal/hr (6×10^6 Btu/hr) combustion test facility designed to simulate the performance of an industrial steam generator. Pulverized coal (70% minus 200 mesh) is burned in the furnace and the combustion products exit at 1800-2000°F, pass through a convective heat transfer section, a recuperative heat exchanger, and a baghouse filter. The temperature of the flue gas leaving the air preheater can be controlled between 300-475°F.

In most of the tests, dry sorbent was injected into the 12 inch diameter flue-gas duct at the exit of the preheater, 26 feet upstream of the baghouse. A few tests were conducted while injecting sorbent at the inlet of the baghouse.

The baghouse is a Mikro-Pulsaire model manufactured by the Pulverizing Machinery Division of the Slick Corporation. It contains 57 Nomex bags, 8 feet long x 4-1/2 inches OD. The unit is normally operated at air/cloth ratios of 4-4.5 ft/min.

A number of operating variables have been examined including baghouse temperature and cycle rate, sorbent particle size, and stoichiometric ratio of alkali to sulfur. In all tests, the excess air levels were maintained at 20%.

Figure 1 shows some results for Pittsburgh seam coal (1.6% S) while injecting nahcolite with a mean particle size of 37 microns. Data at 400°F and 420°F fall on the curve confirming tests which show removal to be fairly independent of temperature above 400°F. Likewise, results are independent of baghouse cycle rate for all sorbents tested.

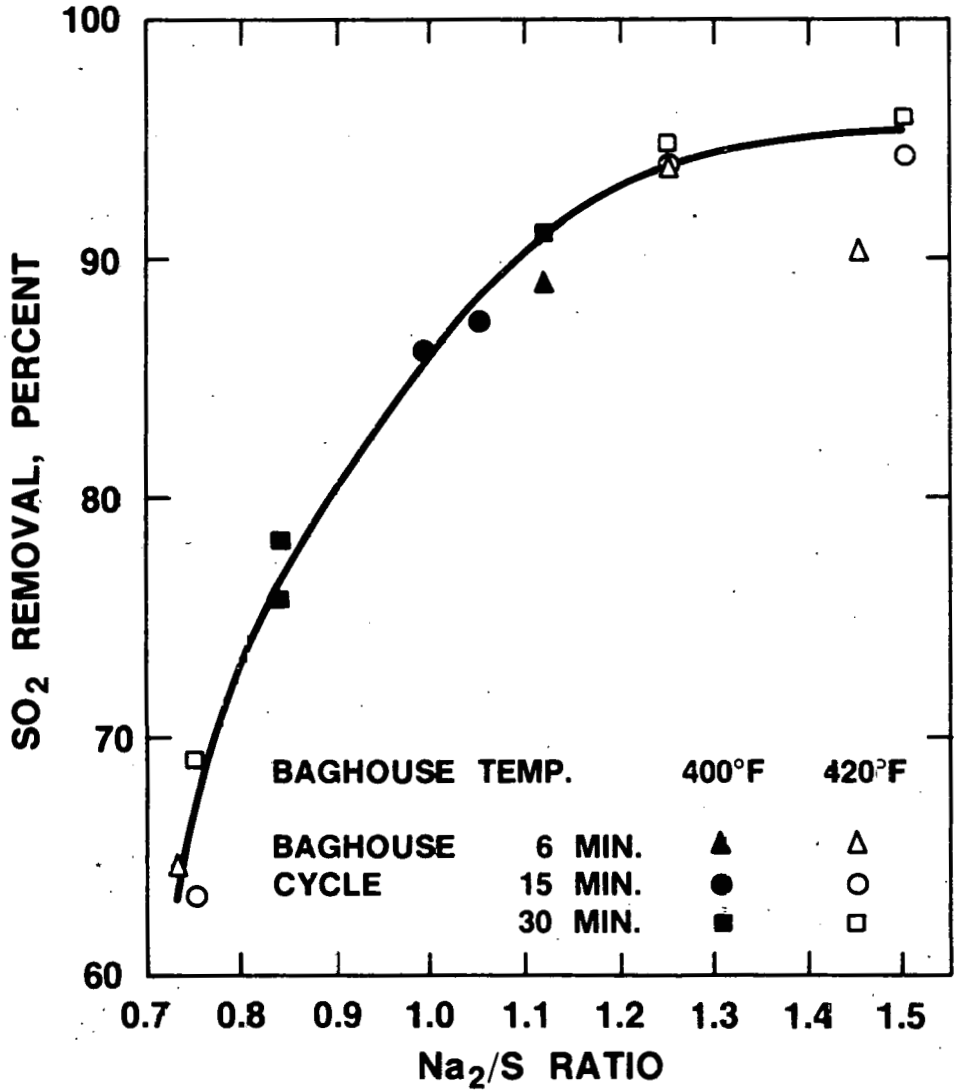


FIGURE 1 – EFFECT OF Na_2/S RATIO ON SO_2 REMOVAL
SORBENT: NAHCOLITE (37 MICRONS)
PITTSBURGH SEAM COAL (1.6% S)

Note that for 90% SO_2 removal, a Na_2/S ratio of 1.1 is needed which corresponds to an 82% sorbent utilization.

Figure 2 shows the effect of sorbent particle size on SO_2 removal with sodium bicarbonate at a Na_2/S ratio of 2 and a baghouse temperature of 400°F. It should be noted that the SO_2 removal varies approximately linearly with the mean particle diameter of the sorbent.

The data indicate that SO_2 removals of 90 percent are achievable at mean sorbent diameters of 65 microns or less. For a stoichiometric ratio of 2, this corresponds to a sorbent utilization of 45 percent. However, in a series of tests with No. 3 sodium bicarbonate (32 micron diameter), it was found that 90 percent SO_2 removal could be attained at a Na_2/S ratio of 1.3, corresponding to about 70 percent sorbent utilization.

Figure 3 compares the effectiveness of nahcolite and trona while burning 3.1% S coal. The nahcolite was clearly more effective over the entire range of Na_2/S ratios considered.

A spray dryer has been purchased to add to this system to enhance gas/solid contacting. Such a system has been shown to provide greater sorbent utilization of various sorbents when injected as solutions or slurries rather than dry powders. Emphasis will be on lime scrubbing of flue gas from medium and high sulfur eastern coals. The spray dryer will be installed in July of 1980.

Fluidized Bed Copper Oxide Process

A regenerative fluidized bed process for simultaneous SO_2/NO_x removal is being investigated. A typical conceptual design is shown in Figure 4. In this concept, flue gas taken before the air preheater at 350-400°C is contacted with a supported copper oxide sorbent in a fluidized bed where the following reaction takes place:

$$CuO + SO_2 + 1/2\ O_2 \rightarrow CuSO_4$$

The sorbent is transported continuously to a fluidized bed solids heater where it is heated to about 440°C and then to a regenerator where it is contacted with methane or other reducing gases to produce concentrated SO_2 via:

$$CuSO_4 + 1/2\ CH_4 \rightarrow Cu + SO_2 + 1/2\ CO_2 + H_2O$$

The sorbent is recirculated to the absorber for another cycle and it immediately reacts with oxygen to reform the CuO via:

$$Cu + 1/2\ O_2 \rightarrow CuO$$

and the cycle is repeated. NO_x removal is accomplished by injecting ammonia upstream of the copper oxide catalyst bed where selective catalytic reduction of the NO_x takes place by reactions such as:

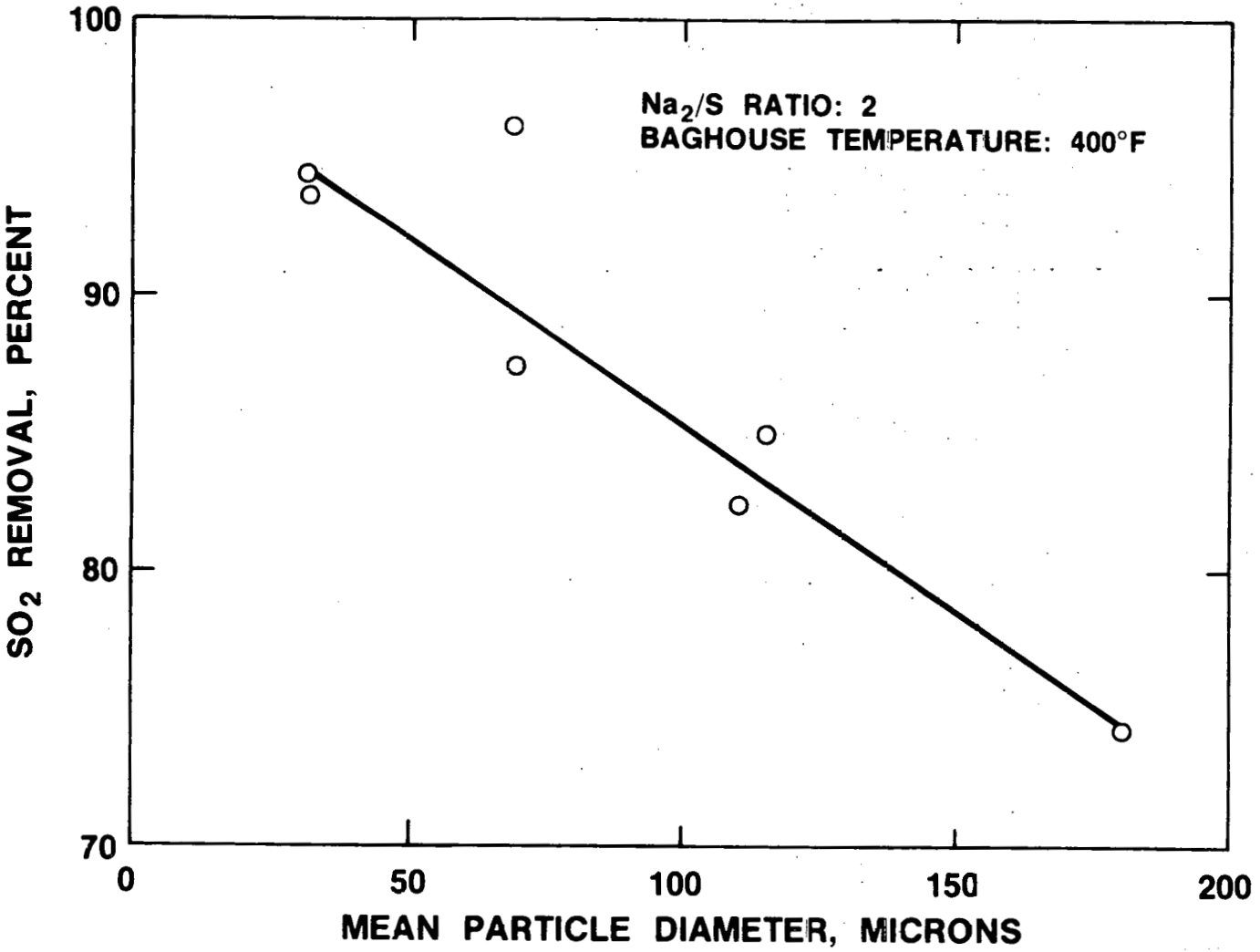


FIGURE 2 - EFFECT OF SORBENT PARTICLE SIZE ON SO_2 REMOVAL SORBENT: SODIUM BICARBONATE PITTSBURGH SEAM COAL (1.6% S)

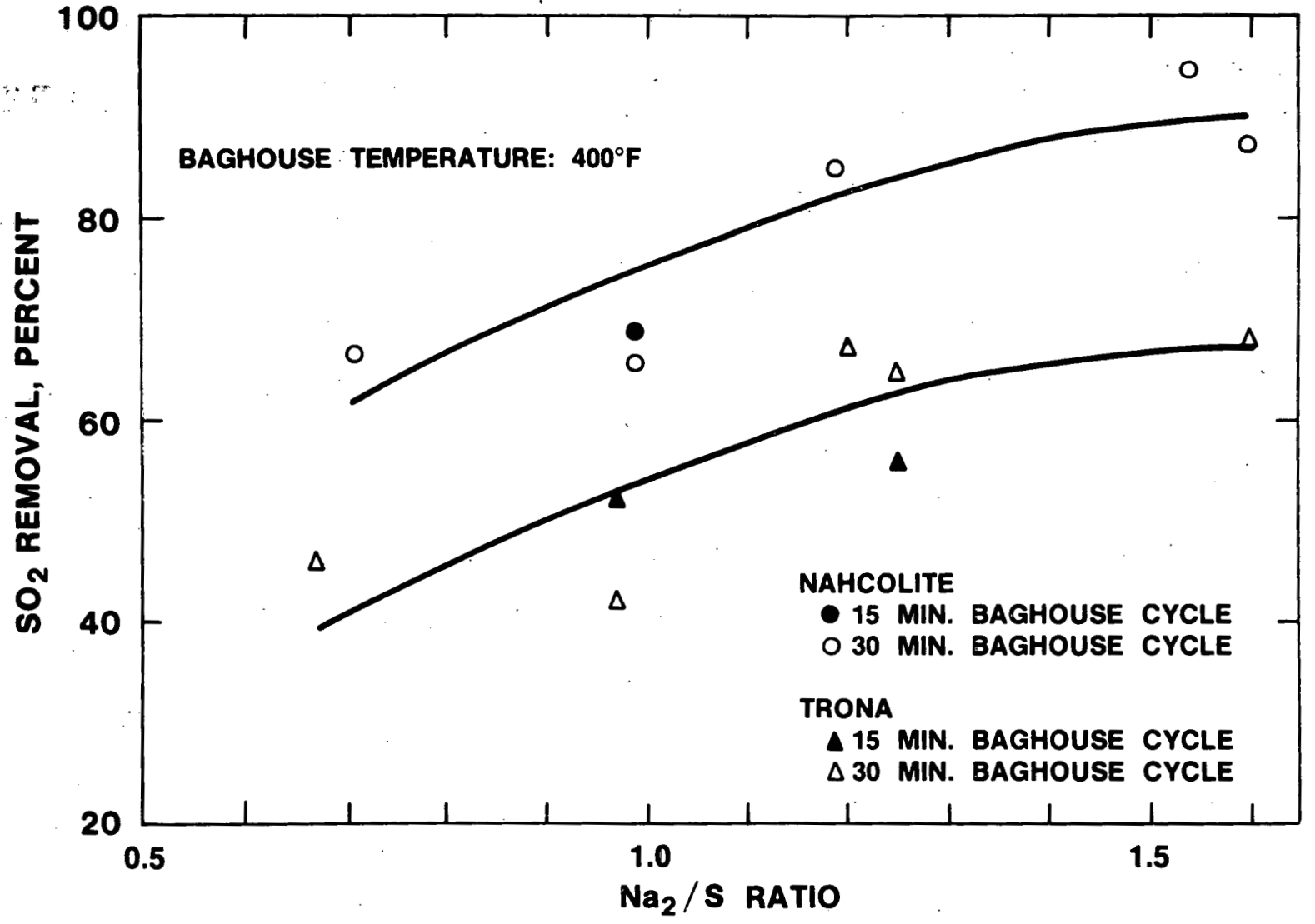


FIGURE 3 - EFFECT OF Na_2/S RATIO ON SO_2 REMOVAL SORBENTS: NAHCOLITE (33 MICRONS) AND TRONA (32 MICRONS) WEST VIRGINIA COAL (3.1% S)

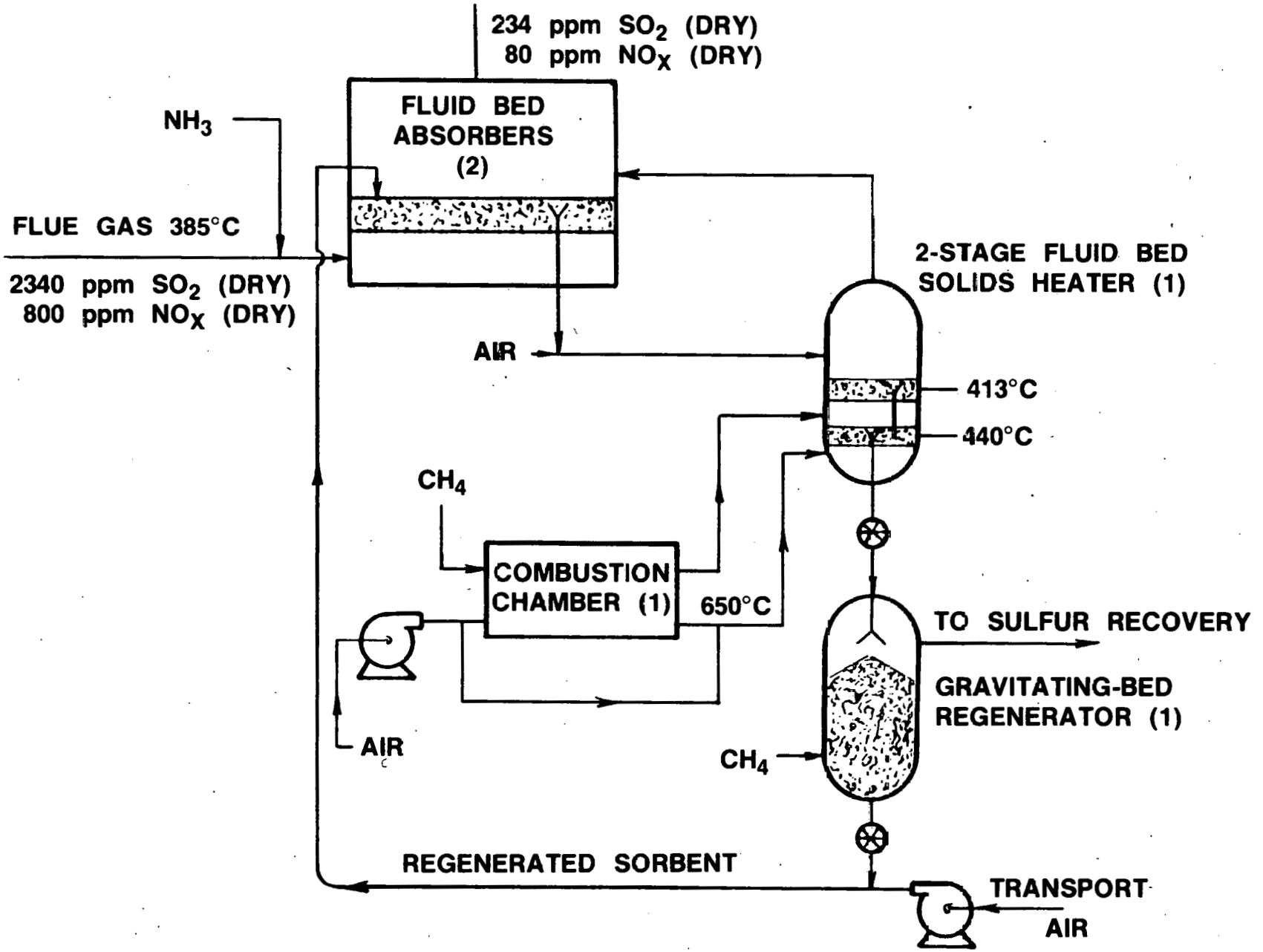


FIGURE 4 – PROCESS FLOWSHEET COPPER OXIDE PROCESS, 550 MWe PLANT.

$$4NO + 4NH_3 + O_2 \xrightarrow{CuO,\ CuSO_4} 4N_2 + 6H_2O$$

$$2NO_2 + 4NH_3 + O_2 \xrightarrow{CuO,\ CuSO_4} 3N_2 + 6H_2O$$

The concentrated SO_2 from the regenerator can be converted to sulfuric acid by commercially available methods or to elemental sulfur using processes currently under development.

The Shell copper oxide process is based on similar chemistry but uses a cyclic fixed-bed contactor in which the supported copper oxide sorbent is contained in parallel trays. Flue gas containing flyash passes between the trays and SO_2 diffuses into the sorbent where it is captured. When the bed becomes saturated it is isolated and regenerated with a reducing gas. This process has been described in numerous publications.[1,2] The process is licensed by the UOP Process Division in this country and is referred to as the UOP/Shell Process.

The fluidized bed design has several significant advantages over a fixed-bed design:

- The absorber and regenerator can operate at different temperatures. Thus turndown can be easily accommodated as the flue gas temperature drops off. Also, retrofitted applications can be handled where the flue gas may be at temperatures significantly below the regeneration temperature.
- No valve problems. No large diameter valves are needed to isolate the absorption from the regeneration as in the fixed bed design.
- Constant regenerator offgas. Fixed beds produce a cyclic feed to the sulfur recovery unit, necessitating an intermediate absorption system to smooth out the feed.
- Flyash should pass through the fluidized bed due to the much smaller particle size, eliminating plugging that can occur in fixed beds and the need for a hot electrostatic precipitator. This assumption has not been tested.

The main disadvantages are:

- Higher pressure drop than in the parallel passage reactor.
- Potential for attrition of the sorbent. Data to date show that this is controllable.

Currently a 45 scfm fluidized bed PDU is being operated at PETC. Flue gas is generated by combustion of natural gas spiked with NH_3 to generate 800 ppm of NO_x. SO_2 is added to the flue gas to give 3000 ppm, simulating high-S coal combustion. To date, no fly ash has been added.

The absorber is a 6-inch diameter fluidized bed operated with bed depths to three feet. The sorbent (1/16" UOP alumina spheres impregnated with CuO) is fed continuously through the bed and is regenerated batch-wise.

Typical data on SO_2 removal is shown in Figure 5. Clearly, removals well above 90% are achievable with bed heights of only three feet.

NO_x removal is shown in Figure 6. Removals in excess of 90% are also typical. Currently, tests are in progress to assess the unreacted ammonia passing through the bed which can be of concern due to formation of ammonium salts which can cause plugging of an air preheater.

Estimates of attrition are quite low - about 0.02% of the bed inventory per hour (5000 hr sorbent life). This will be confirmed by direct attrition determinations in the current test program. Fly ash will also be added to see if it has any detrimental affects on the process.

Further details are available in other publications[3,4].

Direct Reduction of SO_2 to Elemental Sulfur

The objective of this effort is to improve and simplify the process for direct reduction of sulfur dioxide to elemental sulfur using bituminous coal so that it is economically viable for applications in large utility power plants. It should be noted that all direct reduction processes currently under development require an upstream process to concentrate the sulfur dioxide occurring in the flue gas. The proposed process is no exception: the concentrated off-gas from the upstream process is the feed gas to the direct reduction process. Elemental sulfur, formed by the reaction of SO_2 with carbon, is conveyed from the reactor as a vapor and is subsequently separated from the gas using a sulfur condenser.

The initial effort is to provide thermodynamic equilibrium calculations on which to base reactor operating conditions, or to establish from published data that direct reduction is primarily controlled by chemical kinetics.

In later work, a bench-scale reactor will be constructed, and tests with noncaking bituminous or subbituminous coal will be conducted. Efforts will be made to increase SO_2 conversion efficiency, coal utilization, and sulfur purity over existing processes. The sulfur purity has a pronounced effect on the price that can be obtained for the sulfur from a full-scale reactor.

In the later phase, the bench-scale reactor will be operated on caking bituminous coal and process feasibility will be assessed.

SO_2 Absorption/Steam-Stripping Equilibria

The objective of this research is to provide data on SO_2 vapor pressure versus absorbed SO_2 concentration for various organic absorbents considered

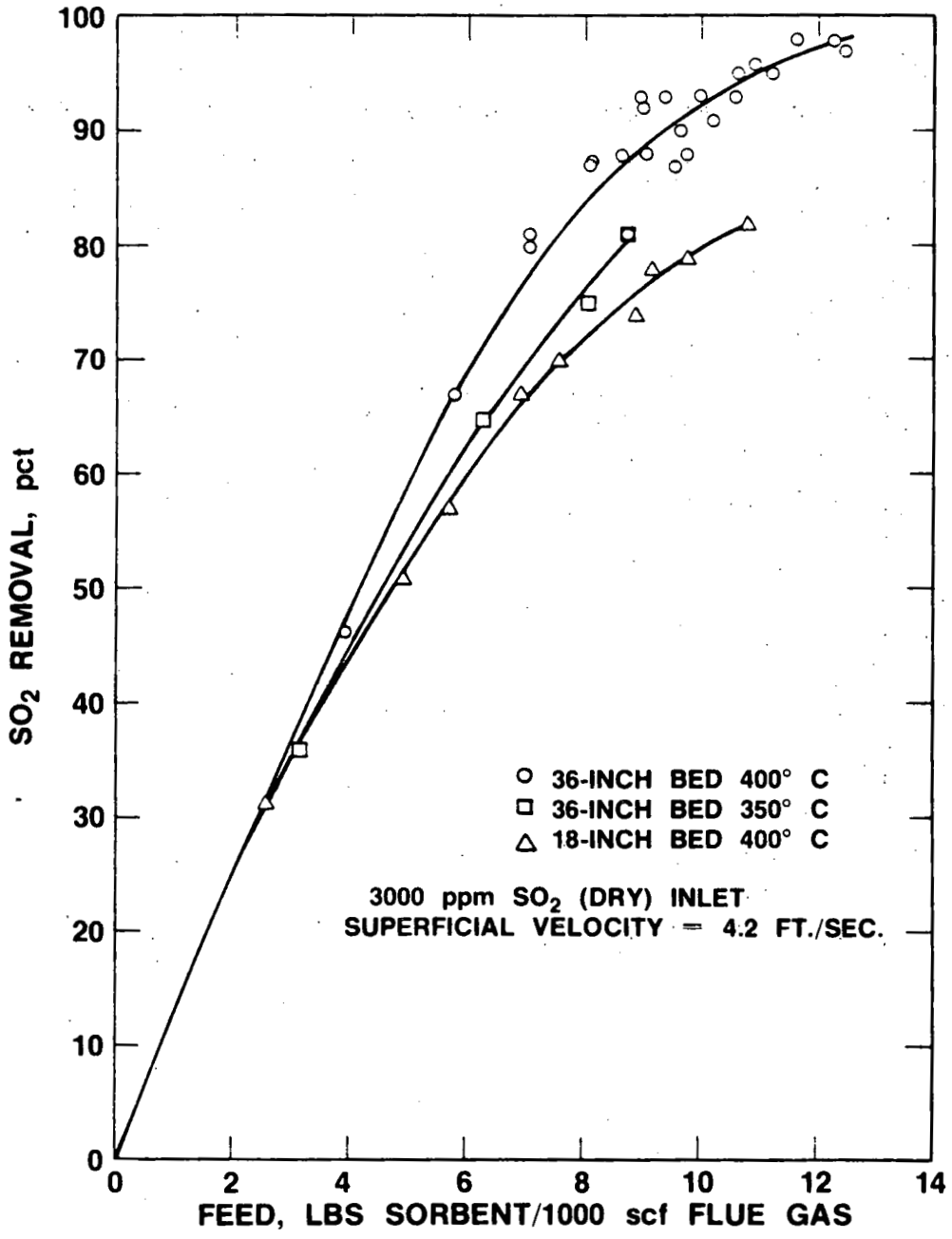


FIGURE 5 - REMOVAL EFFICIENCY IN COPPER OXIDE PDU.

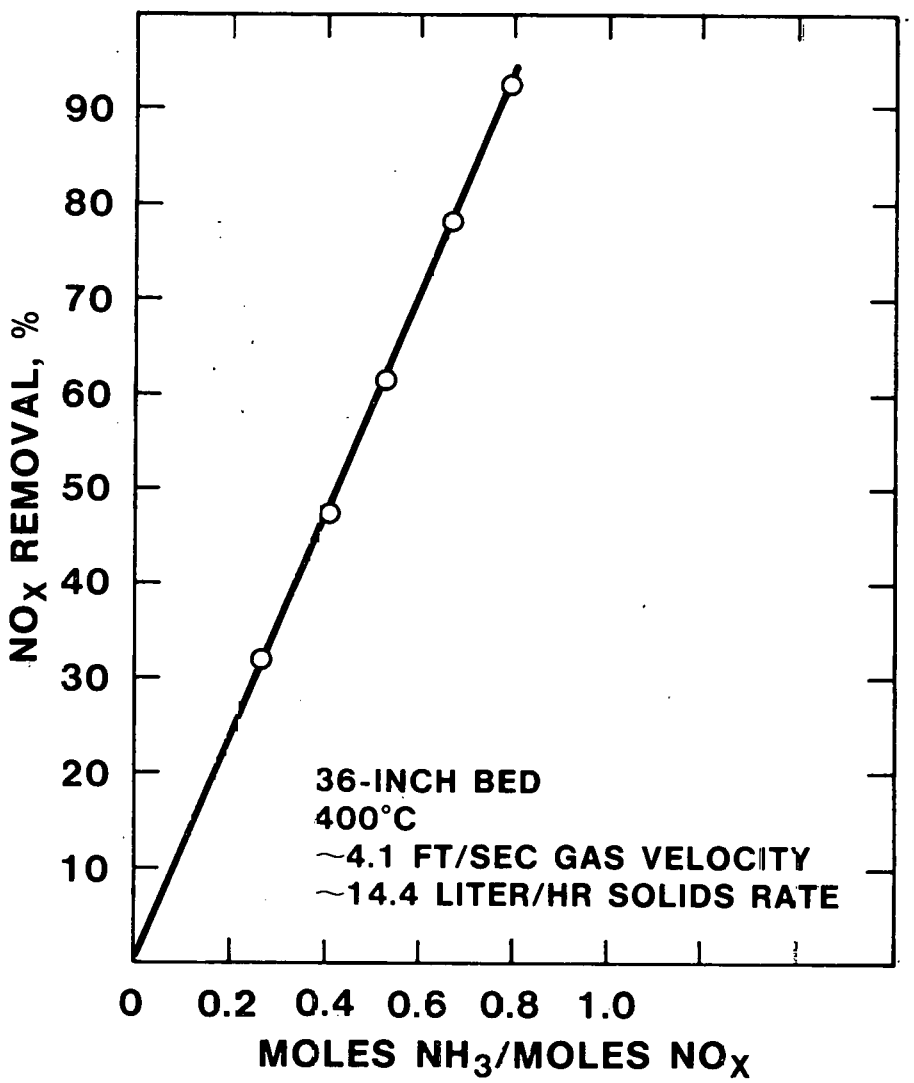


FIGURE 6 – SELECTIVE CATALYTIC REDUCTION OF NOX VIA AMMONIA

to be promising candidates for SO_2 absorption/steam-stripping systems for use in large utility power plants. These data are necessary to optimize the process to reduce energy requirements. Much of the data on such absorbents is proprietary or nonexistent, making it difficult to judge the merits of various proposed absorption/steam-stripping systems.

The experimental program will utilize two techniques to obtain the required data. The first technique involves measurement of SO_2 vapor pressure curves for several absorbents using a reflux condenser/absorber system. The tentative list of candidate absorbents includes citric acid, glycolic acid, ethylenediamine, diethylenetriamine, glyoxalic acid, tri-n-butyl phosphate, and 1-methyl-2-pyrrolidinone. The second technique is based on estimation of the SO_2 vapor pressure from the activity coefficient at infinite dilution obtained from a gas chromatograph. This method should be much faster than the first so may prove useful for screening candidate absorbents.

An economic analysis of SO_2 absorption/steam stripping will be conducted to aid in guiding the experimental program. In addition, theoretical analyses will be carried out to assist in explaining and correlating the experimental vapor pressure curves.

Resource Conservation and Recovery Act (RCRA) Activities

PETC research activities related to assessing the impact of RCRA include the following elements:

- Complete analysis of the legislation and proposed regulations and guidelines for non-hazardous waste disposal, hazardous waste disposal, and resource recovery.
- Assessment of the potential impact of RCRA on conventional combustion and coal conversion programs.
- Evaluation of hazardous waste generation and disposal at PETC and development of a site hazardous waste management program.
- Analysis of leachate extraction procedures through participation in American Society for Testing and Materials (ASTM) and DOE-sponsored collaborative test programs.
- Identification of potential problems and solutions relating to solid waste disposal from large scale/commercial coal conversion facilities.
- Participation in the DOE organic and inorganic characterization program of fossil fuel waste materials.

Further details of the PETC activities are available in two other papers in these proceedings and will not be repeated here.

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TECHNICAL EVALUATION OF RCRA ON SELECTED FOSSIL ENERGY PROGRAMS

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Paper not submitted for publication in Proceedings.

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ENVIRONMENTAL CONTROL IMPLICATIONS OF COAL USE

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1 INTRODUCTION

One of the greatest challenges facing the United States today is the production of energy from coal in ways that are compatible with our environmental goals. If we are to successfully meet this challenge, it will require the timely development and judicious application of environmental control technologies that are capable of reducing potentially adverse impacts to acceptable levels. However, the optimum selection of control technologies is a complex task since there are many different techniques, numerous possible combinations, and great uncertainty regarding interactions between pollutants and the environment.

The Environmental Control Technology for Coal Utilization program at Argonne National Laboratory (ANL) is assisting DOE by providing information required in the planning and guidance of R&D programs for coal utilization technologies and the associated environmental controls. It is a continuing program, begun in 1976, with the following objectives:

- Provide in-depth engineering evaluations of control technologies
- Identify existing or potential problem areas
- Provide DOE with information independent of regulator and developer viewpoints

We analyze both available and developing technologies for the entire energy system from the mine mouth through ultimate waste disposal. The tools of technology assessment and systems analysis are used to provide balanced evaluations of the engineering, environmental, and economic aspects of the technologies, as well as identification of synergistic effects and secondary or indirect impacts.

The remainder of this paper deals with three topics. First, we will briefly review the assessments performed to date and indicate the nature of our current work. Next, the computerized models and data bases utilized in our assessments will be described. Lastly, some of the results from a major ongoing study of environmental controls for industrial boilers will be presented and their implications discussed.

2 TECHNOLOGY ASSESSMENTS

Our approach to evaluating technologies begins with gathering information on the cost, reliability, energy requirements, efficiency, and secondary effects of pollution control systems from reports and discussions with manufacturers, users, and developers of the processes. In this effort, the capabilities of the in-house staff are supplemented by considerable use of subcontractors and consultants with special capabilities and expertise. Evaluation of this information leads to the identification of problems,

inherent process limitations, and high payoff areas for research and development.

For many technologies, extensive short-term studies have been performed to provide a base of information for the program. However, the evaluation process is a continuous one driven by the evolutionary nature of technology and environmental regulations. Thus, a continual updating of information is implicit in the following discussion, although we will be primarily describing discrete studies that have been performed.

2.1 PRECOMBUSTION CONTROLS

Precombustion encompasses all operations from the mine mouth up to the fuel utilization step (the boiler in conventional systems). Our evaluations in this area have included:

- The use of low-sulfur coal
- Coal cleaning
- Solvent refining of coal
- The use of coal-oil mixtures
- Coal transportation

Low-sulfur coal use was one of the first compliance strategies studied under the program. (Ref.1) Although recent regulatory developments (i.e., utility NSPS) have tended to reduce the use of western low-sulfur coals in new power plants, it remains an attractive option for many existing facilities and may be an important factor in the increased industrial use of coal. This is discussed in more detail in Sec. 4.

For some coals of higher sulfur content, physical coal cleaning (washing) can achieve significant reductions in potential SO_2 emissions, as well as reducing the ash content. An extensive study of current and developing industry cleaning practices (including chemical methods) was performed with the aid of the Bechtel Corporation. (Ref.2) Costs for several levels or degrees of cleaning were estimated and problems, such as those associated with fine-coal handling, were identified.

More extensive coal processing is represented by the solvent-refined coal (SRC) process. A preliminary survey of the production and use of SRC was performed by Air Products and Chemicals, Inc. for our program. (Ref.3) Recent efforts have been concentrated on evaluating the environmental control implications of SRC and comparing its use with other control options (see Sec. 4).

Coal-oil mixtures (COM) may prove to be an important fuel option for existing facilities in the near term. Our program is concentrating on determining the environmental control requirements as indicated by the combustion tests now underway or planned.

Fuel transportation is being studied because the associated costs can strongly influence the choice of fuel at a given location. Also, as will be shown later, the energy consumption and environmental residuals from transportation can be a significant portion of the total system values.

2.2 INTEGRAL CONTROLS

Characteristics inherent in a given process, as distinct from add-on devices or fuel changes, can sometimes be used to achieve environmental control goals. One widely applied example is combustion modification for NO_x control. We have analyzed the available modification techniques for coal-fired utility and industrial boilers with the aid of KVB, Inc. (Refs. 4 and 5). Reductions in NO_x in the vicinity of 30% can be achieved with minimal costs, but the results are highly variable, particularly for industrial boilers.

Low NO_x levels can also be achieved by fluidized-bed combustion (FBC) and high SO_2 removal efficiencies are possible. In order to obtain a measure of the developmental status of FBC, we recently had MITRE Corporation prepare an assessment based on the papers of the 5th International Conference. The results and the unique methodology employed are presented in a report now in press. (Ref.6)

Gasification/combined-cycle (G/CC) power systems offer the promise of higher degrees of pollution control. However, these gains are obtained at the expense of greater system complexity and presume the availability of advanced gas turbines and improved gasifiers. Nevertheless, a recent economic comparison of 500 MWe systems prepared by our program from data supplied by United Technologies Research Center found several G/CC systems to be competitive with a conventional power plant equipped with scrubbers.

A combined-cycle approach is also used with magnetohydrodynamic (MHD) power systems to achieve high efficiency. However, the unique nature of this system provides some unusual environmental control challenges. We are currently evaluating the nature and magnitude of these problems, with particular emphasis on control strategies for fine particulates.

2.3 POSTCOMBUSTION CONTROLS

Technologies for the "clean up" of flue gases continue to be at the heart of most environmental control debates. Our program has investigated:

- Particulate control
- Flue-gas desulfurization
- Combined SO_2 and NO_x removal
- Solid waste disposal

Engineering and economic analyses of both conventional (Ref.8) and advanced (Ref.9) particulate-control devices have been made under the program. Based on projected regulatory requirements, the increasing use of baghouses was predicted at an early stage in the program. Our current activities are focused on the control of respirable particulates and on the development of

models for control systems (see Sec. 3).

The costs and performance of flue-gas desulfurization (FGD) systems have been highly controversial and subject to continued change. An initial survey of this technology (Ref.10) is now being updated, and application of FGD to industrial boilers is being analyzed (Sec.4). Significant efforts have also been devoted to modeling these complex systems so as to facilitate tradeoff studies.

Combined SO_2-NO_x removal processes have been surveyed in anticipation of possible lowering of NO_x emission levels. (Ref.11) An investigation of the chemical kinetics of NO_x-removal processes is now being conducted in order to determine the extent of present knowledge and the need for new basic research.

Lastly, the use of flue-gas treatment systems brings about a transfer of pollutants from one medium to another. Salable products may be produced, but in most cases solid wastes are generated. Disposal of these solids can be a major problem, particularly if they should be classified as hazardous under the Resource Conservation and Recovery Act (RCRA). The engineering and cost implications of regulations developed under RCRA are being analyzed in the program and will be factored into future tradeoff studies.

3 COMPUTER MODELS AND DATA BASES

The comparative assessment phase of our program can involve the entire coal to power production system, or it may focus on specific system elements. A modular approach is used wherein each module represents a significant, and technically separable, component of the system. These modules are gradually being computerized as sufficient data become available and adequate models are developed. This computerization permits the rapid evaluation of site-specific control/coal-technology combinations in order to identify the potential role of the technologies as a function of environmental regulations, location, and state of development. In many cases it is possible to identify certain critical process parameters that can alter the existing balance or are especially sensitive to changes in environmental constraints.

3.1 PARTICULATE CONTROL

The ANL staff has under development an advanced particulate control model incorporating performance and economic data for cyclones, hot and cold electrostatic precipitators, baghouses, and scrubbers. This model, named PARTIC II, computes design characteristics and costs for both industrial- and utility-scale particulate-control equipment as a function of coal composition, combustor type, emission regulations, and economic criteria.

An important feature of the program is its ability to calculate precipitator collection efficiency based on an integration of a specific inlet particle-size distribution and size-dependent fractional collection efficiencies.

In addition to determining the required precipitator size for a given emission constraint, the size-dependent calculations predict the size distribution of particles that escape collection.

The program can be used for detailed studies of the technical and economic implications of particulate control for coal utilization. For example, the program has been used in an examination of the effects that differing coal combustor types have on the operation of particulate control equipment. Some results from this study are shown in Table 1.

Table 1. Industrial Boiler
Particulates Control

Coal Firing Rate - 20 TPH (489 x 10^6 Btu/hr)
Coal Type - Illinois #6

Combustor Type	Efficiency Required [a]	Percent of Outlet in Respirable Range [b]	Energy Required (kWh/ton coal burned)	Control Cost[c] ($/ton coal burned)
Pulverized Coal	99.54	96.7	3.87	2.75
Cyclone-Fired	95.84	97.5	2.89	1.78
Fluidized Bed	99.47	99.2	3.75	2.65
Spreader Stoker	99.30	98.5	2.02	0.82

a. Based on 0.03 lb/10^6 Btu emission limit
b. Respirable range of particulates is 15μm to 0.2μm
c. Based on 30 year system life

The use of a spreader stoker for industrial coal combustion clearly is favored, not only due to its low life-cycle cost for control, but also due to its lower energy usage. One interesting facet of this study that deserves mention is the fact that it has been found that virtually all the fly-ash leaving the collectors, regardless of combustor type, is in the respirable range (15 micrometers to 0.2 micrometers). This is illustrated in Fig. 1 for a spreader stoker. The effect that any contemplated emissions limitation on respirable particulates will have on control costs is, at this time, difficult to determine. However, one conclusion can be stated with some certainty -- any attempt to constrain emission of respirable particles will result in drastic increases in control costs.

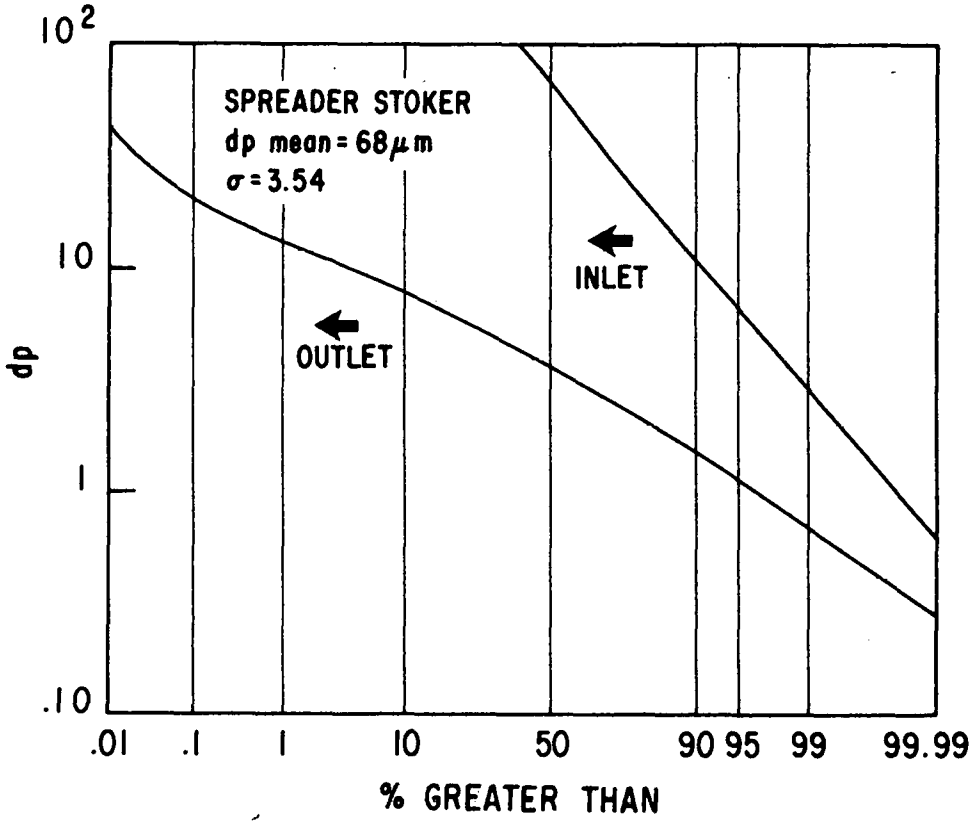


Fig. 1. Effect of a Precipitator on the Size of Fly Ash Emissions.

3.2 FLUE-GAS DESULFURIZATION

Comparative assessments of flue-gas desulfurization (FGD) systems have thus far been carried out at ANL using a wet lime/limestone scrubbing design and cost generator developed by the Tennessee Valley Authority (TVA). The TVA FGD program allows evaluation of performance and costs as a function of variations in coal composition, emissions regulation, scrubber parameters, and economic criteria. In addition, differing modes of sludge disposal are offered, including ponding, filtration, fixation, and combined filtration and fixation. Argonne National Laboratory has supplied its particulate control performance and cost models to TVA. These models have been incorporated into, and form an integral portion of, the most recent TVA scrubbing program. As both organizations continue to upgrade the capabilities of their respective computer programs, a continuing interchange of information is taking place. Argonne views this ongoing relationship with TVA in the development of environmental control assessment models as one of the significant achievements of the program.

Another FGD model designed specifically for comparison of advanced or second generation systems was developed for the program by Battelle Columbus Laboratories. Seven different processes are modeled, as well as five reheat options and five waste disposal options. This model is presently undergoing evaluation before being released for general use.

3.3 SYSTEM MODEL

Development of a total coal energy system model for our program has been underway for several years in cooperation with Carnegie-Mellon University. At the present time, the model can predict costs, environmental residuals to air, land, and water, and energy consumption for systems employing available technologies. Models of several advanced technologies are being integrated into the computer program during this year.

3.4 DATA BASES

Ready access to adequate data is essential if models are to be fully utilized. In order to achieve this, we are now maintaining two on-site data bases. These are based on files obtained from the U.S. Bureau of Mines. One contains analyses of approximately 269,000 coal samples from producing mines, coal loading operations, commercial shipments, and unmined deposits, as well as a file of U.S. coal reserves (tabulated by state, county, and coal bed). This data was recently used in an analysis of U.S. reserves as a function of sulfur content on a state by state basis. (Ref.12) Such information is essential for determining the impacts of different regulatory options for SO_2 control on the coal production in individual states.

Another data base contains the results of merging coal reserve data and coal washability data on a seam by seam basis. About 77.5 billion tons of the demonstrated U.S. reserves of 436.7 billion tons have been successfully characterized in this manner.

4 ENVIRONMENTAL CONTROLS FOR INDUSTRIAL BOILERS

A major objective of the program during the past year has been the development of information on the applicability, performance, and costs of techniques for controlling emissions of atmospheric pollutants from industrial boilers. In accord with provisions of the Clean Air Act Amendments (CAAA) of 1977 requiring the promulgation of performance standards for major industrial emitters, EPA has been reviewing information on industrial boiler emissions and controls with the intent of proposing industrial boiler new source performance standards (IBNSPS) in October 1980. Existing standards for new boilers with heat inputs greater than 250 million Btu/hr are also being reviewed to determine the need for revision. In order to meet its obligation to comment constructively on the EPA proposals, DOE must have access to an independent evaluation of the impacts of possible regulatory initiatives upon fuel use patterns and the development of emerging technologies. It is this need that our program has addressed.

In the latter half of 1978, we engaged the Mittelhauser Corporation to conduct a survey of fuel use in the industrial sector and of the prospects for displacement of gas and oil by coal without serious degradation of the environment. The ultimate objective of this study was to identify energy systems worthy of study in greater detail. Important observations presented in the study are that: 1) the most promising prospects for increased coal use lie in the five two-digit SIC categories that account for more than 75% (8.5 quads/yr) of industrial fuel consumption, as shown in Table 2; 2) the most promising control strategies with respect to near-term availability and cost-effectiveness are post-combustion cleanup (PCC) and atmospheric fluidized-bed combustion (AFBC); 3) gaseous and liquid synfuels, such as substitute natural gas (SNG) and solvent refined coal (SRC-II), from commercial-scale plants offer promise in some applications, and; 4) low-Btu and medium-Btu gasification are cost-effective only in special cases. (Ref.13).

Table 2. Industrial Fuel Use

SIC Code	Industry Group	1974 Fuel Use, Quads[a]	Percent of Total
28	Chemicals, Allied Products	2.5	22
33	Primary Metal Industries	2.1	18
29	Petroleum and Coal Products	1.5	13
32	Stone, Clay, and Glass Products	1.2	11
26	Paper and Allied Products	1.2	11

[a] One quad equals 10^{12} Btu

In defining the scope of a more detailed study, we first used information from recent boiler surveys (Ref.14) to tabulate boiler population and capacity as a function of boiler heat rate and fuel consumed. The results, shown graphically in Fig. 2, indicate peaks in boiler capacity in the size ranges of 1.5-10, 25-50 and 100-250 million Btu/hr. They also reveal that the boiler population per size category increases markedly (by 12,000 boilers) below 50 million Btu/hr, and dramatically (by 183,000 boilers) below 10 million Btu/hr. In view of this distribution, we elected to confine our attention to boilers with heat input rates of 30, 75, 150 and 400 million Btu/hr. Because of the large variation in extent of boiler use in different industries, we saw a need to consider not only a typical load factor (50%) but also a high one, 90%, representative of new boiler use in the petroleum and chemical industries.

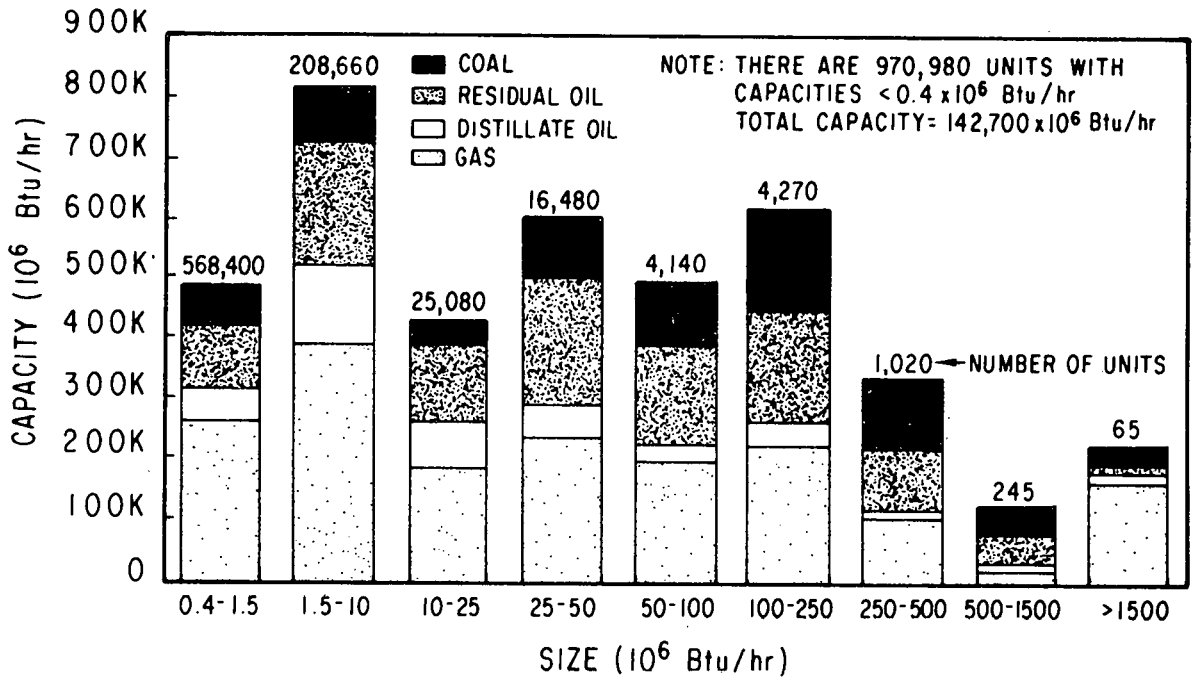


Fig. 2. Commercial and Industrial Boiler Population.

Other aspects of the study reflect the importance we attach to total system analysis and to the desirability of basing costs and impacts on heat output rather than input (to provide an incentive for efficient operation). The systems analysis approach implies the identification of specific sites and system components, and thus gives due consideration to the costs and impacts of fuel transportation. We decided to locate the boilers in Chicago and install them in an existing plant that lacked facilities for coal-handling and on-site disposal of wastes. The selection of fuels, potential SO_2 emission rates, and estimates of delivered prices in 1985 dollars (40% greater than in current dollars) are shown in Table 3. Note that the prices of Illinois high-sulfur coal and Montana low-sulfur coal are considerably lower than those of the fuel oils or coal-derived fuels. Three levels of emission limitations, as shown in Table 4, are considered in the analysis. The least stringent, Level 1, corresponds to limitations found in a number of State Implementation Plans (SIP). Level 2 limitations are similar to those in the existing NSPS for boilers with greater than 250 million Btu/hr input, but do include a percentage removal requirement for SO_2 emissions. The Level 3 requirements, in turn, are similar to the recently adopted NSPS for utility boilers, but include a NO_x limit that is not attainable by currently available technology. This reflects both the 1985 time frame for this study and the current EPA review of NO_x effects and control technology to determine the need for a short-term standard for ambient concentrations of NO_x (as required by the CAAA).

Table 3. Fuels Considered in the Analysis

Fuel	Potential SO_2 (lb/10^6 Btu)	Delivered Price ($/$10^6$ Btu)
Illinois Coal	8.05	2.66
Montana Coal	1.16	3.04
SNG (Montana Plant)	-	8.00
SRC-II (Illinois Plant)	0.35	7.22
Distillate Fuel Oil	0.51	6.19
Residual Fuel Oil	3.14	5.18

Table 4 . Emission Limits Used in the Analysis

Control Level	SO_2	NO_x	Particulates
1	2.5[a] (Coal) 1.2 (Oil)	0.6	0.25 (Coal) 0.10 (Oil)
2	1.2/70% (Coal) 1.0 (Oil)	0.5 (Coal) 0.4 (Oil)	0.10 (Coal) 0.07 (Oil)
3	90% (Coal) 0.8 (Oil)	0.2	0.03

[a] $lb/10^6$ Btu unless a percent removal indicated

The control strategies that we have adopted for the various pollutants and fuels, and the highest level of control considered achievable for each strategy, are shown in Table 5. Note that Level 3 control for SO_2 emissions requires the use of a wet FGD system or of AFBC (with a calcium/sulfur ratio of three). The importance attached to reliability in industrial operations led to the selection of the double alkali process over lime/limestone scrubbing. Note also that attainment of Level 3 NO_x limits for the dirtier fuels requires the use of either the $DeNO_x$ or selective catalytic reduction (SCR) processes in addition to combustion modifications. The more expensive SCR process is required in the case of AFBC because the low flue-gas temperatures preclude use of the $DeNO_x$ process.

Some preliminary conclusions drawn from the as yet incomplete study are presented below. (Ref.15) The cost of steam, in 1985 $/million Btu, is shown in Fig. 3 as a function of SO_2 emission rate for selected systems with heat inputs of 150 million Btu/hr and load factors of 50% and 90%. Note that a low SO_2 emission rate is achieved at least cost by importing low sulfur coal. At the highest required level of control and the higher load factor, AFBC and wet FGD are the favored technologies. The difference in costs between them is regarded to be within the uncertainty in these estimates. At the highest level of control and the lower load factor, the synfuels (and distillate oil, which is not plotted) become competitive economically and favored environmentally because of the lower SO_2 emissions. A similar plot of steam costs vs. SO_2 emission rates is given for smaller boilers, with a heat input of 30 million Btu/hr, in Fig. 4. Note again that use of low sulfur coal is the least-cost option, but that the synfuels are now economically competitive with FGD and AFBC even at the higher load factor and are less expensive at the lower load factor.

Table 5. Control Technology Applications in the Study

Fuel	SO_2		NO_x		Particulates	
Coal	Low-Sulfur Coal	(1)[a]	Combustion Modification	(2)	Cyclone/ESP	(3)
	Dry FGD	(2)	$DeNO_x$	(3)[b]	Cyclone/Baghouse	(3)
	Double Alkali FGD	(3)	SCR	(3)[b]		
	AFBC	(3)				
SRC-II	-		$DeNO_x$	(3)	-	
SNG	-		Combustion Modification	(3)	-	
Distillate Oil	-		Combustion Modification	(3)	-	
Residual Oil	Double Alkali FGD	(3)	Combustion Modification	(2)	ESP	(3)
			$DeNO_x$	(3)		

[a] Highest control level for application

[b] Required for AFBC only

The reasons for the cost-effectiveness of synfuels in the smaller boiler are readily apparent in Fig. 5, which shows the relative contributions of capital charges, fuel costs, and other operational costs to the costs of producing steam in SRC-fired boilers and coal-fired/FGD systems. For the larger boilers and higher load factors, the costs due to fuel, which are relatively insensitive to boiler size or load factor, account for 75% of overall steam costs in the case of SRC. Because the penalties due to capital charges and operating costs associated with scale-down are small in absolute terms for SRC, incremental costs for the smaller boiler and the lower load factor amount to less than 50%. In the FGD case, on the other hand, capital charges and operating costs account for almost two-thirds of the overall cost of steam for the larger boiler. As a result, the cost of steam for the smaller boiler at the low load factor is more than doubled.

The contribution of control costs to the overall cost of steam as a function of boiler size and load factor can be seen in Fig. 6, which presents the costs associated with uncontrolled coal-fired boilers and the incremental costs of meeting Level 3 requirements. The control costs include those attributable to double alkali FGD, combustion modifications, $DeNO_x$, and particulate collection via a baghouse for the small boiler and an electrostatic precipitator for the larger boiler. Note that the control costs represent

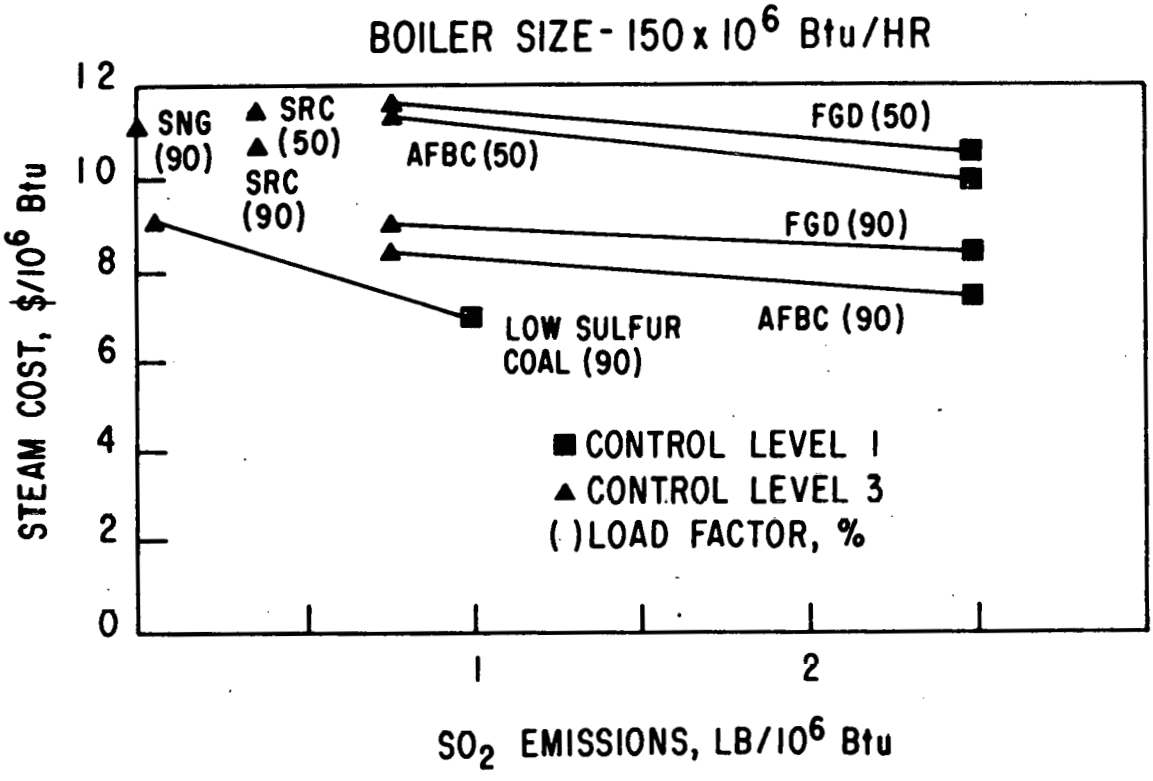


Fig. 3. Steam Cost as a Function of Control Requirements, Strategy, and Load Factor for a 150x10^6 Btu/hr Boiler.

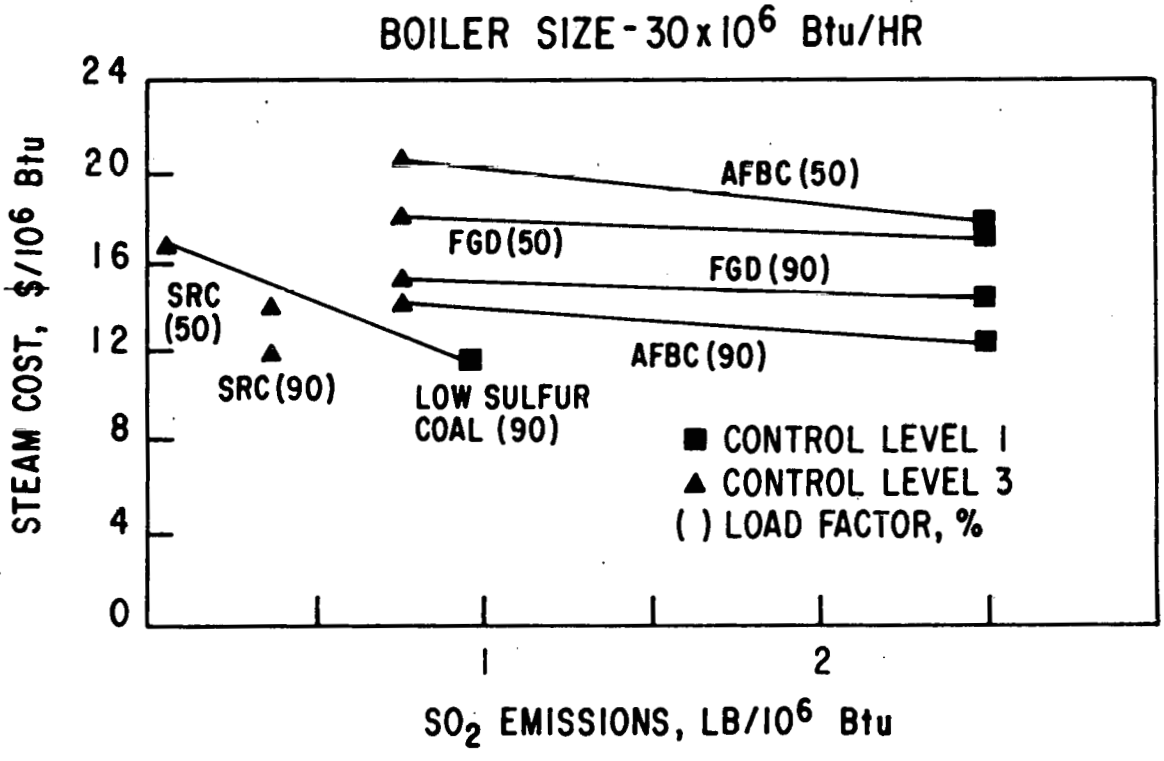


Fig. 4. Steam Cost as a Function of Control Requirements, Strategy, and Load Factor for a 30x10^6 Btu/hr Boiler.

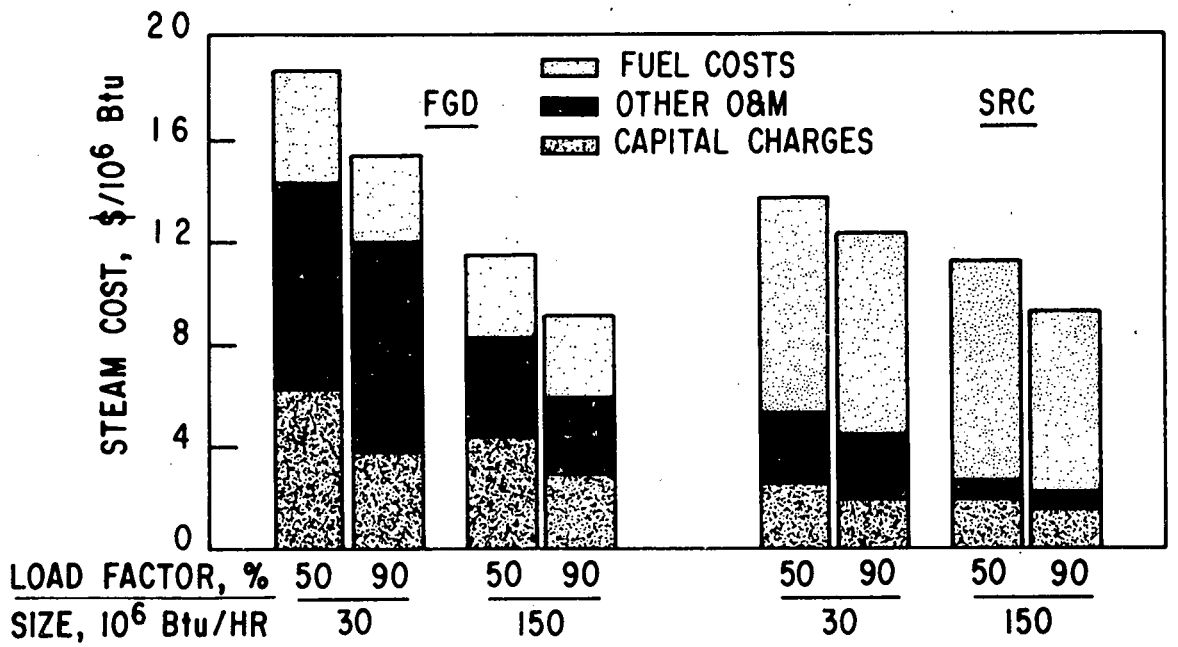


Fig. 5. Variation of Cost Components with Boiler Size and Fuel Choice.

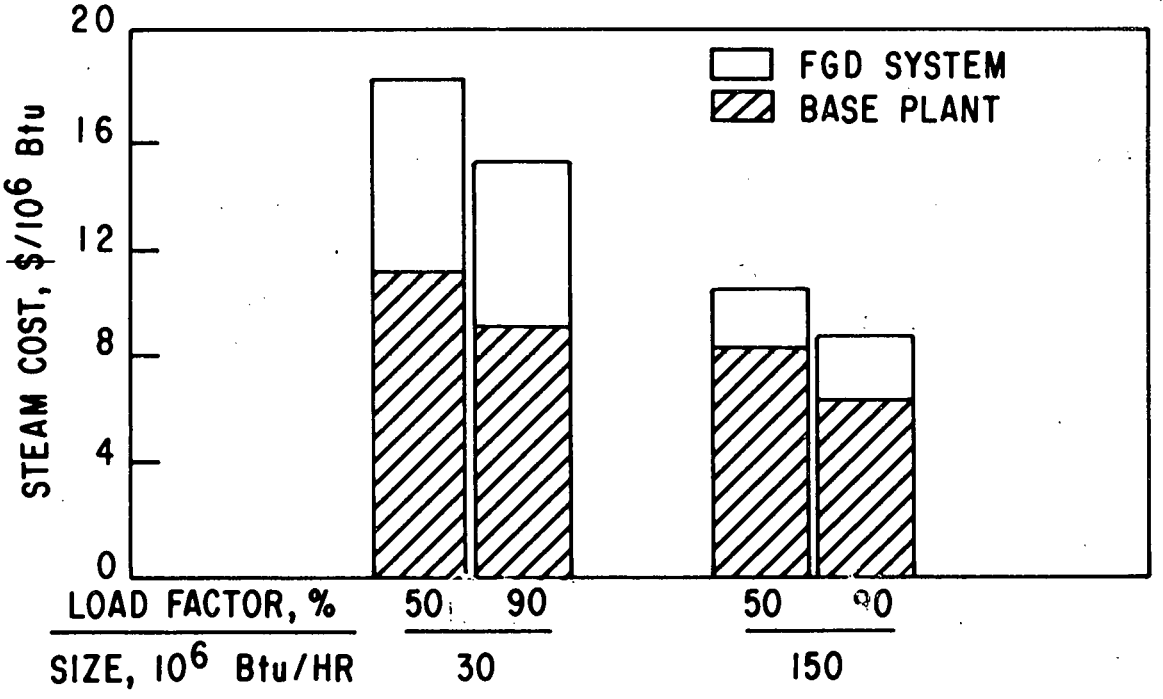


Fig. 6. Contribution of Environmental Controls (Level 3) to Total Steam Cost.

an increasingly larger fraction of overall steam costs as the boiler size and load factor decrease, and that in absolute terms control costs in the smaller boiler become comparable to the total steam generation costs in the larger boiler.

We have thus far been discussing the factors that influence steam production costs. It should be noted, however, that this study addresses a number of other system parameters, including:

- Total coal consumption (a function of system efficiency)
- Non-coal energy consumption
- Water use
- Production of criteria pollutants
- Solid waste production

These factors must be known if one is to assess the true costs of energy production.

The use of a total system perspective can be quite revealing. As an example, we have plotted criteria pollutant production for the FGD and SNG systems (150 x 10^6 Btu/hr, 90% load factor, Level 3 control) in Fig. 7. (Refs. 15, 16 and 17). At the boiler site, the SNG system is indeed much cleaner, emitting only NO_x in appreciable quantities while the boiler with FGD emits a considerable amount of SO_2 and some particulate matter. However, both transportation (pipeline compressors) and processing (gasification) account for sizable NO_x emissions in the SNG system while the corresponding releases in the FGD case are insignificant. We thus have nearly equal total emissions with tradeoffs between SO_2 and NO_x and between localized and distributed sources. If the boundaries of our system were extended farther to include such things as the production of electricity or the refining of diesel fuel, the pollutant burdens would be increased still more. Other factors, such as health and safety considerations in mining and transportation, may also significantly affect the relative cost/benefit ratios of such systems.

These considerations make it imperative that DOE bring this systems perspective to the roundtable where regulatory issues are discussed with the EPA and others. In that way, the perils of a fragmented approach can be avoided and balanced regulatory policies can be developed that are truly cost effective.

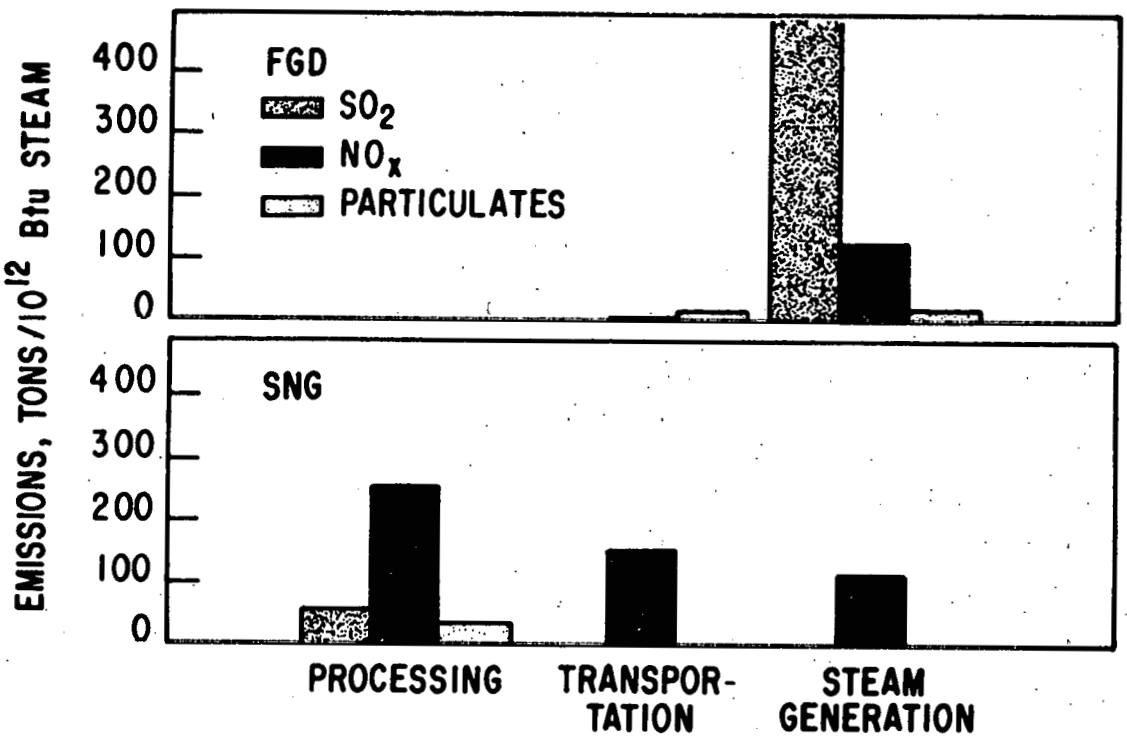


Fig. 7. Analysis of Total System Pollutant Production.

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SESSION 8
ADVANCED COAL UTILIZATION
(FBC, MHD, OCGT, FUEL CELLS)

Chairman: S. Freedman
Co-Chairman: F. Witmer

FLUIDIZED-BED COMBUSTION DEVELOPMENT — AN OVERVIEW

W.L. Buck, H.S. Huang, and B.R. Hubble
Argonne National Laboratory
and
Charles Bliss
The MITRE Corporation/Metrek Division

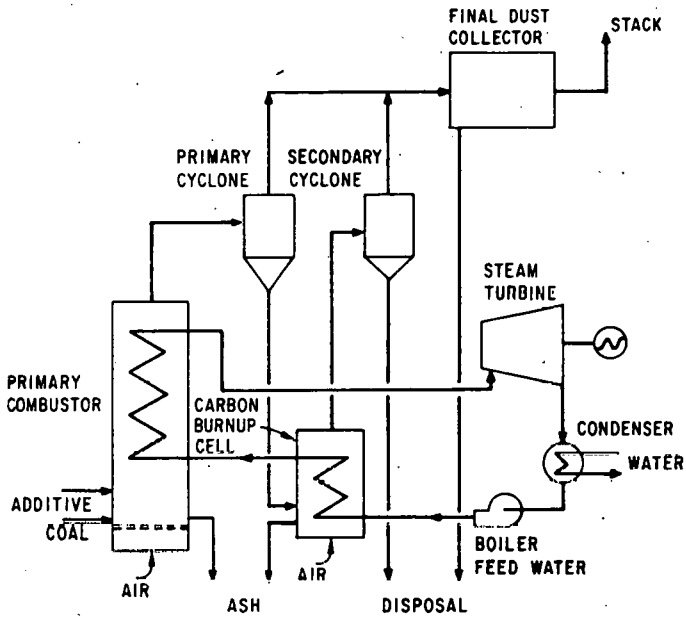
1 INTRODUCTION

Fluidized-bed combustion (FBC) is one of a number of energy options under study in the Environmental Control Technology for Coal Utilization program at Argonne National Laboratory (ANL). This program, which was described at the previous symposium in this series, is a continuing effort sponsored by the Division of Environmental Control Technology under the Assistant Secretary for Environment, U.S. Department of Energy (DOE). The program generates in-depth assessments and comparative evaluations of the engineering, environmental, and economic aspects of control technologies for coal-based energy systems.[1]

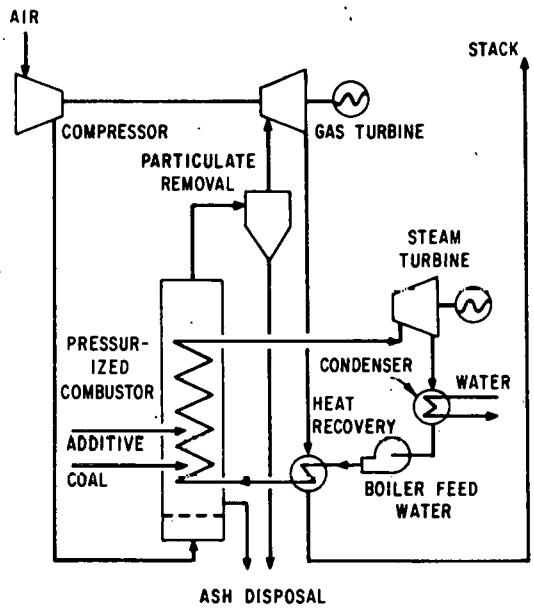
FBC, an alternative to conventional coal combustion, appears to be capable of controlling SO_2 and NO_x emissions to meet current regulatory standards without add-on devices such as scrubbers. Combining multi-fuel capability with the promise of high efficiency and competitive costs, FBC is potentially attractive for both utility and industrial applications.

Figure 1 shows simplified schematics of an atmospheric-pressure fluidized-bed-combustion (AFBC) power plant and three different types of pressurized fluidized-bed-combustion (PFBC)/combined-cycle power plants that serve to illustrate the principles of the technology.[2] In this figure, "additive" means sorbent and "ash" includes spent sorbent. The basic features of FBC are illustrated in the AFBC schematic (Fig. 1a): (i) the upward flow of combustion air maintains fluidization of the bed; (ii) SO_2 released from the burning of coal reacts chemically with the limestone or dolomite sorbent in the bed; (iii) the combustion temperature is maintained in the relatively low range of 1500-1700°F, thus reducing NO formation and trace-element volatilization and precluding slag formation; and (iv) boiler tubes are submerged in the bed and may also be situated in the freeboard region above the bed. Combustion efficiency is enhanced by the carbon-burnup cell (CBC), which burns coal particles and soot elutriated from the primary combustor and collected in the primary cyclone.

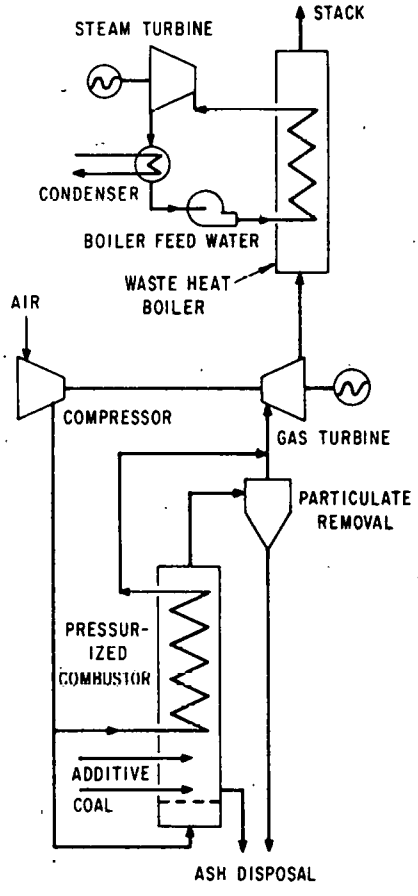
For the purpose of generating electric power, the energy-conversion efficiency can be increased still further by pressurizing the fluidized-bed combustor (say to ~ 10 atm) and generating additional power by expanding the hot, pressurized combustion gases through a gas turbine. All three combined-cycle design configurations shown in the figure require hot-gas cleanup to protect the gas turbine from corrosion, erosion, and deposition. With the water-cooled system (Fig. 1b), steam generation occurs in the bed, as in the AFBC system. In contrast, the adiabatic system (Fig. 1d) has no heat-transfer surface in the combustor, and temperature control is maintained by



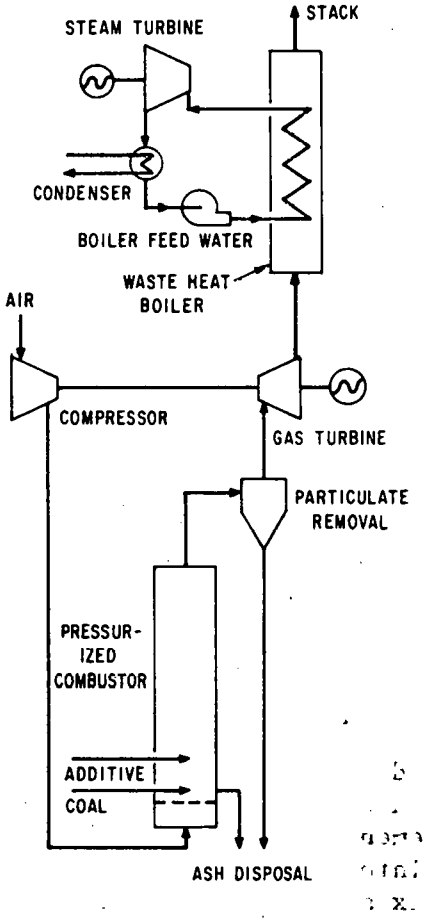
a. ATMOSPHERIC WATER-COOLED COMBUSTOR



b. PRESSURIZED WATER-COOLED COMBUSTOR



c. PRESSURIZED AIR-COOLED COMBUSTOR



d. PRESSURIZED ADIABATIC COMBUSTOR

Fig. 1. Fluidized-Bed Combustion Power-Generation Systems

employing ~ 300% excess air. The air-cooled PFBC system (Fig. 1c) is similar to the adiabatic system in that no steam generation occurs in the bed. In this system, only about one third of the pressurized air is fed to the combustion chamber; the remaining two thirds passes through heat-transfer tubes located in and above the fluidized bed, and the resulting clean, hot, pressurized air is mixed with the combustion-gas stream between the particulate-removal equipment and the gas turbine.

2 A CONFERENCE-BASED TECHNOLOGY ASSESSMENT

A comprehensive assessment of the developmental status of coal-fired FBC technology for electric-power generation has recently been completed, employing a systematic methodology developed by the Metrek Division of The MITRE Corporation. Based on analysis of the 115 individual papers presented at the Fifth International Conference on Fluidized-Bed Combustion held in December, 1977, in Washington, D.C., the assessment depicts the status of information for each element of the technology and identifies the major issues, problems, and information gaps that need to be addressed.

A full report on this study, prepared jointly by The MITRE Corporation and Argonne National Laboratory has been published.[3] Only a brief description of the methodology and summary of the results will be presented here.

2.1 ASSESSMENT METHODOLOGY

FBC technology was first resolved into its fundamental elements (termed technical classifications), encompassing the following constituent topical areas: fuel utilization, heat transfer, emission control, equipment configuration, dynamic response, materials of construction, cost factors, and prospects for commercialization.

Next, the conference papers were reviewed, and a total of 450 information statements bearing on the developmental status of FBC technology were culled from the papers. Each such statement was assigned an accession number and was coded to indicate the technical classification or classifications to which the information pertained, the relevant pressure mode (AFBC, PFBC, or both), and the appropriate information-source classification (such as hardware operation, mathematical modeling, etc.). The information statements were then stored in a computer-managed file from which listings of statements bearing any particular coding or combination of codings could be obtained readily.

The distribution of information statements among the various technical classifications and information-source classifications is conveniently displayed in matrix format, as illustrated in Fig. 2. The numbers appearing in any intersection of this matrix are accession numbers of those information statements that are coded to the corresponding technical classification (row) and information-source classification (column). The information-management matrix shown pertains to AFBC; a similar matrix exists for PFBC.

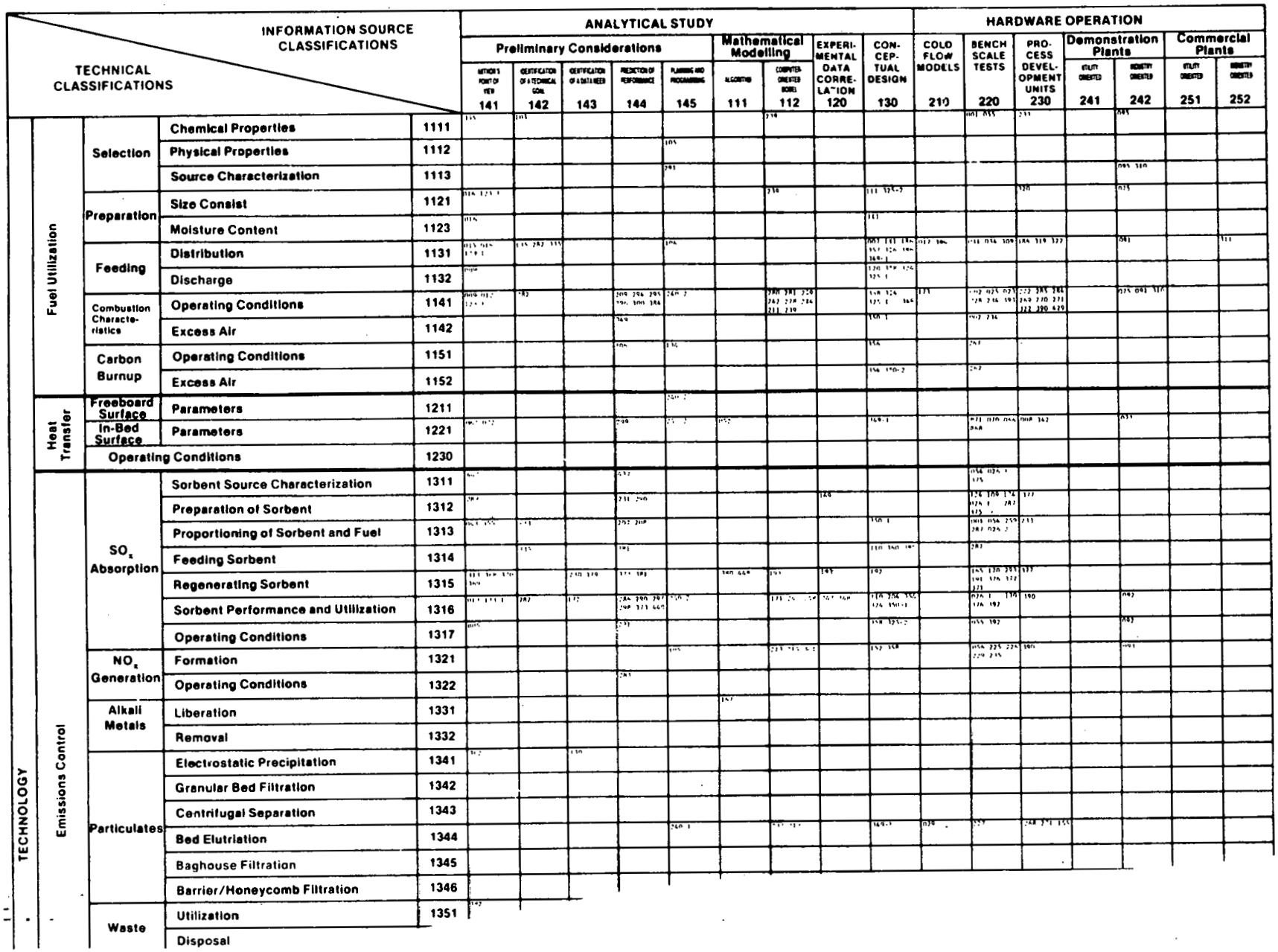


Fig. 2. Portion of Information-Management Matrix for AFBC

For each technical classification, the corresponding information statements were analyzed and summarized in order to characterize the status of information pertaining to that aspect of the technology and to identify relevant elements of uncertainty (issues, problems, and information gaps) that need to be resolved. A level of significance (high, medium, or low) was assigned to each such issue, problem, or information gap, based in part on its relationship to a set of power-generation topics embodying the requirements and concerns of potential users of the technology. These user-oriented topics include cost, environmental compliance, fuels, configuration, downtime, loading, suppliers, and manpower.

2.2 ASSESSMENT RESULTS

The issues, problems, and information gaps identified in the course of this study serve a dual purpose. They are, first of all, an essential element in the characterization of the present developmental status of FBC technology. Also, they point to those areas of the technology wherein future research, development, and demonstration activities may most profitably be concentrated.

Despite their importance, it is not feasible, in the present paper, to enumerate and discuss each of the approximately 50 issues and problems and 45 information gaps brought to light during this assessment of the developmental status of FBC technology. Suffice it to point out here that critical elements of uncertainty were revealed in the following areas:

- Fuel and sorbent feeding,
- Combustion efficiency,
- Corrosion and erosion control,
- Sorbent selection and utilization,
- Load-following capability,
- Emission characterization and control, and
- Solid-waste disposal.

3 CURRENT RESEARCH, DEVELOPMENT, AND DEMONSTRATION PROGRAMS

Selected results from current research, development, and demonstration programs will now be cited to illustrate progress being made in resolving the uncertainties associated with the first four of the areas in the above list. Additional results bearing on these and other areas of uncertainty in FBC will be presented in subsequent papers in this session of the symposium.

Table 1 contains a list of some of the more important FBC units that are currently in service or scheduled for early completion. This list contains both utility-oriented and industry-oriented units; however, the output-power ratings of the units are all given in terms of an equivalent electrical output. Not included in this table are numerous smaller process-development units (PDUs) that are providing valuable support data, as well as various

TABLE 1. ROSTER OF SELECTED FBC FACILITIES

INSTALLATION	TYPE	RATED POWER, EQUIVALENT ELECTRIC	STATUS (1-80)
	ATMOSPHERIC-PRESSURE FBC FACILITIES		
1. POPE, EVANS & ROBBINS, INC. RIVESVILLE, W.V. (DOE)	PILOT PLANT	30 MWe	OPERATIONAL AFTER REPAIRS FOR FIRE.
2. MORGANTOWN ENERGY TECHNOLOGY CENTER MORGANTOWN, W.V. (DOE)	CTIU	6 MWe	UNDER CONSTRUCTION; COMPLETION IN 1981.
3. BABCOCK & WILCOX CO. ALLIANCE, OHIO (EPRI)	PDU	2 MWe	OPERATIONAL.
4. GEORGETOWN UNIVERSITY WASHINGTON, D.C. (DOE)	DEMONSTRATION PLANT	10 MWe	OPERATIONAL.
5. GREAT LAKES NAVAL STATION GREAT LAKES, IL (DOE, STATE OF ILLINOIS)	DEMONSTRATION PLANT	5 MWe	UNDER CONSTRUCTION; COMPLETION IN 1980.
6. TVA SHAWNEE STEAM PLANT PADUCAH, KY (TVA)	PILOT PLANT	20 MWe	CONSTRUCTION TO START OCTOBER 1980.
7. CENTRAL OHIO PSYCHIATRIC HOSPITAL COLUMBUS, OHIO (OHIO DOE)	COMMERICAL PLANT	6 MWe	UNDER CONSTRUCTION; OPERATION IN MAY 1980.
	PRESSURIZED FBC FACILITIES		
8. CURTISS- WRIGHT CORP. WOOD-RIDGE , N.J. (DOE)	PILOT PLANT	13 MWe	UNDER CONSTRUCTION; COMPLETION IN 1981.
9. INTERNATIONAL ENERGY AGENCY GRIMETHORPE, ENGLAND (IEA)	FLEXIBLE TEST FACILITY	27 MWe	UNDER CONSTRUCTION; COMPLETION IN 1981.

ABBREVIATIONS: CTIU = COMPONENTS TEST AND INTEGRATION UNIT
PDU = PROCESS DEVELOPMENT UNIT

larger-scale units in the conceptual-design stage. However, this table serves to illustrate the nature of present activity in terms of FBC developmental effort and will be referred to in the following discussion of progress toward resolving uncertainties in FBC technology.

3.1 FUEL AND SORBENT FEEDING

Two of the FBC facilities listed in Table 1 can be cited as instances of progress in the critical area of fuel and sorbent feeding.

The Babcock & Wilcox Company AFBC PDU, which contains a 6-ft x 6-ft bed, was originally equipped with four under-bed feed points, in accordance with conventional design criteria. However, this unit has since been operated efficiently with only one under-bed feed point (for 36 ft^2 of bed area), indicating that the required feed system can be simplified significantly.[4]

The Georgetown University AFBC unit, which will be discussed in detail in a later paper in this session, completely avoids the plugging and other problems associated with under-bed feed systems.[5] This unit uses an off-the-shelf mechanical stoker that distributes the coal evenly across the top surface of the bed. The limestone feed system employed -- a single gravity-feed pipe into each of the two side-by-side beds, where the limestone is distributed by the fluidizing motion -- shows similar simplicity.

3.2 COMBUSTION EFFICIENCY

The same two units can be referred to in discussing the critical area of combustion efficiency. Neither unit employs a carbon-burnup cell, so a significant capital and operating expense is avoided.

In the Babcock & Wilcox unit, unburned carbon and unreacted limestone are simply recycled from the first cyclone back to the main combustor. This char recycling or fly-ash reinjection, as it is sometimes called, is reported to result in combustion efficiencies of 98% or greater.

A fly-ash reinjection system is also employed in the Georgetown University unit. However, this unit does not rely on cyclones but instead employs baffle plates to route the combustion gases through a series of 180° turns. At the first such turn, unburned carbon particles drop out and are returned to the combustor. Eighty-to-85% combustion efficiency is achieved on the first pass, and the char recycling is expected to raise this level to greater than 95%.

3.3 CORROSION AND EROSION CONTROL

As mentioned previously, one aspect of corrosion and erosion control involves hot-gas cleanup for coal-fired PFBC/combined-cycle systems. Recent test results obtained by Curtiss-Wright Corporation, which is developing the air-cooled type of system shown in Fig. 1c, demonstrate that such a system can be made to operate for at least 1000 hours without incurring significant corrosion or erosion of the gas-turbine blades.[6,7]

The system tested was a 1-MWe coal-fired, air-cooled PFBC rig employing four stages of hot-gas cleanup and a Rover IS-60 single-stage gas turbine. The hot, pressurized combustion gas from the PFBC passed first through a primary cyclone of conventional design, whose purpose was to collect and recycle back to the bed relatively large particles of sorbent and unburned coal. The second through fourth stages of hot-gas cleanup employed more sophisticated cyclone-type devices, namely: a Dynatherm "Whirlaway" separator, a Ducon high-efficiency tangential-entrance cyclone, and an Aerodyne dual-flow cyclone, in that order. For this test, the vortex chamber of the Ducon cyclone was modified to improve the aerodynamic design, and a portion of the clean air from the in-bed heat exchanger was used for the secondary gas flow in the Aerodyne cyclone.

During this test, the turbine drive gas, a mixture of the cleaned combustion gas and the clean air from the in-bed heat exchanger, had a total particulate loading of about 0.05 grain/scf, a mean particle size of 1.4 μm, and a maximum particle size of about 8 μm. After 1000 hours of coal-fired operation, inspection revealed no significant erosion or corrosion of the turbine blades.

For purposes of comparison, it may be mentioned that in an earlier test, run before the modification of the Ducon cyclone and using combustion gas rather than clean air for the secondary flow in the Aerodyne cyclone, the turbine drive gas had a total particulate loading of 0.15 grain/scf, a mean particle size of 3.2 μm, and a maximum particle size of about 27 μm. Under those conditions, significant erosion of the trailing edges of the turbine blades was noted after only 150 hours of operation.

3.4 SORBENT SELECTION AND UTILIZATION

The last examples chosen to illustrate recent progress deal with the area of sorbent selection and utilization. An important parameter of any FBC system is the molar ratio of calcium in the sorbent to sulfur in the coal that is required to achieve the necessary control of SO_2 emission in actual operation. This ratio varies with different sorbents and combustor designs, but values in the range of three to five have been considered typical for AFBC systems.

The fact that the required Ca/S molar ratio is greater than unity indicates that only a fraction of the calcium in the sorbent is being utilized in SO_2 capture. Thus the spent-sorbent waste product from FBC contains unused CaO. This represents an economic penalty and an environmental detriment, in terms of both the amount of sorbent required and the volume of solid waste to be disposed of.

The first example concerns results obtained with the Babcock & Wilcox AFBC PDU. It is reported that the recycling of char and limestone dust from the first cyclone back to the combustor resulted not only in higher combustion efficiency but also in improved sorbent utilization. Specifically, 90% SO_2 removal was achieved with a Ca/S molar ratio of only 2-3, and utilization of the calcium in the sorbent was increased from ~ 20% to ~ 40%.

The second example involves a new method, under development at Argonne National Laboratory, for increasing the utilization of calcium in the sorbent.[8] It has been found that spent sorbent can be reactivated rather simply by treatment with water, and the reactivated sorbent can be fed back to the combustor to pick up additional SO_2 from the combustion gases. This process can be repeated several times, effectively reducing both the amount of fresh sorbent that must be supplied to the combustor and the quantity of solid waste ultimately produced.

This reactivation procedure (not to be confused with sorbent regeneration, in which $CaSO_4$ is reconverted to CaO) depends upon a combination of chemical and physical processes, as illustrated in Fig. 3. In the hydration step, which can be carried out at room temperature, CaO remaining in the interior of the spent-sorbent particle reacts with water for form $Ca(OH)_2$, with a resultant expansion of the particle and cracking of the $CaSO_4$ surface layer. Upon being returned to the combustor, the $Ca(OH)_2$ is converted back to CaO and a completely new, more open pore structure is developed. This results in an increase in both the gas permeability and the exposed surface area of CaO in the particle, thereby making it possible for additional sulfation to take place. As indicated in Fig. 3, the sorbent can be reactivated and reused more than once, substantially increasing the utilization of the calcium in the sorbent.

In laboratory-scale experiments, this method has been applied to a large number of different limestones and dolomites. All stones tested showed a marked increase in sulfation after a single such reactivation. Moreover, those stones that exhibited the lowest extent of sulfation upon initial exposure to SO_2 seemed to benefit the most in terms of increased sulfation capacity after reactivation.

Grove limestone (a relatively unreactive sorbent) was put through five sulfation-hydration cycles in a small AFBC having an inside diameter of 15.5 cm and burning coal containing 5.46% sulfur. The overall calcium utilization increased from 22% after the first pass of the stone through the combustor to ~ 90% after the fifth cycle. Moreover, the molar ratio of available (unsulfated) calcium in the stone to sulfur in the coal required to maintain SO_2 emission at the constant level chosen for this test actually decreased from a value of 3.3 for the virgin stone to a nominal value of 2.0 in cycles one through four.

Optimization studies of this promising new method of enhancing sorbent utilization are in progress, and plans are being finalized to test the process at a suitable larger-scale FBC facility.

4 ECONOMIC COMPARISON OF FBC AND OTHER POWER-GENERATION TECHNOLOGIES

In this section, capital- and operating-cost estimates for both atmospheric and pressurized FBC power-generation systems are compared with those for pulverized-coal-combustion and low-Btu-gasification/combined-cycle systems. The base case for the conceptual design and detailed engineering cost studies is an approximately 500-MWe (net) utility power plant using a representative Illinois bituminous coal with a sulfur content (dry) of about four weight

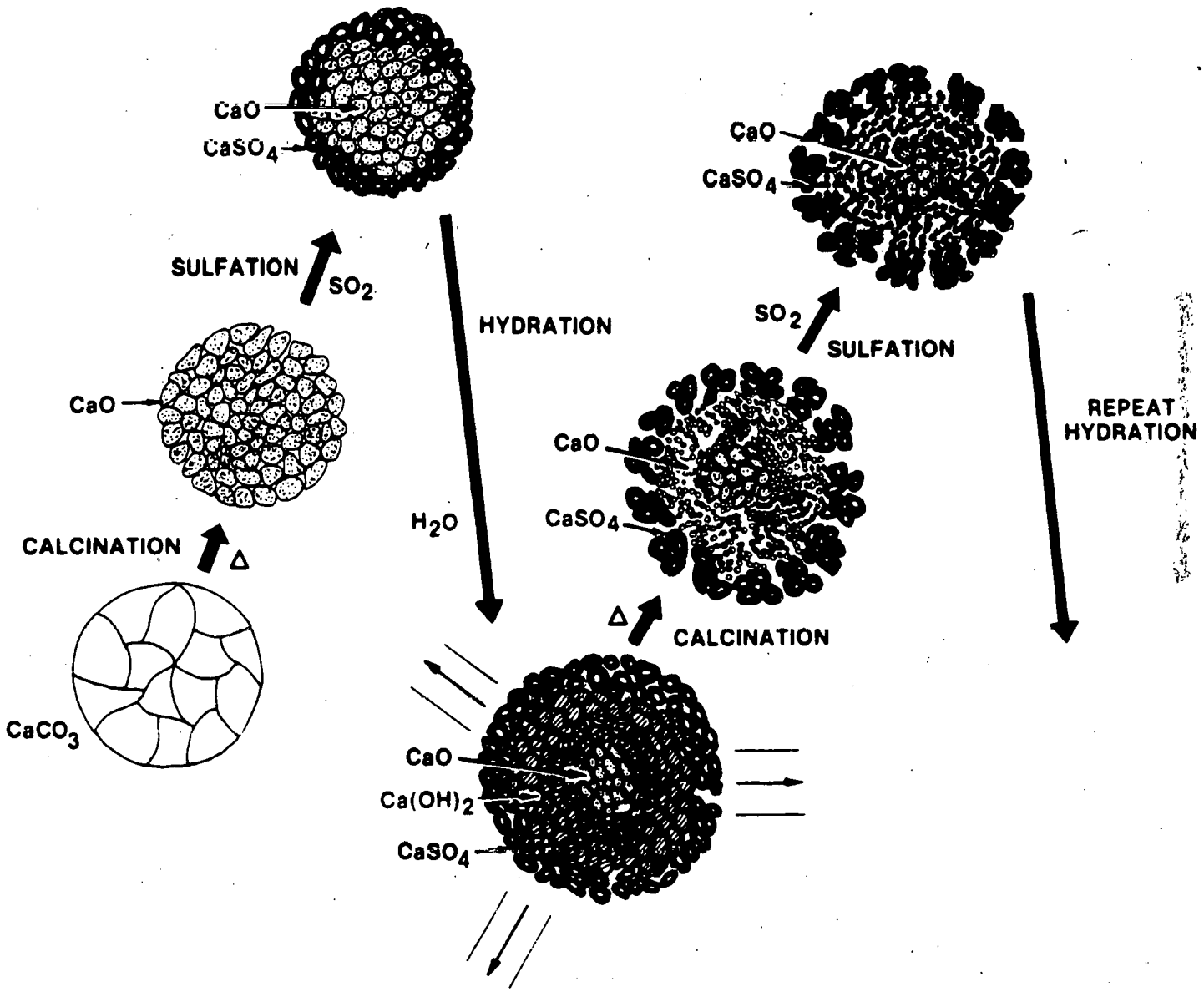


Fig. 3. Enhancement of Limestone Sulfation by Hydration

percent.

The pulverized-coal-combustion boiler and its auxiliaries are of commercial utility designs. The plant uses an electrostatic precipitator (ESP) to remove particulate matter from the flue-gas stream prior to flue-gas desulfurization (FGD). Sulfur-dioxide emission control is performed by a limestone-based FGD system. Normal disposal of FGD sludges is offsite, with an onsite ash pond included to retain scrubber sludges produced during periods when offsite disposal is not available.

The low-Btu-gasification/combined-cycle plant is an integrated facility in that it includes all the components to convert coal into electricity. A simplified plant flow schematic is shown in Fig. 4. Three types of gasifiers have been considered in this analysis: Lurgi fixed-bed, IGT fluidized-bed, and Texaco entrained-flow. Water washing and low-temperature hydrogen-sulfide removal processes are employed to condition the raw fuel gas from the gasifier. Moderately advanced (2,400°F and 16-to-1 pressure-ratio) gas turbines are selected because of their likely availability around 1985.

All of the power plants have been designed to comply with the U.S. EPA New Source Performance Standards (NSPS) promulgated in June, 1979. These standards set the following limits on air pollutants from power plants firing the design coal:

Pollutant	Emission Limit (30-day rolling average)
Sulfur dioxide, SO_2	90% removal
Nitrogen oxides as NO_2	0.6 lb/10^6 Btu
Particulate matter	0.03 lb/10^6 Btu

In the case of the AFBC, a limestone sorbent is used with a calcium-to-sulfur molar ratio of 3.5. For the pressurized FBC, dolomite is used as the sorbent with a calcium-to-sulfur ratio of two. The low-Btu-gasification/combined-cycle plants achieve a high degree of sulfur removal by using standard industrial H_2S-removal processes, such as the Selexol Process with a Claus-sulfur-plant/tail-gas-cleanup system.

A southern Illinois plant site has been chosen for estimating purposes. This would place the plant near several demand centers and in close proximity to extensive coal fields, thus minimizing transportation costs.

Based on the technical criteria briefly described above, the heat rate for each of the power-generation technologies was determined. These rates, which were used for capital costing and revenue-requirement calculations, are given in the following table.

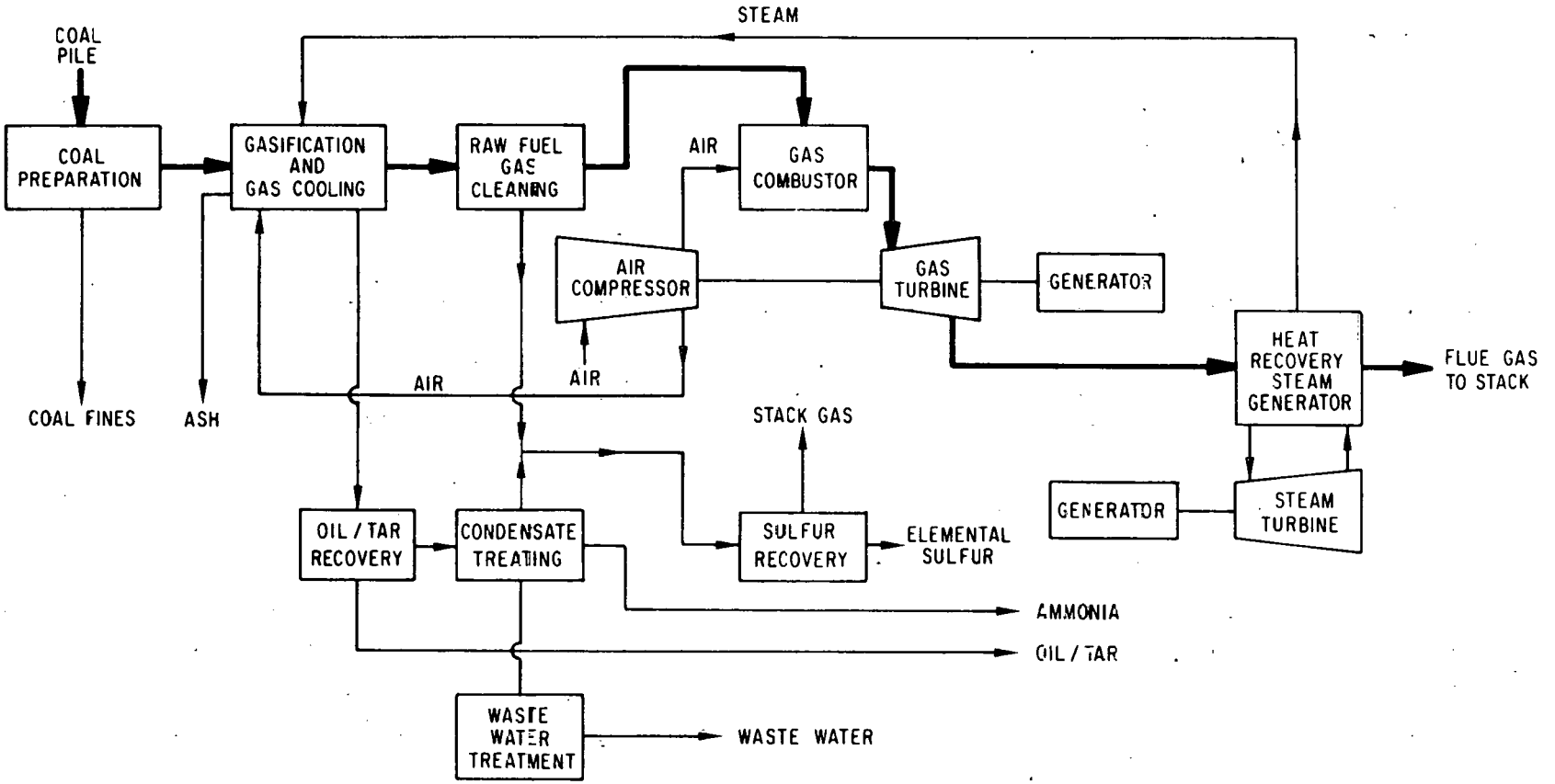


Fig. 4. Gasification/Combined-Cycle Power Plant Schematic

OVERALL HEAT RATES

Technology	Heat Rate (Btu/kWh)
AFBC	9,720
PFBC	8,690
PCC/FGD	9,850
LBG/CC	
Lurgi	10,860
IGT	8,360
Texaco	9,060

4.1 ECONOMIC ASSUMPTIONS

The plant life for each of the systems considered in this analysis is assumed to be 30 years. The design and construction period for these plants is five years. Design and construction are assumed to begin in January 1980, with plant startup in January 1985. All costs are calculated in January-1980 dollars.

4.1.1 Indirect Investment Charges

This includes the materials and labor for equipment and installation and all costs (such as architect and engineering fees, contractor expenses, construction expenses, and in-house engineering) that are necessary for construction of a grass-roots power plant. The engineering design and contingency factors are based on the developmental status of the technology and experience with engineering projects.

The contingency for all of the technologies has been taken as 15% of the overall project investment, plus an additional 10% on equipment costs for the fixed-bed gasifier, acid-gas removal, the atmospheric-pressure FBC boiler, and high-temperature/high-pressure particulate removal; and an additional 20% for the fluidized-bed and entrained-flow gasifiers as well as the pressurized FBC boiler. The interest during construction has been estimated as 30.5% of the sub-total fixed investment for each of the processes, based on a compounded interest rate of 10% per year.

4.1.2 Working Capital

Working capital consists of the money invested in coal and other raw materials carried in stock, accounts receivable, and cash kept on hand for payment of operating expenses. For these cost estimates, working capital

has been taken as equivalent to three weeks of raw-material costs, seven weeks of direct costs, and seven weeks of overhead costs.

4.1.3 Fixed-Charge Rate

The fixed charges include interest on money borrowed to build a plant, income taxes on the equity interest (if the utility is privately owned), property and other taxes, and insurance. Subtracted from this are whatever income-tax credits might be allowed, such as investment-tax credit and depreciation credit. For this analysis, the annual fixed-charge rate was assumed to be 18% of the total capital requirement, with working capital treated the same as depreciable capital.

4.1.4 Overheads

Plant, administrative, and marketing overheads are costs which vary from company to company. With consideration of the various methods used in industry and illustrated in a variety of cost-estimating sources, the following method for estimating overheads is used.

Plant overhead is estimated as 50% of the sub-total conversion costs less utilities, and it includes the projected costs for labor, maintenance, and analyses. Administrative overhead is estimated as 10% of operating labor and supervision. Marketing the product is considered in the estimation of overheads and is defined as 10% of sales revenue.

4.1.5 By-product Sales

In the evaluation of the annual revenue requirements, credit from sale of by-products (such as ammonia or sulfur recovered from low-Btu combined-cycle gasifiers) is deducted from the annual operating costs to obtain the net annual revenue requirements.

4.1.6 Raw-Material Costs

Costs for limestone and dolomite (needed for sulfur-oxides removal in fluidized-bed units) have been taken as $10 per ton. For the basis of calculating annual revenue requirements, a coal price of $1 per million Btu has been assumed. This results in a net coal price of $22.50 per ton of coal. In addition to this fixed coal price, a price range of $0.75-$2.00 per million Btu was also used in order to study the sensitivity of busbar power costs to fuel costs.

4.2 CAPITAL REQUIREMENTS

The capital requirements for the atmospheric and pressurized fluidized bed as well as the pulverized-combustion/FGD power plant, are given in Table 2. The estimate for the pulverized-combustion/FGD system was based on in-

TABLE 2. AFBC, PFBC AND PCC/FGD BASE PLANT CAPITAL COST BREAKDOWN

CATEGORIES	COSTS (MILLIONS OF DOLLARS) ($1980)		
	AFBC (500 MWe)	PFBC (500 MWe)	PCC/FGD (500 MWe)
STEAM GENERATORS	79.8	54.6	83.8
TURBINE GENERATORS	31.5	52.0	31.0
PROCESS MECHANICAL EQUIPMENT	56.1	55.5	67.3
ELECTRICAL	43.2	31.8	43.4
CIVIL AND STRUCTURE	39.6	33.1	45.5
PROCESS PIPING AND INSTRUMENTATION	30.8	49.0	43.8
YARDWORK AND MISCELLANEOUS	5.7	5.2	6.3
TOTAL	286.7	281.2	321.1
A/E HOME OFFICE & FEE @ 10% OF BOP	19.9	17.4	24.8
CONTINGENCY	50.8	57.5	51.9
INTEREST DURING CONSTRUCTION	109.0	108.6	121.3
TOTAL PLANT INVESTMENT	466.4	464.7	519.1
START UP AND MODIFICATION	46.6	46.5	51.9
WORKING CAPITAL	14.1	13.1	14.4
TOTAL CAPITAL REQUIREMENT	521.2	517.8	585.4
UNIT CAPITAL REQUIREMENT, $/kWe	1,042	1,036	1,171

formation developed at Argonne National Laboratory. For the FBC systems, capital costs were determined on the basis of detailed cost estimates prepared by Westinghouse Corporation[9] and Burns and Roe, Inc.[10]

The capital requirements for the three low-Btu-gasification/combined-cycle plants are shown in Table 3. All of the plants include facilities for acid-gas removal and elemental-sulfur recovery, and also ammonia recovery (except for the Texaco process). These estimates were prepared based on yet-to-be-published information supplied by United Technologies Research Center to Argonne National Laboratory.[11]

The Chemical Engineering cost index was used, where necessary, to bring some of the previous capital estimates up to January-1980 dollars.

4.3 ANNUAL REVENUE REQUIREMENTS

The annual revenue requirements for all of the power-generation technologies considered in this economic analysis are shown in Tables 4 and 5. Two cases were considered for each technology; one is for a 0.7 capacity factor (6150 hours per year) and the other for a 0.45 capacity factor (3950 hours per year).

The Lurgi combined-cycle system is clearly the most costly of the power-generation alternatives addressed, being about 10% more costly than the conventional combustion system with FGD. On the other end, the IGT combined-cycle system was found to be the least costly and is about 15% cheaper than the conventional system; however, it should be pointed out that the IGT gasifier is still in an early stage of development. For the rest, the Texaco combined-cycle system shows about the same cost as the conventional PCC/FGD system, while the AFBC and PFBC systems are, respectively about 5% and 10% cheaper.

To investigate further tradeoffs between the technologies, the unit cost of power is plotted as a function of fuel cost in Fig. 5. A change in the cost of coal from 0.5 to 2 dollars per million Btu is shown to have little effect on the economic rankings, although the different technologies do exhibit various degrees of sensitivity to fuel cost.

It should be noted, however, that a variation of up to 20 percent in the cost of power is within the uncertainties inherent in the costing of developing technologies. In addition, all of the advanced processes included in this analysis are, at best, in the pilot or demonstration stage insofar as power generation is concerned. Problems with scale-up, discoveries during development, or changes in regulatory constraints could significantly alter the results that have been shown here.

Table 6 summarizes the operating and economic characteristics of the six power-generation technologies that have been considered in this analysis.

TABLE 3. GASIFICATION COMBINED-CYCLE BASE PLANT
CAPITAL COST BREAKDOWN

CATEGORIES	COSTS (MILLIONS OF DOLLARS) ($1980)		
	LURGI (533 MWe)	IGT (523 MWe)	TEXACO (426 MWe)
COAL HANDLING	12.9	12.7	13.1
OXIDANT FEED	2.5	2.6	4.0
GASIFICATION AND ASH HANDLING	63.5	22.7	35.8
GAS COOLING	30.2	44.4	74.7
ACID GAS REMOVAL AND SULFUR RECOVERY	39.1	32.6	26.9
PROCESS CONDENSATE TREATING	54.4	9.4	---
STEAM, CONDENSATE AND BFW	30.6	1.4	0.5
SUPPORT FACILITIES	26.3	24.1	16.1
COMBINED CYCLE	127.6	162.2	137.9
TOTAL	387.1	312.1	309.0
A/E HOME OFFICE & FEE@ 10% OF ESTIMATED BOP	25.4	20.5	20.3
CONTINGENCY	71.2	56.1	57.5
INTEREST DURING CONSTRUCTION	162.6	118.6	118.0
TOTAL PLANT INVESTMENT	646.3	507.3	504.8
START UP AND MODIFICATIONS	55.0	44.0	41.0
WORKING CAPITAL	17.6	13.8	12.9
TOTAL CAPITAL REQUIREMENT	718.9	565.1	558.7
UNIT CAPITAL REQUIREMENT, $/kWe	1,349	1,080	1,312

TABLE 4. TOTAL ANNUAL REVENUE REQUIREMENT FOR AFBC, PFBC AND PCC/FGD PLANTS

500 MWe NET OUTPUT	ANNUAL COSTS $ x 10^3					
	6,150 HR/YR (0.7 CAPACITY)			3,950 HR/YR (0.45 CAPACITY)		
	AFBC	PFBC	PCC/FGD	AFBC	PFBC	PCC/FGD
DIRECT COSTS						
COAL ($1/MBtu)	29,907.6	26,706.4	30,288.8	19,208.9	17,152.9	19,453.8
SORBENT	5,088.4	5,391.1	1,619.6	3,268.2	3,462.6	1,040.2
ASH AND SLUDGE DISPOSAL	2,753.2	2,009.3	2,678.9	1,768.3	1,290.5	1,720.6
OPERATION AND MAINTENANCE	6,502.0	6,655.8	7,502.0	5,445.9	5,583.7	6,445.9
TOTAL DIRECT COSTS	44,251.2	40,762.6	42,089.3	29,691.3	27,489.7	28,660.5
INDIRECT COSTS						
CAPITAL CHARGES , 18% OF TOTAL CAPITAL REQUIREMENT	93,816.0	93,204.0	105,372.0	93,816.0	93,204.0	105,372.0
OVERHEADS						
PLANT, 50% OF O&M	3,251.0	3,327.9	3,751.0	2,723.0	2,791.9	3,223.0
ADMINISTRATIVE, 10% OF OPERATING LABOR	250.0	250.0	275.0	250.0	250.0	275.0
TOTAL INDIRECT COSTS	97,316.0	96,781.9	109,398.0	96,786.0	96,245.9	108,870.0
TOTAL ANNUAL REVENUE REQUIREMENT	141,567.2	137,544.5	151,487.3	126,477.3	123,753.6	137,530.5
UNIT REVENUE REQUIREMENT, mills/kWh	46.0	44.7	49.3	64.0	62.7	69.6

TABLE 5. TOTAL ANNUAL REVENUE REQUIREMENT FOR LURGI, IGT AND TEXACO COMBINED-CYCLE PLANTS

	ANNUAL COST $ x 10^3					
	6,150 HR/YR (0.7 CAPACITY)			3,950 HR/YR (0.45 CAPACITY)		
	LURGI (533 MWe)	IGT (523 MWe)	TEXACO (426 MWe)	LURGI (533 MWe)	IGT (523 MWe)	TEXACO (426 MWe)
DIRECT COSTS						
COAL ($1/MBtu)	35,649.3	26,628.8	23,743.9	22,896.7	17,103.1	15,244.4
CATALYST & CHEMICALS	549.9	140.4	45.6	353.2	90.2	29.3
UTILITIES	643.1	386.6	744.4	413.1	248.3	478.1
ASH DISPOSAL	559.0	419.4	373.9	359.0	269.4	240.1
OPERATION AND MAINTENANCE	8,417.8	6,312.6	4,697.8	6,095.8	4,705.7	3,017.3
SULFUR CREDIT ($60/TON)	(2,835.5)	(2,291.7)	(1,925.0)	(1,821.2)	(1,471.9)	(1,236.4)
AMMONIA CREDIT ($100/TON)	(1,633.4)	(109.2)	---	(1,049.1)	(70.1)	---
TOTAL DIRECT COSTS	41,350.2	31,486.9	27,680.6	27,247.5	20,874.7	17,772.8
INDIRECT COSTS						
CAPITAL CHARGES, 18% OF TOTAL CAPITAL REQUIREMENT	129,402.0	101,718.0	100,566.0	129,402.0	101,718.0	100,566.0
OVERHEADS						
PLANT, 50% OF O&M	4,208.9	3,156.3	2,348.9	3,047.9	2,352.9	1,508.7
ADMINISTRATIVE, 10% OF OPERATING LABOR	182.5	175.0	162.5	182.5	175.0	162.5
TOTAL INDIRECT COSTS	133,793.4	105,049.3	103,077.4	132,632.4	104,246.9	102,237.2
TOTAL ANNUAL REVENUE REQUIREMENTS	175,143.6	136,536.2	130,758.0	159,879.9	125,121.6	120,010.0
UNIT REVENUE REQUIREMENT, mills/kWh	53.5	42.4	49.9	76.0	60.0	71.3

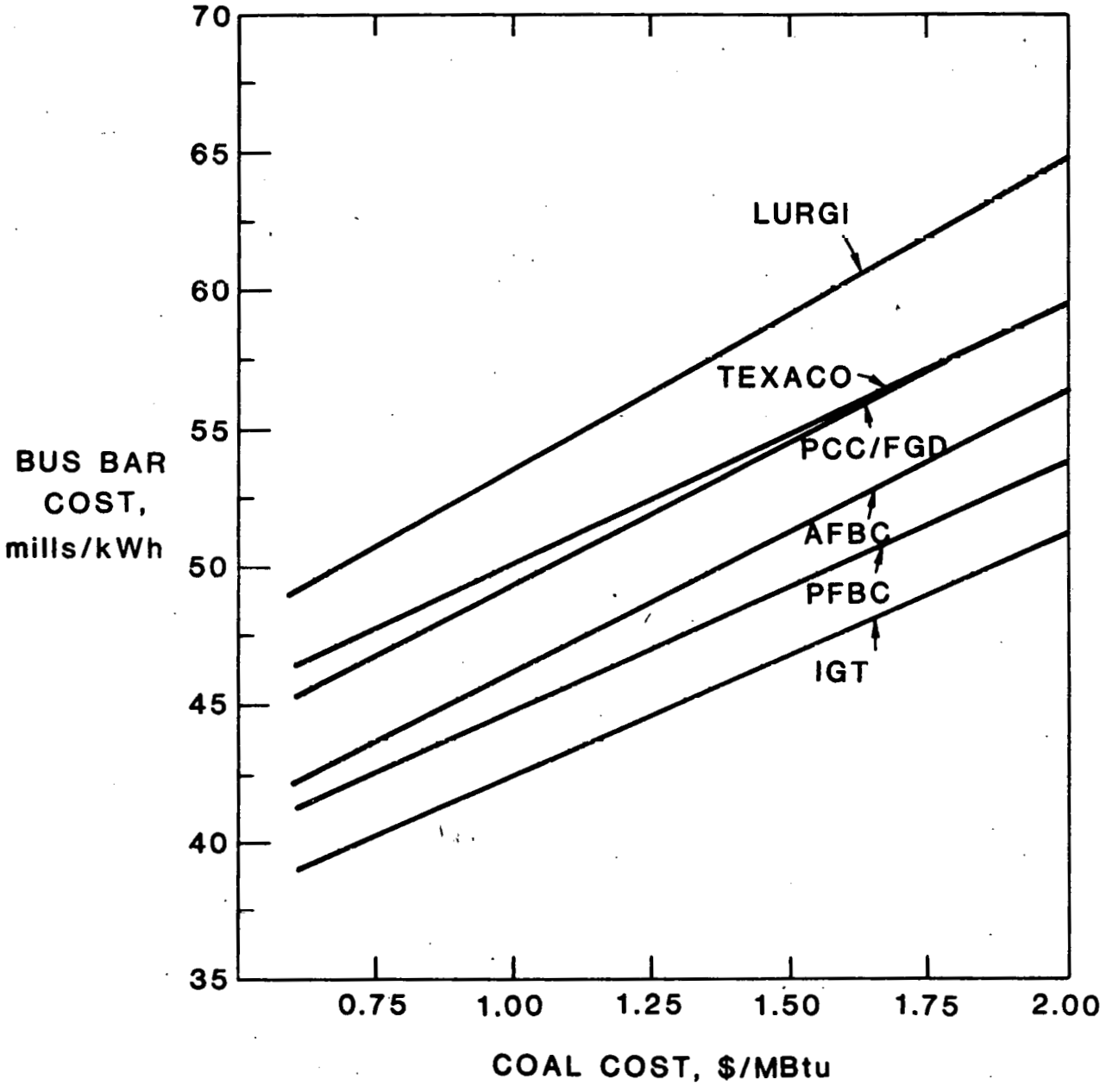


Fig. 5. Effect of Coal Price on Power Cost

TABLE 6. CHARACTERISTICS OF POWER GENERATION TECHNOLOGIES

	AFBC	PFBC	PCC/FGD	GASIF. COMB.-CYCLE SYSTEM		
				LURGI	IGT	TEXACO
MWe NET	500	500	500	533	523	426
OVERALL HEAT RATE Btu/ kWh	9,720	8,690	9,850	10,860	8,360	9,060
UNIT CAPITAL REQUIREMENT $/ kW	1,042	1,036	1,171	1,349	1,080	1,312
CAPITAL COST [a] mills/kWh	30.5	30.3	34.3	39.5	31.6	38.4
FUEL COST [b] mills/kWh	9.7	8.7	9.9	10.9	8.3	9.1
OTHER COSTS mills/kWh	5.8	5.7	5.1	3.1	2.5	2.4
TOTAL POWER COST [c] mills/kWh	46.0	44.7	49.3	53.5	42.4	49.9

[a] BASED ON 18% OF TOTAL CAPITAL REQUIREMENT.

[b] BASED ON $1.0/MBtu BASE COAL COST.

[c] FIRST YEAR COST (IN 1980 DOLLARS), 6,150 HOURS OPERATION.

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CHARACTERIZATION OF EFFLUENTS FROM AN EXPERIMENTAL ATMOSPHERIC PRESSURE FLUIDIZED BED COMBUSTOR

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INTRODUCTION

Over the past three years the Inhalation Toxicology Research Institute (ITRI) and the Morgantown Energy Technology Center (METC) have been engaged in a collaborative research effort to characterize the potential emissions from the atmospheric pressure fluidized bed combustion (AFBC) of coal. The primary purpose of the research is to determine the potential health risks to man from increased use of this technology. The research effort, involves the chemical and physical characterizations of potential effluents from an experimental 18-inch AFBC being operated at METC. Emphasis has been placed on characterizing the potential airborne particulate and hydrocarbon emissions from the AFBC. Characterization is followed by toxicological testing of the potential effluents at ITRI. The approach being used to assess the potential toxicity of the materials collected at METC is the utilization of *in vitro* and *in vivo* screening tests for toxicity and mutagenicity. The screening results are being used to select materials for longer term inhalation studies in experimental animals, including exposures of rodents over their total life span to aerosols of selected AFBC effluents to characterize their potential for producing chronic respiratory disease as well as cancers of the respiratory tract and other organs.

The purpose of this report is to summarize the currently available data from the physicochemical characterization and the toxicological testing of samples that have been obtained from the 18-inch AFBC at METC while it was burning several coal types and operating under various conditions. More detailed presentations of the data have been published previously (1-12).

It should be recognized that the AFBC at METC is a relatively small experimental unit and that such things as control technology for fine particles have not been optimized. However, the data from this unit may be used to approximate the emissions of a full scale AFBC and will supply information on needed control technology until sampling of larger units is possible.

MATERIALS AND METHODS

Figure 1 is a simplified block diagram of the METC 18-inch atmospheric fluidized bed combustor. Inside the combustor a bed of coal and limestone is supported by a conical plate perforated by 1/8-inch holes through which the fluidizing air passes. Water passing through a heat exchanger bank buried in the bed extracts heat from the bed. A screw conveyor meters pre-sized coal into a pneumatic feed tube which conveys fuel into the combustor near the

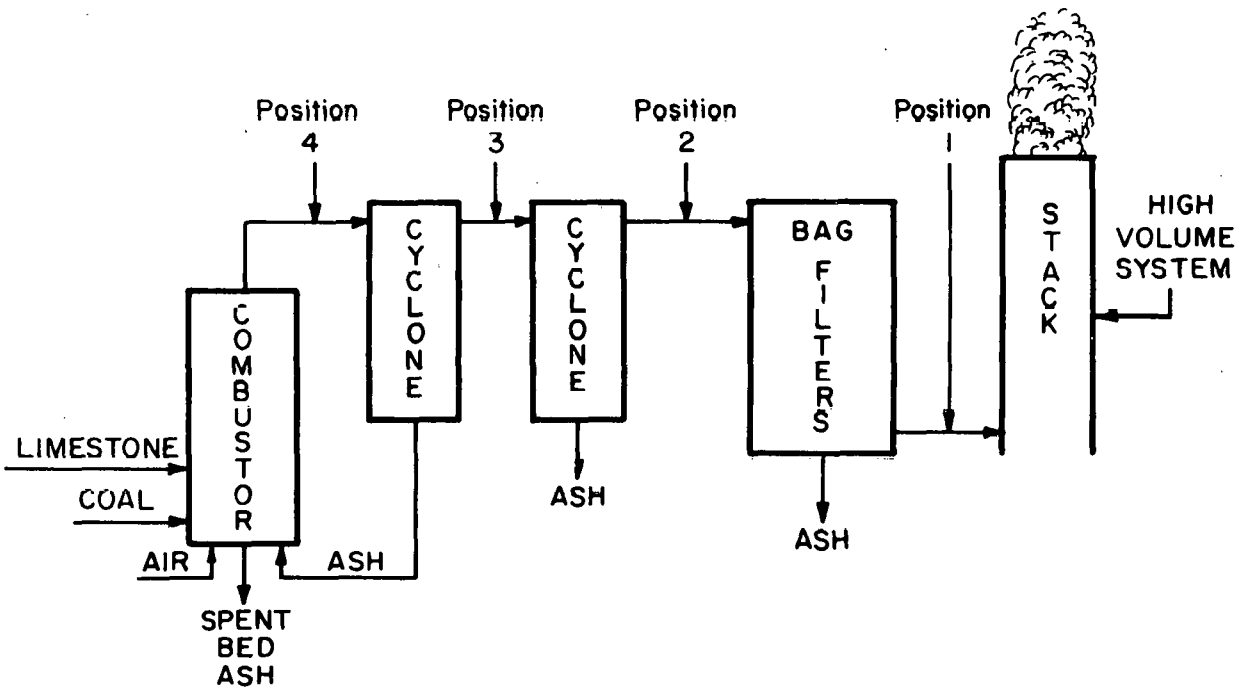


Figure 1. Simplified block diagram of METC experimental atmospheric pressure fluidized bed coal combustor. Samples were obtained at positions noted. Positions 1 and 2 involved sampling from the same port with the baghouse switched in (Position 1) or out (Position 2) of the exhaust stream. Position 1 represented the stack breech with the effluent going through the baghouse. Position 2 represented samples taken when the baghouse was bypassed (baghouse inlet). Position 3 was between the cyclones. Position 4 represented sampling at the top of the combustor freeboard (inlet to the primary cyclone).

bottom of the bed. Limestone or other sorbent may be fed into the combustor by a screw conveyor above the fluidized bed. Combustion products pass through two cyclone separators. Partially cleaned combustion gases pass through a baghouse filter system for final particle removal. Solids from the primary cyclone contain enough unburned fuel to justify reinjection into the combustor. A system of valves allows the baghouse to be placed in the cleanup system or to be bypassed.

The AFBC was sampled at four positions (1-4, in Fig. 1). Samples obtained at Position 1 (stack breech) were of greatest interest as an approximation of atmospheric releases. Samples from Positions 2, 3 and 4 were representative

of source material for potential fugitive emissions to the work place environment. Samples from all four positions provide an engineering assessment of the combustion process and the effectiveness of cleanup devices. Major emphasis has been placed on aerodynamic size-selective sampling because of the critical importance of aerodynamic size in predicting lung deposition of inhaled particles. Similarly, chemical and biological characterization of aerodynamically sized samples is a major goal. A detailed discussion of the sampling system used in these studies has been published (1,2).

Sampling probes in the FBC exhaust system withdrew 15-25 liters per minute (LPM) of AFBC exhaust aerosol which was diluted with 100 LPM of dry ambient air. Immediately after the diluter, a portion of the sample was passed through the Tenax (13) adsorbent to collect vapor phase hydrocarbon samples. The remaining sample was conveyed to a sampling chamber. A battery of aerosol samplers attached to the chamber collected particles (1). These instruments could be changed at will during sampling to supply the mix of samples required for characterization and biological testing. Excess sample is passed through a cleanup system and exhausted.

It is emphasized that the sampling system was designed to have an upper size limit of about 10 μm aerodynamic diameter. The sampling system is thus not directly comparable to the Environmental Protection Agency's compliance type sampling devices.

Samples from the above sampling system as well as coal, bed material, cyclone ash, bag filter ash, and bottom ash have been collected when the AFBC was operating under various conditions with several coal types and bed materials.

Inorganic analysis of the samples from the aerosol sampling system used for the AFBC was done by spark source mass spectrometry (SSMS)* using rhodium and indium as internal standards. The methods for organic analysis of the particle-associated and vapor phase hydrocarbons have been presented elsewhere (5,6). Particles were ultrasonically extracted with methylene chloride while Tenax material was Soxhlet extracted with pentane. Gas chromatography and gas chromatography/mass spectrometry were used to characterize the samples.

Mutagenicity testing of the particle or Tenax (a polymeric absorbant used to trap vapor phase hydrocarbons) extracts was done with strains TA1535, TA100, TA1537, TA1538 and TA98 of *Salmonella typhimurium*** Homogenates for enzyme activation were prepared from the livers of rats treated with Aroclor 1254 (500 mg/kg IP) (14). For mutagenicity testing, samples of particles were extracted ultrasonically with methylene chloride, but Tenax samples were Soxhlet extracted with pentane. The extracts were evaporated to dryness at room temperature and reconstituted in DMSO for the Ames test (14). The cytotoxicity of fly ash from the FBC was evaluated in alveolar macrophages by a modification of the methods of Waters *et al.* (15).

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*All SSMS analyses were done by CDM/Accu Labs, Wheatridge, CO.
**Obtained from B. N. Ames.

RESULTS AND DISCUSSION

Mass concentrations and size parameters of respirable flue gas aerosols produced by the AFBC have been determined for the fuels shown in Table 1 (2). The respirable aerosol released into the stack breech ranged from 2.2 to 2.8 μm mass median aerodynamic diameter (MMAD) for all fuels and AFBC operating conditions studied. This is well below the 10 μm upper size limit of our sampling system and is probably not affected by the sampling system size cut-off. The "< 10 μm fraction" of the flue aerosol entering the exhaust cleanup system from the AFBC ranged from 3.2 to 6.1 μm MMAD and appeared to vary with fuel type and AFBC operation. Insufficient data are currently available to explain the relationship. The 10 μm sampling system cut-off did not appear to influence the observed MMAD at the AFBC cleanup system inlet. For all fuels considered, the observed aerosol size at the sampling point between cyclones was lower than that observed at the cleanup system inlet, evidence that the first cyclone captures large particles elutriated from the bed. The second cyclone and baghouse filter appear to have little effect on observed size distributions, suggesting that the collection efficiency of both devices for particles below 10 μm is not highly size dependent.

Respirable aerosol concentration at the stack breech remained relatively constant as fuel type and AFBC operating conditions varied, ranging from 7×10^{-3} to 7×10^{-2} g/m^3. One exception to this observation was noted. During the bulk Texas lignite combustion studies, an abnormally high stack inlet aerosol mass loading concentration was observed. Upon subsequent disassembly, the baghouse filters were found to have holes.

Cleanup system device penetration by respirable aerosol particles is tabulated in Table 2 as a measure of cleanup efficiency. Penetration is defined as the ratio of device outlet mass loading divided by device inlet mass loading. Fine particle penetration of the exhaust system cleanup devices appeared to be a function of fuel type and combustor operation. The baghouse filter was the most efficient device for fine particle removal, although this efficiency dropped as the filter wore and developed holes.

Morphology of AFBC flue gas aerosol particles was examined by scanning electron microscopy (SEM) and transmission electron microscopy (TEM) of particles collected by electrostatic precipitation and with the Lovelace Aerosol Particle Separator. Although particle size varied, effects of operating the AFBC below the ash fusion temperature were readily seen. For all fuels examined, particles escaping the AFBC were irregularly shaped. Very few fused, spherical particles were seen. This is in contrast to fly ash from pulverized coal combustion which consists mainly of fused, spherical particles.

While emissions from coal fired power plants may have many environmental effects, the size of emitted particles is important in most of them. A primary concern in human health risk estimates is the total mass of emitted particles in the respirable size range (< 10 μm aerodynamic diamter). Assuming power plant efficiencies and fly ash density one can compare data of Ondov *et al.* (16), Lyon (17) and Mesich (18) on conventional pulverized coal combustion (PCC) with ITRI data obtained from the METC AFBC. Table 3 summarizes these data which are expressed as respirable mass loading determined from cumulative size distribution estimates.

Table 1. Summary of Aerosol Size and Mass Concentration at Various Locations in the METC FBC Exhaust Streams for Different Fuels and Operating Conditions

COAL TYPE, ADDITIVE	OPERATING CONDITIONS	PARAMETER MEASURED	Sampling Position 1 STACK BREECH	2 BAGHOUSE INLET	3 BETWEEN CYCLONES	4 TOP OF COMBUSTOR
Montana Rosebud I limestone[d]	790-840°C[a]	MMAD[b]	2.3 ± 0.3	2.3 ± 0.2	2.2 ± 0.1	3.9 ± 0.8
	0.9-1.4[c]	g/m^3[e]	7.0×10^{-2}	0.38	1.2	4.7
Montana Rosebud II limestone	790-900°C	MMAD	2.4 ± 0.2	3.0 ± 0.4	2.7 ± 0.3	6.1 ± 0.9
	0.9-1.0	g/m^3	3.0×10^{-2}	0.56	0.59	3.4
Texas Lignite I (bulk) limestone	810-940	MMAD	2.8 x 0.3	3.2 ± 0.4	3.0 ± 0.3	4.8 ± 2.3
	1.3	g/m^3[f]	1.8	3.1	3.2	- -
Texas Lignite II (washed) glass sand	860-890	MMAD	- -	2.2 ± 0.1	- -	4.5 ± 0.8
	1.2	g/m^3	7.6×10^{-3}	0.24	- -	3.0
Texas Lignite III (refuse) limestone	860-890	MMAD	2.2 ± 0.6	2.7 ± 0.4	- -	3.3 ± 0.9
	1.2	g/m^3	3.3×10^{-2}	1.3	- -	2.6
Texas Lignite IV (refuse) glass sand	860-890	MMAD	2.2 ± 0.4	2.7 ± 0.4	- -	- -
	1.2	g/m^3	2.8×10^{-2}	1.3	- -	- -
Texas Lignite V (refuse) limestone	770-790	MMAD	2.3 ± 0.9	3.2 ± 0.3	- -	5.6 ± 1.6
	1.2	g/m^3	4.3×10^{-2}	0.85	- -	4.9
Texas Lignite VI (refuse) glass sand	790-800	MMAD	2.2 ± 0.1	2.6 ± 0.2	- -	3.2 ± 1.1
	1.2	g/m^3	4.9×10^{-2}	0.88	- -	2.6
Western Kentucky limestone	839-900	MMAD	2.5 ± 0.2	3.0 ± 0.4	2.7 ± 0.3	5.4 ± 1.1
	0.91	g/m^3	2.0×10^{-2}	0.46	0.42	3.4

[a]Mid-bed temperature degrees Celsius. [b]Mass median aerogynamic diameter in μm (geometric standard deviation ranged between 1.6 and 2.1 for all cascade impactor samples). [c]Fluidizing velocity (m/sec). [d]Additive to bed material (Greer limestone or glass sand). [e]Respirable mass loading (g/m^3). [f]High mass loadings and verified leak in baghouse.

Table 2. Respirable (< 10 μm) Aerosol Penetration of Exhaust System Cleanup Devices on an Experimental Atmospheric Pressure FBC

Coal Type	Percent Penetration		
	First Cyclone	Second Cyclone	Baghouse
Montana Rosebud I	26	32	18
Montana Rosebud II	17	95	5
Texas Lignite I	--	97	58[a]
Texas Lignite II	--	--	3
Texas Lignite III-IV	--	--	2-6
Western Kentucky	24	56	4

[a]Verified baghouse filter leak.

Table 3. Comparison of Conventional Pulverized Coal Power Plants and the 18-inch METC FBC

Plant Type and Final Flue Gas Cleanup	Fuel Type	Respirable Mass Loading lb/10^6 Btu
180 MWe Venturi Scrubber	Western Subbituminous	0.16
280 MWe Cold Side ESP	Western Subbituminous	0.12
280 MWe Hot Side ESP	Eastern Subbituminous	0.011
FBC Baghouse	Montana Rosebud	0.02
FBC Baghouse	Lignite (washed)	0.009
FBC Baghouse	Western Kentucky	0.004

Examination of these data demonstrates that the METC AFBC, equipped with a baghouse filter does not emit more respirable particles than the conventional (PCC) power plants. Note that the AFBC mass loading was a function of coal type as is probably true for PCC. Effects of optimizing cleanup devices on an AFBC such as is done for large PCC plants is unknown, although one could assume some decrease in effluent particulate loading.

NO_x and SO_x emissions from the METC 18-inch AFBC have been characterized extensively for a number of fuels. As has been reported by others (19), sulfur retention in the METC AFBC is a function of bed temperature (Fig. 2). Optimum predicted sulfur retention temperatures are in the range of 1550°F and the experimental data show 90% or better sulfur retention over a range of 1490-1620°F. Outside this region, sulfur retention drops sharply below theoretical predictions.

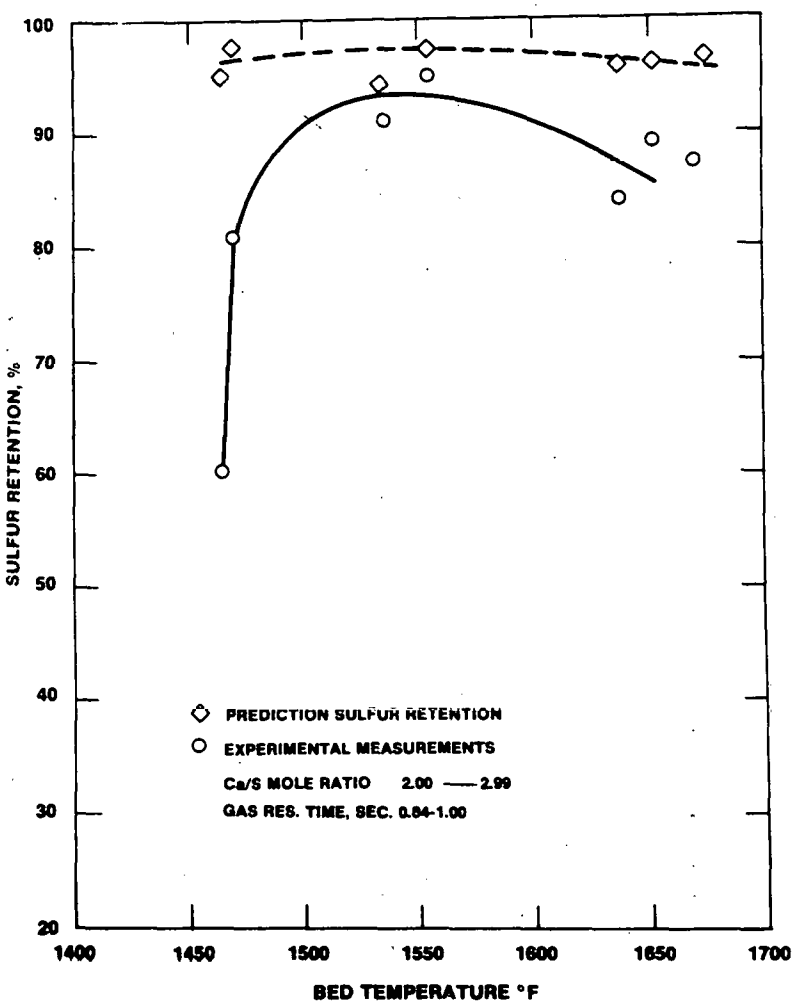


Figure 2. Comparison of predicted sulfur retention with METC experimental Fluidized Bed results as a function of bed temperature [METC data (19)].

NO_x emission from the METC unit were observed to be NO. The release of NO by the AFBC appears to be more complicated than is the case for PCC, but is dependent on bed temperature, excess oxygen and possibly heterogeneous reactions with unburned carbon in the combustor freeboard. Table 4 illustrates typical data from combustion studies at comparable combustor operating conditions. The effect of O_2 content in the flue gas is shown in Figure 3.

Table 4. Effect of Bed Temperature on Nitric Oxide Emissions

Oxygen in Flue Gas (% Vol.)	Gas Residence Time (Sec.)	Bed Temperature (°F)	NO Emission (ppm)
6.10	1.00	1524	570
6.10	1.03	1470	490
6.80	0.87	1533	630
6.80	0.91	1482	360
3.70	0.85	1653	400
3.80	0.92	1507	210

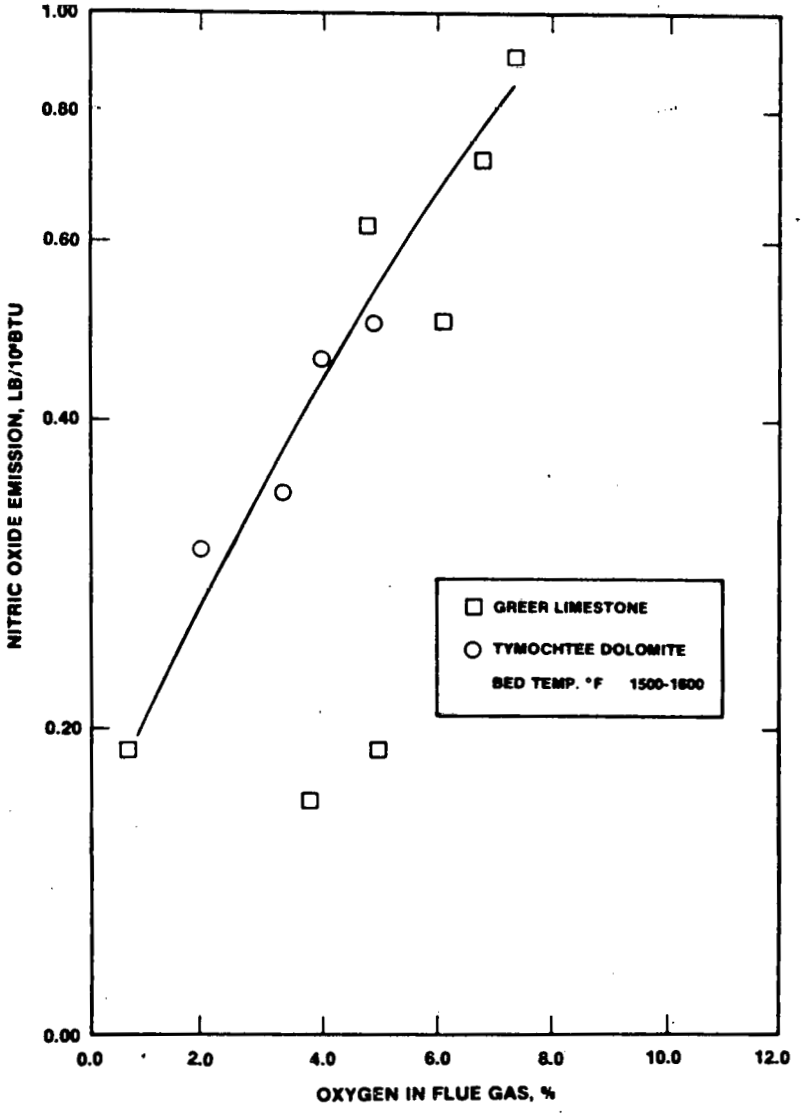


Figure 3. Effect of oxygen in flue gas on NO emissions for two SO_2 sorbents [METC data (19)].

Filter, impactor and hopper ash samples were analyzed for elemental composition using spark source mass spectrometry. Particle trace element concentration varied with position sampled in the effluent stream, fuel and operating parameters. A limited number of elements had concentration variations with particle size. A detailed listing of the inorganic composition of the AFBC effluents has been published (9,12).

The elemental composition of the AFBC ash was a function of sampling location, as indicated by differences in enrichment factors and penetrations (12). Enrichment factors account for enrichment of elements in combustor feed material due to loss of carbon during combustion. Penetrations show the extent of removal of the particulate form of an element by a cleanup device. The reasons for this are being investigated. No elements showed significant differences in penetration through the primary cyclone compared to the inorganic marker Zr. Two elements (Li and Se) showed penetration differences through the secondary cyclone and two elements (I and Li) showed differences through the baghouse. Baghouse ash was significantly depleted in Te and Tl and enriched in Ge. However, for stack breech there were no significant differences between enrichment factors for Te, Tl and Ge in comparison with Zr. Six other elements (Bi, B, Co, F, Li and Sc) were enriched in stack breech fly ash. Eight elements (Cl, Dy, I, Li, Te, Tl, W and Yb) were significantly depleted in the spent bed material, which is primarily ash and limestone (with chemisorbed SO_2).

Differences in elemental concentration were observed for samples obtained under different combustor operating conditions (12). Concentrations of a majority of the elements studied were significantly affected by operating parameters. The elements affected were Be, Bi, B, Br, Ce, Cl, Cr, Co, Er, Eu, Hf, I, La, Pb, Li, Lu, Nd, Ni, P, Pr, Sm, Sc, Se, Na, Sr, Tb, Tl, Tm, W, U, Yb, Y and Zn. Although one of the major changes in operating parameters was combustion temperature, the concentrations of several volatile elements (Sb, As, Cd, and Mo) were not significantly changed. The concentrations of minor and trace elements determined in METC AFBC ash were similar to reported values for other AFBCs and pressurized fluid beds (12). More P and less Cu was found in METC AFBC ash than has been reported for other FBCs.

Emission rates of 9 potentially toxic trace elements as a function of coal type burned in the METC AFBC are summarized in Table 5. These data indicate that the sum of the emitted mass (μg/g of fly ash) range from 200 to 3000 ppm depending on fuel type with uncleaned lignite combustion resulting in about 10 times the emission rate of cleaned lignite or Montana Rosebud. Similarly, data from Ondov *et al.* (16) for PCC power plants are compared for the sum of 8 potentially toxic trace elements with ITRI results on the METC AFBC (Table 6). These data indicate that the sum of Sb, As, Cd, Cr, Cu, Pb, Ni and Se emission is lower for AFBC than for three conventional PCC power plants studied. All trace element emission data to date indicate that AFBC trace element hazards are no more significant than from conventional PCC power plants.

The environmental impact of introducing AFBCs for electrical generation depends partly on whether AFBC and PCC ash differ in elemental composition. The data indicates that ash from the two combustion technologies is similar in elemental concentration. The observed concentration ranges overlap in most cases, usually with the extremes of one range extending beyond that of the other. This was true despite major differences in PCC plant design, fuel, operating conditions, cleanup devices and sampling methodology. The similarity

Table 5. Particulate Trace Element Emissions from the METC Experimental AFBC

Fuel Type	Trace Elements[a] (μg/g)
Lignite Refuse	3×10^3
Raw Lignite	2×10^3
Clean Lignite	5×10^2
Montana Rosebud	2×10^2

[a]Sum of: Sb, As, Be, Cu, Pb, Ni, Se, Il, Zn

Table 6. Particulate Trace Element Emission Comparisons of AFBC and PCC

Plant Type and Final Cleanup System	Emission Rate[a] of 8 Toxic Trace Elements (gm/10^6 Btu)
18" AFBC Baghouse	0.01
350 MWe Pulverized Coal-Venturi Scrubber	0.2
350 MWe Pulverized Coal-Hot Side ESP	0.1
250 MWe Pulverized Coal-Cyclone	0.6

[a]Sum of: Sb, As, Cd, Cr, Cu, Pb, Ni, Se

in ash composition indicates that the two combustion processes will not have radically different environmental impacts.

Several investigators have shown that particles produced by PCC have variations in elemental composition as a function of particle size. We found fewer elements concentrated in small particles with Montana Rosebud combustion effluents than have been reported for PCC. With Montana Rosebud coal (9), only three elements (Be, Ga and Hf) were found enriched in small particles from the AFBC exhaust. Iodine and terbium were found to decrease in concentration with decreasing particle size. The enrichment of I in large particles collected from the stack breech can be attributed to entrainment of limestone particles in the exhaust stream and penetration of the cleanup devices. Our classification of Hf as an element exhibiting small particle enrichment was not expected on the basis of its chemical and physical properties.

The extent of small particle enrichment was also greater for PCC ash compared to AFBC ash (12). The ratio of elemental concentrations in small particles versus large particles for PCC was greater than for AFBC except for Pb.

The largest difference in concentration ratios was found for Cr. Less small particle enrichment was also observed from similar calculations done with data published by Murthy *et al.* (20) on pressurized fluidized bed combustors (PFBC). The reduced small particle enrichment observed for both types of FBC's in comparison with PCC is probably due to the lower combustion temperature for FBC's (800 to 1000°C) compared to that of conventional PCC (1300 to 1500°C). The lower temperatures result in less vaporization, decreasing the extent of selective condensation or adsorption onto small particles.

Vapor and particulate phase samples were analyzed for organic compounds (5,6,12). Following extraction, gas chromatography and gas chromatography mass spectrometry were used for quantitation and tentative compound identification. Vapor phase organic concentrations in stack effluent (after the baghouse) ranged from 0.084-20 mg/m^3. The highest vapor phase organic concentration measurements were obtained with Montana Rosebud subbituminous coal combustion where concentrations as high as 20 mg/m^3 were observed. Although there were variations in vapor phase organic concentrations at different sampling positions, no uniform trend was apparent. For all fuels studied the concentration of vapor phase organics was higher than the extractable particle associated organic concentration. For Texas lignite, 95-98% of the organics present in the exhaust stream at all four sampling locations were in the vapor phase. Similar results were obtained for other coals.

Particle associated hydrocarbon concentrations varied with sampling position. High volume filter samples taken after the bag filter had concentrations of 650-880 µg/g of ash. Samples from ash collected by the cleanup system had considerably lower concentrations, 4.4-50 µg/g. The hydrocarbon concentration in ash increased with distance from combustor as the temperature decreased, suggesting particle adsorption of vapor phase organics with cooling. Samples taken from the stack (after the bag filter) following cooling and dilution had much higher hydrocarbon levels than those taken in front of the bag filter.

There have been relatively few reported measurements of effluent hydrocarbons from coal combustion technologies. The concentrations reported here for vapor and particle phase hydrocarbons are similar to those reported for other atmospheric and pressurized FBC's (20-22) (Table 7). For both vapor and particle phase samples, Argonne National Laboratory (ANL) reported the highest hydrocarbon levels.

Table 7. Reported Concentrations of Organics Associated with Particles and in the Vapor Phase from Various Fluidized Bed Coal Combustors

	ANL PFBC	Exxon PFBC	BCL AFBC	METC AFBC
Vapor Phase (mg/m^3)	2-30	2.2	11.5	0.084-20
Particle Associated (mg/g)	0.8-4	-	0.66-1.1	0.66-0.88

Few hydrocarbon level data are available for PCC. The results of two early studies are compared to some of the results from this study (Table 8). The AFBC appears to have higher vapor phase organic levels. The total of 11 compounds were measured at a PCC plant in 1965 (23). The methodology used in the 1965 study is considerably different from current procedures and may have resulted in smaller polycyclic organic matter (POM) concentration measurements than would be obtained with current techniques. It has been hypothesized that as the effluent stream cools, the vapor-phase hydrocarbons condense onto particles or are adsorbed by particles. Our AFBC measurements for vapor-phase POM and particle-associated hydrocarbons to date, show that even 2 minutes after cooling and diluting, most of the POM's remain in the vapor phase. Although condensation or adsorption may occur in power plant plumes, these effects were not observable in the 2 minute time frame after cooling and diluting.

Table 8. Estimated Aromatic Hydrocarbon Emissions from Conventional and AFBC Combustors

Plant Type	Aromatic Hydrocarbons mg/10^6 Btu
Estimated conventional coal-fired power plant	0.2 - 1
Total of 11 compounds at a conventional PCC plant	1.2
Measurements at METC AFBC	
Montana Rosebud Coal > C_6 Vapor Phase	38 - 12,000
Montana Rosebud extractable from particles	6.1
Texas lignite > C_6 vapor phase	13 - 340
Texas lignite extractable from particles	22 - 24
Texas lignite refuse > C_6 vapor phase	93 - 16,000
Clean Texas lignite refuse > C_6 vapor phase	130 - 970
Western Kentucky > C_6 vapor phase	43 - 3,700

The *Salmonella* mutagenicity (Ames) bioassay has provided a rapid method for detecting potential mutagens at different locations in the process stream and in the cleanup system of the AFBC as well as evaluating changes in mutagenicity associated with different fuel types and operating conditions (7). Samples evaluated to date include: (A) vapor phase hydrocarbons collected on Tenax adsorbent at three different positions in the effluent stream; (B) methylene chloride extracts of material trapped by the primary and secondary cyclones; and (C) methylene chloride or DMSO extracts of fly ash collected in bag filters, on high volume filters placed at the stack breech, and extracts of size separated fly ash collected by cascade impactors placed at the stack breech. Samples

collected while the AFBC was burning Montana Rosebud subbituminous, Western Kentucky bituminous, and Texas lignite coals have been evaluated.

To date, none of the vapor phase hydrocarbons adsorbed from the process stream on Tenax traps have demonstrated any mutagenicity (7). As was noted in the section on organic analysis of the effluent, the majority (over 90% in most cases) of the hydrocarbons in the gaseous effluents were in the vapor phase and no mutagenicity has been detected in these samples.

No mutagenicity was detected in any of the primary cyclone samples and only 3 of the secondary cyclone samples were positive (corresponding to two sampling periods for which mutagenicity of the bag filter ash was the highest). Compounds responsible for mutagenicity may have been adsorbed or condensed more efficiently by the lower temperatures and retained by the smaller sized particles collected in the bag filter than by the larger particles collected at higher temperatures in the cyclones.

When Montana Rosebud baghouse ash samples collected during seven different sampling periods were tested, mutagenicity of bag filter ash extracts varied over 200-fold (7). Two of the seven samples were not mutagenic when up to 2 g of fly ash were extracted and tested. There was some correlation between combustor bed temperature and mutagenicity of the fly ash extracts; the three most mutagenic samples were burned at higher temperatures than most of the negative samples.

Chrisp *et al.* (24) have reported on the mutagenicity of extracts of fly ash collected from a conventional PCC. We also participated in an exchange of fly ash samples and fly ash extracts with the University of California at Davis (Chrisp) and Argonne National Laboratories (Kubitschek) to compare the interlaboratory variation in the results of mutagenicity testing (25). Differences in sample collection and handling techniques and combustor size, make direct comparisons between the AFBC ash collected by us and the PCC ash collected by Chrisp *et al.* difficult. However, none of the AFBC samples tested to date have had mutagenic activity (revertants/mg of ash extracted) as high as that reported by Chrisp *et al.* (24,25). The mutagenic activity of the AFBC ash tested by us has been about one-tenth that of the PCC ash tested. Even though direct comparisons are difficult at this time due to differences in combustor size and sampling techniques, the AFBC effluents (ash and vapor phase hydrocarbons) certainly appear to have no greater and probably less mutagenic activity than similar effluents from PCC plants.

Numerous AFBC and comparable PCC fly ash samples have been evaluated for cytotoxicity against a quartz standard. None of the samples tested to date from either AFBC or PCC have shown significant cytotoxicity in this system.

The expected mode of human exposure to FBC effluents is repeated or continuous inhalation at low doses for long periods of time ranging up to life span. There are no reports of studies of the inhalation of FBC fly ash, but Alarie and coworkers (26-28) have studied the response of Cynomolgus monkeys and guinea pigs to the inhalation of ash from conventional coal combustion. Their research indicated that 1 to 1-1/2 year exposures to 0.5 mg/m^3 of conventional fly ash did not result in biological effects other than accumulation of ash in lung cells and lymph nodes, and some nodules of aggregated macrophages.

These studies, however, did not employ functional measurements such as forced expiratory flow-volume and volume-time indices which have been recommended for use in detecting lung disease from environmental pollutants and demonstrated to be useful in human epidemiologic studies. Thus, there is a critical need for chronic inhalation studies on both FBC and PCC fly ash. We plan to initiate chronic inhalation studies of this type in the near future.

SUMMARY AND CONCLUSION

Based on our studies of the potential emissions of AFBC and comparing them to data available in the literature from PCC, the following conclusions have been made.

- AFBC particle emissions are comparable or lower than from conventional power plants.
- AFBC trace element emissions are comparable or lower than conventional power plant emissions.
- AFBC polycyclic organic emissions appear to be higher than estimated for conventional power plants and are primarily vapor phase as measured.
- Mutagenic activity has not been detected in AFBC vapor phase polycyclic organic AFBC samples tested to date.
- Mutagenic activity has been detected in some fly ash samples from the AFBC bag filter and stack.
- The mutagenic activity per mass of fly ash extracted appears to be less in the METC fluidized bed combustor ash than that reported for one conventional power plant.
- More comparisons are needed between FBC and conventional combustion emissions especially for organic emissions.
- Chronic inhalation studies on both FBC and conventional combustion emissions are needed.

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PRELIMINARY OPERATION AND ENVIRONMENTAL CHARACTERIZATION OF THE GEORGETOWN UNIVERSITY FLUIDIZED BED COMBUSTOR

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ABSTRACT

Georgetown University and Fluidized Combustion Company have completed the construction of an atmospheric-pressure fluidized bed combustion (AFBC) system which is burning high sulfur coal in an environmentally acceptable manner. The Georgetown AFBC has a steam production capacity of 100,000 lb/hr and will burn about 5 tons per hr of bituminous coal when both beds of the boiler are in full operation. It is expected that sufficient data will be obtained from the Georgetown AFBC so that industry can move directly to the design and construction of commercially warranted industrial-size fluidized bed boiler units.

The fluidized bed system has been operated for well over 1000 hours. Due to a low steam demand by the University campus, much of the operation has been restricted such that only one bed has been ignited and producing steam. The emissions monitoring system has been functioning both prior to and during bed operation. It is encouraging that some reasonable correlations have been measured between the sulfur content of the coal being burned, the amount of limestone injected into the bed and the effluent SO_2 and O_2 content of the stack emissions.

The Georgetown AFBC has been partially funded by the Department of Energy with contract EX 76-C-01-2461, and in accordance with the Program Plan for Emissions Monitoring for the Georgetown AFBC the following emissions from the stack have been measured: SO_2, O_2, NO/NO_x, CO, CO_2, opacity, particulates and hydrocarbons including polycyclic aromatic hydrocarbons. The particulate analysis has included POMs, TSP and elemental analysis. Studies of the aromatic hydrocarbons includes GC data from samples at the exit to the stack, near the isokinetic point in the stack and from fly ash and coal samples. Elemental analysis of samples from the stack effluents, passing through a 6-stage impactor, from coal samples and from fly ash samples has been accomplished.

The emissions sampling and analysis systems include: continuous chemiluminescence NO/NO_x, NDIR CO and CO_2, paramagnetic O_2, pulsed UV fluorescence SO_2 and double-pass optical transmissometer opacity monitors; as well as off-line flame ionization and GC hydrocarbon monitors and proton induced X-ray, mass spectrometer, and optical emissions spectrometer elemental analysis apparatus. Clearly, in all cases standard samples, traceable to NBS standards, are used to calibrate each of the data acquisition systems.

We intend this paper to be a status report of the preliminary operation and environmental characterization of the Georgetown AFBC with particular emphasis on data obtained with one of the two beds in operation for over 1000 hours. In addition, the specific problems addressed in the attempts to maximize the on-time for the emissions monitoring apparatus will be discussed.

FACILITY DESCRIPTION

The Georgetown AFBC has been designed and engineered to produce 100,000 lb/hr of saturated steam at 625 psig with the possibility of cogeneration of electrical energy by installation of a backpressure steam turbine and electrical generator in the future[1]. Presently, we supply 250 psig steam to an

existing header through a pressure reducing station and satisfy the changing load conditions of the University complex, including the Hospital and the Medical Center.

Fluidized Bed Combustor

Many of the design features of the fluidized dual-bed combustor are shown in Figs. 1 and 2. Horizontal dimensions of the bed are illustrated in Fig. 2. Vertically the expanded bed depth will be about 4'6" while the freeboard is 8'. Coal is distributed across the top of the beds by conventional spreader stoker feeders which are located two feet above the beds. Limestone is simply dumped on top of the beds, with one feed point per bed.

Adequate combustion efficiency to achieve a fuel to steam/boiler efficiency of just above 80% is provided by several operating factors including the ratio of the size of the coal to the fluidizing velocity which is usually about 8 ft/sec; the recycling of flue gas which first passes through an internal cinder trap to remove suspended unburned carbon as the gas leaves the bed; and the recycling of fine particles of unburned carbon collected in a multicyclone.

The dual beds, when in full operation, are expected to have the adequate turndown and load-following capabilities already demonstrated in one bed operation.

Heat is extracted with the waterwalls, in bed tubes and convective heat transfer surfaces. It should be pointed out that slanted tubes are in the bed and natural circulation occurs so that no forced circulation is required. Also, the divider between the two beds is constructed of water wall tubes with fins.

A balanced draft system is used to provide combustion air. A pressure a little above atmospheric is produced at the top of the bed(s) with a forced air fan before the boiler and an induced draft fan after the fabric filter or bag house.

Spent bed materials are withdrawn through ports in the grid plate shown in Fig. 1; gravity being used. The bed material is cooled by water from about 1600 F to about 250 F and then is transported via a pneumatic system to a bed material crusher. When all works well, which is most of the time, the crusher exposes the core of the calcium oxide in the small spent bed material pieces and a homogeneous mass is formed.

Flue Gas Handling and Particulate Control

The flue gases, prior to leaving the boiler, are cooled by convective heat transfer processes to about 750 F and the large particles are removed by an internal cinder trap. A conventional device, the Multiclone of Joy Manufacturing, Western Precipitation Division, which contains 50 less-than 12" diameter cyclones in parallel is the primary emission control unit. The design specifications of this unit were: a gas flow of 56,000 acfm at 750 T, an inlet particle concentration of 42 gr/scf, an efficiency of 85% and an outlet concentration of 6 gr/scf. After the Multicone the flue gases enter an economizer (feed water preheater) and then are transmitted through the fabric filter (bag house) which is the final particulate removal component in the system preparing the effluents for environmentally acceptable expulsion to the community.

The fabric filter bag house is a 22-compartment unit. Initially, it had 36 100% Teflon fiber Dupont Armalon felt bags in each compartment operating

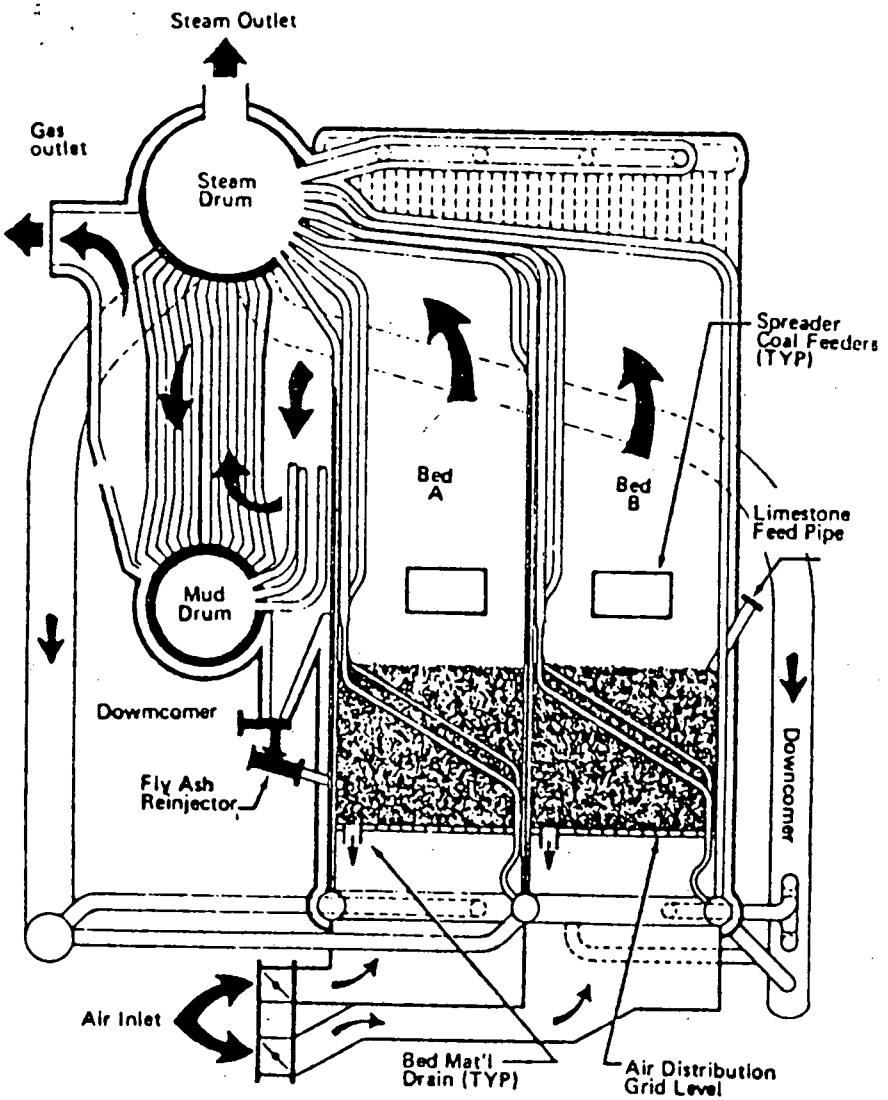


Fig. 1. Side view of Georgetown AFBC

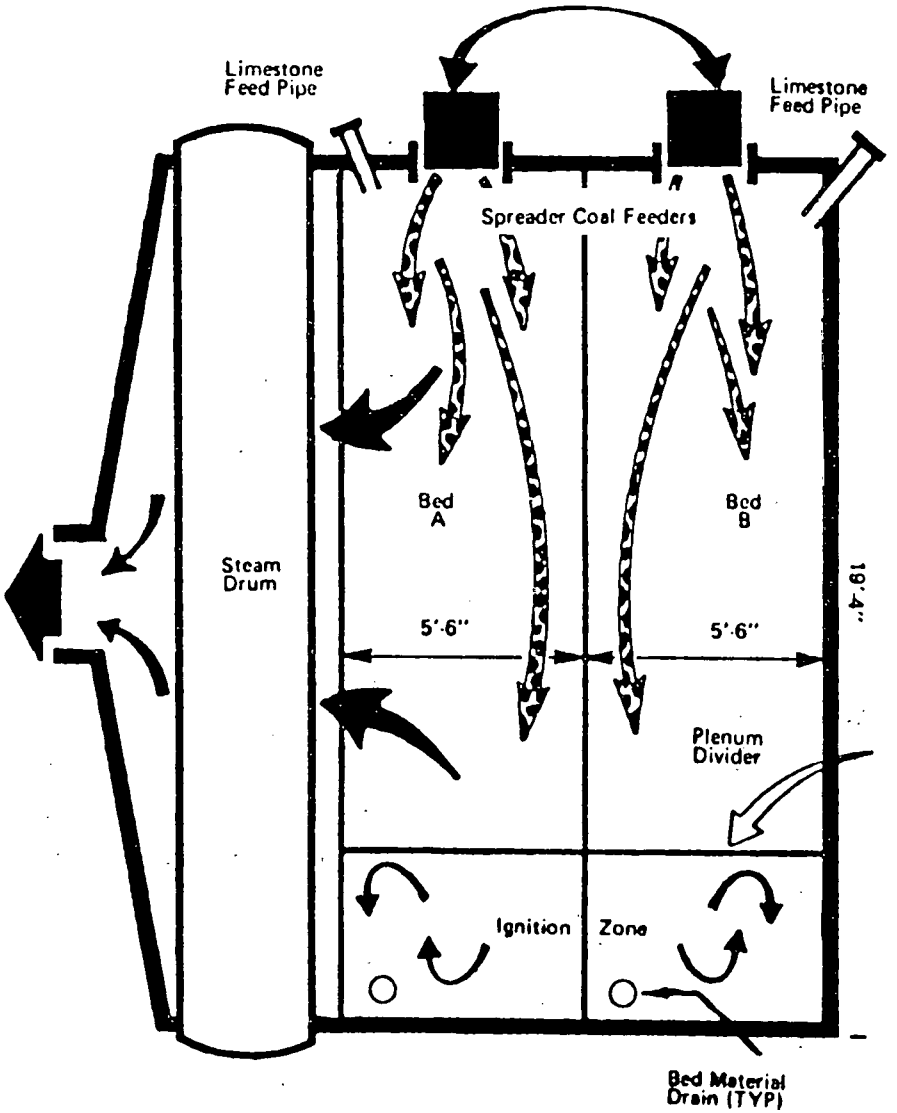


Fig. 2. Top view of Georgetown AFBC

at an air to cloth ratio of about 5:1. The type of bags has been changed to be Nomex fiberglass in 19 compartments, Nomex fiberglass treated with an anticorrosive material in one compartment, regular Nomex in another compartment and the Dupont Armalon felt bags in the remaining compartment. The mixture should allow subsequent selection of the optimum bag material or set of materials. The cost of the initial bags was quite high compared to conventional glass fabric bags, but their higher efficiency was expected to be needed. Although the first arrangement was not completely satisfactory, the new arrangement seems to provide the necessary environmental-control function. Cleaning of the bags is initiated when the pressure drop reaches a predetermined value (6" W.C.); the cleaning is by the novel reverse air method which is called the shock-drag technique by the supplier Enviro-Systems. At this point in time it appears as though the design criteria of 40,000-45,000 acfm gas flow at 400 F and the inlet concentration to outlet concentration ratio of 300 is being satisfied. Particulates collected by the fabric filter in the bag house are transported to a silo; separate silos are provided for spent bed materials and for bag house particulates.

Coal and Limestone Feed

Dry coal is supplied by 20-ton capacity trucks to a hopper and is then conveyed and elevated from the hopper to the top of one of three storage bunkers each having a capacity of approximately 350 tons. To ensure minimal conveyer down time initially, we have been using double screened as-delivered coal with a size of 1 to 1 ¼ inch by ¼ inch. As the plant-operation experience increases, we will move to coal in the size range of 3/8 inch to 2 inches with inplant crushing and screening to reduce the feed to 1 inch by ¼ inch. Coal is removed from the storage bunker to the boiler hoppers shown in Fig. 3 by a pneumatic conveyer. It passes through a weigh scale to the stoker spreader device and is fed to the top of the bed.

Limestone is received as needed for use, 1200-1400 micron size, and is pneumatically unloaded and conveyed to the storage bunker and transport system shown in Fig. 3. Limestone is withdrawn from the bins by a screw feeder, which has caused some operational problems due to an inability to fine tune the amount of limestone reaching the bed in short time spans, and passed through a weigh scale prior to falling into the bed. Clearly, the flow rate of limestone must be variable to control the SO_2 emissions.

Typical coal and limestone characteristics are given in Table I.

TABLE I. Coal and Limestone Characteristics

COAL		LIMESTONE	
Size	1 in. by ¼ in.	Size	1000 μ by 3000 μ
Typical Analysis - Percent by Weight		Typical Analysis - Percent by Weight	
Sulfur	3.3	Fe_2O_3	0.1
Hydrogen	5.0	$CaCO_3$	94.1
Carbon	70.0	$MgCO_3$	1.5
Oxygen	7.3	Al_3O_3	0.2
Nitrogen	1.2	SiO_2	1.2
Ash	8.0	Moisture	3.0
Heating Value	12,750 BTU/hr		

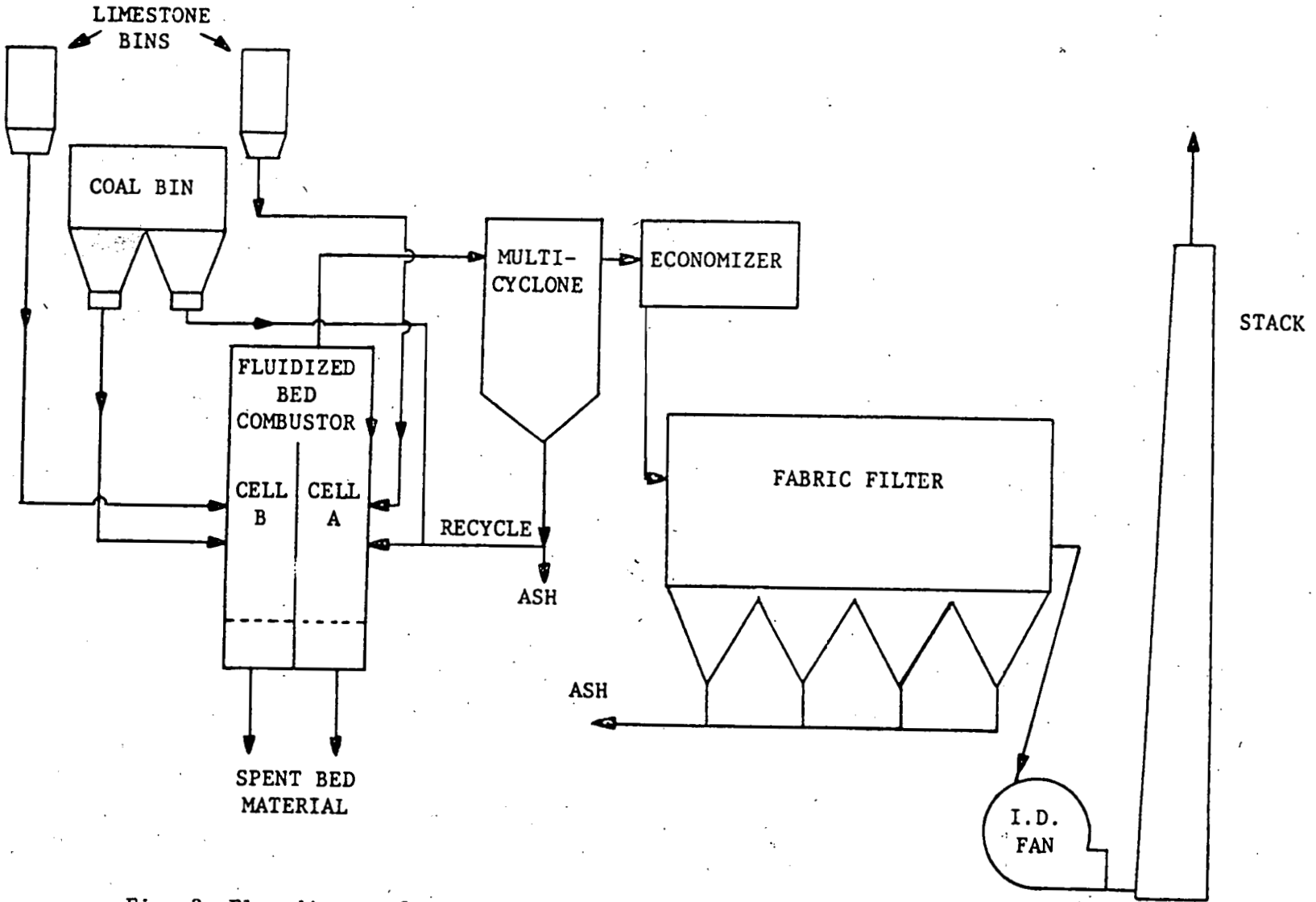


Fig. 3. Flow diagram for the combustion side of the Georgetown AFBC

Water Systems

Essentially no difference exists between conventional steam and cooling systems and those used for the Georgetown AFBC. A cooling tower previously and presently used for the older oil fired boilers on the Georgetown campus (they are located in the adjacent building) is used for the AFBC. This is a two cell Pritchard cooling tower rated at 24,000 gpm; it is wood filled and has a cement-asbestos lining. About two million gallons of make-up water are required per month. Again, as for conventional boilers, blowdown and treatment of make-up water is needed. With the AFBC generating saturated steam at 625 psig, it is necessary (see American Boiler Manufacturers Association standards) that the limits of 3500 ppm of total solids, 700 ppm total alkalinity and 300 ppm of suspended solids not be exceeded for the boiler water. To satisfy these standards, for two-bed operation at 100,000 lb/hr steam flow, it is projected that make-up water and blowdown will each be nearly the same at an average value of approximately 5000 lb/hr. The boiler feed make-up water is from the municipal supply and is treated in a Zeolite ion exchange resin column. It appears as if periodic regeneration when full two-bed operation is routine.

General Information

Typical AFBC operating data are presented in Table II. Emission estimates and typical values for those quantities for which a sufficient amount of data have been obtained (albeit for on-bed operation) are given in Table III. It should be noted that coal, limestone and all solid materials are handled within the AFBC site and shipped offsite for reuse or disposal; there are no onsite leachate streams.

TABLE II. Selected Georgetown University AFBC Operating Data

Steam flow	100,000 lb/hr	Gas temperature, post economizer	400 F
Steam pressure	625 psig	Excess air leaving economizer	22 %
Boiler efficiency	83.75%	Superficial velocity	8 ft/s
Maximum Coal feed	9,565 lb/hr	Expanded bed height	4.5 ft
Maximum Limestone	3,610 lb/hr	Freeboard height	8.0 ft
Bed temperature	1,600 °F	Steam temperature	493 °F
Ca/S ratio (molar) varied to meet SO_2 emission criteria, nominal is 3.5			

TABLE III. Effluent/Emission Values for the Georgetown AFBC

Stack gas emissions, lb/10^6 BTU		Solid Residues, lb/hr	
SO_2	0.78	Bed material	2,086
NO_x	0.295	$CaSO_4$	848
Particulates	0.033	CaO	922
		C	125
Water, gal/min		Ash	191
Boiler makeup	10	Bag house-fabric filter	1,308
Boiler blowdown	8	$CaSO_4$	305
Cooling blowdown	8	CaO	332
Boiler makeup discharge	2	C	111
		Ash	560

EMISSIONS MONITORING DESCRIPTION

During phase I of the Georgetown AFBC project, personnel in the University's Chemistry and Physics Departments formulated an emissions monitoring program plan. The plan was based on information obtained in conferences with numerous individuals having expertise in design, construction, operation and monitoring of similar plants[2], suppliers of monitoring equipment for such plants[3], and attendees of fossil fuel and environmental conferences[4]. The plan was designed to satisfy the environmental assessment factors for a 100,000 lh/hr power plant and to be accomplished with four imposed conditions: maximization of cost-effectiveness; maximization of data quality and applicability to this and similar plants coming on-line presently and in the near future; limitation of total costs to the monies available from the then ERDA, now DOE, and the EPA; and continuation of the emissions monitoring program through the first three years of operational experience of the AFBC plant. In retrospect, it is not clear that any of the conditions have been satisfied precisely, but most should be by the completion of the three-year operational experience. Indeed, as time has passed, the emissions monitoring function has taken on an importance not commensurate with the 100,000 lb/hr size of the plant; this appears to us to be due to the greater impact various non-coal based energy problems have had on the country's economy and populace.

Emissions Monitoring Equipment

The emissions monitoring program is divisible into two components, on-line and off-line; on-line work is accomplished at the site on a continuous or regular periodic basis, while off-line requires removal of samples to support laboratories for data accumulation and reduction. The on-line emissions monitors and ancillary equipment are listed in Tables IV and V. The off-line equipment, which is specifically used for particulate monitoring, is listed in Table VI.

TABLE IV. On-line Emissions Monitors

Pollutant	Analyzer Type	Supplier Model	Pollutant	Analyzer Type	Supplier Model
SO_2	pulsed fluorescence	TECO 40	CO	NDIR	Horiba A1A-21-AS
NO/NO_x	chemiluminescence	TECO 10A			
O_2	paramagnetic double-pass	Westinghouse 209	CO_2	NDIR	Horiba A1A-21
Opacity	transmissometer	Dynatron 1100	Hydro-carbons	Flame ionization	AID,550

All monitors are continuous except for the AID 550 hydrocarbon monitor.

TABLE V. Ancillary On-line Emissions Monitoring Equipment

Description	Supplier
Stack probe and temperature controlled sample tubing	PACE
Gas conditioning system for SO_2, NO/NO_x and CO	TECO, Model 900
Ten-point strip chart recorder for data accumulation	Leeds and Northrup
Double ball valve system for span gas injection at stack	Dupont
Manual calibration-gas injection system (to stack)	Georgetown
Automatic calibration-gas feed system (local to monitors)	PACE
Calibration gases	AIRCO, presently
Backflush and residual pressure compressors	Sears and Grainger's
Equipment enclosure, 7'6" by 11'6"	
Equipment enclosure air conditioner	Sears

TABLE VI. Off-line Particulate Monitoring Equipment

Description	Purpose	Supplier
Method 5 train, with 6 stage cascade impactor and POM collection apparatus	POMs, TSP and elemental analysis	GII Enterprises
Gas chromatograph	Polycyclic aromatic hydrocarbons	Resident in GU
Mass spectrometer Mass spectrograph	Elemental analysis, polycyclic aromatic hydrocarbons	Resident in GU
Microgram balances	Weight by size for impactor samples	Resident in GU
Optical emission spectrometers	Elemental analysis	Resident in GU
Charged-particle accelerators	Elemental analysis	Resident in GU
X-ray detector system	PIXE data for elemental analysis	ORTEC
X-ray data system	PIXE data accumulation and analysis	Tracor

A block diagram of the on-line emissions monitors and associated plumbing is shown in Fig. 4. The monitors and much of the associated plumbing are in an equipment enclosure some 15' from the base of the stack. The schematic of the stack and enclosure are given in Fig. 5. The stack is a rather short one, only 55' high, and is a double-walled stack with 3'6" inside diameter. The stack has a set of ports at four different heights. Ports presently used are at 13', 3.7 stack diameters, from the top of the stack and 30', 8.6 stack diameters up from the induced draft fan exhaust. The Method 5 train is

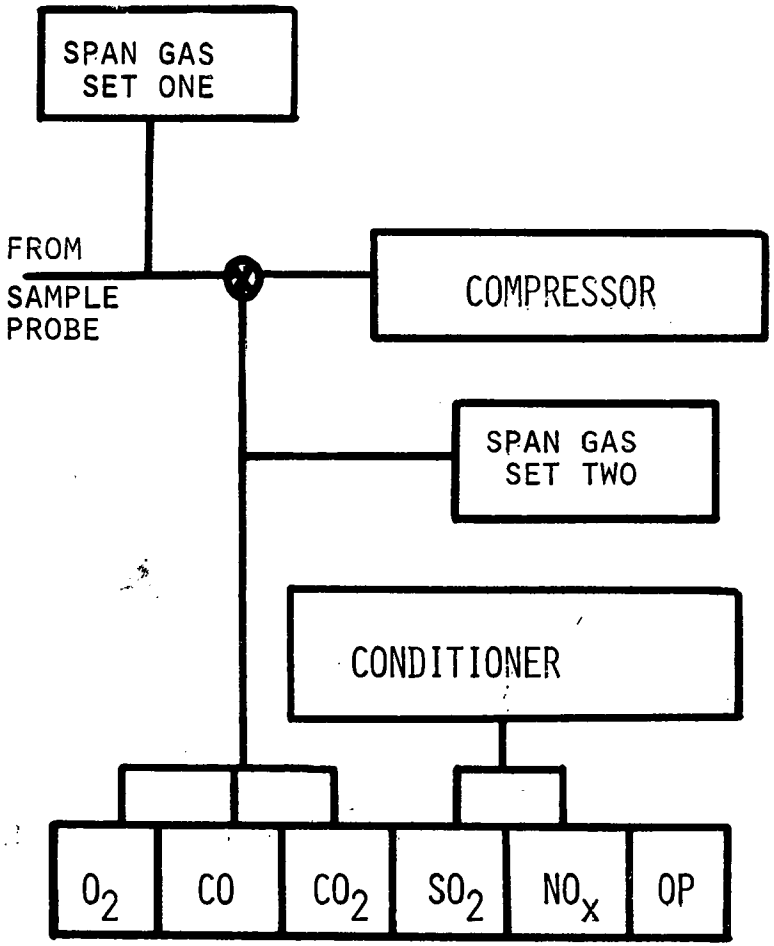


Fig. 4. On-line emissions monitors.

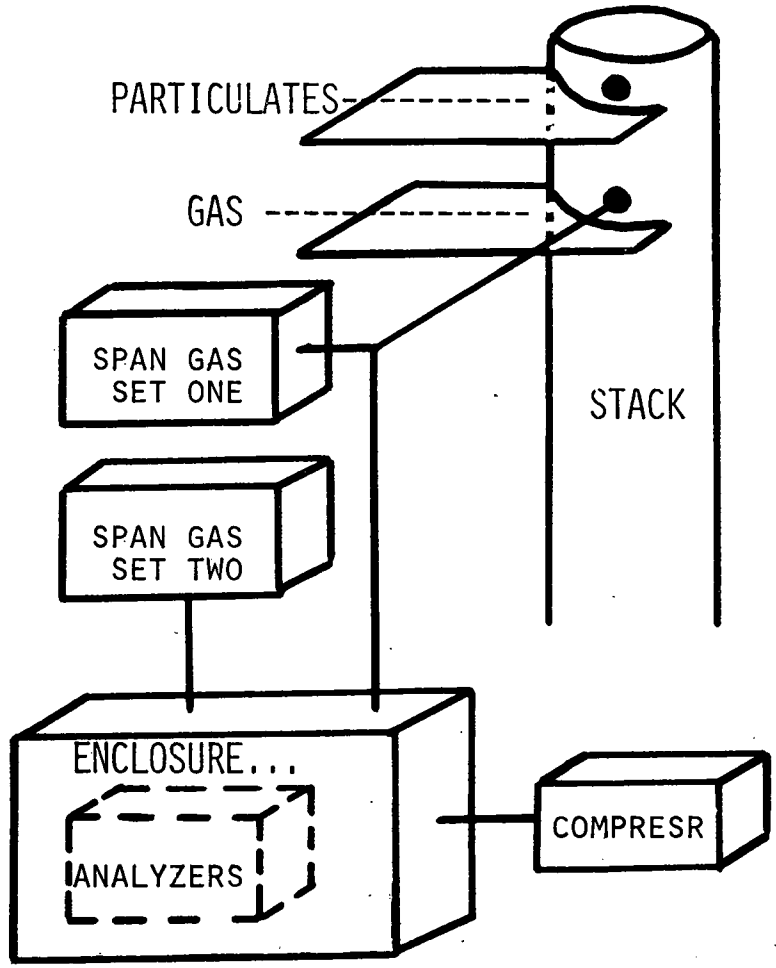


Fig. 5. Stack, analyzers, and enclosure schematic.

located at the upper position and the opacity meter and gas sampling probe are located at the lower position. All systems are now operational and have been producing data for most of the boiler-operation periods; the opacity meter is required for operation of the plant and has been the cause of little or no boiler downtime. It should be noted that continuous operation of the boiler is most efficient when SO_2 and O_2 levels within the bed areas are used in the control feedback loops. Thus, SO_2 and O_2 monitors are in place in the bed and have been providing information to the operational staff as to instantaneous changes in SO_2 and O_2 levels in the beds.

PRELIMINARY AFBC OPERATION

Combustor, Bag House and Auxiliaries

As of March 1, 1980, the AFBC plant has operated for approximately 1175 hours. Of this time approximately 96% of the operating hours was with only bed A fired. The steam load ranged from 26,000 lb/hr to about 58,000 lb/hr for the one-bed operation. Coal with sulfur content from 1.2% to 3.8% has been used; coal with characteristics essentially identical to those given in Table I has been used with successful operational stack emissions. Design parameters have, in general, been satisfactory.

A significant modification of the fabric filtering in the bag house has resulted from a number of minor problems. Also, some problems have been persistent with the limestone feed system, particularly the screw feeder which has been mentioned previously. It has not always been possible to use a limited continuous flow of limestone, and operators have had to be a direct part of the feedback system; they have had to inject larger amounts of limestone than needed, wait for the SO_2 emissions to decrease and then inject limestone by manual rather than automatic control when the SO_2 emissions increase again. This, now, has been corrected and slow limestone feeds are routine.

Upon arrival, the coal shipments are sampled and sizing measurements made. The as-delivered coal information is used in controlling the environmental conditions of the bed. Expected as-delivered coal characteristics were given in Table I. Typical as-delivered coal values are given in Table VII.

TABLE VII. 10 January 80 As-Received Coal and Limestone Analysis

Coal Analysis			Limestone Analysis		
	% By Weight			% By Weight	
Component	Estimated	As Received	Component	Specified	As Received
Inherent Moisture	3	2.53	Calcium Carbonate	94.06	95.00
Volatile Matter	20	22.62	Magnesium Carbonate	1.46	1.00
Fixed Carbon	65.5	60.28	Silicon Dioxide	1.16	1.00
Ash	8	14.70	Aluminum Oxide	0.24	1.00
Sulphur	3.5	2.69	Ferric Oxide	0.08	1.00
Bulk Density	50#/cu.ft	50#/cu.ft	Water	3.00	1.00
HHV, BTU/#		12791			

The values characterizing coal and limestone for the period of use we are discussing have not varied significantly from those given in Table VII, except for the very early running period when the sulfur content of the coal used was normally below 2%. It may be of interest to note that Physics Department personnel have been considering the design, construction of prototype devices and testing of the prototype devices for instantaneous (within 4-5 minutes) measurements of the sulfur content of as-delivered coal. Coring of the 20 ton load of coal would provide 5-6 samples per load for analysis; thus, within 20 minutes the sulfur content of coal to be used in the beds would be known and this is well before the coal would actually arrive at the bed for burning.

Start-up time for the boiler, again generally for single-bed operation, has ranged from four to eight hours; the longer periods occur when minor problems exist with auxiliary systems and have not been caused by in-bed difficulties. The oil used to fire the beds has provided no environmental problems; it is interesting to note that the opacity in the stack is essentially the same with oil in the beds as when coal is being burned.

A summary of the progress for the fourth quarter of 1979 may be of interest and follows: (1) the boiler was operated for 694 hours during 9 separate running periods, (2) 73 hours of the 694 were two-bed operation periods, (3) steam generation ranged from 18,000 to 80,000 lb/hr with the higher values for two-bed operation, (4) the boiler was inspected and various minor modifications were installed in the last three weeks of December, (5) the most important modifications were the installation of grid plate seals within the boiler and changes in the flyash reinjection blowers, (6) the boiler instrumentation was checked and calibrated preparatory to automatic operation of the boiler, and (7) the plant was officially dedicated on 15 November 1979. Fig. 6 depicts the fourth quarter, 1979, operations experience of the boiler.

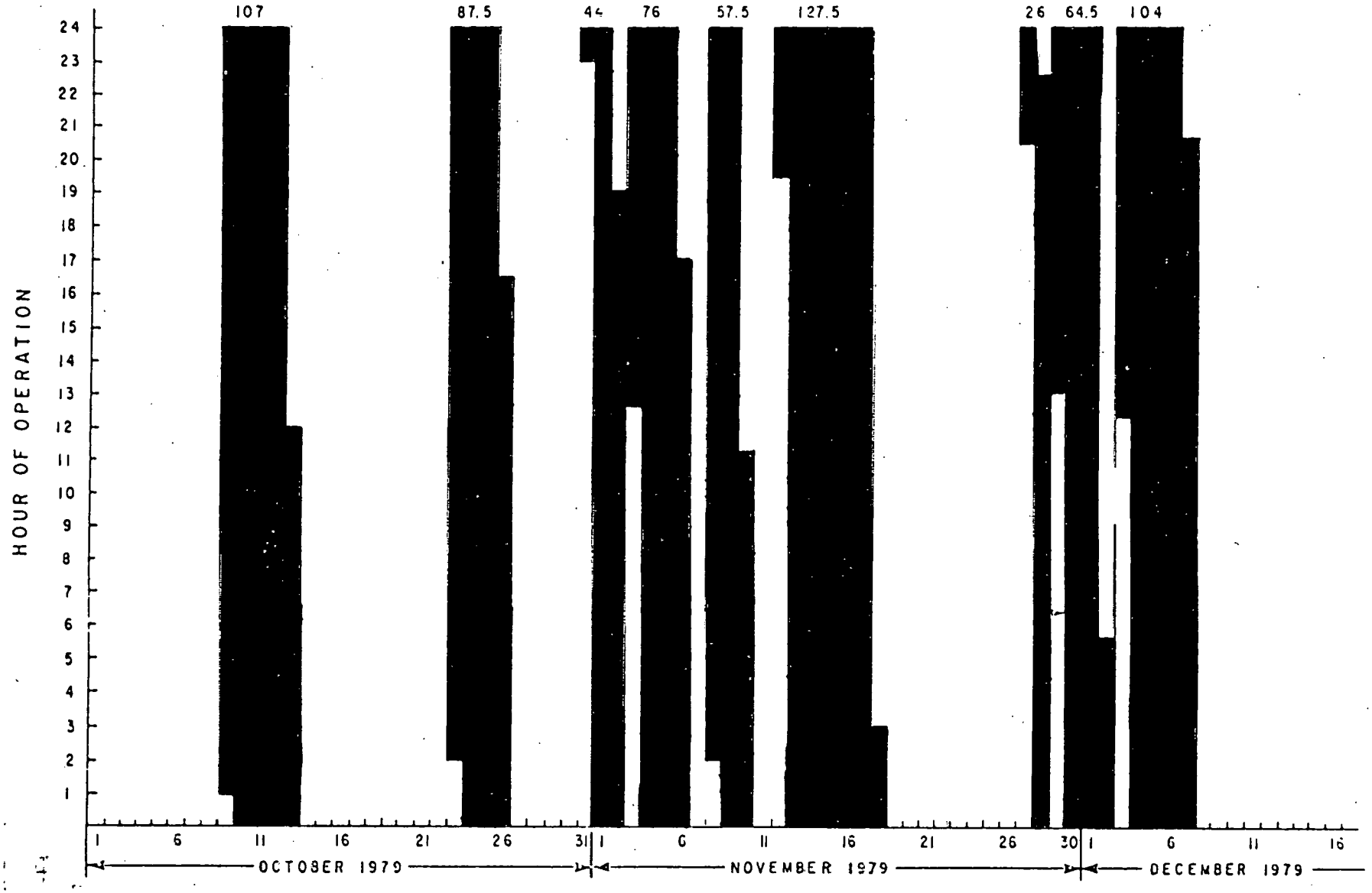


Fig. 6. Boiler operation for the fourth quarter of 1979.

Preliminary Operation of Emissions Monitoring Equipment

Continuous monitoring by instrumental techniques has been used to measure SO_2, NO/NO_x, CO, CO_2, O_2 and opacity with the instruments listed in Table IV and positioned as shown in Fig. 5. Table IX gives a synopsis of operational time during actual boiler operation for each of the 6 monitors. Table X lists the design expectations for the dual bed combustor and the EPA- and D.C.-imposed limits for SO_2, NO_x and particulates, as well as an estimate of the average values for these quantities over the 1300 boiler-operation hours.

Initial testing of the emissions monitoring equipment commenced in April of 1979. Prior to moving the basic system components to the power plant in early summer, 1979, certain electronic problems with the L&N recorder and the opacity monitor and a zero-level offset in the SO_2 monitor were corrected. Also, each individual analyzer for the stack gas emissions system was tested for zero-drift, calibration reproducibility over extended periods up to two weeks, calibration-gas readout as a function of a number of pressures in the system-plumbing both between the gas entrance port and the specific analyzer and within each analyzer's gas distribution system, and reaction to intermittent power failures. With the two exceptions of the gas conditioner pressure differentials being disrupted during some of the simulated power interrupt conditions and of the main vacuum pump showing a tendency to be sluggish on re-start after the power interrup condition, no problems existed with the system when it was ready to be moved to the base of the stack in the plant.

TABLE VIII. Emissions Monitors Operational Time

Monitor	% vs. Boiler	Monitor	% vs. Boiler
Opacity	100%	NO_x	98%
SO_2	98%	O_2	75%
CO	88%	CO_2	93%

TABLE IX. Emissions Expectations, Limits and Experience

Pollutant	Anticipated Experience		Acceptable		Estimates	Experience
	Maximum	Average	EPA	D.C.	lbs/hr	lbs/hr (average)
	$lbs/10^6 BTU$	$lbs/10^6$ BTU				
SO_2	0.678	0.605	147	102	85	76
NO_x	0.324	0.481	86	86	40	60
Particulates	0.032	0.046	12.3	6.9	4	5.8

After installation at the base of the stack, but not in its present equipment enclosure, the gas analysis system operated properly until a particularly dirty plant environment resulted from bag house cleanup. We then moved the equipment inside its present temperature controlled and reasonably dirt-free enclosure. In the time span since initial plant operation, a number of modifications have been completed. The modifications were to meet the needs of the GCA personnel who will perform compliance measurements for particulates, SO_2 and NO_x. These measurements will be accomplished either during the GCA environmental assessment program or during the GCA fabric filter evaluation program[5,6]. Some of the modifications included injection of the span gas at the probe and extra heating of 18" of the trace line at the probe end.

Typical stack emissions data from periods when the boiler was operational are shown in Figs. 7,8 and 9. For comparison with the emissions data given in Fig. 9, boiler parameters for the same day are given in Fig. 10. One can see that when limestone is added to counteract an increase in the SO_2 emissions, the SO_2 emissions do indeed decrease. Fig. 7 shows data from a day in which the boiler was needed to furnish steam for the campus, while Fig. 8 shows data from a day in which significant operating-mode tests were in progress and steam production was not the only intent.

In early November, 1979, the Method 5 train began to be used regularly. Data obtained during sample collection and from the samples collected are given in Tables X and XI and Figs. 11 and 12. Table X gives selected particulate emissions data obtained off-line with the Method 5 train, and Table XI gives much of the on-line data available from a specific day. Fig. 11 shows polycyclic aromatic hydrocarbon data obtained with an interrupted flow GC/IR/MS system located in the Chemistry Department. Sample data from stack wall materials and the final filter of the cyclone impactor are shown. Fig.12 depicts PIXE data from the same filter, and material from the cell of the O_2 analyzer. Clearly, one begins to believe that the white residue found on the O_2 analyzer cell is similar, if not identical, to that trapped in the impactor and that Ca and S are primary elements in the spectra. It is very important to note that no harmful elements, such as arsenic, lead selenium, uranium, radium, or strontium have been found with the PIXE analysis. For completion, Fig. 13 shows a PIXE spectrum of a coal sample. These data are in excellent agreement with an NBS furnished standard coal sample which is used prior to taking any data for the elemental analysis of plant coal samples.

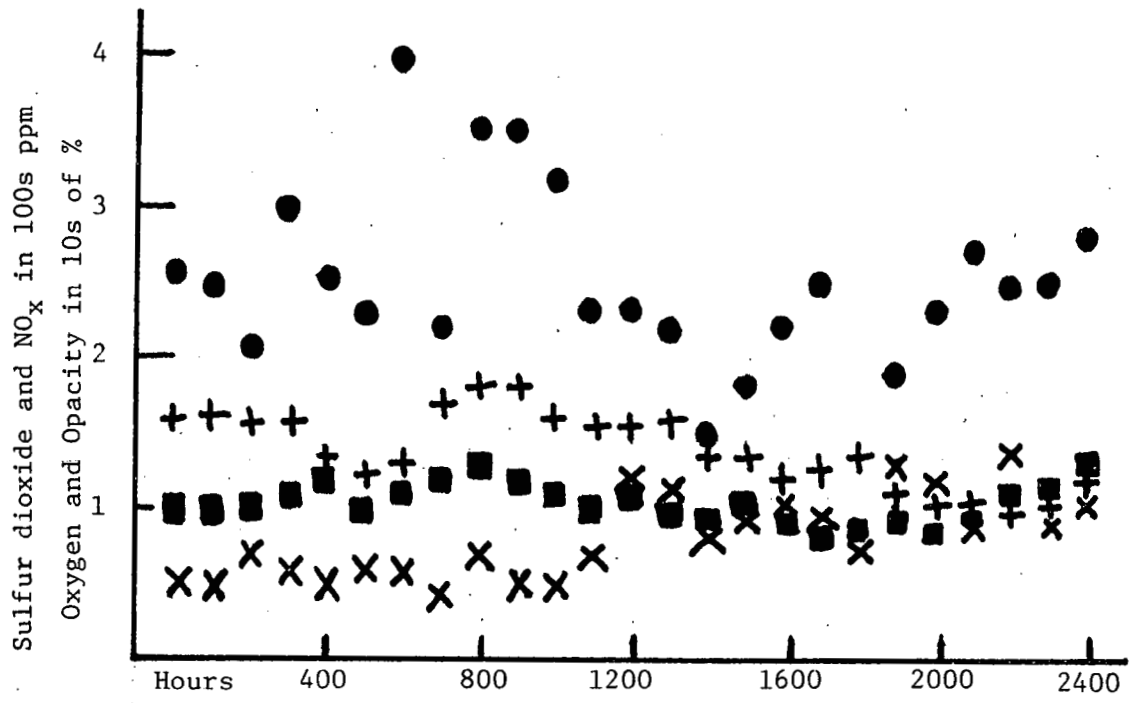


Fig.7. Selected emissions data when steam furnished.

Legend: ● SO_2; ✕ O_2; + NO_x; ■ Opacity.

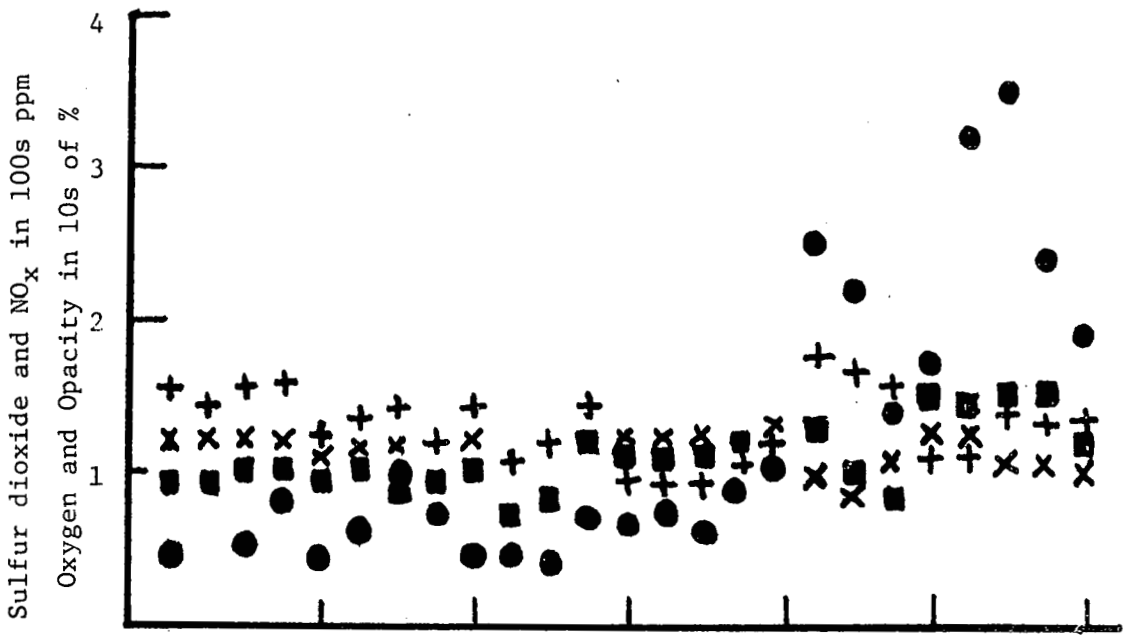


Fig. 8. Selected emissions data when boiler tested.

GEORGETOWN UNIVERSITY FLUIDIZED BED BOILER PLANT

HOURLY STACK GAS EMISSION DATA

TIME	OPACITY	NITROGEN OXIDES	CARBON DIOXIDE	CARBON MONOXIDE	SULFUR OXIDES	OXYGEN	EMISSIONS
	%	PPM	%	PPM	PPM	%	#SO2/MILLION BTU
01	17	153	8.4	562	155	11.8	0.6
02	14	153	11.9	1397	280	11.4	1.0
03	14	173	7.8	504	97	12.2	0.4
04	14	173	10.2	662	164	11.6	0.6
05	14	173	9.8	634	126	11.8	0.5
06	15	173	8.8	605	174	11.8	0.7
07	16	163	10.2	907	213	11.6	0.8
08	17	244	9.8	518	155	11.6	0.6
09	11	183	7.4	490	135	12.8	0.6
10	13	113	4.9	1138	135	14	0.7
11	10	193	8	648	242	12.8	1.0
12	9	183	9	547	145	13.2	0.6
13	8	193	12.3	806	164	13.4	0.7
14	8	183	12.7	1368	242	12.2	0.9
15	8	183	10.6	634	97	12.6	0.4
16	12	178	10.8	706	116	12.6	0.5
17	9	173	12.9	1181	164	11.6	0.6
18	9	173	11.7	720	116	11.6	0.4
19	9	193	10.8	706	135	11.8	0.5
20	9.	173	12.3	850	135	11.6	0.5
21	10	183	13.9		203	11.4	0.7
22	7	173	11.7	648	116	11.8	0.4
23	7	173	13.9	922	15.5	12	0.1
24	10	193	12.5	648	174	12.2	0.7
	==	===	===	====	====	===	===
MEAN	11.	177.0	10.5	774.0	154.1	12.1	0.6
STANDARD DEVIATION	3.	22.	2.	259.	54.	1.	0.21

Fig. 9. Off-line computer printout of hourly stack gas emission data.

TIME	AVG BED TEMP	EXCESS O2	SUPERFICIAL VELOCITY	COAL FEED	BED HEIGHT SLUMPED	BED HEIGHT EXPANDED	LIMESTONE FEED	MAXIMUM OVERBED TEMP
	F	%	FT/SEC	#/HR	INCHES		#/HR	F
01	1480	4.0	6	1800	17.5	12.5	900	1550
02	1500	4.5	5.5	1800	15.8	12.4	700	1600
03	1480	4.0	5.5	1600	15.8	12.4	700	1575
04	1480	4.0	5.5	200	15.8	12.4	700	1550
05	1500	4.5	5.5	200	15.8	12.4	800	1575
06	1550	4.5	5.5	200	15.0	12.4		1550
07	1500	5	6	2000	15.0	12.4	850	1625
08	1550	5	6	2000	15.8	12.5	800	1600
09	1500	5	6	2000	15.0	12.5	800	1600
10								
11	1550	5	6	1800	15.0	12.3	900	1600
12	1550	5	6	2000	15.8	12.5	1000	1550
13	1575		6	2100	19.2	12.4	1000	1550
14	1550	5.5	5.2	2100	18.3	12.4	1000	1550
15	1550	10.0	55	2000	18.3	12.5	1000	1550
16	1550	10.0	5.2	2000	15.8	12.6	1000	1525
17	1525	10.0	5.5	2000	18.3	12.7	900	1525
18	1525	8.0	5.8	2000	19.2	12.8	900	1525
19	1525	11.0	5.8	2000	19.2	12.8	1000	1525
20	1525	9.0	5.8	2000	19.2	12.8	1000	1525
21	1525	11.0	5.8	2000	19.2	12.8	1000	1525
22	1525	8.5	5.8	2000	19.2	12.7	1000	1525
23	1450	3.8	5.8	2000	19.2	12.7	1000	1560
24	1520	5.0	5.8	190	17.5	12.5	600	1550
	====	====	===	====	====	====	====	====
MEAN	1521	6.5	7.9	3303	17.2	12.5	888	1556
STANDARD DEVIATION	30.	2.5	10.1	1352.	1.7	0.2	124.	30.

Fig. 10. Off-line computer printout of hourly (selected) boiler data.

TABLE X. 6 December 79 Particulate Train Data

Barometric pressure (in. HG)	29.740
Average stack gas temperature (^{o}R)	774.000
Pitot Coefficient	0.760
Molecular weight of stack gas	31.000
Avg. Sq. Rt. of velocity head (in. $H_2O)^{\frac{1}{2}}$	0.828
Average stack gas velocity (FPS)	49.292
Volume of dry gas sampled (DCF)	19,129
Average meter temperature (^{o}R)	558.000
Average orifice pressure drop (in. H_2O)	0.500
Stack area (ft^2)	9.621
Sampling nozzle diameter (in.)	0.156
Net time of test (min)	60.000
Total H_2O collected (g)	17.300
Volume of dry gas samples, STD, (DSCF)	18.007
Volume of water vapor, STD, (SCF)	0.816
% moisture in stack gas by volume, STD	4.334
Total particulate collected (g)	0.037
Particulate concentration (gr/CF)	0.030
Particulate STD concentration (gr/SCF)	0.031
% isokinetic	117.546

Emissions Systems Operations Summary

In the past six months, the various components of the stack gas emissions monitoring system have been operating during operation of the combustor between 75% for the O_2 monitor to 100% for the opacity monitor. The major fraction of down time for most of the instruments during combustor operation has been due to intermittent power outages, two of which caused the failure of the main vacuum pump in the system, unauthorized personnel (visitors) playing with switches, a lack of complete closing of the back-flush valve in the system plumbing, a ground-loop with the L&N recorder, the move from the original stack position to the enclosure which required new electrical, water, exhaust and calibration gas lines, a fine white powder build-up in a limited number of plumbing lines and in the O_2 analyzer cell, and a lubrication failing of the chopper motor in the CO analyzer. The particulate train has been operating for four months and little or no difficulty has arisen. From the emissions data it is clear that the plant can operate within satisfactory environmental limits.

To facilitate future plant operation, we will inject span gases at both the sample probe and at the gas emissions plumbing inlet, we will provide the operational staff with a multiplexed system allowing them to monitor the gas emissions in the control room via a switchable meter, we will design,

TABLE XI. Selected Particulate Emissions Data

I. Particulates (grains/hr)

Impactor	Dp50	11/9/79	12/6/79	2/6/80	2/14/80
Cyclone	>20μ	25200	20900	38100	31300
1	>16μ	309	0	277	3210
2	16μ	773	0	461	1280
3	8.6μ	1160	285	738	1090
4	3.9μ	2010	3700	5530	3330
5	2.4μ	2400	4840	9350	4360
6	1.2μ	1240	2470	5440	2370
7	0.61μ	618	569	1380	1030
8	<0.61μ	4330	2370	4430	9620
Total		38000	35100	65700	54400

II. Stack Conditions

Total Flow x 10^6 DSCF/hr	1.034	1.11	1.18	1.09
Percent Isokinetic (%)	33.4	118	121	174
Temperature (°F)	309	314	306	279
Water (%)	4.51	4.33	3.15	3.95
Acidity, N(pH)	--	--	.045(1.3)	.077(1.1)
Total Hydrocarbon (CH4ppm)	>2000	1750	1500	>2000

III. Bag House

Fly Ash (soluble base by wt.)	5.81%	3.93%	--	--

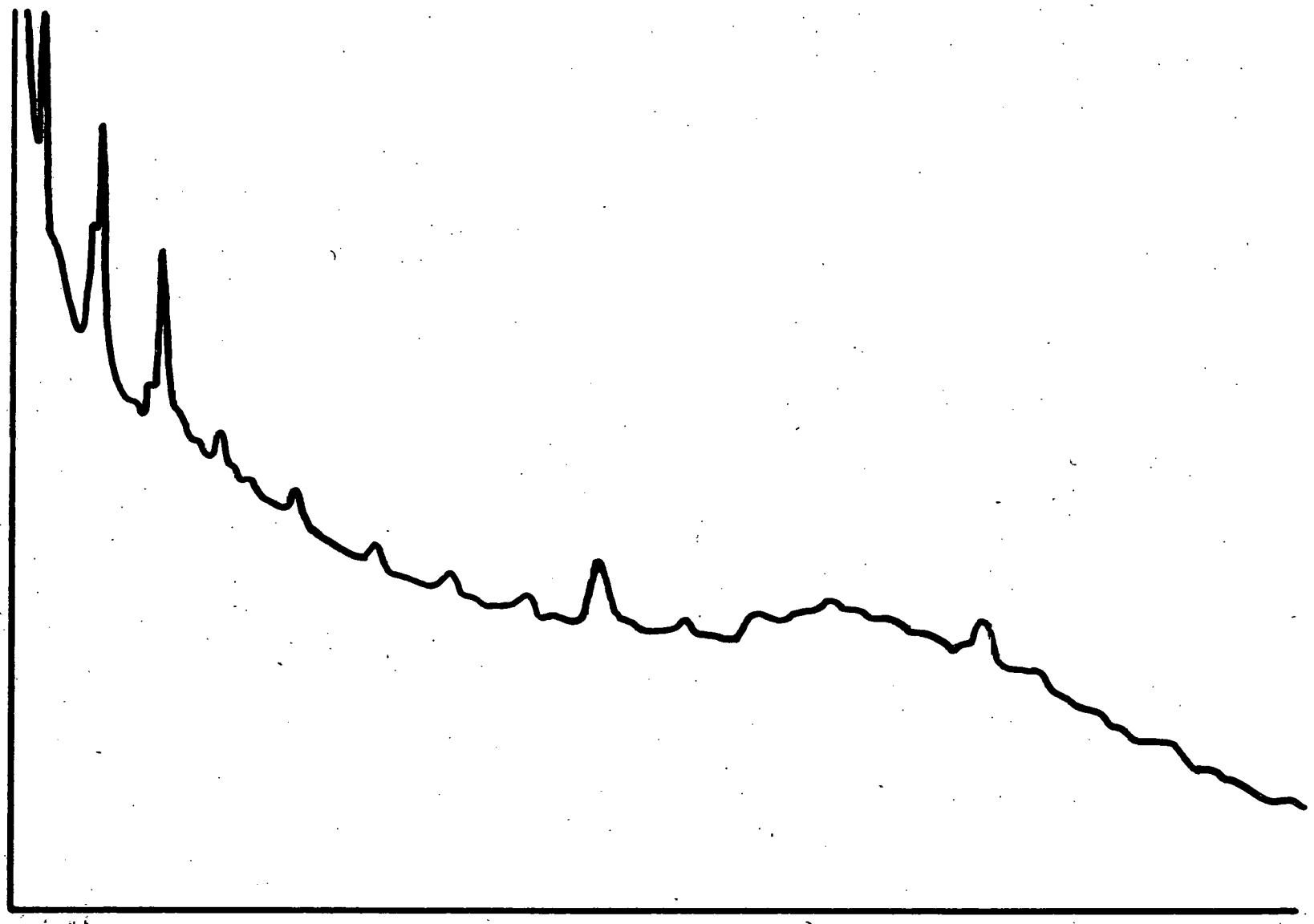


Fig. 11a. Polycyclic aromatic hydrocarbons in impactor cyclone material

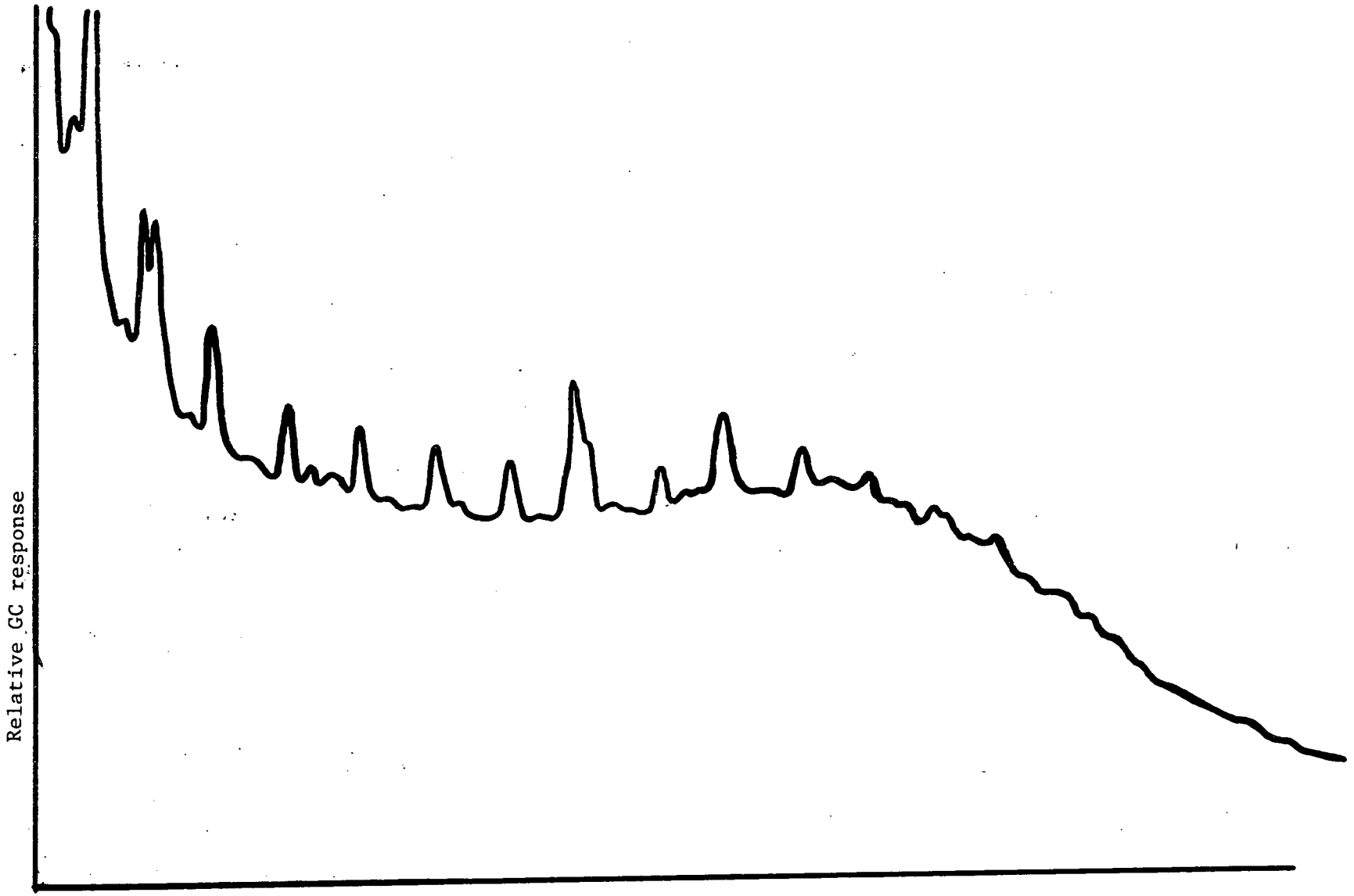


Fig. 11b. Polycyclic aromatic hydrocarbons in fly ash

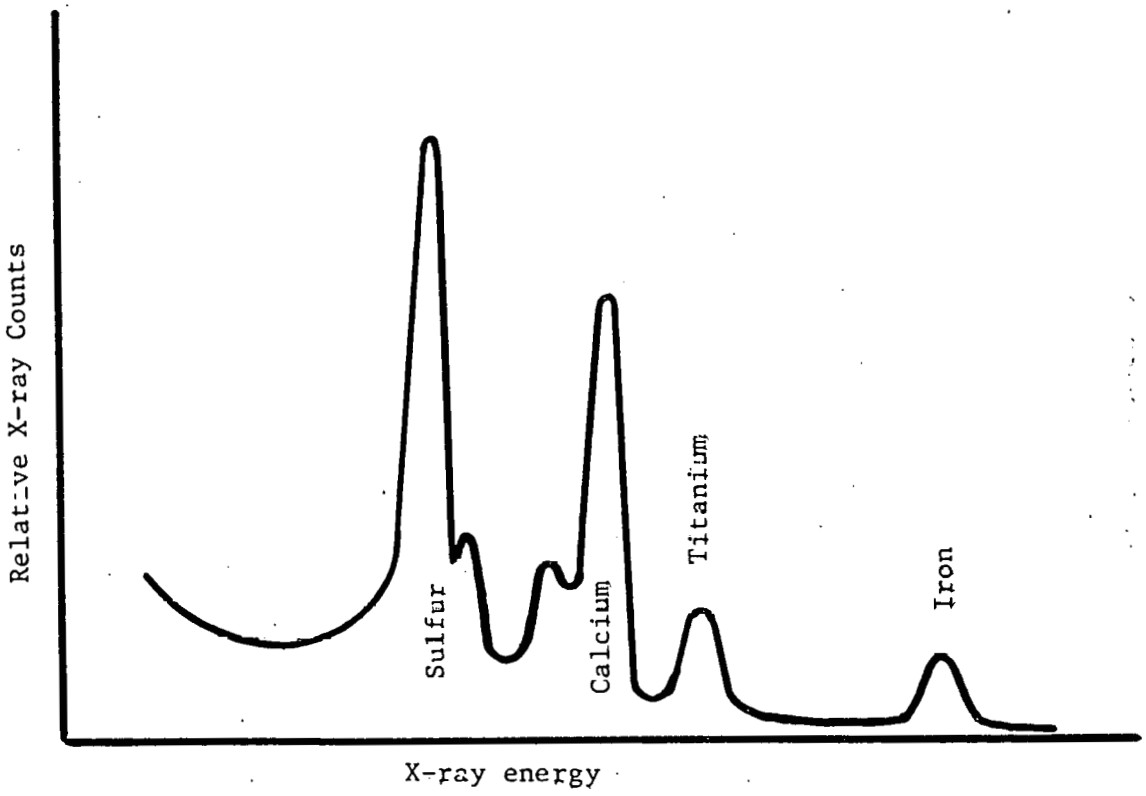


Fig. 12a. PIXE spectrum of impactor cyclone material

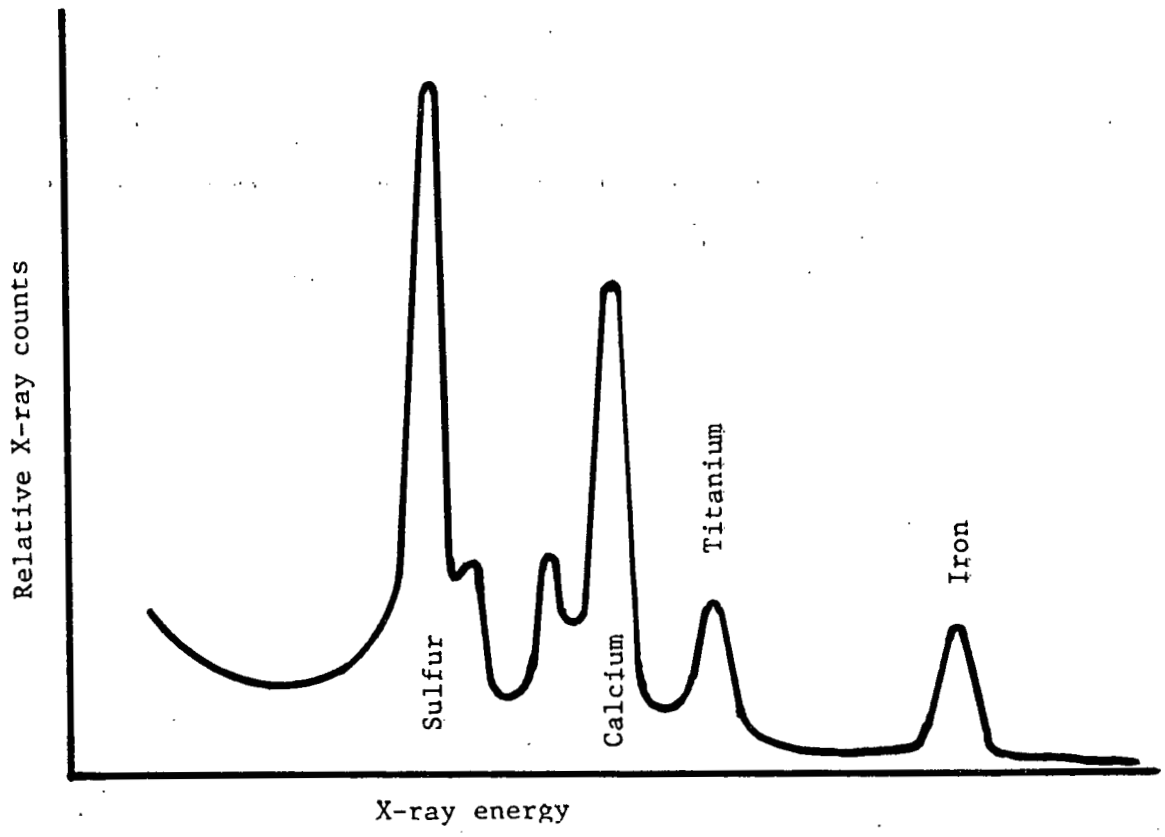


Fig. 12b. PIXE spectrum of O_2 analyzer residue

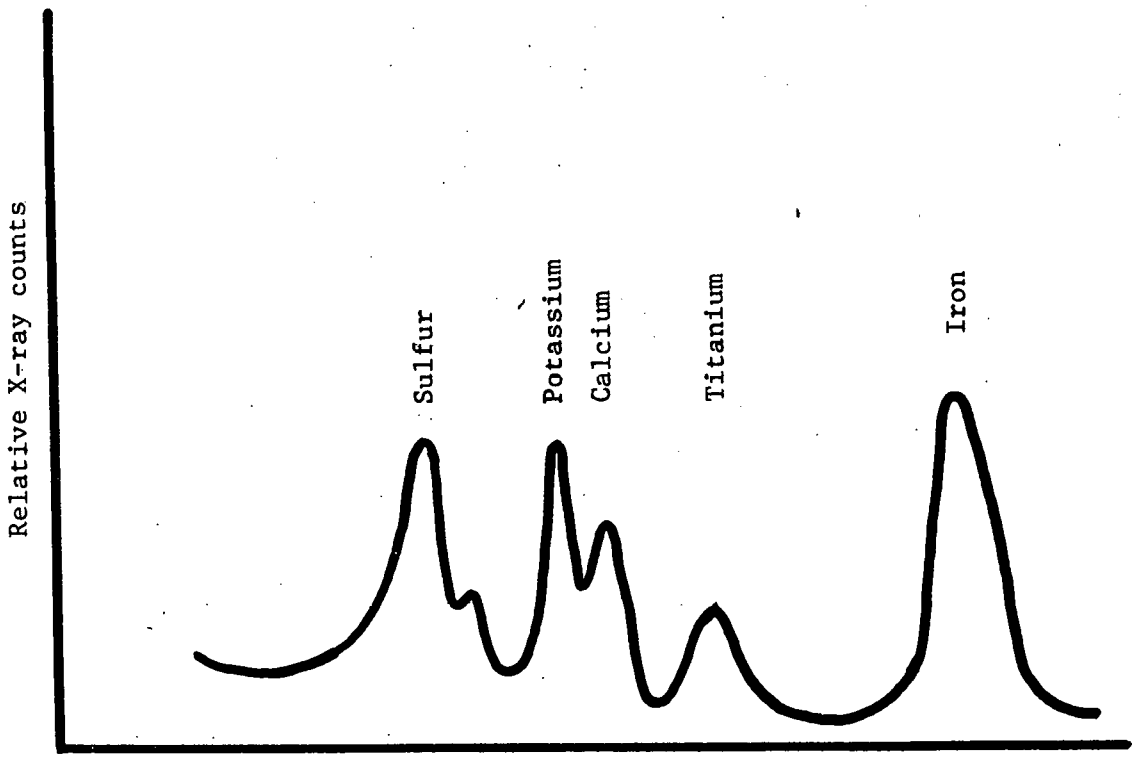


Fig. 13. PIXE spectrum of coal sample

construct and install a computer-based system to provide emissions data for all of the gas emissions and two or three of the particle train parameters with a 5-minute updating, and we will improve our routines for maintaining the equipment by having two independent systems for delivering compressed air for back-flushing and for O_2 monitoring. The back-flush mode for the system must be operational at all times as we have found that from 8 to 12 hours of no back-flushing results in clogging of the sample probe. The computer-based system will allow the operators to monitor the effect of various bed parameters, such as the coal to limestone feed ratio, on actual environmental quantities such as the emitted lbs/10^6 BTU of SO_2.

Acknowledgments:

A number of Georgetown University people have contributed significantly to the work reported in this paper. In particular, Dr. James M. Lambert, Dr. Lutz Leopold, Mr. Al Guron and Mr. Mousa Hawamdah of the Department of Physics and Dr. Charles F. Hammer, Dr. Shing-Bong Chen and Mr. Michael Kornbluth of the Department of Chemistry have been very much involved in every aspect of the emissions monitoring program. Mr. Ben Scarbrough has been involved in the boiler and ancillary systems work from the inception of the project. Personnel from PER and Foster Wheeler, such as C. Sala and H. Wong, have been very cooperative and helpful.

References:

1. Industrial Application Fluidized Bed Combusion, Georgetown University; Environmental Impact Assessment. Prepared by Georgetown University under DOE Contract EX-76-C-01-2461. Revised April 1978.

2. DOE personnel; EPA personnel; Battelle personnel; GCA personnel; Pope, Evans and Robbins personnel; and Foster Wheeler personnel.

3. Engineering and sales personnel from Dupont, Beckman, TECO, PACE, GII, and Environmental Research and Technology companies.

4. Various coal conferences and workshops of DOE and the APA; particularly, the spring Morgantown conferences.

A Status Report on the Environmental Acceptability of Spent FBC Sorbent for Agricultural Uses

O. L. Bennett, W. L. Stout, J. L. Hern,
J. Edwards, and R. Korcak

Large quantities of limestone are used in the Fluidized Bed Combustion Process. The resulting residue consists of various combinations of calcium sulfate, magensium sulfate, calcium oxides and other compounds that may be contained in the limestone or scrubbed from the coal during combustion (1). Therefore, FBC residue represents a tremendous resource of elements and compounds that may prove valuable for agricultural production (5). However, this residue may also contain heavy metals that are toxic to plants, animals and humans if these elements enter the food chain in sufficient amounts. This could seriously limit the use of FBC residue in agricultural production.

Since 1976, an intensive and extensive research program has been conducted by the Agricultural Research branch of the U.S. Department of Agriculture, Science and Education Administration in cooperation with the U.S. Department of Energy to determine agricultural uses of FBC residue. The research is conducted at several locations representing most of the major soil associations and environmental conditions existing in the eastern half of the United States. The research consists of detailed chemical and physical evaluation of the material followed by extensive greenhouse, environmental growth chamber, and field studies. All major plant species including corn, small grain crops, vegetables, nut crops, grass, and legume species are covered in these studies. Final phases of the research will cover metabolic studies using test animals and possibly human feeding trials with feed and food products grown with FBC residue. The purpose of this paper is to give a summary of the nature, extent, and some of the results of this extensive research program.

CHEMICAL EVALUATION

Samples of FBC residue from several locations scattered throughout the United States have been collected for chemical and physical evaluation (2). Chemical analysis of several samples of FBC residue are given in Table 1. A theoretical mineral balance obtained from chemical composition indicates FBC residue contains an average of 28.3 percent calcium sulfate, 33.6 percent calcium oxide, 4 percent aluminum oxide, 2.1 percent iron oxide and 1.8 percent maganesium oxide with 26 percent of the material listed as inert and identified as primary silic dioxide. This leaves 3.2 percent for trace elements and undetermined components. The purpose of the chemical analysis was to determine those constitutents of FBC residue which are 1) essential plant nutrients, 2) toxic metals, 3) possible phytotoxic elements and 4) a soil pH amendment. Essential elements are those required for plant growth and reproduction of crop species. This group consists

TABLE 1 - Variations in some chemical constituents of nine samples of fluidized bed combustion waste (2), FBCW.

	Constituent	FBCW Average	FBCW Range
		ug/g of Dry Matter	
Essential Plant Nutrients	Ca	380,000	240,000-460,000
	Mg	7,100	5,000-12,000
	K	2,500	500-8,000
	P	430	380-500
	S	92,000	72,000-140,000
	Fe	11,000	800-16,000
	Mn	485	210-685
	Mo	0.19	0.12-0.28
	B	110	95-170
	Cu	15	12-19
	Zn	55	29-105
Heavy Metals	Ni	21	13-29
	Pb	3.2	1.5-7.5
	Cd	0.5	---
	Cr	15	9-23
Possibly Phytotoxic	Se	0.29	0.16-0.58
	Al	10,000	4,000-20,000
		% of $CaCO_3$	
Soil pH Amendment	Neutralizing Potential	60	31-100

of calcium, magnesium, potassium, phosphorous and sulfur which are required in macro amounts and iron, manganese, molybdenum, boron, copper and zinc which are required in micro amounts. The heavy metals listed in Table 1 are nickel, lead, cadmium, chromium, selenium and aluminum. Mercury and arsenic (not shown) would be in the same category. The FBC residue samples vary considerably in chemical composition but do not vary significantly from the amounts of micro elements and heavy metals already present in the soil. That was not true for some of the essential plant nutrients such as calcium, magnesium and sulfur. Boron may be present in sufficient amounts to be phytotoxic for some species. The plant availability of many of these elements, especially the micro-nutrients and heavy metals are within the range of those usually found in soils. But, uptake of these elements by plants will depend on the amount applied in the FBC residue, native amounts in the soil, soil pH, interactions with other ions, and the solubility of the compound. Therefore, the application of large amounts of FBC residue over a period of time should be carefully monitored.

Laboratory studies were carried out to determine particle size distribtion, porocity, water rentention capacity and the effects of these physical properties on potential use of FBC residue as an agricultural liming material. Such studies carried out at several locations indicated that particle size will significantly affect chemical reactivity. In general, the smaller size fractions have a much faster rate of reaction and release of potential nutrients for plant growth. Particle size distribution of several samples of FBC residue indicate that 27 percent of the particles were in the 1 - 2 mm size range and about 28 percient in the 1/2 - 1 mm size range (Table 2). An average of 90% of all of the material was less than 2 mm in size. However, the percentage spread is considerable between subsamples.

LEACHING STUDIES

In order to determine possible elemental movement through soils treated with FBC residue, column leaching studies were conducted at several locations. At Morgantown, West Virginia, studies were initiated to evaluate the effects of FBC residue liming rates on the movement of added chemical consistuents in both acid soils and mine spoils (4). This was accomplished by incorporating various rates of FBC residue in the upper portion of the soil or mine spoil material. Sufficient amounts of FBC residue were applied to bring the soil and spoil material to pH(s) of 4.6, 5.0 and 6.0. Since the soil had a higher buffering capacity than the mine spoil, this meant that higher amounts of FBC residue were applied to the soil columns than the mine spoil.

Analysis of the leachate from 14 different leachings for each column, carried out at 10-day intervals, shows that of the elements analyzed in the mine spoil digest, only calcium showed any significant downward migration as a result of the FBC residue treatment. Of the heavy metals analyzed in leachate from mine spoil, all were within an

Table 2. Particle size distribution from 9 subsamples of fluidized bed combustion waste obtained from the Alexandria, WV pilot plant.

Size	%			
	Mean	High	Low	CV
>2 mm	9.2	19.0	0.7	58
1 - 2 mm	46.6	57.9	36.0	19
0.5 - 1 mm	27.9	39.6	19.1	22
0.25 - 0.5 mm	9.4	16.9	1.1	58
0.15 - 0.25 mm	3.4	9.9	0.3	93
0.15 mm	3.5	10.9	0.4	97

Data by W. L. Stout and R. C. Sidle

acceptable range for potable water. Only percolate SO_4^{-2} and manganese concentrations were present in excess of suggested limits for potable water. However, this was true for percolate collected with FBC residue amended as well as control column. Of the elements analyzed in the percolate from soil samples, calcium increased the most due to FBC liming amendment. Mean percolate calcium concentrations for all leaching periods for the high FBC treatment were significantly higher than concentrations for either the low treatment (11.4 ppm) or control (6.7 ppm). Other elements showing downward migration in the soil column were magnesium, manganese, and sulfate. None of the other elements analyzed in the percolate showed any overall FBC residue treatment effect. These studies indicate, in general, that no environmental problems are found with respect to solute transport from liming rate applications of FBC residue on soils or strip mine spoils. Movement of calcium and magnesium into the subsoil would definitely be beneficial to many acid soils in the Eastern United States.

PLANT GROWTH STUDIES

Initial studies with plant species were carried out at several locations in both the greenhouse and in environmental growth chambers. Indicator plants were used such as vegetable crops - swiss chard, cabbage, tomatoes, lettuce, radish, turnips - that tend to accumulate heavy metals (5). By using indicator crops, we were able to get a quick estimate of the potential availability of the heavy metals contained in the FBC residue as compared with regular limestone. In general, these studies indicated that when FBC residue was applied on a lime equivalency basis, soil pH was increased to the same level as where agricultural lime was applied. Greenhouses and growth chambers studies indicated that no significant increases in heavy metals concentrations in plant tissue were obtained and growth rates were equivalent to those obtained with limestone. In some cases, the calcium and sulfur content of the plant material was increased significantly by application of FBC residue. For instance, studies conducted in Maryland using apple seedlings showed that FBC residue applied at rates of 1, 2 or 4 times the lime requirement on three different soils resulted in better or equal apple seedling growth when compared to a non-calcium fertilizer control or calcium carbonate applied at the lime requirements (3). The largest growth responses were obtained when FBC residue was applied at rates equivalent to lime requirement for each soil. When FBC residue was applied at eight times the lime requirement, severe growth reduction occurred.

Greenhouse studies with pecan seedlings in Georgia indicated a significant increase in growth and calcium and magnesium concentrations in seedlings that were treated with equivalent rates of FBC residue generated from dolimite sources. Similar results were obtained using peach seedlings. The use of dolimite in the FBC process would certainly enhance the value of the FBC residue for agricultural uses because of the need for larger amounts of magnesium on most acid soils throughout the Eastern United States.

Other plant species tested in environmental growth chamber and greenhouse conditions include several grass and legume species, various vegetable crops, small grain species, buckwheat and blueberries.

Field studies using most of the major agricultural crops are in progress throughout the Eastern United States representing most major soil series and environmental conditions. Studies extend from Massachusetts to Georgia. Field studies are in progress utilizing apple and peaches as test crops near Amherst, Massachusetts; New Brunswick, New Jersey; Raleigh, North Carolina; Beltsville, Maryland; and peaches and pecans at Byron, Georgia. Studies with forage and grain crops are underway in Virginia, Delaware, Pennsylvania, West Virginia, Kentucky, Maryland, and South Carolina. Vegetable and horticultural crops are being grown in many of the above states using FBC residue.

The results of several field experiments are presented to give an idea of the effect of FBC residue as compared to regular agriculture lime treatment on elemental composition of several plant species. Since no differences in yield were obtained, between FBC residue and lime treatments, only the elemental composition of various plant parts will be given. Elemental analysis of first year field results for corn, soybean, and oats are given in Tables 3 and 4. First year results for broccoli, lettuce, beets and snapbeans are presented in Table 5 for different edible plant parts, i.e., infloresence leaves, roots and pods.

In Table 3 are given the elemental composition of corn leaves and grain, and soybean leaves and grain grown with FBC and calcium hydroxides treatments in field studies at Morgantown, West Virginia. The FBC treatment, when compared to the calcium hydroxide treatment, showed only significant increases in levels of sodium and copper in corn grain and a significant decrease in potassium in corn leaves. Soybean leaves showed increases in calcium and sodium levels and a decrease in potassium level with FBC residue applications. Soybean grain actually had significantly lower cadmium level in the FBC treatment than in the calcium hydroxide treatment. Since soybeans normally have a tendency to accumulate cadmium in the grain, this is of special interest.

Oat grain did show a significant increase in cadmium level with FBC applications (Table 4). Although this increased level is still within a safe range, such increases, if consistent from year to year, could limit the rate of applications of FBC to crop land. Therefore, when repeated application of FBC residue are applied to land over an extended period of time, plant uptake of heavy metals should be carefully monitored. Oat straw showed a significant increase in zinc concentrations with application of FBC residue (Table 4). This increase is probably beneficial since many forages contain inadequate amounts of zinc for nutrition of grazing animals.

TABLE 3 Elemental composition of corn leaves and grain and soybean leaves and grain grown with FBCW and $Ca(OH)_2$ (1978, Morgantown, WV).

Element	Corn				Soybean			
	Leaves		Grain		Leaves		Grain	
	FBCW	$Ca(OH)_2$	FBCW	$Ca(OH)_2$	FBCW	$Ca(OH)_2$	FBCW	$Ca(OH)_2$
	Percent Dry Matter							
Ca	1.05	0.93	0.02	0.02	2.14	1.93*	0.26	0.28
Mg	0.22	0.22	0.14	0.13	0.27	0.28	0.25	0.24
K	1.92	2.05*	1.03	1.02	1.31	1.42*	1.70	1.70
N	3.16	2.85	1.54	1.65	3.77	4.24	5.79	5.97
P	0.32	0.31	0.40	0.35	0.24	0.28	0.49	0.50
S	0.43	0.45	1.49	1.48	0.28	0.30	0.33	0.33
	ug/g Dry Matter							
Na	246	243	64	50*	358	339*	256	240
Fe	162	158	23.4	19.7	148	153	73	111
Zn	45	42	38.5	36.6	41.0	45.5	45	44
Mn	75	73	4.53	2.98	102	105	31	35
Cu	16.6	14.4	3.19	2.68*	8.72	9.71	13.4	13.0
Al	59	60	31.1	29.0	43.3	59.7	16.4	43.9
Ni	1.95	2.08	1.28	1.10	5.02	4.37	3.56	3.32
Sr	12.1	9.5	0.17	0.72	26.8	21.4	5.50	5.79
Cr	1.88	1.68	1.30	1.30	3.54	3.46	0.09	0.10
Cd	0.26	0.31	0.05	0.08	1.71	1.54	0.09	0.15*
Pb	6.00	5.73	0.20	0.30	24.3	22.4	0.16	0.22
Co	1.90	1.80	0.43	0.55	19.3	17.0	0.35	0.18
N/S ratio	7.45	6.53	10.4	11.2	13.7	14.0	18.5	17.7

*Indicates that means are significantly different ($P < .05$) by Duncans Multiple Range Test.

TABLE 4 Elemental composition of oat herbage, grain and straw grown with FBCW and $Ca(OH)_2$, (1978, Morgantown, WV).

Element	Herbage		Grain		Straw	
	FBCW	$Ca(OH)_2$	FBCW	$Ca(OH)_2$	FBCW	$Ca(OH)_2$
	Percent Dry Matter					
Ca	0.53	0.51	0.09	0.09	0.50	0.50
Mg	0.20	0.19	0.12	0.12	0.16	0.15
K	2.00	2.05	1.15	1.16	1.82	1.61
N	0.99	1.04	2.73	2.66	1.31	1.36
P	0.37	0.38	0.48	0.48	0.19	0.17
S	0.34	0.33	0.22	0.22	0.19	0.18
	ug/g Dry Matter					
Na	275	380	108	101	397	436
Fe	723	378	603	755	511	425
Zn	50	51	49	44	25	21*
Mn	108	83	85	68	78	75
Cu	10.7	12.0	8.5	6.0	10.4	5.9
Al	1020	1362	277	200	359	542
Ni	4.0	9.3	3.1	3.1	2.3	1.9
Sr	17.5	18.0	1.72	1.56	11.6	11.1
Cr	3.45	3.00	2.68	2.58	3.00	2.70
Cd	0.87	0.87	0.10	0.04*	0.06	0.70
Pb	2.33	3.05	0.70	0.78	1.73	2.83
Co	2.53	2.45	4.98	4.88	3.55	4.17
N/S ratio	11.1	11.6	11.0	12.5	6.78	7.47*

*Indicates that means are significantly different ($P < .05$) by Duncans Multiple Range Test.

Vegetable crops showed very few differences in elemental concentrations between FBC and calcium hydroxide treatments. Zinc did have a tendency to increase in lettuce leaves. However, this increase would be more beneficial than harmful. It should be pointed out that different plant species accumulate elements at different levels (Tables 3, 4 and 5). For instance, lettuce and soybean leaves have dangerously high levels of lead, even in the calcium hydroxide check area. Therefore, it is very important to use several species to evaluate the effects of FBC on the food chain.

The final phases of the research program will involve extensive metabolic testing of various food and feed products with small animals, large animals and using human subjects. In these studies, animals will be fed plant material grown with either FBC residue or with those grown with regular limestone. Pending favorable results with the animal trials, a human nutrition study is being formulated in cooperation with the West Virginia University Animal Science Division, the Human Nutrition Department, and West Virginia University Medical Center. Complete diets will be formulated from food grown with both FBC and with calcium hydroxide treated land. These diets will include meats, poultry, and dairy products as well as fruits, vegetables, and nut crops.

SUMMARY

A comprehensive research program is in progress to evaluate the potential of using FBC residue for agricultural uses throughout the Eastern United States. The results with field, greenhouse, growth chamber and laboratory studies indicate that the material can be used effectively for food and feed productions. At the present time we have found little evidence to indicate that this material would be detrimental to the food chain. However, studies with plants only indicate the short term effect of FBC residue on heavy metal uptake. It is absolutely essential that studies be conducted over a long period of time with repeated applications to the soil before final conclusions can be drawn. The soil is not a static situation and is continuously changing. Repeated heavy applications of FBC residue to the soil could cause a slow building of certain toxic heavy metals, or solubility and availability to plants can change with time. Therefore, we must evaluate soil management practices relative to FBC residue applications to crop land under as many different environmental conditions as possible before final judgment is made.

TABLE 5 Elemental compcsition of broccoli, lettuce, beets, and snap beans grown with FBCW and $Ca(OH)_2$ (1978, Morgantown, WV).

Elements	Broccoli		Lettuce		Beets		Snap Beans	
	FBCW	$Ca(OH)_2$	FBCW	$Ca(OH)_2$	FBCW	$Ca(OH)_2$	FBCW	$Ca(OH)_2$
	Percent Dry Matter							
Ca	0.46	0.51	1.53	1.63	0.16	0.16	0.48	0.48
Mg	0.17	0.19	0.27	0.26	0.27	0.22	0.20	0.19
K	2.62	2.48	3.18	2.62	2.52	2.56	2.10	2.18
N	6.14	6.18	2.85	2.72	2.50	2.37	3.01	3.13
P	0.86	0.86	0.38	0.35	0.30	0.30	0.43	0.43
S	1.55	1.56	0.33	0.31	0.16	0.14	0.21	0.20
	ug/g Dry Matter							
Na	579	619	1274	1278	436	708	182	178
Fe	91	134	927	867	69	58	73	75
Zn	80	85	40	36*	42	39	30	31
Mn	20	21	104	93	32	28	15	14
Cu	6.0	6.3	8.2	7.7	11.4	10.3	6.6	7.0
Al	17	15	1117	968	13.2	13.7	30	32
Ni	2.26	2.19	1.46	1.48	0.80	1.22	2.48	2.25
Sr	11.6	14.3	23.6	26.0	9.06	8.18	6.01	6.06
Cr	1.16	1.57	3.37	3.34	1.67	1.54	1.43	1.48
Cd	0.08	0.09	0.67	0.69	0.27	0.39	0.10	0.04
Pb	1.71	0.63	8.50	8.45	0.31	0.13	0.55	0.35
Co	0.87	0.88	0.38	0.62	0.41	0.69	1.18	1.25
N/S	3.96	3.96	9.30	9.35	15.5	17.3	14.3	16.1

*Indicates that means are significantly different ($P < .05$) by Duncans Multiple Range Test.

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STATUS REPORT ON INVESTIGATIONS DEALING WITH COMMERCIAL USES FOR ATMOSPHERIC FLUIDIZED BED COMBUSTION RESIDUES

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In November 1976 the U.S. Department of Energy established a research project under Contract No. EF-77-C-01-2549 to evaluate the solid waste from fluidized bed systems for potential commercial uses. In addition, the investigation includes developing methods by which the material can be safely disposed of should commercial applications be slow in developing, or not of sufficient magnitude to account for utilization of all of the waste materials. The program has involved several phases of activity and has used material from eight sources of supply.

Most of the work has been carried out on the fluidized bed drain. The availability of fly ash has been somewhat limited since many of the systems have not finalized the operating design for processing this material. Since it is important to carry out investigations using representative type materials, it has been necessary to delay this part of the project. However, fly ash samples have recently been received from the fluidized bed boiler at Alliance, Ohio and from Georgetown University, and this material has now been incorporated into the ongoing program.

The first phase of the investigation is directed to characterization of the products. This includes the usual wet chemical and physical tests (such as sieve analysis, density, porosity, etc.), X-ray diffraction, optical microscopy, and scanning electron microscopy. Since these materials contain substantial quantities of free lime base, reactivity tests have been used to establish the availability of the free lime, as well as the rate of hydration when mixed with water. An important property which all of the bed drain materials possess is the cementitious characteristics of the residue when used in conjunction with supplementary materials, particularly pulverized coal fly ash. Cementitious reactivity tests have, therefore, been included in the characterization program.

With respect to the fly ash material, it is to be noted that due to the low temperature in the fluidized bed combustion, this material does not resemble the fly ash conventionally produced in pulverized coal boilers. The lack of the small size alumina siliceous glass in the AFB fly ash does not provide the typical pozzolanic reactivity found in pulverized coal fly ash. In addition, the samples that have been received are very high in loss on ignition which indicates the presence of substantial quantities of unburned carbon.

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It should be noted that the presence of free lime in the bed drain and carbon in the fly ash fraction are desirable from the standpoint of utilization of these by-products. Both the free lime and the carbon have economic value in many of the applications being considered for commercial use of the residues.

Tables I, II, and III provide examples of typical chemical analyses. Figure 1 gives the size range found in the majority of the sources that have been tested. The dotted line in this graph shows the average gradation that is used by the engineering profession for fine or "sand" aggregate as defined by ASTM C 33.

PERFORMANCE TESTS

Following the characterization of the material, a number of performance tests are carried out to establish the feasibility of utilizing these materials in commercial compositions. These tests include programs to determine procedures for modification or beneficiation of the material (for example, crushing and grinding of the bed drain), and techniques for separating the lime constituent from the "as received" product. The residues are then blended with other materials to develop compositions that may be useful, particularly in applications for construction type products. Primarily these compositions are designed to develop products that meet existing engineering specifications that have been developed by highway departments, Bureau of Reclamation, ASTM, American Concrete Institute, etc. Some of these formulations are described below.

Many laboratory tests have been carried out to investigate the ability of the bed drain material to stabilize other waste sludges and products. The evaluation of these compositions involve measurements of unconfined compressive strength, shear value, effect of freezing/thawing and wetting/drying, durability, and dimensional stability.

In addition to the above, extensive tests have been made to establish the performance of the material as a chemical reagent for use in neutralizing trade waste acids in the treatment of acid mine drainage, for use in sewage treatment plants, as a sorbent for SO_x scrubbing systems, and as a general reagent for use in the stabilization of other by-product sludges. Laboratory tests have also been carried out to evaluate some of the problem areas that have been observed in the field tests, such as the expansive characteristics of some of the compositions when used in cementitious structures.

A number of these applications utilize additional additives, particularly supplementary aggregates and pulverized coal fly ash. It has been determined that combinations of pulverized coal fly ash with the free lime base and calcium sulfate dihydrate formed in the pretreatment of AFB bed residue result in a cementitious matrix containing the well known compound ettringite. This ingredient serves as a basis for developing the high strength and durability of the products made with these materials. Figure 2 shows presence of gypsum crystals formed in preconditioned residue. Figure 3 shows presence of large numbers of ettringite rods from sample of cured fly ash-AFB residue.

TABLE I

CHEMICAL ANALYSES OF SEVERAL SOURCES OF BED RESIDUE

	Limestone Sorbents				Dolomite Sorbents	
	Alexandria	Rivesville	Battelle	Alliance	Fluidyne	Exxon
LOI	3.78	3.19	11.79	3.72	10.64	12.63
SiO_2	16.68	13.44	13.88	4.12	16.56	6.14
Al_2O_3	2.64	3.92	2.96	1.76	3.06	0.42
Fe_2O_3	3.66	4.20	14.64	3.14	3.14	4.18
CaO	50.13	47.74	41.87	56.55	27.91	35.99
MgO	1.49	0.96	3.19	0.20	11.47	13.71
SO_4	21.61	28.45	17.72	29.48	21.28	25.75

TABLE II

CHEMICAL ANALYSES OF AFB FLY ASHES

	Alexandria			Alliance		
	Sample #1	Sample #2	Sample #3	Sample #1	Sample #2	Windsor, Conn.
LOI	49.96	44.50	49.40	38.73	11.24	30.16
SiO_2	11.64	17.16	17.48	9.64	3.30	30.18
Fe_2O_3	7.85	7.39	7.80	20.92	13.04	10.86
Al_2O_3	5.35	4.31	6.20	5.28	20.86	7.44
CaO	13.03	17.69	10.98	16.15	30.21	10.07
MgO	1.05	2.64	1.92	1.30	3.26	1.81
SO_3	7.08	6.01	3.22	7.32	17.82	4.23

TABLE III

X-RAY DIFFRACTION DATA FOR AFB RESIDUES

Compound	Source of AFB Residue (Bed Material)					Fly Ash*
	Alexandria	Fluidyne	Battelle	Rivesville	Exxon	Alexandria
	Peak Heights (Direct Measurement at 500 Range Factor)					
$CaSO_4$	48	230	84	120	156	70
CaO	64	-	74	90	-	24
$CaCO_3$	-	73	33	10	114	10
αSiO_2	18	62	37	76	10	52
Fe_2O_3	-	-	-	-	-	23
	Compositional Ranges					
$CaSO_4$	Major	Major	Major	Major	Major	Major
CaO	Major	-----	Major	Major	-----	Minor
$CaCO_3$	-----	Major	Minor	Trace	Major	Trace
αSiO_2	Minor	Major	Minor	Major	Trace	Major
Mixed Iron Oxides	Minor	-----	Minor	Minor	-----	Minor

-----	1% or less
Trace	<5%
Minor	5 - 25%
Major	25+%

*A substantial quantity of carbon (amorphous) appears to be present.

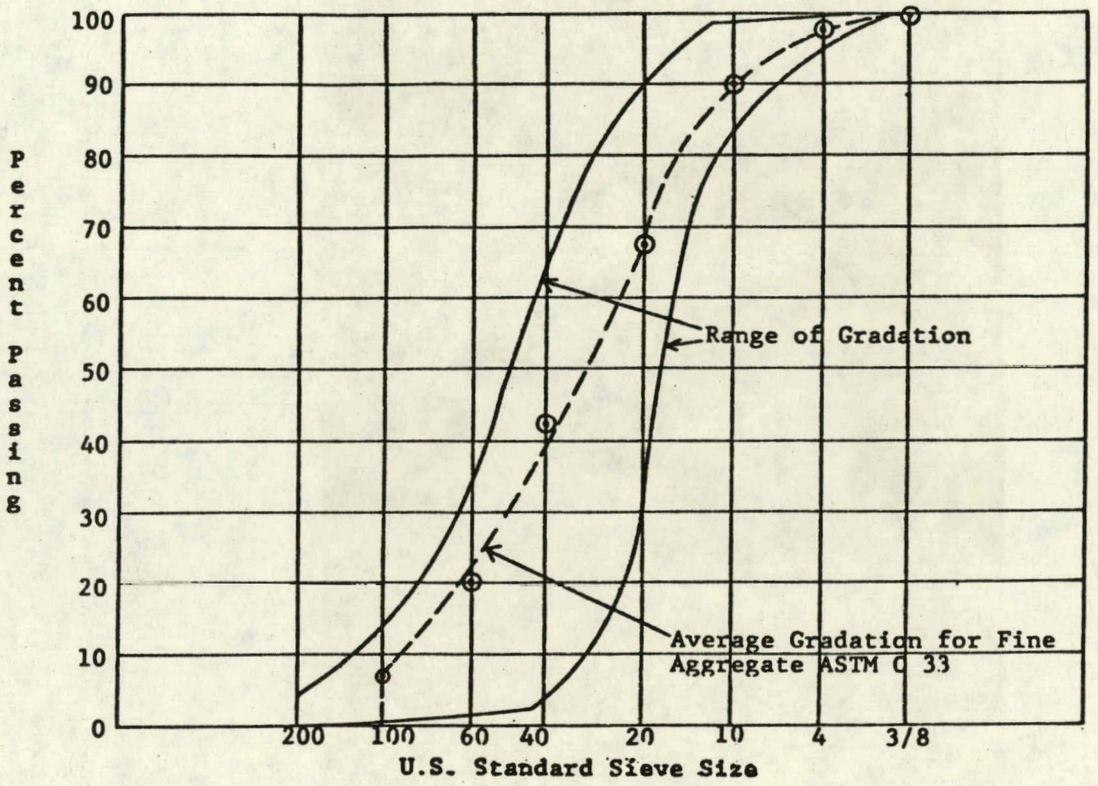


FIGURE 1

GRADATION OF AFB RESIDUE SAMPLES

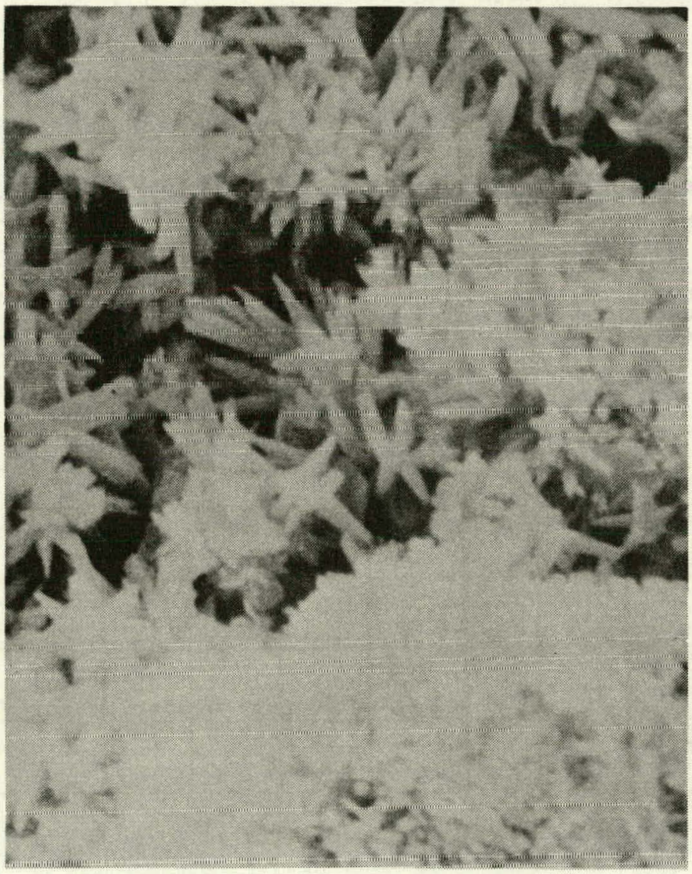


FIGURE 2

HYDRATED AFB RESIDUE SHOWING PRESENCE
OF GYPSUM CRYSTALS (x 10,000)



FIGURE 3

REACTION PRODUCTS OF AFB RESIDUE AND PULVERIZED COAL FLY ASH SHOWING FORMATION OF ETTRINGITE (X 10,000)

It is beyond the scope of this paper to describe these investigations in detail, although some of the results of the program are incorporated into the description of the field demonstrations listed later. The data covering results of these tests are available in quarterly reports and are included in a Users' Manual which is now under preparation

FIELD TESTS

As a supplement to the tests that have been run in the laboratory, a series of tests have been run with commercial hardware. The purpose of this effort is to determine what type of equipment can be used in some of the process steps that are being contemplated for applying the products in the commercial marketplace. Among the types of equipment which have been evaluated are the following:

- Particle size separation by dry tabling
- Blunging and wet tabling
- Air classification
- Magnetic separation
- Elutriation
- Centrifugal separation
- Crushing and grinding
- Hydration and/or slaking of lime

A major concern that has developed in the program is the need for developing proper procedures for handling, storing, and preconditioning of the product. A variety of test programs have been undertaken to study this phase of the problem. These particular tests are also of value in developing suitable procedures for disposal of these residues into landfill type operations. To simply haul AFB bed drain to a dump can create some practical problems and also can be of concern from an environmental standpoint. There is a strong indication that specific process type steps are needed in this area, as well as for developing commercial uses.

DEMONSTRATIONS

Since a major objective of the program is to develop feasibility for specific applications in the commercial market, a number of small scale demonstrations have been carried out and are currently being planned during 1980. A brief description of a few of these is presented in the following tables and photographs.

- *SO_x Scrubber Sorbent*

Two demonstrations have been conducted to evaluate the feasibility of using bed drain material as an SO_X sorbent. One of these used a small pilot

scale horizontal scrubber (Lewis scrubber[1]) which was installed at the Philadelphia Electric Company's Cromby Station in Phoenixville, Pennsylvania. The second test was run on a unit at Southern Illinois University in Carbondale, Illinois. This latter is a wet scrubbing system consisting of a 1500 cfm, two stage open throat (coal burning) boiler system. Figure 4 is a schematic of the set up at the Cromby Station. Figure 5 shows the system used at SIU. Figure 6 illustrates the procedure that was used to prepare the sorbent for applications to the system.

Slaking is achieved by batching the AFB residue with water in a tank equipped with a lightning propellor type mixer. In several instances steam was used to help agitate the mixture as the residue is added slowly to the water. Slaking of the lime increased the ambient water termperature to about 130°F. As soon as the agitation is terminated, the grit settles quickly to the bottom and the supernatant liquor is pumped off into the storage tank used to feed the scrubber.

Table IV gives one set of data using flue gas from the combustion of 2.42 percent sulfur coal.

The bleed stream from the scrubbing system passes to a 5' diameter thickener from which it is pumped to a 3' x 1' diameter rotary vacuum filter. The sludge from the filter which was approximately 40 percent solids was then blended with the grit from the slaking operation. Since the scrubber received small quantities of fly ash from the boiler, the composition that was obtained was sufficient to develop a stabilized mix when placed in a disposal site. The strength of this was adequate for structural and field purposes. Figure 7 presents a block diagram and a material balance for one of the test campaigns on the SIU system.

- *Road Base Demonstrations*

In cooperation with the Ohio Department of Transportation, a road project was carried out in the early fall of 1978 using the design requirements and material specifications provided by ODOT for conventional stabilized road base.[2] A section of roadway was selected which required 6" thickness of stabilized base 25' wide. The three mixes selected are those given in Table V. Included in the table are the quantities of composition used and length of each section of roadway.

A major concern in connection with any road construction project is the question of adequate stockpiling of material in order to schedule delivery in

[1]Clifford J. Lewis, "Lime, Limestone Employed in New Gas Scrubbing Concept", Pit & Quarry, July 1973.

[2]State of Ohio Department of Transportation Supplemental Specification 835, Aggregate Lime-Fly Ash Base, January 13, 1977.

FIGURE 4

SCHEMATIC DIAGRAM OF SO_X SCRUBBER UNIT

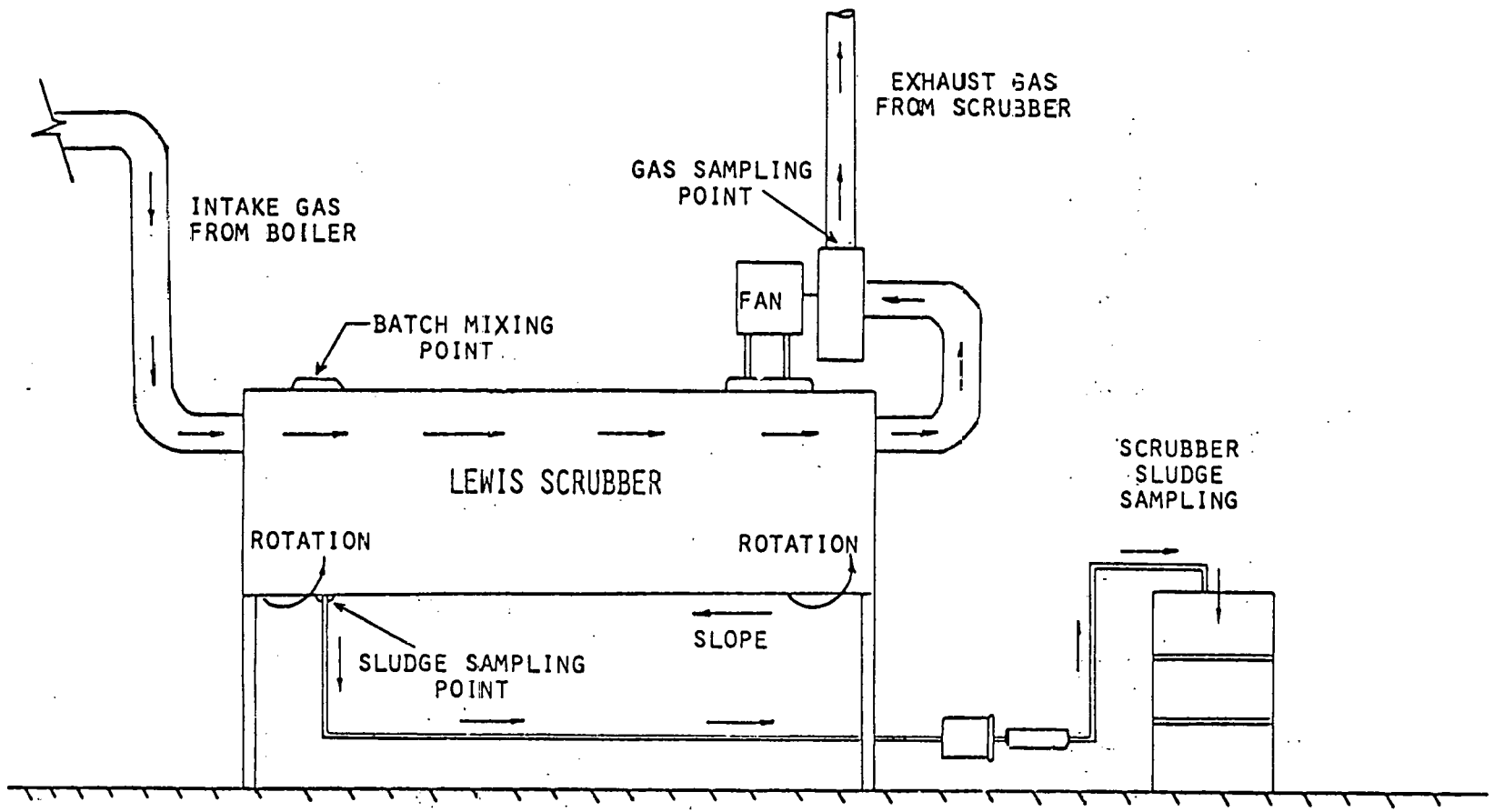


TABLE IV

SCRUBBING SYSTEM OPERATING CONDITIONS

Scrubbing with slaked AFB spent sorbent using flue gas from the combustion of 2.42 percent S coal and 1.58 percent solids (0.82 percent $Ca(OH)_2$) feed slurry at 88.9 percent SO_2 removal. (Based on saturated gas)

	ΔP, "H_2O	v_t, ft/sec	L/G gal/1000 acf	Temp. °F	pH	% Solids	Average tank holdup, min
#1 Venturi	4½	89	25.7				
#1 Separator	1		12.4				
#1 Recycle tank				130	7.3	5	35
#2 Venturi	2	53	29.5				
#2 Separator	1½		8.6				
#2 Recycle tank				128	7.5	3½	35

TABLE V

MIX PROPORTIONS, LABORATORY TESTS, AND QUANTITIES OF AFB PRODUCTS USED IN OHIO ROAD BASE DEMONSTRATION

Mix	Composition (% by Weight)	Demonstration Statistics		Laboratory Tests			
		Average Length of Section (Feet)	Amount Placed (Tons)	Compressive Strength (psi)**		Durability	
				7 Days @ 73° F	7 Days @ 100° F	Vacuum Saturation*** (psi)	Freeze/Thaw**** (% Loss)
A	40% Aggregate* 30% Alliance AFB Residue 30% Fly Ash	50	40	873	1578	1259	0.41
B	75% Aggregate* 15% Alliance AFB Residue 10% Fly Ash	75	60	838	1252	1483	0.60
C	75% Aggregate* 15% Battelle AFB Residue 10% Fly Ash	66	60	222	838	784	0.62

*Canton gravel meeting ODOT 301 specifications
**Average of 3 individual values
***Tested in accordance with ASTM C 593
****Tested in accordance with ASTM D 560

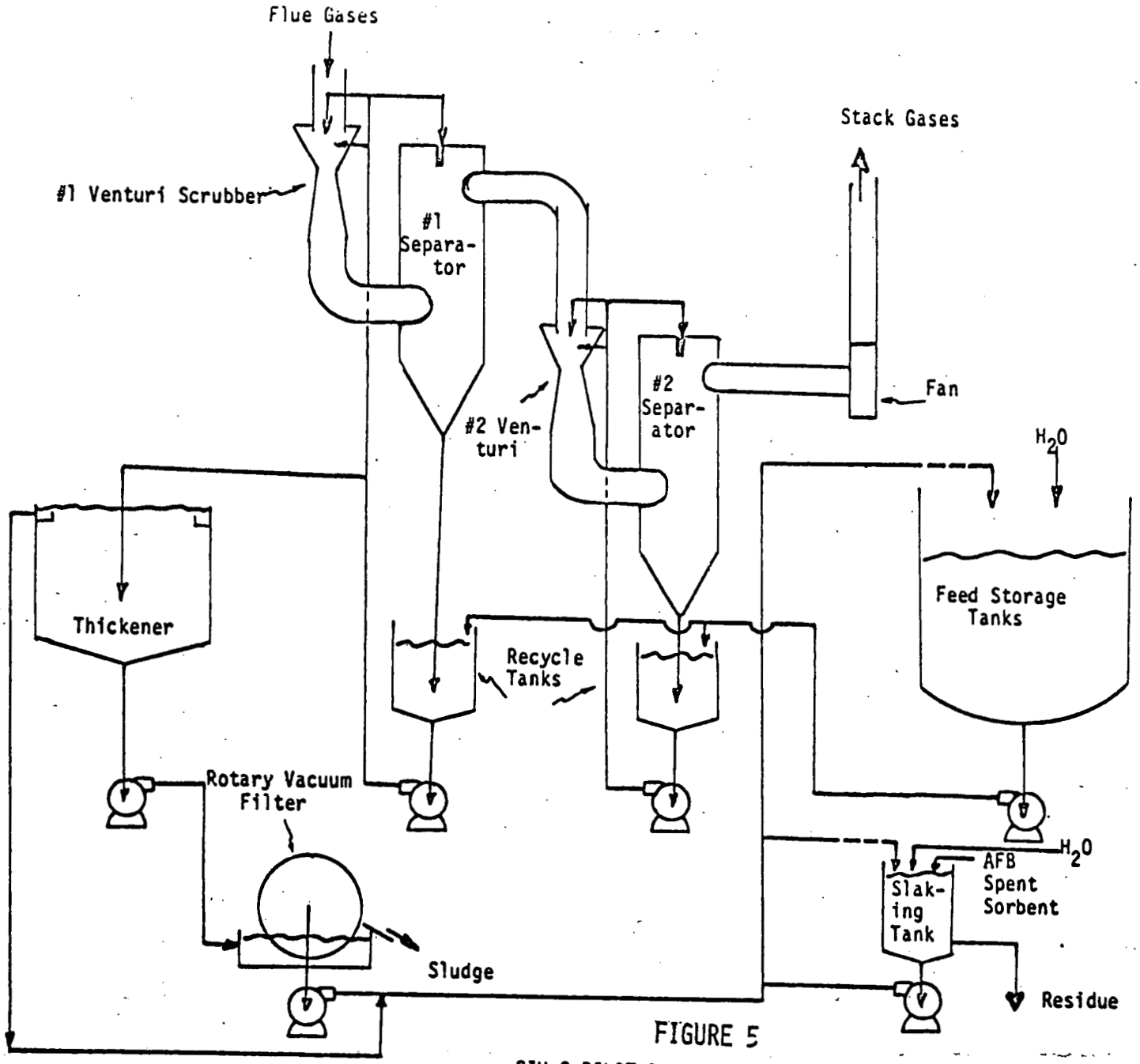


FIGURE 5

SIU-C PILOT PLANT SCRUBBING SYSTEM

FIGURE 6

SLAKER - EXTRACTOR PROCESS

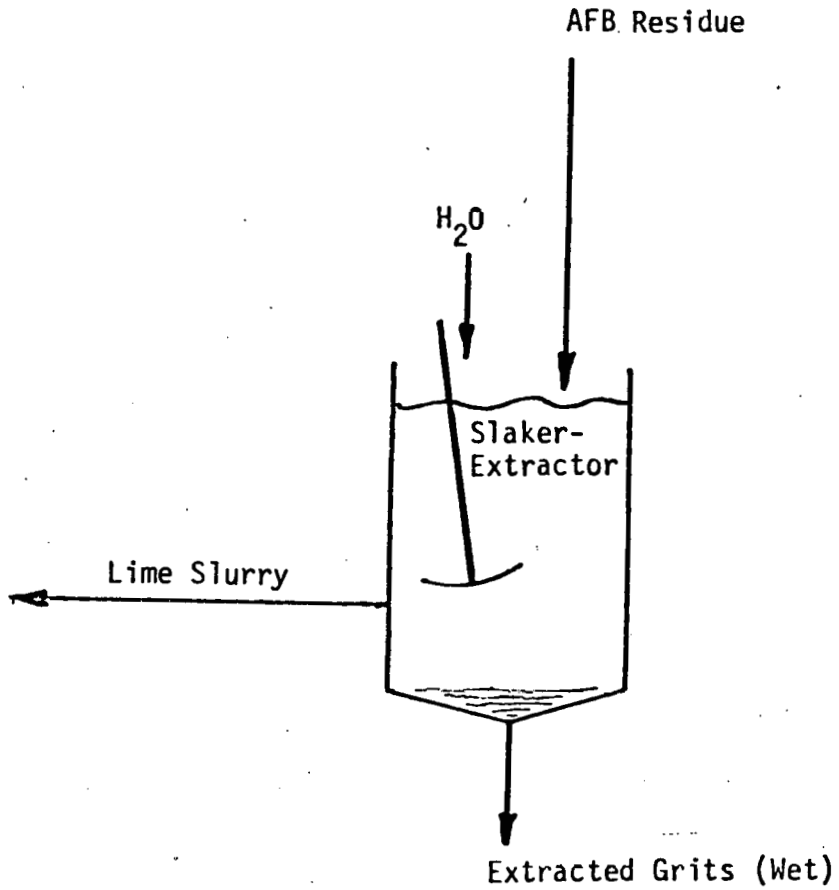
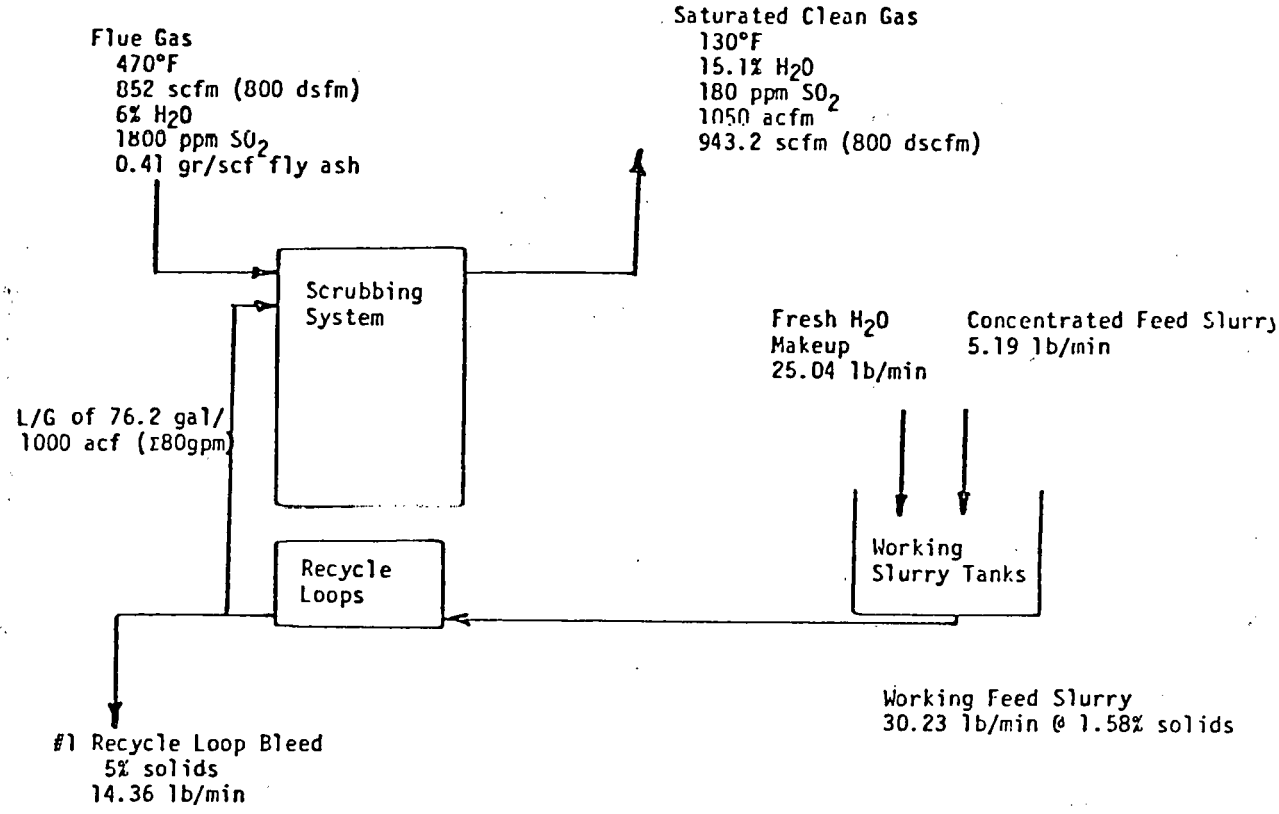


FIGURE 7

Scrubbing System Block Diagram for 88.9% SO_2 Removal



accordance with the contractor's requirements. Therefore, the procedure used for preparing the material involved a premixing of the residue with aggregate and water several weeks in advance of the construction schedule. The stockpiled material was then subjected to a final mixing operation at the time the product was scheduled for shipment to the job. At this point the fly ash and supplementary water were added to provide the desired optimum proportions of all the ingredients in the mix. Figure 8 and 9 show views of the stockpiled material.

Figure 10 shows the mixing operation which was located at the John D. Tonkovich & Son, Inc. plant in Shadyside, Ohio. This plant has been used for a number of years to prepare lime/fly ash/aggregate mixtures for similar type applications. The mixing operation employs a Barber-Greene pug mill with a capacity of approximately 400 tons per hour. Figure 11 is a photograph showing the application of the composition at the construction site. The base course received a final application of an asphaltic mix and wearing course as conventionally used in the State of Ohio.

Several weeks after placing the base, one of the compositions developed linear expansion similar to that which occurs with steel slag aggregate that has not been adequately cured before use. The problem mixture evidentally had not been preconditioned sufficiently to allow the intermediate mixture to completely stabilize. Similar experience has been noted in structural compositions using pulverized coal fly ash derived from lignite and subbituminous coal. In order to properly precondition the latter material before use, the fly ash is first blended with water, then allowed to "cure" for several weeks in a stockpile, after which it is pulverized to a uniform fineness.

An extensive laboratory program, which included preparation of small field plots, was undertaken to study the expansion characteristics of a number of AFB bed materials. While many of the long-term data are not yet available, significant progress has been made in establishing procedures which assure elimination of this problem. Table VI summarizes a few results to illustrate the range and variation obtained with the test compositions.

A number of stockpiles have been prepared of the intermediate product and have been tested periodically to determine the effect of aging on the properties of the final mix.

A second demonstration was carried out in December 1979 in Canton, Ohio. This particular demo has been designed to determine if the laboratory program has adequately developed a procedure for controlling the expansion observed in the program mentioned above. The AFB residue was preconditioned in a commercial fly ash plant at the American Admixtures Corporation conditioning plant in Chicago, Illinois. Figures 12 and 13 show this operation. Figure 14 shows the dimension and mix proportion of the formulations that were placed in this demonstration, as well as the location of control points set in the surface of each test section for use in monitoring dimensional stability that will be carried out during 1980.



FIGURE 8

STOCKPILE OF PREMIXED BLEND OF
BATTELLE RESIDUE AND AGGREGATE

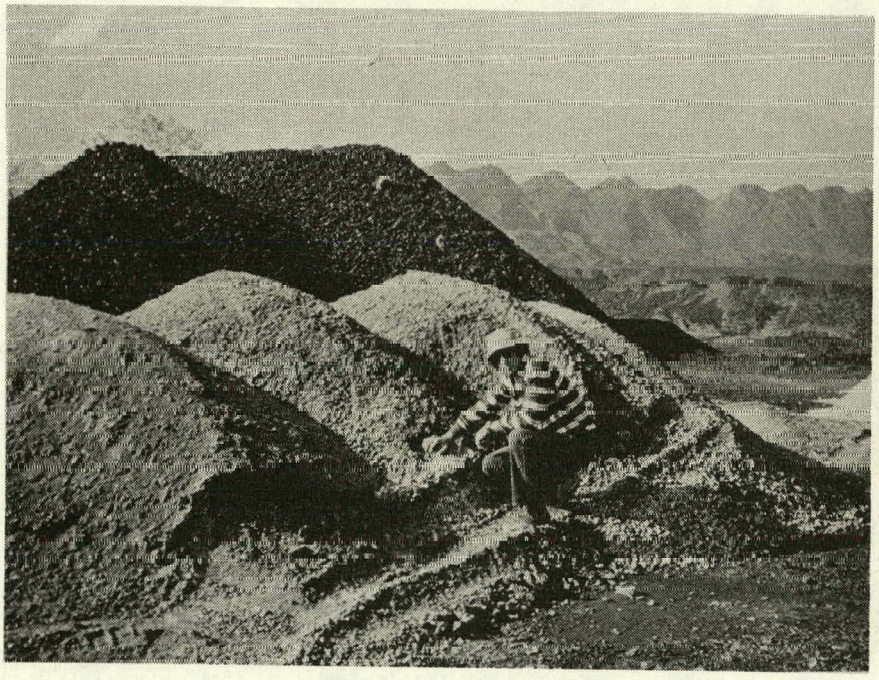


FIGURE 9

STOCKPILE OF PREMIXED BLEND OF
ALLIANCE RESIDUE AND AGGREGATE

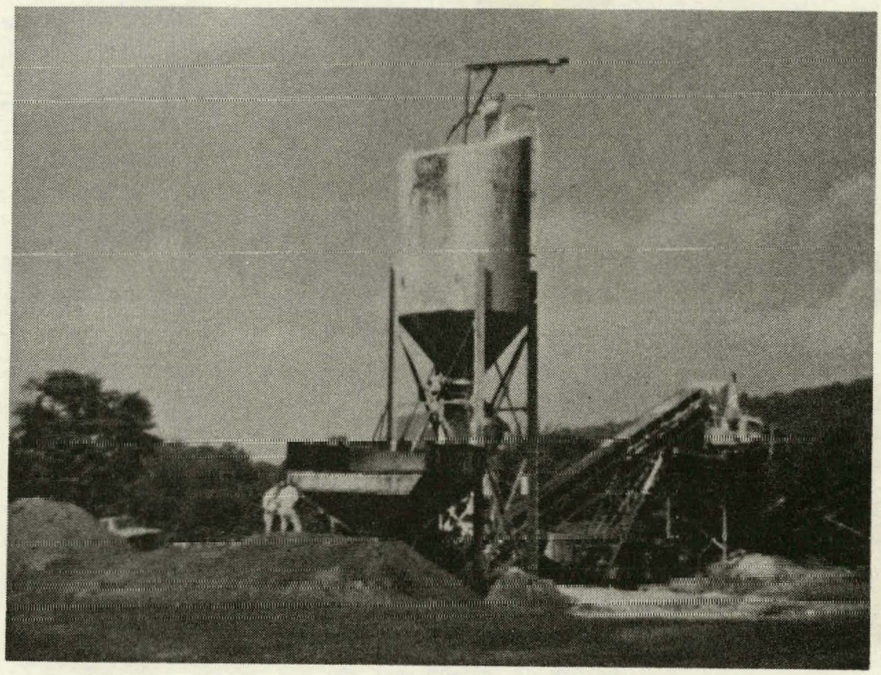


FIGURE 10

VIEW OF STABILIZATION PLANT

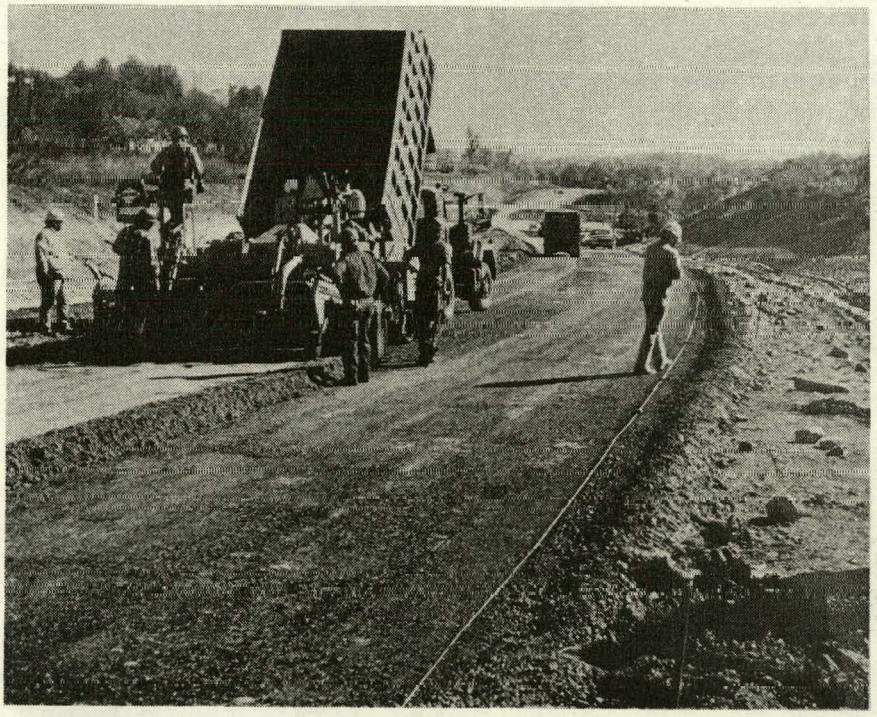


FIGURE 11

SPREADING OF AFB COMPOSITION ON PREPARED SUBBASE

TABLE VI

CHANGE IN LENGTH OF 1" x 1" x 12" EXPANSION BARS CONTAINING CONDITIONED RESIDUE[1]

(AFB residue from Alliance plant, conditioned at American Admixtures plant in Chicago, Illinois)

Sample Designation[2]	Mix Composition (%)			100°F Curing Temperature Change in Length (%) (Number of Days)				73°F Curing Temperature Change in Length (%) (Number of Days)			
	Sand Aggregate	AFB Residue	Fly Ash	7	28	60	120	7	28	60	120
Cr 25%	75	5	20	.04	.06	.05	.05	.03	.09	.10	.10
	70	10	20	.05	.14	.15	.13	.03	.11	.20	.27
	50	15	35	.08	.29	.40	.28	.05	.22	.29	.51
U_1 32%[3]	80	5	15	.05	.06	.04	.04		Broken		
	80	5	15	.05	.05	.04	.04[4]		Broken		
	70	10	20	.08	.10	.10	.10		Broken		
	50	15	35	.11	.16	.16	.15	.04	.12	.18	.22
U_2 32%	75	5	20	.03	.02	.01	.01[4]	.02	.01	.01	.02
	80	5	15	.02	.02	.02	.02[4]	.01	.04	.04	.04
	70	10	20	.03	.06	.06	.06[4]	.03	.13	.17	.15
	75	5	20	.01	.01	.01	.01[4]	.00	.01	.01	.01
	50	15	35	.06	.14	.14	.13	.04	.12	.16	.18
U_3 25%	70	10	20	.05	.05	.05	.05[4]		Broken		
	80	5	15	.03	.04	.04	.04[4]	.03	.03	.03	.04
	50	15	35	.08	.10	.10	.12[4]	.08	.10	.11	.13
	75	5	20	.04	.06	.10	-		Broken		

[1]AFB residue from Alliance and conditioned at American Admixtures plant in Chicago, Illinois.

[2]Sample Designation: Cr - Crushed
U_1 - Uncrushed - Batch No. 1
U_2 - Uncrushed - Batch No. 2
U_3 - Uncrushed - Batch No. 3
25% - Percent of water by weight used for conditioning

[3]U_1 - 40 Percent conditioning water was originally added. The mix was brought to 32 percent moisture by blending additional dry material.

[4]After 60 days, these bars were stored at 55°F.

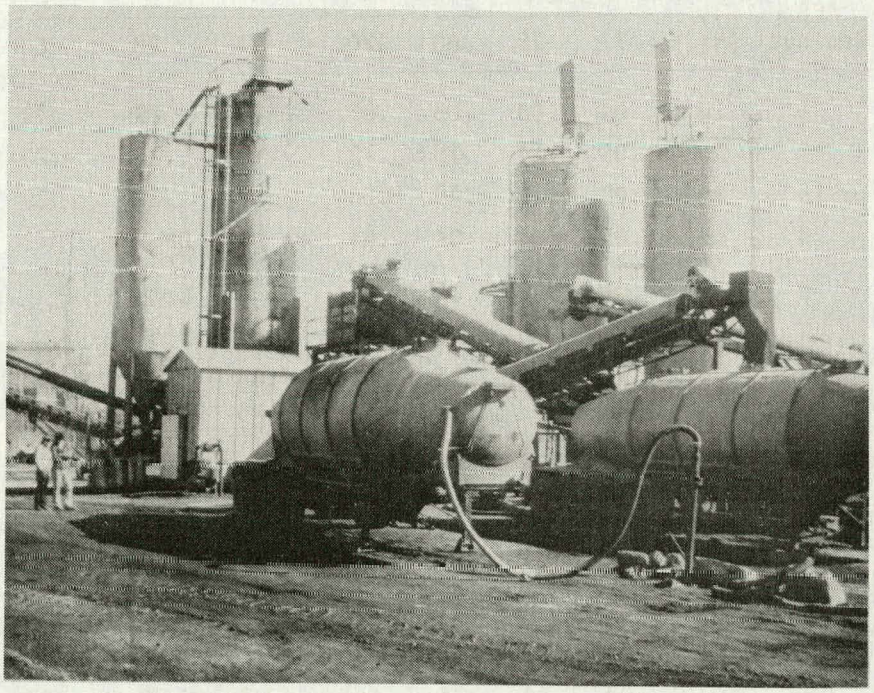


FIGURE 12

FLY ASH CONDITIONING PLANT AT AMERICAN ADMIXTURES CORPORATION, CHICAGO, ILLINOIS

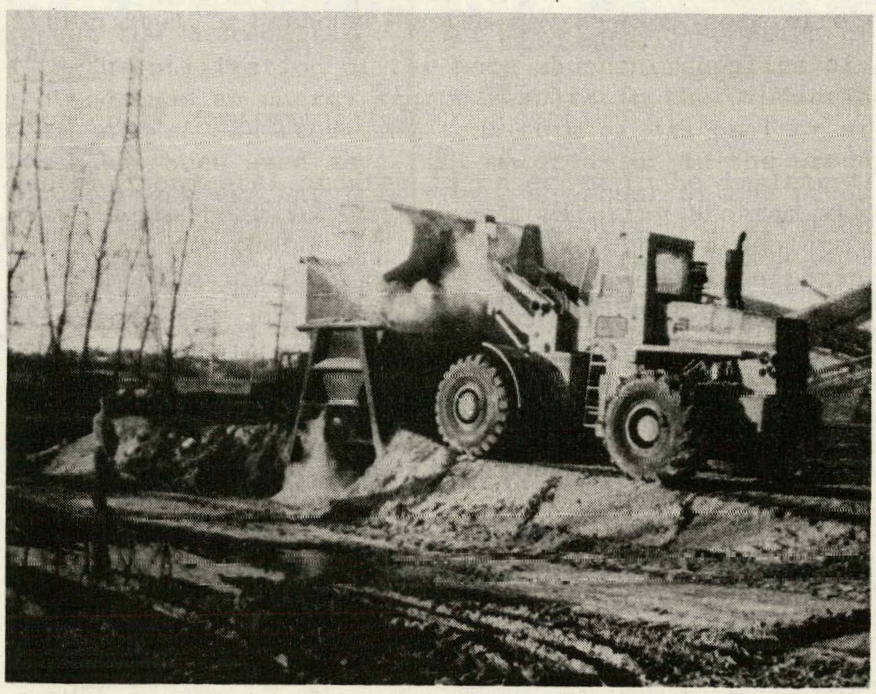
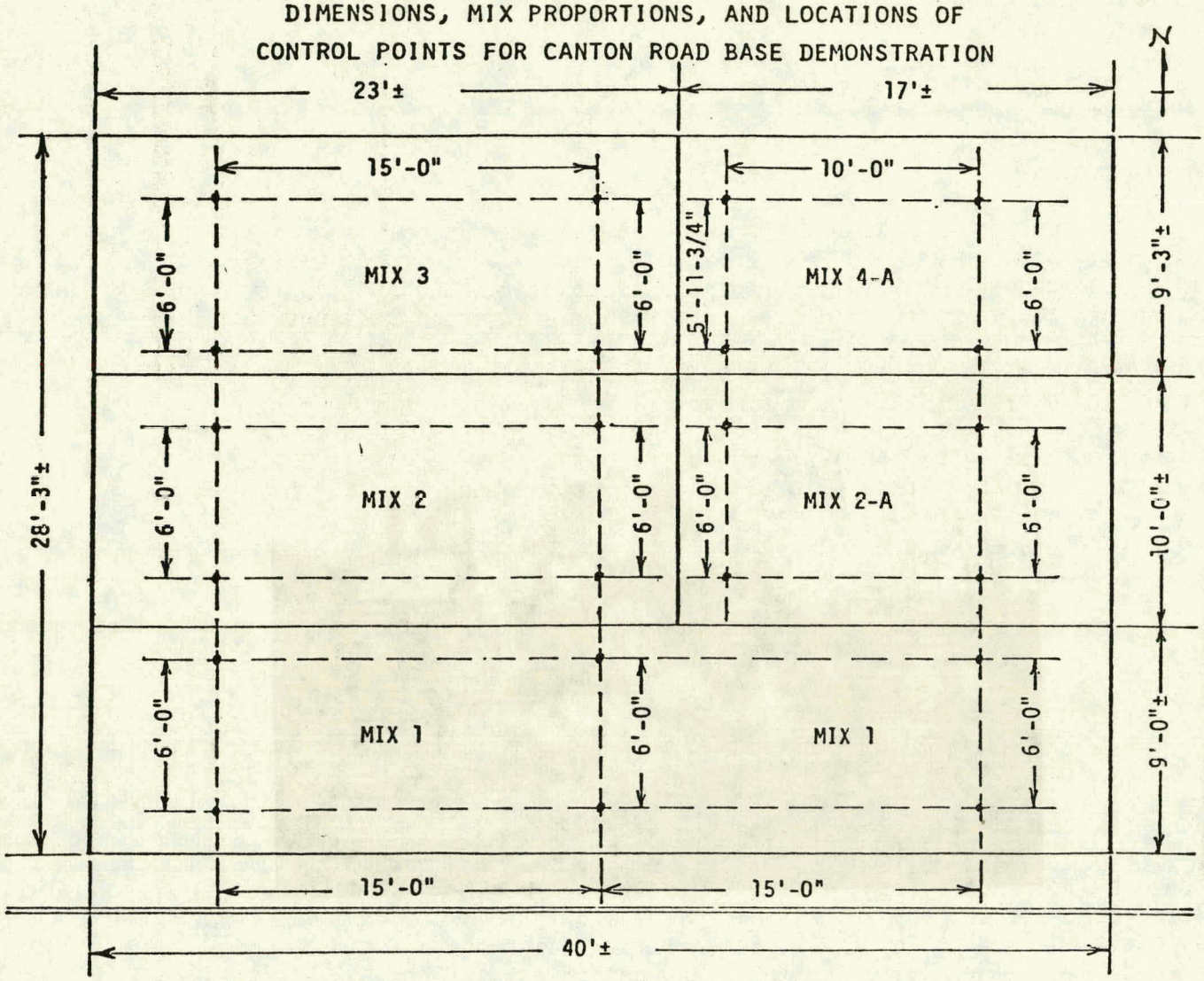


FIGURE 13

AFB RESIDUE BEING FED THROUGH SCALPING SCREEN INTO CONDITIONING PLANT

FIGURE 14

DIMENSIONS, MIX PROPORTIONS, AND LOCATIONS OF CONTROL POINTS FOR CANTON ROAD BASE DEMONSTRATION



Mix	AFB Residue Preparation	Percent Aggregate	Percent AFB Residue	Percent Fly Ash
1	As Received	50	15	35
2	As Received	70	10	20
2-A	Pre-crushed	70	10	20
3	Pre-crushed	75	5	20
4-A	Pre-crushed	80	20	-

- *Structural Masonry Units*

On January 28, 1979 approximately 400 concrete masonry units were molded using AFB residue from the pilot plant in Alexandria, Virginia. The work was performed at the Kurtz Brothers concrete block plant in Ephrate, Pennsylvania.

The control mix was batched at the normal operating capacity of the equipment, both before and after the test program. The trial batches of masonry block were initially cured in a steam heated tunnel kiln for 24 hours at approximately 130°F. The block specimens were stored on trays which were placed in frames of 426 blocks each. The frames were placed in the curing chamber in the order in which the batches were prepared. After the initial overnight cure, they were removed and after two days blocks from each batch were tested in accordance with ASTM C 140, "Sampling and Testing Concrete Masonry Units." Table VII summarizes the batching proportions, compressive strength at 30 days, unit weight, and absorption properties of the mixtures. The color and texture of the test mixes are lighter and finer than the control. Lighter color and fine texture are two features which are promoted in the Lancaster County, Pennsylvania area.

Based on these tests, it appears that AFB residue can be substituted for 40 to 50 percent of the conventional aggregate presently used in block manufacturing and continue to produce block of superior quality. Secondly, the performance of Mixes 1 and 2 suggests that a possible reduction of 20 to 30 percent of portland cement content can provide a product with equal or superior compressive strength potential.

The second block demonstration was conducted January 26, 1980 at the Calcite Block Company in Lebanon, Pennsylvania. The AFB residue was conditioned by means of a ready-mix concrete truck on January 21, 1980 at the Allied Concrete Company in Dresher, Pennsylvania. The conditioned residue was elevated into an aggregate bin for storage and subsequently weighed and batched by conventional equipment. The conditioned or pre-hydrated AFB residue presented no problems in handling with moisture contents ranging from 4 to 19 percent.

A total of eight mixes were investigated for the production of masonry block. Two control mixes and five test mixes were batched during the demonstration program to make 8" x 8" x 16" 2-core hollow masonry units and one additional mix was also used to make solid 8" x 8" x 16" units. The formulations of the seven block mixes that were used in the demonstration to produce hollow blocks are summarized in Table VIII. The results of density and absorption tests performed on these blocks in accordance with ASTM C 140 are summarized in Table VII .

The solid blocks have been included in an experimental reef block program being conducted by the Marine Sciences Research Center of the State University of New York. Figures 15 and 16 show the operation at the Calcite Block Company plant.

TABLE VII

MIX DESIGN AND TEST RESULTS FOR CONCRETE MASONRY UNITS

Composition (Pounds per Cubic Yard)	Mix Designation		
	Control	Mix 1	Mix 2
Portland Cement - Type I	328	349	327
Limestone Screenings (3/8")	3635	2044	1918
Pulverized Coal Fly Ash	71	215	404
AFB Residue	0	1077	1010
Water	246	358	348
Total Weight per Cubic Yard	4279	4043	4008
Compressive Strength @ 30 Days Age	820 psi	1070 psi	1453 psi
Dry Unit Weight @ 30 Days Age	130.7 pcf	119.5 pcf	131.3 pcf
Absorption	8.1%	10.8%	6.9%
% Compaction (Based on theoretical dry unit weight)	87.5%	87.6%	96.8%

TABLE VIII

TRIAL BLOCK FORMULATIONS USED IN MASONRY BLOCK DEMONSTRATION PROGRAM

(Calcite Block Company)

	Mix No.						
	1	2	3	4	5	6	7
Moisture Content (%)	6.2	8.6	8.7	5.7	8.3	20.5	20.2
Wet Block Weight (lbs)	41.9	37.3	34.8	37.9	36.7	27.2	27.3
FORMULATION (% Dry Weight Basis)							
Aggregate	92.6	56.4	57.5	90.4	59.4	-	-
AFB Residue	-	28.2	34.5	-	28.5	82.1	78.1
Fly Ash	-	6.4	8.0	2.5	6.2	17.9	17.1
Cement	7.4	8.9	-	7.1	5.7	-	4.7
ACTUAL WEIGHT BATCHED (lbs)							
Aggregate	3654	910	890	3654	966	-	-
AFB Residue	-	455	533	-	464	1000	1000
Fly Ash	-	103	124	100	100	218	220
Cement	290	144	-	290	96	-	60
Approximate Unit Count	96	39	28	105	45	27	45
Theoretical Unit Count	100	47	48	111	48	54	56
Total Batch Weight Dry (lbs)	3944	1612	1547	4044	1626	1218	1280
Total Batch Weight Wet (lbs)	4189	1750	1680	4275	1761	1468	1539
Theoretical Wet Batch Weight per 100 Blocks	4190	3730	3480	3790	3670	2720	2730

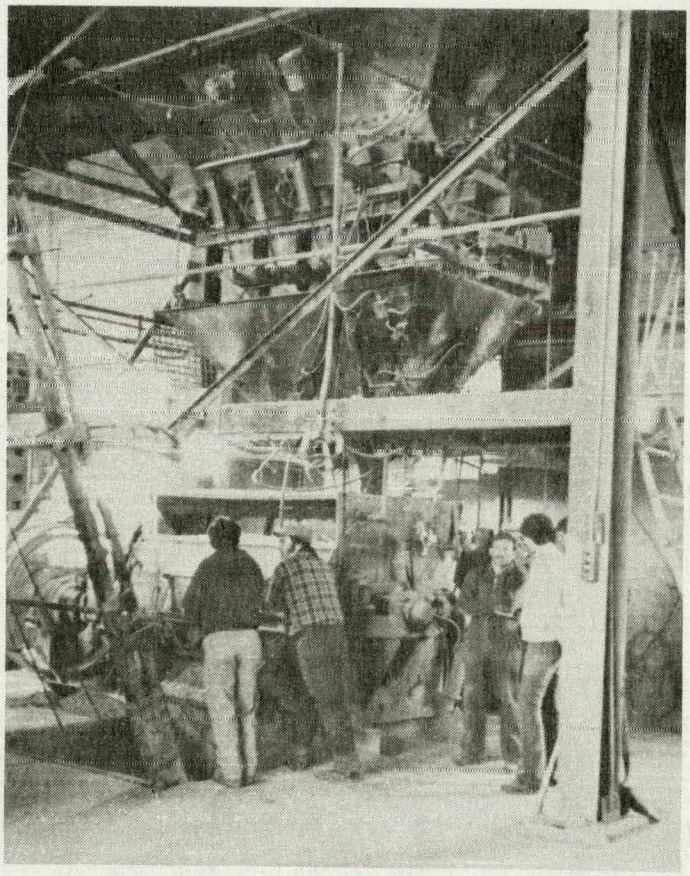


FIGURE 15

BESSER MACHINE USED IN PRODUCTION
OF AFB RESIDUE STRUCTURAL BLOCK

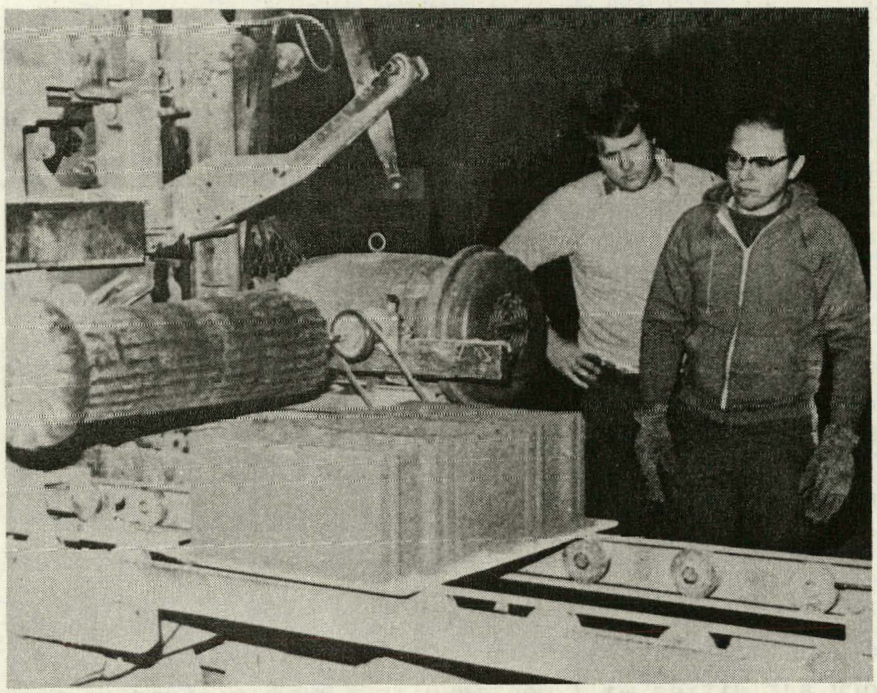


FIGURE 16

VIEW OF AFB BLOCK FORMING
AT CALCITE BLOCK COMPANY

ENVIRONMENTAL FACTORS

Work which has been sponsored by EPA[3] has outlined in early studies that the spent sorbent does have leachable constituents, particularly when it is considered for simple disposal such as ponding or placement in a landfill. As has been described earlier in this report, the residues are quite reactive when first exposed to the environment and, therefore, the management of the landfill can have a substantial effect of the performance of the material when exposed to rainwater or ground water leaching. Note Figure 17.

Since the residues (particularly those that are produced in industrial sized operations) are usually involved with special handling and preconditioning practices, disposal of the material can be coordinated with these procedures. Further, there is a strong possibility that a beneficiation step may be incorporated into the waste handling system which would, therefore, provide a usable product for some commercial application but, at the same time, establish a second generation waste which would have substantially different characteristics to that of the raw material discharged from the combustion unit.

It is also of importance to recognize that the disposal of these products can be more effectively carried out when the material is blended with other waste material using some of the developments outlined in this report. For example, material can be co-disposed with fly ash with pulverized coal combustion, slags, and flue gas desulfurization sludges. Examples of results that are obtained using these blended products are shown in Table IX.

PLANNED PROGRAMS

Laboratory activities will continue in a number of areas such as characterization of spent bed residue and fly ash from AFB systems that are now coming on stream. In addition to the test programs for type of applications described in this paper, demonstrations are also being scheduled for the use of the residue for stabilization of subbase soils in road, trade waste treatment plants, and additional test programs for stabilizing waste sludges.

In addition to these activities, an initial draft of a Users' Manual which has been recently prepared will be updated from time to time to include developments as they become available in the future.

As mentioned earlier, the primary thrust of the program is designed to develop the AFB residues as a national resource which will provide alternate materials to be used as a substitute or replacement for conventional virgin or manufactured materials. Basic issues such as coordinating this program with the operating conditions of AFB units both from the standpoint of changing properties of the residuals as they will be produced in the future and resolving concerns such as availability and uniformity of these products will also receive substantial review.

[3]Ralph Stone, "Environmental Assessment of Solid Residues from Fluidized Bed Processing", EPA Report No. PB-282-940.

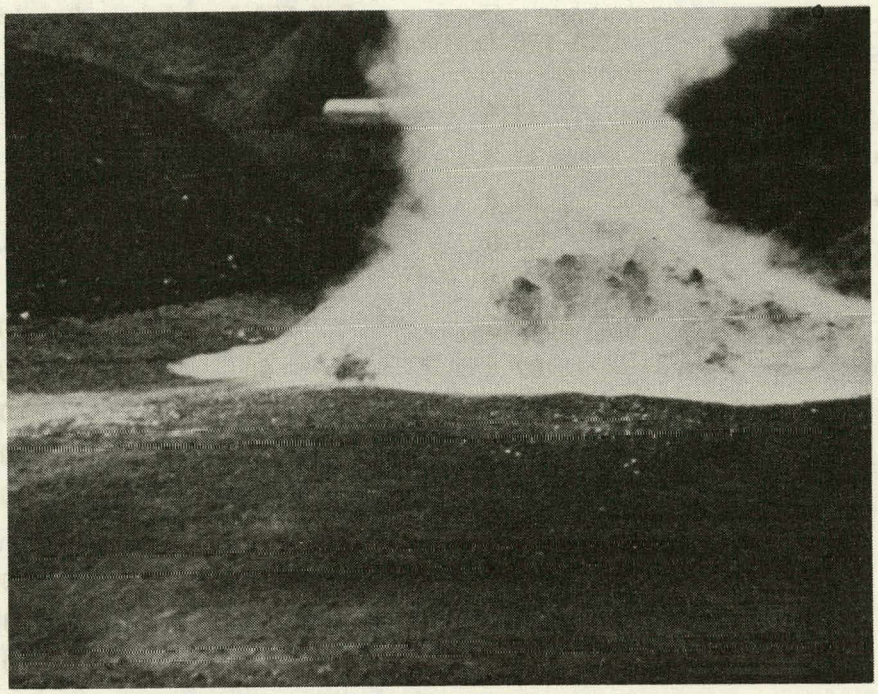


FIGURE 17

STEAM EMISSION FROM AFB RESIDUE STORAGE
PILE PREVIOUSLY MIXED WITH WATER

TABLE IX

48 HOUR SHAKE TEST DATA

(Procedure Outlined by ASTM Committee D-19.12)

	100% FBC Residue	80% FBC Residue 20% Fly Ash	U. S. Dept. of Public Health Drinking Water Standards
pH	11.5	11.7	
Phenolpthalein alkalinity	31.8	26.7	
Total alkalinity	39.8	32.5	
Hardness	53.0	41.7	
Sulfite	7.5	5.0	
Sulfate	1032.5	647.7	250
Chloride	80	40	250
Total dissolved solids	3733	2400	500
Arsenic	0.00	0.00	0.01
Cadmium	0.01	0.01	0.01
Calcium	920	800	
Chromium	0.06	0.02	0.05
Copper	0.04	0.03	1.0
Iron	0.12	0.08	0.30
Mercury	0.00	0.00	
Magnesium	0.02	0.02	
Manganese	0.02	0.01	0.05
Sodium	10	8	
Lead	0.10	0.10	0.05
Zinc	0.02	0.01	5.0

Note 1: pH is expressed in standard pH units. Alkalinity and hardness values are expressed as epm. All other results are expressed as mg/l.

Note 2: Specimens for test were compacted to approximately optimum density in standard proctor molds (4 inch diameter).

THE ENVIRONMENTAL CONTROL REQUIREMENTS OF THE DOE CENTRAL POWER SYSTEMS WHICH UTILIZE COAL DERIVED FUELS

by

W. M. Crim
&
G. B. Manning

The environmental control requirements of the advanced DOE Central Power Systems will have to comply with the EPA Standards of Performance for New Stationary Sources when the new systems are developed. The Central Power Systems which are the subject of this discussion are all advanced energy conversion systems which hopefully will reach a "Technology Readiness" status in about the 1986-1988 time frame, commercialization, which will take another four to six years, should follow.

The Final EPA "Standards of Performance Rule" was promulgated for Stationary Sources on September 10, 1979. This regulation establishes standards of performance which limit emissions of nitrogen oxides and sulfur dioxide.

These standards apply to all new, modified and reconstructed stationary gas turbines whose heat input at peak load is equal to or greater than 10.7 gigajoules per hour (approximately 1000 hp). The standards apply to simple and regenerative cycles as well as the gas turbine portion of a combined cycle generating system.

From 10.7 gigajoules up to and including 107.2 gigajoules per hour (approximately 10,000 hp) the NO_x limits for all applications is 150 ppm(v) in the exhaust gases, but not before 1982. For the sizes larger than 107.2 gigajoules the limits apply now depending on whether it is related to gas and oil transportation or production within a Metropolitan Statistical Area (MSA). All of these are defined on a dry basis with 15% oxygen.

The SO_2 limits are already in effect for all sizes above 10.7 gigajoules. This is 150 ppm(v) or the requirement to fire with a fuel with less than 0.8% sulfur. None of these standards apply to R&D turbines.

The major DOE Cental Power Systems research and development programs are the responsibility of the Assistant Secretary for Fossil Energy.

Coal Technology

The Deputy Assistant Secretary for Coal Technology is responsible for research, development and technology demonstration in the following areas:

- mining research and development
- coal conversion to liquids and gases
- petroleum and natural gas enhanced recovery
- in situ technology (coal and shale)
- fossil power conversion systems
- improved conversion efficiency

All of these responsibilities include compliance with environmental health and safety. The reliability requirements are self-imposed by DOE.

Office of Coal Utilization

This office, under the Deputy Assistant Secretary for Coal Technology is responsibile for:

- the use of gasified, liquefied and solid coal in advanced gas turbine power conversion systems
- cogeneration applications
- utilization of waste heat
- fuel cells
- combustion processes
- topping, bottoming, and combined cycles

Heat Engines and Heat Recovery Division

This division is responsible for:

- central power systems
- dispersed power systems
- heat recovery component technology

Central Power Systems (CPS)

This subactivity is responsible for:

- open/combined cycles
- closed power systems
- engineering analysis, evaluation and assessment (EAEA)

Central Power Systems

Gas turbines, open/combined cycles: integrated with appropriate coal conversion and utilization systems, hold excellent promise for using coal in an economic and environmentally acceptable manner. (This includes both simple cycles and combined gas turbine - steam turbine systems) Such advanced systems offer potentially lower capital costs, lower operating costs, higher availability and better environmental accommodation than conventional steam systems. Water usage and waste products are projected to be significantly reduced as compared to current steam power systems.

The open cycle gas turbine R&D program covers the technology advancement for a turbine inlet gas temperature on the order of 1427°C (2600°F). The High Temperature Turbine Technology (HTTT) program using advanced cooling techniques, ceramics technology, and advanced combustor technology comprise the major development items.

With regard to closed power systems, primary interest is directed toward system definition and primary heater technology for closed cycle gas turbine systems.

The major open cycle program within CPS is the High Temperature Turbine Technology (HTTT) program. The HTTT program as currently defined, consists of three phases of effort to be performed by industrial contractors:

Phase I - Program and System Definition
Phase II - Technology Testing and Test Support Studies
Phase III - Technology Readiness Verification Test Program

Phase I has been completed. Phase II is the present contract activity. Phase III will include the completion of the test vehicle design, fabrication, and tests to verify the technology. One of the key issues of the HTTT program is the specification and selection of a test site for the Phase III test engines. Each of these Phase III machines is to be capable of producing 50 megawatts or more while operating on actual coal-derived fuel.

Background

On the basis of using clean fuels such as petroleum based distillate No. 2 or natural gas, the technology base of the large, utility-sized, open cycle gas turbine is quite advanced. These very large units (30 megawatt sizes and larger) using clean fuel in peaking duty as well as intermediate duty, are already in commercial service. Some of these turbines are also to be used as combined cycles. The commercialized combined cycle plants are capable of an overall efficiency, fuel to bus bar, of approximately 40% using today's clean liquid or gaseous fuels.

When integrating a coal gasification plant with a combined cycle system, the overall coal-pile to bus bar efficiency will drop to about 30% because of the losses in the gasifier. Most of today's utility gas turbines operate with a turbine inlet temperature of 1095°C (2000°F). Some of the best of these can expect 30% efficiency, simple cycle. In order to maintain the overall coal pile to bus bar efficiency above 40%, competitive with today's combined cycle plants operating on petroleum based fuels or natural gas, the combined cycle plants operating on coal gasification must be capable of a turbine inlet temperature on the order of 1427°C (2600°F). This capability does not exist today. This is as true for a coal-derived liquid as for the gasifiers because of the losses in the liquifaction process.

The two HTTT contractors, Curtiss-Wright and General Electric, are attempting to develop gas turbine cooling technologies for their respective machines so that the 1427°C operating temperature can be realized. At the same time, and for the same machines, they are converting to the capability of accepting coal-derived fuels. In addition, the HTTT machines are intended for base-load duty while today's gas turbines are being used only for peaking and intermediate duty. Target lifetime is 30 years. C-W is using the air cooled approach while GE is using the water cooled approach.

These advanced cooling concepts for the gas turbine blades and vanes also include developing alternatives for combustor liners, transition sections and other appropriate hot section parts.

Only after completion of Phase III will commercialization be possible. At least two contractors should be carried to the end of Phase III to assure competition when commercialization begins. Commercialization could conceivably begin in about 1986.

Combined Cycle Power Plant Concepts

A typical flow schematic showing the major features and fluid flows for a combined cycle power plant with an integrated coal gasification plant is shown in Figure 1.

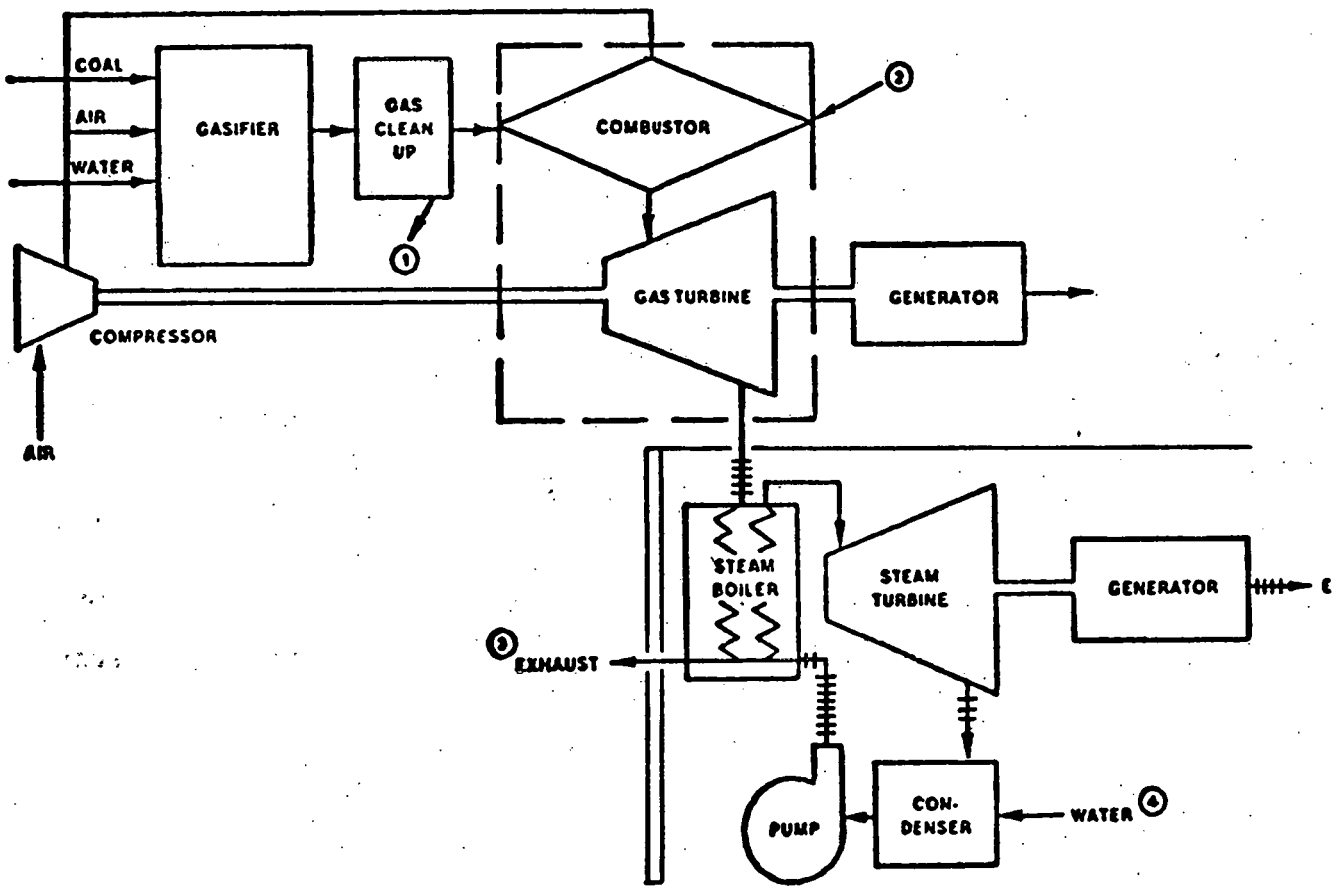


FIGURE 1

The raw coal delivered to the plant site is cleaned and crushed prior to entry into a gasifier, which can be pressurized up to 50 atmospheres depending on the specific gasifier. Partial oxidation of coal takes place in the gasifier with compressed air and steam. This process yields a manufactured fuel gas containing hydrogen, carbon monoxide and small amounts of hydro-carbon gases. In addition, the gas contains some contaminants that enter the gasifier through the coal. These contaminants can include particulates, tars, nitrogen compounds, sulfur compounds and trace metal compounds. They are generally removed from the raw gas leaving the gasifier in the gas cleanup system. A relatively clean fuel gas finally flows to power the gas turbine.

The gas turbine operates on the simple Brayton cycle. Compressed air and fuel gas unite in combustion and expand through a turbine. A portion of this turbine output drives the air compressor. The rest of the gas turbine power can be effectively converted to useful electricity in the generator.

Gaseous combustion products leave the gas turbine at a rather high temperature, generally about 540°C (1000°F). Much of this potential energy can be removed in a waste heat recovery boiler to produce steam. Expansion of this steam in a gas turbine yields additional mechanical work (by means of a Rankine cycle) to drive a second electrical generator.

The combination of a gas turbine with a steam power plant is familiar to many electric utilities. More than 40 such combined cycle plants have been constructed and operated using petroleum and natural gas fuels. Gas turbines have also operated on low-Btu blast furnace gas and on medium-Btu coke oven gas. Thus, most of the individual components of an integrated gasification combined cycle power plant have already been demonstrated. The technical risk of putting together the entire integrated system would appear to be within current industrial practice.

The major environmental advantage of the integrated gasifier combined cycle power concept has to do with cleaning up the hot gases in the process of gasifying coal rather than burning the coal in a furnace, thereby producing steam, and then cleaning up the exhaust stack gases with a flue gas desulfurizer system. The disposal problem associated with the gasifier system waste products are vastly reduced plus the gas turbine combined cycle is considerably more efficient in itself than a steam turbine is.

Actually, an appreciable portion of the gas turbine development is associated with combustor development. When a new gas turbine is designed and built, a new combustor is a large portion of this new design. Because in this case, this combustor is actually a completely new device which must operate at temperatures at least 600°F hotter than today's gas turbines, using fuels which have radically different combustion characteristics means that quite a sizeable combustor development must be successfully completed even to make a machine run, let alone run cleanly. In this case, the basic thrust of the total combustor program is to make the combustor burn cleanly.

The HTTT combustor (Fig. 1a) is used for startup and for other reasons briefly defined as follows:

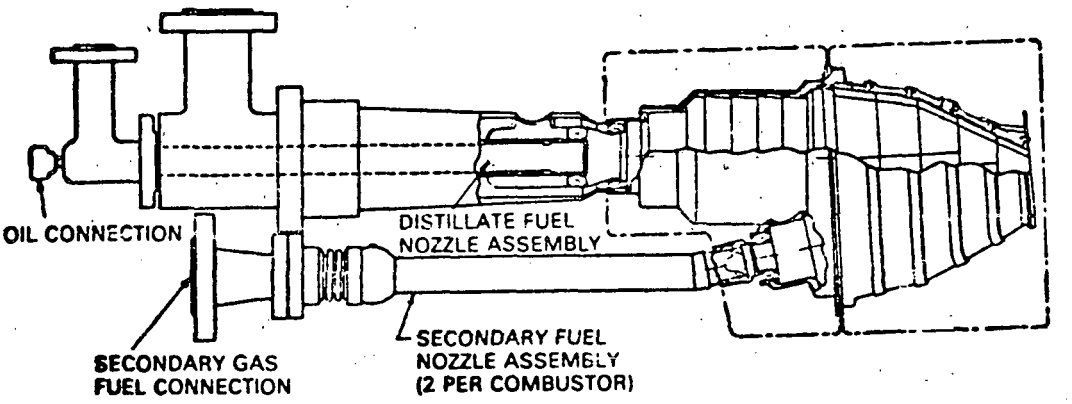


Fig. 1a. HTTT LOW BTU GAS, STAGED, SECTORAL COMBUSTOR

The following discussion is quoted from the G.E. contract quarterly report:

A formal engineering review of the baseline sectoral combustor design was held. An expert review committee was assembled from within General Electric including members from the Aircraft Engine Business Group, Corporate Research and Development, and the Gas Turbine Division.

Stoichiometry

After considering the revised cycle state vector both at the design point and at full speed for various part load conditions, it became necessary to lower the fuel staging point from 49% to 41% load. The fuel split remains approximately within the design flammability limits, but the equivalence ratio at the design point is 1.09 in the pilot burner and 1.32 in the second stage nozzles instead of being equal before this cycle change. The second stage may be too rich to be leaned out by the remaining flow. The fuel and air swirler sizings have been recalculated for the 41% staging point.

Continued evaluation of the transfer point from oil to dual fuel to low-Btu gas is in progress. This transfer may now occur as low as 12% load in lieu of 18% load, as far as the combustion system is concerned. However, the gasifiers may not be able to turn down this low. Further, because of the effect of ambient temperature on performance, the transfer point may have to be defined in some manner other than percent of load.

The baseline sectoral combustor has a two stage fuel injection system. The justification for this is shown in Figure 2. The plot shows the temperature rise across the combustor versus the equivalence ratio in the reaction zone. Two envelopes are shown on the field of the plot. The largest envelope is

dotted and the width approximately represents the burning limits of number two distillate oil. The height of the dotted envelope is the range of the required combustor temperature rise, rising from the minimum at ignition and full speed - no load to the maximum at full speed - full load.

The smallest envelope is drawn with solid lines and the width represents the approximate burning limits for the 127.5 Btu/scf design low-Btu fuel used in Phase II. The vertical component is the combustor temperature rise range from 20% load, the approximate transfer point to coal gas, up to a firing temperature of 1427°C (2600°F) and a compressor pressure ratio of twelve. The curved lines represent the combustor airflow quantity entering the reaction zone. The dotted curved lines show that no more than about 18% of the airflow can enter the reaction zone on distillate or the mixture will be too lean at full speed - no load (lower left corner of the dotted envelope) and no less than 9% of the air can enter the reaction zone or the mixture will be too rich to burn at full speed - full load (upper right corner of the dotted envelope). When burning the 127.5 Btu/scf fuel, the lower left corner requires no more than 28% air and the upper right corner requires no less than 55%. This ratio is impossible without fuel injector staging.

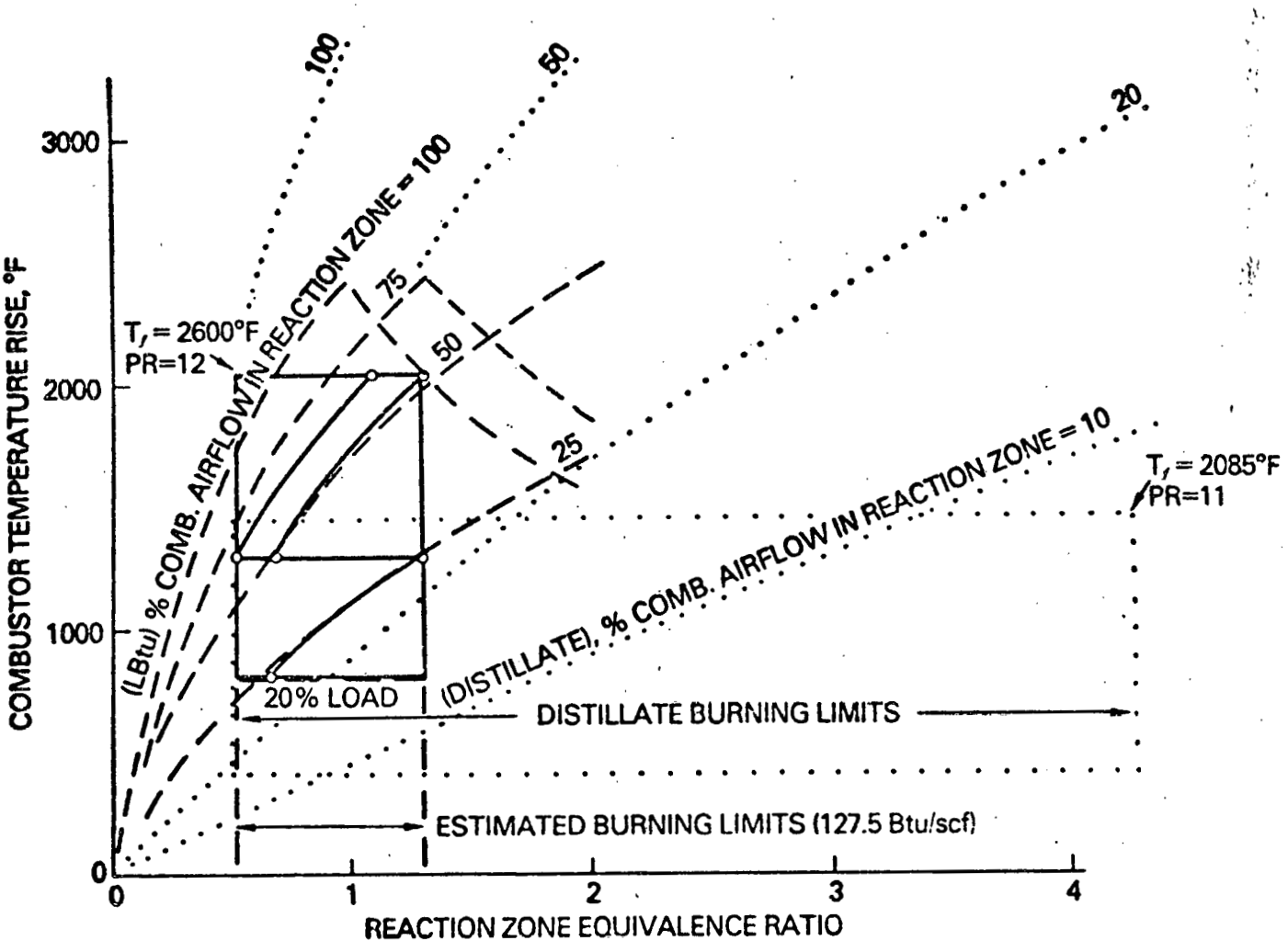


Figure 2 COMBUSTION SYSTEM STOICHIOMETRY

The "Z" shaped lines in the 127.5 Btu/scf burning range envelope represent the percent of combustor air mixing with the fuel in the baseline design. Beginning from the lower left solid line envelope, fuel is supplied to only the pilot stage and mixes with about 25% of the air. When this line reaches the rich burning limit about half way through the load range; i.e., at half the required combustor temperature rise, the fuel flow is split between the pilot burner and the second stage or auxiliary burners. This is shown pictorially by the double solid line beginning approximately from the lean burning limit and ending at the rich burning limit and 1427°C (2600°F) firing temperature. The outcome of a single stage fuel injection system is the base load operating point would burn very rich and the carbon monoxide emissions will be high. A second stage step would help to ameliorate this situation.

Space Rate

The space rate, or heat release, per unit volume per atmosphere of pressure has been calculated for the full load point and is 1.8×10^6 Btu/hr - ft^3 - atm. Space rates of up to 8×10^6 are successful in annular combustors. Space rates for heavy duty gas turbines are typically less than one-third of the HTTT Sectoral combustor.

The Curtiss-Wright HTTT combustor program is described as follows. Within the contract a test facility has been constructed which will simulate low Btu gas by mixing a number of gases from high pressure containers which are transported to the test site on large semi-trailers. These high pressure "bottle trailers" shown in Figure 3 and Figure 4 are then connected to the various mixing systems, Figure 5 and 6, which then supply the pre-programmed mixture to a test cell where the combustors, Figure 7 and Figure 8, are tested.

During the gasification process as conceived by both G.E. and Curtiss-Wright, all of the coal products of combustion include vaporized tars, alkali, particulates, H_2S, sulfur oxides, trace elements, hydrocarbons and oxides of nitrogen. At present, the cleanup train for the gasifier stream appears to require physical cleanup devices such as centrifuges as well as water washes. The water washes are to remove the tars. In the process of removing tars, particulates and tars both are removed rather effectively so that the only contaminants remaining are sulfur oxides and oxides of nitrogen. Some of these nitrogen compounds are in the form of ammonia, which is easily removed, whereas such devices as Benfield systems and Stretford systems will remove the H_2S quite effectively. Conversion to elemental sulfur by using a Claus plant is all that remains.

Closed Power Systems

The closed cycle gas turbine program is presently the major closed power program. The environmental, health and safety aspects of this program are somewhat different, technologically, than the open cycle program. A schematic of a closed cycle system is shown in Figure 9.



Figure 3. Bottle trailers connected to a manifold.

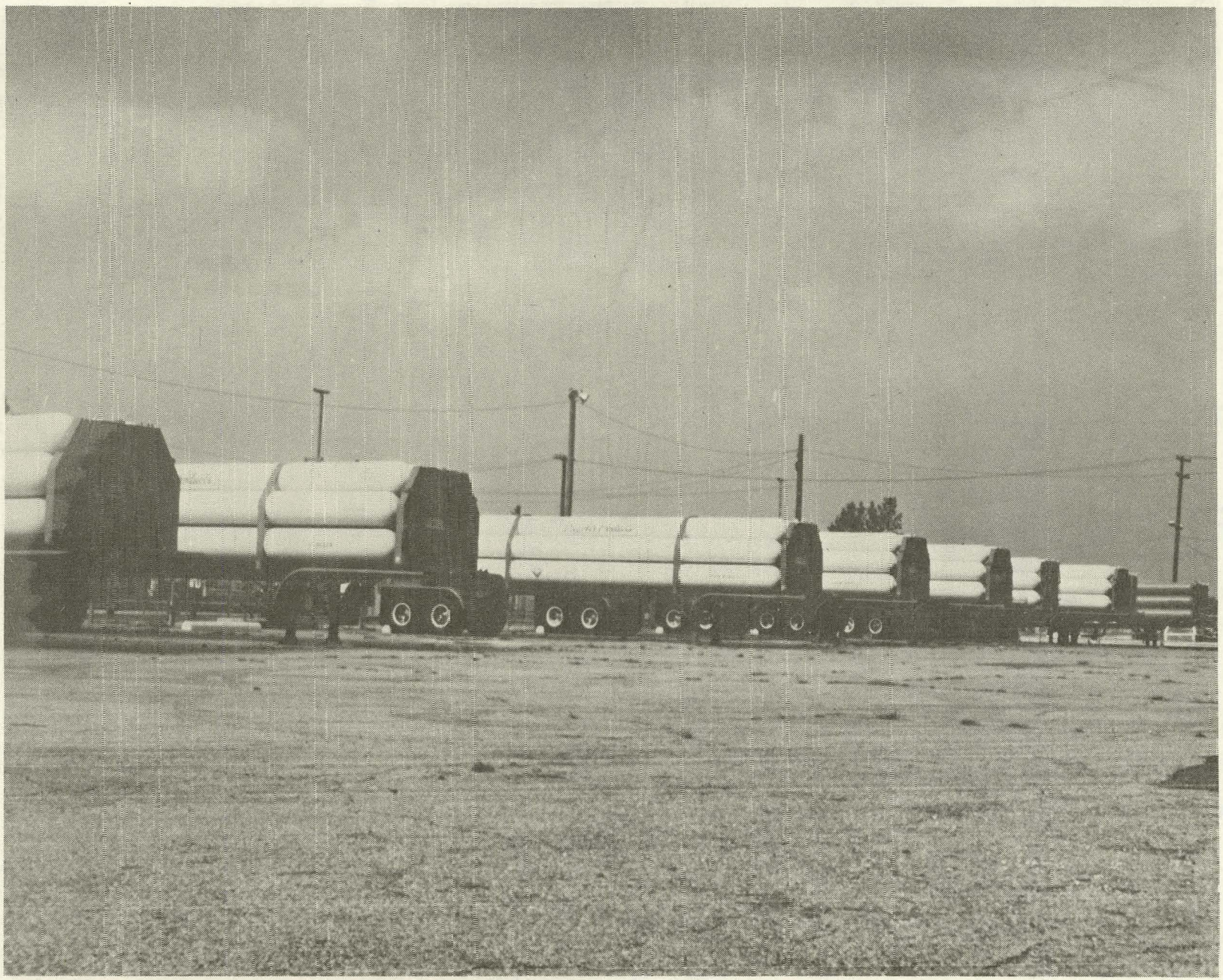


Figure 4. Bottle trailers.

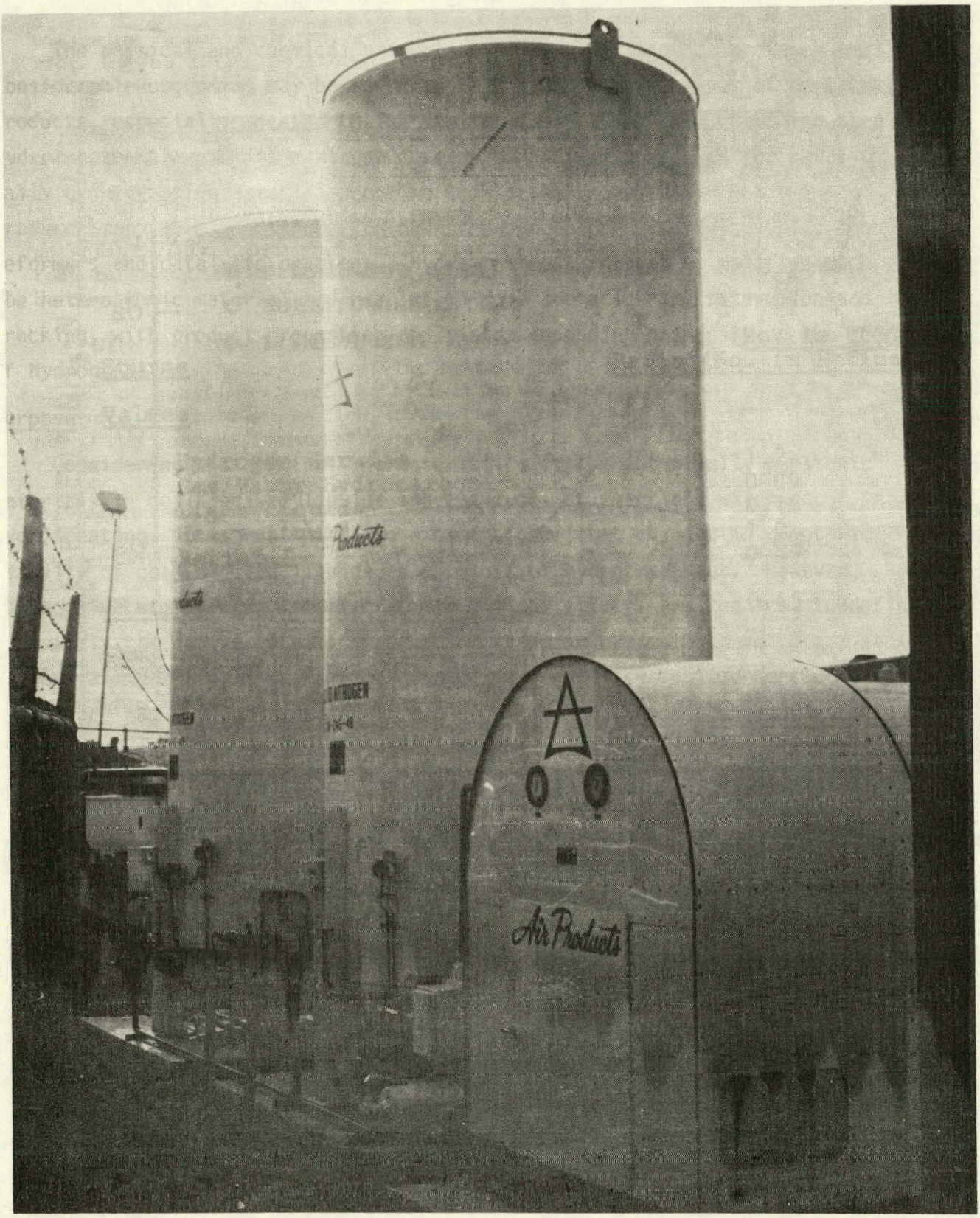


Figure 5. Cryogenic storage tanks.

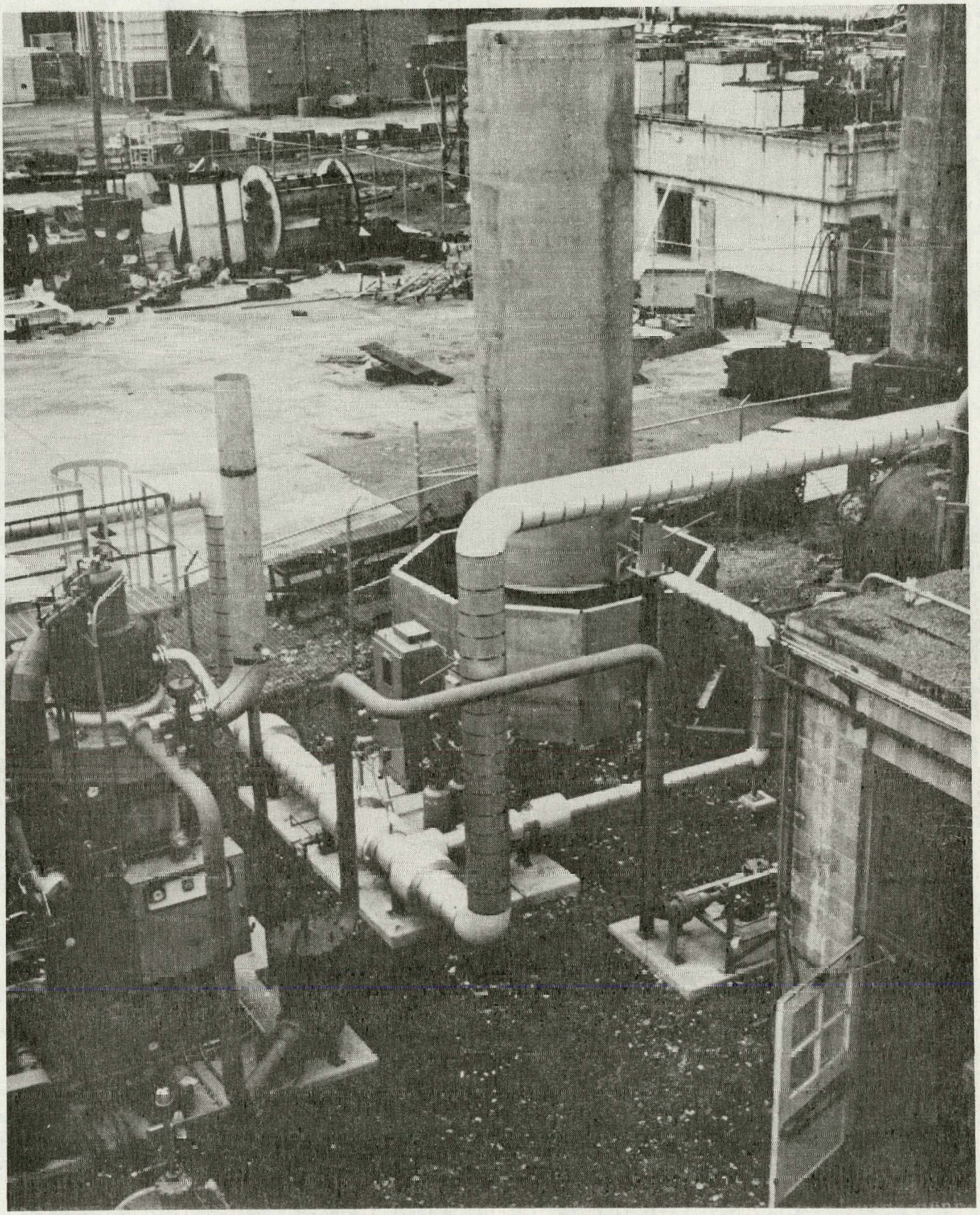
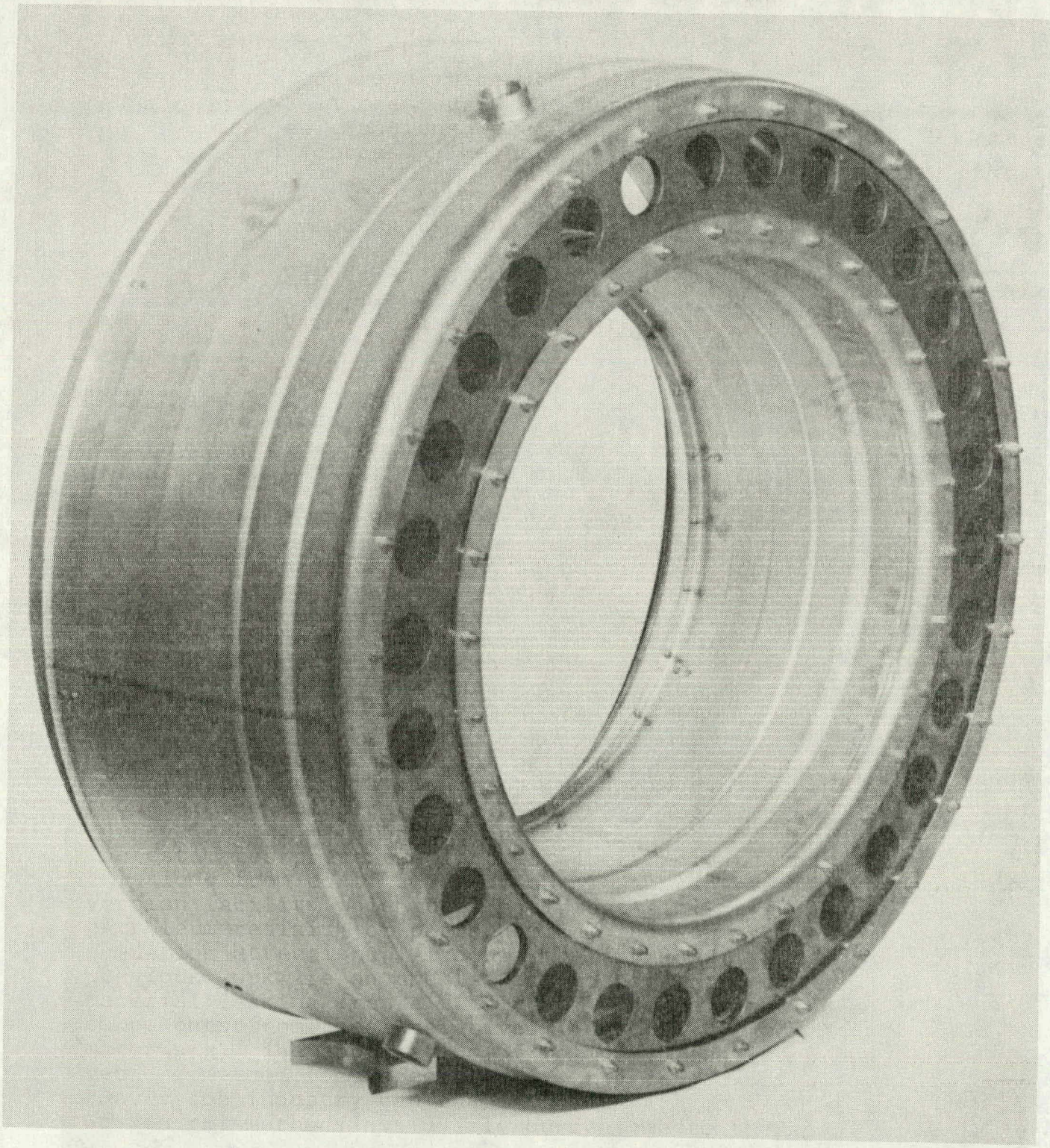


Figure 6. Gas flare and other controls.



TSTR FULL ANNULAR LOW BTU GAS FUEL COMBUSTOR BASKET
WITH COOLING SHROUDS INSTALLED (3/4 FRONT VIEW)

FIGURE 7

HTT-II-426

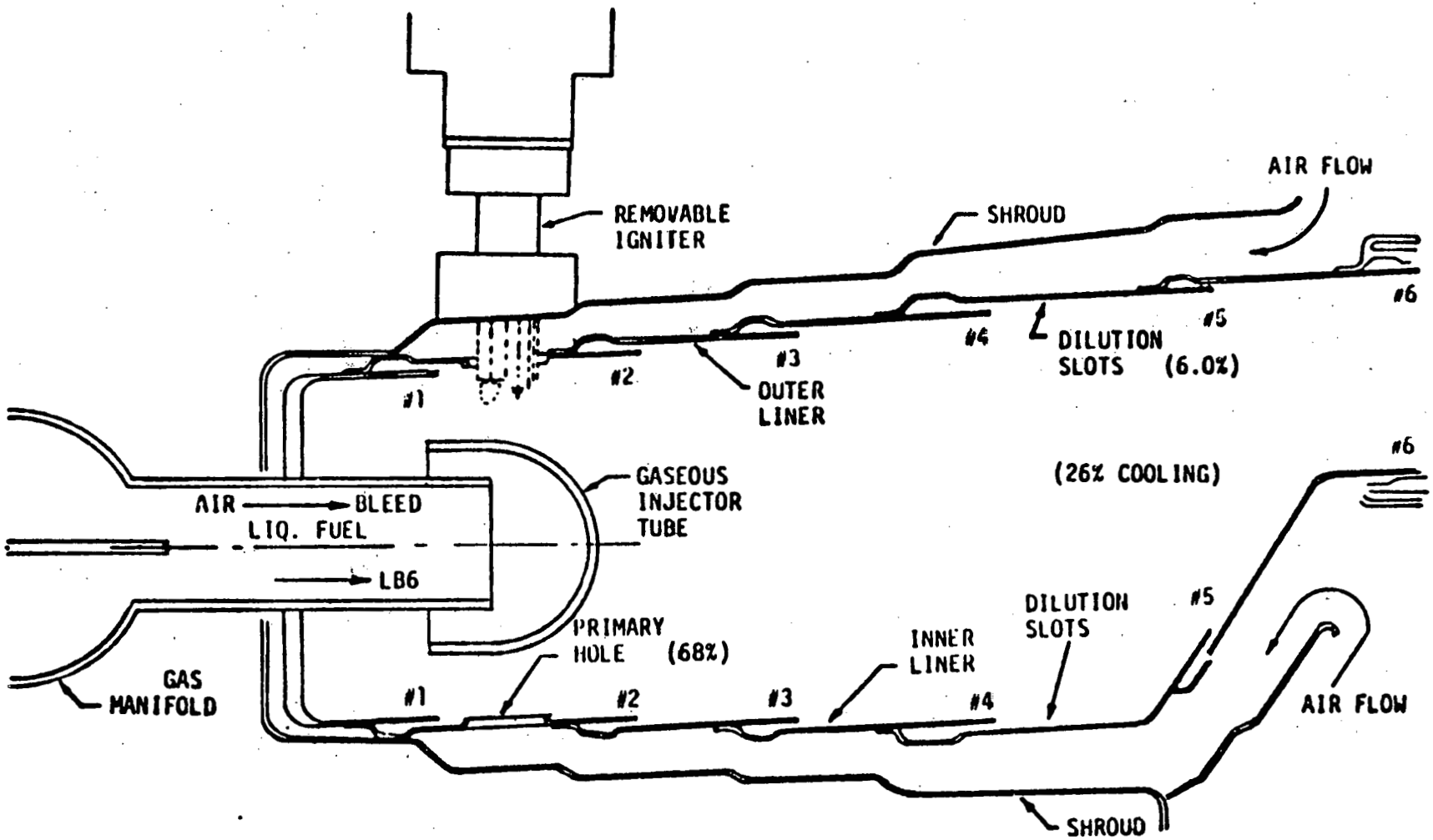


Figure 8 LBG FUEL TEST IN-LINE COMBUSTOR

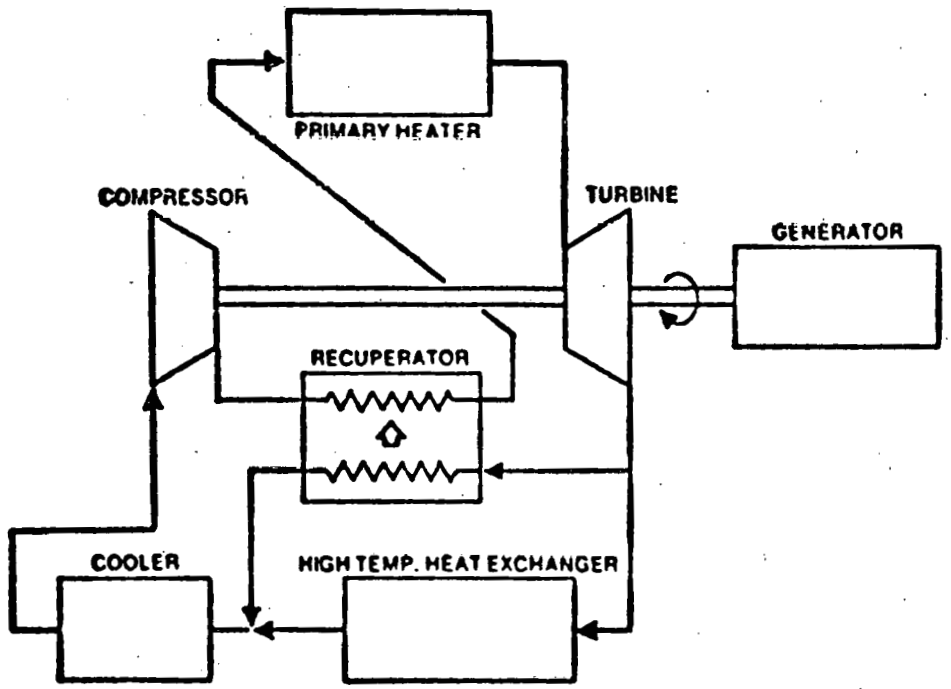

PRIMARY HEATER
COMPRESSOR
TURBINE
GENERATOR
RECUPERATOR
COOLER
HIGH TEMP. HEAT EXCHANGER
CLOSED
CYCLE
GAS TURBINE
POWER
SYSTEM

Figure 9

At the present time the major effort being expended on the DOE closed cycle system is with respect to the primary heater. The two phase I contractors completed simultaneous phase I studies in which they evaluated and finalized their systems analyses on two different cycles, one using air as the working fluid and the other using helium. However, once the systems had been settled on, the single phase II contractor is now concentrating on the primary heater only.

The primary heater is to obtain its heat from burning coal. Two alternatives are being examined-one using a pulverized coal furnace and the other using fluid bed combustion (atmospheric). In the case of the pulverized coal furnace it will require a stack gas scrubber of some kind, however, this DOE program element does not address this because another program element within the Office of Coal Utilization is addressing stack gas cleanup of all kinds. The fluid bed combustor portion of the closed cycle contract effort includes the primary heater element testing in a fluid bed heater, and one of the phase II requirements is to successfully operate a module of such a primary heater.

Figure 10 is a conceptual version of one of the test modules.

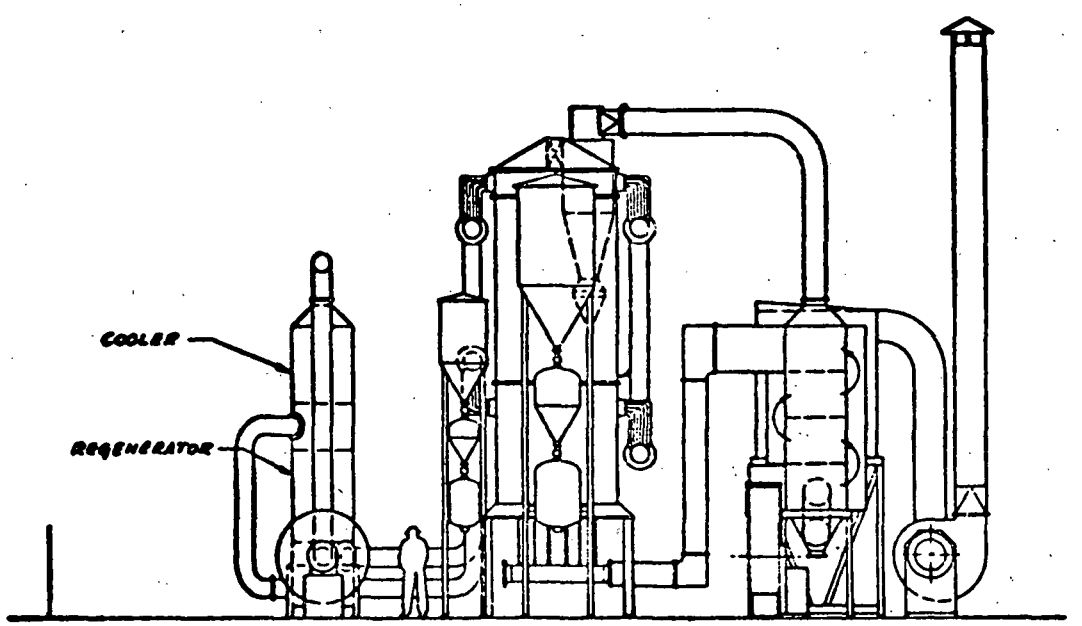


Figure 10

So that the basic R&D contract effort can be placed in proper perspective with regards to the environmental needs, the following point of view reflects what the Rocketdyne (the contractor) understood as far as what DOE requested:

It will not do to spend an inordinate amount of time and money during the startup phase of the 6- x 6-foot bed operation developing diagnostic techniques for use later in the program. Still, there is some hazard that improper operation of the bed during the startup phase of the test program could well initiate sulfidation corrosion and prejudice program results. Neither will it do to risk damage to the 6- x 6-foot bed in conducting some of the hazardous experiments necessary to resolve some of the technical issues involved in the application of the AFB to full system service. Preparatory experimentation with smaller beds, as explained earlier, is planned to be ready to conduct a safe, cost-effective program on the 6- x 6-foot system when it becomes suitable.

During the 6- x 6-foot fluidized bed exploration phase (with perhaps 250 hours at maximum temperature) (1) the experiences of the subscale combustor developments will be transferred to the 6- x 6-foot combustor operations, and operating plus monitoring techniques defined; (2) the interrelationships in operations of the system components will be explored and the most pressing experiments conducted; (3) the adequacy of system components and operating procedures for the long-duration corrosion/erosion testing will be assessed (and modifications made if needed); and (4) the target operating conditions for the corrosion/erosion runs finally defined.

Catalytic Combustors for Coal Derived Fuels

The fuels available for combustion in a gas turbine combined cycle power plant are low and medium Btu gases as well as residual and coal-derived liquids. The reason that residual oil comes under consideration is two fold. First, residuals and coal-derived liquids have a common emission problem - fuel bound nitrogen which is an additional source of NO_x from the combustion process. Secondly, it is possible that residual fuels may be burned in place of distillate fuels prior to coal-derived fuels being available in sufficient quantities. DOE programs have combined residual and coal liquids together as heavy liquids.

This program on catalytic combustors was reported on last year. The change in status in the Engelhard contract is as follows: the contract is now completed. Further, NASA contract work on Low NO_x Heavy Fuel Combustor concepts is only three months old so there isn't much reportable yet.

As stated by Engelhard, the problem associated with the burning of these fuels in conventional combustors is best illustrated by Figure 11. This shows the NO_x emission levels for various fuels plotted against combustor exit temperatures. The plot shows only trends since each manufacturer would have different results depending on the combustor design. The NO_x levels represent thermal NO_x only and assume no entrained nitrogen. As shown, medium Btu gas represents the highest

NO_x output. This is due to the higher hydrogen content which results in a higher stoichiometric temperature. Low Btu gas, on the other hand, is the lowest NO_x generator, how low depends on the gas constituents. The NO_x levels of residual fuel will be in the general neighborhood of the No. 2 oil. As you can see, all fuels except low Btu gas exceed the proposed EPA standards of 75PPM at combustor exit temperatures greater than 1900F.

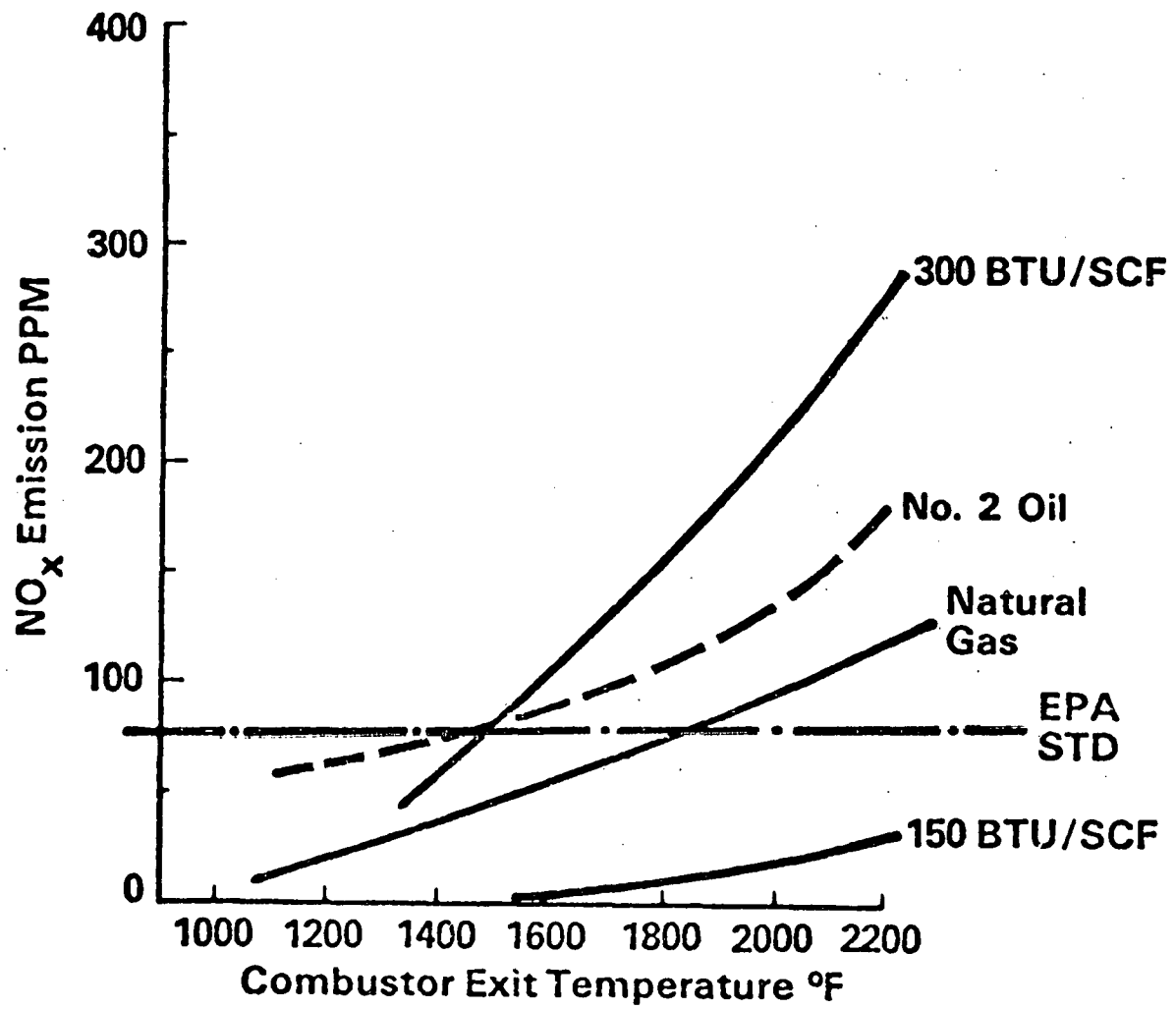


Figure 11 CONVENTIONAL COMBUSTOR EMISSIONS
ZERO ENTRAINED NITROGEN

One solution to the problem is the use of catalytic combustors in gas turbines. Figure 12 is a simplifed explanation of why the NO_x level is drastically reduced when such combustors are used. The illustration at the top shows a conventional combustor operating at its most efficient point under near stoichiometric conditions. The high gas temperature is reduced to the required turbine inlet temperature by means of dilution air. On the bottom chart we have plotted gas temperature versus the axial distance along the combustor. The curve shows that the temperature climbs to over 4000F during the burning process. The catalytic combustor is shown in the center of Figure 12. In this type, the fuel is mixed with air and introduced into the catalytic reactor where it burns under lean conditions. As shown in the bottom diagram the gas temperature gradually builds up to the turbine inlet temperature thus staying below 3000F. The significance of the 3000F level is that thermal NO_x generation is generally produced at gas temperatures in excess of 3000F. Therefore, a combustion process which maintains a gas temperature below 3000F will produce little or no thermal NO_x.

Ceramics Technology Development Program

This program is intended to complement the HTTT by providing an alternate hot section technology for advanced utility turbines using either liquid or gaseous coal-derived fuel. This ceramics effort, which includes the presently emerging carbon-carbon technology, will provide a technology base with design methodology which will support the high temperature needs throughout the development spectrum.

Two contracts have been awarded by DOE for "Conceptual Designs and Material Screening." Contractors are Westinghouse Electric Corporation and AiResearch, (Garrett Corporation). Subsequent phases of these contracts will cover:

Phase II - Materials and Design Methodology Development,
Phase III - Critical Component Design and Development, and
Phase IV - Full Scale Hot Section Test.

Phase II is intended to be contracted in the near future as a result of responses to a DOE Request for Procurement. The time frame involved to achieve technology demonstration of coal-burning ceramic turbines is approximately 8-10 years. It should be noted that simultaneous hardware material screening and testing will be carried out during this period in government facilities.

Any and all contracts in the ceramics development program exceeding $200K will be required to comply with the environmental, health and safety requirements also. However, as presently visualized, these program elements are rather small and not many exceed $200K in size. Because of the experimental nature of the materials involved it is also incumbent upon DOE to make sure of worker safety and environmental compliance.

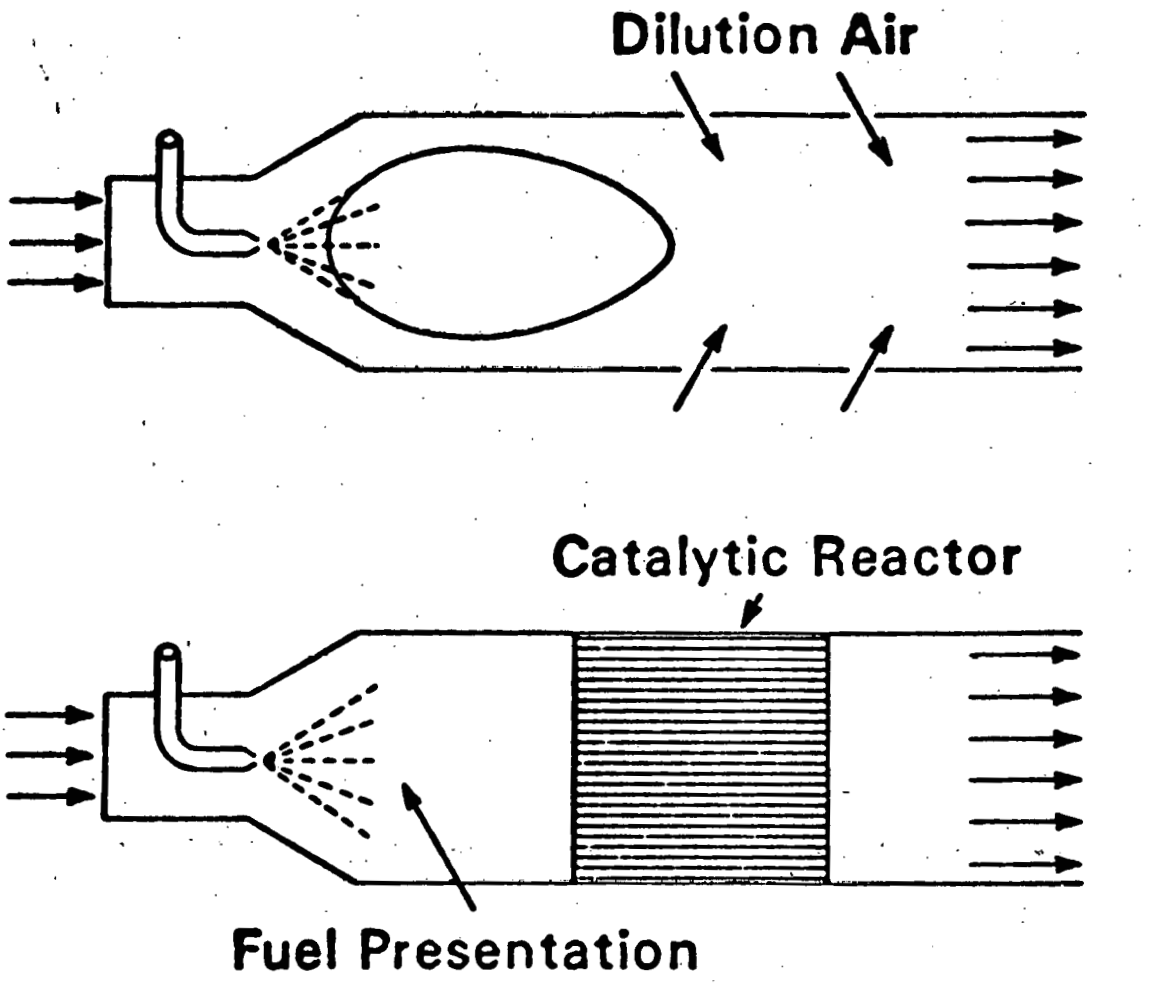


FIGURE 12 GAS TURBINE COMBUSTORS

Health and Safety

The health and safety compliance of both the open and closed cycle programs are required for contracts exceeding $200K, therefore DOE must make sure that all contractor efforts comply under formally defined health and safety regulations monitored both by the states wherein the plants are located and also that they are complying with EPA regulations because these are federally funded programs. This includes all hazardous materials handling, noise pollution, and all OSHA regulations.

EMISSIONS CONTROL FOR COAL-FIRED MHD SYSTEMS

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INTRODUCTION

Rising fossil fuel prices and fuel shortages in the last few years have led to an increased effort to develop magnetohydrodynamics (MHD) for electrical power generation. Much has already been said in the literature about the efficiency potential of MHD cycles and numerous papers have described MHD combustor and generator work and related development efforts. Interest in the bottoming cycle and pollution control has increased recently. For example, the Energy Conversion Alternatives Study[1] defined a bottoming cycle for MHD and a recent paper by J.B. Dicks, et al[2] described a total plant concept being developed by the University of Tennessee Space Institute and Babcock & Wilcox Company. However, except for the USSR development of a gas-fired MHD Electrical Power System[3] there is little experimental data available on the downstream components or pollution control. This paper will describe work sponsored by the Department of Energy and carried out at UTSI to develop an understanding of pollution control aspects while operating coal-fired MHD systems.

BACKGROUND

The shortage of clean fuels and abundance of coal led UTSI to turn to coal firing several years ago for development of MHD concepts at its R&D facility. Several test cells are available at this facility. An earlier paper[4] described results of tests to investigate nitrogen oxide (NO_x) relaxation while operating at about 85 percent of the oxygen required for stoichiometric combustion of the coal. Under the conditions tested, the NO_x relaxed in about 1.5 seconds. Preliminary results[2] indicated that the potassium used to provide the ionized gas for MHD power generation would react with the SO_2 and that the MHD process would be environmentally acceptable with regard to sulfur emissions.

Recent work at UTSI involved the design, fabrication and erection of a secondary combustor to burn the combustibles remaining in the gas stream, and to do so in a manner that minimizes nitrogen oxide formation. This paper will describe that apparatus, and the results of nitrogen oxide and sulfur dioxide measurements made during the ensuing test program. The work is sponsored by the Department of Energy under Contract DE-AC01-79ET10815.

EXPERIMENTAL - R&D FACILITY

The equipment used in these tests, identified as Cell III at the UTSI R&D Facility in Tullahoma, Tennessee, is shown on Figure 1. Major components include a combustor, nozzle, aerodynamic channel, diffuser and cyclone, which were built and installed before this test series began. All components downstream of the cyclone were designed, constructed and installed for this test series to accomplish and evaluate secondary combustion. The principal components of this portion of the train includes the gas sampling section, two secondary oxidant injectors and two in-line tubular heat exchangers. This equipment is connected by annular water-cooled piping and the gases are exhausted to the atmosphere through the stack.

Central Illinois coal, seeded with K_2CO_3, is fed from a pressurized hopper in dense phase into a combustion chamber. A typical coal analyses is shown in Table I. The flow rate of the combined coal/seed mixture for this was a nominal 750 Kg/hr. The capacity of the hoppers allowed for up to two hours of test time. In a coal combustion chamber, the mixture is ignited with a fuel oil flame, then burned with oxygen containing various amounts of nitrogen. Both oxygen and nitrogen are supplied from storage tanks through heat exchangers which vaporize liquid oxygen and nitrogen by utilizing the warm water discharge of the components. The gaseous oxygen and nitrogen flows were controlled by set point controllers and measured by orifice plates in the lines. The system capability allowed for oxygen flow rates to range from reducing to oxidizing stoichiometry in the combustor. Primary nitrogen flows were varied up to about 50 percent of the oxygen flow.

TABLE I

TYPICAL COAL ANALYSIS

Coal Composition	(wt % of coal)
Moisture	3.0
Ash	12.5
Sulfur	3.9
Carbon	65.0
Hydrogen	4.9
Nitrogen	1.2
Oxygen	9.5
Btu/# (HHv)	12,100

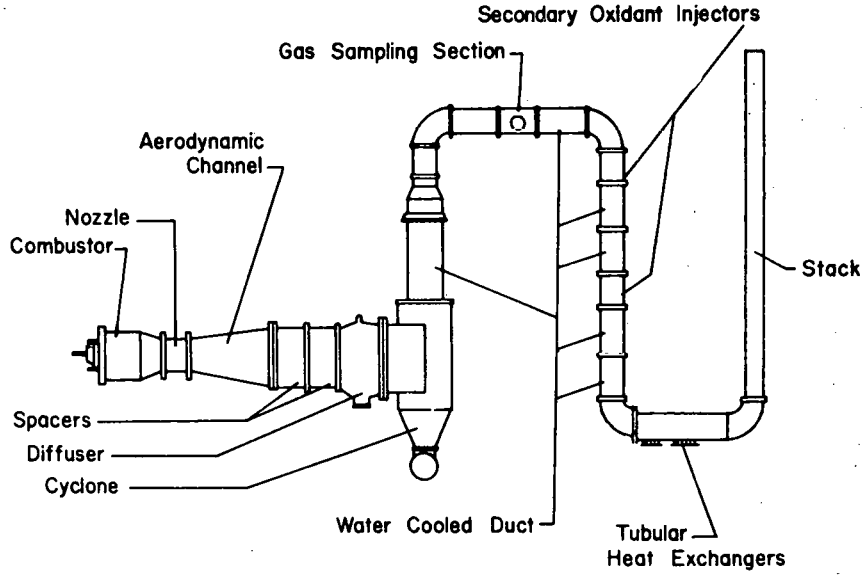


FIGURE I. Cell III Downstream Component Test Facility

Ash Analysis	(wt % of ash)
SiO_2	53.0
AL_2O_3	14.0
Fe_2O_3	21.0
CaO	3.9
K_2O	2.3
NaO_2	0.3
TiO_2	0.9
MgO	0.9

Nominal seeding levels of K_2CO_3 are 17 percent by weight of the total fuel flow.

Shortly after the coal combustor was started and oxygen flows were set to give the desired stoichiometry, oxygen flow to the secondary combustor was initiated and adjusted to get the desired excess oxygen levels. The nitrogen was then introduced at levels that were varied up to about 75 percent of the total oxygen/nitrogen flow rates.

Combustion Gas Analysis

The UTSI facility has gas analyzers available to continuously monitor carbon dioxide (CO_2), carbon monoxide (CO), hydrogen sulfide (H_2S), sulfur dioxide (SO_2), nitrogen oxides (NO_x) and oxygen (O_2). An on-line gas chromatograph is also available for monitoring hydrogen, nitrogen, methane and other gases. The gas analysis system uses an extractive method of sampling to monitor species of interest. A sample is drawn by a teflon diaphragm pump through a heated filter and heated sample line to a sample conditioner in which water is condensed from the gas stream at 5° C and removed from the system. The dry gas is then pumped into the control room to the gas analysis instrumentation.

Instrumentation

During testing, gas samples were obtained and analyzed continuously at the stack for the gases identified earlier. Samples were also taken at two or four minute intervals for gas chromatograph analyses. In selected tests during the latter part of the test schedule, the analytical system was arranged to provide simultaneous samples from the secondary combustor and the stack. However, only one sample conditioner was available. Furthermore, because of the limited number of analyzers, it was necessary to arrange the instruments to measure H_2S and CO (high range) at the secondary combustor inlet and NO_x, SO_2, CO (low range), CO_2 and O_2 at the stack. Periodically, samples were taken at other locations. Coal and ash samples were also collected for each test.

The facility has instrumentation to monitor pressures; flows of coal, kerosene, oxygen, nitrogen and cooling water; gas, water and metal temperatures at various points; gas composition, and additional variables, such as acoustic emissions, vibration and pressure fluctuations.

Test variables were recorded digitally on tape for reduction on a Data General Mini-Computer. The data acquisition system has a 256 channel capability with multiplexing and A/D conversion throughout rates up to 2000 Hz, depending on the test requirements. Selected data are displayed on-line on a CRT.

SECONDARY COMBUSTION

Several techniques for injecting secondary oxygen and nitrogen mixture were investigated. The most satisfactory design tested involved injecting the oxygen and nitrogen almost countercurrent to the direction of flue gas flow. With this arrangement, the performance was dependent on inlet gas temperatures. With inlet gas temperatures above about 750° C, carbon monoxide concentrations at the stack were stable and normally less than 300 ppm (see Figure 2) for inlet carbon monoxide levels between 3 percent and 17 percent.

SULFUR DIOXIDE

The potential for MHD coal-fired systems to reduce high SO_2 levels without the costly scrubbing systems has given increased emphasis to development of MHD systems.[5] When potassium is added to the fuel to produce a conducting plasma at high temperatures, it will later react with the SO_2 in the system to form K_2SO_4. The seeding level in a commercial MHD power plant has been proposed as one percent of the total flue gas mass flow. Using potassium carbonate seed (or any suitable salt) in a coal-fired MHD system allows burning of bituminous coal with high sulfur content without scrubbing systems.

Since an MHD system differs from conventional coal-fired plants in several important aspects, it seems worthwhile to consider the sulfur chemistry. The pathway of sulfur reactions through a conventional coal-fired power plant has been fairly well documented. With excess air levels of 5 percent and higher, more than 98 percent of the sulfur in the coal is converted to SO_2. The remaining two percent or less is converted to sulfur trioxide and metal sulfates. Common overall chemical reactions in conventional coal-fired power plants are listed below.[6]

$$2FeS_2 \text{ (pyrite)} + 5.5\ O_2 \rightarrow Fe_2O_3 + 4SO_2$$

$$\text{R-S (organic sulfur)} + O_2 \rightarrow SO_2 \qquad (1)$$

$$SO_2 + 0.5\ O_2 \rightarrow SO_3 \qquad (2)$$

$$M_2O + SO_3 \rightarrow M_2SO_4 \text{ (M is a metal atom)} \qquad (3)$$

The two-stage combustion process adopted by UTSI is used to achieve low nitrogen oxide emissions. In this process, the primary combustor operates fuel rich. The test train can be considered to be divided into two zones with the primary zone being reducing and the secondary zone being oxidizing. Typical operating parameters are given in Table II.

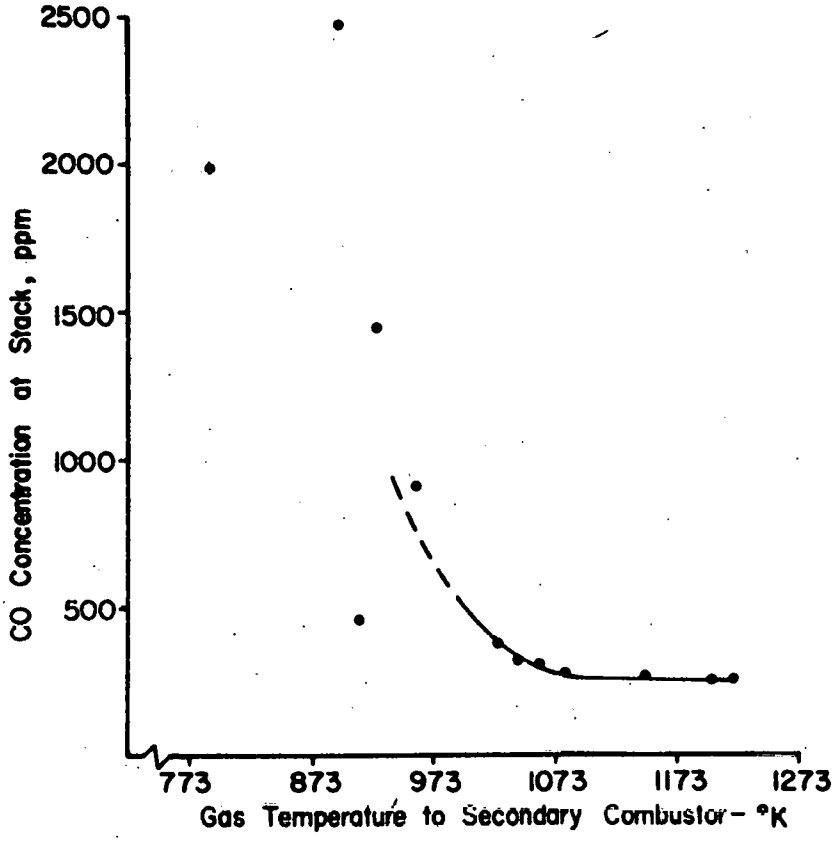


FIGURE 2. CO Level at Stack.

TABLE II

Primary and Secondary Combustor

Typical Operating Parameters

	Primary Combustion Zone	Secondary Combustion Zone
Peak temperature	3000° K	1500° K
Temperature leaving	1200° K	800° K
Pressure - initial	4 atm	1 atm
Pressure - exit	1 atm	1 atm
Residence time	1.5 sec	0.8 sec
Stoichiometric ratio*	0.85	1.15

*Stoichiometric ratio = oxygen actually supplied divided by oxygen required for complete combustion.

The NASA SP-273 program[7] was run over these conditions without potassium to predict the gas phase sulfur forms at equilibrium. A plot of equilibrium sulfur forms (as mole percent of total sulfur) versus temperature is presented in Figure 3. The Free Energy Minimization Program predicts SO_2 along with SO as the predominant sulfur forms in the high temperature region. As the temperature decreases, H_2S, S, and COS become predominant with decreasing concentrations of SO_2 and SO. This relationship has been verified to some extent in the Cell III flow train. More equipment is necessary, however, to determine the levels of COS and other sulfur compounds. These determinations are planned for later work in the UTSI development program.

The reaction pathway of SO_2 to H_2S may be summarized by the overall reaction (4).

$$SO_2 + 2CO + H_2 + H_2S + 2CO_2 \qquad (4)$$

In the oxidizing zone, the sulfur gases are converted from reduced species to oxidized species. Reactions (5) and (6) summarize the oxidation of H_2S and COS.

$$H_2S + O_2 \rightarrow SO_2 + H_2 \xrightarrow{0.5\ O_2} SO_2 + H_2O \qquad (5)$$

$$COS + O_2 \rightarrow CO + SO_2 \xrightarrow{0.5\ O_2} CO_2 + SO_2 \qquad (6)$$

The SO_2 formed in the secondary combustor is stable under the conditions listed above, according the the NASA SP-273 program. A kinetics program now being prepared should give additional insight into the sulfur reactions.

In an MHD system, sulfur reactions are strongly influenced by the potassium in the gas stream, but little information exists on the reaction mechanisms under these conditions. However, the NASA SP-273 program was run for the conditions present in the primary combustion (reducing) zone to obtain information on the potassium behavior. This program predicts several equilibrium potassium forms and these are plotted as mole percent of total potassium versus temperature on Figure 4. The potassium equilibrium forms are primarily atomic K and KOH at high temperatures. As the gas cools, the equili-

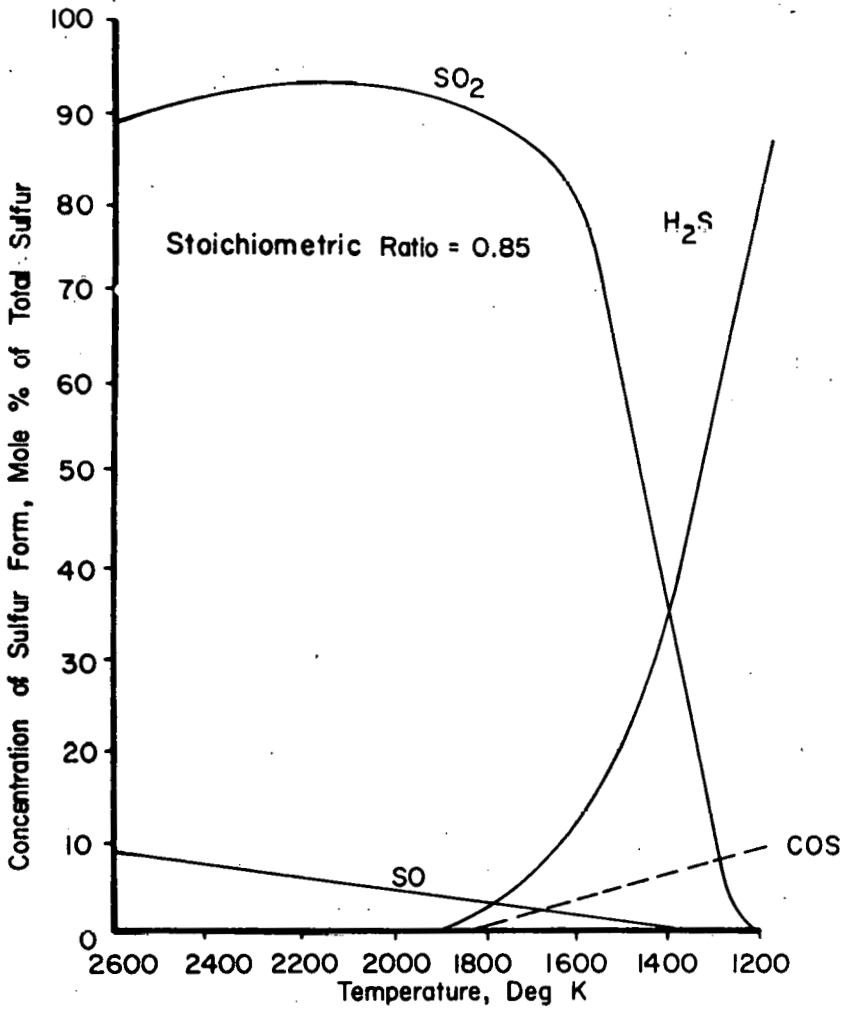


FIGURE 3. Equilibrium Sulfur Forms at Various Temperatures.

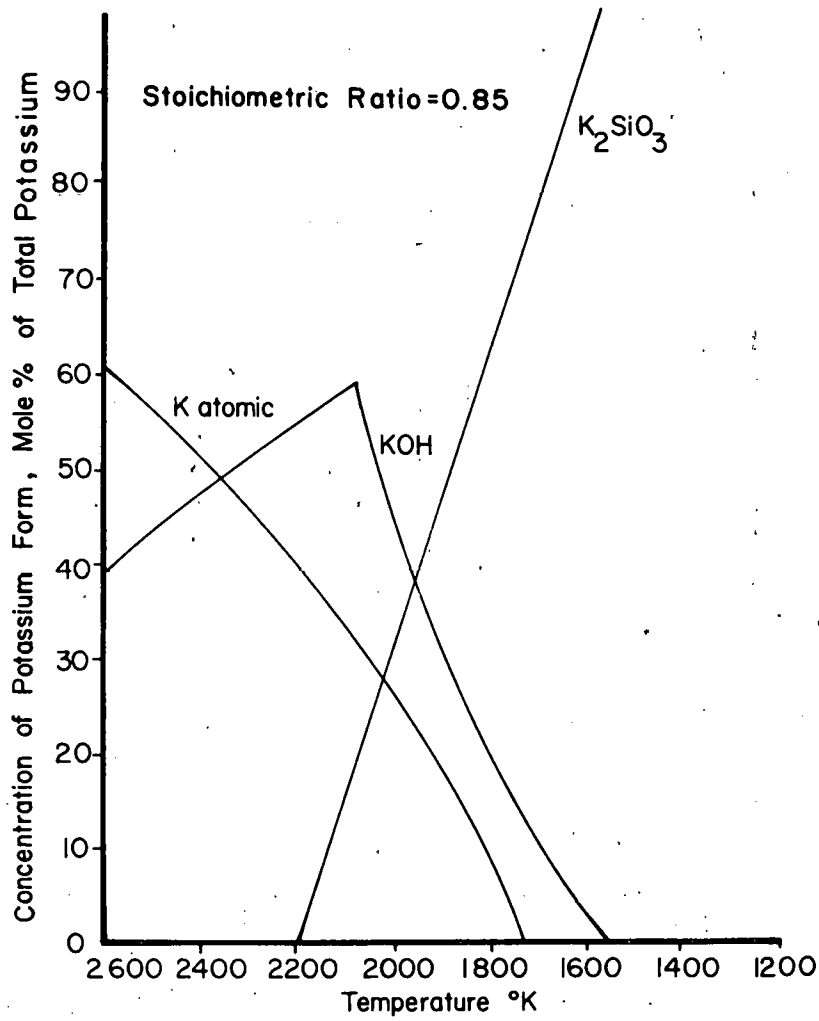


FIGURE 4. Equilibrium Potassium Forms at Various Temp.

brium potassium form favors a stable compound with SiO_2 and at 1600°K, the program predicts that 97 percent of the potassium is in the form of K_2SiO_3. The reactions do not reach equilibrium in the system investigated at UTSI, as evidenced by the fact that slag samples normally contain less than 20 percent insoluble K_2O. Significant amounts of K_2CO_3, K_2SO_4 and K_2S are present in samples collected from reducing zones.

High levels of sodium carbonate are frequently found in sodium recovery systems in the paper industry. Dust and fume collected from the combustion of the liquor residue from pulp making operations (under reducing conditions as the Kraft process) is in the form of sodium carbonate.[8] One potassium form found in the cyclone exhaust in the Cell III facility is potassium carbonate and the formation is probably analagous to the Kraft operation. Potassium hydroxide may be present at higher temperatures and, if so, combines with the CO_2 in the gas stream to form K_2CO_3 on the sampling apparatus through the reaction (7).

$$2\ KOH + CO_2 \rightleftarrows K_2CO_3 + H_2O \qquad \Delta H \simeq -34\ Kcal/mole \qquad (7)$$

The levels of K_2SO_4 found in the cyclone exhaust are also in disagreement with the NASA equilibrium predictions. Potassium sulfate is not predicted as an equilibrium form under fuel rich conditions. Apparently, the K_2SO_4 is formed in the high temperature region of the primary combustion zone. This is a reasonable explanation due to the partial pressure of SO_2 and O_2 in this region. The NASA program did not consider K_2SO_4 (g), which may be formed in this zone, according to recent thermodynamic data.[9]

The operating conditions of the secondary combustor have been mentioned previously. The CO, H_2, H_2S and other reduced species are converted to the oxidized forms at temperatures around 1500°K at oxygen/fuel stoichiometric ratios of 1.05. Potassium hydroxide will react with sulfur dioxide through the overall reaction (8).[10]

$$2\ KOH + SO_2 + 1/2O_2 \rightarrow K_2SO_4 + H_2O \qquad (8)$$

Chemical analyses of samples downstream of the secondary combustor show K_2SO_4 and K_2O·slag as the only potassium forms present, except for one case when K_2CO_3 was present with a K/S molar ratio of 1.5.

Results and Conclusions - SO_2

1. Sulfur dioxide emissions can be reduced more than 95 percent with potassium carbonate seed levels expected for MHD power generation. Sulfur dioxide levels for various seeding levels are shown on Figure 5. This level of SO_2 removal will meet proposed EPA standards.

2. Some K_2SO_4 appears to be formed in the primary combustion zone, which seems to be in disagreement with current NASA equilibrium predictions.

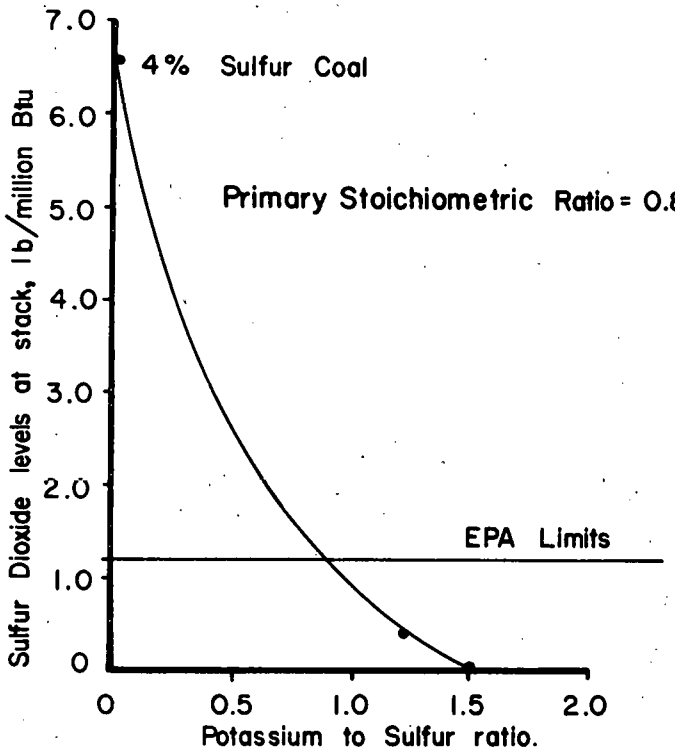


FIGURE 5. Effect of Potassium Addition on SO_2 Removal

NITROGEN OXIDE

The high combustion temperature necessary to produce MHD electrical power (3000°K) leads to high nitrogen oxide formation. Calculated equilibrium nitrogen oxide formation in the combustor is 13 lb/10^6 Btu (5.6 g/J). The current EPA limit for a coal-fired power plant is only 0.7 lb/10^6 Btu (0.3 g/J). It is apparent that the MHD combustion gas must undergo a drastic reduction in NO_x concentration (≃95 percent) between the combustor and stack.

Nitrogen oxide reductions can be carried out in several ways. Methods used in the utility industry are well documented in the EPA periodical NO_x Control Review.[11] An inventory taken in the summer of 1978 included nine methods of controlling NO_x emissions in steam plants now operating. Forty percent of the stations surveyed chose overfire air for NO_x reduction. This method is essentially a staged combustion process where lower burners are operated at theoretical air levels less than 100 percent and additional combustion air is injected above these burners. The residence time under fuel rich conditions is long enough to allow NO_x relaxation (dissociation to N_2 and O_2) in the furnace zone. The other NO_x relaxation methods involve approaches that reduce combustion temperatures. However, NO_x reduction techniques that decrease NO_x formation by lowering peak combustion temperatures are unacceptable in an MHD cycle. Any lowering of temperatures in the MHD cycle drastically decreases efficiency. Therefore, in the MHD system at UTSI, staged combustion was considered as the initial approach for NO_x reduction. However, the combustion zone of an MHD cycle is significantly different from conventional steam plant systems, and it is necessary to obtain system study and experimental data on this NO_x reduction method to confirm predicted results.

A system study was performed to predict the impact of operating the primary MHD combustor at a stoichiometric ratio <1.00. From this study,[4] it was decided that operation of the primary coal combustor at a stoichiometric ratio of about 0.85 would provide the optimum operating point for high plasma conductivity and low NO_x formation. The lower oxygen-to-fuel ratios also permit more rapid relaxation of NO_x (dissociation to N_2 and O_2). Additional system studies have shown that there are other advantages in operating in this range.

An experimental program was implemented to determine the relaxation time needed to obtain NO_x levels sufficiently low to comply with EPA regulations. Figure 6 shows experimentally determined NO_x concentrations in the primary zone combustion gas at various stoichiometric ratios.[3] The residence time in the system was approximately 1.3 seconds. As can be seen, the lowest stoichiometric ratio gave the lowest NO_x concentrations. This experimental data was compared with the Hals and Lewis[12] NO_x relaxation rate predictions. This experimental data agrees well with the predicted concentrations. From these experiments, it was decided that a stoichiometric ratio of ~0.85 was effective in lowering the NO_x concentrations in the combustion gas to the EPA required levels.

The second step in the experimental program included design and testing of the secondary combustor. In this step, additional oxidant is added to the primary zone combustion gases to complete combustion. It is essential that in this component low NO_x levels are formed when operating oxygen rich.

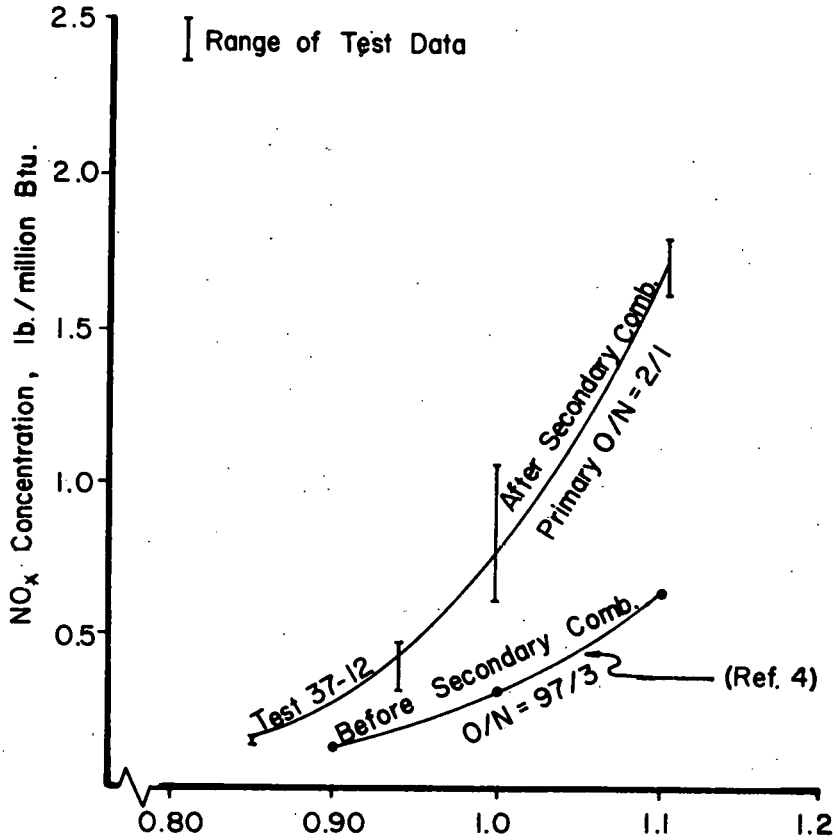


FIGURE 6. Effect of Primary Combustor Stoichiometry

The lower temperatures in the secondary combustion zone keep NO_x formation at low levels. Figure 7 shows predicted equilibrium concentration for NO_x in the secondary combustion gas for various conditions. The maximum concentrations correspond to EPA levels of around 0.25 pounds per million Btu. Experimental data obtained on this test series agreed well with the equilibrium calculations. Experimentally determined nitrogen oxide levels after the secondary combustor are shown in Figure 6. These measured levels are well below the current and more stringent proposed EPA regulations. Since the experiments were carried out with oxygen rich mixtures in the primary combustor, we were also concerned that we were using sufficient nitrogen to simulate combustion with air. Figure 8 indicates that NO_x concentrations reach a maximum at about 25 percent nitrogen under conditions that we can test at the UTSI facilities. Further additions of nitrogen cool the combustion process, thereby producing lower NO_x levels in the flame. Thus, the levels of nitrogen used in the primary combustor in the Cell III experiments were in the range to produce highest NO_x concentrations.

Results and Conclusions - Nitrogen Oxide

1. Nitrogen oxide concentrations in the secondary combustor stack gas gave levels that were expected and consistent with earlier results. Concentrations upstream of the secondary air injector were less than 50 parts per million. Experimental data typically showed 250-300 ppm NO_x after the secondary combustor.

2. The strong dependence of stack NO_x concentrations on the primary oxygen equivalence ratio is shown in Figure 6.

3. Results show that staged combustion is an effective method of controlling NO_x in a coal-fired MHD system. Based on these results, concentrations expected with primary zone stoichiometric ratio of 0.85 and secondary ratio of 1.15 in an air fired system are 0.2 pounds per million Btu, well below the proposed EPA standard of 0.6 lb/million Btu.

FUTURE WORK

Coal-Fired Flow Facility (CFFF)

Since 1976 the Department of Energy and the University of Tennessee Space Institute have been involved in a program to design and build a prototype MHD system to operate at the 25 MW (thermal) level or higher. This facility (CFFF) will test the concepts developed from experimental work in the smaller R&D Facility. The scale-up will be a factor of two and the testing periods can be essentially continuous. Operation of this facility is scheduled for 1980.

Several additional pieces of information concerning power generation and pollution control will come from the extended testing periods available in the CFFF. Staged combustion techniques for NO_x control will be tested with a radiant slagging furnace and secondary combustor more closely resembling hardware expected in a large central power station. Sulfur removal effi-

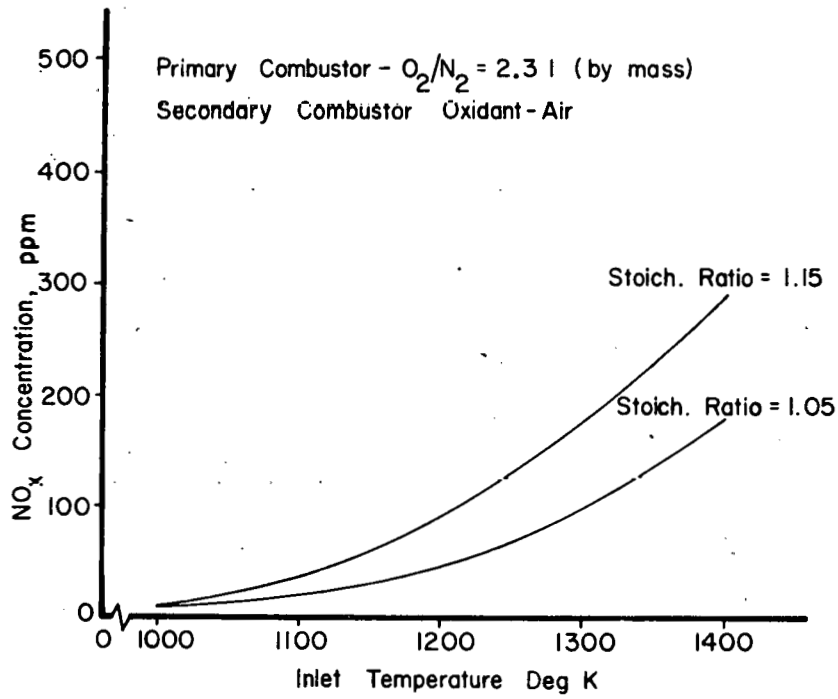


FIGURE 7. Equilibrium Nitrogen Oxide Concentrations.

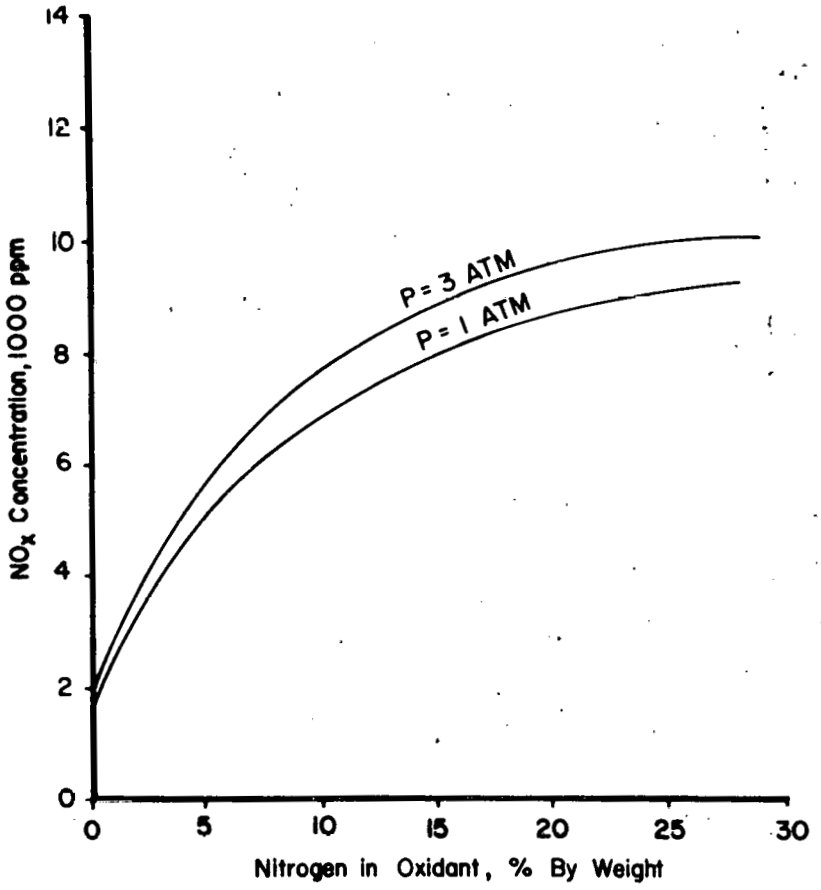


FIGURE 8. Effect of N_2 on NO_x Levels

ciencies will be studied and secondary combustion techniques will be evaluated. Solid waste removal techniques (for slag, ash and potassium) will also be tested with hardware designed for continuous operation.

Ash fouling characteristics of the resulting coal ash and potassium material in the CFFF will be investigated. The ash character will be important in designing solid particulate emissions control equipment and 'soot-blowing' equipment to clean boiler surface. The present program calls for testing of an electrostatic precipitator for ash removal. However, with the new regulations for additional solids removal in new power plants (0.03 pounds per million Btu), a baghouse system may be more cost effective for commercial plants.

Baseline Environmental Monitoring (CFFF)

A baseline environmental program is expected to be implemented in the DOE CFFF program in the near future. This monitoring program will insure that the environmental aspects of coal-fired MHD power generation are properly investigated. This monitoring plan calls for ambient air monitoring, water quality monitoring and solid waste disposal management.

ACKNOWLEDGEMENTS

The work described in this paper required the contributions of many individuals at the Energy Conversion Division of UTSI, which is under the direction of Dr. J.B. Dicks, Jr. The contribution of the late Mr. H.P. Markant was of special value. The pilot plant test work was carried out under the guidance of Dr. J.W. Muehlhauser. The contributions of Dr. Y.C.L. Wu are acknowledged as is the work of Mr. S.S. Strom, who did some of the development leading to this effort.

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SESSION 11
COAL CONVERSION. I – GASIFICATION

Chairman: L. Miller
Co-Chairman: H. Jones

MEASUREMENT AND CONTROL OF FUGITIVE HYDROCARBON EMISSIONS

Presented at:

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MEASUREMENT AND CONTROL OF FUGITIVE HYDROCARBON EMISSIONS

INTRODUCTION

The typical process flow sheet for a synthetic fuels production or processing plant identifies a number of emission sources. The control of these sources, whether gaseous, liquid, or solid, required to meet existing or proposed environmental regulations and criteria has been the subject of many research projects and pilot scale tests. The subject of this paper is an additional emission which can be estimated from the process flow sheets and equipment lists but does not represent a single specified source or control technology. This general source, which may represent a major emission from the plant, is the leakage from fittings and equipment, which results in fugitive emissions.

The primary purpose of this paper is to relate recent experience and data from the petroleum refining industry to the needs of the developing synthetic fuels industry. The major areas of concentration will be point sources resulting from leaks in valves, flanges, pumps, compressors, and miscellaneous sources. Emphasis will be on finding, measuring and controlling leaks. Primary information sources include work done in Los Angeles in the 1950's, the listing of emission factors known as AP-42, and a recent 3-year study of the petroleum refining industry performed by Radian Corporation under EPA sponsorship with full industry participation.

SOURCES OF FUGITIVE EMISSIONS

From a practical measurement standpoint, there are two general classes of fugitive emissions: those that can be enclosed from sampling, termed "baggable" sources; and those which emit from a large surface, termed "area" sources. Baggable sources include valves of all types, flanges, pump seals, compressor seals and floor drains. Area sources include oil-water separators, DAF units and other wastewater handling and treatment facilities such as ditches and ponds, cooling towers, tank storage, and materials handling facilities. For the sake of brevity, this discussion will primarily address the baggable sources for which a large, statistically valid data base is available.

In the Radian fugitive emissions study, 13 refineries were sampled. The results of this sampling led to a set of subclassifications for the baggable fugitive emission sources. Twelve source categories were identified as shown in Table 1. As indicated by the source categories in this table, valves, pumps,

Table 1
CATEGORIES OF BAGGABLE SOURCES

Category	Source Description	Number of Sources Screened
1	Valves, Gas/Vapor Streams	563
2	Valves, Light Liquid/Two-Phase Streams	913
3	Valves, Heavy Liquid Streams	485
4	Valves, Predominantly Hydrogen Streams	135
5	Open-ended Valves (all streams)	129
6	Pump Seals, Light Liquid Streams	470
7	Pump Seals, Heavy Liquid Streams	292
8	Compressor Seals, Hydrocarbon Service	142
9	Compressor Seals, Hydrogen Service	83
10	Flanges (all streams)	2,094
11	Drains (all streams)	257
12	Relief Valves (venting to atmosphere)	148

and compressors each have leak rates dependent upon the stream service for the fitting. Also in Table 1, the number of sources sampled in each of the 12 categories is listed.

The sampling methods used to characterize the fugitive emissions were carefully developed and validated to be applicable to all refinery sources. The same techniques should be directly applicable to synthetic fuels production and processing facilities.

MEASUREMENT METHODS

The number of potential sources leaking in a hydrocarbon processing facility is very large - over 10,000 valves, for example, in a petroleum refinery. For the purposes of locating leaks which require repair, rapid screening techniques are required. The ideal screening methods will permit detection by operator-level personnel and, in addition to showing presence or absence of a leak, give an indication of the magnitude of the leak for decisions as to repair schedule. In Radian's refinery testing, the primary purpose was the creation of a data base sufficient for predictive work. This required statistical selection of a random sample of leakers and, because correlations were sought between leak rates and the process or equipment parameters, the proper coverage of all variables was essential. To illustrate the range of the testing, Table 2 lists the variables investigated and their ranges.

Once sample points were identified based on random selection from process flow sheets, the points were physically located in the refinery and screened to determine the presence of leaks. The screening device was a portable hydrocarbon detector capable of quickly determining the range of hydrocarbon emissions from a given source. Two types of instruments were used: a Bacharach Instrument Company J-W Model TLV Sniffer and a Century Instrument Company Model OVA-108 organic vapor analyzer. Both instruments performed adequately in the field. For the purposes of data base generation, all leaks which screened at over 200 ppmv hydrocarbon, when measured directly at the source, were enclosed or bagged for detailed measurement. Bagging of a fitting simply means enclosing the source with a material such as mylar which is inert but flexible enough to conform to the fitting. Figure 1 illustrates a typical sampling train used to accurately measure leak rates.

This paper will concentrate on the data from non-methane hydrocarbon measurements; however, similar techniques were applied to determine the compositions of the leaks for projection of possible health effects as opposed to compliance with

Table 2

RANGE OF CHOICE VARIABLES FOR SCREENED BAGGABLE SOURCES

Baggable Source	Choice Variable	Variable Ranges for Screened Sources
Valves	Pressure	-10 to 3,000 psig
	Temperature	-190 to 925°F
	Fluid State	Gas, liquid, 2-phase
	Service	In-line, open-ended
	Function	Block, throttling, control
	Size	0.5 to .36 inch
Flanges	Pressure	-14 to 3,000 psig
	Temperature	-30 to 950°F
	Fluid State	Gas, liquid, 2-phase
	Service	Pipe, exchanger, vessel, orifice
	Size	1 to 54 inches
Pump Seals	Pressure	0 to 3,090 psig
	Temperature	0 to 800°F
	Capacity	0 to 100,000 gpm
	Shaft Motion	Centrifugal, reciprocating
	Seal Type	Mechanical seal, packed seal
	Liquid RVP	Complete range
Compressor Seals	Pressure	0 to 3,000 psig
	Temperature	40 to 300°F
	Shaft Motion	Centrifugal, reciprocating
	Seal Type	Packed, labyrinth, mechanical
	Lubrication Method	Hydrocarbon lubricant
	Capacity	0.06 to 66.0 MMSCFD
Drains	Service	Active, wash-up
Relief Valves	Pressure	0 to 1,350 psig
	Temperature	40 to 1,100°F
	Fluid	Gas, liquid

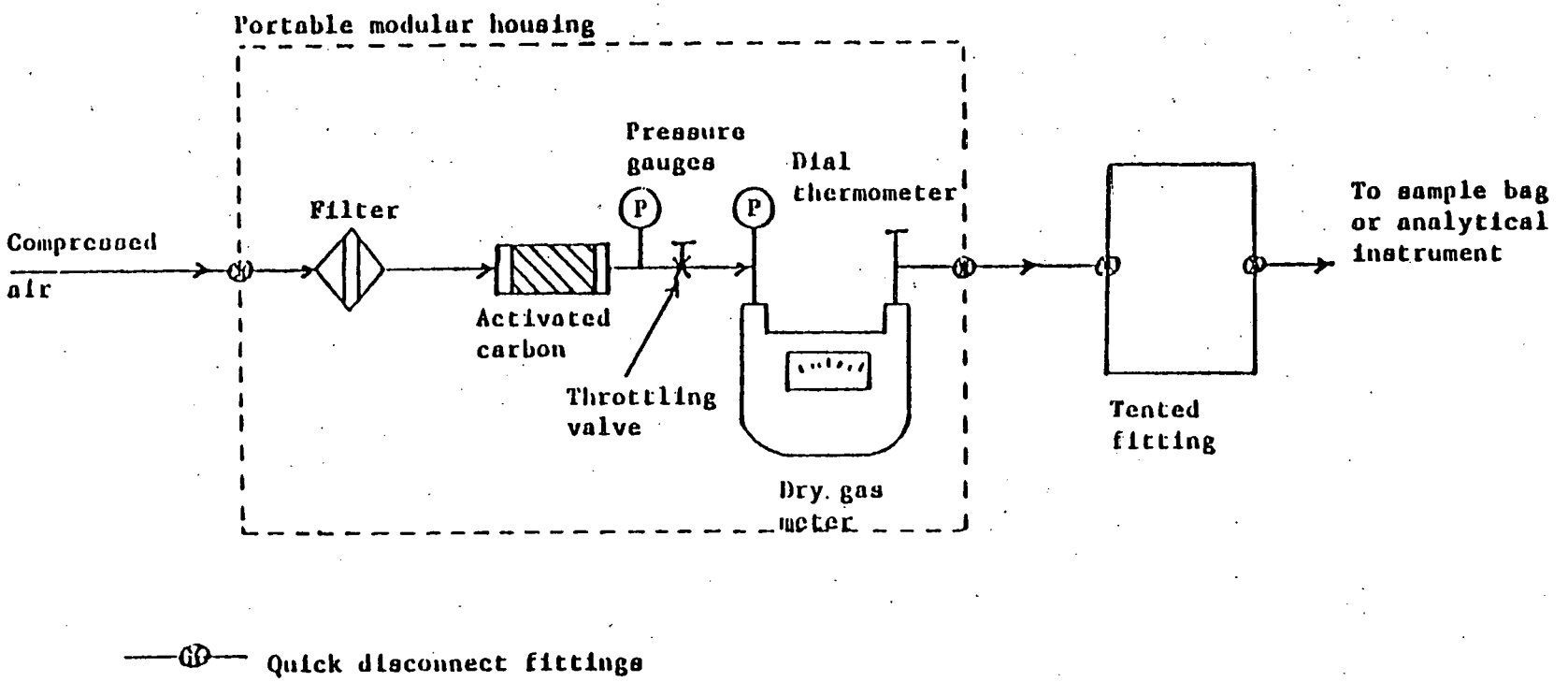


Figure 1

SCHEMATIC DIAGRAM OF THE APPARATUS FOR THE BLOW-THROUGH SAMPLING TECHNIQUE

ambient standards. These data have been the subject of other applications and are in the open literature. From the standpoint of predicting emissions and determining control strategies, emission factors offer a simple, standardized calculational procedure.

EMISSION FACTORS

Statistical evaluation of the data base for refineries resulted in the emission factors given in Table 3. The confidence limits reflect the scatter in the data and the results of an extensive QA/QC program conducted during the field testing. It is of particular significance that the only correlating variable worthy of separate emission factors was stream composition. Fittings in gas service tend to have higher leakage rates than those in liquid or mixed gas/liquid service. Variables such as age, manufacturer, maintenance practices, and size do not yield the correlations intuitively expected. The data base is, however, applicable to the overall population of sources and, within the confidence limits, it is possible for a single facility to deviate greatly from the predicted emissions. This finding is, in fact, what provides hope that effective control strategies can be developed and implemented.

The primary use of emission factor data is in the prediction of fugitive emission levels from either existing or contemplated facilities. As an example, fugitive emissions from a hypothetical 330,000 BPD refinery are shown in Table 4. This estimate projects that such a facility would emit approximately 480 pounds per hour hydrocarbon from fugitive emission sources. Valves are the major source of these emissions (305 pounds per hour), primarily due to the large number required in a refining operation.

APPLICATION TO SYNTHETIC FUELS FACILITIES

To illustrate the use of emission factors in determining areas of concern or opportunities for emission reduction in synthetic fuel projects, we have applied the refinery factors to a hypothetical Exxon Donor Solvent plant. Obviously, the direct application of refinery values is subject to some suspicion but it appears reasonable to expect that a synthetic fuels plant designed and operated by petrochemical companies would share design characteristics with the same company's refineries.

Table 5 illustrates the approximate level of fugitive emissions associated with a 60,000 BPD coal liquefaction facility. The basis for this table is an Exxon Donor Solvent Coal

Table 3

SUMMARY STATISTICS AND ESTIMATED VAPOR EMISSION FACTORS
FOR NONMETHANE HYDROCARBONS FROM BAGGABLE SOURCES

Source Type	Number Screened	Number Leaking	Percent Leaking	95% Confidence Interval for Percent Leaking	Emission Factor Estimate (lb/hr/source)	95% Confidence Interval for Emission Factor (lb/hr/source)
Valves						
Gas Vapor Streams	563	154	27.4	(24, 31)	0.059	(0.030, 0.110)
Light Liquid/Two-Phase	913	330	36.1	(33, 39)	0.024	(0.017, 0.036)
Heavy Liquid	485	32	6.6	(4, 9)	0.0005	(0.0002, 0.0015)
Hydrogen	135	59	43.7	(35, 52)	0.018	(0.007, 0.045)
Open-Ended Valves	129	30	23.3	(16, 31)	0.005	(0.0016, 0.016)
Pumps						
Light Liquid Streams	470	296	63.0	(59, 67)	0.25	(0.16, 0.37)
Heavy Liquid Streams	292	66	22.6	(18, 27)	0.046	(0.019, 0.11)
Drains	257	49	19.1	(14, 24)	0.070	(0.023, 0.20)
Flanges	2,094	62	3.0	(2, 4)	0.00056	(0.0002, 0.0025)
Relief Valves	148	58	39.2	(31, 47)	0.19	(0.070, 0.49)
Compressors						
Hydrocarbon Service	142	102	71.8	(64, 79)	1.4	(0.66, 2.9)
Hydrogen Service	83	69	83.1	(75, 91)	0.11	(0.05, 0.23)

Table 4

HYPOTHETICAL REFINERY: HYDROCARBON EMISSIONS[1]

Process Unit	Number of Valves in Units				Valve Emissions, lb/hr				Relief Valves		Flanges	
	Gas Service	Lt.Liq. Service	Hvy Liq. Service	Total	Gas Service	Lt.Liq. Service	Hvy Liq. Service	Total	Total R.V.	Emissions, lb/hr	Total Flanges	Emissions, lb/hr
Atmospheric Distillation: No. 1	90	280	520	890	5.31	6.72	0.26	12.29	6	1.14	3,560	1.99
Atmospheric Distillation: No. 2	90	280	520	890	5.31	6.72	0.26	12.29	6	1.14	3,560	1.99
Vacuum Distillation	50	50	400	500	2.95	1.20	0.20	4.35	6	1.14	2,000	1.12
Light Ends/Gas Processing	90	80	20	190	5.31	1.92	0.01	7.24	6	1.14	760	0.43
HDS: Reformer Feed	340*	210	100	650	15.88	5.04	0.05	20.97	6	1.14	2,600	1.46
HDS: Light Gas Oil	340*	210	100	650	15.88	5.04	0.05	20.97	6	1.14	2,600	1.46
HDS: Heavy Gas Oil	340*	210	100	650	15.88	5.04	0.05	20.97	6	1.14	2,600	1.46
HDS: Light Cycle Oil	340*	210	100	650	15.88	5.04	0.05	20.97	6	1.14	2,600	1.46
HDS: Vacuum Gas Oil	340*	210	100	650	15.88	5.04	0.05	20.97	6	1.14	2,600	1.46
HDS: Coker Naphtha	340*	210	100	650	15.88	5.04	0.05	20.97	6	1.14	2,600	1.46
FCCU	380	410	510	1,300	22.42	9.84	0.26	32.52	6	1.14	5,200	2.91
Hydrocracking	250*	380	310	940	11.68	9.12	0.16	20.96	6	1.14	3,760	2.11
Catalytic Reformer No. 1	260*	390	40	690	12.14	9.36	0.02	21.52	6	1.14	2,760	1.55
Catalytic Reformer No. 2	260*	390	40	690	12.14	9.36	0.02	21.52	6	1.14	2,760	1.55
Aromatics Extraction	60	500	40	600	3.54	12.00	0.02	15.56	6	1.14	2,400	1.34
Alkylation	230	340	0	570	13.57	8.16	0.00	21.73	6	1.14	2,280	1.28
Coking	30	60	220	310	1.77	1.44	0.11	3.32	6	1.14	1,240	0.69
Hydrogen Production	80*	80	20	180	3.74	1.92	0.01	5.67	4	0.76	640	0.36
	3,910	4,500	3,240	11,650	195.16	108.00	1.63	304.79	106	20.14	46,520	26.08

* Thirty percent of these valves are assumed to be in service in steams containing more than 50 percent hydrogen.

Table 4 (continued)

HYPOTHETICAL REFINERY: HYDROCARBON EMISSIONS[1]

Process Unit	Number of Pump Seals			Pump Seal Emissions, lb/hr			Compressor		Drains	
	Lt.Liq. Service	Hvy Liq. Service	Total	Lt.Liq. Service	Hvy Liq. Service	Total	Total Seals	Emissions, lb/hr	Total Drains	Emissions, lb/hr
Atmospheric Distillation: No. 1	15	28	43	3.75	1.29	5.04	2	2.80	69	4.83
Atmospheric Distillation: No. 2	15	28	43	3.75	1.29	5.04	2	2.80	69	4.83
Vacuum Distillation	2	19	21	0.50	0.87	1.37	-	--	35	2.45
Light Ends/Gas Processing	4	0	4	1.00	0.00	1.00	4	5.20	11	0.77
HDS: Reformer Feed	9	5	14	2.25	0.23	2.48	6	0.66	22	1.54
HDS: Light Gas Oil	9	5	14	2.25	0.23	2.48	6	0.66	22	1.54
HDS: Heavy Gas Oil	9	5	14	2.25	0.23	2.48	6	0.66	22	1.54
HDS: Light Cycle Oil	9	5	14	2.25	0.23	2.48	6	0.66	22	1.54
HDS: Vacuum Gas Oil	9	5	14	2.25	0.23	2.48	6	0.66	22	1.54
HDS: Coker Naphtha	9	5	14	2.25	0.23	2.48	6	0.66	22	1.54
FCCU	18	24	42	4.50	1.10	5.60	6	8.40	65	4.55
Hydrocracking	17	14	31	4.25	0.64	4.89	6	0.66	58	4.06
Catalytic Reformer No. 1	18	2	20	4.50	0.09	4.59	6	0.66	49	3.43
Catalytic Reformer No. 2	18	2	20	4.50	0.09	4.59	6	0.66	49	3.43
Aromatics Extraction	15	2	17	3.75	0.09	3.84	0	--	41	2.87
Alkylation	15	0	15	3.75	0.00	3.75	0	--	41	2.87
Coking	3	10	13	0.75	0.46	1.21	0	--	28	1.96
	194	159	353	48.50	7.30	55.80	68	25.14	647	45.29

[1]Emissions from within the battery limits of the respective process units.

Table 5

FUGITIVE HYDROCARBON EMISSIONS
FROM 60,000 BPD COAL LIQUEFACTION FACILITY

Fugitive Emission Sources	Number of Sources	Emission Factors (lb/hr-Source)	Fugitive Emissions (lb/hr)	
Valves				
H_2 Service	695	0.018	12.5	
Gas/Vapor Service	185	0.059	10.9	
Light HC Liquid	496	0.024	11.9	
Heavy HC Liquid	2,232	0.0005	1.1	
				36.4
Pump Seals				
Light HC Liquid	22	0.25	5.5	
Heavy HC Liquid	101	0.046	4.6	
				10.1
Compressor Seals				
H_2 Service	18	0.11	2.0	
HC Service	24	1.4	33.6	
				35.6
Flanges	14,432	0.00056		8.1
Relief Valves	36	0.19		6.8
Drains	118	0.07		8.3
TOTAL FUGITIVE EMISSIONS				105.3

Liquefaction Commercial Plant Study performed for the Department of Energy. The number of pumps and compressors were counted from flow sheets and equipment lists provided in the Exxon study. Valves, pump seals, compressor seals, flanges and relief valves were estimated using equipment ratios developed in the Radian fugitive emission project. The number of drains was estimated from refinery data.

Table 5 shows that approximately 105 pounds per hour of hydrocarbon emissions from fugitive sources may be anticipated from the 60,000 BPD facility. (This emission estimate does not include emissions from pumps and valves in the tank farms which were considered to be off-site.)

On a capacity basis, this is very consistent with the previous estimates for a hypothetical refinery, indicating (as would be expected) similar equipment requirements. However, in the synthetic fuel facility, compressors as well as valves appear to be a major source of emissions. The relatively greater contribution from compressors seems reasonable because of the greater hydrogen (compressor) requirement in most synthetic fuel operations.

To put these estimated fugitive emissions in perspective, Table 6 lists the other atmospheric emission levels cited in the Exxon commercial plant study. Although not as great as the SO_2 and NO_x levels resulting from combustion, it is evident that fugitive sources will be the primary contributors of hydrocarbon emissions from synthetic fuel processes.

DETECTION AND CONTROL

The reduction of fugitive emissions relies on two strategies, the selection and proper installation of appropriate equipment and the rapid detection and repair of leaks. The detection of leaks is complicated by the fact that available data show that the bulk of the fugitive emissions result from a small fraction of the total number of sources in a category. For example, using refinery data some 93 percent of the total measured emissions from valves in gas service were emitted from only 1.4 percent of the valves. For flanges, 89 percent of the measured hydrocarbons resulted from less than 1 percent of the total number of flanges. At present there a number of techniques which have been suggested for leak detection which rely on area measurements or automatic equipment but none have proven effective. The state-of-the-art today requires manual screening of each fitting to detect a leak.

Table 6

ATMOSPHERIC EMISSION SUMMARY FOR 60,000 BPD COAL LIQUEFACTION PLANT[1]

SO_2	1,714 lbs/hr.
NO_x	532 lbs/hr.
CO	124 lbs/hr.
Particulates	38 lbs/hr.
Hydrocarbons[2]	2 lbs/hr.
Estimated Hydrocarbons from Fugitive Emissions	[105 lbs/hr.]

Source: Exxon Donor Solvent Coal Liquefaction Commercial Plant Study Design, Exxon Research and Engineering Company, January 1978 (FE-2353-13).

[1]These atmospheric emission levels represent only the emissions from continuous sources.

[2]Hydrocarbon emissions from the tank farms are not included. Tank forms were considered to be off-site.

To minimize labor and time requirements, leak detection or screening must be rapid, convenient, and provide at least a semiquantitative estimate of the magnitude of the leak. Present day technology does not permit a zero leak system and judgements must be made as to the level of emission that requires repair.

As previously mentioned, the screening of sources during the Radian fugitive emission study was accomplished with sensitive portable hydrocarbon detectors. The instruments give direct readings of hydrocarbon concentration in ppm by volume. This instrumentation and methodology has been very effective in refinery applications where the prepondernace of the process streams are hydrocarbons. Table 7 summarizes the estimates of fitting and equipment counts from the "typical" 330,000 BPD petroleum refinery and the 60,000 BPD EDS plant. It is useful to comment here that the total source count is relatively independent of capacity of the refinery, depending more on complexity. A larger refinery would frequently use larger equipment with the same number of pumps and control loops. In contrast, the EDS plant is a commercial module. Expansion to a larger capacity would require additional trains with a corresponding additional number of fittings. (Downstream processing of the liquids would more probably follow the refinery pattern.) Referring to Table 7 it may be seen that a very different distribution of fittings and equipment as a function of service is expected for the EDS plant versus a refinery. The product and processing streams in which hydrogen is a major component are relatively much higher in an EDS plant. As is shown in Table 8, almost 20 percent of the valves in an EDS unit are projected to be in hydrogen service compared with about 8 percent in a typical refinery. In contrast, the heavy liquid valves predominate for the EDS unit, some 62 percent as compared to 28 percent for the refinery.

Application of refinery techniques to a liquefaction plant must then be made with care. The existing instrumentation responds differently to hydrogen than to hydrocarbons and either new, more specific instrumentation or different calibration procedures may have to be developed. In this light it is useful to outline the system which proved effective in the refining industry for developing correlations between screening factors and actual leak rates. The method relied on a large number of screening experiments which were correlated with a statistically selected number of detailed measurements by bagging sources.

Screening values were obtained when the source was first located and then the source was rescreened when it was sampled. Least squares linear regression equations were then developed for predicting leak rates from unsampled sources in the

Table 7

NORMALIZED RATIO OF EDS SOURCE ESTIMATES

TO REFINERY ESTIMATES

Source	Ratio (No. in EDS) / (No. in Refinery)
Valves	
Hydrogen Service	1.2
Gas/Vapor Hydrocarbon	0.09
Light Liquids	0.16
Heavy Liquids	1.0
Relief	0.49
Flanges	0.45
Pump Seals	
Light Liquids	0.16
Heavy Liquids	0.92
Compressors	0.90
Drains	0.26

Table 8

DISTRIBUTION OF VALVES AS A FUNCTION OF SERVICE

- Comparison of EDS with Refinery -

Service	Fraction in Refinery	Fraction in EDS
Hydrogen	0.07	0.19
Gas/Vapor	0.26	0.05
Light Liquid	0.39	0.14
Heavy Liquid	0.28	0.62

data base. For prediction outside the data base, a statistical analysis of covariance was performed to determine whether different linear equations were required for each source category. It was found that the source and stream types could be grouped such that seven equations were adequate for predicting leak rates from screened sources. The seven groups are as follow:

- Pumps in light liquid/two-phase streams, compressors, and relief valves in gas/vapor streams;
- Valves and compressor seals in hydrogen service;
- Valves in gas/vapor streams;
- Valves in light liquid/two-phase streams;
- Flanges;
- Drains;
- Pump seals in heavy liquid streams.

Nomographs were subsequently developed for predicting leak rates from screening values for the various source categories. Each nomograph gives the predicted mean leak rate as a function of the maximum TLV Sniffer screening readings taken directly at the source of the leak. An example nomograph is shown in Figure 2. The 90 percent confidence intervals shown on the nomographs are for the mean leak rate.

Since the correlation between screening values and actual leak rates is imperfect, the nomographs should not be used to determine emission rates. However, the nomographs are useful for evaluating maintenance and control options and/or priorities. The estimates presented in this paper indicate that fugitive emissions from coal liquefaction or, indeed, from any coal conversion facility which uses equipment similar to that in the petroleum refining or petrochemical industries are a matter requiring attention. Although the emphasis of this paper and previous work are on the leakage of non-methane hydrocarbons, the material leaking from a fitting will contain a wide range of components from those relatively innocuous to potentially toxic materials. The application of refinery techniques and development of methodology specifically targeted toward the coal conversion industry can enable the selection and implementation of control methods not overly burdensome to the plant operator but yet protecting both the worker and the environment from possible hazardous leaks.

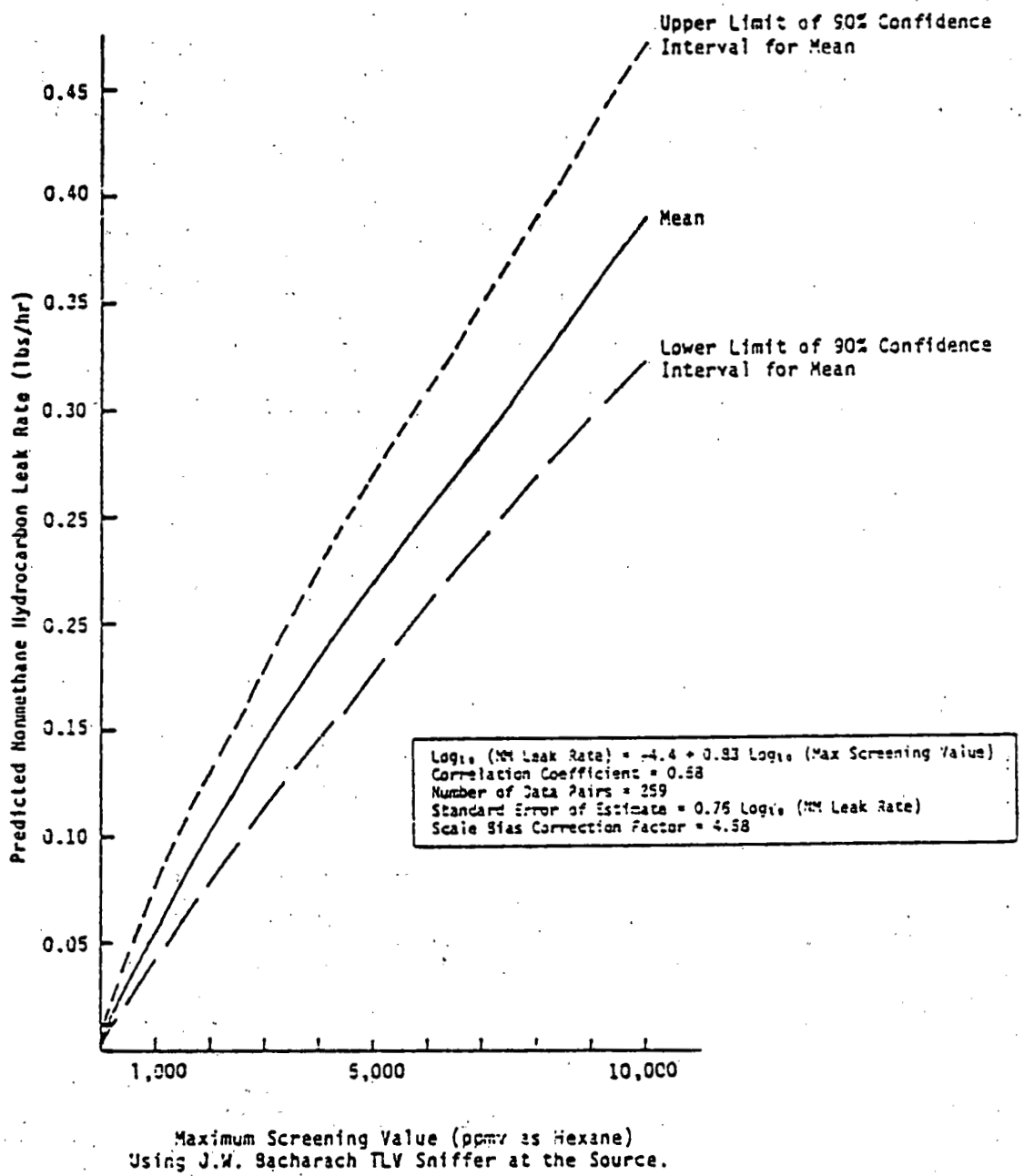


Figure 2

NOMOGRAPH FOR PREDICTING TOTAL HYDROCARBON LEAK RATES FROM MAXIMUM SCREENING VALUES - PUMPS (LIGHT LIQUIDS), COMPRESSORS, RELIEF VALVES (GAS/VAPOR STREAMS) (Part I: Screening Values from 0 to 10,000 ppm)

SUMMARY

The control of fugitive emissions has received significant attention over the past several years. Until recently, the prevailing attitudes were that existing maintenance programs were effective in preventing leaks. This has largely been true from the standpoint of explosion hazard but, as the results of the three year refinery study show, not necessarily true from the standpoint of preventing significant hydrocarbon emissions. The crude estimates made in this paper for an EDS plant indicate that essentially all of the hydrocarbon emissions will result from leaks. It has not been possible to eliminate leaks from petroleum refineries but directed screening and maintenance programs can potentially reduce leaks by over 50 percent, and even more in critical leak areas.

Equipment design, selection and maintenance are the keys to reducing leaks when coupled to a rapid, efficient detection and measurement program. With suitable modification in instrumentation or procedures, the leak reduction methodology developed for the petroleum refining industry should be readily adaptable to the new synfuels industry. In fact, including fugitive emission control as a design consideration in the new plants should provide even more effective and economically less burdensome leak control than that possible in a refinery which was built some years ago with controls now being superimposed on an existing system.

IMPLICATIONS OF ENVIRONMENTAL COMPLIANCE ON DOE GASIFICATION ECT DEVELOPMENT

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1.0 INTRODUCTION

Department of Energy coal gasification projects must be planned and implemented in concert with the development of effective and cost efficient control technology, sufficient to meet present and future environmental requirements. Environmental regulations will influence the timing and cost of commercialization, and will affect decisions regarding plant siting, process selection and design, and operation. It is therefore necessary to identify present and future regulations affecting gasification and to develop options to provide adequate control.

2.0 ENVIRONMENTAL REGULATIONS AFFECTING GASIFICATION

Environmental regulations are continually evolving and expanding. The last several years have seen increased emphasis on the regulation of toxic substances (especially carcinogens), as evidenced by the arrival of the Toxic Substances Control Act (TSCA), National Emission Standards for Hazardous Air Pollutants (NESHAP's), and the OSHA Cancer Policy. In the next five years several developments will significantly impact the commercialization of gasification plants. Among these are the publication of EPA "guidance documents" and the promulgation of New Source Performance Standards for gasifiers. The progression of TSCA regulations from the information-gathering phase to the enforcement phase may also affect gasification plants. It is possible that several gasification intermediates and products/by-products will ultimately be listed on various "priority lists" for regulation such as the NESHAP's hazardous substances list, the TSCA "50 list" and the OSHA Category I and II lists. These and other developments could markedly change the regulatory framework in which gasifiers must be developed and operated.

The current status and anticipated future developments of federal environmental acts and regulations affecting gasification are discussed below. These include the Clean Air Act, Clean Water Act, Resource Conservation and Recovery Act, Toxic Substances Control Act, and OSHA.

AIR QUALITY REGULATION

The National Ambient Quality Standards (NAAQS) set ambient air concentration limits for seven criteria pollutants. Of particular importance to gasification are sulfur dioxide, particulates (including fine particulates) and nitrogen dioxide. Revisions to the NAAQS for these three pollutants are expected during 1980, and may include a short-term standard for nitrogen dioxide.[1] The number of pollutants regulated under the NAAQS will increase in the future. If a facility is attempting to locate in an area which has not attained the NAAQS for pollutants which it will emit, the operators must arrange for offsetting reductions from existing sources. In addition, the Lowest Achievable Emission Rate (LAER) must be achieved by the new source/modification. The LAER is the lowest emission rate achieved in practice or required by any SIP. By definition, the LAER will become more stringent as new control technology is developed. If the proposed plant location has attained the NAAQS for emitted pollutants the plant will be subject to Prevention of Significant Deterioration (PSD) rules. PSD regulations set maximum permissible increments of air quality degradation for areas having better-than-standard air quality. Current regulations set increments for sulfur dioxide and particulates. Regulations setting standards for other NAAQS pollutants are expected in 1980-1981. Amendments to the regulations have been proposed as the result of the Alabama Power Co. vs. Costle decision, which invalidated key provisions of the current rules.[2]

The proposed amendments define a "major" source or modification based on emissions after, rather than before, controls.[3] However, for sources defined as major, the amendments would tend to increase the number of pollutants requiring Best Available Control Technology (BACT) and monitoring beyond the seven criteria pollutants, and would reduce the level of emissions considered significant. They would also allow the consideration of fugitive dust in assessing the impact of a source. The proposed amendments indicate the need to provide efficient controls for non-criteria pollutants such as trace metals and various sulfur compounds.

The National Emission Standards for Hazardous Air Pollutants define acceptable control technology, emission levels and/or ambient air concentrations for designated hazardous pollutants. Current standards cover asbestos, beryllium, mercury and vinyl chloride. Benzene and radionuclides have been listed as hazardous, and coke oven emissions are to be listed soon.[4] In October of 1979 the EPA proposed rules for identifying, assessing and regulating airborne carcinogens, which will ultimately result in the listing and regulation of a large number of carcinogenic substances.[5] The trend toward regulation of carcinogens emphasizes the need to control organic species, especially aromatic compounds.

Probably the most significant regulations affecting gasification are not even in existence at present. New Source Performance Standards set industry or process-specific standards for certain source categories which are generally more stringent than BACT requirements. Existing NSPS affect coal preparation plants, and other could be applied to gasification plants generating electricity on-site. However, standards specific to gasification processes are not expected until 1983 or later.[6] In the meanwhile, EPA plans to publish guidance documents which, while not legally binding, are

intended to direct the early development of the industry, avoiding expensive retrofitting when the NSPS for gasification are promulgated.

Visibility regulations will affect plants locating near mandatory Class I areas. One-hundred and fifty-six Class I areas have been designated for visibility protection. Final rules in this area are expected by November, 1980.[7]

WATER QUALITY REGULATION

Air pollution control as well as gasification processes themselves, result in the generation of liquid and solid wastes, the disposal of which is regulated under several federal acts. The Clean Water Act mandated the NPDES program, which regulates discharges into navigable streams. Permits set standards on a case-by-case basis, based on process-specific federal effluent guidelines and state water quality standards. Effluent guidelines for gasifiers do not exist at present. Contamination of groundwater by injected fluids is to be regulated by the Underground Injection Control Program (UIC), the final rules of which are expected in 1980.[8] Both NPDES and UIC regulations could affect liquid disposal procedures in a gasification plant.

SOLID AND HAZARDOUS WASTE REGULATION

The Resource Conservation and Recovery Act complements the functions of the CAA and CWA by addressing pollution of the terrestrial environment by solid/hazardous wastes. EPA issued proposed regulations implementing the Act in 1978 and 1979. Final regulations are now expected by April of 1980.

The most significant part of RCRA affecting gasification plants is Subtitle C, which deals with hazardous wastes. It is possible that a number of process wastes from gasification plants will ultimately be listed as hazardous under section 3001. Listing will mean that the substances must be stored, treated, labeled and transported according to hazardous waste regulations; and ultimately disposed of in a permitted hazardous waste disposal facility. EPA estimates that eighty percent of all generators dispose of wastes on-site, and would therefore required a disposal permit.

Hazardous waste permits will be developed on a case-by-case basis, integrating applicable regulatory requirements for storage, treatment, and disposal. Facilities approved for hazardous waste disposal will have to meet criteria for siting, design, and operation, as well as standards protecting human health and environment.

The impact of RCRA on gasification plants will depend largely on the specific wastes generated and the final regulatory status of those wastes. Certain high-volume, hazardous wastes considered to have a relatively low hazard potential are to be classified as "special wastes". EPA intends to promulgate specific regulations pertaining to these wastes, which at this time include mining wastes.' High volume wastes are intended for eventual recycle/reuse. Whether the high-volume solid wastes generated by a

gasification plant (e.g., slag, ash) would come under this classification is uncertain. It is likely however that a number of gasification wastes will be given hazardous status.

TOXIC CHEMICAL REGULATION

The Toxic Substances Control Act gives EPA authority to regulate toxic chemicals in all areas of commerce. Although the Act does not deal directly with emissions or control technology, it gives EPA authority to regulate any chemicals entering commerce. Regulation may range from warning label requirements to bans on production or distribution. The regulation of end products in commerce may affect the selection of gasifier designs and cleanup equipment.

OSHA

The Occupational Safety and Health Act is concerned with hazards in the workplace environment. Considerably more chemicals are regulated under the Act at present than by EPA regulations. Standards generally specify the maximum 8-hour exposure level which is permitted for a given chemical. The number of chemicals regulated under the Act is expected to increase as the recently-published OSHA Cancer Policy is implemented.[9] Compliance will require proper design and operational procedures to minimize worker exposure to hazardous substances, such as certain organics and trace elements.

3.0 CURRENT CONTROL OPTIONS

The following section identifies a number of currently available control technology options which could be used in gasification plants to achieve regulatory compliance. Whether these options are sufficient to meet current or expected standards can only be determined on a project-specific basis, where the variables of size, design, feedstock, location, land and water availability are known. As important as the technological efficiency of a control option is the economics of the option. Both control efficiency and economics contribute to the selection of ECT. The discussion which follows will briefly describe the application of environmental control technology options under consideration in DOE gasification programs for control of air, water and solid waste pollutants. It is followed by a discussion of advanced technology R&D efforts and future control needs.

AIR POLLUTION CONTROL TECHNOLOGY

Gasifiers are expected to emit large amounts of SO_2 from such sources as tail gases from sulfur recovery units and coal-fired boilers for steam generation. A number of control options are available for this criteria pollutant. The Wellman-Lord FGD unit can achieve approximately 95 percent SO_2 removal and is well demonstrated. Less efficient options include the Shell FGD system and the SNPA/Lurgi Sulfreen Process. SCOT and Beavon systems may provide more efficient removal, but are more limited in their application.

Acid gas removal from the raw gas stream is necessary both for product upgrading and for regulatory compliance. (Proposed PSD amendments set low emission levels for H_2S, above which BACT and monitoring are required). The Rectisol process provides for H_2S and CO_2 removal. It releases CO_2 and reduced sulfur compounds and can operate at relatively low pressure. Other options include the Purisol and Selexol processes. Acid gas removal processes vary as to selectivity and operating pressure and must be selected according to process requirements.

Sulfur recovery options are desirable to reduce several regulated emissions and to produce saleable by-products. The Claus Unit is a well-demonstrated option. It produces elemental sulfur and SO_2 emissions requiring additional cleanup. On-site sulfuric acid production is another option, but requires additional cleanup of acid mist and SO_2.

Regulations controlling particulates are expected to become more stringent in the future. EPA has indicated its intention to regulate fugitive emissions under PSD and to place increased emphasis on fine particulates (2 microns). Gasification plants will generate significant quantities of particulates from coal transportation and handling, coal fired boilers for steam generation and within the raw gas stream. Coal and solid waste storage piles require spraying for particulate suppression. Water sprays provide only temporary, partial suppression. Crusting agents such as sprayed polymers provide more effective suppression, but require reapplication upon disturbance. Dust from transportation and handling units (e.g., conveyors, hoppers, crushers, etc.) may be controlled with vacuum hoods, baghouse systems as well as water and chemical sprays. These options tend to provide inadequate control, especially of fine particulates. The electrostatic precipitator can provide efficient cleanup of fine particulates in the gas stream. It may not be sufficient to meet more future regulations however. Cyclones provide a less effective means of particulate removal, but are useful as a first step in particulate cleanup. Baghouse cleanup is not generally applicable to hot gas cleanup. The Venturi scrubber is useful as a part of cleanup system but is not completely effective against very fine particulates.

COOLING OPTIONS

Waste heat generated by various heat exchangers in a gasification plant must be dispersed in a manner which will not alter the surrounding aquatic ecosystem. Options for controlled waste heat dispersal vary considerably in their design and environmental impacts. Cooling ponds and spray channels require significant land area and have uncertain effectiveness. Dry cooling has limited effectiveness, and may be costly in some applications. Various cooling tower designs using both forced and natural draft are effective, but have their own environmental impacts. These include blowdown wastewater, the generation of fog and ice in the local area, and the deposition of salts on the surrounding landscape.

WATER TREATMENT TECHNOLOGY

One approach to water pollution prevention is zero-discharge design. It may be accomplished both by cleanup and recycling of process fluids and by

evaporation of wastewater. Evaporation imposes a significant energy penalty on the process. In practice zero discharge will probably be used only for selected wastestreams at present due to costs and design problems. Increased regulatory stringency could make this option more necessary in the future; however, the value of the water, and the additional burden of evaporative salts disposal must be incorporated into the decision.

The other alternative, waste stream treatment and discharge/recycle, requires a number of different processes on the contaminants present and the destination of the cleaned stream (i.e., discharge or recycle).

Gasifier blowdown is expected to be high in TDS and TSS and to contain ammonia, cyanide and toxic organics. The ability of these compounds to induce toxic effects at low levels suggests that the evaporation option may be necessary despite the energy penalty. Discharge of the blowdown would require a number of physical and biological treatment processes. These include clarification, nitrification, denitrification, reverse osmosis, activated carbon filtering and incineration. Various combination of these processes would be required for treatment of other blowdown streams (e.g., FGD units or cooling tower) for reuse or discharge.

SOLID WASTE DISPOSAL

Protecting the environment from damage by solid wastes may require a combination of several control measures. Process design may be modified to reduce the volume or hazardous properties of solid wastes. Waste may be treated to render it less hazardous or more stable. The reuse of waste products in other commercial applications is another option being considered.

A number of solid wastes generated at the gasification plant will probably require disposal in approved hazardous waste disposal sites under RCRA. These include spent catalysts and tars, and potentially slag, fly ash and other wastes. Disposal in lined (impermeable) pits will be required as well as runoff capture and groundwater monitoring. Problems associated with hazardous waste disposal include leaks in the liners and cover soil, run-off control and general long-term maintenance. Even the 20-year maintenance period required under RCRA will not preclude long-term environmental damage. For this reason, hazardous waste treatment methods should be used in conjunction with proper disposal. These include neutralization and other forms of chemical treatment to render the wastes inert and/or non-reactive.

A second goal of RCRA beyond safe disposal is the reuse of solid wastes. Reuse of coal ash is already being done on a large scale. Ash and slag from gasification plants as well as produced gypsum may find commercial markets. The development of these options must include a careful analysis of the environmental effects of reuse.

4.0 FUTURE NEEDS AND ADVANCED TECHNOLOGY R&D

Pilot and demonstration plants must be designed with control technologies capable of complying with federal, state, and local regulations. The appropriate NEPA documents must be prepared and reviewed at each major

scale-up step. Environmental Readiness Documents analyze the suitability of existing technology to control a given process on a larger scale, and identify areas requiring further study. Achieving compliance on the demonstration scale is not enough to guarantee environmental compliance at the commercial level, however. The size of a commercial industry alone would tend to increase the stringency of regulatory requirements, particularly for plants locating in relative proximity to each other. Identical processes would tend to have similar emissions and would therefore be in competition for available air quality increments. Furthermore, environmental regulations will continue to develop and change during the long lead time required for commercial-scale plant construction. It is therefore necessary not only to achieve compliance at the demonstration level, but to develop advanced control technology capable of meeting the control requirements of the future.

THE AECT PROGRAM[10]

To meet the challenge the developing coal combustion and gasification technology in an environmentally acceptable manner the Department of Energy (FE) has initiated the Advanced Environmental Control Technology (AECT) Program. The objective of the program is to provide technology to meet environmental regulations and to meet the gas stream input requirements for advanced energy conversion equipment. The development of effective control technology demonstrating reliability, acceptable cost, and energy efficiency are principal goals of the program.

The AECT Program consists of the development, improvement, and technical and economic evaluation of existing and promising new methods for cleaning undesirable pollutants released during the combustion or gasification of coal. Development, improvement, and evaluation are accomplished through a number of laboratory or bench-scale explorations, pilot-plant tests, and full-scale cleanup system evaluations at large electric utility and industrial facilities in cooperation with the owners of these facilities.

The program is directed toward conducting full-scale verifications of equipment that will reliably and economically provide solutions to the environmental degradation and equipment damage problems associated with coal utilization.

The three disciplines are described as follows:

- The Flue Gas Cleanup Category concerns the technology of removing particulates, sulfur oxides, nitrogen oxides, and other harmful species from exhaust gases to meet environmental requirements.

- The Gas Stream Cleanup Category encompasses the technology for improving gas stream quality. This means removal of contaminants both with hardware and with in-process controls, to protect downstream equipment as well as the environment.

- The Cleanup Base Technology Category will provide the crosscutting base technology development and systems engineering evaluations for the program.

Flue Gas Cleanup

A major emphasis of the AECT program is flue gas cleanup. Although this process is chiefly associated with coal combustion, it is discussed here because it provides one option for meeting environmental standards for sulfur compounds during the combustion of coal to produce steam for gasification and the combustion of low-Btu gasifier product gas. Several of the low-Btu gasifiers currently operating in the U.S. would not have sulfur control equipment sufficient to meet NSPS were their products to be used for electric utility steam generating. The future development of advanced FGD systems may affect the relative cost of the pre- and post-combustion sulfur cleanup options.

The near-term focus of the flow gas cleanup program is on SO_2 removal. Current FGD operating designs consist of scrubbers using a slurry of lime or limestone to absorb SO_2 from flue gas; but these scrubbers generally have process weaknesses such as scaling and corrosion. The first project in Flue Gas Cleanup is therefore the improvement of the operational aspects of these first generation units. Wet scrubber systems also have certain inherent drawbacks including the generation of large amounts of waste, the need for frequent and intensive maintenance, and high initial capital equipment costs. To address these drawbacks, the AECT program will, in parallel, pursue a project to develop advanced FGD systems that will cost-effectively eliminate the drawbacks. However, they will not be available until the 1985 time frame. A third project, Combined Flue Gas Cleanup, has been established to develop new and/or improved technology for flue gas cleanup of particulates and NO_x interfaced with the cleanup of SO_2 as well.

Gas Stream Cleanup

Combined-cycle generating plants powered by high temperature, low-Btu gases from direct coal gasification may prove to be an extremely attractive approach to large-scale coal utilization. The Gas Stream Cleanup Project will develop and demonstrate systems for removing particulate matter, sulfur compounds, alkali metals and other substances that may damage power equipment and thus prevent the direct use of coal gases. It will also demonstrate technology to limit emissions of SO_x, NO_x, and other pollutants via process stream cleanup.

In addition to meeting the needs of turbines and fuel cells, gas stream cleanup may provide a more cost effective means of meeting environmental and combustion engine requirements. It may be used to achieve a more desirable end-product from the standpoint of TSCA regulations. The Hot Gas Cleanup Program Research and Development Announcement (PRDA) released by DOE in 1979 will provide a nucleus of techniques for development.

Cleanup Base Technology

A critical DOE role for fossil energy cleanup is to act as an integrator of technology being developed by industry, other government agencies, and within DOE itself. Many technology issues cut across interrelated cleanup and powerplant areas in general. The purpose of this Cleanup Base Technology category is to provide these critical crosscutting services for both Flue Gas and Gas Stream Cleanup. The four projects included in this category are Waste Management, Systems and Economic Comparisons, Instrumentation, and Applied Research.

The objective of the Waste Management Project is to develop improved methods of handling, reuse, and disposal and combustion of cleanup wastes. Efforts will include the study of FGD sludge utilization options as well as improving the performance of dewatering equipment. The Systems and Economics Comparisons Project will perform economic and technical trade-off analyses of various cleanup alternatives to ensure that the best system combinations are provided. The Instrumentation Project will try to develop monitoring technology capable of measuring process variables during operation. Instrumentation that is accurate and precise, and capable of functioning at temperature and pressure present in the process stream will continue to be a critical requirement. Applied Research efforts will focus on understanding of the scientific bases for flue gas and process stream cleanup technologies. This project will include studies of materials erosion and corrosion, and chemical/physical characteristics of products, contaminants, sorbents, etc.

THE EFFECTS OF REGULATORY DEVELOPMENTS ON FUTURE DOE ACTIVITIES

The developing nature of environmental regulations suggests that DOE activities may need to undergo parallel modifications as time goes on. Areas which are likely to receive increased emphasis in the future include control technology for organics and trace elements, recycling of solid wastes, and in-plant controls preventing worker exposure.

The increased emphasis which recent legislation has placed upon toxic (carcinogenic) substances will ultimately result in regulations which specifically address a large number of suspected or proven carcingoens. Experience indicates that many carcinogens are organic species, some of which are found in fossil fuel processes. Current efforts to identify the components of gasification streams in conjunction with ongoing and future toxicologic tests will give a better understanding of the chemical species requiring control. Standards are expected to be stringent for carcinogenic substances and may require the development of advanced control technology.

Waste waters from gasifiers generally contain various organics and trace elements. Phenol appears to be the major organic constituent, and phenolics as a class constitute 60 to 80 percent of the total organic carbon (TOC) in the wastewater. Other classes of organics, such as mono- and polycyclic nitrogen-containing aromatics, oxygen- and sulfur-containing heterocyclics, and polunuclear aromatic hydrocarbons, appear to be present at significant

concentrations. Conventional wastewater treating schemes are believed to be adequate for reducing concentrations of major contaminants to within the limits of applicable effluent standards. However, zero discharges of certain toxics, e.g., carcinogens, may be required. In the case of zero discharge, the only certain treatment is forced-evaporation followed by incineration of the concentrated wastes. The drawbacks of this treatment scheme are heavy energy penalty, high capital costs, and increased toxic emissions to the air which may not be desirable after all. Development of advanced control technology to control the highly toxic contaminants from coal gasification wastewasters may be necessary. Evaluation of coal conversion wastewater treatability of coal conversion wastewater being carried out at the University of North Carolina under EPA's sponsorship has shown promising results.

Regulations under RCRA will increase the cost of solid waste disposal and will encourage the recycling of useable solids. Efforts to study options for the reuse of gasifiers solid wastes may need to be stepped up in the future. The environmental and health effects of these options, together with development of ways to render the wastes inert should parallel these efforts.

The recent publication of the OSHA cancer policy is a significant event which establishes a methodology for categorizing, testing, and regulating suspected or proven carcinogens. It will ultimately result in the addition of numerous chemicals to OSHA regulations limiting worker exposure; and may require the development of more effective controls.

FOOTNOTES

1. Calendar of Federal Regulations, U.S. Regulatory Council, November 28 1979 (44 FR 68247)

2. Alabama Power Co., et al., Petitioners, v. Douglas M. Costle, as Administrator, EPA et al., Respondents, Sierra Club, et al., Intervenors, No. 78-1006, June 18, 1979, as reported in the Environmental Reporter, 13 ERC 1225, July 13, 1979.

3. EPA Proposed Amendments to Prevention of Significant Deterioration Regulations, September 5, 1979 (44 FR 51924)

4. Calendar of Federal Regulations (44 FR 68238-68239)

5. National Emission Standards for Identifying, Assessing and Regulating Airborne Substances Posing a Risk of Cancer, EPA, October 10, 1979 (44 FR 58642)

6. Gage, Stephen J., Assistant Administrator for Research and Development, EPA, Statement before the Subcommittee on Energy and Power, Committee on Interstate and Foreign Commerce, October 18, 1979.

7. Calendar of Federal Regulations (44 FR 68249)

8. See State Underground Injection Control Programs; Minimum Requirements and Grant Regulations (proposed UIC regulations); (44 FR 23738)

9. Identification, Classification and Regulation of Potential Occupational Carcinogens, OSHA, DOL, January 22, 1980, (45 FR 5002)

10. Major portions of this section are taken from the Multiyear Program Plan for Advanced Environmental Control Technology, December 14, 1979, prepared for Fossil Energy, DOE, by TRW.

GLOSSARY OF ACRONYMS AND ABBREVIATIONS

AECT	Advanced Environmental Control Technology
ASEV	Assistant Secretary for Environment (DOE)
BACT	Best Available Control Technology
CAA	Clean Air Act
CFR	Code of Federal Regulations
CWA	Clean Water Act
EA	Environmental Assessment
EDP	Environmental Development Plan
EIS	Environmental Impact Statement
ERD	Environmental Readiness Document
FE	Fossil Energy
FGD	Flue Gas Desulfurization
FR	Federal Register
LAER	Lowest Achievable Emission Rate
NAAQS	National Ambient Air Quality Standards
NEPA	National Environmental Policy Act
NESHAP('s)	National Emission Standards for Hazardous Air Pollutants
NIOSH	National Institute for Occupational Safety and Health
NO_x	Nitrogen Oxide(s)
NPDES	National Pollutant Discharge Elimination System
NSPS	New Source Performance Standards
OSHA	Occupational Safety and Health Administration (DOL) or Occupational Safety and Health Act
PMN	Premanufacture Notice
POM	Polycyclic Organic Material
RCRA	Resource Conservation and Recovery Act
SIP	State Implementation Plan
SO_2	Sulfur Dioxide
SO_x	Sulfur Oxide(s)
TSCA	Toxic Substances Control Act
TSP	Total Suspended Particulates
UIC	Underground Injection Control

ZERO LIQUID DISCHARGE FOR THE ILLINOIS COAL GASIFICATION GROUP DEMONSTRATION PLANT

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ZERO LIQUID DISCHARGE FOR THE ILLINOIS COAL GASIFICATION GROUP DEMONSTRATION PLANT

The waste treatment and disposal system being designed into the Illinois Coal Gasification Group Pipeline Gas Demonstration Plant is one of zero discharge. All water streams are recovered, treated and recycled, and all solid wastes are placed in landfills. The decision to design the plant in this manner has been made by ICGG in the early program phase, actually when the proposal to DOE was being prepared.

The Demonstration Plant is designed to process 2,300 tons per day of Illinois coal, with provisions to process Western and Pennsylvania coals as part of the program. The architect-engineer for the work is the Chemical Plants Division of Dravo Engineers and Constructors, who are designing all areas, including water and waste. This paper will confine itself to the Illinois case. The coal is pyrolyzed and gasified to obtain liquids and synthesis gas. The liquids are treated to produce 2,100 barrels per day of naphtha and fuel oils. The synthesis gas is purified and then methanated to produce nearly 24 million cubic feet per day of pipeline gas. The water demand is approximately 900 gallons per minute, which is obtained from the Mississippi River, at a point nearly 20 miles away from the plant. The Wastewater treatment recovers 417 GPM to be recycled. The remaining water is lost by evaporation in the Cooling Towers and in process consumption.

There are three main wastewater streams emanating from the main coal gasification process units. Two of these streams consist of the wastewater from ammonia strippers, one of which is high in phenolics. The other stream is the process sewer which picks up any waste liquid leakage from any of the other process areas. This water is treated in the Wastewater Treatment Plant and then returned to the Water Treatment Section where it is blended with filtered river water, further treated, and utilized as cooling water and boiler water make-up. The solids removed from the wastewater by the Wastewater Treatment Plant are disposed of in landfills along with any of the other process areas solids wastes.

Process wastewaters high in dissolved solids are not dumped to the Process Sewer, but rather are pumped to an Inorganic Waste Evaporator. The recovered water is conveyed to Water Treatment and is finally utilized as boiler water make-up. All of the rainwater runoff at the plant perimeter is collected through the Clean Storm Sewer System to the Clean Stormwater Basin, where it is treated for solids removal and returned to the Raw Water Reservoir. Runoff collected in process areas flows through the Contaminated Storm Sewer System to the Contaminated Stormwater Basin, where it is treated and pumped to the Wastewater Treatment Plant for further handling. Figures I and II show the general flow scheme.

An emergency overflow and storage system is provided to accept wastes from the plant in the event an upset occurs in the wastewater treating. This water then is processed through the treatment system when the operation returns to normal.

Primary Separation and Equalization

The Process Sewer and Stripper wastewaters are pumped into one main stream, which flows into Oil-Water Separator No. 1. The separator removes all free floating oil and settleable solids. The separated oil (slop oil) is collected and pumped to the Oil Recovery Area of the plant for recycling. The settled solids collect at the bottom of the separator and are pumped out to the Primary Sludge Holding Tank. A stream of water sprayed into the bottom of the separator prevents solids bridging and ratholing.

The separator's wastewater effluent is pumped to the Equalization Tanks, which have approximately a two day detention capacity based on design flow, to dampen out any minor hydraulic and/or contaminant loading surges in the wastewater flow. In the event major hydraulic surges and/or contaminant shock loadings occur, the wastewater stream or streams in question will be diverted to the Emergency Storage Basin.

In order to keep the wastewater well mixed and prevent any settling of suspended solids, the Equalization Tanks are agitated by bubbling air. An added benefit to using air mixing is that it would aid in stripping and/or oxidizing any hydrogen sulfide and mercaptans that might be present in the wastewater. Hydrogen sulfide or mercaptans stripped from the wastewater, are treated with ozone as the tank air passes through an Ozone Odor Control System before venting to the atmosphere.

Lime-Soda Softening

From the Equalization Tanks the wastewater is pumped to the Lime-Soda Softening System. The system consists of two tanks, each with a mixer, a mixing zone, a sludge concentration zone, and a clarification zone. The system is used to reduce the concentration of calcium,(Ca) and magnesium,(Mg) in the Wastewater to levels approximately equivalent to those found in the river water. Slaked lime, $Ca(OH)_2$ and soda ash, Na_2CO_3, are added to the wastewater. for softening and a primary coagulant is also added to the wastewater to hasten precipitate settling.

Excess slaked lime may have to be added to the wastewater to effect the desired amount of $Mg(OH)_2$ precipitation. If this is the case, and if there is not sufficient carbonate in the wastewater to react with the Ca++ from the excess lime, then a recarbonation step following lime or lime-soda softening may be necessary.

Carbon Dioxide, which has been scrubbed from the synthesis gas, is bubbled through the wastewater as it passes through the Recarbonation Tank. The wastewater then flows through a flocculation tank and a recarbonation clarifier where the precipitate is removed. The softening sludge from both the Lime-Soda Softening System and Recarbonation Clarifier is pumped to the Softening Sludge Press.

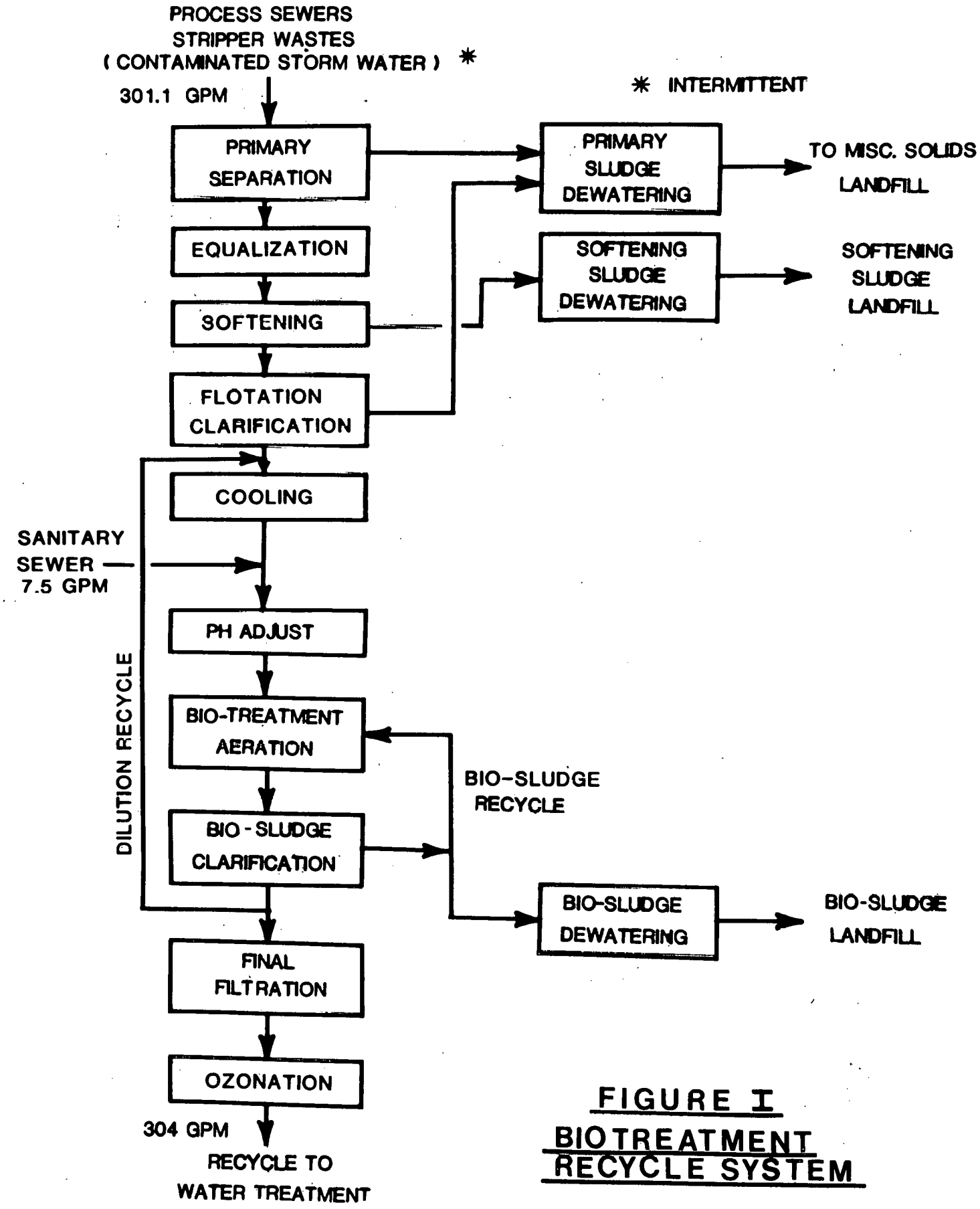


FIGURE I
BIOTREATMENT RECYCLE SYSTEM

Flotation Clarification and Cooling

The wastewater flows from softening proceed to the Flotation Clarifier where it is blended with a coagulant. The coagulant effects particle charge destabilization among the suspended and colloidal solids and emulsified oil droplets in the wastewater. Wastewater then flows into two flocculation tanks where it is joined by a secondary flocculant and gently mixed. The wastewater finally flows into two flotation tanks, where air bubbles capture the solids and oil flocs and float them to the water surface to be scraped into a sludge box. The floc sludge is pumped to the Primary Sludge Holding Tank.

The wastewater is now virtually free of all solids and oil particles and has a pH range of 7 to 10, and is pumped to the Bio-Treatment Plant Influent Coolers. A dilution recycle is added to the wastewater to lower the phenolics concentration in the wastewater to a concentration not toxic to activated bio-sludge. The combined stream flows through one or both of the coolers to bring the wastewater to 90°F, the optimum activated sludge bio-treatment temperature.

After cooling, the wastewater is joined by the Sanitary Sewer (after it has passed through the Septic Tank), sludge press filtrate, sand filter back-wash, and possibly phosphoric acid and ammonia. The latter two streams are cellular growth nutrients, in the event they are not in the wastewater in sufficient quantities. The combination of streams, which constitute the influent to the Bio-Treatment Plant are blended and pH adjusted by either adding sodium hydroxide or sulfuric acid.

Bio-Treatment

The Bio-Treatment Plant consists of a covered, multi-cell, activated sludge aeration tank with an aerator in each cell and a high purity oxygen atmosphere. As the wastewater passes through the tank, activated sludge absorbs and digests the soluble organics in the wastewater releasing CO_2 and forming additional biological growth. In order to maintain a constant optimum activated sludge concentration in the aeration tank, it is necessary to remove activated sludge at a rate equivalent to the rate new biological growths are being synthesized. As the wastewater flows out of the aeration tank into the clarifiers, it takes with it an equivalent concentration of activated sludge which settles to the bottom of the clarifier. A portion of this settled sludge is pumped to the Bio-Sludge Thickener and the rest is recycled back to the aeration tank.

A oxygen atmosphere is maintained in the aeration tank to provide the oxygen for respiration and cellular synthesis. The cover over the aeration tank is used to contain the high purity oxygen atmosphere and to maintain the proper temperature, particularly during winter operations. After the activated sludge has settled from the wastewater in the Bio-Sludge Clarifiers, the wastewater overflows the clarifier weirs to the Final Effluent Filter System. Floating material found in the Bio-Sludge Clarifiers is collected and is pumped to the Bio-Sludge Thickener.

Final Effluent Treatment

The wastewater flows into the Final Effluent Filter System through the deep bed gravity filters to remove any bio-sludge solids that were in the wastewater. The filtered wastewater overflows to the Ozone Contactor.

The ozone is bubbled through the wastewater as it passes through the Ozone Contact Tanks to oxidize residual organics, and destroy any bacteria and viruses. The treated wastewater is pumped to the water treatment area where it is further treated for use as cooling tower and boiler water make-up.

Primary Sludge Dewatering

Primary sludge from several sources previously mentioned is collected in the Primary Sludge Holding Tank. The sludge is then mixed with a sludge conditioning polymer and pumped to the Primary Sludge Presses. The sludge is dewatered and conveyed to the Miscellaneous Solids Landfill. The filtrate is pumped to the influent of the Bio-Treatment Plant System.

Bio-Sludge Digestion and Dewatering

Waste activated sludge and bio-sludge skimmings are pumped from the Bio-Sludge Clarifier to the flocculation tanks of the Bio-Sludge Thickener. The bio-sludge is gently blended with a flocculant. The bio-sludge then flows into the flotation tanks where air bubbles float the bio-sludge solids to the water surface, to be skimmed off into a sludge box. The thickened bio-sludge is then pumped to the Aerobic Digester Tanks. The thickened bio-sludge is thoroughly mixed and aerated in the Aerobic Digester Tanks in order to effect the process of auto-digestion to render most of the bio-mass inert. The thickened and stabilized bio-sludge is then mixed with a sludge conditioning agent and pumped to the Bio-Sludge Presses. The bio-sludge is dewatered and conveyed to the Bio-Sludge Landfill. The filtrate is pumped to the influent of the Bio-Treatment Plant System.

Softening Sludge Dewatering

Softening sludge from the Lime-Soda Softening System and the Recarbonation Clarifier is mixed with a sludge conditioning polymer then is pumped to the Softening Sludge Press. The sludge is dewatered in the press and conveyed to the Softening Sludge Landfill. The filtrate is pumped to the influent of the Bio-Treatment Plant System.

Inorganic Waste Evaporation

Wastewaters high in dissolved solids are pumped to the Inorganic Waste Hold Tank from the following sources:

Lime Reactor Regenerant
Cooling Tower Blowdown
Filtered Water Deionizer Backwash and Regenerant
Condensate Deionizer Backwash and Regenerant
Cooling Tower Water Cation Exchanger Regenerant
Process and Potable Water Cation Exchanger Regenerant
Live Coal Pile Stormwater Runoff (intermittent)

In addition, sulfuric acid and caustic are added to the tank, as required, for pH control. After blending, the wastewater is pumped to the Inorganic Waste Evaporator System. This system consists of a triple effect, horizontal forced circulation evaporator and all the other ancillary equipment necessary, such as pumps and compressors, to effect the required process performance. The dissolved solids are deposited in slurry form on a dryer and delivered to the Evaporator Solids Landfill. The evaporator distillate is returned for use as boiler water make-up.

Stormwater Treatment

Contaminated stormwater runoff is collected from three sources, the Dead Coal Pile, the Oil Storage Area, and the Contaminated Storm Sewer. The contaminated runoff is then pumped to Oil-Water Separator No. 2 which removes all free floating oil and settleable solids from the contaminated runoff. The separated oil (slop oil) is intermittently pumped to the oil recovery section of the plant. The settled solids are pumped from the bottom of the separator to the Primary Sludge Holding Tank. A spray pump is used to prevent solids bridging or ratholing in the bottom of the separator. The separator effluent flows through an Inline Mixer to the Contaminated Stormwater Basin. The inline mixer is used to blend any sulfuric acid or caustic added for pH control. The contaminated stormwater is surged in the basin, then pumped at a controlled rate to the head end of the Wastewater Treatment Plant for further treatment.

Clean stormwater runoff is collected in the Clean Stormwater Sewer System, pumped to the Stormwater Clarifier, where settleable solids are removed, and stored in the Clean Stormwater Basin. The water is returned to the Raw Water Reservoir or alternately to the Wastewater Treatment Plant, if contaminated.

Solids Disposal Systems

The following is a list of the landfills:

Bio-Sludge
Softening Sludge
Evaporator Solids
Slag
Calcium Sulfite/Sulfate from SO_2 Removal
Miscellaneous Solids

With the exception of some of the solids dumped in the Miscellaneous Solids Landfill, all of the solids and sludges are transported to their respective landfills by conveyors. They are then placed in layers, or lifts, by a bulldozer and covered with soil at the end of each day's activity. The sides and bottoms of the landfills are lined with an impermeable native clay layer to prevent any landfill leachate from percolating into the groundwater. The bottoms of the landfills are slightly sloped so that any leachate within the landfills will flow to collection sumps and be pumped to the Wastewater Treatment Plant for treatment. The various solids are not dumped into a common landfill so that separate leachate analysis may be made. The use of native clays as pit lining material is preferable to synthetics, as they have a demonstrated stability not present in those synthetics.

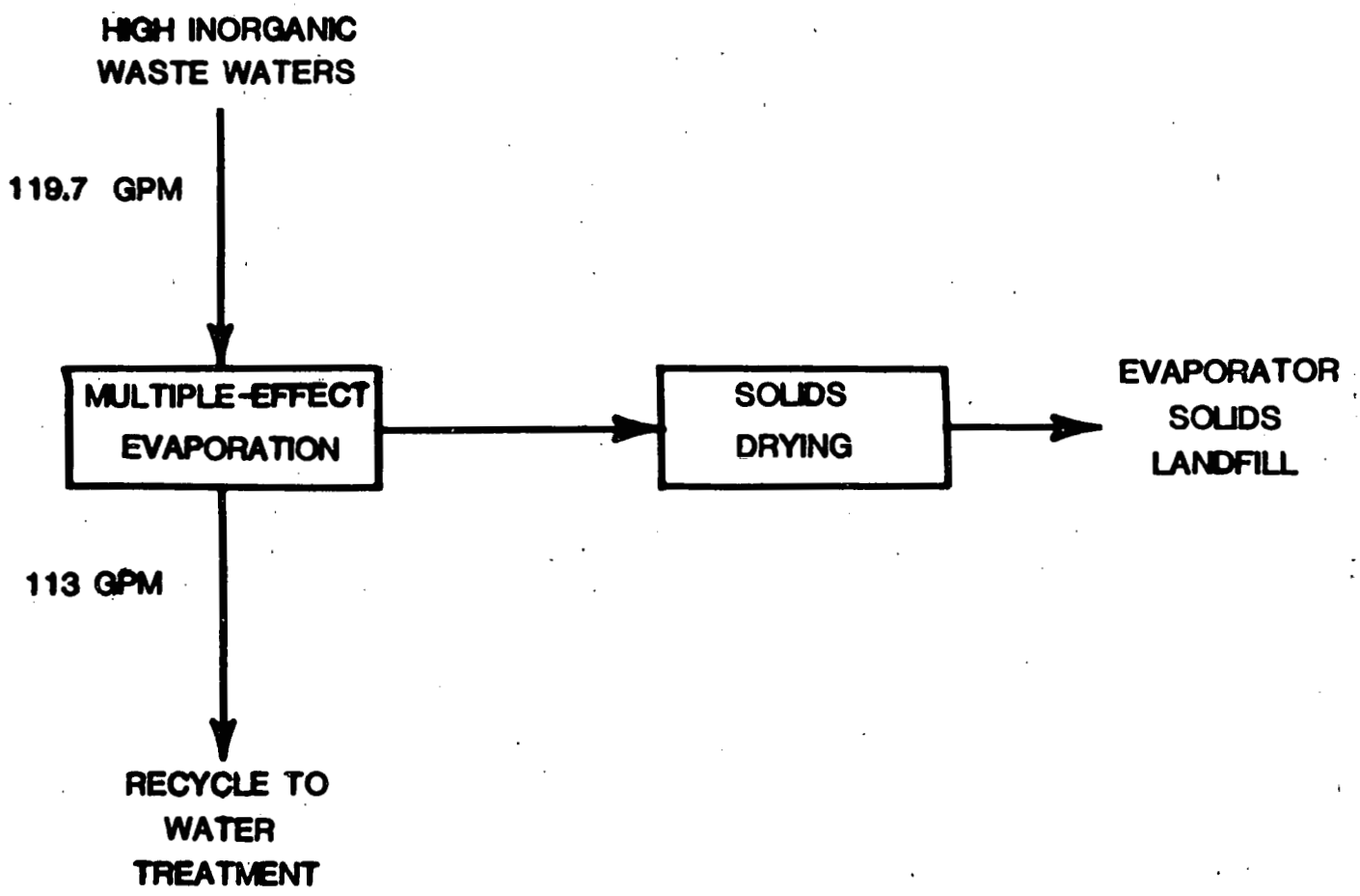


FIGURE II
EVAPORATOR
RECYCLE SYSTEM

Capital Costs

The capital cost of the facility, as designed for the Demonstration plant is approximately $22,500,000. This cost includes engineering, detailed design, procurement, construction and contractor's fees. It does not include interest on construction funds, client project management costs, start up costs or working capital.

Operating Costs

The cost of operating the waste system is an incremental portion of the total plant operating cost. As such, it is not meaningful to calculate a separate cost. However, the systems require the following materials to process the wastewate. Data here is given for the case of processing Ill. No. 5 and 6 coals.

Total Wastewater - To Biotreatment - 308.6 GPM
- To Evaporation - 119.7 GPM

Chemical Consumption

$Ca(OH)_2$	- 435 Tons/Year
H_2SO_4 (93% solution)	- 4,380 Gal./Year
Cationic Polymer	- 14,000 Gal./Year
Anionic Polymer	- 7,100 Gal./Year

Utilities

Steam	- 30,000 Lb./Hour
Cooling Water	- 2,100 GPM
Electric Power	- 1,100 KW

Thermal Efficiency Impact

The biotreatment system is not a major energy consumer, and it can be considered that its energy demands would not add significantly to the overall energy consumption. Indeed, it would approximate that needed for open discharge. However, the concept of the total recycle of water does give an energy credit by reducing the pumping demand. The water supply from the plant comes from the Mississippi River, 20 miles from the plant. This power saving is estimated at 143 HP, or equivalent to 0.05 percent of the coal fed to the Demonstration Plant.

The use of the evaporator, however, has a negative impact on the thermal efficiency of the facility. Generating the 30,000 lbs./hour of steam will require an addition of coal feed to the plant. That quantity of coal is approximately 1.9 percent of the feed, and has the effect of reducing the plant thermal efficiency by that amount. The evaporator is required, however, since brackish water cannot be discharged from new plants in the State of Illinois.

Summary and Conclusion

The concept of zero liquid discharge is viable and can be accomplished using current technology. It does save water, however, it is at the expense of overall thermal efficiency of the facility.

Dup

LEACHING STUDIES OF COAL GASIFICATION SOLID WASTE TO MEET RCRA REQUIREMENTS FOR LAND DISPOSAL

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INTRODUCTION

The 1977 National Energy Plan (NEP) proposes that utilities and industries throughout the United States shift from the consumption of oil and natural gas to the utilization of the more abundant supplies of coal.[1] Utilization of coal as an energy source results in the production of significant amounts of ash requiring some form of disposal or utilization. Coal ash has been used as a fill material or in the production of building products; however, at this time the amount of ash produced is far in excess of the demand. Although the Resource Conservation and Recovery Act of 1976 (RCRA) will stimulate the recovery and utilization of waste materials, it also imposes stringent regulations on the methods used for the disposal of all solid wastes.[2] A key feature of RCRA is the designation of certain solid wastes as hazardous wastes. These types of wastes must be disposed in such a manner as to prevent any significant degradation of the environment.

Resource Conservation and Recovery Act defines a hazardous waste as:[2]

> "a solid waste, or combination of solid wastes, which because of its quantity, concentration, or physical, chemical or infectious characteristics may -
>
> (A) cause, or significantly contribute to an increase in mortality or an increase in serious irreversible, or incapacitating reversible, illness; or
>
> (B) pose a substantial present or potential hazard to human health or the environment when improperly treated, stored, transported, or disposed of, or otherwise managed."

In the latest version of the hazardous waste regulations proposed by EPA to implement RCRA, solid wastes will be designated as hazardous using two sets of guidelines: (1) determining if the waste is listed as being a known hazardous waste under other federal regulations, and (2) a set of characteristics that define the hazard.[3] Eight characteristics have been suggested: ignitibility, corrosivity, reactivity, toxicity, radioactivity, infectiousness, phytotoxicity, and terato- and mutagenicity. In the draft regulations proposed for public comment on December 18, 1978, only the first four characteristics were considered, with the others deferred for inclusion in the regulations at a later date.[3] Of these four characteristics, toxicity is the major concern for gasifier ash. In these regulations, an extraction test is proposed to define a waste as toxic if the leachate concentration of any one of eight trace elements exceeds ten times the maximum concentrations listed in the EPA Interim Primary Drinking Water Standards (IPDWS).[4] Because

comments on these draft regulations were so numerous, the final regulations have not yet been issued. Thus, the conclusions and observations presented in this paper regarding the hazardous nature of the waste will require a reexamination when the final regulations are published.

To date, much of the expressed concern regarding RCRA has centered on the costs of hazardous waste disposal, and on the extraction procedure proposed to determine if a waste is toxic (and thus, would be classified as hazardous). For a hazardous waste, RCRA defines very strict requirements of liners and leachate collection systems; whereas, for non-hazardous wastes, EPA has recently published criteria which will be used to determine if the disposal operation is an acceptable landfill or an illegal operation ("open dump").[5] One of the key features of the criteria is that groundwater cannot be contaminated by leachate in excess of the allowable levels specified in the Interim Primary and Secondary Drinking Water Standards at the solid waste boundary (see Table 1).[1,6] Thus, the burden of proof that a non-hazardous waste landfill is acceptable will remain with the facility owner. Regardless of whether the waste is hazardous or non-hazardous, all landfills that comply with RCRA will have to evaluate the effects of leachate from the solid waste and its subsequent transport to groundwater.

The purpose of this paper is to describe the research currently underway at ORNL related to the land disposal of coal gasification ash.[7,8] Included are data on the chemical composition and properties of ash from five of six proposed gasification/liquefaction demonstration plants and of several selected soils. Batch leaching results are presented which determine compliance with RCRA, along with other suggested batch leaching procedures. Leaching studies with ash/soil columns are also presented. The ultimate goal of this study is to provide design information and procedures to insure that solid wastes from gasification plants will comply with RCRA regardless of whether the waste is classified as hazardous or non-hazardous.

PHYSICAL AND CHEMICAL CHARACTERIZATION OF ASH AND SOIL

A number of ash/slags have been obtained from various pilot-scale gasification facilities; however, the major emphasis in the program is currently being directed to the six plants included in the DOE Demonstration Plant Program. These are COGAS (ICGG), British Gas/Lurgi (Conoco), U-Gas (Memphis Light, Gas and Water), Texaco (Grace/Ebasco), SRC-I (Southern Services Corp), and SRC-II (Gulf Minerals). Relatively large (> 100 kg) amounts of five of the six solid wastes have been obtained and are stored at ORNL (no SRC-I material was available at the time this paper was prepared). To date, soil samples have been obtained from the plant sites for ICGG, Conoco, Grace/Ebasco, and SRC-I.

Chemical and Physical Properties of Ash/Slags

Leachability of solid wastes depends on the physical properties of the

STANDARDS APPLICABLE IN RCRA ANALYSES

LEACHING

(all values in ppm)

ARSENIC	0.5
BARIUM	10.0
CADMIUM	0.10
CHROMIUM	0.10
LEAD	0.50
MERCURY	0.02
SELENIUM	0.10
SILVER	0.50
PESTICIDES	VARIOUS LIMITS

} MAXIMUM CONCENTRATION IN EPA-EP EXTRACTANT (40 CFR 250)

GROUNDWATER MONITORING

(all values in ppm)

ARSENIC	0.05
BARIUM	1.0
CADMIUM	0.010
CHROMIUM	0.05
LEAD	0.05
MERCURY	0.002
NITRATE (as N)	10.0
SELENIUM	0.01
SILVER	0.05

} INTERIM PRIMARY DRINKING WATER STANDARDS (40 CFR 257)

(units as noted)

CHLORIDE	250 ppm
COLOR	15 COLOR UNITS
COPPER	1 ppm
FOAMING AGENTS	0.5 ppm
IRON	0.3 ppm
MANGANESE	0.05 ppm
ODOR	3 THRESHOLD ODOR NO.
pH	6.5-8.5
SULFATE	250 ppm
TDS	500 ppm
ZINC	5 ppm

} MAXIMUM CONTAMINANT LEVELS IN NATIONAL SECONDARY DRINKING WATER REGULATIONS (40 CFR 143)

Table 1 Interim Primary and Secondary Drinking Water Standards used for RCRA compliance analysis

solid, chemical form of its components, the composition of the aqueous leaching medium, and the amount and distribution of the elements in the wastes. Figure 1 is included for illustrative purposes and shows scanning electron micrographs and the x-ray spectra of waste E.* Figure 1A shows the general character and appearance of the waste. The remaining photos show the different types of selected particles and the x-ray spectra revealing the chemical composition of different particles and parts of particles. In Table 2, the major and minor elements of four waste types are listed. Since the "as received" gasifier wastes have a magnetic and nonmagnetic fraction, analyses of two of the magnetic fractions are included. The contribution of the magnetic fractions are 5 and 7% by weight of wastes E and I, respectively.

In waste C, the calcium and magnesium concentrations are high relative to their concentrations in the other wastes. The increased concentrations of these elements in this waste are due to the addition of limestone flux during the gasification process. Although the limestone flux would lower the relative concentrations of the other elements, it appears that the iron content is relatively low in this waste. Wastes I and H contain significantly more sulfur than in waste C and E. In addition, waste H contains about 20% carbon. Since the analysis of this waste is for the fine size fraction which represent about 1/3 of the waste, the high carbon content, which is not anticipated in the coarser fraction, would be proportionately reduced. Interestingly, the iron concentration in the magnetic fraction of waste I has doubled from that in the unsegregated waste; however, the iron in the magnetic fraction of waste E remains nearly the same as the unsegregated waste. Likely, the iron in waste I is present as iron sulfide plus iron oxide or silicate; whereas, the iron in waste E is present mainly as the oxide or silicate.

Of the trace elements, manganese is high in waste C by over an order of magnitude compared with the other wastes. Trace elements such as Ni, Co, Cu, Zn, and Mo commonly associated with iron minerals increased in the magnetic fraction. On the other hand, the trace elements commonly associated with silicate minerals and organic fractions in coal were decreased in the magnetic fraction.

Properties of Site Soils

Of four site soils collected thus far, only the Illinois and Kentucky site soils have been characterized to any significant degree. Furthermore, since ash/soil column testing is being conducted only on the Illinois soil, this soil has been more fully characterized. Properties included pH, particle size distribution, carbonate mineral content, hydraulic conductivity, bulk density, porosity, and the distribution coefficients of several trace elements. These properties are being evaluated for application in depicting the migration of trace elements if and when the wastes are disposed of at the proposed site.

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*Demonstration plant waste data have been coded since results are preliminary and waste compositions are subject to change prior to plant operation.

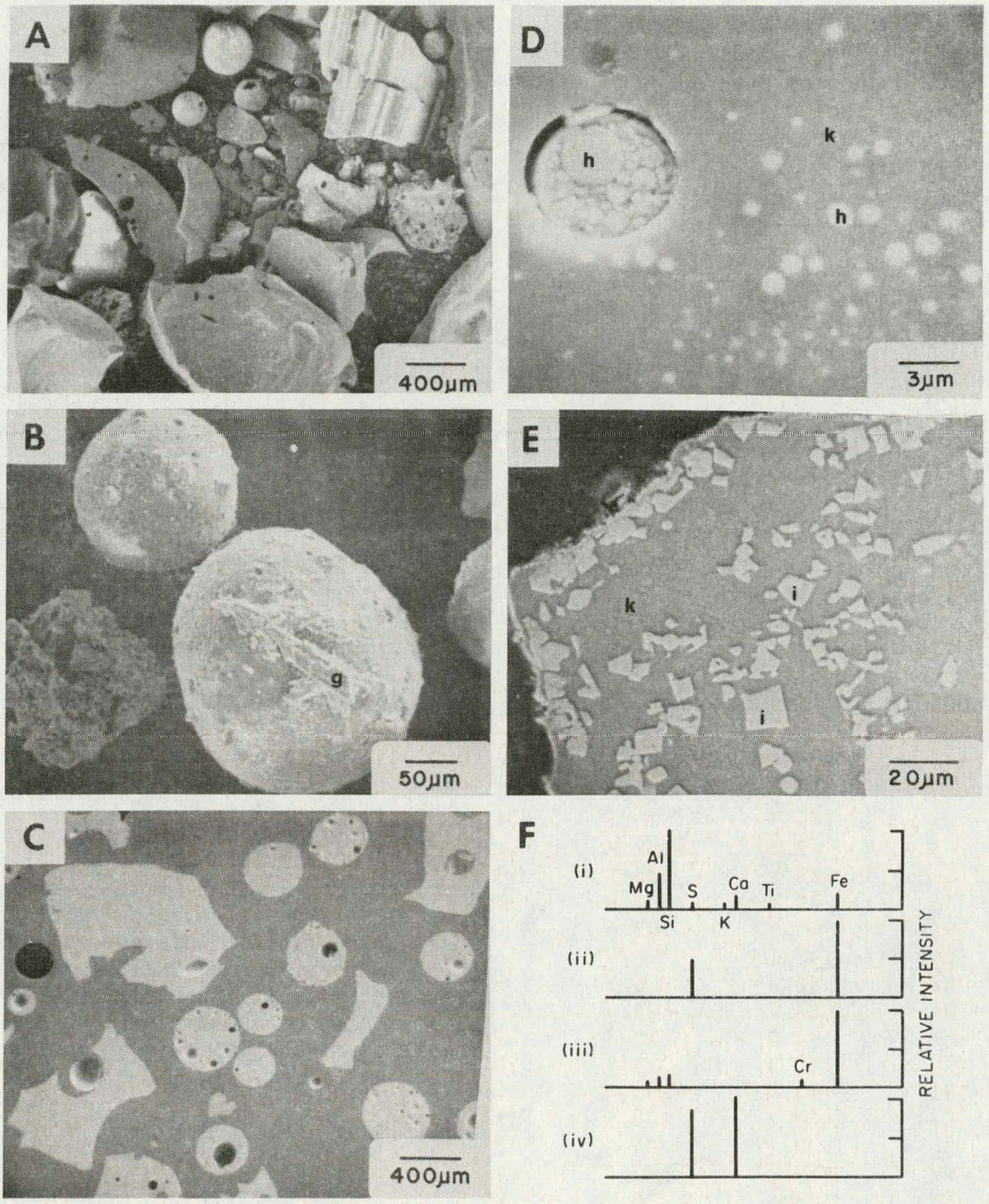


Fig. 1 Scanning electron micrographs and X-ray spectra of Waste E: (A) general view of waste particles; (B) closeup of spherical particles with a gypsum crystal (mark g) on the surface; (C) cross section of magnetic particles; (D) closeup of iron sulfide inclusion (mark h) in a magnetic particle (mark K); (E) closeup of iron oxide (mark i) in a magnetic particle; and (F) X-ray spectrum of; (i) matrix of magnetic and non-magnetic particles, (ii) iron sulfide inclusion, (iii) iron oxide, and (iv) gypsum.

Table 2. Chemical Composition of Unfractionated and Magnetic Fractions of Coal Conversion Solid Wastes

Element	Waste C	Waste E		Waste I		Waste H
	Unfractionated	Unfractionated	Magnetic Fraction	Unfractionated	Magnetic Fraction	Unfractionated
	wt. %					
Al	8.8	10.1	10.2	8.8	6.3	6.7
Ca	18.5	2.9	2.7	2.2	1.4	2.4
Fe	3.8	13.4	14.1	17.2	34.1	13.3
K	0.6	1.5	1.3	1.4	0.9	1.4
Mg	4.9	0.8	0.7	0.5	0.3	0.5
Na	0.3	1.8	1.6	0.2	0.1	0.3
Ti	0.5	0.6	0.5	0.6	0.4	0.4
Si	17.9	22.5	20.4	20.1	13.7	16.4
S	0.4	0.3	0.8	3.8	11.8	4.0
C	1.0	1.8	--[a]	1.7	--[a]	20.2
	µg/g					
Ag	1.0	0.3	0.4	0.3	0.9	0.5
B	287.3	1302.2	1153.0	590.7	335.0	386.4
Ba	654.5	454.0	427.0	531.0	219.0	1013.0
Be	10.3	18.1	20.3	12.6	8.5	6.3
Cd	1.0	0.8	--[a]	1.6	--[a]	5.0
Ce	146.5	85.2	93.8	25.9	53.4	49.6
Co	7.2	137.3	139.9	33.7	117.0	16.3
Cr	78.1	386.1	360.0	642.0	435.0	145.4
Cu	29.8	61.9	120.0	93.5	322.0	58.7
Ga	65.9	103.6	--[a]	106.0	--[a]	98.6
La	152.1	92.5	--[a]	89.2	--[a]	61.4
Li	86.3	80.7	69.1	63.7	37.6	41.4
Mn	3987.2	425.4	450.0	293.2	228.0	249.4
Mo	4.0	18.8	37.6	72.6	273.0	43.5
Nb	17.2	11.9	16.7	1.7	--[a]	1.3
Ni	73.0	254.0	348.0	150.0	488.0	148.0
P	466.7	275.5	333.0	436.3	359.9	544.8
Sc	30.2	24.4	20.4	19.3	13.3	12.4
Sr	519.8	503.3	448.0	182.1	120.0	139.1
Th	28.8	16.2	19.8	15.8	15.1	12.2
V	154.3	237.2	220.0	449.5	408.0	416.8
Y	54.8	53.6	46.1	41.1	30.9	23.8
Zn	8.3	65.7	103.0	96.1	97.3	413.2
Zr	191.7	196.6	173.0	170.2	105.0	97.4

[a] Not determined

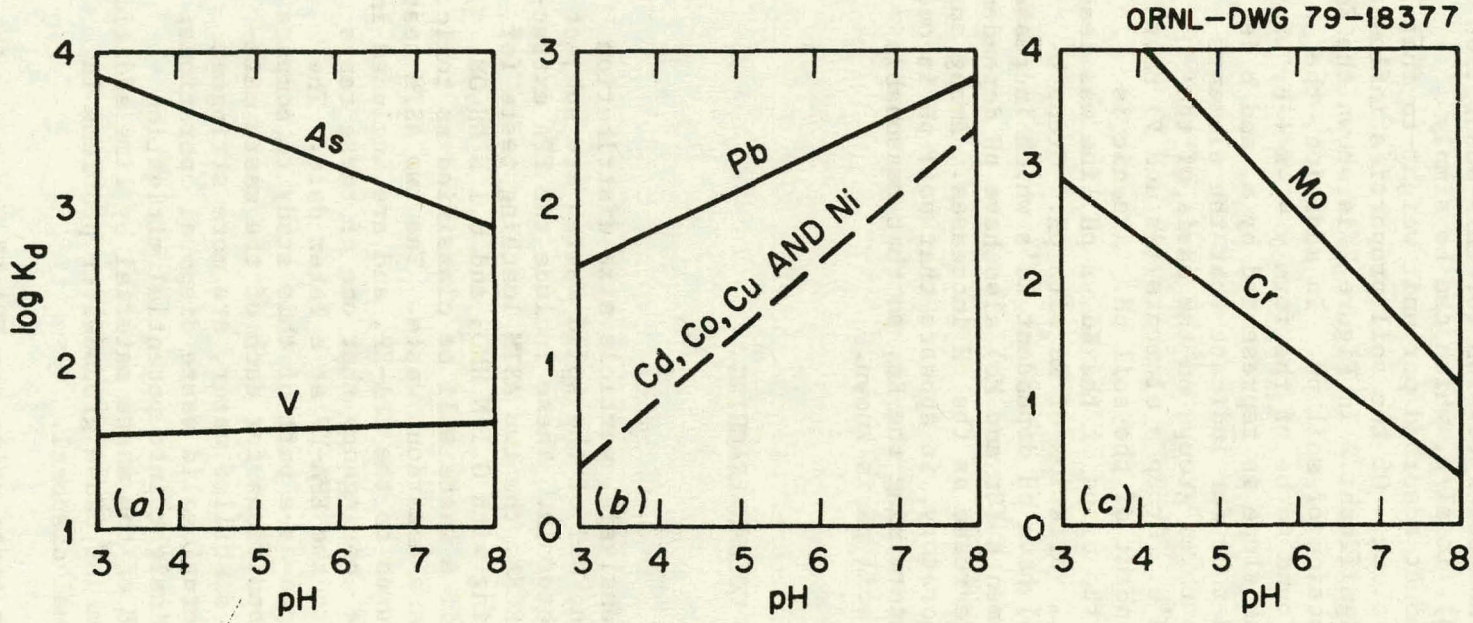
In preventing leached trace elements from migrating from a disposal site, one of the most important mechanisms for retention of trace elements is soil adsorption. A common expression for this adsorption is the distribution coefficient (Kd), in ml/g, which can be simply expressed as the ratio of the amount adsorbed per unit weight to that remaining in solution per unit volume. Of the soil properties influencing Kd, pH is one of the most significant. In Figure 2 is shown the Kd for nine trace elements as a function of soil pH. In addition, the equation relating Kd to pH was found to be of the form $y = ax + b$, where y is the log Kd and x is pH. The slope is represented by a, and b is the intercept. Results obtained thus far indicate that the elements investigated can be divided into three groups on the basis of the measured Kd values at various pH's. Group a elements (As and V) have Kd's which are relatively independent of the soil pH. Arsenic is included in this category since the slope of the Kd vs pH line was less than 0.2, indicating a very small variation of Kd with pH. Group b elements (Ni, Cd, Co, Cu, and Pb) have pH dependent Kd's which increase with increasing pH. Group c elements (Cr and Mo) also have pH dependent Kd's, but these values tend to decrease as the pH increases. Among soil factors investigated at this laboratory, it appears that soil pH is one of the most important factors determining the Kd, so that reasonable estimation of Kd can be made if soil pH is known.

BATCH AND COLUMN LEACHING

Batch Leaching

In addition to routine chemical analysis, particle size distribution measurement, and loss on ignition, all of the solid wastes are subject to a number of batch leaching protocols. These include the EPA extraction procedure (EP) required by RCRA, the two ASTM leaching tests for solid waste materials, and leaching with 0.1 N HNO_3 and 0.1 N NH_4OH. The EPA-EP is used to determine if a waste will be classified as toxic, and therefore, must be handled as a hazardous waste. The two ASTM tests are suggested alternative procedures to the EPA-EP, and are included in the leaching program to cover the contingency that one of these tests might be listed as an alternate to the EPA-EP at a later date. The final two tests have been developed as a part of this study to compare strong acid and basic leaching conditions for each of the waste materials. These procedures, except distilled water, are more stringent than could ever be expected in actual solid waste disposal operations; however, the results do provide insight into potential mitigation measures, such as altering the pH of the waste material by lime addition or removing trace elements that might cause groundwater problems in disposal operations prior to actual disposal.

The results of the batch leaching tests using the EPA-EP are given in Table 3 for the five wastes studied. Also included in Table 3 are the RCRA criteria for determining if the waste is toxic or hazardous. These criteria are ten times the trace elements listed in the Interim Primary Drinking Water Standards.[4] Certain organic materials are also listed in



	a	b
As	−0.194	4.432
V	0.014	1.535

	a	b
Pb	0.242	0.886
Cd	0.397	−0.651
Ni	0.383	−0.792
Cu	0.437	−0.985
Co	0.464	−1.171

	a	b
Mo	−0.712	6.902
Cr	−0.493	4.367

Fig. 2 Variation of log Kd of different trace elements as a function of soil pH's. "a" and "b" are the slope and intercept, respectively, in the equation y = ax + b. The broken line in (b) represents the approximate position of the Cd, Co, Cu, and Ni lines.

Table 3 EPA-EP leaching results for five gasification/liquifaction solid wastes

Element	Waste C	Waste E	Waste G	Waste H	Waste I	RCRA standards[a]
			(all concentrations in ppb)			
Arsenic	0.27	0.06	<1	<1	0.53	500
Barium	<200	<500	20	80	<500	10000
Cadmium	0.054	0.97	<1	28	3.4	100
Chromium	1.6	0.44	<5	<5	0.13	500
Copper	2.7	3.7	10	10	0.94	b
Lead	<0.3	0.26	<10	<10	1.6	500
Mercury	0.64	0.03	<1	1	0.191	20
Selenium	<5	2	<1	<1	<1	100
Silver	<0.03	<0.03	<2	<2	0.07	500
Nickel	281	219	30	540	758	b
Zinc	63	10	13	2240	385	b

[a] RCRA standards are ten times the interim primary drinking water standards

[b] no standards have been established for these elements at this time

the criteria, but thus far, have not been found in detectable amounts in the ash/slag leachates. It can be seen in Table 3 that none of the wastes listed exceed the criteria, and thus, these gasifier ashes will likely be designated as non-hazardous solid wastes. Of the elements considered, cadmium in waste H comes closest to exceeding the RCRA standard; the other elements are on the order of 1% of the permissible values.

Table 4 illustrates the results of all five types of batch leaching observed for a typical gasifier ash (waste G). This ash does not exceed the RCRA definition of a hazardous waste, in fact, none of the values measured exceeded one percent of the allowable standards. Both of the ASTM leaches gave about the same values as the EPA-EP; however, the ASTM (pH 4.5) gave slightly higher values for Ba and Cr which are elements listed in the IPDWS, as well as higher values for Ni and Zn. In waste H, the ASTM (pH 4.5) gave only 1/4 the cadmium concentration as compared to the EP. Only in the case of the 0.1 N HNO_3 leach were trace element concentrations approaching the IPDWS. Thus, it appears that this gasifier ash would probably be classified as non-hazardous regardless of any minor modifications in the EPA-EP.

Ash/Soil Column Leaching

In addition to the small-scale batch leaching experiments, leachate production and soil attenuation in large-scale ash/soil columns have also been investigated. Six leaching columns (56 cm in diameter) were loaded with 120 kg (depth of 30.5 cm) of site soil from the Waste E plant, and overlaid with a 30.5 cm depth (approximately 100 kg) of Waste E. Figure 3 gives some indication of the size and scale of the leaching column (lysimeter) experiments. The purpose of this large-scale leaching experiment was to examine the ability of the disposal site soil to attenuate the movement of trace metals known to be released from the solid waste.

Each of the six waste-soil lysimeters was subjected to a series of simulated rainfalls of 2.44 cm per week; totaling, to date, 34 applications covering a period of approximately ten months. Leachate samples resulting from each simulated rainfall are periodically checked for changes in pH and electrical conductivity. The data thus far indicate that the leachate pH from all six lysimeters has remained in the neutral range (6.2-8.2), and the pH does not appear to be increasing or decreasing with time. Laboratory-scale experiments with this same waste showed that the leachate pH was in the range of 3.7 to 4.1 as a result of the acidic nature of the waste. The observed neutral pH range of the leachate pH is evidence of the strong buffering capacity of the soil. It should be mentioned that this site soil showed a slightly basic pH; whereas, other site soils have shown pH in the range of 4.5-5.0. Thus, leachate pH would depend on the waste, as well as the soil. Values of the electrical conductivity have remained relatively constant averaging 3200 μmhos/cm, and as with pH, have shown no signs of increasing or decreasing over the ten-month study period suggesting no breakthrough of components leached from the waste.

Table 4 Atomic absorption analysis of leachates derived from various batch leaching protocols

ELEMENT	EPA EP	ASTM H_2O	ASTM pH 4.5	0.1 N HNO_3	0.1 N NH_4OH	RCRA STANDARDS[a]
			(all concentrations given in ppm)			
ARSENIC	<0.001	<0.001	<0.001	<0.011	<0.002	0.50
BARIUM	0.02	0.01	0.06	2.8	0.02	10.0
CADMIUM	<0.001	<0.001	<0.001	<0.001	<0.001	0.10
CHROMIUM	<0.005	<0.005	0.006	0.07	0.005	0.50
COPPER	0.01	<0.01	<0.01	<0.01	<0.01	b
LEAD	<0.01	<0.01	<0.01	<0.01	<0.01	0.50
MERCURY	<0.001	<0.001	<0.001	<0.001	<0.001	0.02
NICKEL	0.03	<0.005	0.055	1.4	<0.005	b
SELENIUM	<0.001	<0.001	<0.001	<0.001	<0.007	0.10
SILVER	<0.002	<0.002	<0.002	<0.002	<0.002	0.50
ZINC	0.013	<0.001	0.066	0.359	<0.001	b

[a] RCRA standards (as proposed December 18,1978) are ten times the EPA Interim Primary Drinking Water Standards

[b] no standards have been established for copper, nickel and zinc



Fig. 3 Ash/soil lysimeters loaded with soil prior to adding waste. Water is being added to saturate the soil prior to hydraulic conductivity measurement.

After 30 water applications (eight months), one of the lysimeters was disassembled to examine the release of metals from the waste and their movement through the soil layer. The waste layer was removed in 3 cm increments and the soil layer was removed in 1.5 cm increments for the first 7.5 cm depth, followed by 7.5 cm increments until all of the soil had been removed from the lysimeter.

Each increment of soil was air-dried and a representative sample was submitted for complete elemental analysis by neutron activation methods. This type data representing element concentration versus soil depth should reveal the distance of migration of an element in the eight month period. Furthermore, since the downward migration was mathematically modeled, the data should provide valuable information for validation of the model. To date, the analyses by neutron activation have not been completed.

A separate aliquot of sample was taken and an extraction was performed on each soil increment using distilled water, 0.1 M hydrochloric acid, and a 1.0 M ammonium acetate (pH 7). A 1:1 soil to liquid ratio was shaken for a 24-hour period, centrifuged, filtered, and the resulting leachate analyzed. To date, only the results of the nickel determinations have been obtained. In addition, pH and electrical conductivity measurements were made on the distilled water extract. These results are tabulated in Table 5. The pH of each increment of soil remains relatively constant, but the electrical conductivity increased with depth and is approaching the value obtained from soil only. Possible explanations for the increasing conductivity is that the deeper increments of soil were in contact with the leachate longer than the increments near the surface, and thus, were nearer equilibrium in solute content when conductivity was measured, or that soluble materials were being leached from the upper layers of the soil and are being distributed downward in the soil.

The distribution of nickel shows that it is distributed about 6 cm into the soil. The first 1.5 cm increment contains the highest nickel content based on all the extracts. The ammonium acetate extraction was applied in order to evaluate the exchangeable nickel concentration; the water extract should reflect the water-soluble fraction. The difference between the acid and ammonium acetate extract values may be considered the "fixed" nickel concentration.

Using the acid soluble values as the amount on the solid phase and the concentration in the water as the liquid phase, the Kd was calculated. The simplified mathematical model used to depict the distribution is based on incremental additions to the column for thirty (30) "simulated rains" and is defined as:

$$C_w^n = \frac{C_w^{n-1} + p\, C_s^{n-1}/n_e}{R_d}$$

and

$$R_d = 1 + \frac{p\ Kd}{n_e}$$

where C_w and C_s is the concentration of nickel in the water and solid phase, n is the number of applications of rain, p is the bulk density, n_e is the effective porosity, R_d is the retardation factor, and Kd the distribution coefficient as defined earlier. The bulk density as determined in the container was 1.4 g/cm^3 and the effective porosity was 46%. The value obtained was 10-20 ml/g depending on the assumption made, which appeared to be low based on the value for nickel at the slightly basic pH (pH = 7.5) reported in Figure 2. Since the mathematical model had been prepared to depict the downward transport of trace metals, the observed distribution in the first four layers of segmented soil was compared using Kd values of either 20 or 100; the latter being the expected equilibrium Kd value. The results in Table 6 suggest that the Kd of 20 more nearly depicts the observed distribution. Furthermore, since dispersion was not considered in the present model, the results suggest the possibility of closer agreement if this parameter is included. The possible disagreement of the expected Kd and the observed Kd may lie in the time dependent function of achieving equilibrium. The considerations of dispersion and time dependency of Kd are now being examined.

Since the remaining lysimeters are still under operation, they will provide further opportunities to improve the mathematical model, as well as the model providing insight to obtaining necessary parametric information. It is envisioned that the information being obtained in the lysimeter tests will be the basis for performing experiments under field conditions.

TABLE 5. Soil-Extracted Nickel Concentrations Using Selected Solvents (1:1 soil-solution ratio). Soil pH and Conductivity Measured in Distilled Water Extract.

Soil Depth (cm)	Nickel in Extract (µg/ml)			pH	Conductivity (µmhos/cm)
	H_2O	NH_3OAc	HCl		
0-1.5	0.210	1.061	2.039	7.6	2240
1.5-3.0	0.035	0.197	0.408	7.6	2240
3.0-4.5	0.027	0.189	0.245	7.7	2260
4.5-6.0	0.025	0.113	0.152	7.7	2290
6.0-7.5	0.022	0.066	0.109	7.7	2320
7.5-15.0	0.022	0.036	0.072	7.7	2610
15.0-22.5	0.012	0.044	0.041	7.6	2630
22.5-31.0	0.027	0.063	0.110	7.7	2770
control soil[a]	0.022	0.066	0.084	7.7	3250

[a]Not subjected to the 30 water applications.

TABLE 6. Calculated and Observed Distribution of Nickel in Top Four Layers of Soil After Eight Months.

Depth (cm)	Calculated Based on Kd of 100	20	10	Observed
0-1.5	96	80	66	78
1.5-3.0	4	17	26	13
3.0-4.5	0	3	7	6
4.5-6.0	0	0	2	3

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STRATEGIES FOR CHARACTERIZING THE FATE OF BIOACTIVE MATERIALS DURING COAL LIQUEFACTION PRODUCT UPGRADING

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ABSTRACT

An interdisciplinary strategy is outlined for characterizing the disposition of bioactive (toxic, teratogenic, mutagenic, and/or carcinogenic) materials in coal-derived hydrocarbon liquids during upgrading processing. Engineering input is required to select representative PDU and pilot-scale samples and appropriate processing schemes and conditions for upgrading experiments to ensure reliable extrapolation of results to demonstration and commercial-scale. Biology expertise is required to perform and interpret short-term *in vitro* cellular assays and whole-animal toxicity and carcinogenesis testing on raw and upgraded samples. Chemical separation and identification of active classes and components in the samples aids in interpreting bio-activity results and in quantifying effects of various upgrading processes and conditions. The end result will be a data base for reliably assessing and addressing potential occupational and environmental safety and health concerns associated with upgraded coal-derived liquids.

An example of the value of this interdisciplinary approach is given by work performed on generically representative raw and hydrotreated SRC-II gas oil samples. Biological and chemical characterization indicates significant loss of bio-activity during hydrotreatment, with one postulated mechanism being removal of primary amine groups from multi-ring aromatic compounds.

INTRODUCTION

One of the goals of current U.S. energy policy is the development of a coal-derived liquid fuels industry. Such an industry will involve both coal liquefaction plants and refineries for upgrading the liquid products into marketable transportation and power generation fuels. A major concern in developing the coal-liquids industry is to ensure the acceptability of associated health and environmental impacts. The potential for genotoxic (e.g., carcinogenic) effects in humans exposed to certain coal-derived liquid materials is of special concern. Understanding the fate of potentially genotoxic materials in refinery upgrading operations is thus important in determining the potential human health impacts of a coal-liquids industry. Such an understanding requires an interdisciplinary effort involving biology, chemistry, and engineering to ensure that a useful and reliable data base can be created for assessment and resolution of potential health concerns associated with the coal-liquids industry. This paper presents the results of exploratory work which indicates that a significant reduction in the microbial genotoxic activity of a coal-derived liquid results when hydrotreatment is employed as an initial upgrading step.

Background

Coal-derived liquids consist primarily of complex mixtures of aromatic and hydroaromatic compounds together with larger concentrations of heteroatomic species than are typically present in comparable petroleum fractions.[1] In addition, these complex mixtures may contain genotoxically active classes of compounds such as polynuclear aromatic hydrocarbons (PAH), heterocyclic PAH, and primary aromatic amines (PAA).[1,2] Limited epidemiological data suggest that at least some coal-derived liquids may exhibit carcinogen activity.[3] In addition, certain coal liquids have been shown to be both carcinogenic in small animal skin painting tests and mutagenic in submammalian mutagenesis assays.[4] Two classes of compounds, namely multi-ring nitrogen heterocycles and polynuclear aromatics, both of which are present in coal liquids in low concentrations[1,2,4,5], have been implicated as possible causative agents in eliciting the carcinogenic and/or mutagenic responses observed upon exposure to coal-derived liquids.

The physical and chemical properties of raw coal liquids are such that considerable upgrading may be required to produce certain types of marketable products, especially transportation fuels. A likely initial upgrading step is hydrotreatment, which is a standard petroleum refinery process for catalytically hydrogenating materials ranging from naphthas to heavy residual to produce acceptable feedstocks for downstream refinery processing units such as reformers and catalytic crackers. Hydrotreatment removes or modifies much of the heteroatomic material and results in some aromatic ring saturation and cracking, with product properties and yields depending primarily on the degree of hydrogenation.

Purpose

Considering the chemical characteristics of the potentially genotoxic materials in coal-derived liquids and the types of reactions which occur in hydrotreating, it is reasonable to expect significant changes in genotoxic activity of coal-derived liquids as a result of hydrotreatment. However, cooperative engineering, chemistry, and biology efforts are required to define adequately the nature of such changes and their relevance to development and commercialization of a coal-liquids industry. Battelle Pacific Northwest Laboratory has performed exploratory biological and chemical characterization work on generically representative raw and hydrotreated coal liquids which offers initial confirmation of the expected decrease in genotoxic activity due to hydrotreatment. This paper summarizes the results of this work as an example of the interdisciplinary approach required in characterizing the potential health and environmental impacts associated with upgrading complex, coal-derived materials.

This work was performed on coal liquids produced by the Pittsburg & Midway Coal Mining Company's SRC-II coal liquefaction pilot plant which were hydrotreated by UOP, Inc. in laboratory-scale reactors. While the pilot plant materials characterized thus may not be strictly representative of expected commercial-scale materials, they do have generic process significance and have been shown to be biologically active. This paper, therefore, provides an engineering assessment of the process relevance of the materials studied and

describes the biological and chemical characterization work in the context of an initial effort in an area requiring further delineation of process, biological, and chemical relationships and their significance. Each of the disciplinary efforts involved is discussed separately in this paper, followed by an integrated discussion of the implications of this work.

ENGINEERING ASSESSMENT OF SAMPLE MATERIALS

Biological and chemical characterization work was performed on three SRC-II samples obtained from UOP, Inc. These were an SRC-II pilot plant distillate blend (boiling points 400 to 800°F) and the 400°F+ products resulting from moderate and severe hydrotreating of this pilot plant material by UOP. The engineering assessment of these materials consists of a general characterization of the pilot plant operation during sample collection and the hydrotreating conditions employed in relation to projected commercial-scale operations.

Pilot Plant Conditions

The SRC-II distillate blend sample was collected for UOP by the Pittsburg & Midway Coal Mining Company from its SRC-II pilot plant in Fort Lewis, Washington, in March 1979. The material is a 2.9 to 1.0 blend of middle and heavy distillates produced over a series of pilot plant runs. These runs extended from October 1978 to February 1979 and were all made with Powhaton No. 5 bituminous coal. The middle to heavy distillate blending ratio was based on the best available estimate of what would constitute the eventual demonstration plant liquid fuel. Eight material balance runs were included in this period (78SR-22 through 78SR-29), with the same single set of target operating conditions for each run. However, the distillates stored during this period and subsequently sampled included a considerable quantity of material produced during upset or poorly defined operating conditions.[6] For this reason, the sample can only be considered as being generically representative of SRC-II product during operation with Powhaton No. 5 coal. In addition, the relationship of the sample to a commercial or demonstration scale material is only generic because the significance of differences between the pilot plant process conditions and those for projected large-scale operation is not fully known at present.

Hydrotreating Conditions

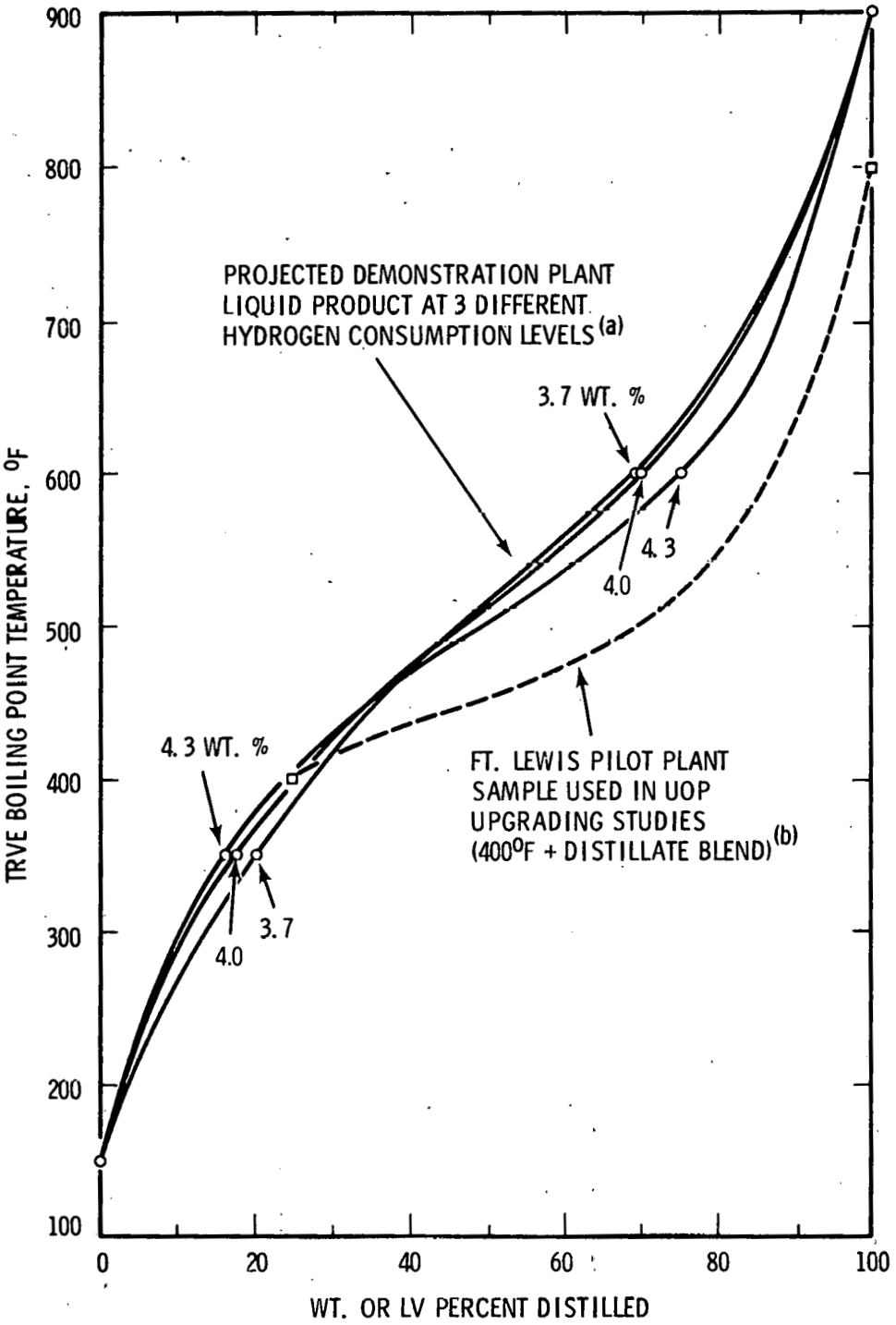
The SCR-II distillate blend sample was hydrotreated by UOP[7] in its own standard pilot plant reactors using a commercial UOP catalyst (Group VI

and VIII metals on a high surface area refractory support). Two extended runs of over 300 hours were made in July 1979 under different temperature, pressure, and residence time conditions to produce mildly and severely hydrotreated products. Reaction conditions for this type of hydrotreating can range from 650 to 900°F temperature, 700 to 3000 psi pressure, and 0.2 to 5.0 hours residence time.[(a)] The two runs resulted in hydrogen consumption rates of about 1300 SCF H_2 per barrel of feed under mild conditions and about 1900 SCF/bbl under severe conditions. This increased the hydrogen content of the products to 10.4 wt% and 11.2 wt%, respectively, compared to 8.7 wt% hydrogen in the feed. Table 1 summarizes the feed and whole liquid product inspections made by UOP, as well as the overall yields for the two hydrotreating runs. Sulfur levels were reduced by over 95% in each run, while nitrogen and oxygen were removed to a lesser degree (32% to 79% removal for nitrogen and 46% to 61% removal for oxygen for mild and severe hydrotreatment, respectively). The whole liquid products were distilled by UOP to give 400°F end-point naphthas and 400°F+ gas oils. PNL received samples of the two 400°F+ materials, the UOP inspections of which are also included in Table 1.

Sample Relevance

The SRC-II pilot plant distillate blend sample hydrotreated by UOP is not strictly representative of expected demonstration or commercial scale material. While the sample is qualitatively representative of the type of material expected from a commercial SRC-II plant, it was produced over a series of runs under a range of both steady and upset conditions which in some cases could differ significantly from those expected for a commercial plant. In addition, the pilot plant distillate blend sample is a lighter boiling range material than the projected demonstration scale fuel oil product. This is shown by Figure 1, which compares the UOP sample distillation curve with the whole liquid product distillation curves for the demonstration plant design.[(a)(6)] The UOP sample has a lighter end-point than the projected demonstration scale product (800° vs. 900°F) due primarily to limitations in the pilot plant

(a) Equivalent to 5.0 to 0.2 liquid hourly space velocity (volume of oil per hour per volume of catalyst), respectively.



(a) PROJECTED WEIGHT PERCENT YIELDS OF 180-350°F NAPHTHA, 350-600°F MIDDLE DISTILLATE, AND 600-900°F HEAVY DISTILLATE FROM DEMONSTRATION PLANT DESIGN DESCRIPTION. (b)

(b) VOLUME PERCENT DISTILLED BY UOP USING ASTM D-1160 METHOD. (s)

FIGURE 1. Comparison of Projected Demonstration Plant Product and Pilot Plant Sample Distillaton Curves

TABLE 1. UOP Inspections of SRC-II Distillate and Hydrotreated Products[5]

	Feed		Mildly[a] Hydrotreated		Severely[b] Hydrotreated	
	Drum 1*	/Drum 2	WLP[c]	400°F+*	WLP[c]	400°F+*
UOP Sample No.	3777-6	3777-7	3777-21	3777-34	3777-28	3777-41
°API @ 60°F	9.7	10.1	17.0	13.6	23.4	17.7
Specific Gravity @ 60°F	1.0021	0.9993	0.9529	0.9752	0.9135	0.9484
Wt. Pct.						
Hydrogen	8.68	8.72	10.38	9.98	11.18	10.59
Carbon	85.83	86.13	86.91	86.84	87.17	84.86
Oxygen	2.02	1.73	1.08	0.98	0.67	0.83
Wt. ppm						
Sulfur	3300	3815	129	106	98	109
Nitrogen	8100	9040	5510	6000	1900	1730
FIA, Vol. Pct.						
Color Band[d]	-	36.1	19.7	19.4	6.3	-
A	90.1	54.5	59.1	69.9	50.8	73.9
P&N	9.9	9.4	21.2	10.7	42.9	26.1
ASTM D 1160 Distillation, LV%, °F						
IBP/5	386/407	335/395	280/350	418/428	234/302	408/440
10/30	417/445	410/444	374/422	436/462	331/400	448/463
50	186	472	460	487	446	490
70/90	335/645	512/656	505/611	539/641	490/575	536/625
95/EP	711/799	705/810	687/779	691/790	628/724	668/748
% Over	99.0	99.0	99.0	99.0	99.0	99.0
Product Distribution, Wt%						
C_1-C_4	0.09	0.21				
C_5-C_6	0.33	0.26				
400°F EP naphtha	21.4	30.0				
400°F+ bottoms	78.1	69.4				
H_2O	1.42	1.70				
H_2S	0.32	0.39				
NH_3	0.32	0.89				
Total	101.95	102.85				
H_2 Consumption, SCF/bbl	1290	1870				

(a) Feed was Drum 1.
(b) Feed was Drum 2.
(c) Whole liquid product.
(d) Highly polar compounds
* Indicates samples to PNL.

vacuum flash tower operation. In addition, the UOP sample contains less heavy distillate material (550°F+) than the demonstration scale product due to a combination of: 1) difficulties in determining the relative middle to heavy distillate blend ratio which best approximated eventual demo plant products, and 2) possible differences in yield structures caused by different reactor operating conditions. These differences between the UOP pilot plant sample and projected demonstration scale product in end-point and heavy distillate content may have a major impact in assessing both the hydrotreating processing requirements and the potential genotoxic effects of SRC-II distillate materials.

The hydrotreating conditions employed by UOP should be technically feasible on a commercial scale based on comparison with representative conditions for hydrotreating a typical Arabian crude vacuum gas oil.[5] However, the hydrotreating conditions and severities which would be used in commercial refining of coal-derived liquids have not yet been precisely defined because of various technical and economic uncertainties. The UOP hydrotreated samples have, therefore, simply generic relevance to possible commercial scale hydrotreated materials.

As a final note on sample representativity, the UOP fuel oil sample contained about 9 wt% diphenyl ether. This is a major component of Dowtherm A, which is a heat transfer fluid used extensively in the Fort Lewis pilot plant. Dowtherm contamination of fuel oil material at the pilot plant is not uncommon, although 9% contamination is unusually high.[4] The effect of this contamination on the hydrotreating and bio-assay results outside of simple dilution is unclear at present.

(a) The demonstration plant design distillations are on a weight percent basis, while the UOP sample distillation is on a liquid volume percent basis, because data was not available to convert the two to a common basis. Converting the demonstration plant design distillations to a volumetric basis would shift the distillation curves slightly to the right (i.e. higher naphtha and lower fuel oil yields are obtained on a volume basis than on a weight basis).

CHEMICAL CHARACTERIZATION OF SAMPLE MATERIALS

Chemical characterization of the raw and hydrotreated SRC-II samples was performed by gas chromatographic mass spectrometry. In addition, the samples were fractionated by solvent partitioning and by distillation to aid in the biological and chemical identification and quantification of genotoxically active compound classes. The chemical characterization and fractionation methods and results are briefly described below.

Methods

Solvent Fractionation

Separation of the raw and hydrotreated samples into fractions was carried out by dissolving the coal-derived liquids in isooctane and then partitioning sequentially with 1N HCl, 1N NaOH and dimethylsulfoxide. The resulting fractions are isooctane-insoluble tar, basic, acid-induced tar, acidic, base-induced tar, neutral and polynuclear aromatic hydrocarbon (PAH).[9] The recoveries of the feedstock, moderately and severely hydrotreated products in this procedure were 98%, 64% and 88% by weight, respectively. The losses are attributed to evaporation of low-boiling components during the concentration step for removal of isooctane from the acidic, basic, neutral and PAH fractions.

Fractional Distillation

The raw distillate blend feedstock was subjected to fractional distillation under continuous nitrogen flow. Fractions were collected at approximately 10°C intervals. Collections were initiated and terminated as the temperature within the distillation vessel peaked and subsequently dropped. Twenty fractions were collected, fraction No. 20 being the pot residue at 265°C (510°F). Number 19 solidified in the condenser and was removed only by heating the glassware.

GC-MS Analysis

Both electron impact and chemical ionization mode GC-MS analyses were performed on a Hewlett Packard 5985-A GC-MS system using either a 60 m x 0.25 mm

ID wall-coated open tubing glass column coated with SP-2250 liquid phase or a specially prepared 25 m x 0.25 mm ID WCOT glass column coated with SE-52 phase. Splitless mode injection was employed for the capillary columns and the eluent stream was split to allow simultaneous flame ionization (FID) and mass spectrometric detection. The FID trace was automatically integrated for GC peak quantitation and the MS data were used for peak identification. Concentrations of those PAH compounds having four or more rings were determined by gas chromatography alone using a 4 mm ID x 2 m glass column packed with SP-301 (liquid crystal) stationary phase at 270°C isothermal.

PAH concentrations were determined both in the raw samples and in the PAH fractions using benzo(a)pyrene, benzp(e)pyrene and perlyene as external standards. Primary aromatic amine and nitrogen heterocycle concentrations were estimated from the basic and tar fractions on both the SP-2250 and SE-52 columns using methylene dianiline and d_{10} anthracene as internal standards. Phenolic, aromatic and hydroaromatic concentrations were determined in the raw sample using the SE-52 column. Undetermined amounts of the more volatile anilines, pyridines, and alkyl benzenes were lost during the fractionation procedure; hence, no quantitative data are presented for these lower molecular weight components.

Results

As expected, the chemical composition of the SRC-II distillate blend material was drastically altered by catalytic hydrotreatment. This is illustrated by the summary in Table 2 of the concentrations of selected chemical class compounds in the raw and hydrotreated samples. Overall, compounds having lower boiling points were produced, suggesting that the higher molecular weight aromatic compounds in the SRC-II feedstock had undergone extensive hydrogenation. This resulted in the formation of a series of hydroaromatic compounds along with their alkylated homologs. Inspection of total ion chromatograms, single ion chromatograms and mass spectra generated also indicated a substantial decrease in the concentration of larger heteroatomic species. However, sulfur and oxygen containing compounds were detected in the intact hydrotreated materials, the sulfur being in thiophenic species and the oxygen in the form of

TABLE 2. Alteration in Chemical Composition of SRC-II Distillate Due to Hydrotreatment for Five Compound Classes[d]

Material	Phenols[a]		N-heterocycles[b]		Primary Aromatic Amines[b]		Aromatics and Hydroaromatics[a]		Polynuclear Aromatics[c]	
Feedstock	∑phenols	130	∑N-heterocycles	28	∑primary aromatic amines	1.9	∑aromatics + hydroaromatics	450	∑polynuclear aromatics	110
	C_1 phenols	41	quinoline	3.6	aminonaphthalenes	0.09	naphthalene	97	$C_{14}H_{10}$	38
	C_2 phenols	35	C_1 quinoline	1.4	aminoanthracene/ aminophenanthrene	0.07	C_1 naphthalenes	82	$C_{16}H_{10}$	9.2
	phenol	27	carbazole	1.3	aminobiphenyls	0.03	C_2 naphthalenes	65	$C_{18}H_{12}$	3.5
	C_3 phenols	16	C_2 quinoline	0.8	aminopyrene/ aminofluoranthene	0.03	tetralin	57	benzo(a)pyrene	0.041
	o-cresol	9	acridine	0.1	aminochrysene	0.02	C_1 tetralin	26	benzo(e)pyrene	0.077
					aminocarbazoles	trace	biphenyl	24		
Moderately Hydrotreated	∑phenols	30	∑N-heterocycles	1.2	∑primary aromatic amines	≤0.005	∑aromatics + hydroaromatics	660	∑polynuclear aromatics	18
	C_1 phenols	5.5	tetrahydroquinoline	0.08			tetralin	71	$C_{14}H_{10}$	2.5
	C_2 phenols	2.6	tetrahydrocarbazole	0.06	none detected	≤0.005	C_2 tetralins	51	$C_{16}H_{10}$	0.8
	phenol	1.6	carbazole	0.04			C_1 tetralins	48	$C_{18}H_{12}$	0.4
	C_3 phenols	1.2	C_1 quinoline	0.03			C_1 naphthalenes	41	benzo(a)pyrene	≤0.010
			tetrahydroazapyrene	0.02					benzo(e)pyrene	≤0.010
Severely Hydrotreated	∑phenols	17	∑N-heterocycles	1.0	∑primary aromatic amines	≤0.005	∑aromatics + hydroaromatics	780	∑polynuclear aromatics	7.5
	C_1 phenols	4.3	tetrahydrocarbazole	0.07	1		C_1 tetralins	120	$C_{14}H_{10}$	1.9
	C_2 phenols	2.1	tetrahydroquinoline	0.05	none detected	≤0.005	C_2 tetralins	41	$C_{16}H_{10}$	0.5
	phenol	1.2	carbazole	trace			tetralin	34	benzo(a)pyrene	≤0.010
	C_3 phenol	0.8	C_1 quinoline	trace			C_3 tetralins	27	benzo(e)pyrene	≤0.005

(a) Estimated directly in the unfractionated material by GC and GCMS.
(b) Estimated in the basic fraction by GCMS. Concentrations given have been calculated for the unfractionated material.
(c) Estimated in the unfractionated material and in the PAH fraction by GC and GCMS. Concentrations given have been calculated for the unfractionated material.
(d) The contributions listed do not total 100% due to the presence of compound classes not listed (e.g., aliphatics) and losses during extraction. Specific compounds listed under each heading are those found in the highest concentrations within that class.

benzofurans, phenols and phenylether. Tetrahydroquinolines were the only nitrogen containing species detectable in the hydrogenated oils prior to their fractionation.

Acid Fraction

The total ion chromatogram of the acid fraction from the hydrotreated SRC-II feedstock was dominated by alkyl phenols having molecular weights of 122 (C_2 phenols, 4 isomers), 136 (C_3 phenols, 3 isomers), 150 (C_4 phenols, 2 isomers), 164 and 178 according to the mass spectra. Comparison of the reconstructed single ion and total ion chromatograms from the hydrogenated products with those from the feedstock indicated that the concentrations of phenolic compounds were lowered (Table 2), and that some other acidic compounds (probably sulfur containing) were not detectable after hydrotreatment. Overall, phenolic content of the hydrotreated products was between 13% and 23% of that in the feedstock, depending on the hydrotreating severity.

Basic Fraction

Table 2 lists the approximate concentrations of several nitrogen compounds detected in the three materials. As can be seen, the feedstock contained relatively large amounts of several nitrogen heterocycles along with lower concentrations of several primary aromatic amines. More than 100 peaks were resolved in the FID chromatograms; however, most represented insufficient material to allow mass spectral identification.

After severe hydrotreatment, the basic fractions constituted only about 0.8% of the total recovered sample weight compared to 2.4% for the untreated starting material. Nitrogen compounds which were detected were present in low concentrations and consisted essentially of tetrahydroquinolines, tetrahydrocarbazoles, carbazoles and alkyl quinolines. Hydroaromatic and small amounts of phenolic compounds which partitioned into the basic and tar fractions of the hydrotreated materials contributed to their weight percentages, making these higher than would be indicated by the concentrations of nitrogen bases present. No primary aromatic amines were detected in any of the hydrotreated fractions.

Neutral and PAH Fractions

Changes brought about by hydrotreatment were most apparent in the neutral and PAH fractions. While aromatic compounds such as naphthalenes, phenanthrenes, biphenyls and pyrenes were in high concentrations in the feedstock (Table 2), a homologous series of hydroaromatics having molecular ions at m/e 132, 146, 160, 174 and 186 were the most prominent in the gas chromatogram of the hydrotreated products. Dihydro-, tetrahydro-, hexahydro-, octahydro- and decahydro-aromatic species having up to four rings were detected in the hydrotreated products, along with traces of some aromatics such as naphthalenes, acenaphthenes, anthracenes and phenanthrenes. PAH compounds detected having four or more rings constituted a total concentration of 1.3 parts per thousand in the feedstock. Their concentrations were reduced substantially by hydrotreatment; however, the amount of reduction was not uniform for the various species present. Electronically integrated area percent ratios from the FID chromatograms indicated that between 90% and 95% of the neutral fraction weight in the severely treated product was comprised of hydrogenated or partially hydrogenated species.

Tar Fractions

The acid-induced and isooctane-insoluble tar fractions obtained from the distillate blend feedstock were relatively rich in carbazoles and contained other nitrogen bases including primary aromatic amines. As has been characteristic of these two types of tars in the coal liquids studied thus far, higher molecular weight nitrogen compounds, particularly azapyrenes and amino pyrenes, were present in higher relative concentrations than in any other fraction.[13] The same tar fractions from the hydrotreated materials contained lower concentrations of carbazoles, partially hydrogenated carbazoles, and phenanthridine as well as tetrahydroazapyrenes and azapyrenes.

BIOLOGICAL CHARACTERIZATON OF SAMPLE MATERIALS

While PNL has performed a variety of *in vitro* and *in vivo* bio-assays on SRC-II pilot plant materials[4], only the rapid, inexpensive, and widely used Ames assay for *in vitro* microbial mutagenesis was used to provide a screening characterization of the effect of hydrotreatment on the genotoxic activity of generically representative SRC-II samples. Although it should be emphasized that a quantitative link between mutagenic potency in the Ames test and other biological effects (e.g., carcinogenicity) remains to be established, it has been shown that the mutagenic potencies of SRC-II materials, as determined by the Ames test, are at least roughly related to their carcinogenic potency in small-animal skin painting studies.[4] The Ames assay, therefore, is a valuable tool in screening or exploratory studies such as the one summarized here.

Methods

The Ames assay is performed by mixing the test materials with mutant strain-*Salmonella Typhimurium* cells in the presence or absence of mammalian liver microsomal enzymes (S9) and determining the number of bacteria which undergo reverse mutation from dependency on histidine in the medium to non-dependency. Assay in the presence of S9 detects mutagens which require metabolic activation to effect mutagenesis while assay in the absence of S9 detects mutagens which do not require metabolic activation. Use of appropriate strains of *Salmonella* permits determination of the nature of the mutation (frame shift or point mutation) which is a function of the biochemical properties of the test materials. For each material assay results are quantified by the slope of the initial linear portion of the dose-response curve (revertants per microgram) obtained by testing over a range of test material concentrations.

Agar plate mutagenicity assays were carried out essentially as described by Ames, et al.[10] All tests were conducted with *Salmonella* strain TA98 in the presence of S9 activating enzyme. This combination has been shown to give optimum assay response when testing SRC-II materials.[4] Dimethylsulfoxide was used as the solvent for all of the standard control chemicals and the

sample fractions. After the top agar layer was poured onto the 37°C plates, they were incubated in the upright position for several hours to allow hardening of the semisolid top agars. The assay plates were then inverted and incubated for 24 to 36 hours to allow expression of mutant colonies. Colonies were counted using an automated colony counter.

Results

Mutagenic response for the moderately and severely hydrotreated materials in the Ames test was substantially reduced compared to that observed for the distillate blend sample. As shown in Table 3 and Figure 2, the mutagenic activity of the basic fraction was significantly reduced and the activities of the various tar fractions were undetectable after moderate or severe hydrotreatment. The total weighted activities of the hydrotreated products (weighted sum of the individual fraction activities) were reduced by 97 to 99%, depending on the hydrotreating severity. This is due to both the reduced activity of the fractions and to the reduced yield of the fractions after hydrotreatment (Table 3).

In agreement with previous observations from the analysis of various SRC materials, there is good correspondence between the concentrations of three and four ring PAA and total mutagenic activity.[11] The decrease of PAA concentrations in the hydrotreated samples and the loss of mutagenicity in these materials were in agreement with the earlier observations. It is particularly noteworthy that the highly mutagenic three and four ring primary aromatic amines were not detectable in basic and tar fractions of the hydrotreated materials; hence, the quantitative relationship between the drastic reduction of mutagenic activity of the moderately and severely hydrotreated products and the reduction in PAA content could not be rigorously established. Nevertheless, it should be noted that the implied 100-fold or so reduction in PAA content would render these compounds undetectable by the methods described here.

Ames testing was also performed on the 20 cuts obtained from fractional distillation of the raw SRC-II distillate blend samples. The results are depicted in Figure 3, and clearly suggest that the heavier molecular weight components in this material have the greatest mutagenic potential.

TABLE 3. The Effect of Catalytic Hydrogenation on the Mutagenicity of SRC-II Coal Liquid

Material	Chemical Fraction(b)	Percent of Total Wt.	Revertants per μg Fraction(c)	Weighted Response, rev/μg(a)	Total Weighted Response, rev/μg	Total Revertants Unfractionated Material, rev/μg
Feedstock	Basic	5.37	16.2	0.86	$\sum$ = 1.20	2.54
	Acid Induced Tar	5.97	2.7	0.16		
	Base Induced Tar	1.40	5.6	0.08		
	Isooctane Insoluble Tar	1.16	8.9	0.10		
Moderately Hydrotreated	Basic	1.44	2.2	0.03	$\sum$ = 0.03	None detected above backbround
	Acid Induced Tar	0.06	0	0		
	Base Induced Tar	0.03	0	0		
	Isooctane Insoluble Tar	0.44	0	0		
Severely Hydrotreated	Basic	0.99	0.79	0.01	$\sum$ = 0.01	None detected above background
	Acid Induced Tar	1.31	0	0		
	Base Induced Tar	0.03	0	0		
	Isooctane Insoluble Tar	0.44	0	0		

(a) (Revertants per μg) x (percent total weight)/100.
(b) Other fractions were not active.
(c) Strain TA98 with S9 enzyme activation.

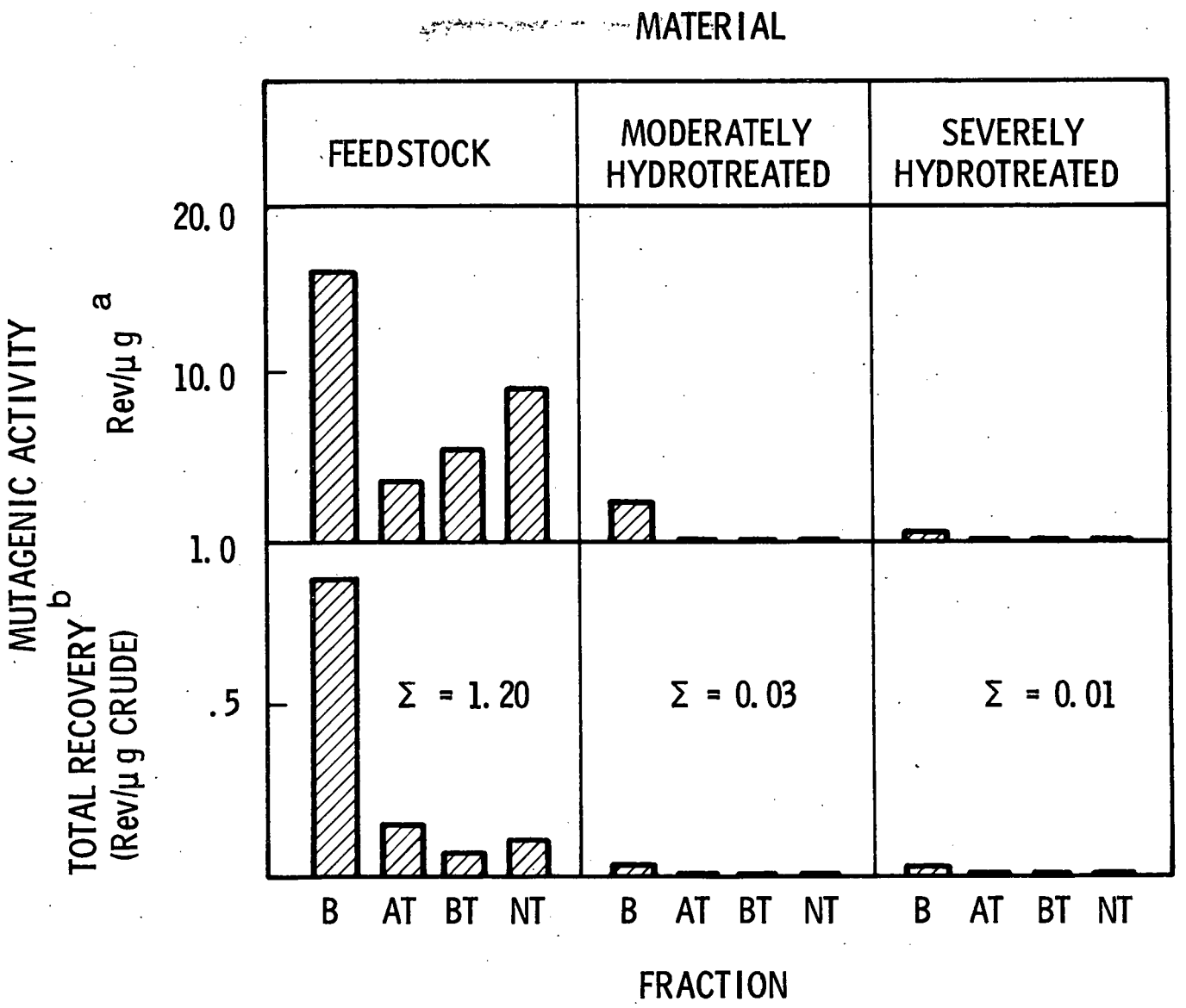


FIGURE 2. Specific and Weighted Activity Test Results for the Basic (B), Base Induced tar (AT) acid induced for (BT) and isooctone induced for (NT) from Raw and Hydrotreated SRC-II Distillate Blend.
(a) Strain TA98 with S9 enzyme activation.
(b) Specific activity weighted by the gravimetric yield of the fraction.

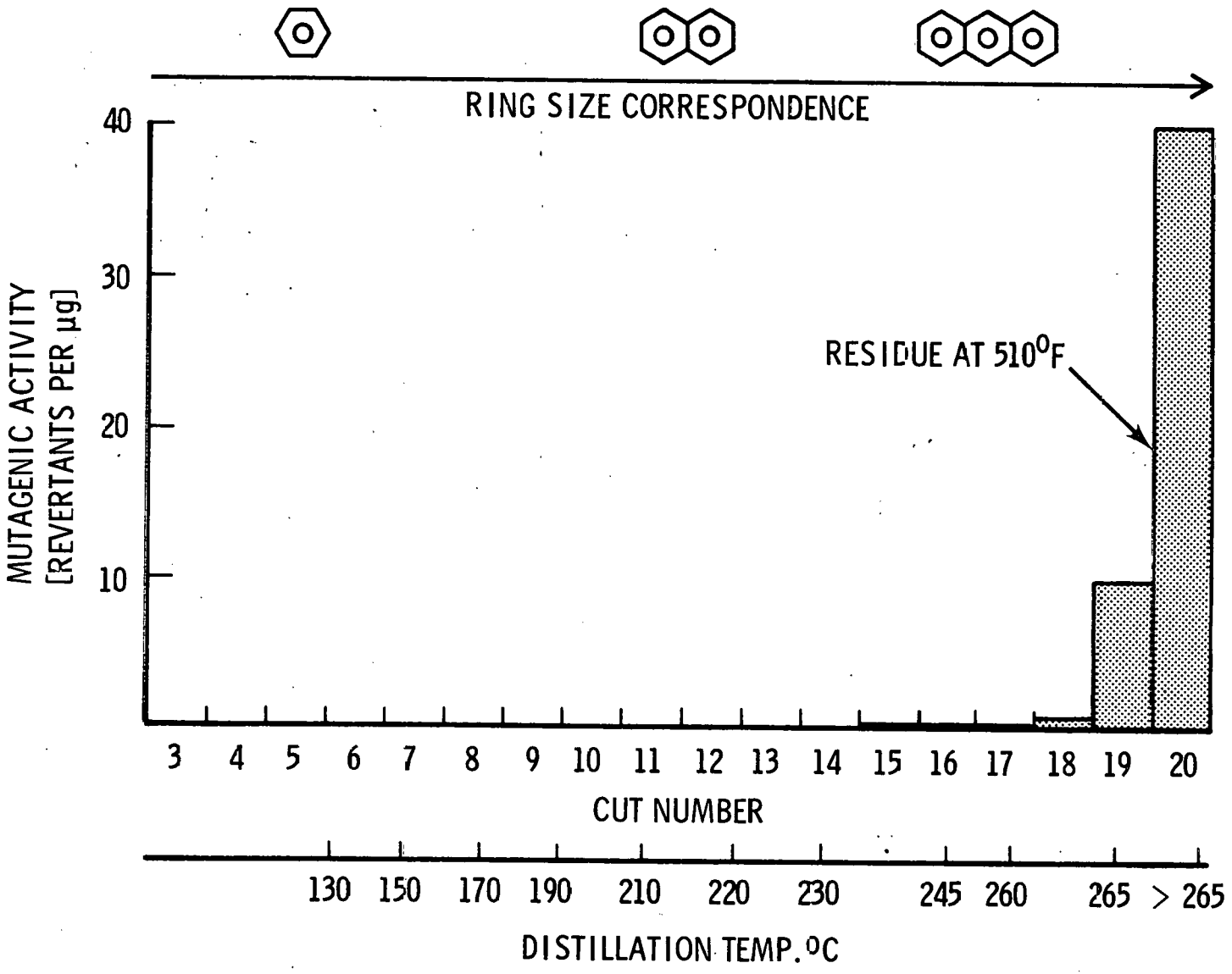


FIGURE 3. Relationship of Mutagenic Activity to Distillation Temperature

DISCUSSION OF PRELIMINARY SCREENING RESULTS

While the specific effects of hydrotreatment on the chemical composition and biological activity of a given coal-derived fuel product depends on parameters such as reaction conditions, catalysts and starting material composition, it appears certain that such treatment will, in general, result in products of reduced microbial genotoxic activity. This is due to the fact that compound classes in coal liquids thought to be primarily responsible for inducing genetic damage, namely the nitrogen containing aromatics and polynuclear aromatic hydrocarbons, are susceptible to hydrogenation, and therefore substantially altered or destroyed during hydrotreatment. The biological and chemical screening characterization results summarized here support this expectation, and also offer an initial indication that hydrotreating conditions can affect the degree to which genotoxic activity is reduced (Tables 2 and 3). It is noteworthy, however, that compared to differences from the feedstock, the moderately and severely hydrotreated materials do not differ greatly in microbial mutagenic activity (Table 3) or PAH and PAA content (Table 2). Considering the almost 50% increase in hydrogen consumption between moderate and severe hydrotreatment (Table 1), this seems to indicate that the genotoxic activity of coal-derived liquids may be readily and significantly reduced by hydrotreating.

While the marked reduction in the microbial mutagenic activity of the hydrotreated products is of substantial significance by itself, the additional understanding of the likely causes of this reduction which is provided by the chemical characterization data increases the reliability and utility of this work. The near total elimination of PAA content observed in the hydrotreated products (Table 3), for example, is consistent with other evidence that primary aromatic amines play a major role in the mutagenic response of heavy SRC-II distillates. In addition, the observation of substantial reductions in phenolics is of interest since certain compounds in this class may be associated with promotion of carcinogenesis.[12]

The most probable series of reactions leading to eventual loss of heterocyclic nitrogen begins with the addition of hydrogen across carbon-carbon bonds

followed by carbon-nitrogen bond cleavage and addition of hydrogen to form primary amino functionalities[13] which in turn are rapidly deaminated. The presence of compounds such as alkyl tetrahydroquinolines and tetrahydrocarbazoles, as major constituents of the residual basic components in the hydrotreated product, lend support to this view. PAA themselves are thought to deaminate very quickly under such conditions. Thus, the overall process can be seen as one of successive destruction of larger ring systems to form lighter weight alkylated and/or hydrogenated species with overall loss of sulphur, nitrogen and oxygen in the form of H_2S, NH_3, and H_2O, respectively. A second possible mechanism which could also be important for removal of nitrogen during hydrotreating is one in which the nitrogen ends up in alkyl anilines or other relatively volatile constituents which are subsequently removed during "topping" (separation of the naphtha and gas oil products) and may also have been lost during sample fractionation.

Finally, the engineering assessment of the materials characterized is important in evaluating the significance of the biological and chemical results obtained. The results presented here (Figure 3) and related work on SRC-II materials[4] indicate that significant genotoxic activity is primarily associated with the higher molecular weight components of SRC-II distillates. This suggests that the differences between the pilot plant materials studied and projected demonstration scale distillates in heavy end content and cut-point (Figure 1) may be important in assessing the commercial scale significance of these results. Heavier components will likely change both the genotoxic properties of the hydrotreating feedstocks and the hydrotreating conditions employed.

SUMMARY AND RECOMMENDATIONS

Summary

Initial biological and chemical screening characterization of generically representative raw and hydrotreated SRC-II coal-derived liquid indicates that catalytic hydrogenation substantially reduces the genotoxic activity of the feed material. Chemical analyses suggest that the decrease in microbial mutagenic activity is due principally to the destruction or transformation of primary aromatic amines and/or other nitrogen containing species during hydrotreatment.

Recommendations

The Ames microbial mutagenic assay results reported here represent only the first tier in bioactivity assessment. Additional tests which characterize other biological end points at several tier levels are required for a more definitive understanding of the effect of hydrotreatment on the genotoxicity of coal-derived liquids.

Some of the data obtained in this work underscore the need to characterize materials which are more representative of projected demonstration scale products with respect to heavy-end components. In addition, samples having better documented histories which are as closely representative as possible of projected demonstration plant operation are needed.

The extent of upgrading which will be required to yield marketable coal-derived liquids is still being investigated and may change as economics change. Biological and chemical characterization is required as a part of parametric upgrading studies to provide input to the technical, economic, environmental, and health trade-off evaluations involved in optimizing coal liquids refining schemes. Processes other than hydrotreatment need to be assessed, with perhaps some creative effort in seeking other means for reducing the genotoxic activity of coal-derived liquids. The results summarized here represent a single point in a matrix of process and life science parameters which must be understood to assess potential occupational and environmental concerns with a developing coal liquids industry.

ACKNOWLEDGMENTS

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TREATMENT OF PHENOLIC COAL GASIFICATION EFFLUENTS

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Several research projects recently conducted at Carnegie-Mellon University have been directed towards evaluation of environmental problems associated with coal conversion processes. A portion of this work has focused on treatment of phenolic coal gasification process condensates. The purpose of these studies has been to define physicochemical and biological treatment characteristics of those wastewaters in order to obtain basic engineering and design data. The following discussion summarizes the general scope and conclusions of these treatability studies with high-BTU coal gasification wastewaters

BIOLOGICAL OXIDATION STUDIES

Biological oxidation experiments have been performed with gasification process effluents obtained from the Hygas pilot plant operated by the Institute of Gas Technology in Chicago, Illinois and the slagging fixed-bed pilot plant operated by the Grand Forks Energy Technology Center (GFETC) in Grand Forks, North Dakota. The objectives of these experimental investigations are summarized below:

1. Investigate coal gasification wastewater compositional characteristics, and assess how these characteristics impact pretreatment prior to biological oxidation.

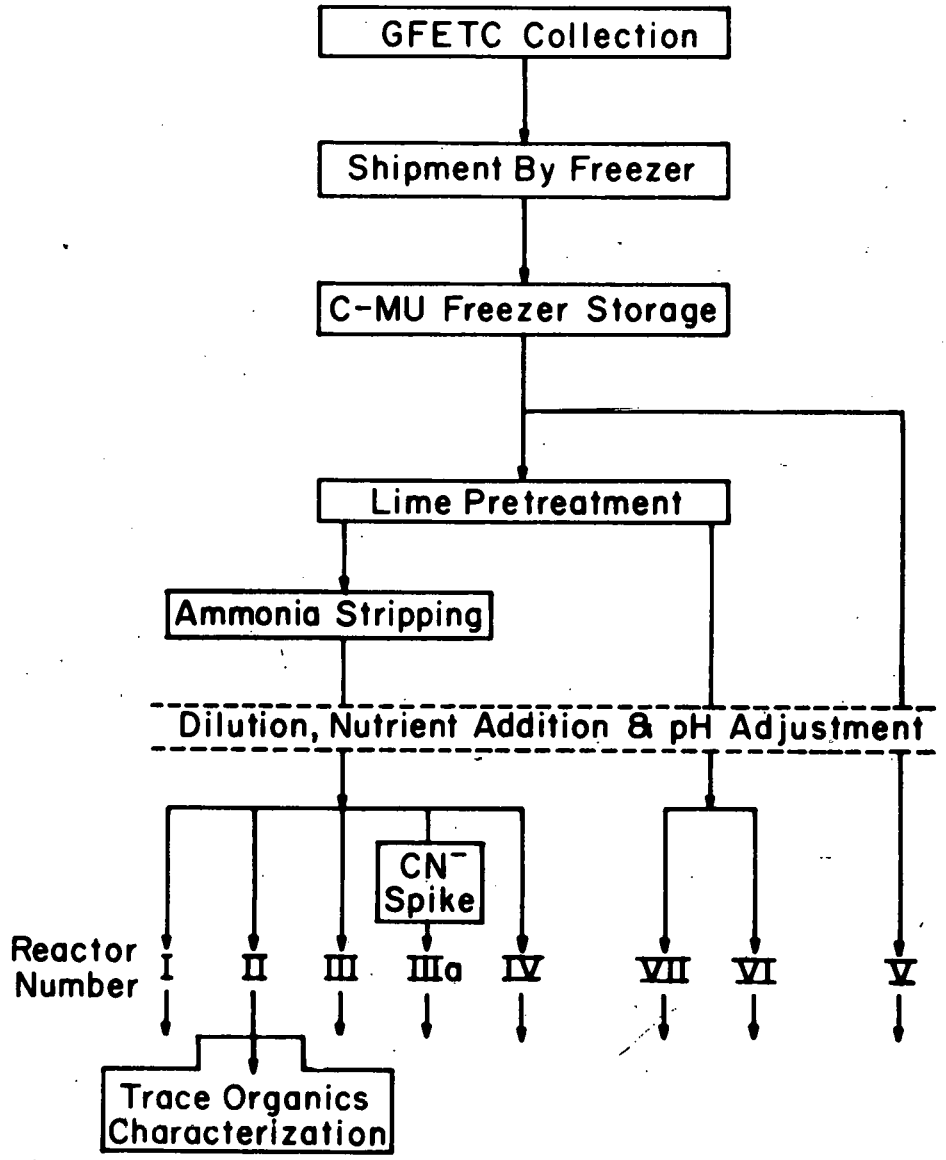
2. Identify minimum dilution requirements for biological treatment of coal gasification effluents, and evaluate biological oxidation of coal gasification effluents receiving different types of pretreatment.

3. Determine biological oxidation growth constants for treatment of coal gasification effluents, and determine removal efficiencies for primary effluent contaminants,

4. Investigate parameters which effect biological oxidation of cyanide and thiocyanate, and determine the fate of cyanogen-nitrogen, and evaluate the potential for single-stage nitrification of ammonia liquors, and

5. Determine removal efficiencies for coal gasification wastewater trace organic compounds.

Figure 1 shows the experimental design employed to investigate biological treatability characteristics of GFETC wastewater. This design permitted study of raw, lime pretreated, and ammonia stripped wastewater, as well as wastewater receiving an addition of cyanide. Influent and effluent samples for Reactor II on Figure 1 were



Nominal Hyd. Res. Time θ, days	9.2	9.2	13.8	13.8	18.4	11.8	11.8	11.8
Mean Cell Res. Time θ_c, days	10	15	20	20	40	20	20	20
% Wastewater Concentration	33	33	33	33	33	40	20	40

For All Reactors pH = 7.0-7.5; Temperature = 20-25°C; D.O. > 3 mg/ℓ

Figure 1
Experimental design for biological oxidation study with GFETC quench condensate

characterized for trace organic compounds. A similar experimental design with somewhat different objectives was employed in studies with Hygas effluent. The biological systems in all of these tests were complete-mix, single stage air activated sludge reactors with internal clarifiers.

Table I lists the source of wastewaters employed in the biological oxidation studies and the form of pretreatment employed prior to biological oxidation. General results of biological treatment investigations with Run 64 Hygas and Run RA-52 slagging fixed-bed gasification effluents are summarized in references (1) and (2) respectively. Information presented in reference (3) compares the results of these studies with investigations performed with other coal refinery effluents, and provides data on interpretation of results from biological treatment. In addition, reference (3) presents results for wastewater pretreatment by solvent extraction and ammonia stripping. Reference (4) summarizes results of combined gas chromatography-mass spectrometry analysis for estimation of removal of organic contaminants during biological oxidation of coal gasification wastewaters. General observations from these investigations are discussed below.

Quenchwater Buffer Capacity Coal gasification quench waters contain high concentrations of dissolved carbon dioxide and ammonia. Quench waters employed in these investigations may be envisioned as containing 0.25 to 0.8 m/l ammonium bicarbonate; this results in a very strongly buffered solution for which estimated buffer capacities are in the range of 0.025 to 0.1 m/l or more. Calculated values of base neutralizing capacities are in the range of 0.5 to 1.7 m/l, and are approximately twice as great as acid neutralizing capacities. These results show that it is impractical to consider pH adjustments to raw gasification quench waters until much of the ammonia and carbon dioxide have been removed from the solution.

Ammonia Stripping Characteristics It has been shown in theory and in bench-scale stripping experiments that 95 to 99% of the total ammonia in quench condensates may be liberated from solution by steam stripping without the need for addition of caustic or lime. Nonetheless, because of the high ammonia levels, a residual ammonia concentration of up to several hundred mg/l NH_3-N may remain after free-leg ammonia stripping and will require addition of base in order to be stripped from solution.

Acceptable Ammonia Levels Investigations conducted with unstripped Hygas wastewater showed that ammonia concentrations of up to 1600 mg/l NH_3-N may be present in reactor mixed liquor without inhibiting biological oxidation, while ambient concentrations of 3200 mg/l NH_3-N impaired biological activity. It was also shown that raw GFETC gasifier quench condensate could be processed at 40% strength with an influent ammonia concentration of approximately 2700 mg/l. However, in this case nitrification reduced ammonia concentrations in reactor mixed liquor to approximately 1000 mg/l NH_3-N. These results show that gasifier quench waters may be processed with ambient ammonia concentrations in the range of 1000-1600 mg/l at pH = 7.0-7.5, which is substantially higher than residual ammonia concentration that would remain after free-leg ammonia stripping.

Table I

Wastewater Source and Form of Pretreatment
Employed in Biological Oxidation Studies
With Coal Gasification Condensates

TYPE OF WASTEWATER	PROCESS RUN - COAL TYPE	TYPE OF BIOLOGICAL REACTOR INFLUENT
Hygas process, 1:1 blend of cyclone and quench condensates	Run 64; Bitminous coal, Illinois No. 6	*(i)* Raw wastewater without pretreatment *(ii)* Diluted and undiluted lime pretreated wastewater *(iii)* Diluted and undiluted ammonia stripped wastewater
Hygas process, quench condensate	Run 72; bituminous coal, Illinois No. 6	*(i)* Ammonia stripped wastewater *(ii)* Solvent extracted, ammonia stripped wastewater
Hygas process, quench condensate	Run 79; bituminous coal, Illinois No. 6	*(i)* Ammonia stripped wastewater
GFETC process, quench condensate	Run RA-52, Indian Head lignite	*(i)* Diluted raw wastewater *(ii)* Diluted lime-pretreated wastewater *(iii)* Diluted and undiluted ammonia stripped wastewater

Dilution Requirements It has been determined that Hygas quench water and coke plant ammonia still effluent, with COD values in the range of 3000-5000 mg/l, can be processed reliably at moderate values of COD removal rate (e.g. 0.2-0.5 mg COD removed/mg MLVSS-day) without dilution. However, it was shown by a series of parallel and sequential experiments that ammonia stripped GFETC wastewater with an average COD of approximately 22,000 mg/l could not be processed at full strength with COD removal rates in the range of 0.3 to 0.5 day.$^{-1}$ Stable biological oxidation was obtained in that range of COD removal rates by diluting the wastewater to 33% strength. Factors which impose limitations on influent strength are not well understood, although the presence of inhibitory organic compounds are suspect. British researchers belive that inhibition to biological oxidation of phenolic liquors may be due to oxidized or polymerized substances of unknown composition, but which may be associated with the residal COD and color of biologically treated phenolic wastes.

Performance In general best removal efficiencies and operational stability have been associated with relatively long values of mean bacterial cell residence time (sludge age) and corresponding low values of substrate removal rate. Recommended values of sludge age are in the range of twenty to forty days.

Biological reactors employed in these studies showed relatively low sludge yields. This may be explained in part by long values of mean bacterial cell residence times and also by the presence of inhibitory substances. In addition, calculations show that compounds such as phenol and thiocyanate do not yield as much energy for biological synthesis as compared to organic compounds common to less complex effluents. It was demonstrated that low values of sludge yield do not adversely effect biological reactor performance at recommended operating conditions. In fact it may be desirable to have minimum sludge yield as this presents less of a solids disposal problem.

Various studies have shown that under suitable operating conditions high removal efficiencies may be attained for primary wastewater contaminants, viz. phenolics, BOD, organic-nitrogen, and thiocyanate. COD removal efficiencies were typically in the range of 80% with BOD removals of 95-99%. However, effluent COD concentrations can be quite large because of high influent COD levels. Nitrification has been observed with coke plant wastewater, and GFETC and Hygas condensates with the exception of Hygas wastewater from Run 64. The extent of nitrification has been found to be dependent on substrate removal rate when processing ammonia stripped GFETC and coke plant wastewater. It is necessary to consider the fate of cyanogen-nitrogen when evaluating nitrification, as degradation of cyanide and thiocyanate results in increased wastewater ammonia concentration. For example, nitrogen mass balances for biological oxidation of coke plant ammonia still waste revealed that in the absence of substantial nitrification, biological reactor effluent concentration of ammonia-nitrogen was significantly greater than influent values owing to release of ammonia-nitrogen from degradation of thiocyanate.

Removal of Organics The removal of organic compounds by activated sludge treatment of Hygas and GFETC wastewater was estimated by capillary column gas chromatography/mass spectrometry (GM/MC) of extracts from wastewater sample composites. In both cases nearly 99% of the total extractable and chromatographable organic material was comprised of phenol and alkylated phenols. Activated sludge treatment removed these compounds almost completely. Removal efficiencies of base compounds was generally good with the exception of certain alkylated pyridines. Removal efficiencies for certain compounds in the neutral fraction were poor, i.e. alkylated benzenes, cycloalkanes, and cycloalkenes. The Hygas sample also showed poor removal efficiency for polycyclic aromatic hydrocarbons.

SOLVENT EXTRACTION STUDIES

Coal gasification quench waters that contain high levels of phenolic compounds may be processed for phenol recovery by solvent extraction. High phenolic concentrations may provide several economic incentives for recovery. Recovered phenol may be used as a fuel or possibly sold as a chemical commodity, also phenol recovery would reduce the organic loading to a biological treatment facility. Solvent extraction may also serve to protect biological oxidation systems from shock loads, and it may provide a means for removal of slowly degradable or non-degradable trace organic compounds. The latter issue may be especially important with regard to reduction of toxic/hazardous organic compounds.

Hygas Run 72 quench condensate was employed in screening solvent extraction experiments. The wastewater was processed by solvent extraction, followed by high temperature stripping and biological oxidation. N-butyl acetate was the solvent used in these studies, which gave a phenolic distribution coefficient in the range of 50 to 55.

Pretreatment by solvent extraction was designed to remove 99% of wastewater phenolics. This resulted in approximately 75% reduction of wastewater COD from an initial value of 10,000 mg/l. Biological oxidation of solvent extracted wastewater gave an additional 78% reduction in COD. This was significant considering that easily oxidizable phenolic material had been removed by pretreatment. Organic matter remaining after solvent extraction of gasifier wastewater appeared to be no more refractory to biological oxidation than organics in raw stripped wastewater. It was observed also that wastewater pretreated by solvent extraction showed much less tendency to foam during biological oxidation. Additional experiments are in progress to assess the removal of polycyclic aromatic hydrocarbons by solvent extraction and to evaluate biological oxidation of solvent extracted GFETC wastewater. The GFETC quench condensate to be used in these studies has a raw phenolic concentration of 4000-6000 mg/l.

BIOLOGICAL OXIDATION WITH ADDITION OF POWDERED ACTIVATED CARBON

Although biological treatment of gasification wastewaters can result in good to excellent BOD removal efficiencies, treated wastewater may contain appreciable residual organic material owing to high influent COD concentrations. This residual organic material may present problems for reuse of this wastewater as cooling tower makeup water or as makeup to boiler feed water preparation. For this reason a series of studies were initiated to evaluate powdered and granular activated carbon treatment of a coal gasification wastewater. These studies assessed treatment technologies which would achieve additional removal of residual organic contaminants during wastewater processing. The experimental design employed in these studies is shown in Figure 2; and the results will be summarized in a forthcoming report.

Powdered activated carbon (PAC) treatment was evaluated at sludge ages of twenty and forty days with mixed liquor carbon concentrations ranging from 0 to 5000 mg/l. A high surface area powdered activated carbon was employed in these investigations, and GFETC wastewater at 33% dilution was used for purposes of comparing the results with the previous biological oxidation experiments. The PAC tests were performed under optimal biological reactor operating conditions and results showed that treatment without addition of powdered carbon gave an effluent BOD of about 30 mg/l from an influent value of 3700 mg/l. Addition of powdered activated carbon gave lower residual COD and color, and somewhat lower values of BOD. However, screening GC/MC analyses of soluble base and neutral fraction organics in effluents of PAC reactors showed that these soluble organics are not removed substantially below the low levels observed in biological reactor effluent with no addition of powdered activated carbon.

WASTEWATER DEMINERALIZATION STUDIES

A conceptual diagram of major wastewater streams in a coal gasification process is shown in Figure 3. These streams include cooling tower and boiler feed water streams, process condensates, blowdowns, and water for slurry of coal and sludges. Possible choices for reuse of water which has come into contact with either coal or product gas include: (i) water for coal slurry feeding, (ii) recycle slurry water for gasifier slag, ash, or char removal, (iii) direct contact quench water, and (iv) water for the CO shift reactor(5). Other plant water needs which may be partially or completely satisfied by use of treated wastewater include: (i) cooling water makeup, (ii) boiler feed water make up, and (iii) water for solids disposal.

If it is assumed that there has been maximum reuse of minimally treated water in the gasification process, then excess water will require treatment to meet quality constraints governing one or more plant needs. It is most likely that wastewater not completely reused in the gasification process will be used primarily as cooling tower makeup water

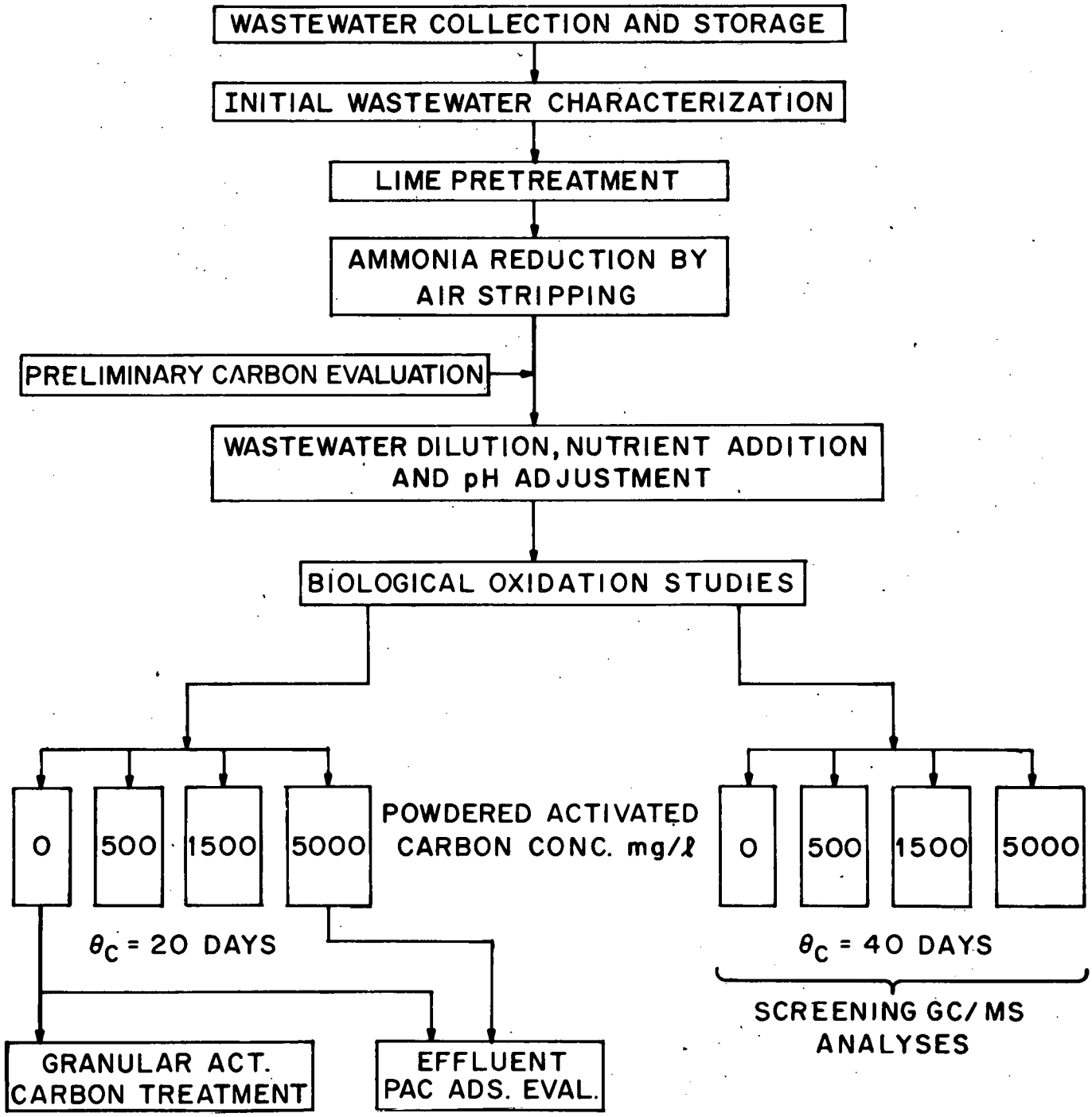


Figure 2
Experimental design for evaluation of GAC and PACtreatment of Hygas quench condensate

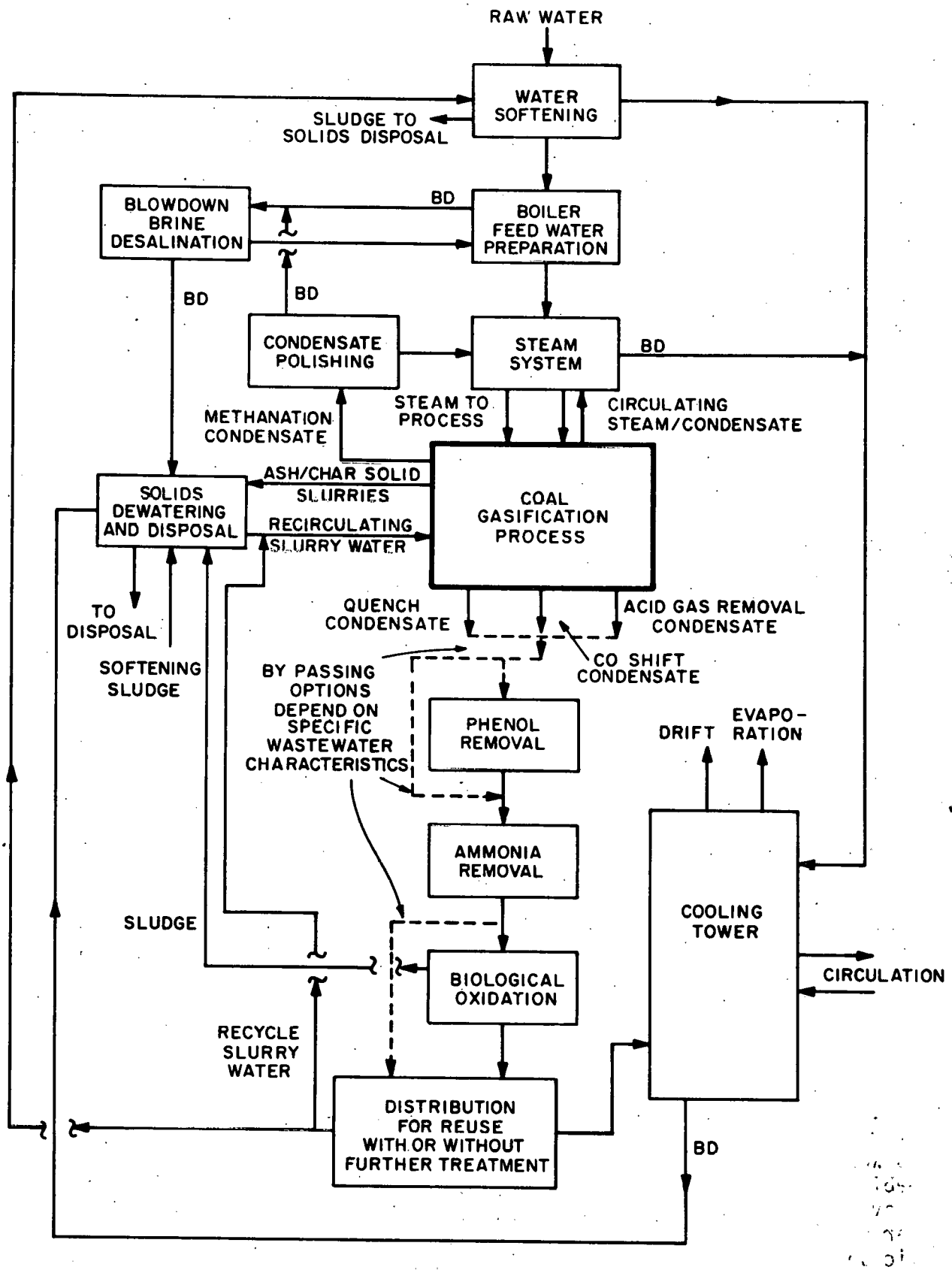


Figure 3
Major water streams in a coal gasification process water balance

since cooling water quality constraints are less than those for boiler feed water. Cooling water quality constraints include the need to control chemical scaling and fouling, biological activity, and corrosion. Although species which cause scaling problems can be predicted using solubility relationships, little can be predicted regarding the extent to which refractory organic compounds such as biological reactor effluent COD may undergo decomposition in a cooling tower system and promote biological activity.

Figure 4 shows a schematic of a wastewater treatment train employed to evaluate advanced wastewater processing of a coal gasification quench condensate. This study allowed for evaluation of lime-soda softening, activated carbon adsorption, and reverse osmosis. These unit processes represent a sequence of treatment steps which may be employed to process quench condensate for reuse as makeup water to a cooling tower or to a boiler feed water polishing facility. While detailed discussion of the results of this investigation will be available in the near future, summary analyses are presented in Table II which shows quench water quality characteristics through successive treatment steps. In these investigations, ammonia removal simulated free-and fix-leg steam stripping by liming and air stripping. However, in this case, sulfide was eventually oxidized to sulfate, rather than being stripped from solution as would occur during high temperature free-leg stripping operations.

Biological oxidation removed 99% of BOD and approximately 90% of COD. Nitrification resulted in partial conversion of organic-N, SCN^--N, and NH_3-N to nitrate. Lime-soda softening removed hardness to practical limits; however, this step required large soda dosages to remove noncarbonate hardness since most of the quench water alkalinity was consumed during biological oxidation. Activated carbon treatment reduced wastewater COD to 110 mg/l and color to 130 Pt-Co units.

Reverse osmosis experiments conducted with a hollow fiber polyamide membrane operated at 75% conversion and 400 psi produced a high quality permeate, although low levels of COD (20 mg/l) passed through the membrane. The reverse osmosis studies reported here were relatively short term and additional work needs to be performed to evaluate problems with membrane fouling and also to study membrane cleaning techniques.

DISCUSSION

Investigations performed at C-MU and elsewhere have helped to identify wastewater treatment characteristics for coal gasification condensates. This work has provided initial estimates of specific treatment process capabilities and limitations. Further studies need to be performed to: (a) evaluate minimal cost and innovative treatment systems, (b) assess water reuse strategies at reasonable scale, and (c) determine the fate of toxic and hazardous wastewater contaminants.

It has been estimated that treatment cost for phenolic process

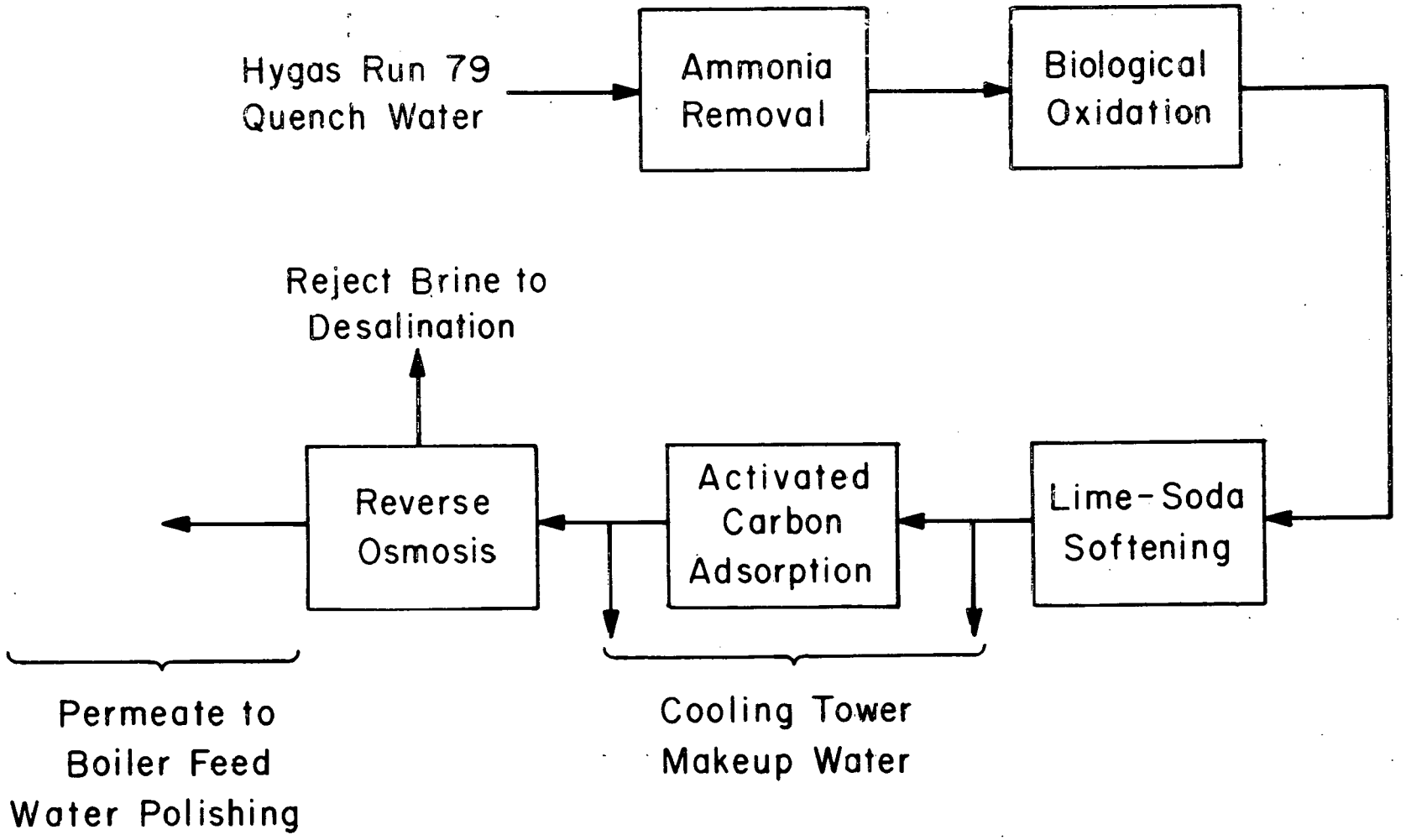


Figure 4
Bench Scale Treatment Train to Evaluate Processing Characteristics of Hygas Process Quench Condensate

Table II

TREATMENT OF A
COAL GASIFICATION QUENCH CONDENSATE

Specification[1]	BOD	COD	Phenolics	Org-N	SCN^-	CN^-	NH_3-N	NO_3^--N	S^{2-}	SO_4^{2-}	Total Freon Extractable	Calcium Hardness as $CaCO_3$	Total Hardness as $CaCO_3$	Alkalinity as $CaCO_3$	pH units	Cond µmhos/cm	Color Pt-Co units
Raw	-	10,400	1950	70	260	3.8	13,200	<2	620	225	120	56	56	46,200	7.7	44,300	-
Lime Pretreated	-	10,200	1970	60	290	3.9	10,800	<2	530	-	105	3100	3090	42,300	10.8	6,630	-
Ammonia Stripped	3450	6,930	1140	26	235	5.5	150	<2	25	-	75	1950	1950	2,000	9.5	3,150	-
Biological Effluent	30	715	0.74	11	9.0	6.0	100	150	<5	2380	45	1240	1240	170	7.0	4,640	-
Lime-Soda Softened	30	600	0.50	10	8.3	6.0	85	140	<5	2025	-	33	35	3,000	10.3	6,300	2400
Activated Carbon	23	110	0.23	5	2.1	5.0	80	160	<5	2540	<10	45	45	1,080	7.8	6,500	130
Reverse Osmosis Product[2]	4	20	0.04	2	0.4	0.1	0.5	0.55	-	10	-	0	0	100	7.6	180	<5

Notes: 1. Hygas Run 79 quench water, mg/l except as noted.

2. Reverse osmosis tests were conducted at 400 psi and 75% conversion with a hollow fiber polyamide membrane

condensates can exceed $50 per 1,000 gallons (6). It is important therefore for both reasons of cost and water availability that wastewater management be considered an integral part of any coal conversion process. Since high BTU coal gasification processes are net consumers of water, strong incentives exist for limiting discharge of aqueous streams, and wherever possible process modifications should be considered to facilitate water reuse.

One example of process modification is the use of a two stage quench condensation process proposed by Arthur G. McKee and Co. (7). This system accomplishes a preconcentration of inorganic salts in one quench condensate stream while leaving a second stream with predominantly volatile species. Another example of process modification to facilitate wastewater treatment relates to changing gasifier operation and/or configuration. Studies by Nakles, et al. (8) and Fillo (9) have shown that the production of organics during gasification is especially sensitive to operating variables such as coal devolatization temperature, gas-solids mixing, and gas residence time. Their results suggest that there are exploitable process modifications which may help to reduce or eliminate the production of organic contaminants. A third example is direct injection of concentrated process wastewater back into the gasifier. This feature has been incorporated in the Texaco entrained bed slagging gasifier, where it is reported that quench water organics are recycled to thermal extinction.(10). Feasibility and cost studies need to be conducted to evaluate the advantages of direct use of condensate for steam purposes; a possible drawback is that larger oxygen plant and gas handling systems would be needed (6).

The biological oxidation studies reported here and in the bibliography of reference (3), have defined the basic biological oxidation characteristics for phenolic gasification wastewaters by activated sludge treatment. Consideration should be given to alternative biological treatment systems in order to evaluate processes which may offer lower treatment costs and/or energy requirements. Candidate processes include rotating disk biological treatment and anaerobic biological contact filters.

The cooling tower is the most probable target for reuse of phenolic wastewaters. Unfortunately, there is lack of information to predict minimum makeup water quality criteria with respect to acceptable loadings of organics and trace contaminants. Hence, it would be prudent for the first demonstration plants to be designed with a conservative approach towards reuse of wastewater as a cooling tower makeup source. This strategy is exemplified by the Continental Oil Company design for a Lurgi slagging gasifier in which gas liquor is processed as makeup to the utilities cooling tower. The treatment system includes solvent extraction, ammonia recovery, biological oxidation, sand filtration, and activated carbon adsorption (11). In contrast, the Lurgi process design for El Paso Natural Gas Company called for only phenol extraction and ammonia recovery prior to reuse in the main plant cooling tower (12). This water management plan presents questions regarding cooling tower fouling, as well as justifiable concern for contamination via cooling tower drift and stripping/evaporation.

The problem of ultimate disposal of residual salts and sludges also

needs additional study. In many instances it is clear that the goal of zero discharge of aqueous streams can only be achieved by a high degree of brine concentration which necessarily results in a salt slurry. Possible disposal alternatives of the salt solutions include solar evaporation ponds, deepwell injection, or land filling. Inorganic sludges disposed by landfilling will require some form of chemical fixation or glassification to render them non-leachable. Where feasible, dilute salt streams may be returned to the ocean or other natural body with a large assimilative capacity. Organic sludges may ultimately be disposed of by recycle to the gasifier, by incineration, or by controlled landfilling. At this time, it does not appear that technical feasibilities, economic incentives, and policy implications are sufficiently clear to permit rational choice between these alternatives.

Finally, there is need to address issues relevant to environmental control of coal gasification facilities from a more fundamental point of view. In the past, much of the coal gasification environmental research has taken the form of specific studies focusing on individual processes. Although this research has provided a solid basis upon which to understand certain environmental issues, the current need is to consider critical wastewater treatment problems in greater detail. For example, work now being planned at C-MU will investigate adsorption of polycyclic aromatic hydrocarbons (PAH) in coal gasification wastewaters. PAH have been identified in some coal conversion wastewaters, and preliminary studies indicate that PAH may be largely associated with suspended particulates in these wastewaters. It is proposed to evaluate several important issues including the effect of PAH molecular structure on adsorption, the effect on adsorption due to competition for adsorption sites, and the effect on adsorption due to the presence of aqueous phase organic solvents which enhance PAH solubility. Information gained from this study will aid understanding of the fate and transport of PAH during and following wastewater treatment.

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POTENTIAL FOR CONTROL OF POLLUTANT PRODUCTION THROUGH PROCESS OPTIMIZATION

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INTRODUCTION

The eventual commercial-scale development of coal conversion processes requires an assessment of their technical feasibility, potential environmental impacts and economic merit. An economical processing scheme must be developed that produces the primary product(s) while impacting on the environment at a minimum, as dictated by expected regulatory guidelines. The environmental characteristics of the process determine the need for utilizing environmental controls, their type and consequently their cost. As such, it is necessary to identify and evaluate potential routes in the total processing scheme that economically control the release of pollutants to the environment.

Figure 1 illustrates a generalized process in which raw materials are reacted to produce both products/intermediates and potential waste materials. Reactor effluents are subsequently processed (individually and/or combined) to recover heat, separate phases, upgrade and process products/intermediates and remove waste materials. Specific control technology is most often invoked to bring process waste streams into compliance with regulations prior to their discharge from the plant. It may also be necessary to utilize "control technology" to alter potentially hazardous properties of products.

The ability to impact on the nature of control hardware exists across the network -- in production and distribution, as well as the control phases of the process. There is potential for reducing the need for environmental controls or changing the type of controls by altering the fate of pollutants (or their predecessors) within the process. While process development always includes experiments that seek to determine the response of the reactor to changes in its operation, it is becoming increasingly clear that the "response" being examined must include the fate of pollutants. A knowledge of process variabilities that affect the fate of pollutants during production and distribution preserves options for control, and consequently permits economic optimization across both production and environmental unit operations. It is the economic optimization across both process and environmental unit operations that is the driving force for gathering environmental data as a part of process development. This paper addresses two aspects of this problem which are relevant to coal gasification: 1) the fate of potential pollutants during gasification; and 2) generic pollutant production patterns which might aid in extrapolation of PDU/pilot-scale data to demonstration/commercial scales of development.

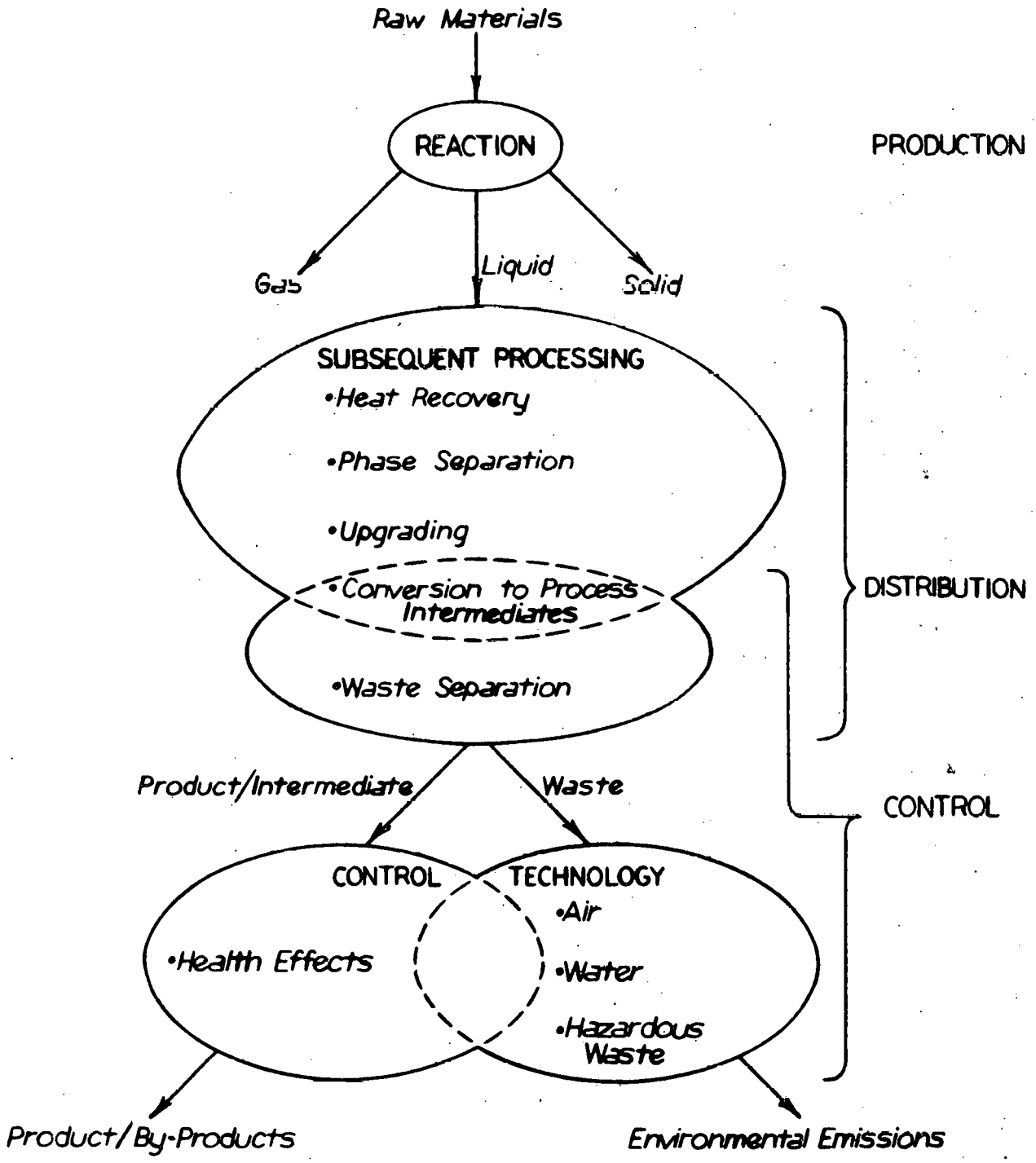


FIGURE 1. OVERLAPPING OF ELEMENTS IN PRODUCTION AND ENVIRONMENTAL PROCESSING.

ALTERNATIVES FOR CONTROL OF GASIFICATION ENVIRONMENTAL CHARACTERISTICS

The environmental characteristics of any coal gasification process are a complicated function of the main processing scheme (i.e., gas production) and the types of control technology used to reduce pollutant emissions. As illustrated in Figure 2, the primary processing blocks consist of:

- Production - release of potential pollutants from coal via chemical reaction during pretreatment and gasification,
- Distribution - pollutant species partitioning during raw process gas quenching and gas processing, and
- Control - removal of pollutant species from process streams that will eventually be discharged to the environment.

The function of each of these blocks, as well as their role in affecting environmental characteristics, is discusssed below.

Pollutant Production

Pollutant species are produced during thermal treatment of coal to produce gas. This occurs primarily in the gasification process where coal is reacted with mixtures of steam, air or oxygen to produce hydrogen, carbon oxides and hydrocarbon gases. Gasification of agglomerating bituminous coal requires oxidative pretreatment (i.e., steam plus air) prior to gasification, also resulting in pollutant release. Vent gases from pretreatment can be routed through the gasifier with pretreated coal or separately treated, depending upon the particular process configuration.

Pollutant production consists of an initial release from coal via chemical reaction followed by secondary reactions within the gasification environment(1,2).* Materials which typically report as potential pollutants include coal volatile matter (e.g., hydrocarbon tars, oils and phenols), nitrogen (e.g., NH_3, HCN), sulfur (e.g., H_2S, COS, CS_2, mercaptans) and trace elements (e.g., volatile and char/ash-bound). The extent to which these materials are released and their ultimate chemical form is determined by physical and chemical characteristics of the gasification environment.

Distribution of Pollutants

The first step in the distribution of reaction products (including pollutants) is the gasifier quench. Recirculating condensate (i.e., most often water) cools hot process gas and removes liquid condensates, including water (e.g., unreacted steam, coal moisture) and/or hydrocarbons (e.g., tars, oils, phenols). Pollutants produced during gasification, both organic and inorganic, are removed from raw product gas in the quench and report to all phases - water and tar/oil. Distribution of species by the quench system depends upon process configuration (e.g., single pass, recycle), process operation (e.g., temperature, pressure, recycle ratio) and chemical interactions in the quench environment (e.g., aqueous/hydrocarbon phase partitioning, aqueous phase specie dissociation).

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* Numbers in parentheses are references, listed at the end of the paper.

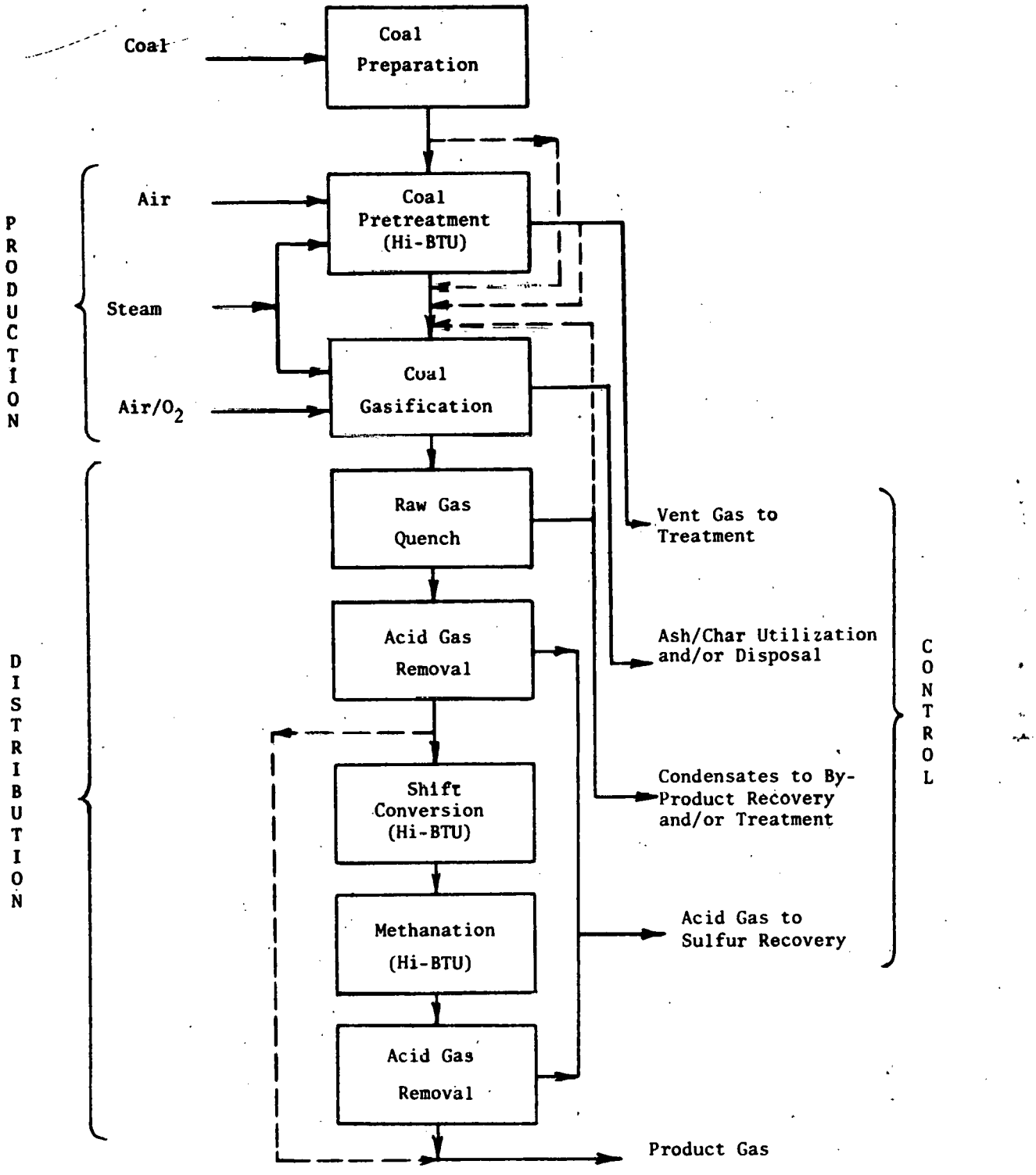


FIGURE 2. PRODUCTION, DISTRIBUTION AND CONTROL OF ENVIRONMENTAL POLLUTANTS IN COAL GASIFICATION PROCESSING.

Further processing of quenched gas usually consists of acid gas removal to provide a clean gas stream. In the case of high-BTU processing, some combination of shift conversion and/or methanation is required to upgrade product gas heating value. Acid gas removal prior to shift conversion and methanation also facilitates operability, as the potential for catalyst poisoning decreases. Trace amounts of pollutants not removed with acid gases can undergo chemical transformations (e.g., COS hydrolysis over shift catalyst) during shift conversion/methanation.

Control of Gasification Process Emissions

Methods for controlling pollutant emissions generally fall into two categories: 1) removal and recovery as by-products; and 2) destructive treatment. By-product removal is a useful alternative where sufficient quantities of pollutants are produced. Specific examples include recovery of NH_3 and phenols from aqueous condensate and processing of acid gases to recover H_2S as elemental sulfur. Where quantities are not sufficient to justify by-product recovery, destructive treatment of pollutant-bearing process streams can be utilized. Examples here include biological treatment of wastewater and incineration of gaseous, liquid and solid waste streams.

EFFECTS OF PROCESS CONDITIONS ON PRODUCTION OF POLLUTANTS DURING GASIFICATION

In order to achieve optimal control of coal gasification pollutant emissions, it is necessary to evaluate all potential control options in developing an environmental control network. This requires that the sensitivities for achieving pollutant control be identified for each process unit operation. This discussion addresses the fate of two potential pollutants during coal gasification: 1) condensable hydrocarbons; and 2) nitrogen-bearing species.

Condensable Hydrocarbon Production Characteristics

Condensable hydrocarbons produced during gasification include heavy tars, oils and phenols. Production is highly variable (see Table 1), both within and between processes, and can be attributed to differences in temperature, vapor residence time, reaction environment (e.g., hydrogen partial pressure), coal heating rate and gas/solids contacting. Given the widely different processing concepts available, and thus expected variations in operating conditions, production variations are not surprising.

To date, two of the most definitive studies addressing condensable hydrocarbon production characteristics were conducted on the Synthane PDU, and consisted of: 1) evaluating the effects of coal feed location(5); and 2) studying the effects of controlled coal devolatilization conditions(6). Results of these studies are summarized in Figure 3.

Production, lb/ton MAF Coal		Coal Feed Conditions		Production, lb/ton MAF Coal		
Tars/Oils	Aqueous Phenols			Tars	Oils	Aqueous Phenols
74 ± 3	12 ± 1	Free Fall ~400°C	50μ	13.0 ± 3.0	54 ± 11	8 ± 3
		Top Bed ~700°C	50μ	0.4 ± 0.4	49 ± 4	7 ± 4
			220μ	0.3 ± 0.2	4	6 ± 1
10 ± 5	4 ± 2	Shallow Bed				
6 ± 2	0.5 ± 0.6	Deep Bed ~900°C				

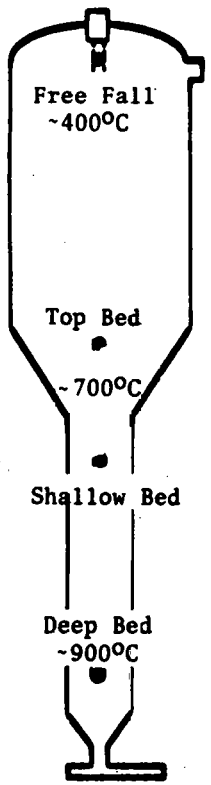


FIGURE 3. SENSITIVITY OF HYDROCARBON PRODUCTION TO CHANGES IN COAL FEED GEOMETRY IN THE SYNTHANE PDU.

TABLE 1: SUMMARY OF RANGES OF HYDROCARBON PRODUCTION FROM COAL GASIFICATION PROCESSES[a]

Process	Production, lb/ton MAF Coal		
	Tar	Oils	Aqueous Phenols
CO_2-Acceptor	0.1	2[b]	0.1
Hygas	-	40-140	1-16
Lurgi			
Westfield Semi-Plant	50-110	7-64	7-17
Slagging Fixed Bed	50-100[c]	-	10-30
Synthane PDU	0.1-180[c]	-	1-12

(a) Summary data reported in references 1-4; (b) Primarily benzene, measured in gasifier raw process gas. See reference 4; and (c) Includes tar and oil production, normally not segregated.

The first study resulted in achieving substantial reductions in tar/oil (i.e., measured in bulk as one entity) and phenol production as coal was injected deeper into the gasifier (i.e., free-fall, shallow and deep fluidized bed injection). Note that the severity of gasifier process conditions increased accordingly, including reaction temperatures, residence times in the hot fluidized char bed, coal heating rates and gas/solid contacting. Of primary importance were the comparative reductions observed for tars/oils and phenols (see Table 2), suggesting the following behavioral characteristics: 1) production of hydrocarbon tars/oils is determined primarily by process variabilities that affect release during initial coal devolatilization; and 2) production of phenols is determined primarily by process variabilities that enhance thermal/catalytic decomposition in the gasification environment. While the effects of thermal/catalytic decomposition could not be completely segregated, the experiments strongly suggested that these distinctly different mechanisms were responsible for the measured production characteristics.

The second series of experiments was designed to study the effects of changes in coal devolatilization conditions on production of condensable hydrocarbons. Coal particle size (i.e., 50 vs. 220 μm mean diameter) and coal feed geometry (i.e., free-fall vs. top bed-injection) were varied to study the effects of conditions that would enhance release and transport of volatiles from the coal particle (e.g., heating/diffusion rates, gas/solid contacting). Thermal/catalytic decomposition effects were minimized by injecting coal on top of the gasifier's fluidized bed to achieve enhanced gas/solid contacting. Results of these experiments indicated that tar and oil production could be substantially altered by changing initial coal devolatilization conditions. Within the variability observed in the data, production of phenols did not change significantly. These results, coupled with the demonstrated susceptibility of phenols to thermal/catalytic decomposition (7,12), confirmed the previously cited hydrocarbon production phenomena (see Table 2). Note also that observed reductions in condensable hydrocarbon production did not result in significant changes in equivalent methane or total gas production during either study.

TABLE 2: RELATIVE IMPACTS OF CHANGES IN MAJOR PROCESS VARIABLES ON SYNTHANE GASIFIER CONDENSABLE HYDROCARBON PRODUCTION

PROCESS VARIABLE	NATURE OF INCREASE[a]	EFFLUENT PRODUCTION DECREASE		
		TAR	OIL	AQUEOUS PHENOLS
	SHALLOW VS. FREE FALL INJECTION[b]			
Reaction Temperature	Major			
Coal Heating Rate	Major			
Residence Time	Moderate	- 86% -		71%
Gas/Solid Contacting	Major			
	DEEP- VS. SHALLOW-BED INJECTION[b]			
Reaction Temperature	Minor			
Coal Heating Rate	Negligible			
Residence Time	Major	- 38% -		86%
Gas/Solid Contacting	Negligible			
	TOP BED VS. FREE FALL INJECTION - 50 μm PARTICLES[c]			
Reaction Temperature	Major			
Coal Heating Rate	Major			
Residence Time	Negligible	97%	9%	13%
Gas/Solid Contacting	Major			
	220 VS. 50 μm PARTICLES - TOP BED INJECTION[c]			
Reaction Temperature	Negligible			
Coal Heating/Diffusion Rates	(Major)	25%	92%	14%
Residence Time	Negligible			
Gas/Solid Contacting	Negligible			

NOTES:

(a) Variable change which caused reduction in condensable hydrocarbon production. Changes in parentheses indicate directional variable decreases.
(b) Study evaluating effects of changes in coal feed geometry. See Ref. 5.
(c) Study evaluating effects of controlled devolatilization conditions. See Ref. 6.

Production of Nitrogen-Bearing Pollutants

Coal nitrogen is released to the product gas via reaction during gasification, and can report as molecular nitrogen, NH_3, HCN and nitrogen-bearing hydrocarbons. Both the conditions of initial release from coal and subsequent reaction in the gasification environment are important in determining characteristic pollutant production patterns.

The release of coal nitrogen during gasification is a function of gasifier carbon conversion. As illustrated in Figure 4, data from both Hygas(3,11) and CO_2-Acceptor pilot plants(4,9,11) support this conclusion. While variabilities in reactor pressure, temperature and gas composition (e.g., steam and hydrogen partial pressure) are not accounted for in this correlation, a definitive trend is evident and provides a basis for estimating nitrogen release from coal during gasification.

Identification and quantification of nitrogen-bearing pollutant production patterns from pilot plant data is clearly not a simple task. Significant quantities of molecular nitrogen used as purge gas in the gasifier precludes direct measurement of N_2. In addition, difficulties (e.g., quench system lag times, analytical and sampling interferences, aqueous phase pollutant dissociation) associated with quantitative characterization of pollutant production from pilot plant facilities further complicates matters. However, data are available that quantify production patterns of nitrogen-bearing pollutant production during gasification, and are summarized in Figure 5 and Table 3.

TABLE 3: COMPARISON OF NITROGEN-BEARING POLLUTANT PRODUCTION FROM THE CO_2-ACCEPTOR GASIFIER

Sampling Location	Pollutant Production, lb/ton MAF Coal		
	Ammonia-N[a]	Cyanide	Thiocyanate ($x10^3$)
	RUN 47A		
Middle Probe	14 ± 4	0.4 ± 0.09	12 ± 1
Gasifier Overhead	22 ± 4	0.2 ± 0.06	59 ± 10
	RUN 47B		
Bottom Probe	18 ± 1	0.04 ± 0.008	9
Middle Probe	17 ± 4	0.2 ± 0.2	4 ± 1
Top Probe	15 ± 1	0.2 ± 0.2	2
Gasifier Overhead	18 ± 2	0.07 ± 0.02[b]	-

(a) Coal nitrogen was 20 and 17 lb/ton MAF coal for Runs 47A and 47B, respectively; (b) Does not include HCN remaining in unquenched product gas.

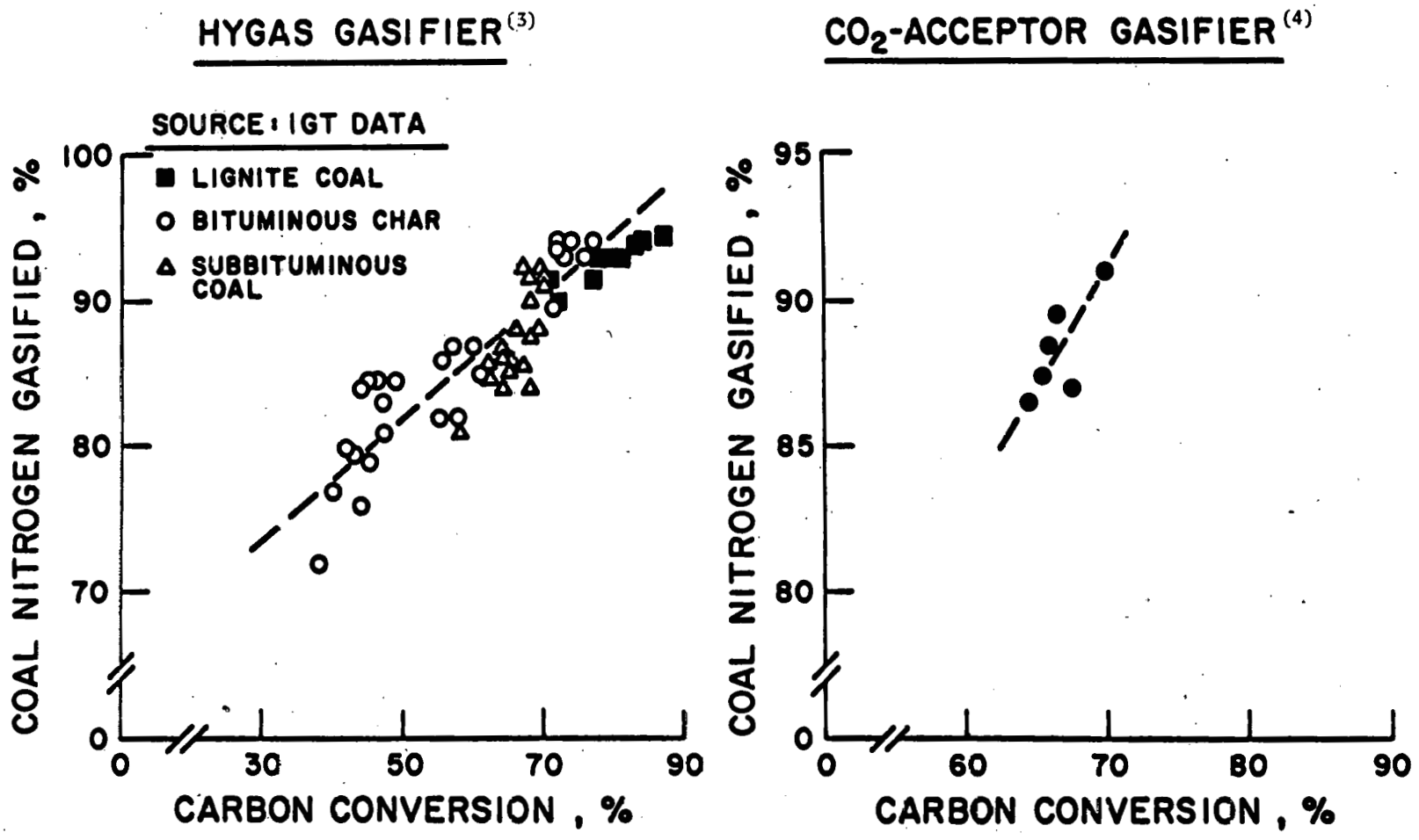


FIGURE 4. STEADY STATE HYGAS AND CO_2-ACCEPTOR COAL NITROGEN CONVERSION AS A FUNCTION OF GASIFIER CARBON CONVERSION.

As illustrated in Figure 5, conversion of coal nitrogen to ammonia in the Hygas gasifier(3,11) correlates with gasifier carbon conversion. While the bulk of gasified coal nitrogen appears to report as ammonia, scatter introduced by varying coal types and the use of data from self-sustained (i.e., as opposed to steady state) plant operating periods casts some doubt on this conclusion. Unfortunately, published information on production of HCN is not currently available.

Data summarized in Table 3 for the CO_2-Acceptor gasifier(4,8) shows production characteristics for ammonia, cyanide and thiocyanate measured at two locations in the gasifier. These include: 1) gasifier outlet as determined by quench condensate analyses; and 2) probe measurement of the gasifier's internal chemical composition at and around the point of fresh coal feed in the base of the gasifier. Interesting characteristics of this dataset include:

- essentially complete conversion of coal nitrogen to ammonia,
- less than 0.5 percent of coal nitrogen reporting to cyanide and thiocyanate, and
- within the variability in the data, ammonia production at the base of the gasifier is not significantly different than that measured at the gasifier outlet.

Again, as in the case of the Hygas, while available data are scattered, evidence points in the direction of substantial conversion of coal nitrogen to ammonia.

GENERIC COAL GASIFICATION POLLUTANT PRODUCTION PATTERNS

In order to design demonstration- and commercial-scale coal gasification processes which effectively optimize control of environmental characteristics, it is necessary to first estimate pollutant production patterns for the gasification step. The primary source of this data is generated at the pilot plant. However, since physical configuration and operating conditions of pilot plant and demonstration/commercial facilities are usually not identical, the effects of these differences must be taken into consideration. Generic pollutant production patterns for hydrocarbon, nitrogen- and sulfur-bearing pollutants are presented, as they can potentially aid in the extrapolation of PDU/pilot plant environmental databases.

Hydrocarbon Production Patterns

Production of hydrocarbons during gasification is a function of coal devolatilization conditions and/or conditions which enhance thermal/catalytic decomposition of hydrocarbons. Variabilities in production seen between various pilot plant processes are shown in Table 4(1) and follow the identified trends, consisting of:

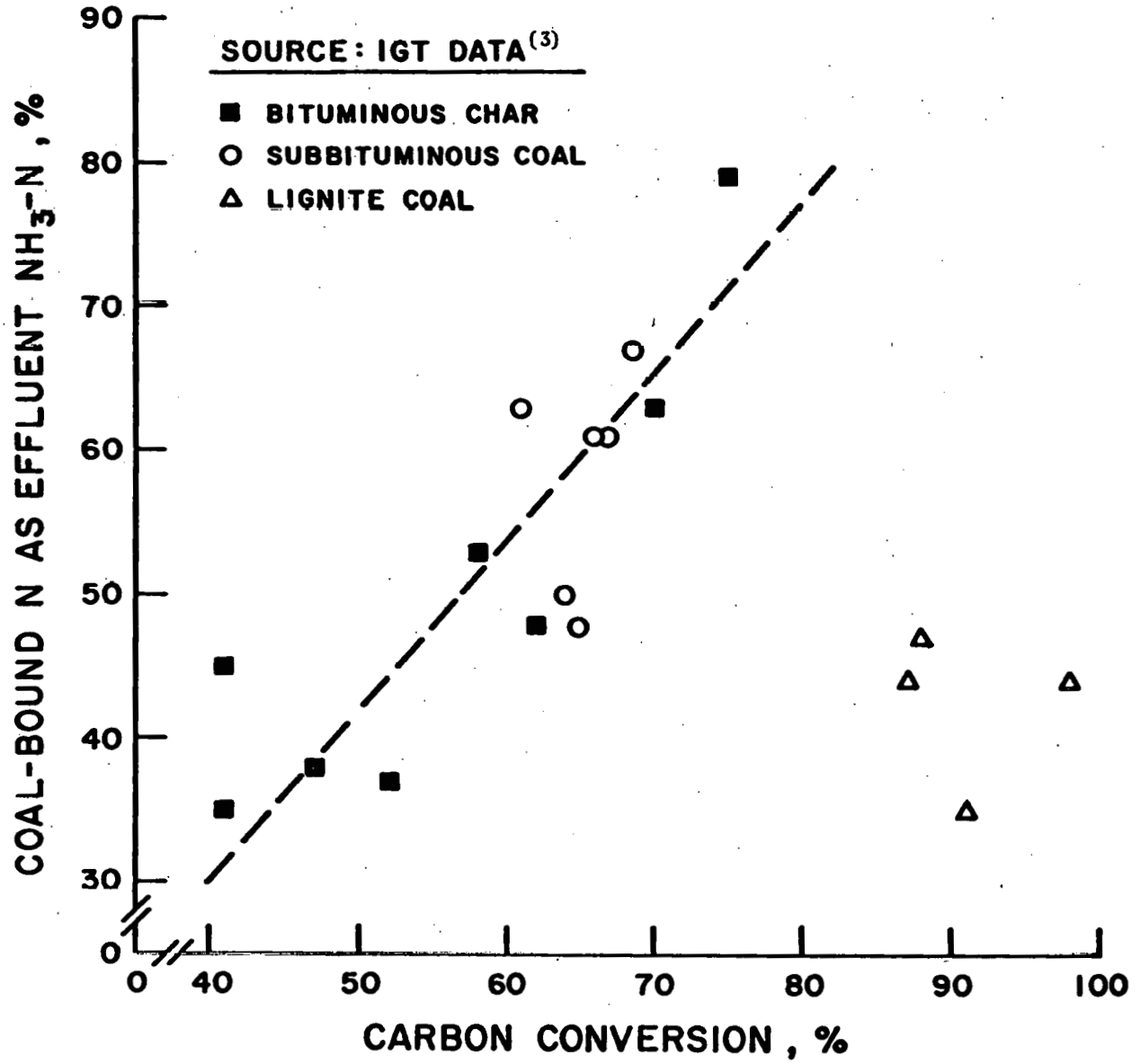


FIGURE 5. VARIATION OF NH_3-N YIELDS WITH CHANGES IN CARBON CONVERSION IN THE HYGAS GASIFIER.

1) Minimal gas/solid contacting, temperature and gas residence time results in high tar, oil and phenol production.

2) Extensive gas/solid contacting and temperature with minimal gas residence time results in low tar production, high oil and phenols production.

3) Extensive gas/solid contacting, temperature and gas residence time results in low production rates for tar, oil and phenols.

The extent to which these processing conditions are quantitatively replicated in demonstration/commercial facilities will determine whether pilot plant environmental data bases are adequate for extrapolating to larger facilities. In the case of the Synthane process, variabilities determined at the PDU-scale were fully demonstrated at the pilot-scale; substantial production of hydrocarbon tars, oils and phenols occurred during free-fall coal feeding, negligible production of these pollutants occurred during deep bed-injection coal feeding(10). In cases where process conditions and configurations are substantially different, more fundamental behavioral characteristics (e.g., hydrocarbon decomposition kinetics, coal devolatilization characteristics) will be necessary to properly effect database extrapolation.

TABLE 4: PROCESS VARIABLE AND HYDROCARBON PRODUCTION PATTERNS FOR SELECTED COAL GASIFICATION PROCESSES

	Process Variable		Pollutant Production		
Process	Gas/Solid Contacting During Devolatilization	Residence Time at Temperature	Tars	Oils	Phenols
Synthane[a]	Extensive	Extensive	Negl.	Negl.	Negl.
CO_2-Acceptor	Extensive	Extensive	Negl.	Low	Negl.
Hygas	Extensive	Minimal	Negl.	High	High
Lurgi[b]	Minimal	Minimal	High	High	High
Synthane[c]	Minimal	Minimal	High	High	High

(a) Operating with deep bed-injection of coal; (b) Either dry ash or slagging operation; and (c) Operating with free-fall coal injection.

Production Patterns of Nitrogen- and Sulfur-Bearing Pollutants

Patterns of release of coal nitrogen to the gasification environment have been demonstrated from both Hygas and CO_2-Acceptor data bases. Correlation of the extent of nitrogen release with gasifier carbon conversion suggests that at minimum proposed commercial design carbon conversion levels of 90 percent, 90 to 100 percent of coal bound nitrogen should be released. To the extent that production trends observed at both Hygas and CO_2-Acceptor pilot plants are directionally correct, the bulk of nitrogen released from the coal should report as ammonia.

A more basic understanding of pollutant characteristics can be obtained from the CO_2-Acceptor pilot plant data base for both nitrogen- and sulfur-bearing species. Gasifier pollutant production(9) and probe study data(8) were analyzed for the following equilibrium reactions:

$$H_2S + CaCO_3 \rightleftarrows CO_2 + H_2O + CaS \qquad (a)$$

$$HCN + H_2O \rightleftarrows NH_3 + CO \qquad (b)$$

Equilibrium constants were calculated using raw process gas and probe study data for reactions (a) and (b), respectively, and were individually plotted on a semi-logarithmic scale versus inverse absolute temperature (see Figure 6). Considering that pilot plant data was used in this analysis, good correspondence with equilibrium conditions in the gasifier was demonstrated. To the extent that correspondence with equilibrium conditions in the gasifier was demonstrated. To the extent that correspondence or approach to specific equilibrium conditions can be demonstrated for gas phase pollutant species, a useful tool for prediction of speciation in demonstration/commercial facilities could be available.

FUTURE NEEDS FOR ACHIEVING OPTIMAL CONTROL OF GASIFICATION PROCESS ENVIRONMENTAL CHARACTERISTICS

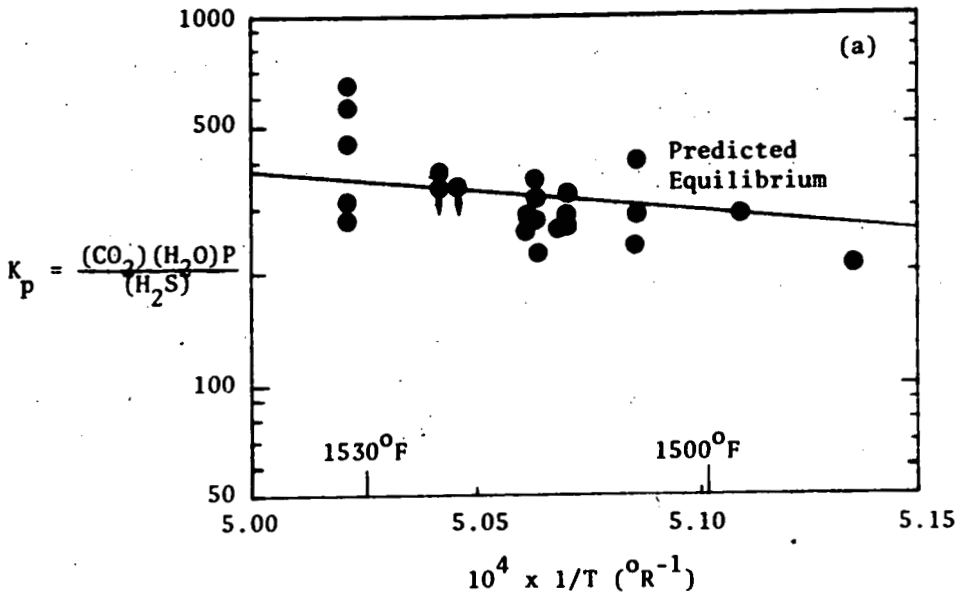
In order to optimize control of pollutant production from coal gasification processes, it is necessary to thoroughly understand variabilities inherent to production, distribution and residual emissions control. Areas which require further efforts include:

1) Production - Better characterization of pollutant production from pilot plant facilities is needed, especially for trace sulfur species and trace elements. Characterization data from low-BTU facilities is needed in particular.

2) Distribution - Capabilities for precise simulation of raw gas quench systems must be developed. They must necessarily be based on the behavior of operating pilot plant quench systems. Similarly, behavior of trace pollutants across processes inherent to gas production must be quantified (e.g., COS hydrolysis over shift catalysts).

3) Control - Quantification of control system performance on coal gasification process pollutant-bearing streams must be completed (e.g., biological wastewater treatment on the full range of aqueous pollutants).

The extent to which the full range of options can be utilized to effectively and economically minimize environmental impacts will determine the feasibility of eventual coal gasification technology commercialization.



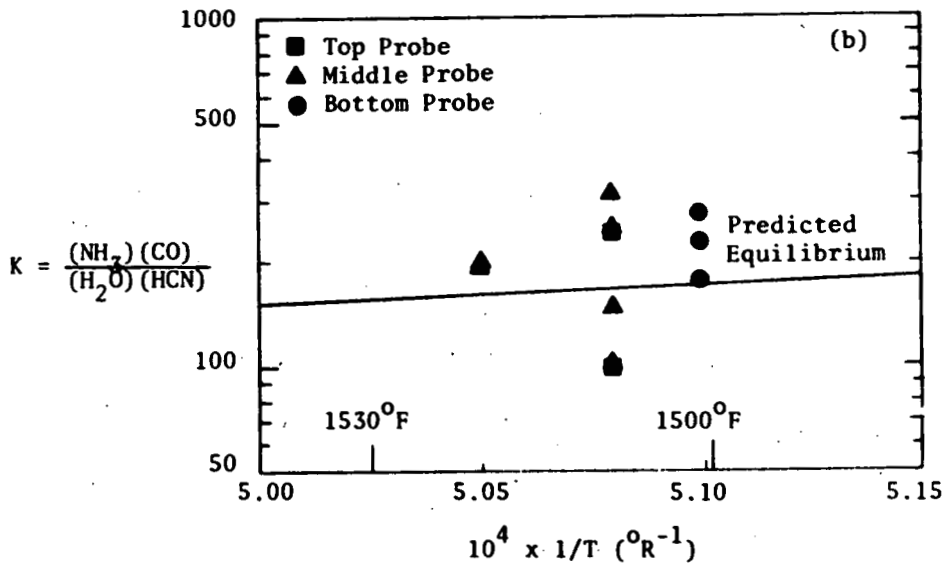


FIGURE 6. EQUILIBRIUM ANALYSIS OF CO_2-ACCEPTOR GASIFIER POLLUTANT PRODUCTION DATA: (a) $H_2S + CaCO_3 \rightleftarrows CO_2 + H_2O + CaS$, (b) $HCN + H_2O \rightleftarrows NH_3 + CO$.

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PROCESSING NEEDS AND METHODOLOGY FOR CONDENSATE WATERS FROM COAL CONVERSION

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INTRODUCTION

A contractors' workshop on the subject "Processing Needs and Methodology for Wastewater from Coal, Oil Shale and Biomass Synfuel Processes" was held in Germantown MD on June 14/15, 1979. The sponsor was the Division of Environmental Control Technology (ECT), Office of Environmental Compliance and Overview (ECO), Assistant Secretary for Environment, U.S. Department of Energy. Results of that workshop are include in a report of the same name, published Spring 1980. Copies may be obtained from the Division of Environmental Control Technology. This paper summarizes that report, which includes general conclusions from the workshop, as well as status reports of the projects represented by the participants.

Purposes of the workshop were several-fold. Water usages and general effluent situations were first surveyed. Next an effort was made to identify probable and possible water-treatment goals and regulations which will be in effect at the time of construction of synfuels plants. Various components of present water-processing technology were identified, and the capabilities, shortcomings and probable costs of these were assessed. Particular attention was given to process reliability, which is a critical point for plants of the size and cost projected for synfuels operations. This then led to identification of water-related environmental-control problems which seem to be particularly severe. Finally, overall conclusions and recommendations were made.

Although it was recognized that there are many different types of effluent waters from coal-conversion or other synfuels processes, it was decided to focus upon the process condensates -- water formed by condensation during cooling of reactor effluents. For a coal-gasification process this is the condensate from the main gasification reactor and from the shift converter. For oil shale, it is the retort water. The other water effluents will require treatment, as well, but most require less processing than the highly contaminated condensate waters.

Although concentrations of various substances in condensate waters vary widely, there are several common compositional characteristics:

(1) High dissolved ammonia contents, ranging up to 20,000 ppm w/w.

(2) High dissolved carbon dioxide contents, and, depending upon the sulfur level of the substrate, high H_2S contents.

(3) In most cases the molar concentration of dissolved acid gases (CO_2, H_2S) is roughly equal to the molar concentrations of dissolved NH_3. Exceptions include in-situ oil-shale retort

waters where there can be a large sodium-ion concentration from natural trona, with the result that C_{CO_2} exceeds C_{NH_3}, and some coal-conversion waters where chloride and/or sulfate are present, and C_{NH_3} exceeds $C_{CO_2} + C_{H_2S}$.

(4) Since NH_3 is a stronger base than CO_2 and H_2S are acids, the pH of condensate waters is usually high, typically in the range 8.0 to 9.5.

(5) Because of (1) and (2), the waters are strongly buffered.

(6) Organics loadings are often high, with chemical oxygen demand (COD) ranging up to 40,000 ppm and above. For coal-conversion waters the principal organics are phenols; for oil-shale retort waters they are carboxylic acids.

(7) Some known toxic substances are present, including polynuclear aromatic hydrocarbons, nitrogen heterocyclics, primary aromatic amines and arsenic.

Coking effluent waters from the iron and steel industry have similar characteristics. However, important differences are that synfuels condensate waters have (1) much larger flow rates; (2) much greater proportions of dissolved CO_2; (3) greater buffering; (4) often higher concentrations of organics and ammonia; and (5) possibly a greater proportion of polyhydric phenols and problem trace organics.

CAPABILITIES AND COSTS OF PRESENT TECHNOLOGY

Table 1 lists current-technology processes, along with an indication of substances removed and approximate costs. It should be recognized that costs will be highly variable from situation to situation, depending upon the specific locale, the coal or other feedstock used, the particular conversion process, etc. In the case of steam strippong for ammonia removal, the high cost reflects the large steam boil-up ratios required, resulting from lowering of the volatility of ammonia by acid-base interactions in solution. Costs in Table 1 are those which would be associated with clean-up to an extent allowing release to the environment.

Figure 1 shows a possible treatment scenario, giving costs of 7 to 30 $/1000 gallons for the more contaminated waters to meet present standards, and costs up to $50/1000 gallons projected to meet possible future standards. Although these costs may seem high by water-treatment standards, it should be recognized that the waters in question are usually highly contamined. Taking typical water throughputs of coal-conversion processes, the costs indicated in Table 1 and Figure 1 might correspond to roughly 5% of the total costs for the conversion process.

It is reasonable to attempt to estimate such costs now, in spite of the uncertainty regarding future standards and process capabilities. The total costs of synfuels plants are also uncertain, and, even though water treatment costs are a small percentage of the total cost, they are large enough to give substantial economic incentive for improvement.

Table 1. PRESENT TECHNOLOGY

Process	Comments	Cost ($/1000 gal)
Gravity Separation	Suspended matter with SG ≠ 1	0.10 - 0.20
Steam Stripping	NH_3, H_2S, HCN, CO_2, light organics	10
Solvent Extraction	Phenols, other organics, COD	5
Biological Treatment	Incomplete removal of COD? Surges, high loadings	10 - 20*
Carbon Adsorption	Prior ozonation helps Expensive if no regeneration	6 - 40*
Iron Precipitation	Scavenges heavy metals	var.
Ozonation	May be broadbrush	10 - 50*
Wet-Air oxidation	Broadbrush; poorly tested	25 or more
Ion Exchange		
Incineration		
Deep-well Injection		
Concentration for Inorganics		
Process Modification (i.e., RECYCLE)		

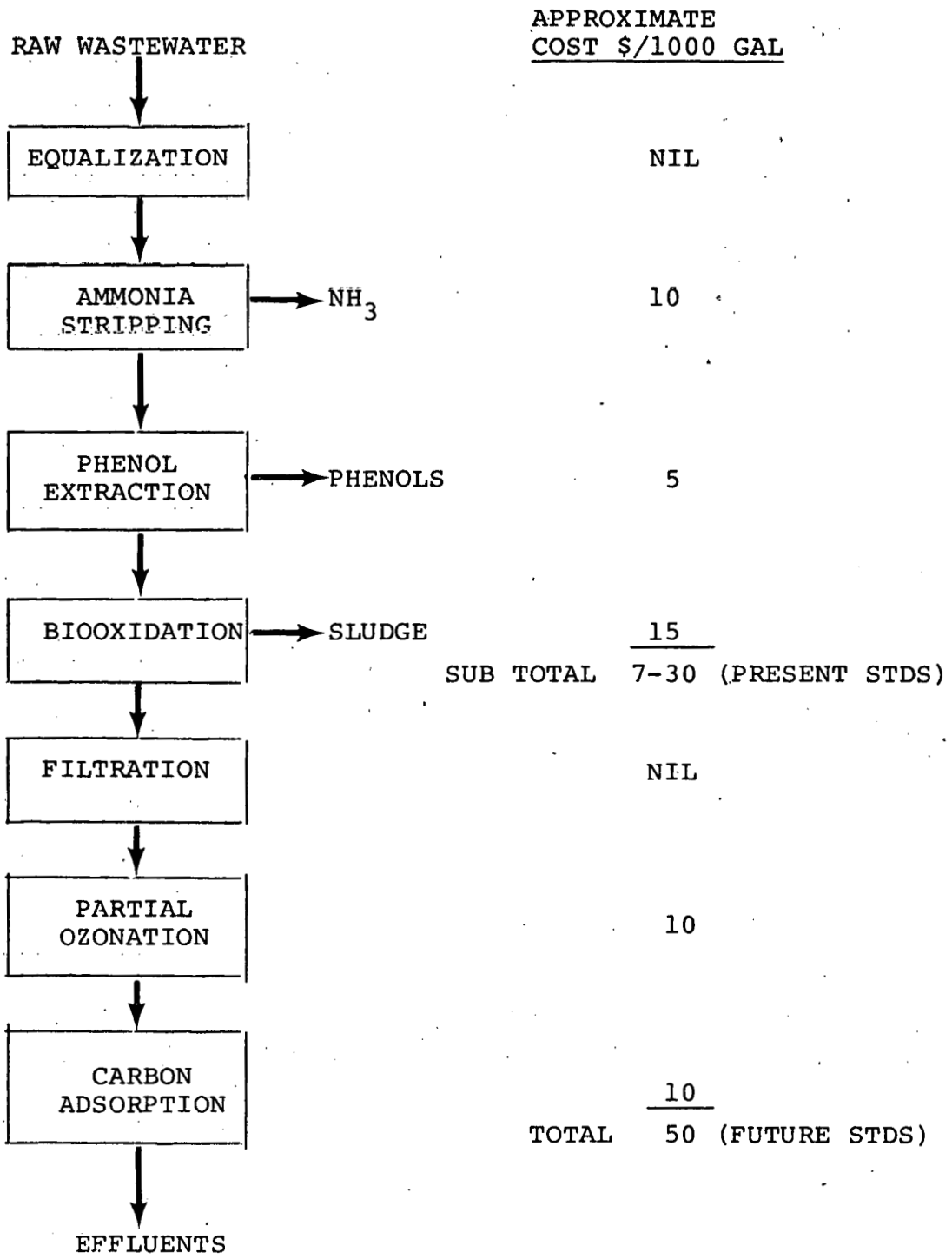
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* - Costs based on no significant prior roughing treatment. If used as a finishing step, cost will be less.

Figure 1

REPRESENTATIVE WASTE WATER TREATMENT TRAIN

FOR COAL CONVERSION EFFLUENTS



It is useful to categorize the available processing steps for condensate waters. One classification would separate those processes suitable for organics (biotreatment, extraction, adsorption, ozonation, incineration, wet-air oxidation) from those suitable for inorganics (evaporation, reverse osmosis, ion exchange, $Fe(OH)_3$ precipitation). Another classification is that shown in Table 2, differentiating processes favored for more concentrated waters from those favored for more dilute waters. Table 3 breaks these processes down still another way, distinguishing between those which are suited for recovery of substances in unchanged form, those which are best as finishing steps, and those which serve to give bulk destruction.

It is important to identify those synfuels processes which are likely to be net consumers of water (conversion of high-grade coals, above-ground shale retorting) and to contrast them with those processes which are likely to be net producers of water (conversion of peat and lignite, in-situ retorting below the water table, biomass pyrolysis). Processes in the latter category lead to processing of more dilute waters, while for the net water consumers there is a very large incentive for recycle and building water concentrations up to high levels in smaller water volumes, which will therefore be less expensive to process.

In view of the substantial costs projected for waters to be released from the process, there is a great incentive to develop technology for substantial recycle. A relatively straightforward recycle would be as cooling-tower make-up. However, it is also important to recognize that the gasifier itself in a coal-gasification process can serve for ultimate disposal of many pollutants. Even though there will be an energy loss associated with vaporization of water recycled to the gasifier, it is important to quantify what that energy loss would be and to identify the extent of recycle possible without excessive processing difficulties, since recycle to the gasifier would greatly alleviate the water-processing problem. Recycle of water to the gasifier has been proposed for use with the Texaco entrained-bed slagging gasifier, and in a combination of the Texaco gasifier and the slagging Lurgi moving-bed gasifier.

CRITICAL ENVIRONMENTAL CONTROL ISSUES

The following appear to be particularly important environmental-control issues, for which solutions are either not apparent or are untested:

(1) Total dissolved solids. Condensate waters with a high concentration of non-volatile inorganic solutes pose problems for release to natural waterways. Recycle to the gasifier may be a way of incorporating these substances with the ash. Alternatively, expensive saline-water treatment technology will be needed, with disposal by deep-well injection or conversion into a non-leachable landfill.

(2) Polynuclear aromatic hydrocarbons, nitrogen heterocyclics, etc. Fragmentary evidence says that biological treatment does not handle these well, and that carbon adsorption may not be fully effective either. Ozonation, followed by carbon adsorption, may be effective. The problem is probably to a large extent one of particulates removal.

Table 2

CATEGORIZATION

Concentrated	Dilute
Extraction	Biological Treatment
Stripping	Adsorption
Evaporation	Ozonation
	$Fe(OH)_3$ Precipitation
	Ion Exchange

Table 3

CATEGORIZATION

Recovery	Finishing	Bulk-Destruction
Extraction	Carbon Adsorption	Recycle to Gasifier
Stripping	Ozonation	Wet-Air Oxidation
		Biological Treatment
		Incineration

(3) Ammonia or nitrate. Allowable effluent concentrations for these substances may be very low. Complications include the facts that the last ammonia may be held in solution chemically and that these compounds can be products of biological processing.

(4) Color. Many synfuels condensate waters discolor severely; in many cases this is attributable to polyhydric phenols. Some of these are resistant to biological oxidation and also difficult to extract from water.

(5) Arsenic. It is conceivable that standards may become severe enough so that they are very close to the detection limit. The toxicological situation is quite uncertain, however.

(6) Boron. Boron is undesirable in waters to be used for irrigation, and appears to pose a problem in in-situ oil-shale retort waters.

(7) Toxicity safeguard. A broadbrush finishing step in the treatment train is desirable. Greater knowledge is needed in order to evaluate the effectiveness of various finishing steps as toxicity safeguards.

(8) Disposal of sludges. How to do this is uncertain at this point, but the question should not provide a barrier to commercialization.

(9) Carbon regeneration effluent and other secondary effluents. Attention must be paid to these, as well.

CONCLUSIONS AND RECOMMENDATIONS

1. There appear to be no insurmountable barriers to commercialization resulting from water-pollution problems. However, in several cases novel technology appears to be needed and is not well tested.

2. There are a number of generic problem areas which cut across different synfuels processes. These include ammonia removal, gross COD reduction, handling trace levels of toxic organics, and removal of color bodies. It would be cost-effective to direct more research toward these generic problems, as opposed to processing techniques for specific processes, many of which can be expected to change substantially (or disappear) before commercialization.

3. For the more contaminated condensate waters, processing costs for water to be released can reach or exceed $50/1000 gallons.

4. Water handling should be considered as an integral part of the main synfuels process, rather than as an add-on.

5. Especially for feedstocks for which the process will be a net consumer of water, there is a strong incentive for water recycle.

6. Physicochemical processing (stripping, extraction, etc.) is relatively more favorable under conditions of substantial recycle; biological treatment, ozonation, etc., are more favored for water to be released.
7. Ultimate disposal of sludges and secondary effluents requires attention.
8. Some sort of final, broadbrush, safeguard treatment is desirable.
9. In many cases biotreatment has not been able to accomplish more than a 60 to 75% reduction in COD. It may be promising to look at innovative approaches for biological processing.
10. Solvent extraction should be an effective alternative for gross reduction of COD.
11. Wet-air oxidation may be desirable for broadbrush treatment of small volumes of highly concentrated condensate water. It should be better characterized.
12. Polyhydric phenols have received little attention in the past. They are problematic compounds, requiring more intensive consideration.
13. A preliminary separation of inorganic solutes from organic solutes may be useful.
14. Evaluation of water-processing methods is considerably complicated by uncertainty regarding future standards.
15. Waters with high total dissolved solids contents pose special problems.
16. Processing approaches for polynuclear compounds should receive more attention.
17. Effects of strong and moderately strong acids on ammonia volatility should be better characterized, in cases where there may be unexpected association complexes.

SESSION 13
FOSSIL RESOURCE EXTRACTION

Chairman: A. Sikri
Co-Chairman: J. Pell

"An Overview of the Status of Enhanced Oil Recovery in the U.S., and Related Environmental Concerns"

by

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and

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Introduction

The objective of this paper is to present a brief overview of the status of enhanced oil recovery (EOR) in the U.S., with particular emphasis on the activities of the DOE Secretariats for Fossil Energy and the Environment. As the activity in EOR expands, due to the economic pressures to produce domestic oil, many new field tests, both developmental and commercial, are getting underway. This involves the use of the newer thermal and chemical techniques which present possible air and water pollution problems. Thus a need to alleviate enviornmental concerns arises.

In the two Secretariats involved, work on EOR environmental problems has been accelerating. The timing of the EOR expansion technically and commercially is such that the necessary environmental planning, although not entirely completed, is adequate and ready. The environmental problems and probable solutions are presented.

Where We Are in Enhanced Oil Recovery (EOR) in the U.S.

Conventional primary and secondary oil recovery from existing U.S. reservoirs has left behind two-thirds of the original oil in place. Thus the target for EOR is large, perhaps the largest liquid hydrocarbon source in the U.S. (other than shale oil). Out of roughly 440 billion barrels discovered, we have recovered 106 billion and have reserves by conventional methods of 34 billion. This leaves as the EOR target 300 billion barrels which can be further subdivided into 230 billion barrels of light oil, roughly 90 billion of heavy, and 80 billion of recoverable bitumen from tar sands.

Enhanced oil recovery is finally beginning to receive the attention it deserves. Our greatest need is for transportation hydrocarbon fuels, and the light and heavy residual oil in place is an attractive target. Although the oil industry has researched enhanced recovery for 20 years, production by EOR has been constrained by incomplete technology and unfavorable economics. Only in the past few years has the technology advanced enough to give some confidence of predictability in favorable reservoirs, and only in the past 18 months have the prices been adequate to encourage some techniques. The technology as a whole is not complete, and the vital roles of reservoir description and mineraology have come to be recognized.

In order to reduce any future potential environmental problems associated with expanding EOR application, DOE has formulated an "EOR Environmental Development Plan." This plan identifies EOR environmental concerns which require study in order to assure environmental acceptability. Many of these studies are already underway, and others are planned for our future EOR tests. Fortunately in most cases these environmental concerns are not insurmountable. The target productions of oil by EOR are significant: 0.6 to 0.8 million bpd by 1985 and 1.6 to 2.0 million by 1990.

The Federal Role In EOR

Research and development on EOR began in the 1950's in the Bureau of Mines, and slowly expanded through ERDA into DOE, where two major secretariats are involved. EOR technology in DOE/ERDA expanded rapidly between 1975 and 1979 up to a maximum 1979 budget of $54 million. In these years two-thirds of the budget went into cost sharing of twenty-seven field tests, twenty-three of which continue. These are tabulated in Table 1. (2).

TABLE 1

DOE CONTRACTS FOR EOR FIELD TESTS

(Million Dollars)

Program	Total Cost	DOE Share	Operator	Field Location	Planned Completion Date
Micellar Polymer Flooding	13.1	5.4	Cities Service, Inc.	El Dorado, KS	11/82
	9.8	3.4	Phillips Petroleum Co.	Burbank Field, OK	8/79
	4.2	2.2	Penn Grade Crude Oil Assoc.	Bradford Field, PA	6/80
	5.0	2.5	Gary Operating Co.	Bell Creek Field, MT	6/81
	7.0	3.5	City of Long Beach	Wilmington Field, CA	12/80
	44.0	14.0	Marathon Oil Co.	Robinson Field, IL	12/86
	35.5	9.5	Continental Oil Co.	Big Muddy Field, WY	1/88
Total	118.6	40.5			
CO_2 Flooding	2.8	2.8	Gulf Oil Co.	Little Knife Field, ND	5/82
	1.4	0.5	Columbia Gas Trans. Corp.	Granny's Creek Field, WV	6/79
	2.6	1.0	Pennzoil Co.	Rock Creek Field, WV	3/81
	5.5	2.4	Shell Oil Company	Weeks Island Field, LA	8/81
Total	12.3	6.7			
Improved Waterflooding	3.9	1.2	Kewanee Oil Co.	Stanley Stringer Field, OK	5/79
	7.5	2.2	Shell Oil Co.	East Coalinga Field, CA	6/81
	14.0	5.6	City of Long Beach	Wilmington Field, CA	9/81
	2.0	0.5	Aminoil	Huntington Beach, CA	7/79
	2.2	1.1	ERCO	Storms Pool Unit, IL	12/81
Total	29.6	10.6			
Thermal Recovery	7.3	2.5	Husky Oil Co.	Paris Valley Field, CA	1/80
	0.8	0.7	Carmel Energy Co.	Carlyle Field, KS	6/79
	8.7	2.0	Getty Oil Co.	Cat Canyon Field, CA	5/81
	8.2	3.1	Cities Service, Inc.	Bellevue Field, LA	6/82
	8.2	1.7	Chanslor Western Co.	Midway Sunset Field, CA	6/83
	11.3	4.4	General Crude Oil Co.	Lynch Canyon Field, CA	9/85
Total	44.5	14.4			

In FY 1980 the DOE Management instructed the ERA to formulate and authorize rule-making to permit self-certifying incentive field testing by raising the price of controlled oil in sufficient quantity to world market price to accumulate $20 million for each property tested. By February 15, 1980 about sixty applications were received. Forty-one are tabulated (through February 7, 1980) as Table 2. (3). This permits reduction in the DOE/EOR budget for continuation of its R&D effort, and establishment and analysis of an EOR data base.

With the expansion of field testing and DOE's commitment to technology environmentally acceptable, the Environmental Development Plan mentioned earlier plays a key role in assuring that appropriate environmental R&D effort is conducted either in-house or by universities or contractors.

In addition, each field test contract includes environmental monitoring provisions and any required mitigation measures necessary to fully comply with federal, state, and local environmental permits and regulations. DOE Fossil Energy has also initiated action for the development of a Programmatic Enhanced Oil Recovery Impact Statement. This Statement when finalized will further assess technology-wide environmental impacts and will provide information regarding any additional measures that should be taken to assure environmental compliance for the outyear expansion of EOR.

The Processes

These have been described adequately in preceding documentation enough to require only the briefest description here. In the thermal processes, applied mainly to viscous (heavy) oil or tar sands reservoirs, steam or steam and flue gas are injected into oil sands thru injection wells. The partially condensed steam and heated oil are forced toward producing wells. An alternative is to inject compressed air and partially burn the heavy ends of the oil in place and force the remaining lighter components and products of combustion toward producing wells. Water may be injected with the air, once in situ combustion is established.

The chemical processes are varied in nature. The simplest is perhaps the injection of dilute caustic soda or sodium orthosilicate into oil sands, where crude detergents may be formed with the organic acid components. These reduce surface tension, and permit greater oil recovery. Where mobile oil still remains in the reservoir, polymer-thickened water may be used as a mobility control agent to improve sweep efficiency.

The most sophisticated, and perhaps the most versatile profess, micellar-polymer or microemulsion, is slowly gaining recognition because of its potential cost effectiveness. After preflush, if necessary, a microemulsion slug of surfactant, cosurfactant (higher alcohols), light hydrocarbon oil

TABLE 2

RESULTS OF RA/ERA FINANCIAL INCENTIVE APPLICATIONS AS OF FEB. 7, 1980

- 41 Projects have been Received as of February 7, 1980
- 18 Projects Use Existing Technology; Will Add Little New Technology
- 23 are Advanced Technology, but Few are Aimed High Production Targets

• The Projects Received to Date are Summarized Below:

	Number of Proposals	Target: Ultimate Recovery (Billion Bls)	Target: 1990 Production (M B/D)
• Current Technologies			
Heavy Oil: Shallow Steam/ Combustion	12	9	300-500
Light Oil: CO_2 in SW Carbonates/ Polymer	6	6	300
	18	15	600-800
• Low Risk, Low Yield Technologies			
Heavy Oil: Improved Combustion	4	0.1	10
Light Oil: Improved Waterflood	7	0.1	10
	11	0.2	20
• Higher Risk, Highest Yield Technologies			
Heavy Oil: Steam w/ Additives	0	3.6	150
Deep Steam	1	3.7	80
Non-Petroleum Fuels	0	1.6	130
Environment/Institut.	0	-	130
Light Oil: CO_2 w/ Mobility Control	0	5.8	360
CO_2 in Other Carbonate, Sandstone	2	6.1	250
CO_2 Offshore	0	1.7	20
CO_2 Supplies	1	-	50
Improved Chemical	4	1.8	100
Thermal w/ Light Oil	0	2.7	110
Tar Sands and Special Targets:	4	2.1	-
	12	29.2	1380

and water or brine is injected to the extent of perhaps 10 percent of the pore volume. This reduces surface tension and releases residual oil. The banked oil is then swept efficiently toward producing wells thereafter with a tapered polymer-thickened water flush. The viscosity of the polymer solution is carefully adjusted. The total volume of polymer solution may reach 10 pore volumes.

Finally, carbon dioxide, either liquid or as the gas, often alternated with water, may be injected in oil sands. It will do several favorable things, such as reduce viscosity, reduce surface tension, swell the oil, and distill light components to enhance production. Combination processes are now appearing such as carbon dioxide - surfactant foams, steam with additives, and others.

The Environmental Problems

In the study of the environmental aspects of EOR, eight areas of concern are highlighted in the EDP: air pollution, ground water pollution, water use, waste water effluents, solid wastes, occupational safety and health, physical disturbance and noise (6). The greatest problems occur from air or water pollution, and these will be discussed separately.

I. Air Pollution: The principal problems arise from the thermal processes processes of steamflooding and in situ combustion. The former has been applied applied most often to heavy oil fields in California, beginning about 1960. Dozens of installations of oil field steam generators exist, primarily in four large fields, i.e., Kern River, Midway-Sunset, San Ardo and Coalinga. (7). The air pollution problems arise mainly from the steam generator stack gases. The generator sizes are commonly 20 million or 50 million Btu/hour.

Attention has centered on SO_2, NO_X and particulates, although carbon monoxide and hydrocarbons are not overlooked. For the typical size steam generators burning a typical 1.1 percent sulfur produced heavy crude, the following quantities of these 3 principal pollutants will be emitted (8).

Table 3 (see attached sheet)

If these quantities are multiplied by 275 generators, the current estimate, the pollution is significant for the heavy oil fields of California. In other states the problem is not as severe. Roughly half of the U.S. heavy oil reserves are in California, and the reservoirs are amenable to steam production.

For flue gas desulfurization, alkaline scrubbers are now being installed in many California oil field steam generators. Using non-regenerable sodium carbonate or sodium hydroxide, these scrubbers are 90 percent efficient, and will do the job for now.

TABLE 3

EMISSIONS FROM TWO SIZES OF STEAM GENERATORS

	SO_2			NO_2			PARTICIPATORS		
	Lbs/Bbl	Lbs/MMBtu	Lbs/Hr	Lbs/Bbl	Lbs/MMBtu	Lbs/Hr	Lbs/Bbl	Lbs/MMBtu	Lbs/Hr
20MMBtu/Hr	8.0	1.3	27	3.5	0.58	12	0.66	0.11	2.2
50MMBtu/Hr	8.0	1.3	67	3.5	0.58	29	0.66	0.11	5.5

NO_X presents more difficult problems. Low excess air, low NO_X burners, ammonia injection and catalytic reduction are under consideration for new permits. The Exxon-developed ammonia injection method is often effective, but not in all cases.

The particulate removal problems may be partially solved by the alkaline scrubbers. If the removal efficiency is not 85 percent or better, however, then other methods such as cyclones, bag filters or electrostatic precipators may be required.

At the present time, in view of the urgent need to reduce oil imports, the California oil producers and California Air Resources Board (CARB) are cooperating and compromising so that many new steamfloods are planned in California and in other states.

The air pollution problems from in situ combustion are not dissimilar to those of stack gas emissions from steam generators. After passing through the stock tanks, the light hydrocarbons must be recovered by natural gasoline type processing, after which the pollutants from combustion must be handled similarly to the steam generators.

II Ground and Surface Water Pollution: The more serious environmental problems are presented by the possible contamination from EOR processes in underground aquifers. Without DOE's current studies this could go undetected for long periods of time, after which little could be done about it. Most useful fresh water aquifers are fortunately not at great depths, and the petroleum industry on the whole in recent years has learned to meet the required rules with respect to disposal of produced brine, oil spills, leaks from corroded casings or natural fractures, and fugitive hydrocarbon leaks. This has not always been 100 percent true, although the record of the oil industry as a whole in recent years has been quite good. This undoubtedly comes from simple economics plus pressure from regulatory bodies.

Somewhat greater risks arise with EOR, particularly the chemical processes. The risks from the thermal processes would be represented by leaks of condensed steam, or oil emulsions into aquifers. Carbon dioxide per se presents little risk and is generally non-toxic unless it contains H_2S.

Generally speaking it is economically imperative that EOR fluids be contained in and pass through the intended oil sand areas. In developmental, small tests to date this has not always occurred, but sophistication is developing rapidly. Alkaline solutions will be consumed to a considerable extent in passing through oil sands, either by reaction with reservoir rock or clays, or crude oil reactions. That which may be in the produced brine must either be reinjected or neutralized.

A list of some of the most common chemicals that are being used today in oil fields is presented in Table IV. The chemicals are generally well known organic products, and their toxicity and limiting concentrations in fresh water established. Toxicity will vary widely. Surfactant slugs will contain 50 to 70 percent water, with the remainder being surfactant, cosurfactant, hydrocarbon and bactericides. Polymer solutions will usually have 0.1 percent have 0.1 percent concentration or less. BETC completed a review of the toxicity of EOR chemicals in February 1980. This work will be published as soon as feasible this year and it may also be presented in summary form at the annual Society of Petroleum Engineers Meeting in October 1980, Dallas, Texas.

These micellar chemicals, if released from the oil sands or wells, will decrease in concentration with time and distance in travelling through underground geological strata by adsorption, dilution, chemical decomposition and biodegradation. Thus in the unlikely event that such chemicals are released, their concentrations will usually be below toxic levels. Many aquifers near oil reservoirs are saline and thus not useful to humans or animals. Most useful aquifers are above the oil sands to be flooded and contamination is thus unlikely. Current studies are underway at the Bartlesville Energy Technology Center to assure long-term chemical acceptability from an environmental point of view.

In some cases disposal of produced brines containing small quantities of these chemicals may not be practical by injection into deep geological strata. In these cases either recycle (usually difficult), biodegradation or chemical destruction will be necessary.

The impacts of EOR on surface waters are minimal and appear to be controlled adequately by the Clean Water Act and state regulations. Many EOR operations will have no surface discharge of water. Accidental spills of oil, chemicals or brines must be handled by Spill Prevention Control. (1) These preventive measures are required in DOE test contracts.

Water use for chemical flooding purposes has been studied by areas, and supply problems may occur in some. This study is incomplete.

III. Other Environmental Problems: Physical disturbances of a seismic nature have occurred in a few cases by pressure injection of fluids, particularly near geological faults. It is a hazard which must be considered as possible in specific types of geological structures. BETC is presently initiating a study of induced seismicity and subsidence caused by the injection of chemical solutions and chemical breakdown of the rock skeleton.

TABLE 4

COMMON CHEMICALS USED IN POLYMER OR MICROEMULSION FLOODING

Surfactants	Cosurfactants	Polymers	Bactericides
Olefin Sulfonates	Amino Compounds	CMC	Sodium Dichloro-Phenol
Alkyl Aryl Sulfonates	N. Butanol	Polyacrylamide	Dosium Pentachloro-Phenol
Diethyleneglycol Sulfate	Cyclohexanol	Polysaccharides	Aldehydes
Dodecyltrimethyl Ammonium Chloride	Isobutanol	Polyethylene Oxide	Alkyl Amines
Polyglycerol Monolaurate	Isopropanol	Carboxyvinyl Polymer	Alky Phosphates
Sodium Lauryl Sulfonate	Ketones	Ketoses	Chlorinated Phenols
	Gluteraldehyde	Aldoses	
	Zpentanol		

Noise pollution from compressors, pumps and steam generators lends itself to conventional remedies. The same can be said of occupational safety and health rules governing the handling of toxic chemicals, flammable liquids and gases, hydrogen sulfide, and oil field machinery. Few unusual hazards are presented, and these concerns have associated mitigating measures.

IV. Monitoring Systems for Air and Water Pollution: Reference (5) prepared in 1978 is a four volume compendium of proposed monitoring systems for air and water pollution prepared for the Office of Environmental Activities, Division of Program Control and Support, DOE. It contains detailed descriptions of pollutants, their toxicity, test methods, governing regulations and much more. It is beyond the scope of this paper to describe these, but this reference is ready for the expansion of EOR. The resource requirements in manpower and equipment are relatively modest. This document has not been released as a public document.

DOE/EOR Environmental Research

The DOE environmental research effort for oil production is centered at BETC. In-house research is being conducted to determine the long-term migration properties of injected EOR chemical in a subsurface environment. In addition, the rates and products of chemical degradation of these compounds at subsurface conditions is being studied. Grants have been made to universities to determine the biological rates of decomposition and the toxicity of the chemicals to soil bacteria. Research contracts with various research institutes have been negotiated to determine the toxicity of the EOR chemicals and the potential for induced seismicity due to injection of chemical compounds into reservoirs because of reactions of the chemicals with the rock matrix.

The Environmental Development Plan (EDP), Enhanced Oil Recovery (November 1979)

This important document was originally prepared in May 1978, and has now been revised in November 1979 at the direction of the Assistant Secretaries for Environment and Fossil Energy. An EDP is timed to precede key technology program decisions as the technology moves from exploratory to the engineering and commercialization stages. It is believed that EOR is now entering these stages. Hence the EDP for EOR addresses the environmental concerns springing from the technology expansion, further reseaarch if necessary and assuring that the environmental safety and health considerations are adequately recognized. It is believed that this EDP and supporting documents adequately prepares the U.S. for gradual but major commercialization of EOR in an environmentally acceptable manner. In order to assure that environmental concerns and regulations are fully considered in the planning stages, our EOR RFP's or PON's will require that the proposers outline an environmental strategy. This proposed strategy will be evaluated in addition to technical and economic provisions in determinations for contract awards. It is considered that this approach will reduce any potential environmental delays during contract testing operations.

Conclusions

The role of DOE is to accelerate the technology of EOR by research, developmental and field testing in existing reservoirs. Its efforts parallel and complement those of the oil industry. DOE's Office of Oil, Gas and Shale Technology becomes the selected agency to collect and analyze the data from the cost-shared and incentives field tests and form a common data base available to the public.

Paralleling the technological effort has been the DOE environmental research, development and documentation of procedures to be used. This includes specification of the environmental risks, the monitoring and test methods to be used, and finally a revised Environmental Development Plan to cover all contingencies. This is an ongoing effort that will undergo constant refinement and improvement.

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COPING WITH ENVIRONMENTAL PROBLEMS OF HEAVY OIL PRODUCTION

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INTRODUCTION

The production of heavy oil is receiving increased attention as a means of reducing our dependence on foreign oil imports. Last year the President decontrolled heavy crude pricing in recognition of the production difficulties involved and to provide additional economic incentive. Most United States production of heavy crude occurs in California, where air quality problems are especially difficult. This paper looks at the impact of environmental regulations adopted in Kern County, California exclusively for the oil industry. The general conclusion is that growth of oil production and maintenance of air quality can both occur.

THERMAL ENHANCED OIL RECOVERY DESCRIPTION

Two different EOR techniques are used to recover very heavy crudes, steam injection and in situ combustion. Both techniques use heat to lower the crude viscosity, thus increasing flow thru the reservoir. In situ combustion generates heat within the reservoir by burning part of the crude in place. Compressed air is injected to maintain combustion and reservoir pressure. The more widely used technique involves steam injection. Steam is generated on the surface and injected into the reservoir to provide heat and pressure. Steam is continuously injected in one well to drive oil to a production well. Cyclic steam injection is also used where steam is injected into a well for one or two weeks, the well left to soak for a week and then produced. The cycle will be repeated every 6 to 10 months.

The process equipment of primary interest with respect to environmental needs is the air compressor in the in situ combustion process and the steam generator in the steam injection process. Air compressors are generally driven by diesel engines. Electric motors can be used, but electricity costs may significantly affect the economics of the process. If diesel engines are used emissions of NOx and particulates will occur.

The steam injection process generally relies on steam generated from the combustion of lease crude oil. Two sizes of steam generators are used, 22 million Btu per hour and 50 million Btu per hour. These units are one-pass water tube steam generators rather than boilers. Generated steam is only about 80 percent quality to prevent tube scaling from the high solids content water used. The fuel used is heavy crude oil high in both sulfur and nitrogen. Sulfur content is mostly in the range of 1.0 to 1.5 percent, but may be up to 5 percent from some fields. Nitrogen is in the range of 0.5 to 0.8 percent. Therefore, uncontrolled emissions of SOx, NOx and particulates can be significant.

THERMAL EOR GROWTH

Injecting steam for the recovery of heavy oil has been commercially practiced for about 15 years. Early production was from cyclic steam stimulation whereas current production is mostly from steam drive. Cyclic projects will normally be converted to drive projects as the resource recovery can increase from roughly 20 percent to 50 percent. Thermal production increased rapidly in the mid sixties once the technology was demonstrated, as shown in Table 1. Production is increasing again in response to the higher prices since 1974. Based on resource availability DOE expects thermal production to reach about 500,000 barrels per day by 1985-1990. This estimate is contingent, however, on maintaining ambient air quality standards. Both the regulatory "climate" and the availability of emissions control technology are important to reaching the 500,000 barrel per day estimate.

In situ combustion production is currently about 10,000 barrels per day. The process is somewhat more difficult to design and operate and generally not used in fields where steam injection methods have proven successful. Combustion production may double or triple by 1985-1990.

TABLE 1

Growth of Thermal Enhanced Oil Recovery in California

Year	1964	1968	1972	1976	1980	1985
Production, thousands of barrels per day	16	128	139	162	*275	*500

* Estimate

AIR QUALITY CONSIDERATIONS

Kern County is located at the south end of California's San Joaquin Valley. The valley is bounded by the Sierra Nevada mountains to the east, the Tehachapi range to the south and the Temblor range to the west. The elevations in the Sierra's and the Tehachapi's are generally greater than 5000 feet. The Temblor range is much lower, but as it lies to the west, it is not as important in restricting air transport from the basin. Figure 1 is a simplified map of the lower two-thirds of California showing the valley and Kern County heavy oilfields.

In the summer months a predominant high pressure area exists over the Pacific Ocean and a predominant low pressure area exists in the valley. The resulting winds transport pollutants from the San Francisco Bay area into the valley. In the fall and winter months light winds and atmospheric stability allow local pollutants to accumulate. The highest hourly ambient pollutant concentrations occur in these months. The overall result is periods of poor air quality, in spite of the basically rural environment.

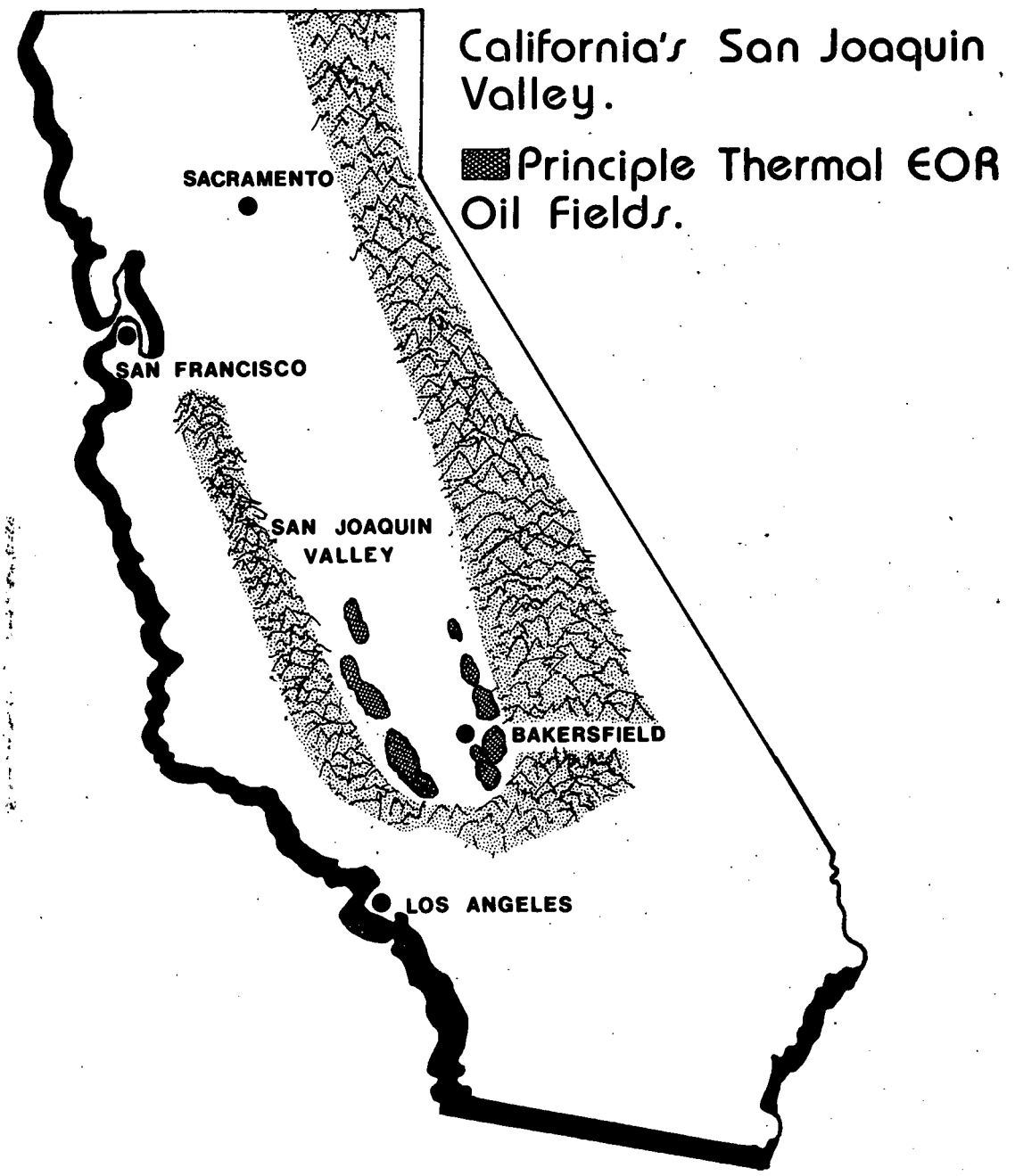

California's San Joaquin Valley.
Principle Thermal EOR Oil Fields.
SACRAMENTO
SAN FRANCISCO
SAN JOAQUIN VALLEY
BAKERSFIELD
LOS ANGELES
XBL 803-8457

Figure 1

Visibility, for instance, can be limited to a few miles on any day of the year.

The attainment status of Kern County is shown in Table 2. The attainment status for SO2 is in question as the county may redesignate a small area north of Bakersfield as a separate SO2 nonattainment area. The rest of the county would revert to a Class II area under Prevention of Significant Deterioration (PSD) for SO2. Both National and State 24 hour standards have been violated in the small "redesignation" area. The only National violation was during December 25 and 26 of 1978. The State 24 hour standard, only one third of the National standard, has been exceeded on many occasions. The rest of the county is within both State and National standards.

The county is attainment for NO2, although 1 hour levels have been approaching the State standard in recent years.

Oxidant levels have exceeded the National standard by up to 50 percent on a few occasions and on numerous occasions have been at or near National or State standards. The problem is compounded in the summer months by a background level about one third the National standard. Transport into the county is part of the background problem.

Total Suspended Particulate (TSP) levels exceeded the National standard on several occasions. The State 24 hour standard, only 40 percent of the National standard, is violated on over 80 percent of recorded measurements. Agricultural activities undoubtedly contribute to the problem.

TABLE 2

Kern County Air Quality Status

Pollutant	SO2	NO2	O3	TSP
National Standard	NA (?)	A	NA	NA
California Standard	NA (?)	A	NA	NA

? Redesignation pending.

PERMITTING PROCEDURES

One of the largest complaints from the Kern County oil industry is over the very long time elapsed before air quality permits are granted. Delays of about two years have occured. These delays appear attributable to the changing regulatory requirements and to the degree of air quality impact assessment required in permit applications.

The permit sought by the industry is the "authority to construct" for new steam generators. Permits must be received from both the Kern County Air Pollution Control District in Bakersfield and from the EPA Region IX office in San Francisco. Although the process has been lengthy, a large number of additional permits were granted in 1979. The permitted steam generation capacity in Kern County today is more than double the capacity operating in 1976. The figures are approximately 19 billion Btu/hr in 1976 and 40 billion Btu/hr in 1979. Another 5 billion Btu/hr of capacity has been applied for but not yet granted. These applications were made prior to the July 1979 Clean Air Act deadline and could potentially be granted. The Kern County portion of the California State Implementation Plan (SIP) could be completed this year so that the permitting ban in force now could be lifted.

The EPA Region IX will retain authority for Prevention of Significant Deterioration (PSD) permitting for Kern County, once the ban is lifted. Kern County will issue both PSD and New Source Review (NSR) permits. The California Air Resources Board (ARB) in Sacramento has the ultimate State authority for promulgating air quality regulations. The ARB has on several occasions mandated regulations for local APCD's to enforce. A lengthy public hearing process takes place before the ARB takes such actions. Some regulations have been adopted for Kern County by the ARB specifically for the oil industry.

One example is Kern County Rule 424 for the control of sulfur oxides from steam generators. The rule was originally proposed by the ARB in April of 1978 and finally approved in September of 1979. Several days of public hearings were interspersed in that period to allow for industry and other interested parties to testify. Some modifications to the rule were accepted by the ARB. The rule is summarized in Table 3.

A rule currently under consideration is 425, a modification to the Kern County New Source Review regulation. This rule is for the control of NOx emissions from steam generators and the debate has been especially active. The ARB regards the regulatory process as technology forcing with regard to emission controls. The initial ARB proposal was premised upon availability of processes to reduce NOx emissions by 68 percent. Industry has contested this proposal and it appears the ARB may accept changes. The original proposal was made in September of 1979 and the third hearing on the subject was held March 5 and 6, 1980.

The regulatory process can have great impacts on the future development of the California heavy oil resource. The sulfur oxide rule, for instance, requires 80 percent retrofit control of SO2 from existing generators. This will greatly reduce the potential emission pool available for offsetting emissions from new steam generators. Implementing the SO2 rule has not proven too difficult as several vendors offer relatively well developed processes.

Implementation of the NOx rule will be a more difficult problem. Low NOx burners were not available for steam generators prior to 1979. Some companies are now offering low NOx burners, but only after a period of field application testing in 1979. The Exxon Thermal De NOx process is now being tested by two oil companies. The process involves ammonia injection into the flue gas within a narrow temperature range to reduce NOx to nitrogen and water vapor. The degree of NOx reduction to be attained is not certain and long term operating experience on steam generators is not available. Both low NOx burners and Thermal De NOx may be attractive control technologies. Implementing use of new controls is somewhat of a "chicken or the egg" problem. The technologies may not be developed and applied to their maximum extent unless required by regulatory agencies. Controls, however, cannot generally be required until developed. Which comes first?

TABLE 3

Regulations Adopted For Thermal EOR Emissions Control In Kern County

Rule 411	Rule 424	Rule 425
HC Control	SO2 Control	NOx Control
o 93% retrofit control on vapors from thermal EOR wells	o 80% retrofit control on existing generators	o 30% retrofit control on existing generators
	o 90% control on new generators	o Higher control required if standards approached or exceeded
	o Offsets required for new permits	o Offsets required for new generators
		o BACT required on new generators

DEPARTMENT OF ENERGY ROLE

About five years ago a comprehensive program aimed at resolving environmental constraints was outlined by the Energy Research and Development Administration (ERDA), one of the predecessors to DOE. As the program developed it became clear that large DOE funding would not be required. The oil industry has taken constructive actions to help foster the application of control technologies for steam generators. Flue Gas Desulfurization (FGD) processes for SO2 control are now commercially available from several vendors. Many problems arose on the first units operated, but these problems appear to have been satisfactorily resolved. Nearly all of the scrubbers in use today dispose of a liquid waste stream. In the future, solid waste systems could become the "second generation" choice. DOE has contracted a study of 12 alternative FGD processes which can serve as a guide to the industry in pursuing future actions.

The industry has been testing low NOx burners and ammonia injection systems for about one year. Results have not yet been published. The biggest questions are the degree of NOx reduction possible and long term operating performance. DOE hosted a small, informal workshop on the subject but does not plan any further work.

The DOE activity of most interest to the industry and regulatory agencies has been an ongoing contracted study of potential environmental limitation to thermal EOR growth. The study primarily looks at the costs of meeting environmental regulations, the availability of emission offsets and will also perform limited modeling of air quality impacts of thermal EOR.

Because of this study and other related projects DOE has been able to provide some middle ground between the regulators and industry. We have given testimony at ARB hearings on proposed regulations and supplied information to the ARB on potential production growth. As environmental issues escalate this DOE role appears to be gaining significance. The potential influence of DOE should not, however, be over estimated. The hearings process allows all parties to comment and the ARB has been careful to independently evaluate information before making decisions. DOE recognizes the trend towards greater emission controls will continue and our aim is to provide balance to energy and environmental deliberation. The strongest mediator appears to be the lengthy, complicated and sometimes frustrating process of public hearings to allow input from all concerned.

FUTURE DIRECTION

The single largest future issue is one of alternative energy sources for generating injection steam. Currently about one of every three barrels of produced oil from a steam injection project is burned for steam generation. Several alternative approaches are possible. DOE has completed contracted studies on the use of coal and petroleum coke. Using either appears to be compatible with environmental needs, through either gasification or fluidized bed combustion (FBC). The capital investment required for using either solid fuel would be greatly increased over that for the current oil fired generators, even including SO2 and NOx control. But the steeply rising price of oil appears about to justify conversion. An oil price of $25 - 30 per barrel is needed for either gasification or FBC to be competitive and heavy oil prices are approaching $25 per barrel. A windfall profit tax could pose a constraint to conversion and some special treatment of this situation could be helpful.

Another alternative is oil field cogeneration of steam and electricity. Oil, petroleum coke, coal or combinations of the three might be starting fuels. The fuel would be gasified and the gas burned to spin turbines for generation of electricity. The exhaust gas would go to boilers for steam generation. The produced steam would be injected in the field for oil recovery. Discussions have been held between California utilities and oil companies for several years. DOE favors the use of coal or coke as use of oil may not be allowed by the Fuel Use Act. The State of California is also very interested and a strong proponent of cogeneration processes.

Solar steam generation is also being investigated. DOE has three contracts now in study/design phases. Solar generated steam is unlikely to ever completely replace fossil generated steam but may find application in hybrid systems with solar reducing fossil steam during daylight hours.

CONCLUSIONS

California heavy oil production is in a period of rapid growth. Maintenance of air quality has required increased regulation and emission controls for steam generators. This has resulted in delays in the granting of permits for new steam generation capacity, but not in any substantial denial of permits. Emission control technology is available for SO2 and under development and field testing for NOx. The degree of NOx control to be required on new steam generators and the availability of emission offsets are major concerns. Particulate control could be the next major issue. The California Air Resources Board has taken firm actions to protect air quality but has not adopted overly restrictive regulations.

ENVIRONMENTAL EFFECTS AND CONTROLS ASSOCIATED WITH EXTRACTION OF UNCONVENTIONAL GAS

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Introduction

The U.S. Department of Energy has initiated a multi-year research and development program to bring the unconventional gas resources to commercial readiness. The Enhanced Gas Recovery Program (EGR), is composed of four projects - the Eastern Gas Shale Project (EGSP), the Methane from Coal (MFC) Project, the Western Gas Sands Project (WGSP) and the Geopressured Aquifers Project (GPA). Broad program goals are to add 10 Tcf of producible reserves to existing recoverable reserves by 1985, increase gas production by an 3 Bcf/day by 1985, and accelerate development of cost-effective technology that can be readily transferred to the private sector (U.S. Department of Energy, 1978).

The purpose of this paper is to provide the reader with background information on the R&D program, the resource base and the technology; present an overview of the environmental problems associated with development of the unconventional gas resource; and delineate the environmental control strategies and technologies which can properly be applied to eliminate or reduce these problems.

The information presented herein was developed during the preparation of the programmatic environmental impact statement for the Enhanced Gas Recovery Program (U.S. DOE, 1980 draft) and is completely referenced in that document.

Resource Location and Technology Development

Deposited during the Devonian Periods some 350-400 million years ago the brown and black shales located in the Appalachian, Illinois and Michigan Basins are the most gas productive shales (Figure 1). The Chattanooga, Marcellus, Ohio and New Albany Devonian shales which vary in thickness from 20-200 feet are located between 700 and 7000 feet. In the past, recovery of eastern shale gas has been hampered by a lack of resource definition and marginal economics. Consequently, the eight year Eastern Gas Shales Project has several technological objectives.

- Develop reliable and efficient surface mapping and remote sensing techniques for locating and exploiting the Devonian shale resource.
- Examine the lithological, geochemical and physical properties of the shales to better delineate the shale/gas characteristics.
- Apply traditional and novel fracturing and stimulation techniques and modify them as appropriate to enhance shale productivity.
- Transfer this information to industry.

For the Methane from Coal project, twelve coal basins or regions are being considered: Illinois, Northern Appalachian, Central Appalachian, Warrior, Arkoma, San Juan, Raton, Uinta, Piceance, Green River, Wind River and Powder River (Figure 2). Three drilling technologies, horizontal drilling from an active mine face, directional drilling in advance of the coal mining operation and vertical drilling and fracturing in unmineable seams, are being examined in relation to the twelve coal regions. Directional drilling and horizontal drilling technologies are expected to be more heavily utilized in the deeper, gassier seams of the first four coal regions; vertical drilling and fracturing in unmineable seams is expected to be more evenly distributed throughout the twelve basins. The Methane from Coal Project involves:

- Designing, developing and testing extraction and utilization technology systems which are efficient, cost-effective, and specifically designed for coalbed methane application.
- Locate and delineate coalbed methane resources and develop recovery prodiction techniques.
- Field test the most promising systems to stimulate interest and transfer information to the private sector concerning the technology and its economics.

The Western Gas Sands Project is aimed at developing the low-permeability or "tight" sandstone reservoirs. Both lenticular and blanket type deposits are being examined. Approximately twenty potential sandstone resource bases exist west of the Mississippi River; four of these regions with the greatest prospects, the Greater Green River Basin, the Northern Great Plains Province, the Piceance Basin and the Uinta Basin, have been singled out for closer scrutiny (Figure 3). Besides general and specific studies in mineralogy,

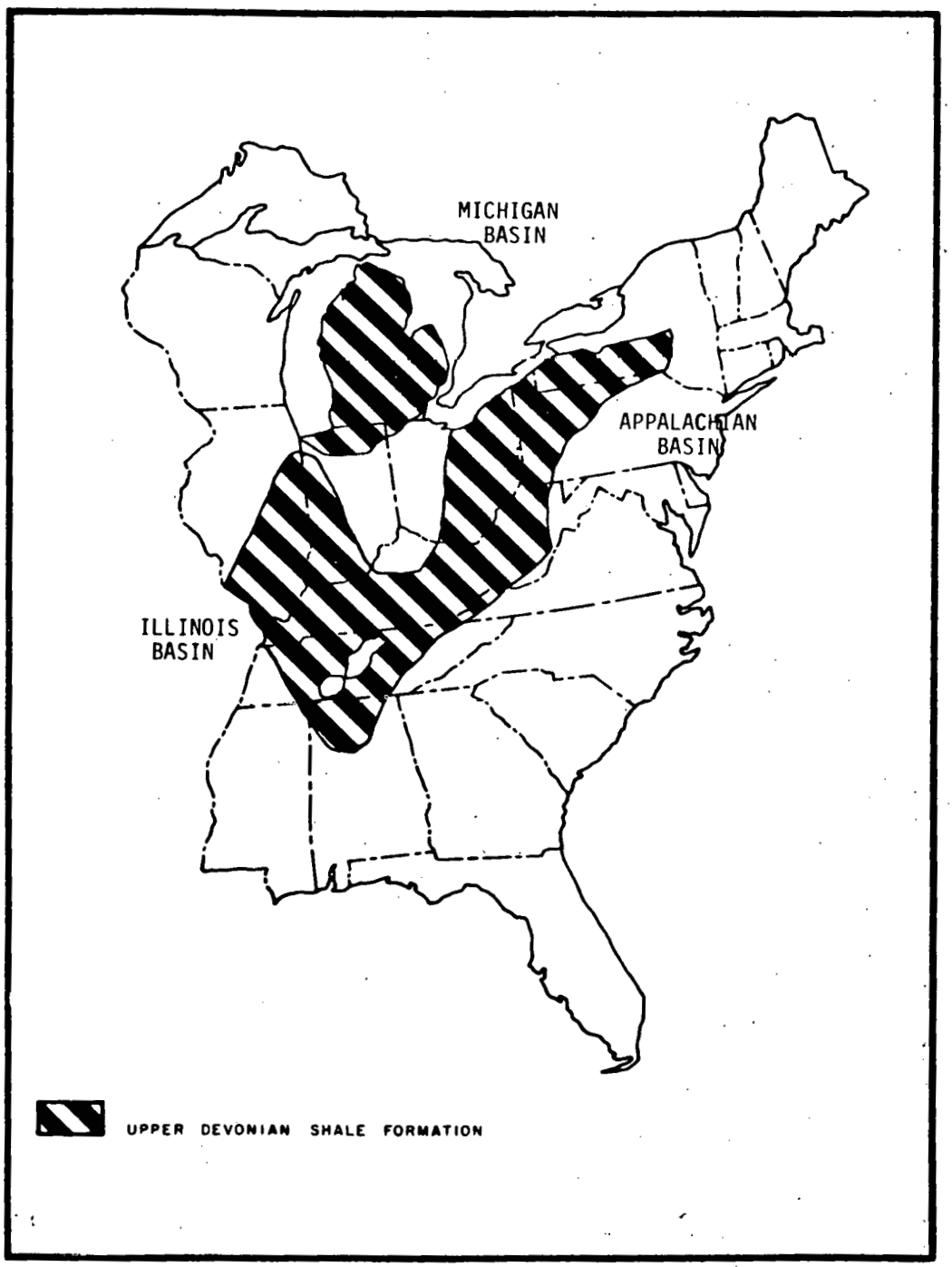
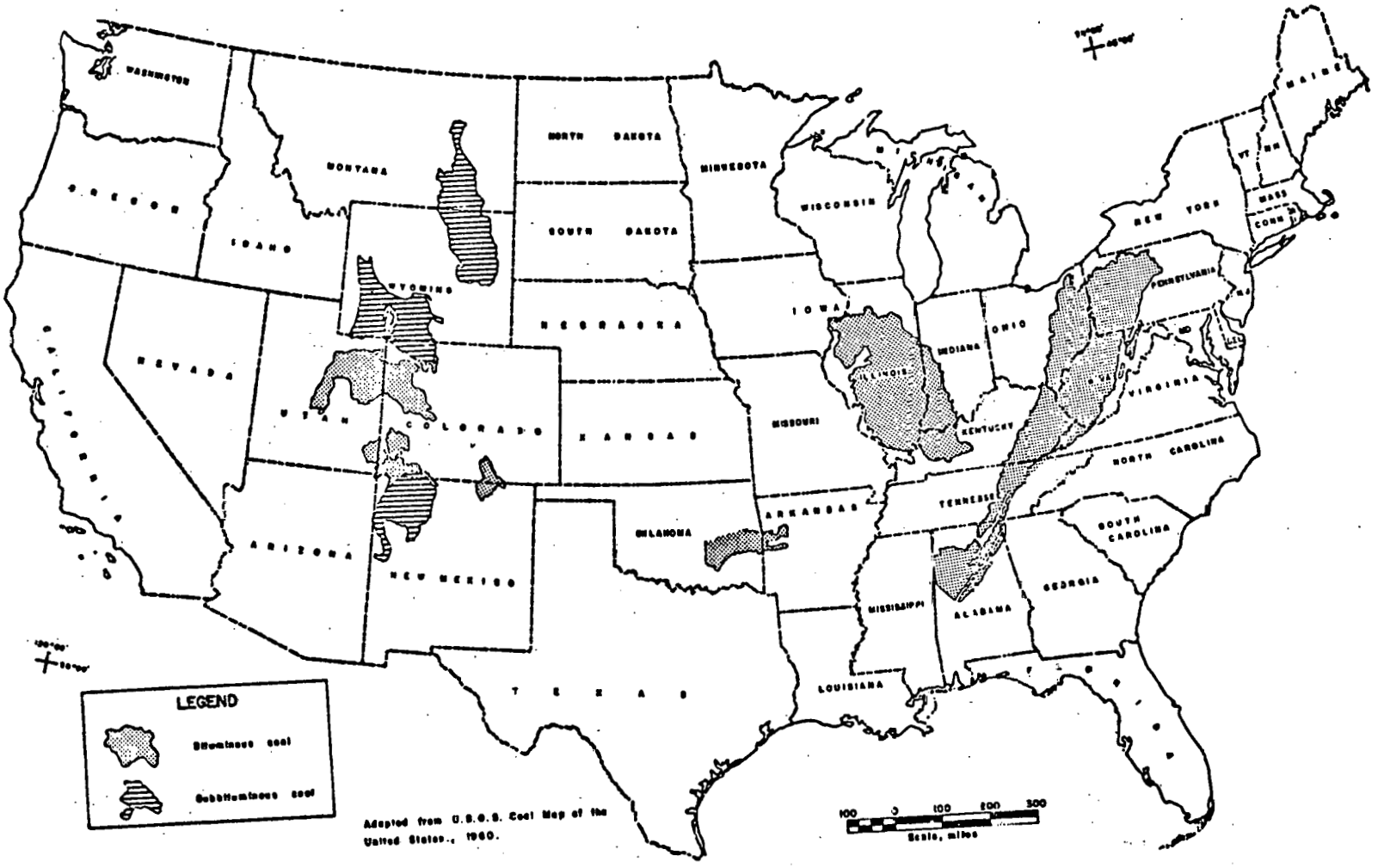


Figure 1
LOCATION OF DEVONIAN SHALE DEPOSITS



SOURCE: TRW, 1978.

Figure 2

TARGET AREAS FOR INITIAL RESOURCE DELINEATION ACTIVITIES

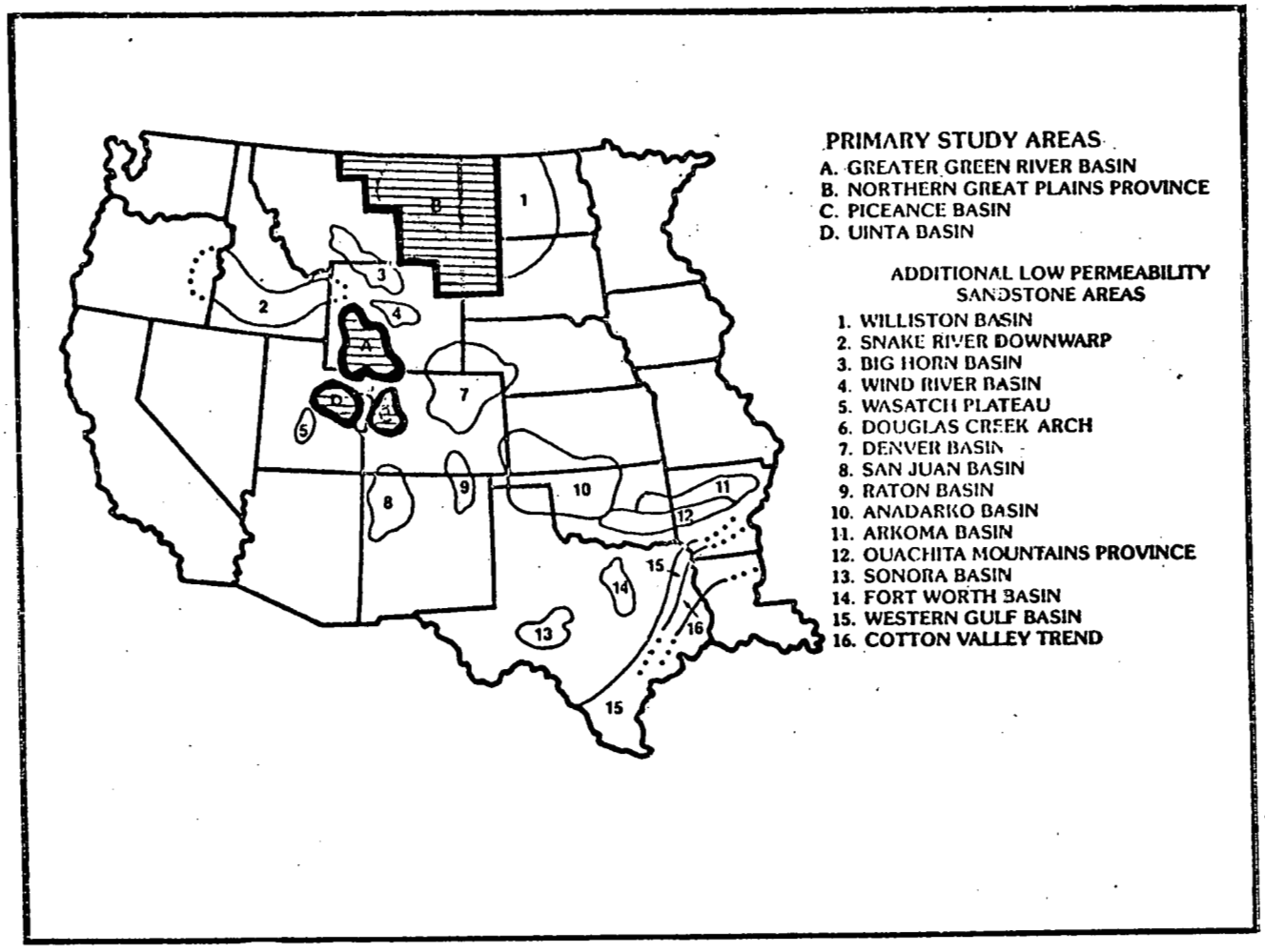


Figure 3

Map of Western United States Showing Western Tight Sands Areas of Interest

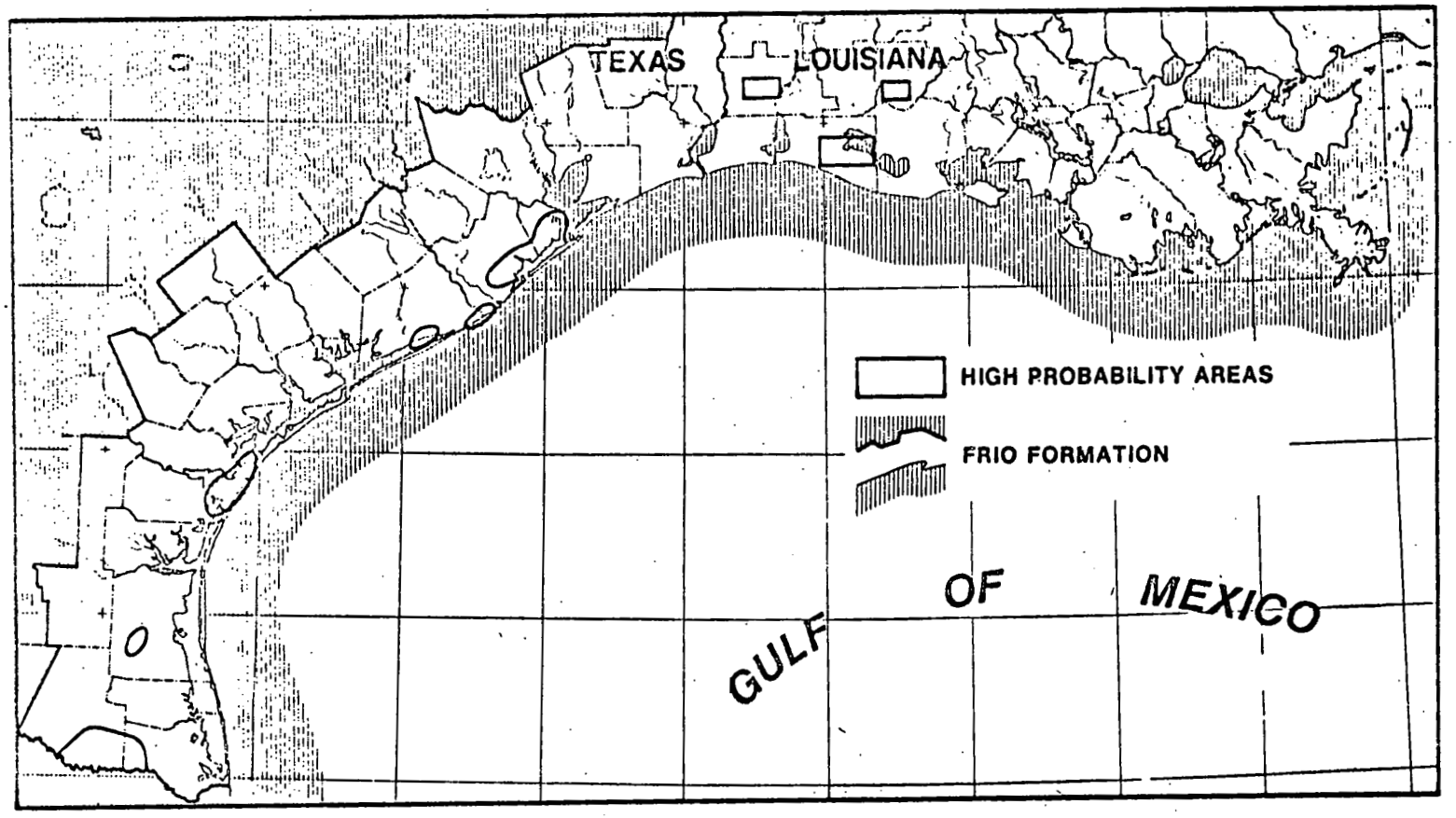
Source: U.S. DOE, 1978a.

paleontology, geophysics, geochemistry, petrology, outcroping and data bank coordination, the WGSP will focus attention on:

- o Developing new logging and coring tools
- o Modeling rock mechanics and gas productivity from low permeability reservoirs
- o Devising new coring and fracturing analysis techniques.

The Geopressured Aquifers Project intends to exploit the methane gas, high pressure and high temperature to produce pipeline quality gas and electricity from the deep brine of the Louisiana - Texas Gulf Coast (Figure 4). Several formations such as the Frio Formation and the Upper Cretaceous Tuscaloosa sands have been identified and hot spots within these geopressured fairways located. Along with resource delineation, the project objectives are to:

- o Estimate reservoir size and geometric distribution
- o Drill test wells in high prospect formations and then in other secondary formations
- o Examine methods for utilizing the three geopressured energy forms
- o Study water disposal and subsidence issues
- o Detail cost analysis of potential production.



SOURCE: U. S. DOE, 1978c.

Figure 4

GEOPRESSURED FAIRWAYS

Environmental Impacts Associated with EGR

The environmental impacts associated with the EGR program are very similar in most respects to those associated with drilling and producing more permeable, conventional gas reservoirs. Two additional activities, however, fracturing of well bores and massive subsurface fluid withdrawal, could cause impacts not generally associated with conventional gas drilling. All impacts will be discussed generically and related to the programs where they are expected to be most substantial.

Soil erosion and potential stream sedimentation are impacts associated with any construction site. Access roadways and drilling sites have to be cleared and leveled prior to drilling. The amount of erosion expected is a function of rainfall amount and duration, soil type, slope length, slope steepness, vegetative cover and erosion control practices. Generally, drilling contractors can only control the last factor. The impacts associated with soil erosion are loss of fertile topsoil, leaching of essential soil nutrients and cations, and subsequent decrease in agricultural or biological productivity. If eroded soil enters nearby surface waters, some or all of the following impacts could be induced: Increase in water temperature, change in pH, increases in dissolved chemicals and total suspended sediments, increases in both biological and chemical oxygen demand, decrease in light penetration and photosynthesis, reduction of dissolved oxygen in the water and associated metabolic activity in organisms, interference of feeding behavior in filter feeders, reduction of habitat diversity and desirability through bottom infilling between rocks, and settling of phytoplankton from the water column. Both the amount of sediments which enter the water body and the duration of the loading will determine the extent of the impacts. Due to the relatively rugged topography in the EGSP, MFC and WGSP regions, more cut and fill and leveling activities would be expected, and consequently, more erosion. The scarcity of surface water in the west, however, decreases the chances for stream sedimentation in WGSP and some MFC project areas. Erosion in the GPA regions are expected to be lower due to the flatter terrain.

Well stimulating or fracturing has three potential impacts associated with it which are not common with conventional gas drilling - water availability, surface water pollution, and ground water pollution. Depending on the depth of the well to be stimulated, up to 400,000 gallons of water or frac fluid could be necessary. In the eastern regions (EGSP and some MFC regions), water availability should not be a problem, except in localized situations in low-flow dry years. During drought seasons in the west (WGSP and some MFC regions), a water availability problem could occur, especially if there are competing demands with agricultural or mining interests. Strict water rights laws are in effect and even small, one-time users may be required to get a permit which allows water withdrawl only after more senior appropriations are met. A water availability problem is not anticipated for the GPA region as no well fractures are planned.

After a massive hydraulic fracture, the frac fluid is allowed to flow back up the borehole and into a retention pit. Fluids used in massive hydraulic fractures range from gelled waters to complex foam fluids to crosslinked polymer systems and emulsifying agents. The potential exists for retention pit leakage to potable aquifers or overflow during periods of heavy

rain. Vegetative impacts to local flow and potential fish and invertebrate impacts in neighboring water bodies exist on the surface; local ground water supplies for domestic or irrigation wells could be affected on the subsurface.

The third potential impact from well stimulation is the connection of two subsurface aquifers of varying qualities. During a massive hydraulic fracture or chemical explosive fracture, the theoretical shape of the fracture is an ellipse in the horizontal plane, the same plane in which the gas is found. The potential for the fracture branches to migrate in the vertical direction also exists, and concomitantly, the potential for a lower saline aquifer to migrate to higher potable aquifers and pollute agricultural or domestic water supplies likewise exists. In a similar manner, improperly cased or cemented wells also present a migratory fairway for subsurface aquifer connection. Potential impacts from well fracturing could be realized from all three programs utilizing this technology (EGSP, MFC, and WGSP); potential impacts from well bore migration could occur associated with all four resource areas, especially with the geopressured aquifers where high pressure and corrosive fluids are anticipated.

Air pollution and noise impacts are expected to be short-term or negligible. No air pollution violations, except possibly NO_x in some western regions, are expected from drilling operations. Worst case clearing and burning situations in a single day period would violate all pollutant levels; however, intermittent burning over a 5-10 day period would cause no violations. Noise levels would increase during drilling, coring and stimulation activities and would be noticeable and annoying to nearby residents. In many cases, fauna would be forced to emigrate to neighboring environments, possibly abandoning their young. Impacts would be more severe in quiet rural areas, but fewer people would be affected. Maximum duration of noise is expected to be a few months.

Biological productivity losses on agricultural lands, rangelands and forestlands, along with a decrease in faunal habitat, would be expected with each program. The magnitude of the losses would be a function of the land disturbed for each type of commercial development and the regional land use pattern. In general, on a per quad energy basis, the impacts would be considerably higher in those technologies expected to have lower flow rates per well (MFC and EGSP), as substantially more land disturbance would result from the higher number of access roads and drill sites required.

Waters produced during gas operations could have a substantial impact in the Geopressured Aquifers Project, and might be a problem in the Methane from Coal Project. Coal seams may contain significant quantities of groundwater which often contains undesirable dissolved solids. If so, the discharge may have to be treated before release to surface waters or be reinjected. Otherwise, water pollutant violations could result along with attendent impacts on fish and aquatic life.

Hot geopressured brines, with dissolved solid concentrations ranging from one-third to twice that of sea water, have to be treated or reinjected to subsurface strata to protect the environment. Accidental surface releases of geopressured brines would substantially degrade water quality; chloride, sodium,

potassium, ammonia, boron, and zinc levels would be especially high. Biota may be killed by thermal shock or adversely affected by salinity, pH changes or metal bioaccumulation.

Even reinjected geopressured brines, due to their massive volumes, could cause substantial impacts. Brines would probably not be returned to the source strata but to shallower zones which are presently used for petrochemical wastes. If the geopressured brines are not compatible with injection strata, fluids may clog the strata, cause pressure buildup or permeability reductions, and potentially, fracturing of the confining beds and migration of saline brines to potable aquifers. Irrigation, industrial or domestic water supplies could be degraded.

With the expected massive withdrawal of geopressured brines for a commercial facility, subsidence of overlying surface lands is a real possibility. The amount of subsidence would be a function of many parameters such as pressure drop due to fluid production, rock compaction, lateral reservoir extent, depth below the surface, reservoir properties, well completion technique and the type, thicknesses and degree of cementation of overlying strata. Potential impacts associated with subsidence would be fault activation; groundwater migration; connection of aquifers of varying qualities; disruption of surface features (e.g., pipelines, roadways, structures); flooding of industrial, residential or agricultural sites with surface water or saline coastal waters; increase in areas flooded by high tides and hurricanes and their associated effects including wetland, fish, and shellfish losses.

Loss, attention or degradation of wetlands could be substantial in only the Geopressured Aquifers Project. While EGSP, MFC, and WGSP projects could impact wetlands on a site specific basis by poorly planned or located access roads or drill sites, the potential for wetlands impacts is substantially greater along the Gulf Coast where marshes, occupying a 10 to 50 mile ribbon along the coast, overlie a significant portion of the geopressured resources. Dredging of access canals and drilling large turning areas would affect water quality (increase in turbidity, BOD and COD, chemical desorption, and siltation), marsh drainage, salt-water intrusion (species composition changes), canal bank erosion, fish and shellfish spawning and feeding areas, and marsh alteration due to spoils placement (loss of productive marsh and modification of marsh flooding patterns). The magnitude of the impact would be a function of the number of canals and drill sites dredged and the orientation of the canals.

Socioeconomic impacts associated with projected population increases and their attendent pressure on local services would in general be minimal. In most situations, the projected transient and permanent population increases are expected to be absorbed by existing community infrastructures. Localized housing shortages could be realized in a few cases. Two potential impacts could arise, however. First, if both the WGSP and the MFC projects in the west are successful, there could be substantial socioeconomic impacts in areas which are already under intense development from coal, nuclear, oil conventional gas and synfuels interests. And secondly, if the GPA project attains full commercial status and geopressured electrical generating/processing plants are sited in rural counties, local populations and services could be

overwhelmed by projected population increases associated with construction of the plant. Boom town population increases of up to 16 percent of the base population could occur.

Environmental Control Strategy to Mitigate Expected EGR Impacts

The environmental control strategy to mitigate expected EGR impacts is not a control strategy in the sense of materials balance and effluent control; instead, it involves extensive planning in the earlier states, proper housekeeping methods during the construction phase, and constant monitoring during the operational phase. In most cases, the potential or the magnitude for impact can be decreased by proper planning; however, if the impacts are sustained in certain circumstances, such as potable aquifer pollution or subsidence, the effects will be long-lived and severe.

Soil erosion and potential stream sedimentation can best be ameliorated during the site planning phase by proper site selection and layout. The following factors should be considered: avoid road construction on slopes greater than twenty percent, minimize cut and fill ratios and stream crossings, retain natural buffer strips beside streams and surface water bodies, avoid floodplains, schedule heavy construction during dry seasons and plan for topsoil separation and retention in locations with good quality soils. During the actual construction of access roads and drilling sites, the velocity of water can be regulated by filter berms, check dams, and jute mesh; storm water can be deflected by dikes made of soil, stone, straw babs or brush; storm water can be channeled with chutes, flumes, flexible downdrains and gabions; and sediment can be trapped before it enters surface water bodies by sedimentation basins, gravel filters and straw bale walls. Between 50 and 70 percent erosion/sedimentation prevention efficiencies can be obtained with these devices. Subsequent to construction and drilling activities, bare surfaces should be graded, seeded with fast growing vegetation and mulched with hay or other suitable materials.

Well stimulation and fracturing could cause water availability, surface water pollution or ground water contamination problems. Water availability is only projected to be a localized problem during drought periods in the West. To mitigate this situation, water can be drawn slowly from surface sources or ground water sources over a period of three or four weeks before the fracture. If water resources would still be taxed or water rights infringed upon, the well stimulation could be postponed until more favorable conditions exist, or water could be transported from a more distant adequate supply by truck.

Surface water pollution can be prevented by excavating an adequately sized and lined (clay or plastic) retention pond for drilling wastes and fracturing fluid. Fracturing fluid which flows back from the well bore after the stimulation, should be directed to the retention pond. In high water evaporation regions, the wastes can be scraped up and properly disposed after the water evaporates. In medium evaporation rate regions, the pond would maintain its level from rainfall and runoff input; eventually, water quality changes would permit wildlife and cattle to use the pond and thereby, enhance the local environment. If the retention pond has the potential to overflow from stormwater, or if the land is to be reclaimed more quickly, the frac-fluid wastes would have to be removed from the pond and transported to a waste water processing facility.

Ground water pollution from fracturing fluid or from the fracturing process could occur by migration of frac-fluid or saline brine along the well bore or along newly created fracture lines. Frac-fluid migration can be avoided by proper well casing, cementing and testing before stimulation, and monitoring thereafter. Planning for migration along newly created fracture lines, however, is more difficult. Theoretically, well stimulations are predominantly propagated in the horizontal plan, but a worst case fracture would assume a spherical shape with a five hundred foot radius. Therefore, if the zone to be fractured is more than 500 feet below potable aquifers, the potential for subsurface aquifer connection is decreased. If it is not, then local information on the quality and depth of the aquifer should be obtained; an estimate of the domestic, agricultural and industrial water use assertained; and an evaluation made on the economic potential from enhanced gas production versus the cost obtaining a new water source if the aquifer is contaminated. Once degraded, a potable aquifer may never regain its original quality.

Air pollution is expected to be negligible during drilling and fracturing phases and may only be a problem in worst case clearing and burning during site preparation. To avoid such a situation, burning should be carried out intermittently over a five or ten-day period and care should be taken to ensure that visibility is not impaired on public rights-of-way.

Noise impacts may be annoying and would be persistent as most drilling operations require round the clock drilling for engineering and financial reasons. Consequently, the drilling and fracturing equipment should have properly muffled engines which are checked periodically. In certain locations where a large number of residents could be impacted at night, the possibility of erecting a noise barrier should be examined.

To prevent impacts on prime wildlife habitat such as critical habitat for Endangered and Threatened Species, the U.S. Fish and Wildlife Service or the State Fish and Game Department should be contacted. If such critical habitats are present or if other sensitive wildlife areas such as marshes are encountered, these sites should be avoided by realigning access roads or directionally drilling from a nearby site.

Agricultural productivity losses can be minimized during the construction and drilling phases by segregating the topsoil into a separate pile before the subsoil is excavated, temporarily seeding the topsoil pile with a fast growing annual, and avoiding fluid flow back from contaminating it. After well stimulation and well completion activities have ceased, the excess drill pad area and unnecessary roads should have the subsoil graded, the topsoil replaced, and the site fertilized, seeded and mulched.

Produced waters from the MFC and GPA projects should be handled to prevent their release into the environment or into subsurface potable aquifers. As mentioned previously, during drilling and casing, the steel pipe and surrounding cement should be tested for its integrity and strength. During the production phase, both surface and subsurface pipes and well bores should be tested for corrosion and leaks and repairs initiated when required. Surface spills and subsurface aquifer connections along well bores can be more easily prevented than corrected. If subsurface aquifers of varying qualities are connected, it may take several to many years before the pollutants appear in residential,

agricultural or industrial water supplies. Subsequently, even when the problem is corrected, it may take years before the pollutants are flushed from the aquifers. In the intervening period, the water supply could be rendered useless. Therefore, preventative maintenance, possibly in combination with a ground water monitoring program, would best serve to avoid this potentially severe impact.

Subsidence from reservoir pressure drop could be a substantial impact above geopressured reservoirs. Mathematical predictions indicate that 30 to 40 percent or more of the subsidence could be alleviated by reinjecting the saline brines to the producing strata. This would have the added advantage of potentially doubling the amount of fluids which could be produced from the reservoir; however, it may not be economically feasible to reinject the fluids to the producing reservoir and they might also lower the reservoir temperature. Reinjection of salt brines to a shallower, lower pressured zone might be more economically and technically feasible. The amount of subsidence that this activity might prevent is not known and the Department of Energy is continuing to evaluate this problem during its GPA R&D program. Commercial siting of GPA plants in rural areas would decrease the economic impact to cities, their residents and their businesses, but not necessarily decrease the impact to the natural environment.

The impact on wetlands, predominantly in the geopressured region, can be decreased by either dredging few canals or by properly constructing the ones which are required. During the pre-exploratory and seismic phase, helicopters should be used to access remote wetlands, or if this is not possible, balloon-tired vehicles should be used as they are less destructive than tracked vehicles. Construction of new canals should be minimized by multiple use of existing canals, integrated planning with other commercial interests, common use of pipeline canals and directional drilling from upland sites or existing access canals.

When the dredging of new canals is required, the following steps should be incorporated into the planning and construction phases:

- Align canals to take advantage of existing natural or man-made channels.
- Minimize salt water intrusion by siting canals perpendicular to the coast, and obtain access to the coast from an existing perpendicular canal if possible.
- Avoid dredging canals which exceed the euphotic zone or the depth of the water body in which the canal terminates in order to prevent formation of stagnant pockets of water.
- Avoid crossing natural drainage patterns where possible or use adequate bulkheading to protect and maintain waterflows when not possible.
- Minimize the drilling area disturbed by using space efficiently.
- Stagger the borrow pits on each side of the roadway when constructing accessways on higher marsh elevations.

- o Use the push pipeline method over the flotation method when possible and use the double ditching method if revegetation is planned or the canal plugging method if it is not.

- o Minimize canal boat traffic and boat speed to reduce canal bank erosion.

- o Refill, restore and revegetate upon termination of production.

While the socioeconomic impacts from EGR programs are not expected to be substantial by themselves, coupled with other energy development, especially in several of the western regions, the impacts could be significant. Additionally, construction of geopressured electrical generating/gas processing plants in rural Gulf Coast areas could cause severe strain on the housing and social service systems. Local communities and county planning agencies should be given adequate funds to ameliorate the impact of accelerated growth. To designate the areas most likely to be impacted, either a Federal agency of a Federal Agency in combination with state planning agencies should project where the growth will occur and supply the necessary funds for local planning boards to ready the community for the population increase.

Summary

Environmental Impacts from the Enhanced Gas Recovery Programs will be similar in most respects to those previously experienced in conventional gas drilling operations such as soil erosion, stream sedimentation, air pollution, noise pollution, critical habitat destruction, degradation of high quality farmland and wetlands, and socioeconomic stresses or communities. A preventative strategy has been outlined to avoid or at least mitigate the severity of these problems. Well stimulation (EGSP, MFC, WGSP), fluid withdrawl (GPA and potentially MFC) and fluid reinjection (GPA and potentially MFC) are processes inherently different from those encountered in conventional gas drilling. The potential impacts are ground water pollution from fracturing fluid, connection of subsurface aquifers of varing qualities, and subsidence of the overlying land surface. Methods to eliminate or ameliorate these impacts have also been outlined. It must be stressed, however, that unlike many others energy categories or facilities where effluents are controlled and processed, the environmental control strategy for the extraction of unconventional gas is one of preventative planning, good housekeeping and successful monitoring programs.

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MECHANISMS OF MINE ACID DRAINAGE FORMATION AND FEASIBILITY OF ABATEMENT METHODS

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ABSTRACT

The mining of coal is frequently associated with the production of an acidic effluent which is caused by the degradation and dissolution of pyrite present in the majority of coal deposits. This problem is particularly pronounced and evident in the northern half of the Appalachian region and is considerably more severe in underground mining where acid production can continue and actually increase long after mine abandonment. One reason for this is that in underground mining, as compared to surface or strip mining, an appreciable fraction of the coal must be left in place for roof support. Furthermore, the strata covering the coal bed frequently also contain appreciable concentrations of pyrite. As compared to an unmined seam, this remaining coal, as well as the overburden, are now, however, fairly freely accessible to water and air, the reactants necessary for the decomposition of pyrite and the formation of acid.

Coal is the one energy resource of the United States which is both abundant and for which recovery techniques are well established. It is therefore the one resource where increased production is both feasible as well as capable of making a significant impact in regard to the dependency of the United States on foreign oil imports within a relatively short period of time. However, increased rates of coal extraction from underground seams may result in an increase of total mine acid production which, if not corrected, may be a high price to pay.

In order to make possible a significant increase in coal production from underground mines without harmful effects on the environment or drastically increased treatment costs, the Department of Energy initiated this program with the objective to determine the mechanisms and kinetics of the acid formation processes and to identify technically and economically feasible methods of abatement and, ideally, complete prevention.

Coal mine acid drainage results from the "transformation" of inorganic sulfides and polysulfides, present in virtually all coal deposits, into oxidized products which form strongly acidic aqueous solutions. The details of this overall "transformation", e.g., the mechanisms and the rates of the reaction steps involved, have so far not been elucidated, based on the information available in the literature, despite the existence of numerous reports and publications dealing with isolated, readily identifiable and controllable processes under specific conditions. As a matter of fact, the problem of acid mine drainage formation in its entirety has not been addressed at all when compared to the efforts made to neutralize its adverse effects.

Over 40 years ago, the basic reactions leading to mine acid production (slide 1) were postulated by Carpenter and Herndon, later expanded by Weiss, and since then referred to by practically every investigator in the field. The possibility of bacterial involvement in iron precipitation was mentioned as early as 1919; however, it was only in the late 1940's that bacteria became definitely identified as being present in mine waters and affecting FeS_2 transformation. Since that time, a tremendous amount of work has been carried out on the various aspects of mine acid production as attested by the publications cited in various reviews.

There are several reasons why a comprehensive and consistent description of the mechanisms and rates of all processes leading from inorganic sulfides to acid drainage has not been developed. The number of interdependent variables affecting acid formation is huge - to name just a few: the type and mix of minerals present, their degree of dispersion, the large number of sulfur compounds most likely involved in the overall process, the permeability of the coal bed, the nature and activity of the overburden, the pH and hardness of incoming water, the type and quantity of other water borne or leached species including catalysts or nutrients, or the variety of microorganisms not only capable of survival, but able to adapt and even change via mutation. In establishing the kinetics and mechanisms of the acid forming reactions, all these variables need to be considered in a systematic manner.

To accomplish this, the experimental investigations were carried out along two lines: the reactions of "pure" iron disulfides, e.g. pyrite and marcasite, and the reactions of iron disulfide as occurring in bituminous coals.

The results of these investigations show that marcasite in water in the presence of air decomposes almost twice as fast as pyrite (S-2), that the amount of soluble iron produced is strictly dependent on the quantity of pyrite (S-3) or marcasite (S-4) present, and that, most importantly, it is the degree of distribution, e.g. the available surface area, which determines how much iron is being solubilized in a given time (S-5).

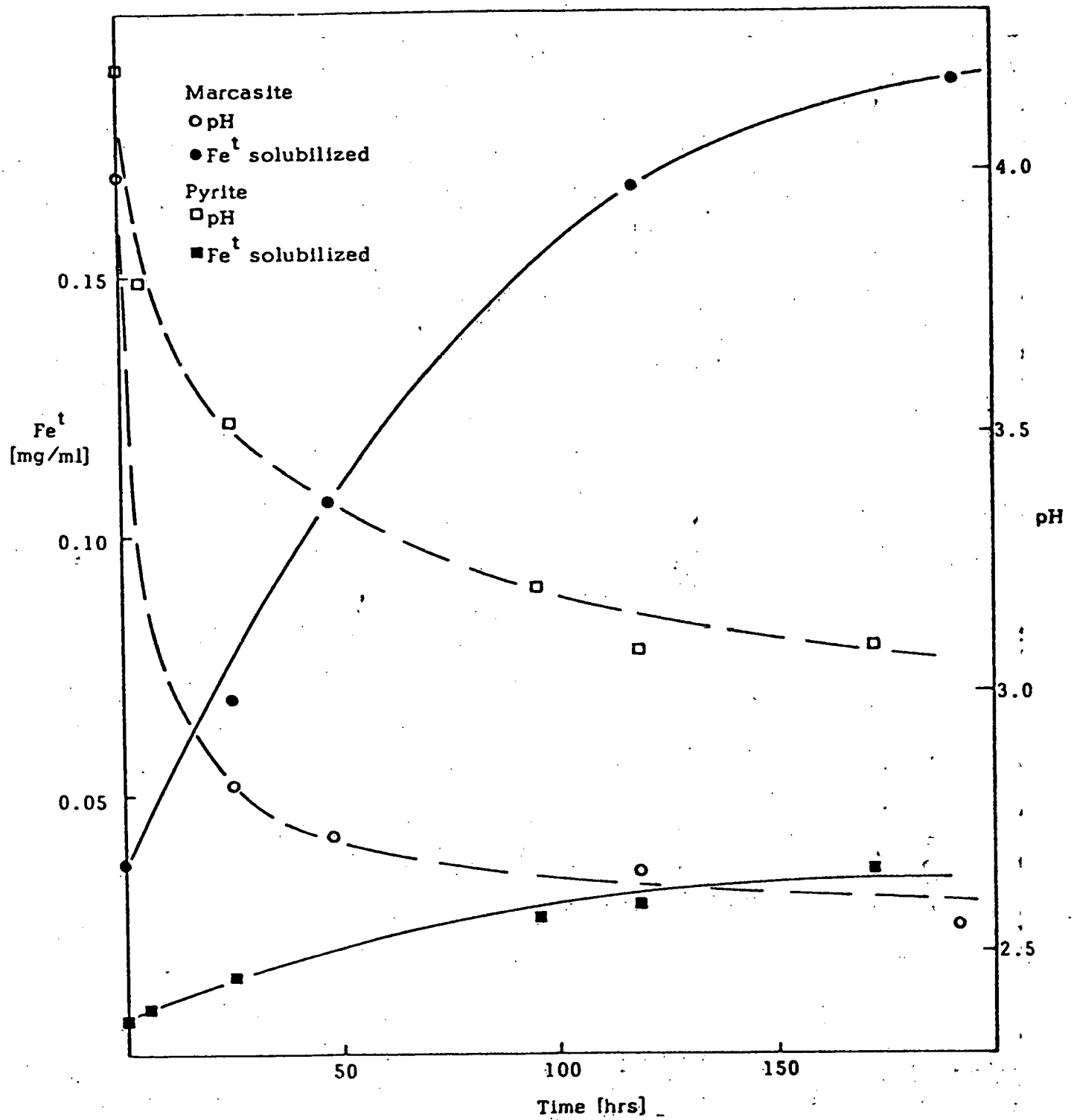
$$2\,FeS_2 + 7\,O_2 + 2\,H_2O \longrightarrow 2\,FeSO_4 + 2\,H_2SO_4$$

$$2\,FeSO_4 + H_2SO_4 + 1/2\,O_2 \longrightarrow Fe_2(SO_4)_3 + H_2O$$

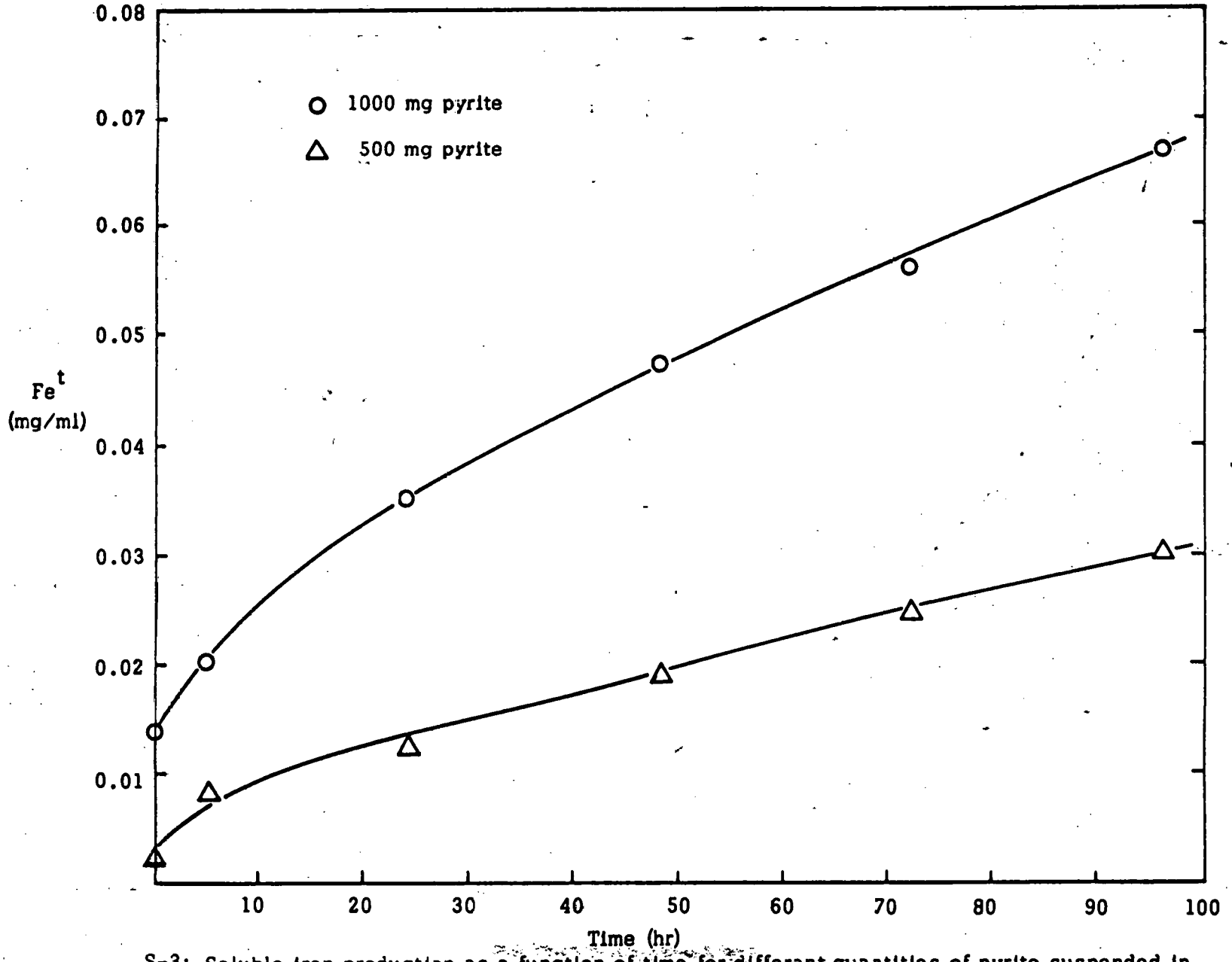
$$Fe_2(SO_4)_3 + 6\,H_2O \longrightarrow 2\,Fe(OH)_3 + 3\,H_2SO_4$$

$$2\,FeS_2 + 7.5\,O_2 + 7\,H_2O \longrightarrow 2\,Fe(OH)_3 + 4\,H_2SO_4$$

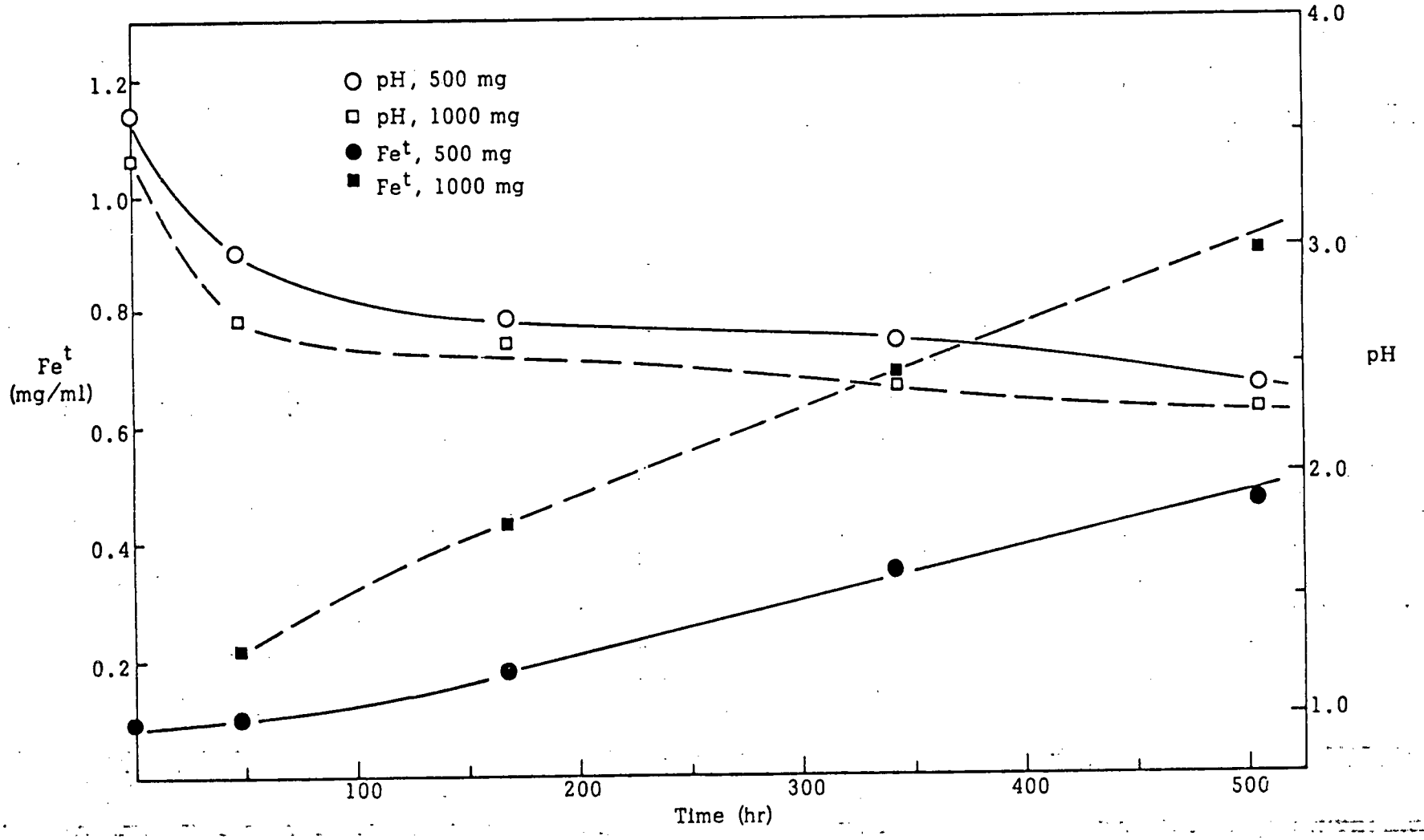
S-1 : Basic Reactions



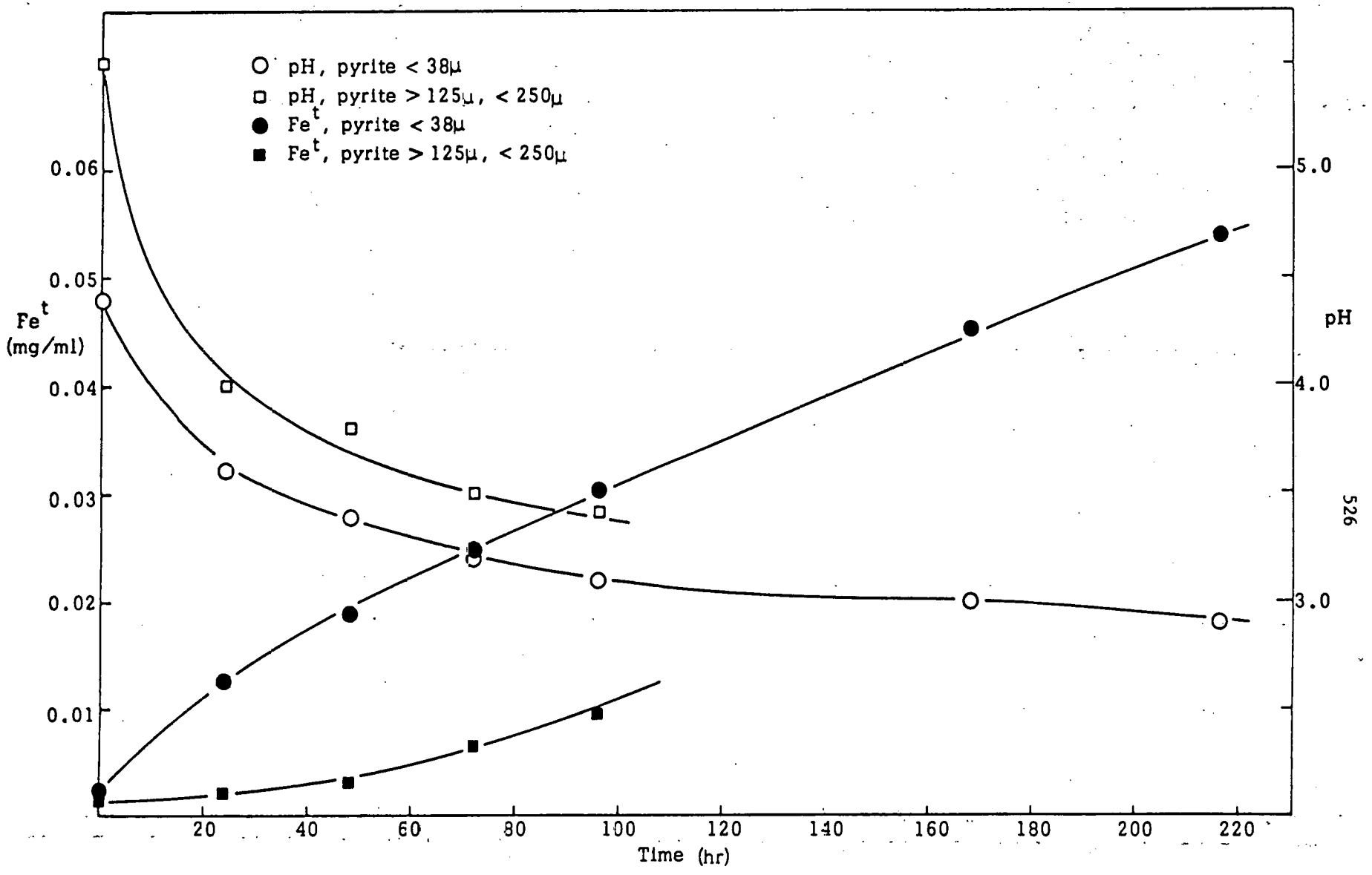
S-2: Plot of Fe^t and pH versus Time for Marcasite and Pyrite (<38μm, ~500 mg FeS_2/100 ml H_2O Samples)



S-3: Soluble iron production as a function of time for different quantities of pyrite suspended in 100 ml of water.



S-4: Changes in pH and soluble iron production as a function of time for different quantities of marcasite suspended in 100 ml of water.



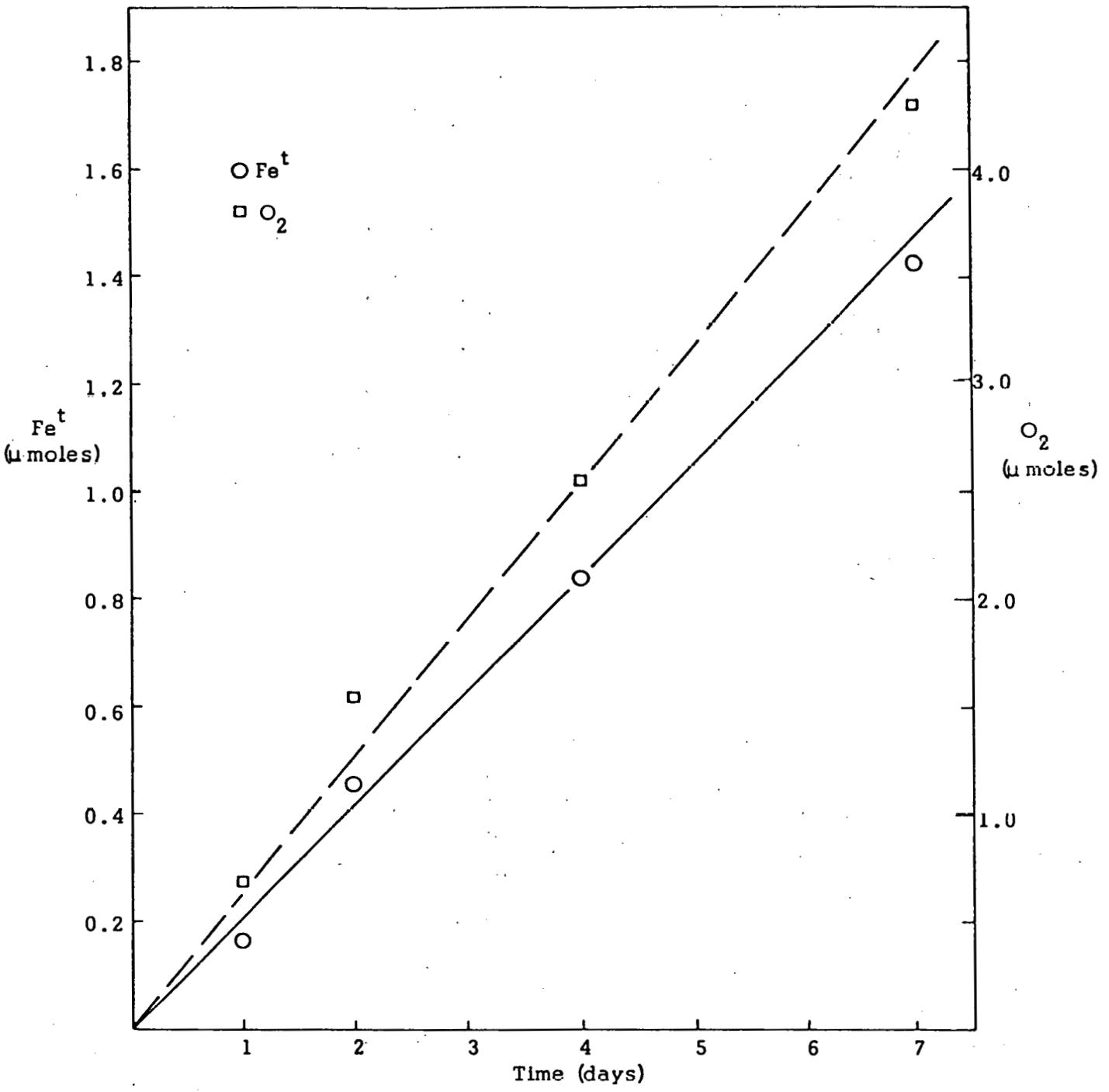
S-5: Effect of particle size upon pyrite solubilization.

One of the reactants needed for pyrite degradation is oxygen and since 7.5 moles of oxygen are needed for each two moles of pyrite to form ferric iron and sulfuric acid the measurement of the oxygen consumption rate should be a very good indicator of the progress of the reaction. However, thus far, the theoretically required ratio could not be experimentally verified. Oxygen consumption always lags behind iron production (S-6) indicating that sulfur species of an oxidation state lower than six may be formed. To complicate matters, it appears that in the initial stages of reaction more oxygen is consumed than required (S-7) and at later stages considerably less than would be expected on the basis of iron produced. This is much more pronounced with marcasite (S-8), but here it may be obscured by the presence of other sulfides, because the sample available was only 78% marcasite.

In the initial studies with pyrite it appeared that two successive processes are taking place, an initially fast production of iron followed by a slower iron release process (S-9). This has been found to be caused by the structure of the surface of the pyrite particles and to be due to sample preparation. The grinding of museum grade pyrite apparently produces particles of high surface irregularity and therefore areas of high surface energy. At these points the rate of iron solubilization is much higher than on the remainder of the surface causing the high iron relaese rate. In the course of the experiment these high surface energy spots are ground away and particles of a smooth surface structure are produced, which react at a slower rate. When such "polished" pyrite is subjected to the same exposure conditions the iron release rates are constant (S-10).

Cupric and ferric ion have in the past been described as accelerators for pyrite dissolution. However, no such effect was found for cupric ion (S-11), whereas the action of ferric ion, which definitely was evident, as measured in this investigation did not follow either one of two previously proposed mechanisms. Trivalent iron can be formed in two ways, one the oxidation of ferrous iron by T. ferrooxidans, the other the reaction of ferrous iron with oxygen (S-12). The two previously proposed schemes of ferric iron reaction are a) the oxidation of the sulfide ion in pyrite to elemental sulfur and b) the complete oxidation to sulfate. The first process would consume 2 moles of ferric iron for each mole of pyrite solubilized, the second would require 14 (S-12). The present investigations show that the addition of ferric ion to a pyrite suspension does increase the rate of pyrite solubilization (S-13), however, the ratios of ferric iron reduced to ferrous iron produced from pyrite vary from 4 to 7, thus indicating that the oxidation of sulfide by trivalent iron neither stops at the elemental sulfur stage nor does it proceed to the oxidation state of plus six as present in sulfate (S-14).

One objective of this investigation is to evaluate the effects of various bacteria on pyrite solubilization. Accordingly, methods of sterilization had



S-6: Plot of oxygen uptake and soluble iron production versus time for 25 mg FeS_2/5 ml H_2O at 14°C.

OXYGEN UPTAKE AND IRON PRODUCTION DATA
FOR PYRITE IN WATER AT 14°C [a]

Sampling Period day	pH [b]	$Fe^{t,b}$ µmoles	O_2 [b] µmoles	Mole Ratio of Species Produced during a given time interval Fe : O_2
1	3.8	0.184	0.68 (0.73_8)	1 : 3.71
2	3.7	0.452	1.53 (1.46_5)	1 : 3.17
4	3.4	0.842	2.55 (2.81_3)	1 : 2.60
7	3.3	1.424	4.29 (4.42_2)	1 : 3.00

a) All the tests were performed at 14°C using 25 mg of pyrite per 5 ml of deionized water. The values given for the specific time periods are corrected for the zero time sampling, i.e., the values obtained at zero time sampling are subtracted out.
b) The value given is the real value for the sample, while the value given in the parenthesis is the average value for this time period and the subscript value is the number of samples averaged.

OXYGEN UPTAKE AND IRON PRODUCTION DATA

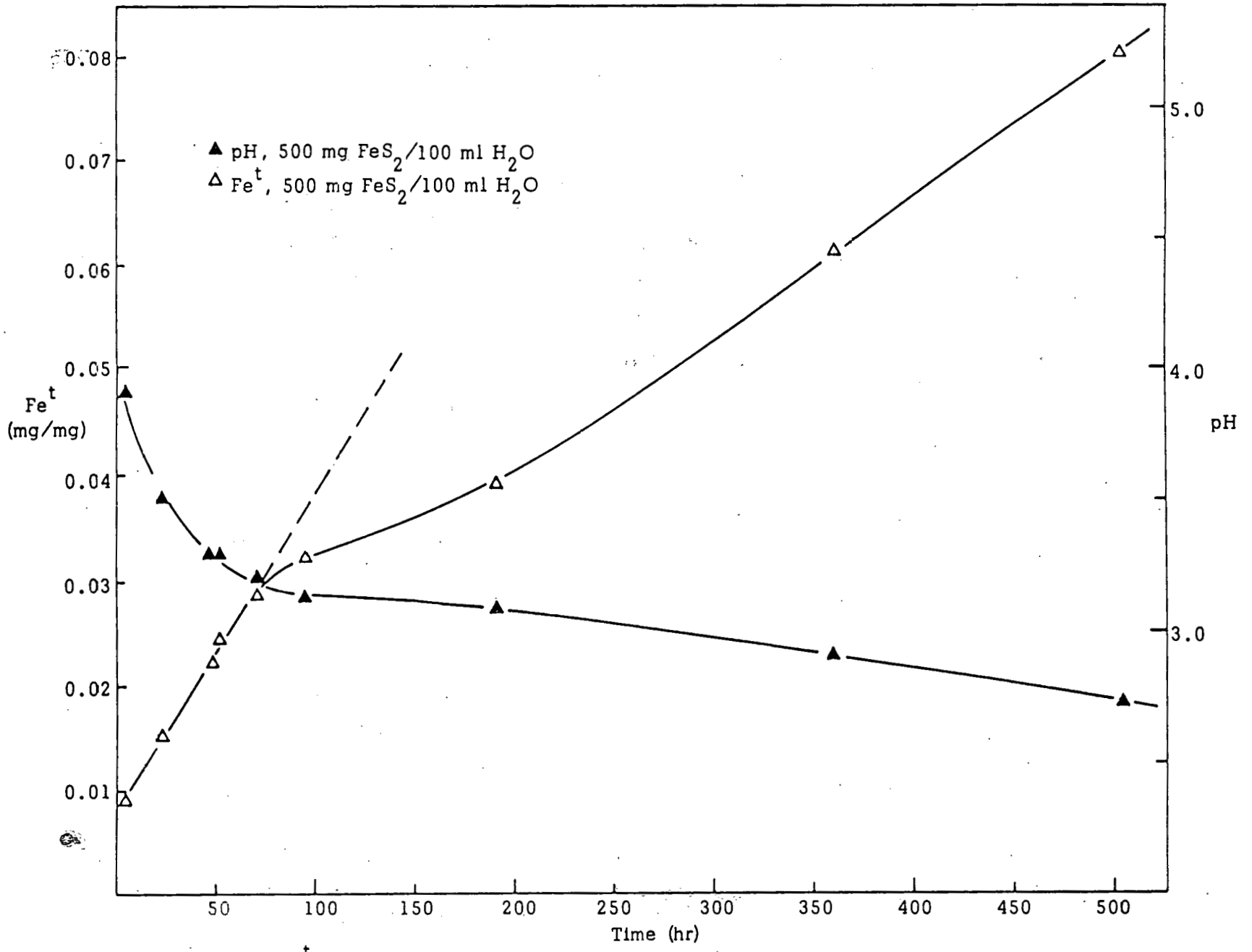
FOR MARCASITE IN WATER AT 14°C [a]

Sampling Period day	pH [b]	$Fe^{t,b}$ µmoles	O_2 [b] µmoles	Mole Ratio of Species Produced during a given time interval Fe : O_2
1	3.0	7.49	4.38 (4.05_{13})	1 : 17
2	3.0	7.55	7.41 (7.85_{11})	1 : 51
3	2.9	8.48	10.45 (10.78_{10})	1 : 3.3
6	2.8	10.20	17.58 (17.26_{8})	1 : 4.1
7	2.8	10.72	17.63 (17.98_{6})	1 : 0.1
8	2.8	11.91	19.26 (19.31_{4})	1 : 1.4
9	2.8	12.27	20.98	- : -

a) All the tests were performed at 14°C using marcasite, < 38µ, 25 mg per 5 ml of deionized water. The values given for the specific time periods are corrected for the zero time sampling, i.e., the values obtained at zero time sampling are subtracted out.

b) The value given is the average for two samples, while the value given in parenthesis is the average value for this time period and the subscript value is the number of samples averaged.

S-8



S-9: Plot of Fe^t and pH versus time for ~ 500 mg FeS_2/100 ml H_2O.

EFFECTS OF PREVIOUS TREATMENTS UPON PYRITE SOLUBILIZATION[a]

(Pyrite, water)

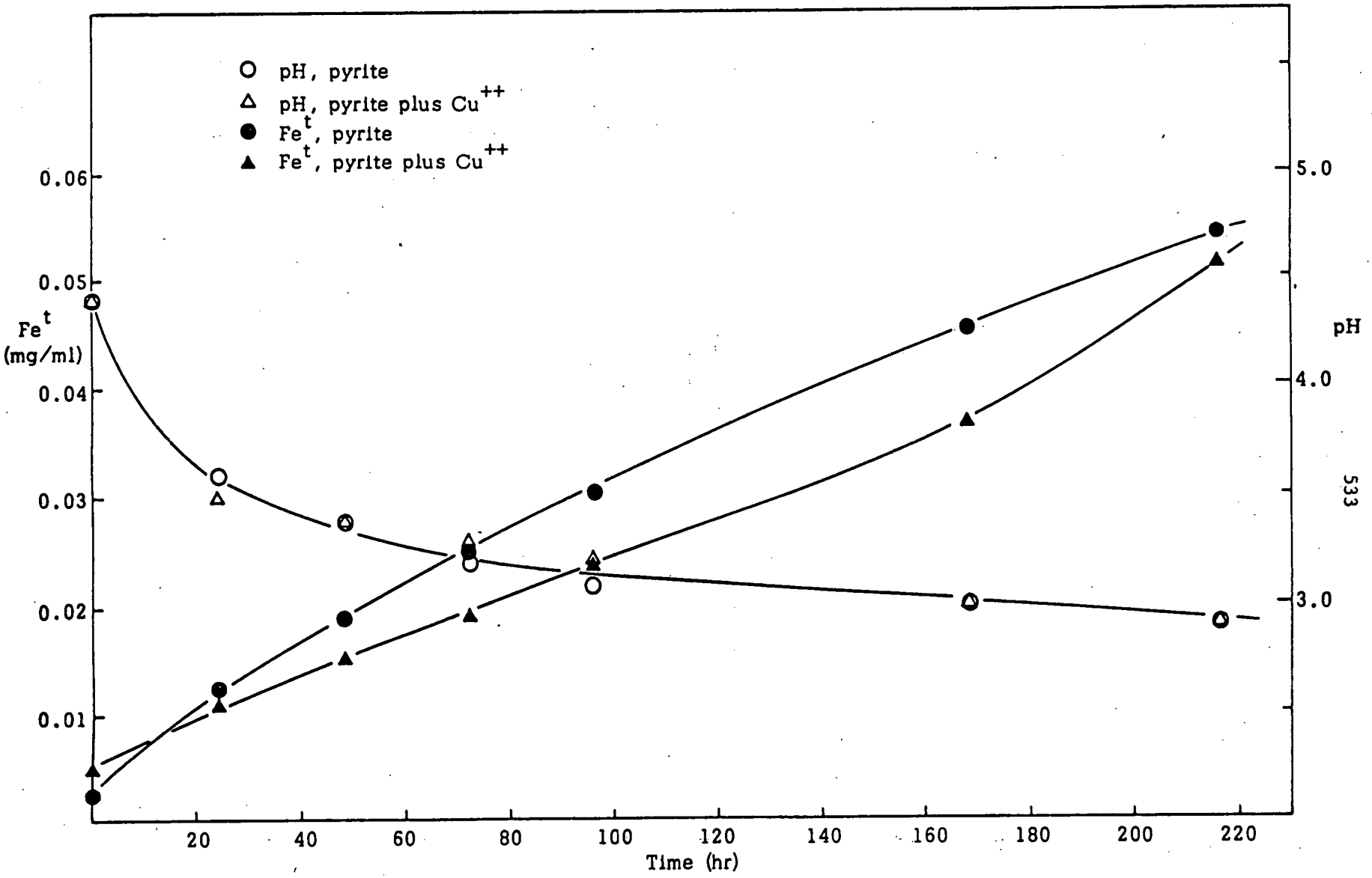
Time Interval hr	pH	$Fe^{t,b}$ 10^{-3}	Rate $Fe^{t,c}$ 10^{-4}
0	5.1	0.1	-
24-0	3.9	0.9	0.3
48-24	3.8	1.3	0.2
120-48	3.6	3.8	0.3
168-120	3.5	6.3	0.5
216-168	3.3	7.9	0.3
288-216	3.2	11.2	0.4

a) In these tests, museum grade pyrite, < 38μ, recovered from the tests performed previously was used. The test conditions (~ 500 mg in 100 ml deionized water, room temperature agitation) were the same as for previous series.

b) Fe^t is the total soluble iron in mg/ml.

c) The rate is the total soluble iron produced per ml of solution per hr during the time interval specified.

S-10



S-11: Effect of cupric ion presence upon pyrite solubilization.

Fe^{+3} PRODUCTION

1) MICROBIAL $Fe^{+2} - e \xrightarrow{T.f.} Fe^{+3}$

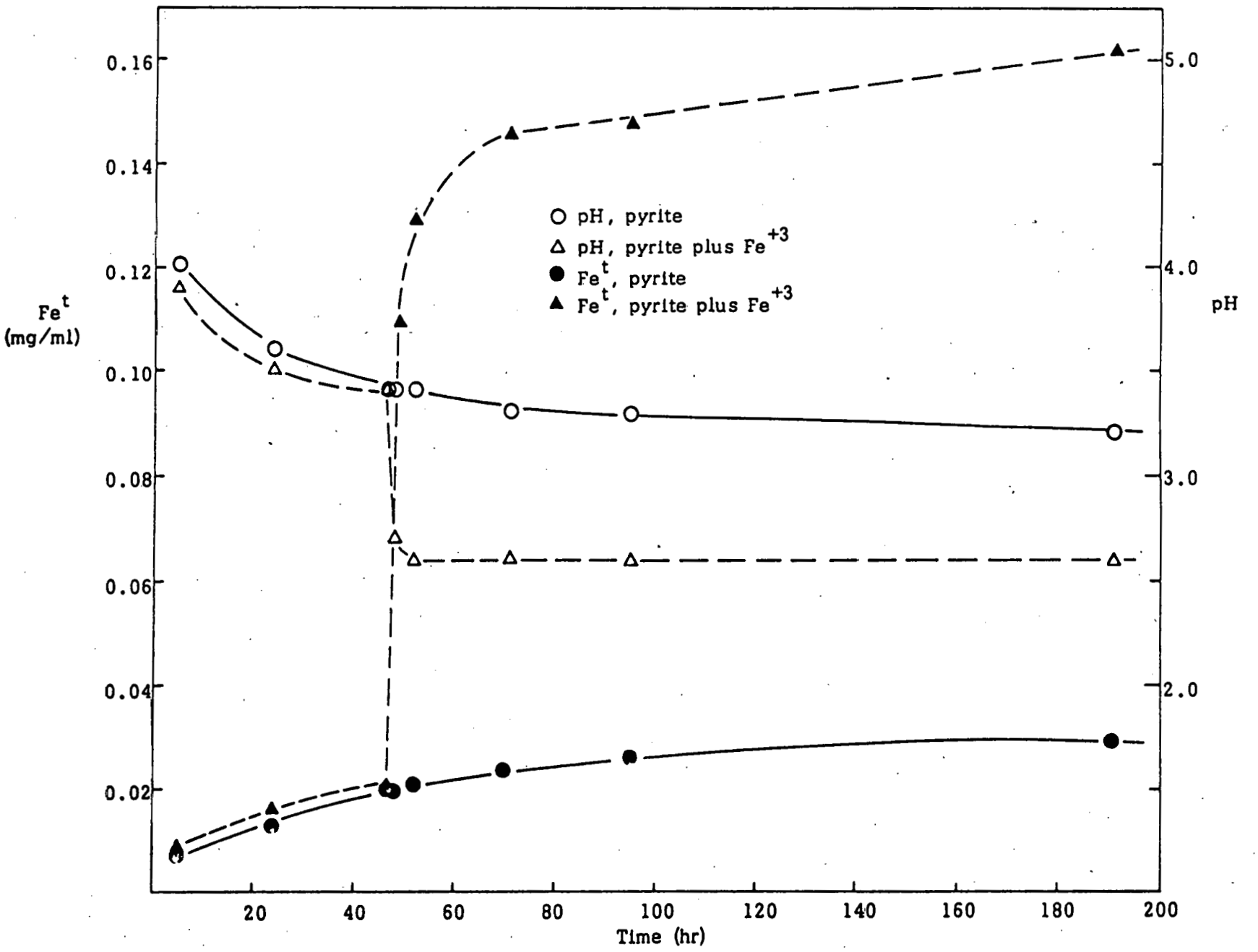
2) INORGANIC $2\,Fe^{+2} + H_2O + O \longrightarrow 2\,Fe^{+3} + 2\,OH^-$

Fe^{+3} CONSUMPTION

$$Fe^{+2}S_2^{-2} + 2\,Fe^{+3} \longrightarrow 3\,Fe^{+2} + 2\,S^0$$

$$S^0 + 2\,O_2 \longrightarrow SO_4^{=}$$

$$Fe^{+2}S_2^{-2} + 14\,Fe^{+3} \longrightarrow 2\,S^{+6} + 15\,Fe^{+2}$$



S-13: Effect of ferric ion upon pyrite dissolution (high ferric ion concentration).

QUANTITATIVE PRESENTATION OF Fe^{+3} EFFECT UPON PYRITE SOLUBILIZATION [a]

Time	Fe^{t}	Fe^{+3}	$Fe^{+3,b}_{reduced}$	$Fe^{+2,c}_{liberated\ found}$	Ratio $\frac{Fe^{+3}_{reduced}}{Fe^{+2}_{liberated}}$
hr	10^{-3}	10^{-3}	10^{-3}	10^{-3}	
71	1441	846	507	75	6.8
77	1478	821	532	112	4.8
102	1549	575	778	179	4.3
191	1574	249	1104	180	6.1

a) All the species' concentrations are given in mg/ml and all are averages of QQ-3 and QQ-4 Runs. The total Fe^{+3}_{added} was 1.353 mg/ml.

b) $Fe^{+3}_{reduced} = Fe^{+3}_{added} - Fe^{+3}$.

c) $Fe^{+2}_{liberated\ found} = Fe^{t} - Fe^{+3}_{added} - Fe_{control}$; $Fe_{control}$ = average Fe^{t} of QQ-1 and QQ-2 Runs.

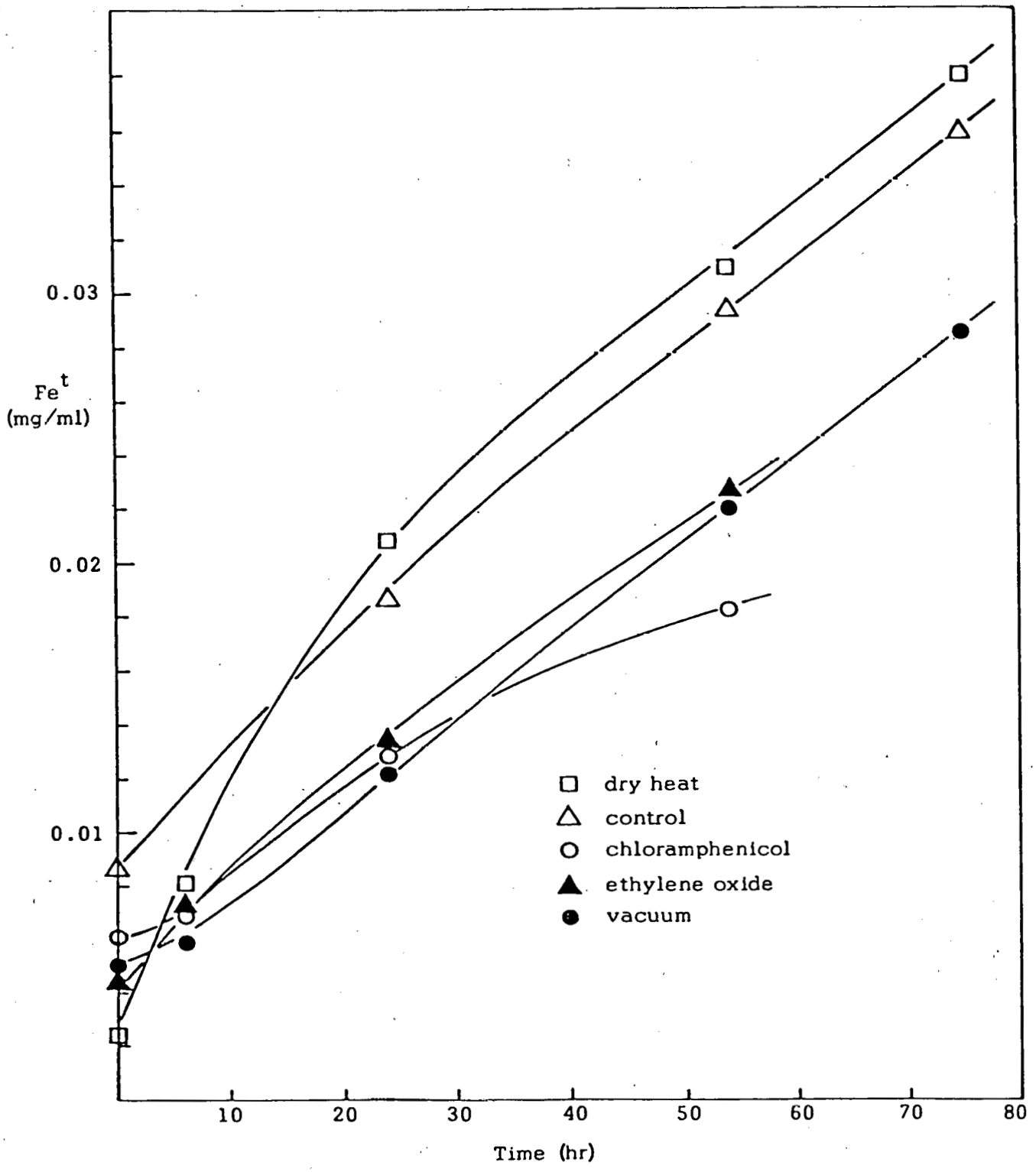
to be found which do not affect the reactivity of pyrite, yet assure the elimination of all microorganisms. Dry heat and ethylene oxide treatments were found acceptable in both respects (S-15), whereas chloramphenicol and steam sterilization were found to alter the reactivity of pyrite.

The addition of T.ferrooxidans to a suspension of pyrite was found to increase its solubilization rate, particularly when a nutrient solution was added simultaneously (S-17). The same effect was found with marcasite (S-18). The addition of T.thiooxidans to a marcasite suspension had a minimal yet discernible effect (S-19), whereas on pyrite T.thiooxidans showed no effect at all when compared to a sterile control.

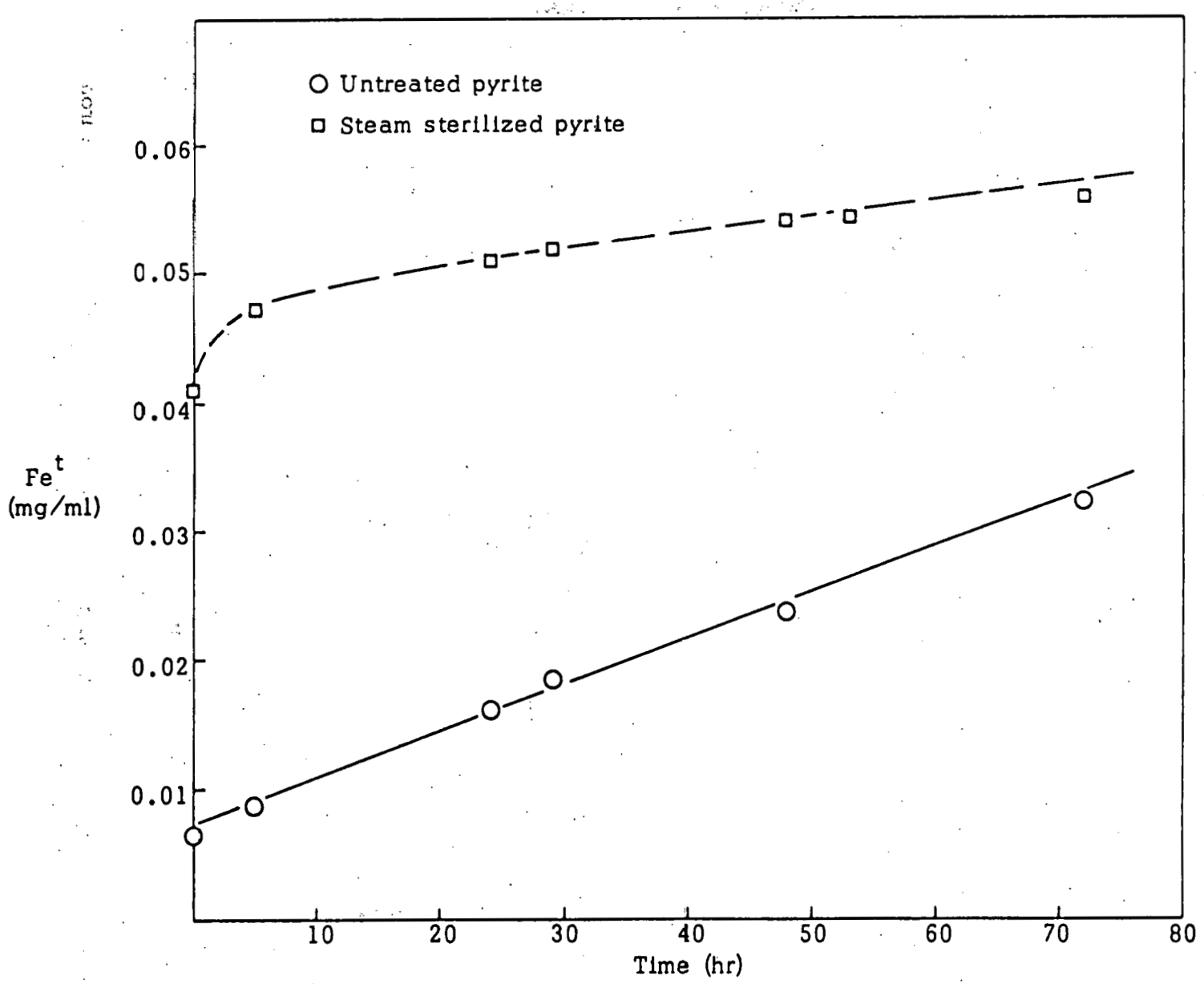
Analysis of field samples for microorganisms showed the presence of a variety of species on both the solids as well as in the water samples. Practically all the coals, shales, and waters taken from an abandoned underground mine and the water collected from near-by overflow bore holes showed the presence of T.thioparus, T.thiooxidans, T.ferrooxidans, as well as sulfate reducers (S-20). Interestingly, in none of the samples could Metallogenium be identified although it is said to be a critical link in establishing conditions for T.ferrooxidans to become effective. The same results were obtained on the samples collected in an active mine in the Pittsburgh seam (S-21).

Based on the results obtained the coal from the Pittsburgh seam mine, which contained about 2% pyrite, exhibited large variations between samples depending on the location where they were taken from. A sample from a freshly cut face and a roof coal sample at a sump did not produce measurable amounts of iron for over 20 days, whereas a roof sample from an old haulage way and a sample from the wall did (S-22). The same trend was evident in the production of sulfate (S-23), where sulfate concentrations on the first two samples remained essentially constant for up to 20 days, whereas the latter two samples started producing sulfate immediately. The reason for this discrepancy was found to be the presence of varying amounts of calcite. The coal from the freshly cut face did start releasing iron after about 35 days (S-24), apparently after all calcite had been consumed under formation of calcium sulfate (S-25). T.ferrooxidans was found to increase the rate of reaction of pyrite embedded in coal in the same way as it did with museum grade pyrite (S-26). Interestingly, T.thiooxidans increased the iron solubilization rate for pyrite in coal although it showed no measurable effect in the case of museum grade pyrite (S-27).

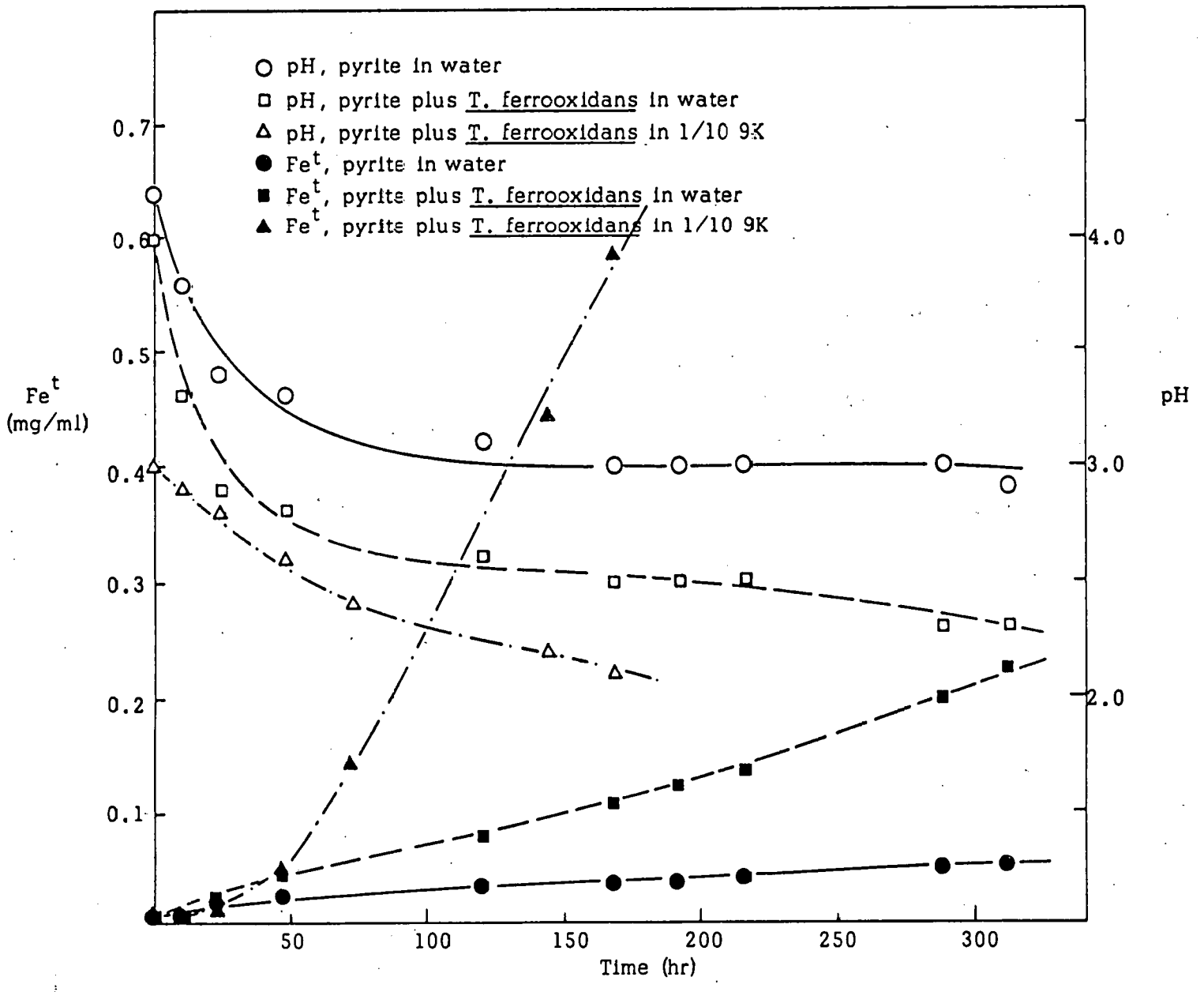
The results obtained thus far show that pyrite will undergo dissolution upon exposure to air and water and that the rate of solubilization is a function of available surface area and temperature. Ferric ion does accelerate this process, cupric ion does not, and carbonates present prevent acid formation until exhausted. T.ferrooxidans and to a degree T.thiooxidans accelerate the rate of pyritic iron solubilization in coal. Both of these organisms were



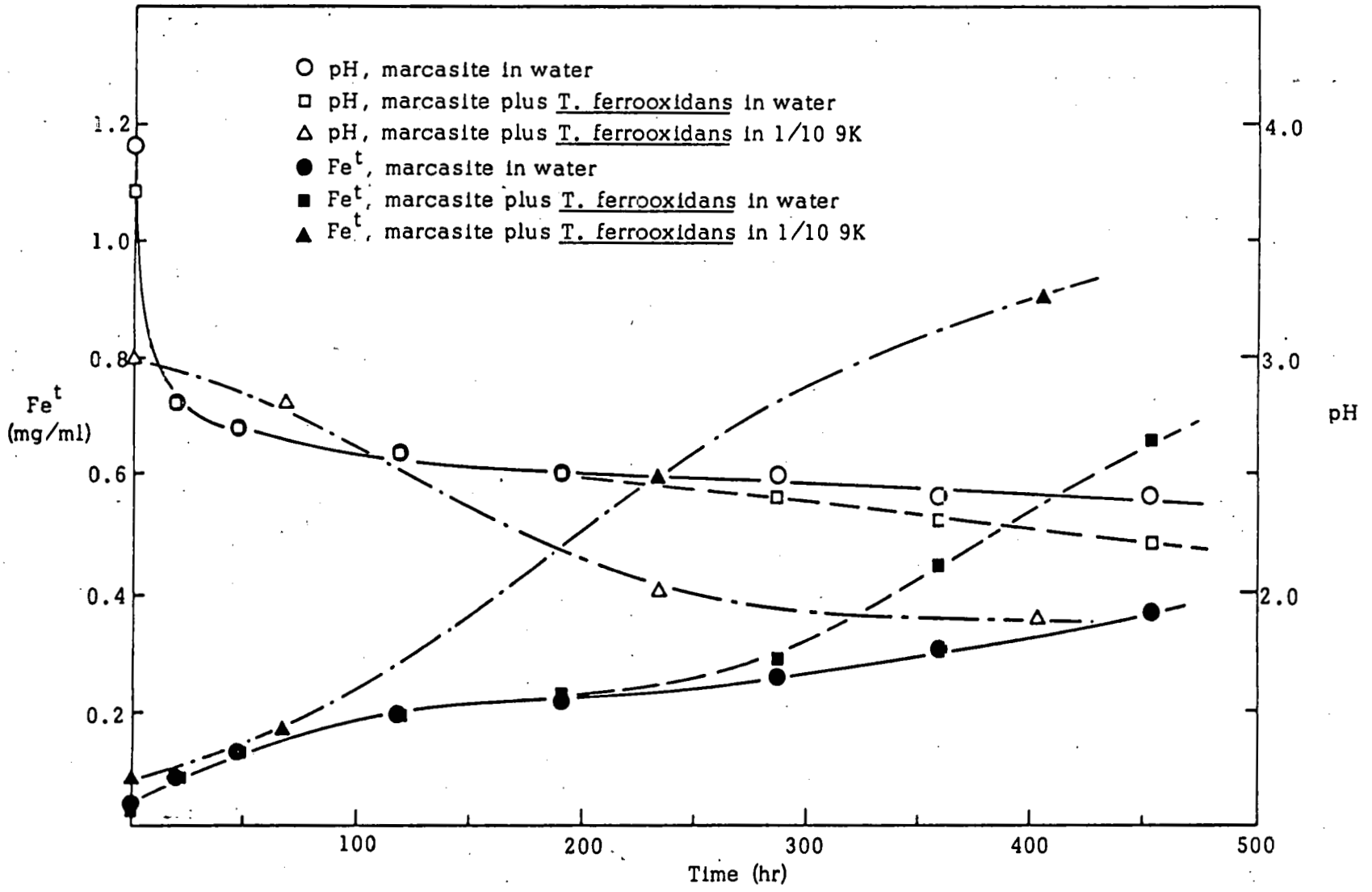
S-15: Effect of sterilization procedures upon pyrite dissolution, total iron versus time.



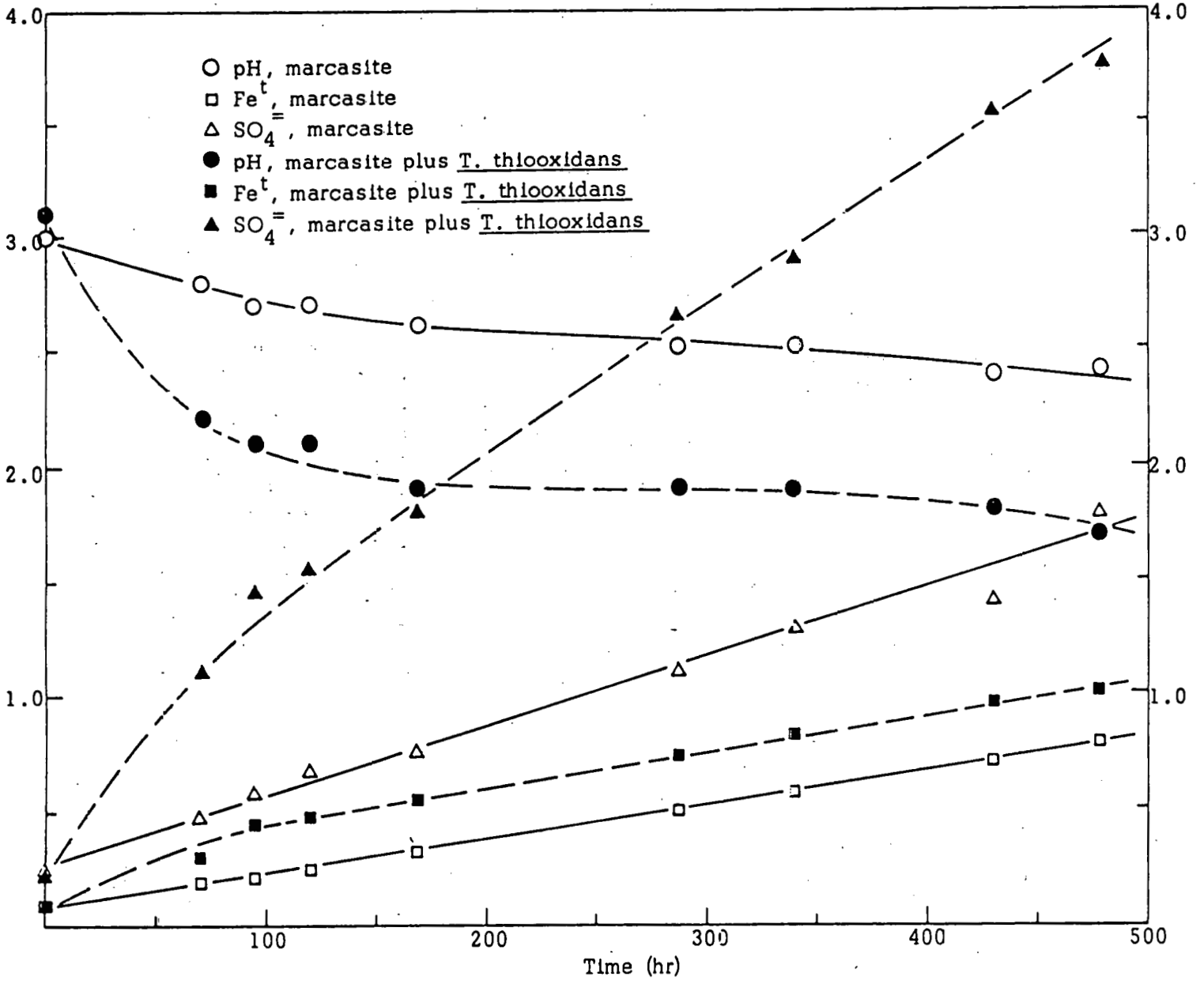
S-16: Effect of steam sterilization upon pyrite solubilization.



S-17: Effect of T. ferrooxidans upon pyrite dissolution in various media.



S-18: Effect of T. ferrooxidans upon marcasite dissolution in different media.



S-19: Effect of T. thiooxidans upon marcasite dissolution.

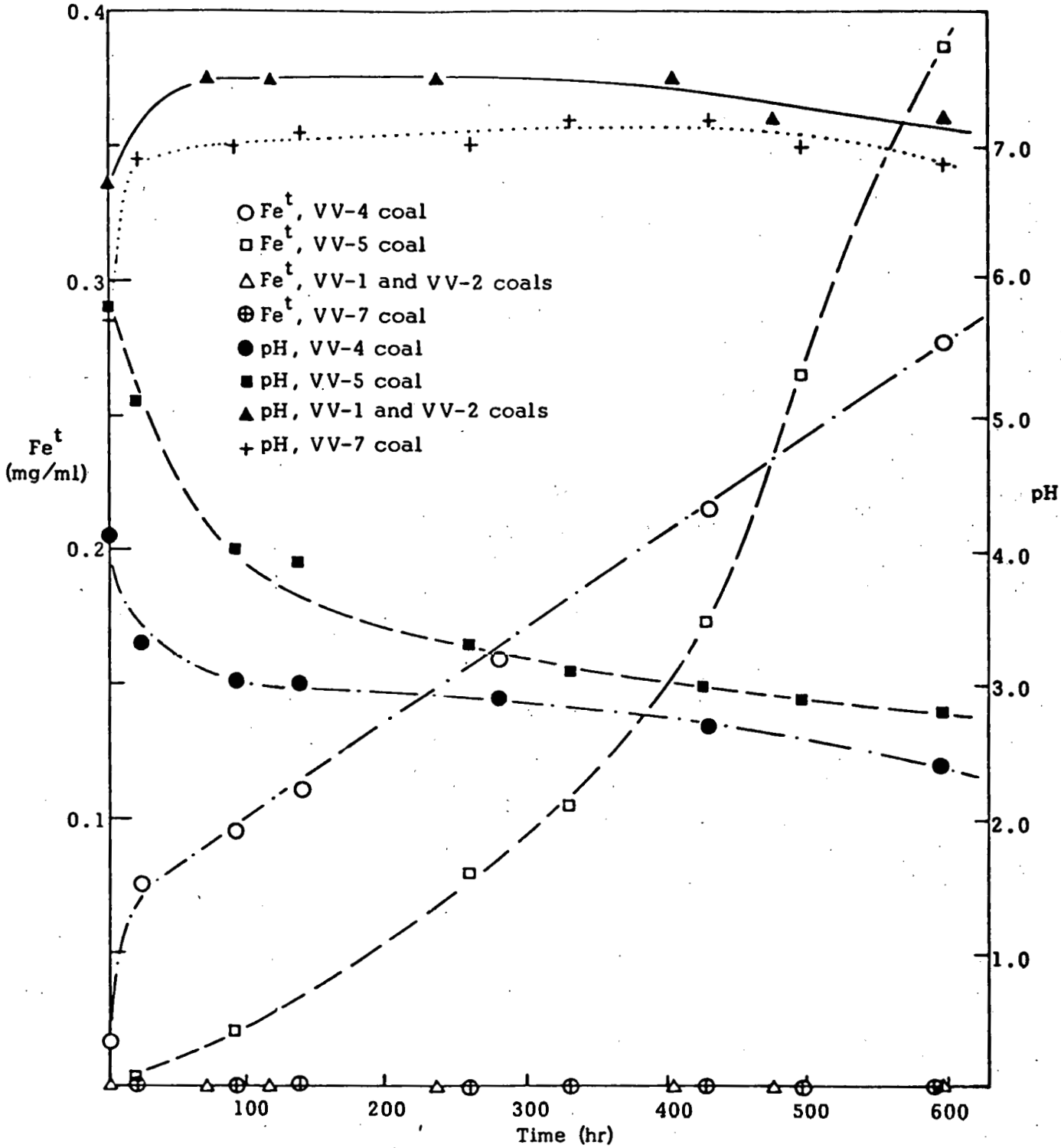
ANALYSIS OF SAMPLES FROM AN
ABANDONED MINE AND BORE HOLE OVERFLOW

No.	Description		pH	Fe Total ppm	T. thioparus	T. thiooxidans	T. ferrooxidans	Metallogenium	$SO_4^=$ reducers	Heterotrophic Population	Yeast Population
1	water, free flow	Bed No. 1	4.6	1.5	+	+	+	-	+	+	+
2	water, muddy	Bed No. 2	5.2	0.2	+	+	+	-	+	+	+
3	water, stagnant	Bore hole	4.7	107	+	+	+	-	+	+	+
4	water, froth	Bore hole	4.6	67	+	+	+	-	+	+	+
5	water, muddy	Bore hole	4.4	62	+	+	+	-	+	+	+
6	water, free flow	Bore hole	5.5	114	+	-	-	-	+	+	+
7	yellowboy	Bed No. 1	n.d.	n.d.	-	+	+	-	+	n.d.	n.d.
8	"stalactite"	Bed No. 2	n.d.	n.d.	+	+	+	-	+	n.d.	n.d.
9	coal	Bed No. 2	n.d.	n.d.	+	+	+	-	+	n.d.	n.d.
10	rock	Bed No. 2	n.d.	n.d.	-	+	+	-	-	n.d.	n.d.

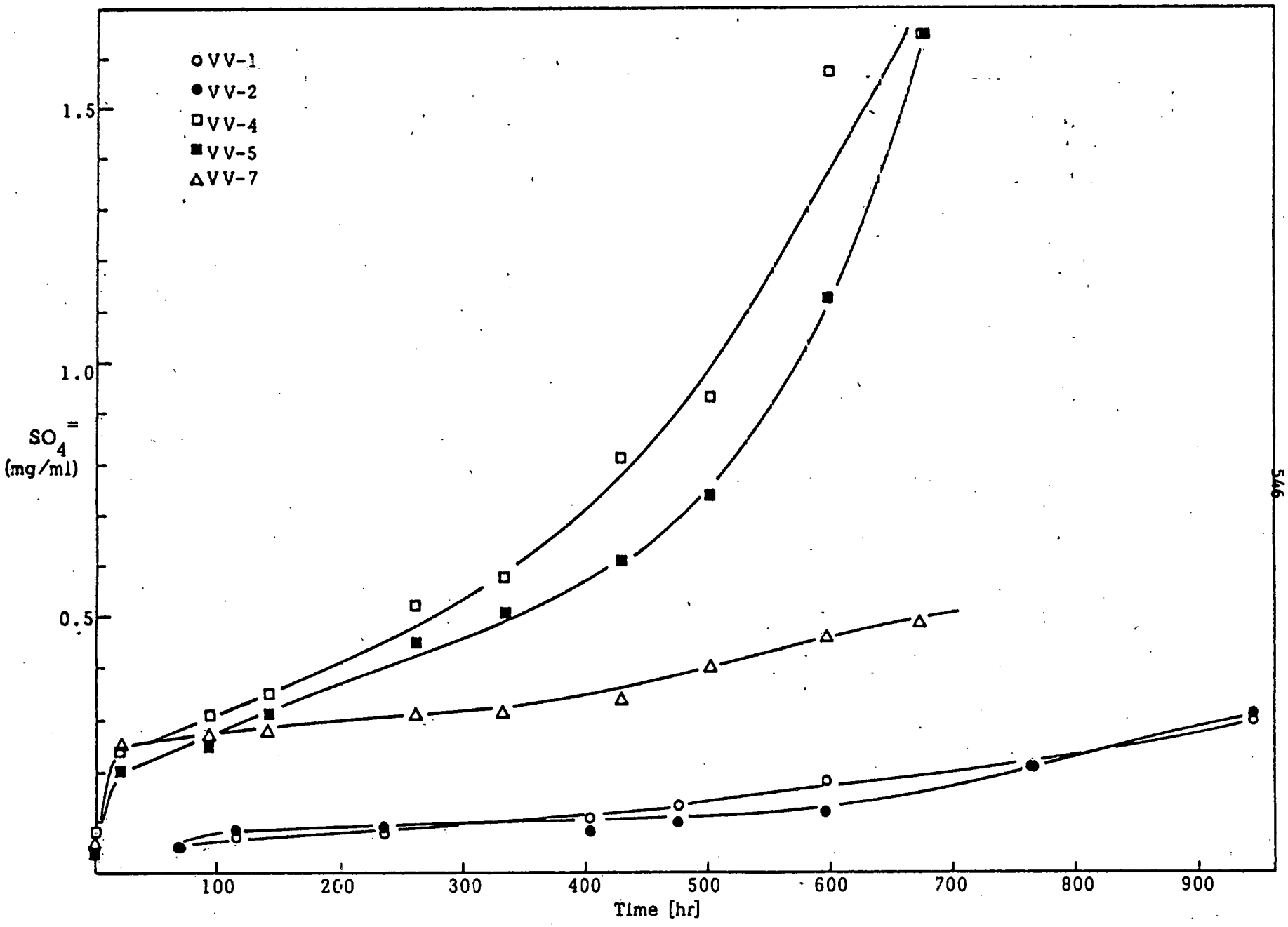
S-20

RESULTS OF THE BACTERIAL ANALYSIS OF VV-MINE SAMPLES

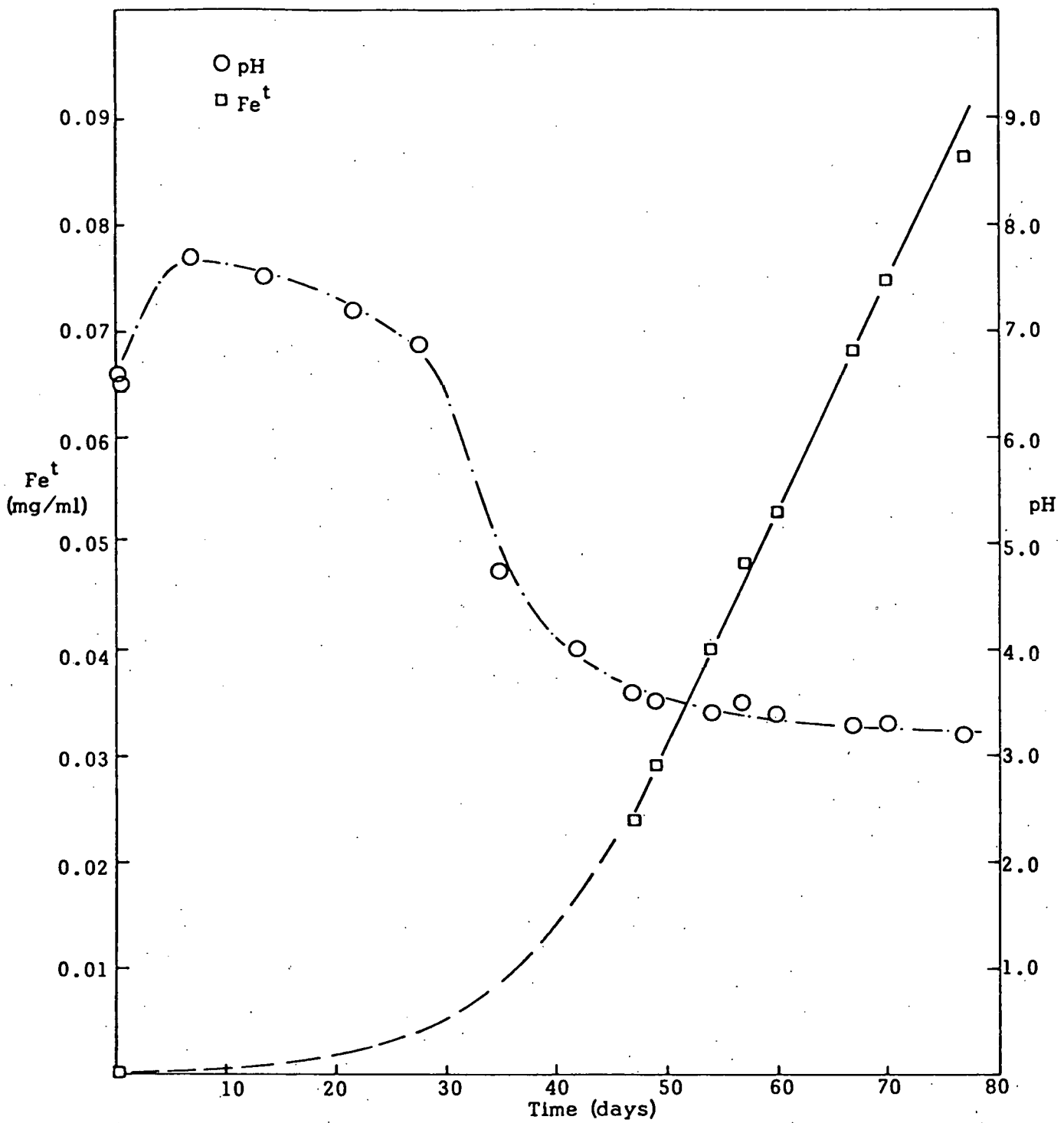
Mine Sample	pH~7 S-oxid	pH=2.7 S-oxid	pH=2.7 Fe-oxid	Metallogenium	S-red	Heterotrophs	Yeast
VV-1 (coal)	-	-	?<3	-[j]	+	2.6×10^4	5.0×10
VV-2 (coal)	(+)[k]	-	?<3	-	+	5.4×10^4	1.3×10^3
VV-9 (water)	$<10^5->10^3$	-	4.0×10^2	-	+	7.4×10^5	1.0×10^4
VV-12 (water-coal)	-	-	?<3	-	+	4.2×10^4	8.0×10
VV-11 (water)	$<10^7->10^5$	-	4.3×10^4	-	+	2.8×10^7	5.0×10^3
VV-3 (shale)	-	-	?<3	-	+	1.9×10^2	1.7×10^2
VV-4 (coal)	-	-	?<3	-	-	1.0×10	6.0×10
VV-5 (coal)	-	-	?<3	-	-	0	0
VV-6 (shale)	-	-	?<3	-	-	1.1×10^3	9.1×10^2
VV-7 (coal)	-	-	?<3	-	-	5.0×10	0
VV-8 (shale)	-	-	?<3	-	-	2.3×10^3	1.7×10^3
VV-10 (water)	$<10^7->10^5$	$<10^7->10^5$	9.3×10^6	-	+	3.5×10^2	2.9×10
W-3 (water)	4.3×10^3	<3	?<3	-	2.4×10^4	3.6×10^3	2.4×10^2
W-4 (water)	9.3×10^4	2.4×10^4	4.3×10^5	-	4.6×10^5	2.9×10^4	1.0×10^2



S-22: pH drop and soluble iron production as a function of time for coals obtained from different locations of VV-mine.



S-23: Soluble sulfate production from coals obtained from different locations of VV-mine.



S-24: Effect of prolonged exposure of VV-1 coal to water and air.

$$2\,FeS_2 + 2\,H_2O + 7\,O_2 \longrightarrow 2\,FeSO_4 + 2\,H_2SO_4$$

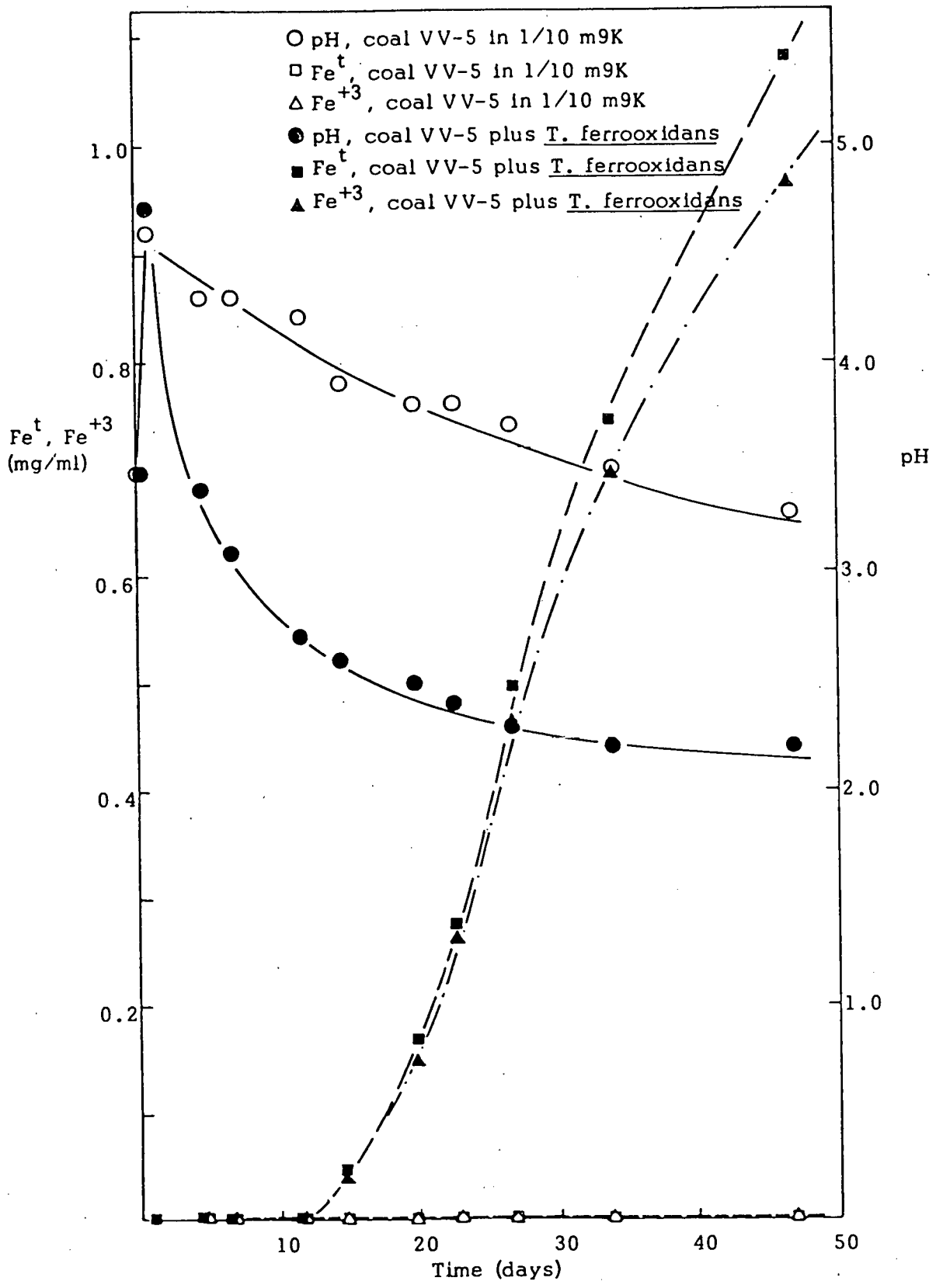
$$CaCO_3 + H_2SO_4 \longrightarrow CaSO_4 + H_2O + CO_2$$

At pH ~ 7:

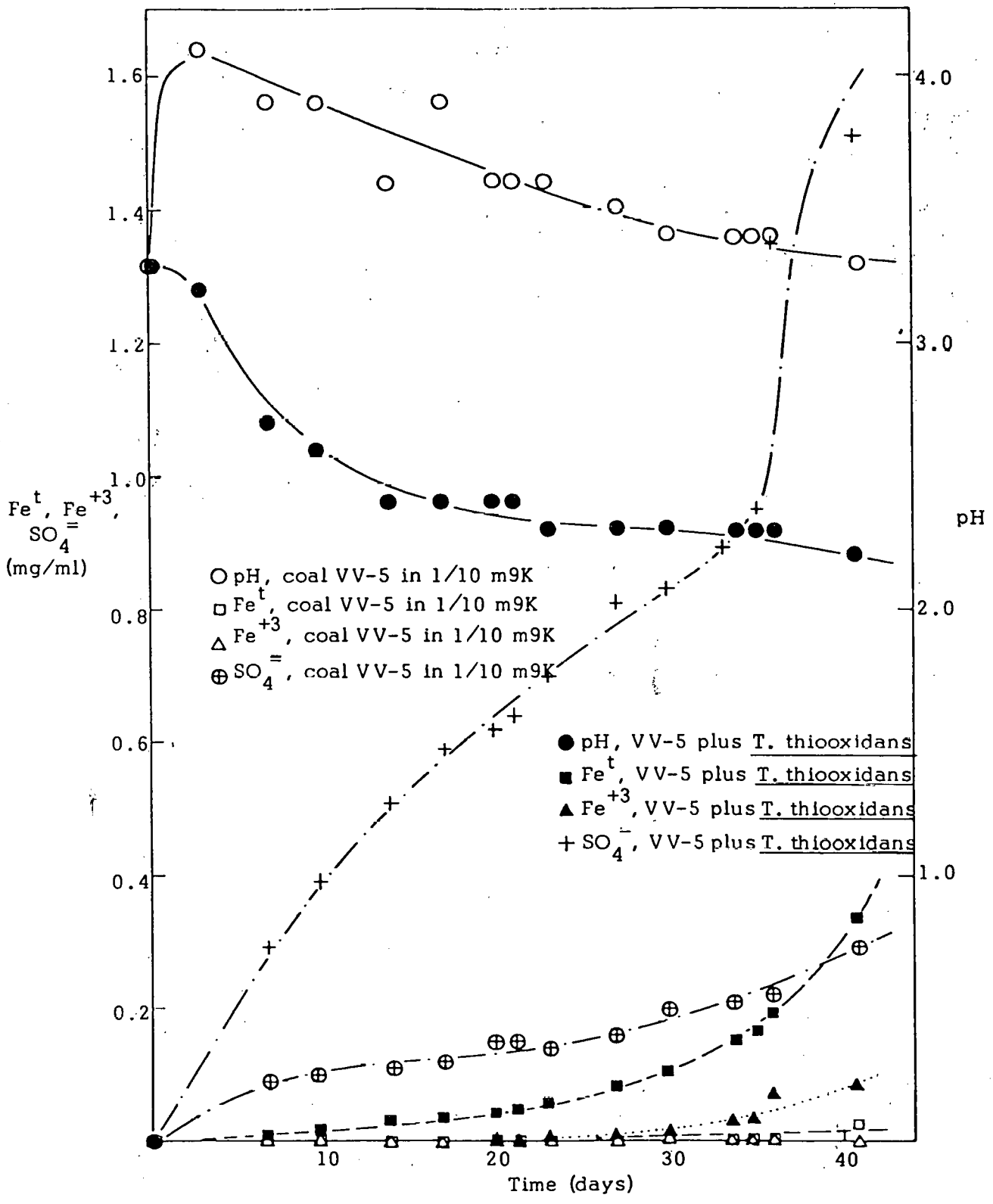
$$2\,FeSO_4 + 1/2\,O_2 + H_2O \longrightarrow 2\,Fe(OH)SO_4$$

$$2\,Fe(OH)SO_4 + 4\,H_2O \longrightarrow 2\,Fe(OH)_3 + 2\,H_2SO_4$$

S-25: Effect of Calcite



S-26: Effect of T. ferrooxidans, ATCC strain, upon coal solubilization.



S-27: Effect of T. thiooxidans, ATCC strain, upon coal solubilization.

found in field samples, whereas Metallogenium could not be detected. In regard to abatement methods the application of bactericides is by itself pollution creating and will have only a temporary effect; recycling of ferrous iron containing water is ineffective based on the results obtained thus far, and mine sealing or flooding may be hard, if not impossible to achieve to exclude all oxygen. Promising approaches include making available carbonates present in coal and overburden to produce ferric oxides and hydroxides together with calcium sulfate; these would precipitate within the mine. Backfilling to reduce the amounts of water and air , which possibly could enter, to a minimum would offer another avenue with the additional benefit of subsidence control.

We would like to express our appreciation for the support of the Department of Energy under Contract No. ET-78-C-01-8977, without which this study would have been impossible. We also would like to thank the officials and engineers from the mining companies, the Pennsylvania Department of Environmental Resources, the Bureau of Mines, the Corps of Engineers, the Appalachian Regional Commission, and the Bituminous Coal Association for all the help and advise they gave us. Finally, it is a pleasure to acknowledge the generous assistance and guidance of Mr. R. Wenzel, Mr. D. Uthus, and Dr. A. Hartstein of the Department of Energy, whose continuous encouragement made a significant contribution to this program.

ENVIRONMENTAL CONTROLS FOR UNDERGROUND COAL GASIFICATION. PART I. ENVIRONMENTAL CONTROL TECHNOLOGY AND RESEARCH FOR UNDERGROUND COAL GASIFICATION

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Paper not submitted for publication in Proceedings.

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ENVIRONMENTAL CONTROLS FOR UNDERGROUND COAL GASIFICATION: GROUND-WATER EFFECTS AND CONTROL TECHNOLOGIES *

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ABSTRACT

Underground coal gasification (UCG) promises to provide economic access to an enormous deep-coal resource. It is, therefore, of considerable importance to develop appropriate environmental controls for use in conjunction with the UCG process. The Lawrence Livermore Laboratory has conducted three UCG experiments at its Hoe Creek site in northeastern Wyoming. We are conducting environmental studies in conjunction with these UCG experiments, including an investigation of changes in local ground-water quality and subsidence effects. Ground-water monitoring and geotechnical measurements have helped to clarify the environmental significance of reaction-product contaminants that remain underground following gasification, and the implications of cavity roof collapse and aquifer interconnection. These investigations have led to the development of preliminary plans for a specific method of groundwater quality restoration utilizing activated carbon adsorption. We are also investigating unconventional technologies that may be appropriate for restoring ground water that has been contaminated as a result of UCG operations. These water treatment technologies are being explored as possible supplements to natural controls and process restrictions.

INTRODUCTION

The conversion of coal into combustible gases, as a source for synthetic fuels, promises to become an important method of coal utilization. If the conversion process is carried out with the coal in place underground - in situ gasification or Underground Coal Gasification (UCG) - there are important economic and environmental advantages. However, the exploration and assessment of this prospective technology must include a careful evaluation of potential environmental problems, together with efforts to identify effective environmental controls.

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The Lawrence Livermore Laboratory (LLL) has carried out three underground coal gasification experiments at its Hoe Creek site in northeastern Wyoming. We are conducting environmental studies in conjunction with these UCG experiments, including an investigation of changes in ground-water quality and subsidence effects. Our objectives are to characterize any ground-water or subsidence problems that may exist, and to identify appropriate environmental control technologies. The ground-water investigations are designed, primarily, to evaluate the magnitude and extent of hydraulic and chemical changes that could result from UCG. In some instances, UCG has led to cavity roof collapse and interconnection of aquifers. It is important to understand the altered hydrologic regime that will result under such circumstances, and its effect on contaminant dispersal. An understanding of both chemical and hydrologic factors is essential to the design of effective environmental controls. This paper summarizes the results of our ongoing ground-water studies at the Hoe Creek site and presents our preliminary ideas and investigations concerning possible control technologies and mitigation measures that may be applicable to ground-water quality changes that result from UCG.

BACKGROUND

In order to evaluate the environmental concerns and constraints associated with UCG, it is important to have an understanding of the process itself. Although underground coal gasification generally involves a complex series of chemical reactions, it can be simply characterized as the heating of coal in the presence of gasifying agents such as oxygen and steam. Some of the coal is burned to provide heat to drive the gasification reactions. In the simplest form of UCG, two or more process wells drilled into the coal seam are used, after the coal is ignited, to inject air or other gasifying agents and to withdraw the resulting combustible gas mixture (Figure 1). Usually, the coal's permeability must be enhanced, before gasification, along a path connecting the process wells. This may be accomplished by explosive fracturing (as was done at Hoe Creek I), reverse burn linking (Hoe Creek II), directional drilling (Hoe Creek III), hydrofracturing, or electrolinking[1]. The need to achieve this preliminary connection, reliably and economically, represents an important current challenge in UCG technology.

The possibility of ground-water contamination arises because some of the gasification reaction products remain underground in the vicinity of the gasified coal seam, which is typically an aquifer. The residual materials include coal ash, char, some coal tars, and roughly 10% of the product gases, which escape into the surrounding permeable strata. During gasification, these escaping product gases can transport small amounts of volatile contaminants up to 600 ft (200 m) or more, from the gasification cavity. Following the gasification process, the ground water, which has been prevented from entering the gasification cavity by product-gas pressure - and perhaps in part by dewatering operations - returns to the cavity, leaches inorganic materials from the ash, and dissolves some of the organic species. A contaminated ground-water plume develops and begins to move through the coal seam under the influence of the natural ground-water flow. This contaminated ground water would be of environmental significance if it found its way, in sufficient concentrations, into surface waters or into aquifers from which water is extracted for drinking or agricultural purposes. Fortunately, the concentrations of many contaminants are significantly reduced as a result of sorption by the surrounding coal.

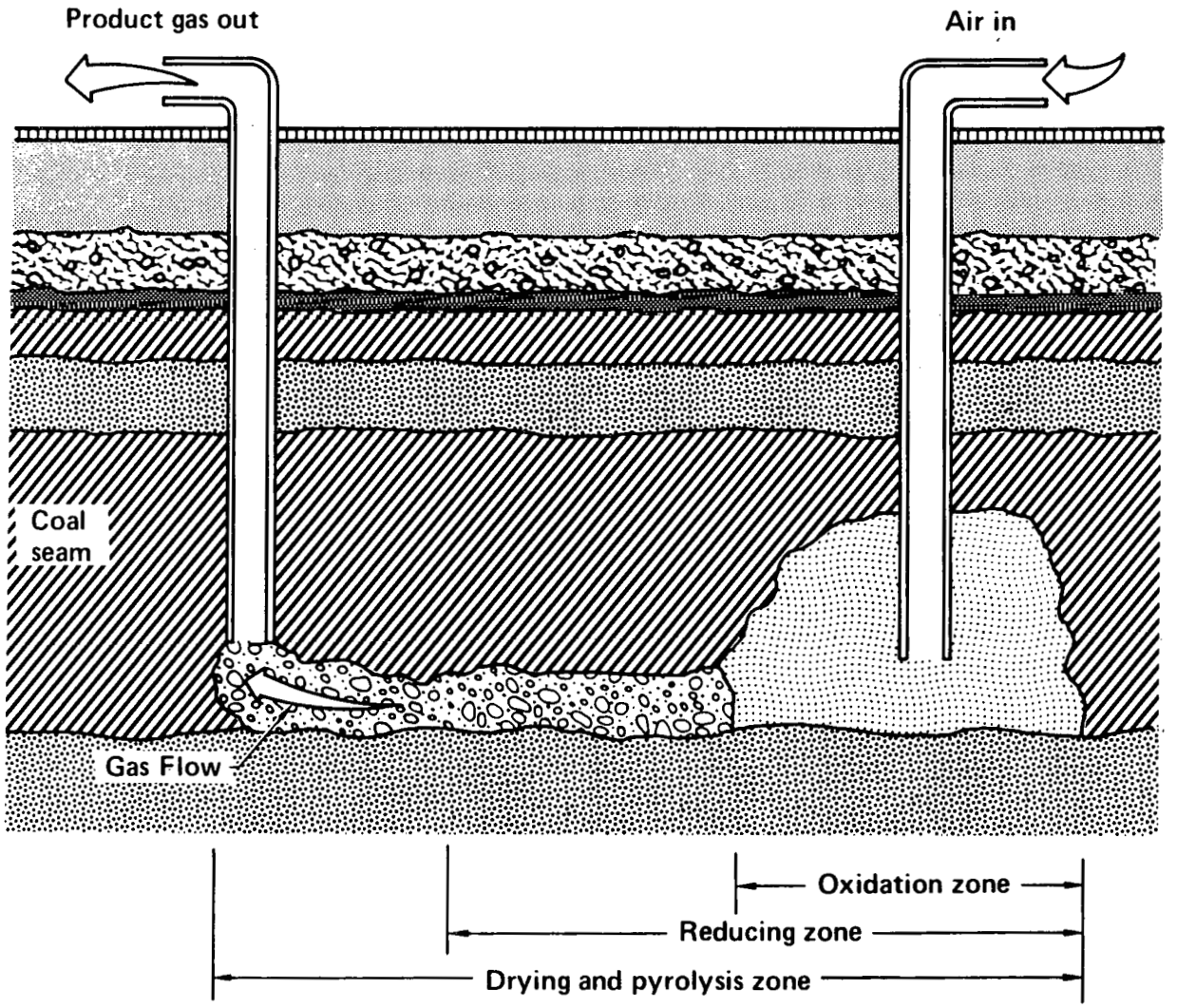


Figure 1. Schematic representation of the underground coal gasification process. The region ahead of the oxidation zone has been modified before gasification to provide a path of increased permeability that will permit adequate gas flow.

We have monitored ground-water quality before, during and after the three Hoe Creek UCG experiments. The first experiment, performed in 1976, was comparatively small, involving gasification of only 130 tons of coal. The gasified coal seam (Felix No. 2) is 25 ft (7.6m) thick and lies at a depth of 125 ft (38 m). Phenolic materials are among the contaminants that showed large increases near the burn zone following gasification. However, the concentrations decreased rapidly with time and distance from the burn zone, as indicated in Figure 2. At distances of about 50 ft (15m) from the burn zone, concentrations have returned to baseline values. It is important to note that normal ground-water flow rates in the vicinity of Hoe Creek are quite slow - perhaps a few meters a year - and that the results exhibited in Figure 2 do not, for the most part, represent contaminant transport as a result of ground-water flow. Our laboratory measurements provide confirmation that the decrease in phenol concentrations with time is largely a result of sorption on the coal.

Some important new factors affected contaminant distribution at the sites of the more recent UCG experiments at Hoe Creek: Hoe Creek II (2300 tons of coal gasified, 1977) and Hoe Creek III (3600 tons gasified, 1979). A primary difference between these large gasification experiments and the Hoe Creek I experiment is the fact that roof collapse and the resulting gasification of an overlying coal seam (Felix No. 1) led to the interconnection of the Felix No. 2 Coal aquifer with the Felix No. 1 Coal aquifer and with an overlying sand aquifer. Roof collapse was documented by an extensive array of subsurface geotechnical instruments[2], and the nature of the permeable collapse zone was delineated in detail by post-burn coring at site II (Fig. 3)[3].

Since the Hoe Creek site is an area of natural recharge to ground water[4], we expected that water from the overlying aquifers would flow downward toward the bottom of the gasification cavity and radially outward into the Felix No. 2 Coal seam. Our measurements of ground-water contaminants and hydraulic heads as a function of time confirm the expected behavior. The radial ground-water flow is the dominant ground-water movement within 100 ft (30 m), or so, of the burn zone.

An example of contaminant transport that is believed to be a result of the accelerated ground-water motion due to aquifer interconnection is shown in Figure 4.[5] The initial high concentrations of the aromatic hydrocarbons are probably due to the rapid outward transport of these materials in the vapor phase during gasification[6]. After a decrease, perhaps due to sorption, the contaminants increase slowly as a result of ground-water transport from the more concentrated source near the gasification zone.

In Figure 5, we have plotted boron concentrations in several outer wells at various times after gasification. These results also indicate increasing concentrations in some outer wells with time, as would be expected if boron is following the natural ground-water flow and being transported outward with the moving ground water.

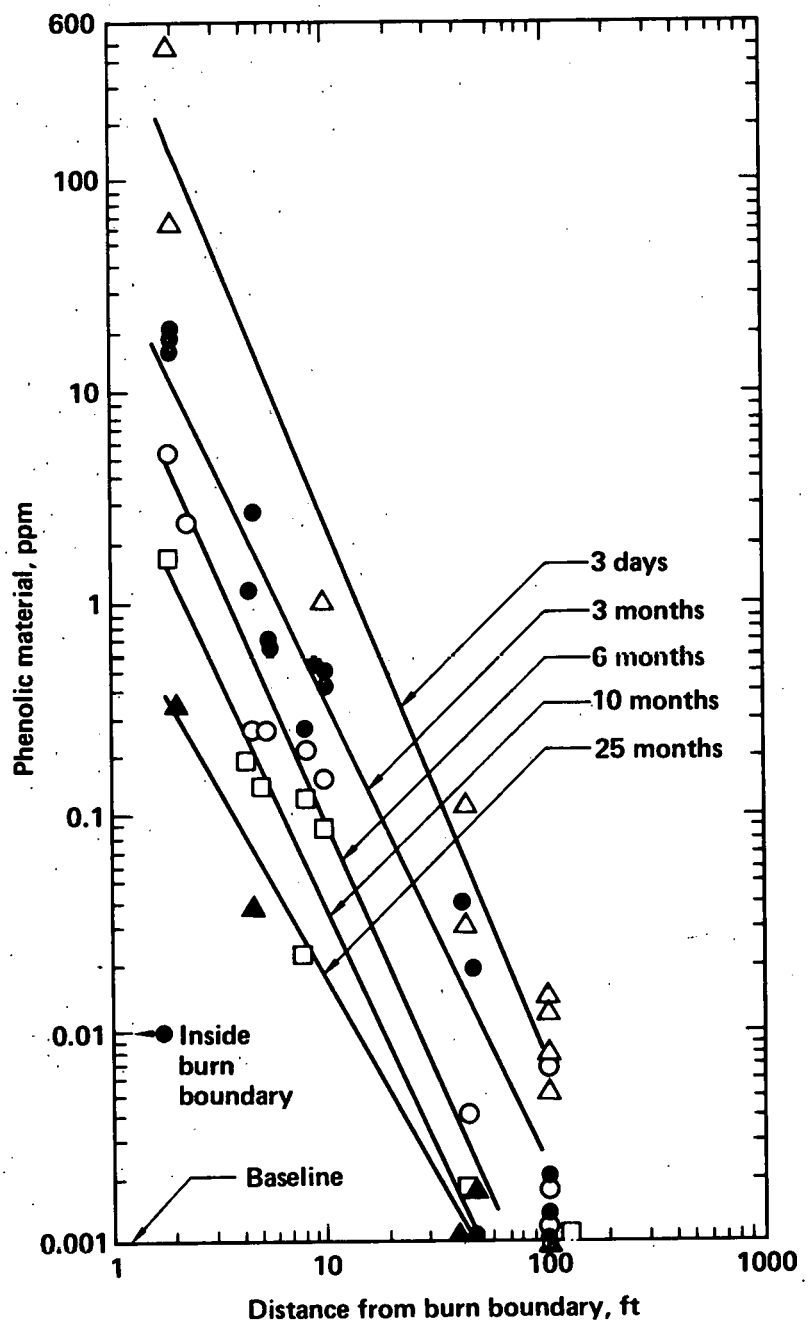


Figure 2. Concentrations of phenolic materials in the ground water as a function of distance from the nearest burn boundary of the Hoe Creek I gasification experiment. Times are measured from the end of gasification. The sampling wells are completed in the gasified coal seam, and located in various directions from the gasification zone.

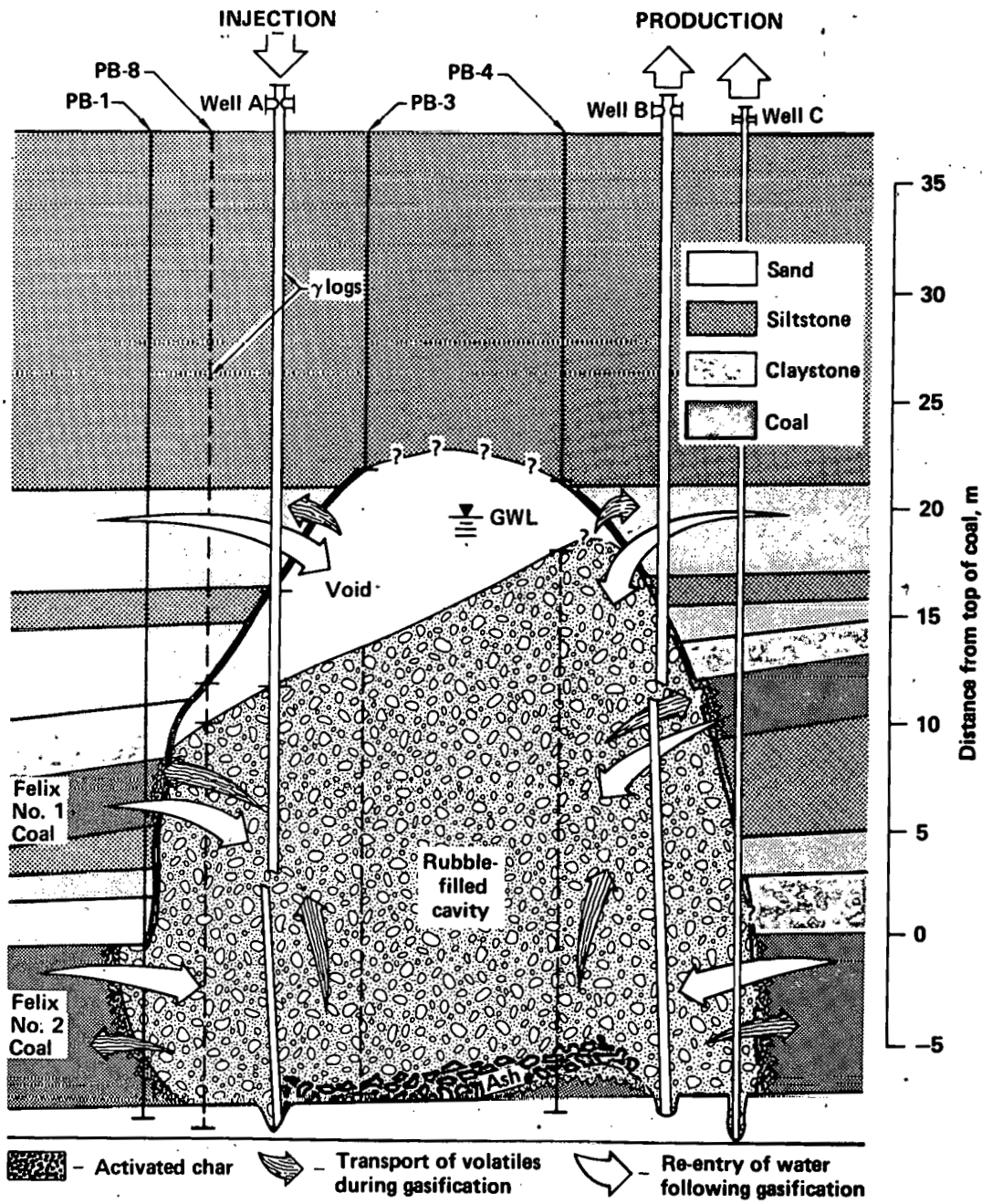


Figure 3. Inferred shape of the Hoe Creek II gasification cavity on the basis of post-burn coring and logging investigations. Roof collapse and gasification of the overlying Felix No. 1 Coal contributed to the vertical extension of the cavity.

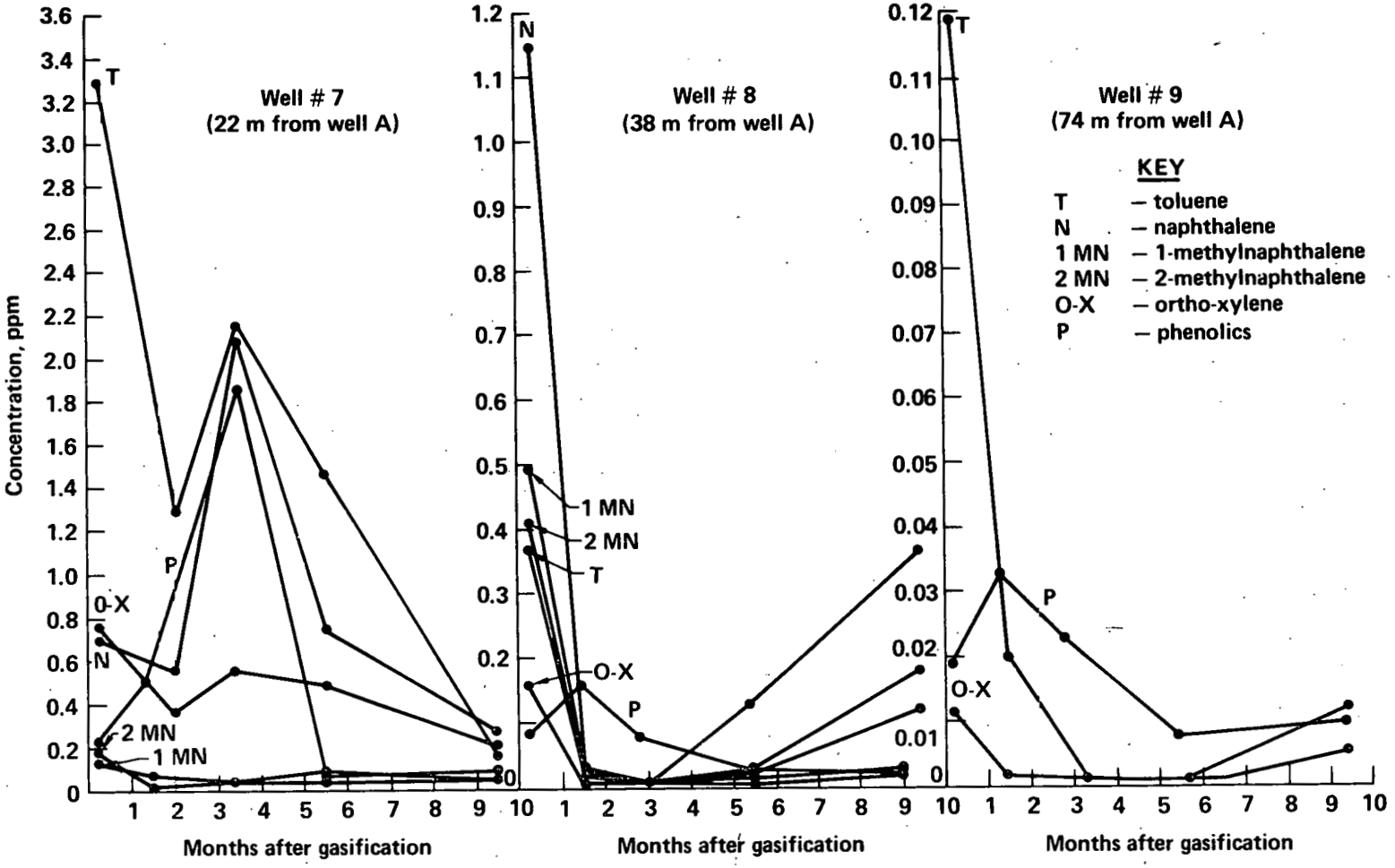


Figure 4. Changes in the concentrations of aromatic hydrocarbons and phenols as a function of time in three wells near the Hoe Creek II gasification experiment.

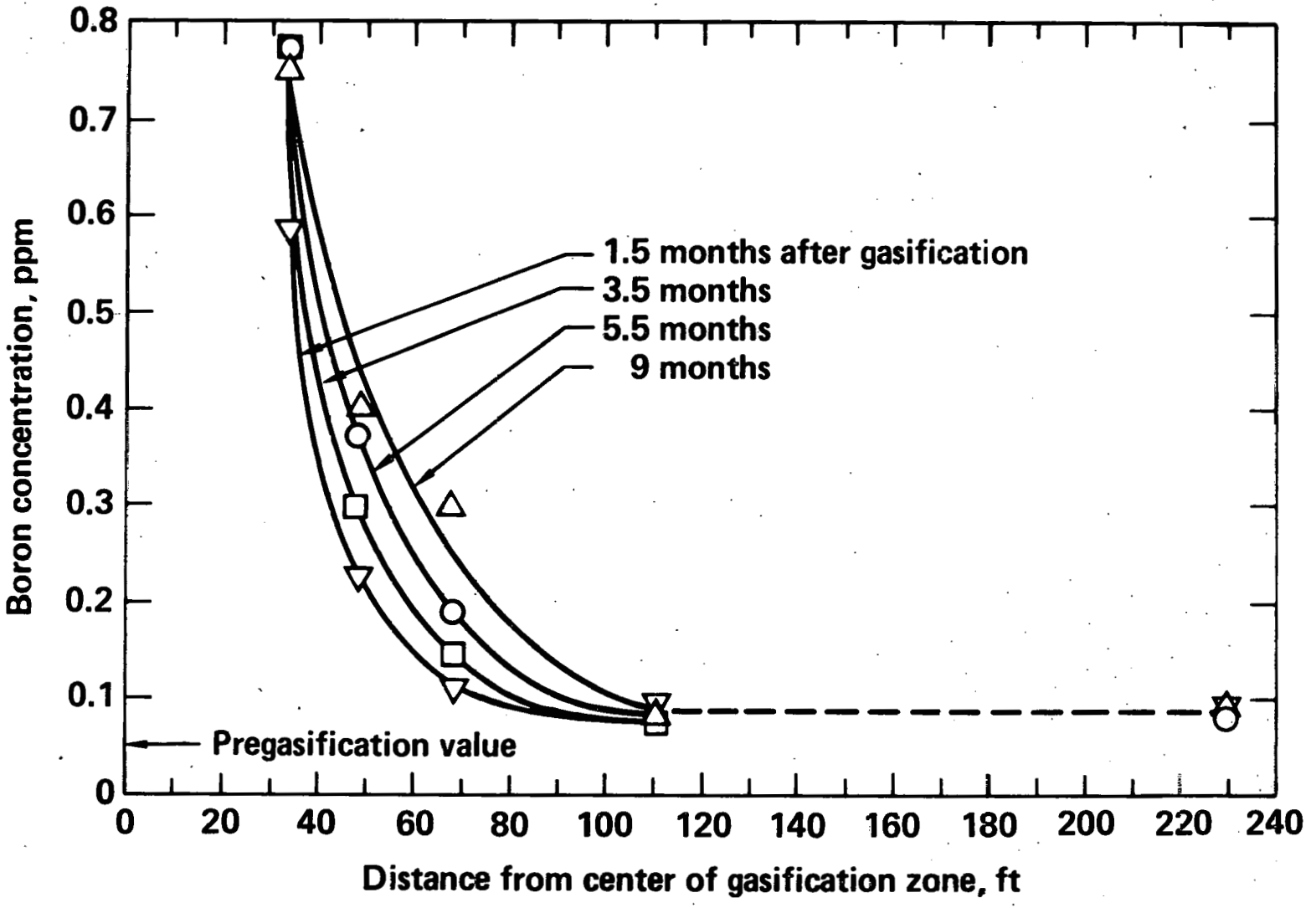


Figure 5. Changes in the boron concentrations measured in ground-water samples obtained near the Hoe Creek II gasification site.

Another interesting feature of the contaminant distribution that resulted from the Hoe Creek II and III experiments is the fact that the highest phenol concentrations occur in the overlying Felix No. 1 Coal seam. This may be because the hydrostatic pressure within the Felix No. 1 Coal is less than that in the underlying Felix No. 2, and the cavity gas pressure is therefore more effective in driving vaporized contaminants out into the Felix No. 1 Coal seam.

ENVIRONMENTAL CONTROLS

We have begun an investigation aimed at identifying effective and economically feasible methods for controlling or mitigating ground-water quality changes caused by UCG. Our investigation has included laboratory studies to assist in evaluating the effectiveness of promising control technologies. It is important to remember that natural controls - in particular, ground-water cleansing by the surrounding coal - and UCG operational restrictions are likely to play a major role in the control and limitation of ground-water contamination.

An essential prerequisite to the development of meaningful ground-water controls is a knowledge of the applicable water quality standards. The task is complicated by the broad range of organic and inorganic products that are found in the ground water as a result of underground coal gasification (Table 1). Furthermore, the water quality standards themselves are certain to change with increased understanding of the environmental significance of coal gasification by-products. In an effort to provide a tentative basis for control technology development, we have assembled in Table 2 a listing of water quality standards as specified by the Environmental Protection Agency and the Wyoming Department of Environmental Quality. We have also listed some recommended values that may provide insight concerning future regulations.

Operational Limitations and Natural Controls

We are beginning to recognize operational characteristics of the UCG process that affect contaminant dispersal and that may be altered so as to limit contamination - often with advantageous effects on process economics. For example, the extent of contaminant deposition that results from product gas escape is, in part, dependent on cavity pressure. By keeping cavity pressure as low as possible, consistent with the need to restrict ground-water influx, it should be possible to limit the initial dispersal of gaseous contaminants, as well as the loss of valuable product gases.

Site selection criteria that preclude weak overburdens and nearby aquifers may also be beneficial - if not essential - in achieving successful process operations and effective limitations on contaminant migration.

The principal natural control that restricts ground-water contamination is the sorption by the coal surrounding the gasification zone. Our ground-water monitoring studies suggest that coal effectively sorbs many of the contaminants introduced by the UCG process.

Table 1

Ground-Water Contaminants that Increased Following Gasification at Hoe Creek Sites[5]
(Listed in approximate order of abundance.)

Organics

Volatile Hydrocarbons:	methane, ethane, ethylene, propane
Aromatic Hydrocarbons:	benzene, touluene, C_2-C_4-benzenes, napthalenes, 3- and 4-ring aromatics, indans
Organic Acids:	phenol, alkylphenols, naphthol, alkylnaphthols
Organic Bases:	pyridine, methyl pyridine, C_2-C_4-pyridines, aniline, indolines, quinolines, isoquinolines
Saturated and Cyclic Hydrocarbons:	n-alkanes, branched alkanes, cyclic alkanes
Unsaturated Hydrocarbons:	olefins

Inorganics: boron, flouride, bromide, chloride, lead, lithium, sulfate, manganese ammonia, sodium, sulfide, thiocyanate, iron, calcium, cyanide, barium, potassium, magnesium

It is important to consider the mechanisms that appear to be involved in various kinds of coal sorption. The coal network is generally assumed to be formed from small aromatic units held together by short cross-linkers - mainly methylene, but also including ethytene, propylene and ethers. A coal particle appears to act like a sponge. It is permeated by large and small fissures or pores (from a few tenths to 10 nm) that are more or less accessible to small molecules such as ammonia and low molecular weight hydrocarbons. Most of these volatile materials are trapped in the pores of the coal and are not actually chemically bonded[12]. In the case of small pores, the foreign molecules are able to enter them only at high temperatures and pressures, but are trapped therein upon cooling. Larger pores permit unrestricted entrance and exit of molecules, but other sorption processes may occur.

We have conducted preliminary laboratory studies on the sorption capacities of coal[13]. However, there are difficulties in duplicating the two geologic colloid systems that appear to exist underground (gas in solid phase and liquid in solid phase). The sorption of gas or vapor by coal can be described by the Langmuir isotherm[14], whereas the sorption from solution by coals is

TABLE 2

Water Quality Standards and Recommendations (Future)

Contaminant	EPA Requirements (ppm) (Future - Present)	Wyoming DEQ Requirements (ppm) (Domestic - Livestock)
Phenols	0.001 - 9.5	0.001
Carboxylic acids	? - 100	--
Organic bases	0.1 - 10	--
Polynuclear bases	10^{-5} - 10^{-3}	--
Polynuclear aromatics	10^{-6} - 10^{-3}	--
Polynuclear aromatic hydrocarbons	10^{-6} - 10^{-3}	--
Oil and Grease	1 - 10	10.0
Organic Sulfur	.1 - 10	--
Endrin	? - .0002	--
Lindane	? - .004	--
Methoxyclor	? - .1	--
Toxaphene	? - .005	--
Chlorophenoxys	.01 - .1	--
BOD	10 - 30	--
COD (State & Municipal)	30 - 500	--
CCE	0.3 - ?	
CAE	1.5 - ?	
Inorganics		
Ammonia (NH_3)	0.5 - 10	0.5 - ?
Sulfide ($S^=$)	.03 - 0.3	
Carbonate ($CO_3^=$)	--	
Cyanide (CN^-)	0.02 - 0.2	0.2 - ?
COS	--	
SCN^-	--	
Fluoride (F^-)	1.4 - 2.4	1.4 - 2.4
Cadmium (Cd)	.001 - 0.01	0.01 - 0.05
Chloride (Cl^-)	250 - ?	250 - 2,000
Aluminium (Al)	--	- 5.0
Copper (Cu)	1.0 - ?	1.0 - 0.5
Hydrogen Sulfide (H_2S)	--	0.05 - ?
Iron (Fe)	0.3 - ?	0.3 - ?
Manganese (Mn)	0.05 - ?	0.05 - ?
Sulfate ($SO_4^=$)	250 - ?	250 - 10,000
Uranium (U)	--	5.0
Zinc (Zn)	5.0 - ?	5.0
Cobalt (Co)	--	? - 1.0
Mercury (Hg)	0.0005 - 0.002	0.002 - 0.00005
Arsenic (As)	10^{-6} - 10^{-3}	0.5 - 0.2
Silver (Ag)	? - 0.05	0.05 - ?
Selenium (Sc)	.001 - 0.01	0.01 - 0.05
Lead (Pb)	.005 - 0.05	0.05 - 0.10
Boron (B)	0.5 - 2.0	.75 - 5.0
Barium (Ba)	? - 1.0	1.0
Chromium (Cr)	? - 0.05	0.05
Nitrate (as N)	? - 10.0	1.0 - 10.0
Total Dissolved Solids	500 - 5000	500 - 10,000
Color - Turbidity	1.0 NTU	
Odor	Insignificant	
Coliform Bacteria	four/100 ml	
Ph	6 - 9 s.u.	6.5 - 8.5 s.u.
Ames test for Mutagenicity	Negative	
SAR	8	8
RSC	1.25 meq/l	1.25 meq/l
Combined Total Radium - 226 and Radium - 228	5 pCi/l	5 pCi/l
Total Strontium	8 pCi/l	8 pCi/l
Gross alpha particle radioactivity	15 pCi/l	15 pCi/l
Tritium	20,000 PCi/l	--

References: (7), (8), (9), (10), (11)

best described by the Freundlich isotherm[14]. The main difference is that sorption of gases and vapors onto solids is primarily a function of temperature and pressure, while the sorption capacity of solids from solution depends upon the pH of the solution, concentration of the solute, contact time, and competition adsorption reactions between species. Although we have measured, in the laboratory, the sorption of many ground-water contaminants in solution on granular coal at pH 7, we have not yet been able to predict absolute sorption characteristics under field conditions[13]. In many geologic colloid systems, such as coal, adsorption is expected to play a significant role. It is also important to consider the rate at which desorption takes place. Desorption depends upon many factors including changing solution characteristics and the type of adsorption process that occurred initially. Furthermore, thermodynamic equations demonstrate that if adsorption occurs from a solution, the surface excess (number of adsorbed layers) increases with increasing concentration of the adsorbate in solution. If the adsorption occurs from the gaseous phase, the surface excess increases with increasing partial pressure of the adsorbate[14].

The outstanding ability of activated carbon to adsorb various organics and inorganics from solution is well known[12]. Our recent laboratory experiments have shown that bituminous coal is the best source of activated carbon for the removal of organics that are present in the ground water affected by UCG operations. The first step in the production of activated carbon is the formation of a char from the source material (carbonization). This is accomplished by heating the source material (usually in the absence of air) to a temperature that is sufficiently high to dry and volatilize substances in the carbon[12]. To increase the surface area, the carbon is then activated by the action of oxidizing agents such as steam, air or CO_2 at elevated temperatures. This results in the development of an extremely porous structure and an extensive internal surface area with much greater adsorption capacity. The adsorptive properties of the finished product depend heavily on the oxidizing gas, its concentration and the temperature during oxidation.

Since activated char is formed during the gasification process[15], it may be possible to provide increased adsorption capabilities in the surrounding coal by promoting the formation of this uniquely effective adsorbent. The experiment at Hoe Creek I used explosive fracturing to enhance permeability prior to gasification. This may have provided additional surface area for activation, thereby leading to the formation of more highly activated coal surfaces. In fact, contaminant levels have decreased most conspicuously at Hoe Creek I (compared to Hoe Creek II) but there are many other factors that could equally well account for the observed differences. Nevertheless, the possibility of providing increased adsorption through special activation procedures deserves further consideration.

Supplementary Control Measures

If a combination of process controls and sorption by the surrounding coal proves inadequate for effective control of ground-water quality, then supplementary measures will need to be implemented. There are three approaches that can be explored: (1) minimizing contaminant transport (2) external removal of contaminants or (3) converting contaminants to innocuous

substances. We have begun to evaluate possible control technologies that could be both effective and economically feasible. Figure 6 suggests the steps involved in assessing potential cleanup techniques. Much of the required information is already available to us as a result of our ground-water sampling investigations.

Our current investigations include a consideration of conventional water treatment methods which involve pumping the contaminated water to the surface. If pumping can be initiated soon enough after gasification - before the normal ground-water flow has extended the region of contamination - it may be possible to create a flow pattern that prevents further contaminant dispersal. Preliminary estimates suggest that reasonable pumping capabilities (less than 100 gpm) may be adequate. Although this approach seems straightforward, we are uncertain of its ultimate effectiveness - primarily because slow desorption of residual contaminants may prolong the effective lifetime of the contaminant source. Experiments designed to provide an estimate of this effect are under consideration. Of course, chemical additives might hasten the desorption process. In any case, it must be remembered that a combination of several techniques may be most effective.

We are presently involved in process feasibility and engineering design studies to determine system effectiveness and cost economics for ground-water treatment in connection with large scale UCG operations. We are evaluating a combination of conventional wastewater treatment techniques, as well as some possible in situ methods (Fig. 6). In situ treatment might involve oxidation, ozonation, biological, chemical or containment methods. We have contracted with both National Technical Services (NTS), Corvallis, Oregon, and NUS Corporation of Pittsburgh, PA to develop design criteria and cost estimates for conventional treatment methods that may be applicable to UCG operations. We have conducted laboratory jar tests and bench scale studies (involving Hoe Creek water samples) in collaboration with NTS. The techniques studied included activated carbon adsorption, wet-air oxidation, aeration and ozonation. Our results suggest that certain powdered activated carbons in appropriate amounts are effective in removing problem organics. As indicated previously, activated carbon prepared from bituminous coal was found to be the most effective adsorbent. Total organic carbon concentrations were reduced to <0.1 ppm in Hoe Creek water samples whose initial TOC values were ~75 ppm. Concentrated synthetic solutions made up in Hoe Creek water using typical contaminants and having TOC concentrations of about 280 ppm were lowered to <10 ppm in these bench scale studies. Aeration and ozonation were found to be effective preliminary treatments and might be incorporated into the system design, since air and oxygen are both available on site. A preliminary design for surface treatment of UCG-contaminated ground water is indicated in Figure 7. Note that carbon regeneration is involved. It is of interest that some treatment methods which have been considered too costly to be used in conjunction with surface gasification may be cost effective when applied under the conditions that prevail during UCG operations. The disposal of treated water may involve reinjection or, possibly, repeated use in continuing gasification process operations.

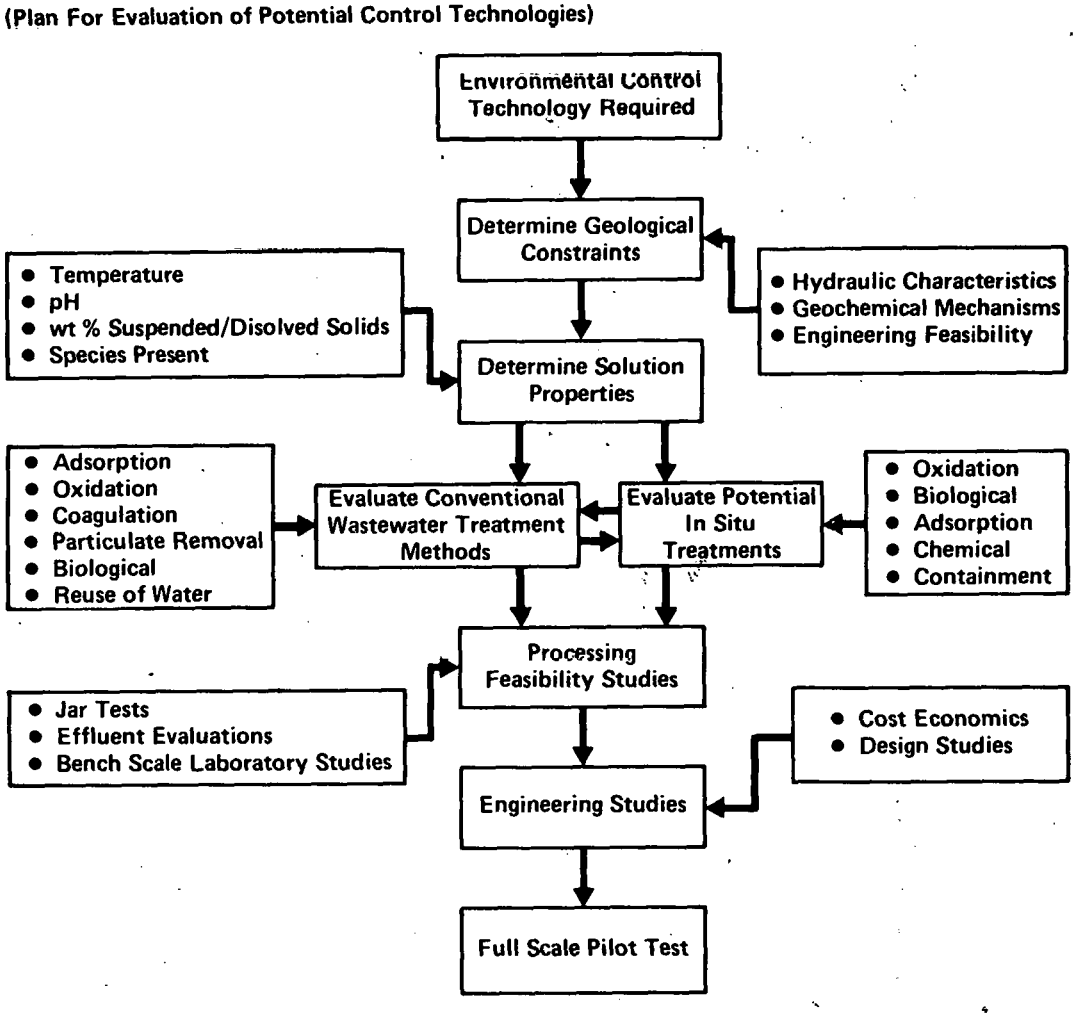


Figure 6. Flow diagram suggesting the methodology necessary to evaluate environmental control technologies that may be applicable to ground-water quality changes resulting from underground coal gasification.

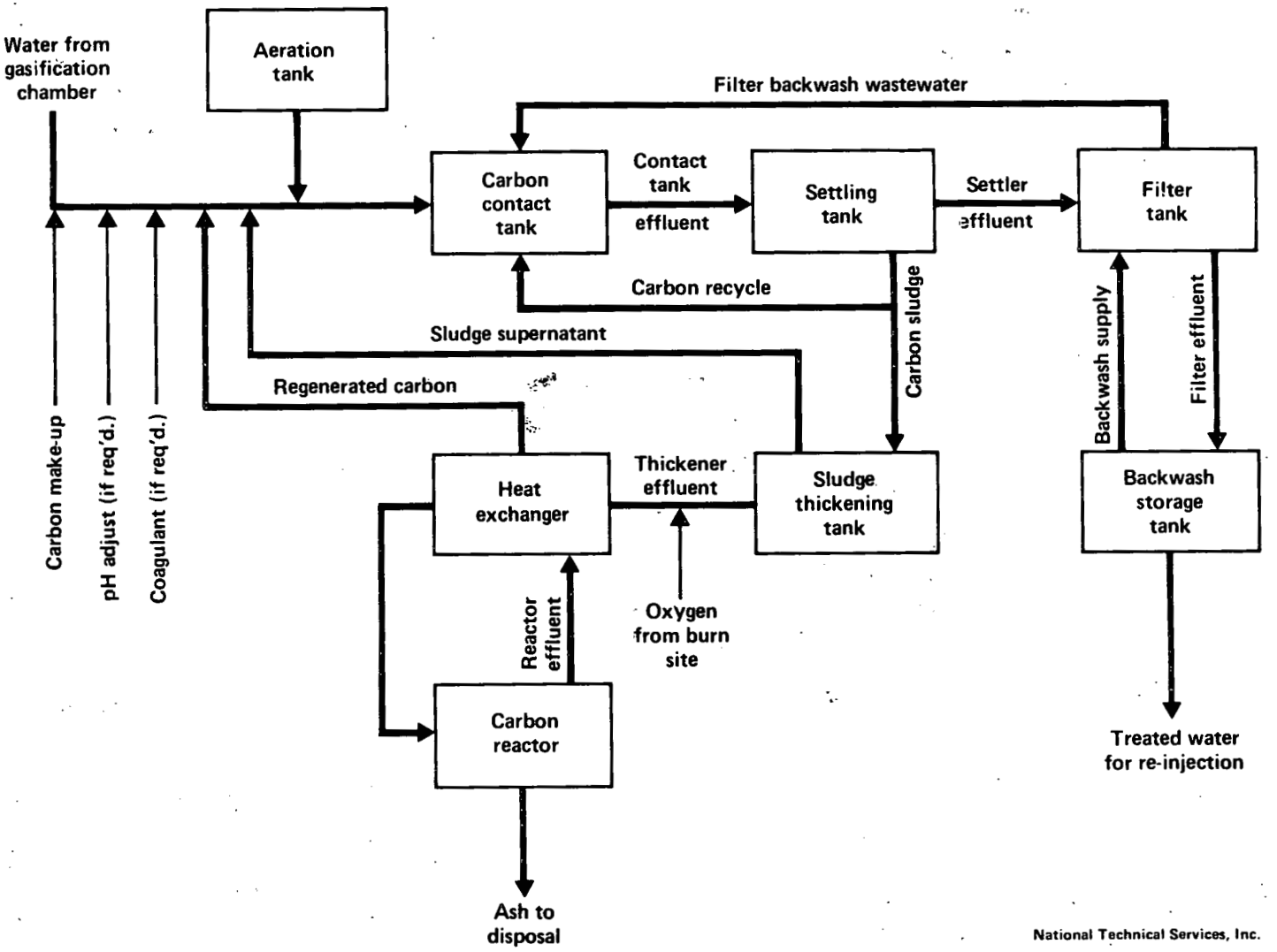


Figure 7. Schematic representation of a possible wastewater treatment facility for surface cleanup of ground waters affected by UCG operations. This system, designed by National Technical Services, Corvallis, Oregon, utilizes activated carbon adsorption.

In summary, we emphasize that underground coal gasification is a promising technology that may provide an important contribution to our needs for clean, easily transportable fuels. To insure that UCG development is not unnecessarily delayed, it is imperative that significant environmental effects be anticipated. Our studies show that a broad range of organic and inorganic contaminants are introduced into the ground water, but that most of these are substantially reduced and circumscribed as a result of sorption by the surrounding coal. In recognition of the possibility that coal cleansing and operational limitations may be judged inadequate, we are evaluating the cost and effectiveness of various ground-water restoration methodologies.

ACKNOWLEDGMENTS

The extensive program of ground-water quality sampling and analysis at Hoe Creek - which forms the essential basis for our efforts to develop effective control technologies - is carried out under the supervision of Francis T. Wang and Daniel H. Stuermer. We are also grateful to Harold Ganow for the geotechnical measurements and post-burn coring investigations, and to Randolph Stone for measurements and interpretations of the hydrologic regime at Hoe Creek.

Robert E. Thompson, National Technical Services, Corvallis, Oregon, has been of considerable assistance in our efforts to evaluate current water treatment techniques and explore unconventional technologies that may be appropriate for restoring ground water that has been contaminated by UCG operations.

Finally, it is a pleasure to acknowledge the continued support and assistance provided by Douglas R. Stephens, Project Director for LLL's In Situ Coal Program.

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ANTHRACITE MINING: ENVIRONMENTAL CONSIDERATIONS PAST, PRESENT AND FUTURE

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INTRODUCTION

There are some indications that low sulfur Pennsylvania anthracite may once again play a larger role among national and world energy sources. Previously it was the main source fueling the American industrial revolution. The exact nature of its new role is not clear, but some developments have occurred, and certain trends are beginning to develop.

Due to anthracite's unique geology, conventional anthracite mining has associated costs which contribute to competitive marketing disadvantages, particularly when compared to bituminous coal. Traditional anthracite mining methods have unique environmental considerations. New or expanded markets, to be more competitive, require improved mining methods which also have unique environmental problems and solutions. Any of these mining methods must interact with the Region's abandoned mine conditions and current laws/regulations.

ACKNOWLEDGEMENTS

Berger Associates is currently providing anthracite program support services[1] to the Division of Anthracite, Office of Coal Supply Development, Resource Applications, U.S. Department of Energy (DOE). The work is under the direction of Dr. Jerry Pell, C.C.M., Director of the Division of Anthracite. Our tasks presently consist of:

1. Preliminary assessment of the 1977 Federal Anthracite Task Force Recommendations.

2. Impact of the NSPS exemption for anthracite-fueled electric utility steam generating units.

3. Inventory of Federally-funded current anthracite projects and programs.

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[1]Contract DE-AC01-79 RA 20005.

WHERE AND WHAT IS ANTHRACITE?

All of the reported output of anthracite in recent years has been from the northeastern Pennsylvania Region, although smaller amounts are located in Virginia, the Narragansett Basin and elsewhere. According to the U.S. Geological Survey, 96 percent of the estimated domestic reserves of anthracite are located in four geological fields of the Region ---- Northern, Eastern Middle, Western Middle and Southern.

In 1975 Berger Associates completed a comprehensive study of anthracite for the Department of Interior, Bureau of Mines[1]. As part of this study we made a basic analytical study of the remaining Pennsylvania anthracite resources, and estimated this to be 17.4 billion tons. This independent estimate appears to be reasonable since the U.S. Geological Survey had previously estimated 18.4 billion tons (1945), and the Pennsylvania Bureau of Topographic and Geologic Survey, 16 billion tons (1970). The recoverable reserves have been estimated by others at 7 to 8 billion tons.

Since the 1960's anthracite has generally been ignored, especially in the research and development area ---- until some recent activity. It suffers from what can be called the "one percent syndrome"; it is only one percent of the national coal resources. However, 7 to 8 billion tons of recoverable coal is still a lot of coal, located as it is within 150 miles of 1/8 of the population of the United States. This amount of coal represents 200 quads of energy. It should not continue to be ignored.

To the above reserves should be added 910 million C.Y.[2] of surface coal refuse in some 860 banks covering 12,000 acres in the Region. The coal content of these banks ranges from 10 to 50 percent with a conservative figure being 20 percent, since the material consists of breaker refuse, silt, mine refuse, tunnel rock and combinations thereof. Conversion to a tonnage basis indicates approximately 230 million tons of recoverable coal.

Anthracite is a high rank, high fixed carbon, low sulfur coal with a relatively high ignition temperature. The definition of anthracite varies throughout the world, but ASTM defines it as a nonagglomerating coal having more than 92 percent and less than 98 percent fixed carbon, 8 percent or less and more than 2 percent of volatile matter, as measured on a dry, mineral-matter-free basis. Anthracite's inherently low sulfur content should be viewed favorably in light of the environmental benefit derived from the use of fossil fuels which exhibit this quality.

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[1] Evaluation of Mining Constraints to the Revitalization of Pennsylvania Anthracite, NTIS No. PB 242 580/AS, March, 1975, 336 pp.

[2] McCartney, James G. and Whaite, Ralph H., Pennsylvania Anthracite Refuse - A Survey of Solid Waste from Mining and Preparation, Bureau of Mines, IC-8409, 1969, 77 pp.

ANTHRACITE RELATIVE TO THE NORTHEASTERN UNITED STATES

In the current energy situation anthracite is important because it is geographically located near the densely populated and highly industrialized northeastern region of the United States. Stated in other terms the ten northeastern anthracite counties of Pennsylvania are located near a potentially large market which is now heavily dependent on oil, much of it imported. In 1974 the New England area depended on oil to produce approximately 60 percent of their total electrical output, while the New York-New Jersey area used oil to produce 50 percent of its electrical needs.

The EPA New Source Performance Standards (NSPS) for new power plants, issued June 11, 1979, exempted anthracite from the percentage reduction requirement of the SO_2 standard, except for the previous ambient standard of 1.2 lbs SO_2 per million BTU. Anthracite is also subject to all other provisions of the NSPS, including particulate matter and NO_x standards[1]. The preamble to the NSPS Regulations states that the exemption from the percentage reduction requirement of the SO_2 standard was granted by the EPA Administrator based on conclusions that the higher SO_2 emmissions were acceptable because of the other environmental improvements that will result. Some of these are discussed in this paper. EPA's action has caused a number of utility companies, both within the state and outside the state, to at least take a closer look at anthracite. Many of these companies would not have otherwise done so.

CURRENT MINING LAWS/REGULATIONS AND THEIR RELATIONSHIP TO ANTHRACITE MINING AND THE ENVIRONMENT

Historically under Pennsylvania State law, there has been two sets of mining laws relative to bituminous and anthracite coal mining, principally because of the unique geologic and mining characteristics of the coals ---- one lying essentially level and the other steeply pitched.

The Federal Coal Mine Health and Safety Act did not take this into consideration and resulted in a single law with some regulations that were unrealistic for the anthracite deep mining industry. The industry has generally admitted that they were not represented to provide input to the Bill at critical times. While this Act had some detrimental effects it was by no means the sole reason for the near demise of the anthracite deep mining industry, accounting as it does for less than 10 percent of current production. There were many reasons for this decline, not the least of which was the trend to cheaper surface mining as in bituminous coal mining.

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[1] 40 CFR Part 60, 44 FR 33590.

The above was not the case with the Federal Surface Mining Control and Reclamation Act of 1977. The unique features of anthracite mining are considered. Section 529 of that law pertains to anthracite mines, and authorizes acceptance of the environmental protection performance standards of the State regulatory program, in lieu of the environmental performance standards (Section 515 and 516) of the Federal Act. Sections 509 and 519 are applicable except for specified bond limits and period of revegetation responsibility. All other provisions of the Act apply and must be reflected in the State's regulatory program. The Secretary of the Interior shall also issue such additional regulations as necessary, and shall report to the Congress biennually on the effectiveness of the State anthracite regulatory program; hence the Office of Surface Mining (OSM) still has oversight authority.

Pennsylvania's Act 147, the 1971 Surface Mining Conservation and Reclamation Act, was the first State legislation to regulate both anthracite and bituminous coal mining. Along with the Pennsylvania Clean Streams Act and the Coal Refuse Disposal Act, this Act basically controls the environmental performance standards for anthracite mining. These three Acts are included in a bundle of five which are in the process of being amended by the Pennsylvania Legislature to gain primacy under the Federal Surface Mine Act. The State mining law provides for reclamation by contouring (approximate original contour) as well as terracing. The latter must be approved by the State Regulatory authority. It limits the highwall to 35 degrees, instead of the maximum 20 degrees in the Federal law, P.L. 95-87. The table portion of the restored area is required to be a relatively level terrace without depressions to hold water. This reclamation method is applied in the anthracite region, although quite a bit of approximate original contour (AOC) is practiced too, expecially in basin-type mining where all of the coal is normally taken. The allowance of 35 degree maximum slopes takes recognition of such factors as: (1) the bottom rock from which the coal is removed is often 70± degrees, or more (2) spoil material for reclamation backfill may be deficient where past surface mining has occurred (double and even triple casting of spoil material to the side by dragline was not unusual), and (3) relative depth of mining on the pitch compared to the smaller lateral movement.

EFFECT OF CURRENT RECLAMATION LAWS/REGULATIONS ON FUTURE ANTHRACITE SURFACE MINING

Over the span of years, equipment, methods and market changes effect stripping ratios in surface mining. With the advent of larger equipment availability operators often reaffect an area by second and even later third cuts to greater depths ---- especially from pre-law open face highwalls. However, under current laws and regulations it becomes imperative to extract the maximum reserves in current and future mining areas. Because of the pitch of the coal (70± degrees is not uncommon in the Southern Field), reaffecting a reclaimed area in subsequent years by deeper stripping may require such expensive handling of

spoil material as to make the operation uneconomic. Therefore, it becomes more imperative that surface mining recover the maximum amount of resource. This adds importance to the deep moving pit mining concept, described below.

DEEP MOVING PIT MINING CONCEPT AND ENVIRONMENTAL CONSIDERATIONS

Although a number of engineering studies have been performed on this concept, more engineering is continuing (see attached illustrations). It does appear that the large scale of this type of mining presents no mining problems that cannot be solved. In fact the concept is really not new since very similar open pit mining is already being practiced to considerable depths by Reading Anthracite Company and Bethlehem Mines Corp. Another firm is considering it.

Several analogies to this concept are frequently mentioned which, in fact, are not directly applicable. The first of these, for example, is the Kennecott Copper-type of ore mining operations in the west. The expanse at the ground surface in ore mining increases as the mine pit goes deeper. This contrasts with the moving deep pit concept which follows the outcrop of the multiple coal veins, and has a relatively uniform depth of, say, 800± feet.

Secondly, an analogy is often made to the open pit mining as practiced in West Germany and East Germany. This does have similarities since it is a moving deep pit, except it is in so-called brown coal, or lignite, and the overburden is relatively shallow and friable. Hence large bucketwheel excavators are used which are impractical in the dense conglomerate found in anthracite overburdens.

Alternative production techniques considered in deep moving pit mining involve dragline/loader/truck, shovel/truck, shovel/dragline/truck, or shovel/conveyor methods with appropriate benching. Some problems can be expected, most of which have environmental considerations. These include final cut reclamation. A working base of 600 to 800 feet is required in the bottom of the pit. Since the pit may eventually move a number of miles, obtaining material for reclamation of this final cut may pose a problem.

Another costly problem will be the pumping, handling and treatment of large volumes of water at depth. Any type of anthracite mining cannot be discussed without addressing the problems of water ---- a perennial problem to operators. However, several of the largest operators are now handling and treating large amounts of water within the economic constraints of similar open pit mining. Because of the large volumes of water to be encountered in deep moving pit mining, it may be advantageous to consider trying to transform the water problem from a negative factor to a plus. This might include hydraulic hoisting from the pit and hydraulic transport to the nearby generating plant, providing

sufficient coal volumes can be attained to make this a viable operation. Whether hydraulic disintegration of the coal should be considered in open pit mining vs. conventional crushing is a matter of conjecture. It has previously been shown in tests that in-place anthracite can be hydraulically pulverized at easily attainable pressures of 3000 to 5000 psi.

Other possible problems having some environmental and social consequences, include stream encroachments and restorations, highway alterations or restorations, and dwelling or possibly even village relocations. One potentially difficult problem may be the hydrologic consequences, including effects on adjacent wells and ground water quality. More will be discussed later about existing huge abandoned mine pools from past deep mining. However, deep moving pit mining would completely mine out these mine pools and their large acidic discharges. This would be a considerable benefit to the streams and people of the Commonwealth.

FEASIBILITY STUDIES OF ANTHRACITE-FIRED GENERATION PLANTS WITH EMPHASIS ON ENVIRONMENTAL MINING EFFECTS

In recent years the Pennsylvania Power and Light Co. (PP&L) engineers and a number of consultants engaged by PP&L undertook studies to determine the feasibility of an anthracite-fired power generation plant. This included an extensive drilling program. Following this initial period of study PP&L shelved the project, probably because of reduced load growth patterns and uncertainties as to the need for scrubbers. This took place prior to the EPA NSPS anthracite exemption of June 11, 1979. Since then they have announced that they will join with Allegheny Electric Cooperative Inc. in further exploring the project feasibility. The previous PP&L studies, although not entirely complete, did reach some conclusions:

- From the drilling program and reserve studies, sufficient coal is available for the life of the plant.
- Economics are greatly influenced negatively if scrubbers are required. The project is possibly economic if large scale deep moving pit mining is used, rather than traditional small operations.
- The Southern and Western Middle Fields have the most potential.
- The open pit method provides land rehabilitation while extracting much needed resources for energy production. Deep mining is out of the question because of lack of new technology, leads times, etc.
- Only one or two areas would be developed, instead of many locations. Each location would involve a pit of approximately 1/4 square mile moving over a total site of about 2 to 3 square miles with constant

reclamation as mining proceeds. The pit would be from 400 to 800 feet deep.

- The backfill can be tailored to future land use requirements with the reclamation plan fully developed in advance before the first bucket of earth is moved. This planning would be in conjunction with the adjacent communities and their land use planning.

- An anthracite plant will be able to meet the required air quality standards without scrubbers.

The EPA NSPS exemption for new power plants is causing a number of utilities, including some from adjacent states, to at least review anthracite. However, because of lagging technology developments in anthracite combustion, inherent risks, uncertain economics (for example, an anthracite-fired plant costs approximately one-third more than an equivalent bituminous plant), rail transportation and other problems, it has been difficult to translate interest into action. Because of the uncertainties and the improved economics of a mine-mouth plant, it is believed that if the concept is developed, it will be a Pennsylvania entity which first undertakes it. It is also likely that only large deep moving pit mining can provide the economies of scale for an anthracite-fired plant.

Pennsylvania State government elected officials and agencies are also interested in seeing such a market develop for anthracite. Good cooperation in this respect has taken place in the past and can be expected to continue.

ANTHRACITE MINING EFFECTS ON WATER, LAND AND AIR

Operations in the Region have been somewhat slower to fully comply with environmental mining regulations due to the high percentage of marginally profitable small operators and loss of markets, accompanied by a long steady production decline. Mine inspectors are well acquainted with the need for environmental protection and take the necessary strides within the constraints of reaffecting abandoned deep and surface mines. Recent hopeful market improvement trends have been noted along with improving compliance. Some of these emerging improved markets appear to be in export, heating fuel, and potentially in power generation and other applications. However, anthracite like all U.S. coals, remains demand limited.

Water

The phrase "water, land and air" is purposely reversed from the usual because revitalization of anthracite production must necessarily address the problems created by water. This includes, as previously mentioned, the handling, disposal and/or treatment of water. Unlike the bituminous coal industry, anthracite surface mine operators thrive on

previously deep mined coals where as much as 50 percent of the in-place coal may already have been removed. Large scale deep moving pit mining "below drainage" necessarily involves these large colliery underground mines of the past 100 years. Many of them extend to depths of 800 feet or more, approximately that planned for the deep moving pit concept. Hence large quantities of water are involved.

Present data indicate that the cessation of most underground mining has created at least 167 known mine pools. The Northern Field, in particular, is one continuous pool, more or less. The estimates of the total amount of water contained in the mine pools of the various fields are as follows:

Northern	-	262,000,000,000 gallons
Eastern Middle	-	14,000,000,000 gallons
Western Middle	-	61,000,000,000 gallons
Southern	-	38,000,000,000 gallons

In addition to the necessity to partially drawdown the static pool of any given mine pool, infiltration is a factor, although the latter can be minimized somewhat by diversion ditches and other techniques.

All of the above mine pools discharge at some point into area streams. These abandoned mine discharges are by far the major sources of acid mine drainage. In one Berger Associates' study completed in an area in the Southern Field under Operation Scarlift for the Pennsylvania Department of Environmental Resources[1], it was found that although there were nine small deep mines in the watershed, they collectively produced 8 percent of the flow and only 2 percent of the acid load of all discharges. The worst acid mine drainage pollution sources are abandoned deep mine/mine pools, coal refuse banks, and abandoned strip mines, in that order.

Because of its reduced sulfur content (0.6 to 1.2± percent), it can be generalized that acid mine drainage (AMD) from anthracite mining tends to be somewhat less acidic than AMD from bituminous mining. Assuming the absence of limestone in a given area (the Region has almost none), typical anthracite mine discharges may vary upwards to 400± mg/l of acidity, while mine discharges in bituminous regions of Pennsylvania may vary upwards to 1,000 mg/l, or more. Acidic mine discharges of 10,000 mg/l have been recorded. However, this lowered acidity associated with anthracite does not mean that streams in the Region are any less devoid of aquatic life. Deep moving pit mining, as previously discussed, could eliminate some of the large discharging abandoned mine pools ---- the principal pollution contributors to area streams. The potential hydraulic heads above mine drainage audits for

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[1]Berger Associates, Inc., Swatara Creek Mine Drainage Pollution Abatement Project - Part Two, Operation Scarlift, Pennsylvania Department of Environmental Resources, SL 126-2, December, 1972, 166 pp.

the most part are too large for mine sealing, and mine drainage treatment of abandoned sources is not a viable answer ---- it goes on essentially forever.

Land

There have been numerous estimates of the amounts of unreclaimed surface mined lands by the Soil Conservation Service, Bureau of Mines, State, and others. The recently published fourth inventory by SCS is the first ever to list this information by Counties. Of the States in the nation Pennsylvania leads the list with 240,000 acres of abandoned coal-mined land. Of this total 46,000 acres are located in the anthracite Region. For those familiar with the Region, Schuylkill followed by Northumberland County, lead the list. These two counties are located in the Southern and Western Middle Fields where the major anthracite reserves remain.

Some of this acreage will continue to be reclaimed under Pennsylvania's ten year old Operation Scarlift Program, and primarily through the emerging OSM Abandoned Mine Land Reclamation Program, with the State and SCS as cooperators. However, as in bituminous mining "second mining" under current law reaffects abandoned strip mine areas and hence achieves reclamation. Often operators reclaim more acreage than normally required. The revitalization of anthracite would do much to remove the scars of past surface mining. Considerable acreages of these open pits date to World War II mining which, of course, was pre-law surface mining.

Recovery of coal from anthracite refuse remains an important energy source with the totals included in the annual reported coal production. This source consistently ranges from 30 to 40 percent of total anthracite production. The environmental aspects of using this material can be, for the most part, positive. Since the banks are the result of pre-law mining, they are not correctable under precent surface mining legislation. When these banks were reprocessed in the past large quantities of reject material were returned to the pile. However, under current regulations a mining permit is required and reclamation can be expected for reaffected banks. This can only be beneficial as the 910 million C.Y. of coal refuse covering some 12,000 acres remains a blight on the Region, often with coal refuse banks located within towns and city limits. They are not only unsightly but often are unstable with highly erodable conditions. Many are located adjacent to streams with resulting erosion, sedimentation, and mine drainage to the streams. Almost all of the current production goes to the Pennsylvania Power and Light Co. at their Sunbury and Holtwood plants or to the UGI Corporation at their Hunlock Creek generating plant. Some of the silt material which originated from early wet processing plants is used directly by the utilities. Other coarse refuse is reprocessed leaving, say, 75 percent bony material behind, as discussed. However, currently in reclaiming the banks, the residue can be stabilized, drainage controlled, and the area reseeded.

There is an inflexibility in the law preventing "mining" of refuse within 100 feet of a stream. Normally this is a sound regulation, since it minimizes erosion and sedimentation to the stream. However, allowing the reworking of the culm bank will yield far greater long term benefits, while employing short term operator controls. Again, State law applies (Pennsylvania Coal Refuse Disposal Control Act of 1968) in lieu of the environmental performance standards of Federal Act 95-87. However, both laws have the same 100 foot restriction.

The Department of Energy (DOE) presently has planning underway, along with others, for three Atmospheric Fluidized Bed Combustion (AFBC) demonstration projects at Shamokin, Wilkes Barre and possibly Towanda, Pennsylvania. In this process a limestone or dolomite bed serves as a high temperature "host" for the anthracite culm fuel. The bed is fluidized by high velocity air currents from the bottom of the combustor which lifts the coal and limestone causing it to churn so that it behaves like a boiling fluid in suspension. The limestone in this mixture reportedly captures up to 90 percent of the sulfur released from the burning coal, negating the need for sulfur dioxide emission controls. The coal and heat of the fluidized bed are reportedly below the sinter level. Temperatures are 1500 to 1650°F compared to an average of 2700°F in burning conventional anthracite. Low temperatures also reportedly decrease considerably the formation of nitrogen oxides, another serious air pollutant produced in burning coal. Tests on culm material have been conducted at the DOE Morgantown Energy Research Center[1] and others planned at the Georgetown University FBC installation. The process does eliminate the traditional environmental problems, such as AMD, from coal refuse banks; the residue also does not have the ground and surface water contamination problems associated with SO_2 scrubber sludges. In wide industrial/commercial applications FBC could help to reduce somewhat the enormous quantities of refuse in the Region. However, very considerable ash disposal problems would still exist. Perhaps 60 percent of the material may be accumulated as ash. Low quality culm has about 3500 BTU per lb., compared to 12,500 BTU per lb. for anthracite. Therefore, three to four times as much fuel must be burned to obtain the same amount of heat value. Development of alternative utilization or disposal practices such as recovery of alumina, use in highway materials, building materials and in mining backfill would be required.

Additionally, the Bureau of Mines is reported to annually use some 3 million tons of anthracite waste in subsidence control activity, especially under the densely settled areas of the Northern Field. Use of FBC ash should be considered if the transport costs are within an economic range.

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[1] Wilson, John S. et al, Preliminary Report on Fluidized-Bed Combustion of Anthracite Wastes, Fourth International Fluidized-Bed Combustion Conference, McLean, Va., December 7-11, 1975.

Various estimates have been made of the number of years in which anthracite refuse will remain as a viable energy source. Such estimates vary widely which indicates they are risky at best. Variable factors to be considered include:

1. The many constituent sources of the refuse; each source having a relative residual coal content.

2. Highly variable coal recovery factors even within individual banks.

3. Some banks have been totally or partially reprocessed in the past.

4. Power companies supplement low quality silt material with reprocessed coarse refuse, and sometimes fresh mined anthracite.

5. Uncertain usage rates in the future for power generation, FBC and other applications.

Silt material from slurry ponds is generally screened only and delivered to power companies. Coarse refuse is generally reprocessed through a wet processing plant; the product may go to power or to industrial customers. Further, there will likely not be any anthracite refuse-fired power plants in use past the year 2000. The 1978 washery and bank production was reported by PennDER to be 1.5 million tons. Based on this rate of use and estimated energy values, it can be generalized that it may take from 50 to several hundred years to recover the energy contained in anthracite refuse, despite the fact that the quality of silt material is already declining. Using the reject material for subsidence control at the reported annual rate would not alter this estimate.

Air

The major problems associated with air pollution from anthracite mining activities are not greatly different from bituminous mining. In surface mining some problems can be created by fugitive dust emissions. Again, state law would control in lieu of the environmental performance standards of the Federal Surface Mine Act. This would include the Pennsylvania Air Pollution Control Act of 1968 and the State Surface Mining Conservation and Control Act. EPA is understood to have dropped its fugitive dust rule for surface mines.[1]

Coal refuse can create wind blown dust problems, particularly from the fine material in silt dams. The Penna. Coal Refuse Disposal Control Act of 1968 states that coal refuse disposal piles shall not be operated in such a condition that would create hazards of health and safety to the public. All actively operated banks are to be rendered unsusceptible

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[1] Coal Outlook, EPA To Drop Fugitive Dust Rule, Sept. 10, 1979.

to sliding, shifting or burning. The latter is the cause of nauseous and possibly lethal gases for nearby residents. However, the problem relates both to burning abandoned refuse banks and mine fires. The Bureau of Mines and the Penna. Dept. of Environmental Resources have been successful, supported in part by Appalachian Region Commission funds, in controlling or extinguishing a number of these fires. However, severe problems still persist because of the very large expense involved. Success has been particularly good with bank fire extinguishment since the work is not done remotely as in most mine fire control work.

SUMMARY

An estimated 200 quads of potential energy lie essentially unused within close proximity to the densely populated and highly industrialized northeastern United States. The 1917 anthracite production of 100 million tons declined to 5.7 million tons[1] last year.

There are signs of a limited renewed interest in anthracite spurred by the 1979 EPA NSPS exemption for new power plants, refinements in the deep moving pit mining concept, recent U.S. DOE studies and FBC demonstration projects using anthracite refuse, and somewhat improved export and heating fuel markets. Certain exemptions from the Federal Surface Mine Act requiring continued reliance on the State environmental protection performance standards partially provided a regulatory respite for the anthracite industry. However, anthracite like all U.S. coals, remains demand limited. A new anthracite-fired power plant in the Region, for example, would double the current production of fresh-mined anthracite.

Both traditional and improved mining techniques must interact with the Region's abandoned mine conditions and current laws/regulations. The major environmental problem relating to both active and abandoned mining involves water. Area streams have been adversely impacted chiefly by acid mine drainage discharges from abandoned deep mine/mine pools, followed by AMD sources from coal refuse banks and abandoned surface mines. The deep moving pit mining concept would entirely mine out some of these large colliery underground mines of the past 100 years ---- thus eliminating at least some large pollution contributors to area streams. A revitalization of anthracite would also do much to reclaim abandoned coal mined land, along with the ten year old Pennsylvania Scarlift Program, and the emerging OSM, SCS, and State Abandoned Mine Land Program under Title IV of the Federal Act, P.L. 95-87.

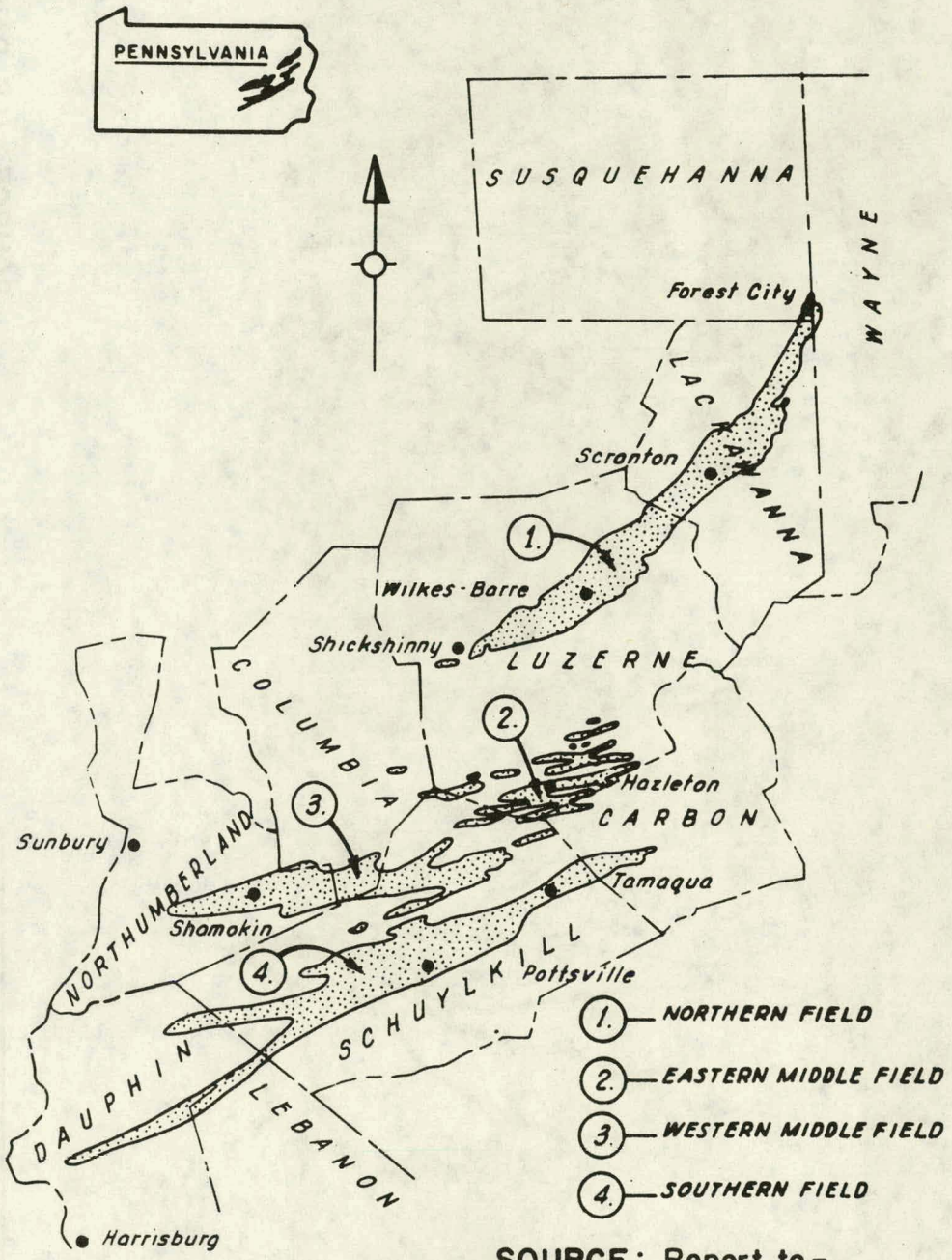
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[1] Pennsylvania Anthracite Weekly Production, Energy Information Administration, U.S. Department of Energy, January 4, 1980.

If the FBC demonstration projects are successful, they should provide a source of energy while somewhat reducing the large quantities of coal refuse from past mining. An estimated 60 percent would still remain in the form of ash, requiring new utilization or disposal practices. Continued reclaiming of coal refuse, mainly for power production, along with the use of reject material for subsidence control will also help reduce this blight on the Region.

Air pollution problems associated with active mining are not great and relate to fugitive dust in surface mining and wind blown silt from slurry ponds. More serious problems relate to nauseous and possibly lethal gases from abandoned burning mine fires and mine refuse bank fires.

ANTHRACITE FIELDS OF NORTHEASTERN PENNSYLVANIA

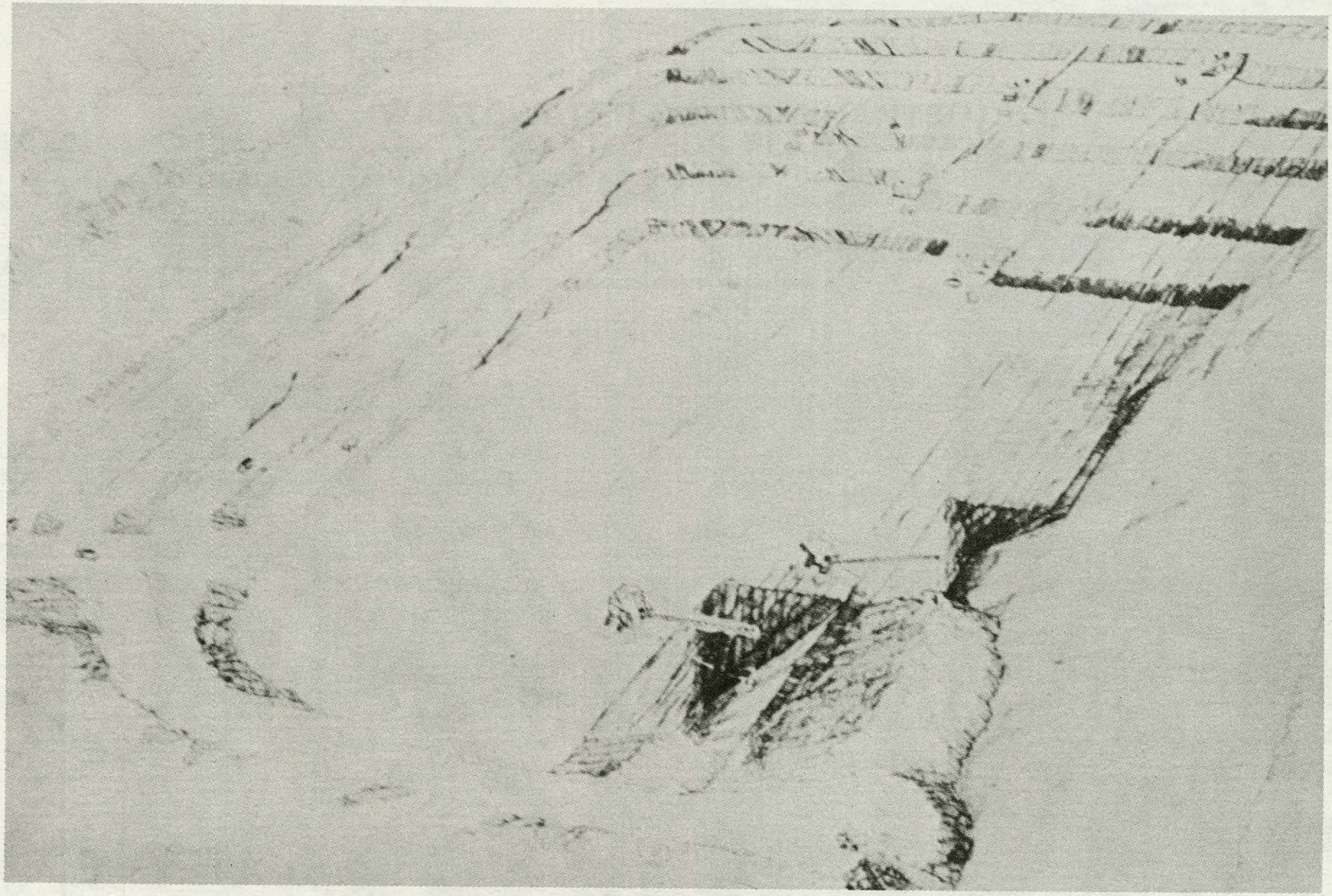


SOURCE: Report to -
U.S. Department of Interior
Bureau of Mines
By -
Berger Assoc., Inc. March, 1975



BEFORE MINING

SOURCE: U.S. Department of Interior
Bureau of Mines



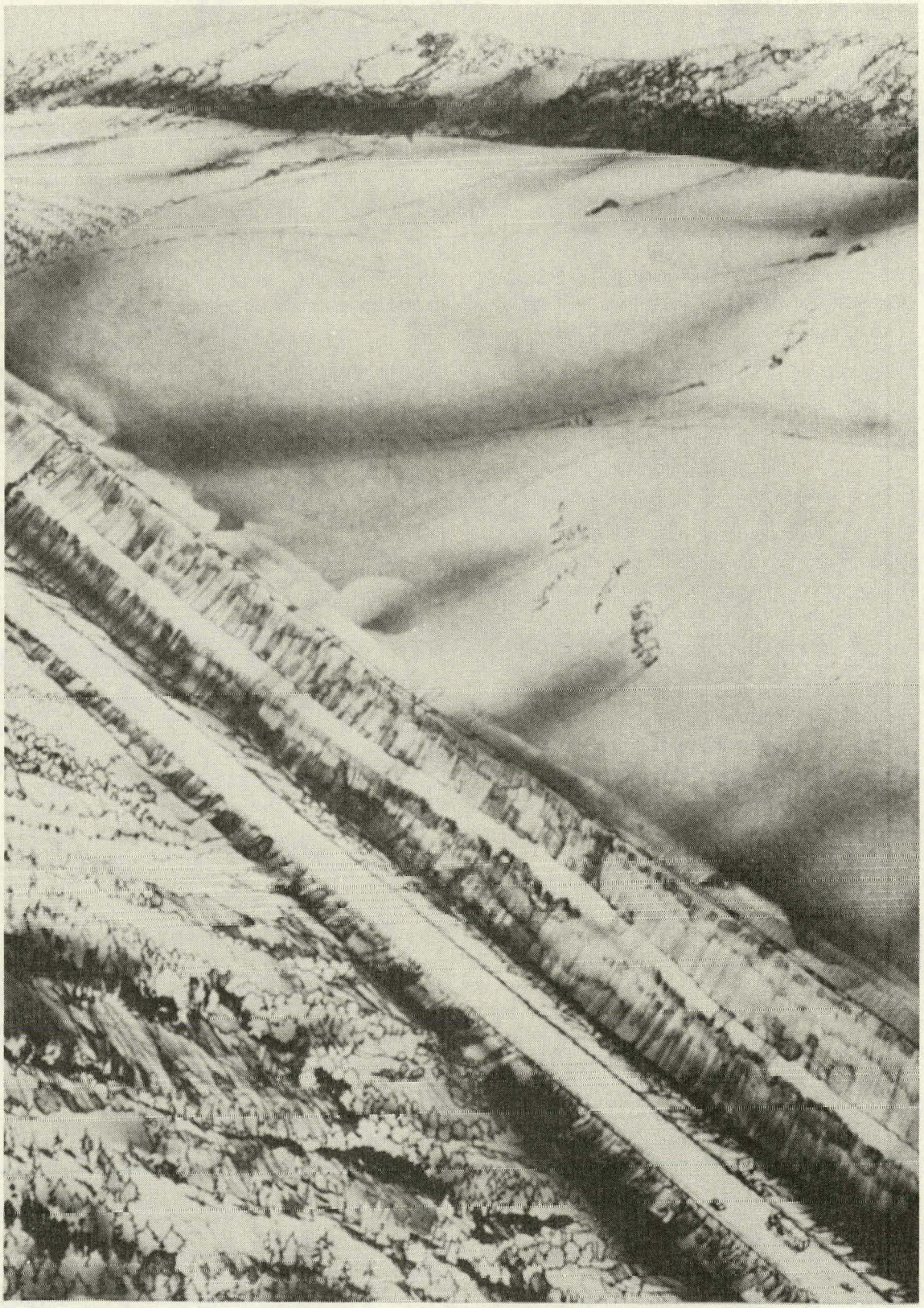
EXAMPLE OF DEEP MOVING PIT MINE

SOURCE : Pennsylvania Power & Light Co.
Anthracite Feasibility Study



DURING MINING

SOURCE: Pennsylvania Power & Light Co.
Anthracite Feasibility Study



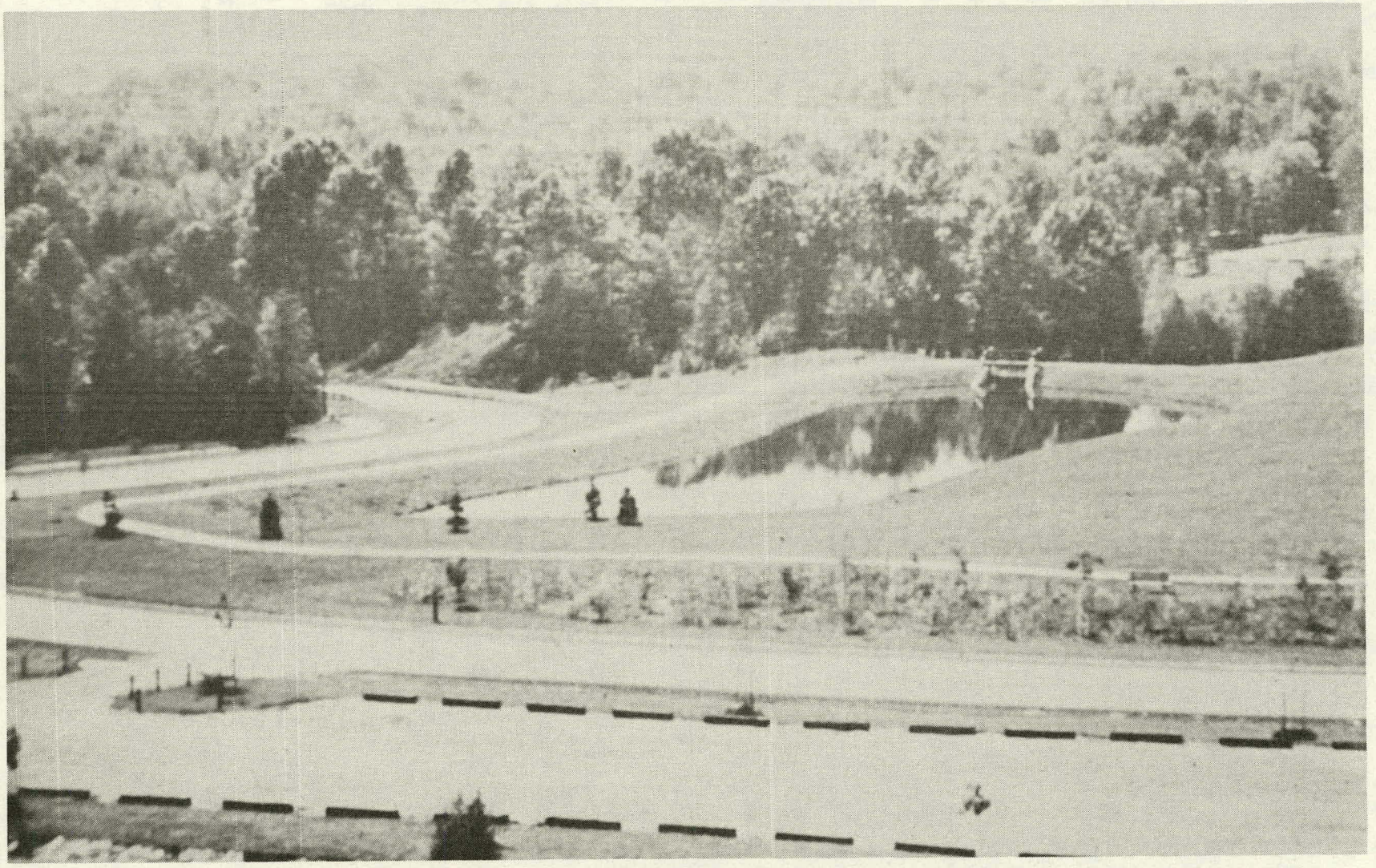
AFTER MINING

SOURCE: Pennsylvania Power & Light Co.
Anthracite Feasibility Study



AFTER MINING

SOURCE: U.S. Department of Interior
Bureau of Mines



AFTER MINING

SOURCE: U.S. Department of Interior
Bureau of Mines

SESSION 15
COAL CONVERSION. II – LIQUIDS

Chairman: J. Batchelor
Co-Chairman: M. Singer

ENVIRONMENTAL CONTROL SYSTEMS OF THE SRC-I DEMONSTRATION PLANT

by John C. Tao and A. F. Yen

Air Products/Wheelabrator-Frye Joint Venture

INTRODUCTION

The 6000 Tons Per Day SRC-I Demonstration Plant that is planned to be constructed near Newman, Kentucky, to produce solid solvent refined coal, liquid fuels, and anode coke presents a two-fold environmental challenge:

(1) How to begin with an environmentally dirty feedstock, high-sulfur coal, and end with environmentally clean products.

(2) How to operate at an environmentally acceptable level throughout the refining process.

The first challenge has already been met. Pilot Plant products have been evaluated in extensive burn tests and found to meet strict emissions standards for air pollutants. The second challenge is being addressed in the design of the Demonstration Plant, which will not only comply with existing environmental regulations, but also anticipate future requirements.

The SRC-I process will generate air emissions containing sulfur dioxide, particulates, hydrocarbons, carbon monoxide, oxides of nitrogen, and reduced sulfur compounds. The best available control technology will be employed in the Demonstration Plant to eliminate or reduce these contaminants to an environmentally acceptable level.

Wastewater from the Demonstration Plant will be treated in an advanced wastewater treatment facility located on the plant site. Phenolic compounds will be the major contaminant in the wastewater; some cyanides, thiocyanates, ammonia, and trace organic constituents will also be present, along with toxic metals. Streams that contain toxic metals will be pretreated by physical-chemical methods before biological treatment. The biological system will remove the organic contaminants, cyanides, thiocyanates, and ammonia. The effluent from the biological system will be polished by filtration and activated carbon adsorption before discharge to the river or reclamation for

reuse. Possible techniques to eliminate all wastewater discharge to surface waters are also being evaluated.

Three major types of solid waste will result from the SRC-I Process. The largest volume will be the mineral residue from the gasifier; this material will either be stored onsite in accordance with best engineering practice or be sold for further processing. Hazardous wastes from the physical-chemical section of the wastewater treatment facility will be disposed of in a permitted and secure landfill located onsite. (Sludge fixation processes that will convert hazardous waste to nonhazardous waste are also being evaluated.) The third type of solid, nonhazardous waste that is primarily biological sludge, will be recycled to the process for ultimate degradation.

This report covers the following subjects:

Process description
Product environmental compliance
Status of environmental controls
Air emissions control
Handling of aqueous wastes
Solid waste disposal
Sulfur balance
Investment in pollution control

A. PROCESS DESCRIPTION

Refer to Figure 1 (three pages) for a flow sheet of the SRC-I Coal Refinery. The process encompasses the following steps:

Washed Kentucky #9 coal is delivered to the site by unit train, weighed, unloaded, and delivered by conveyor to process silos. It is fed to pulverizers/dryers where the coal is ground, dried and pulverized to 200 mesh coal.

The coal is slurried in the process solvent and pumped to reaction pressure (roughly 2000 psig). Hydrogen-rich recycled gas is mixed with the slurry and heated to reaction temperature in a fired heater. At the exit of the fired heater, hot hydrogen makeup gas from a hydrogen purification area is added to the slurry and this mixture flows to a dissolver for further hydrogenation and desulfurization.

After the dissolving step, the slurry is flashed--and the gases and the hydrogen are separated in stages and recovered for recycle to the reaction section after being treated by a diethanolamine (DEA) system, an oil scrub for heavy hydrocarbon removal, and a cryogenic methane separation. The vapors from these stages are partially condensed and the water is decanted from the hydrocarbon phase. This water is sent to the ammonium sulfide stripper in a gasification area. The hydrocarbon liquid streams are mixed, heated, and charged into a

Figure 1a
SRC-I Process

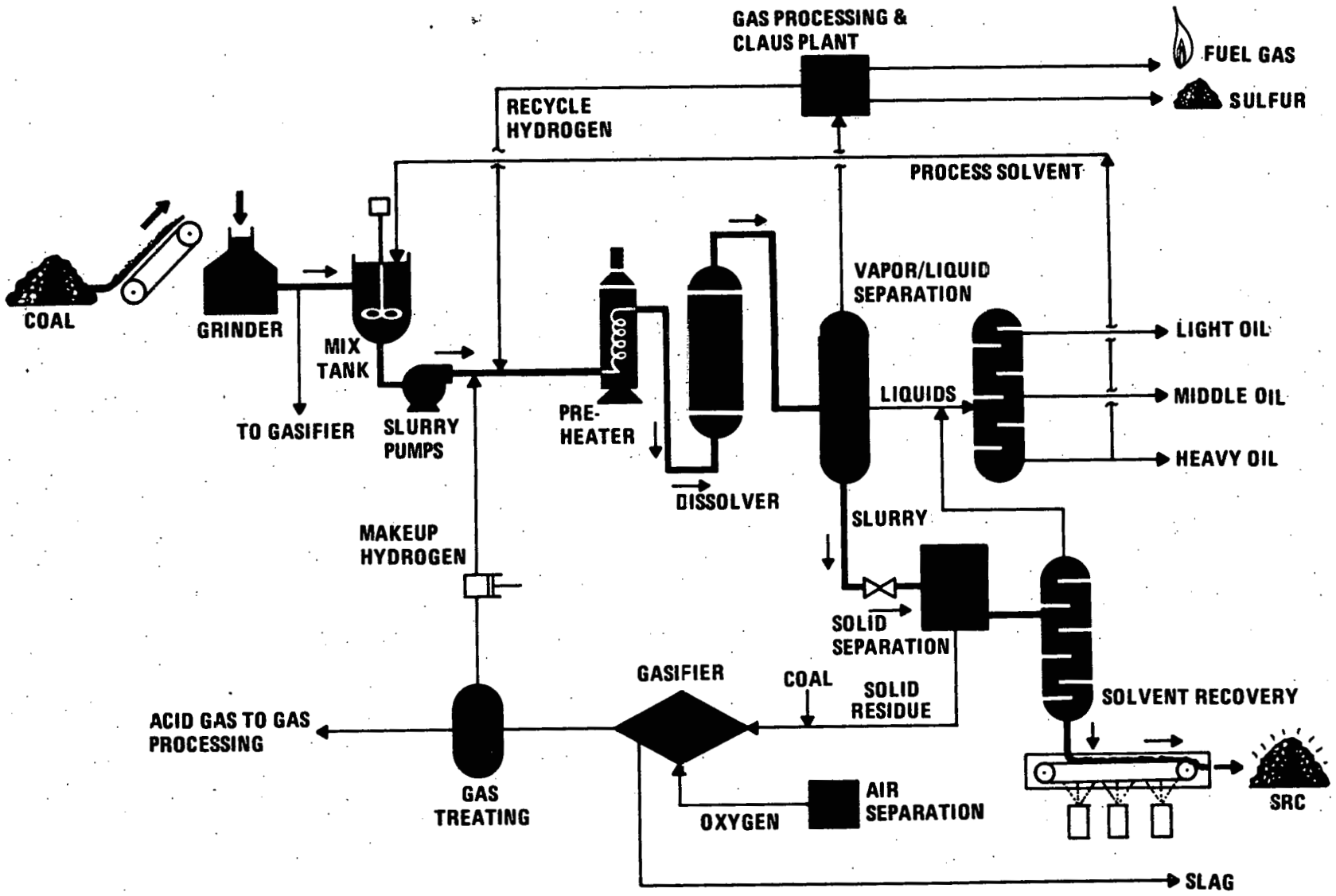


Figure 1b
Anode Coke From SRC-I

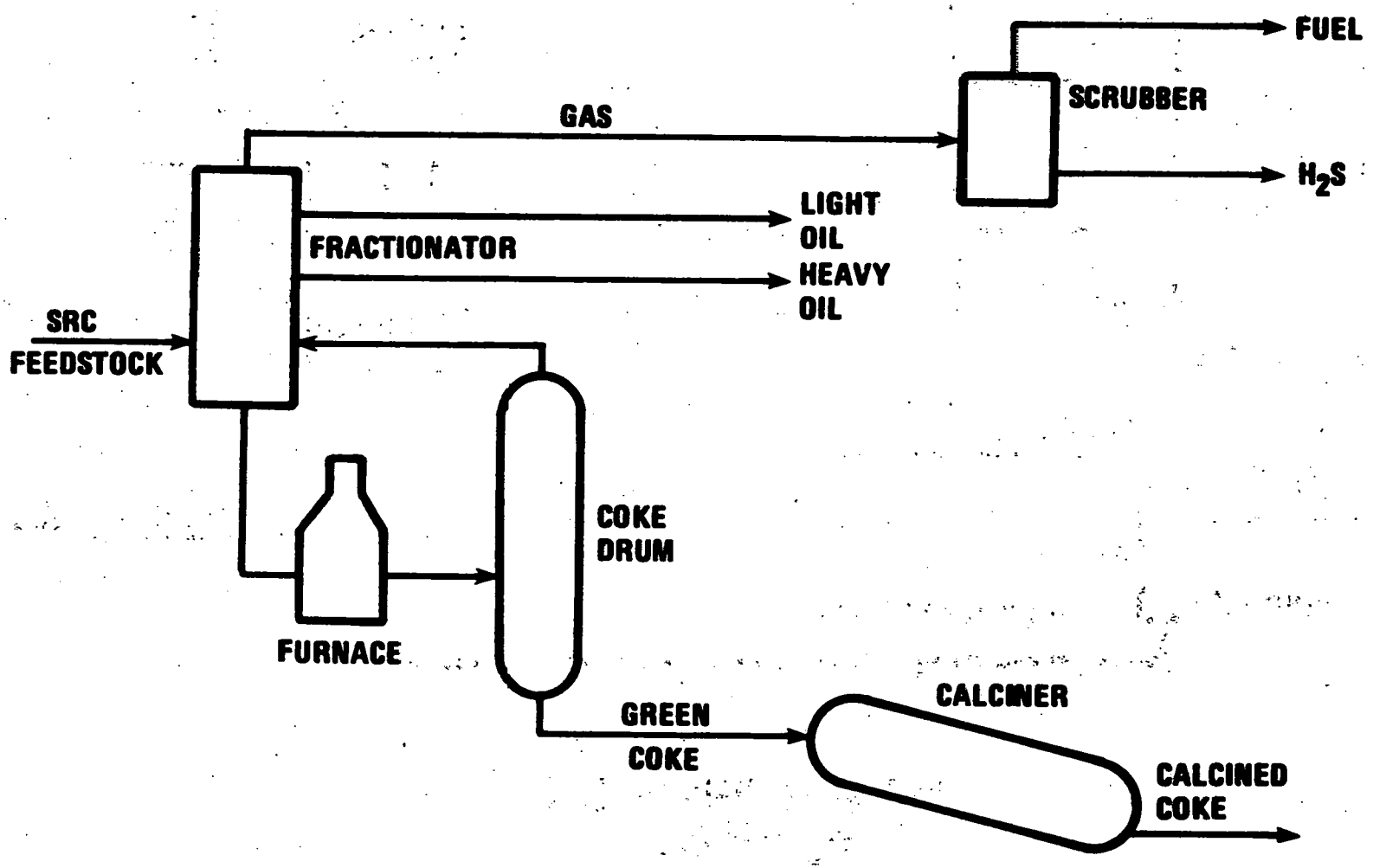
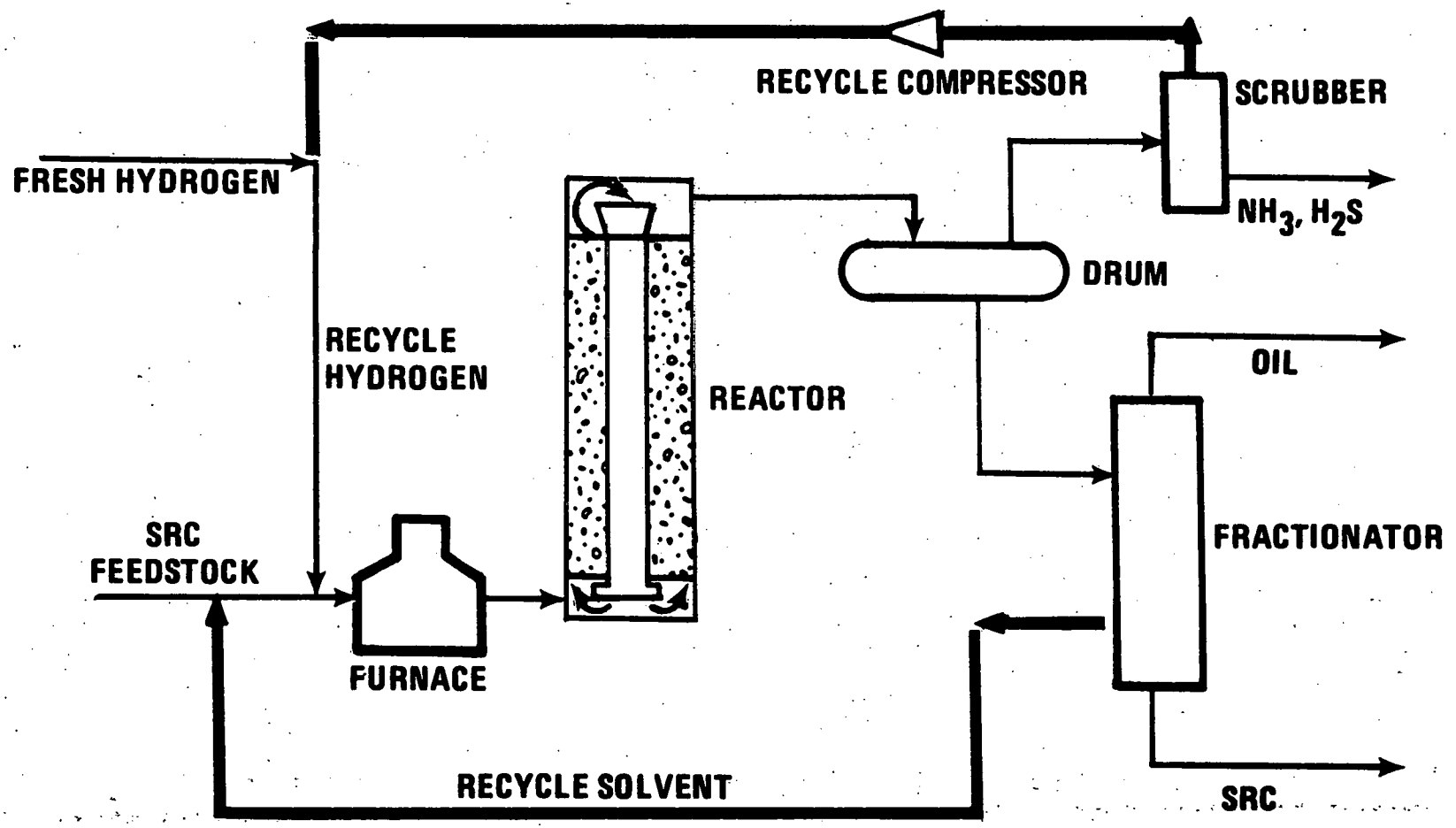


Figure 1c
LC-Fining Process



process solvent column in a fractionation section. The gas is compressed, combined, and forwarded to acid gas removal.

The low pressure slurry containing unconverted coal and ash from the final separation stage goes directly to a vacuum column in an SRC recovery area. Here the process solvent and lighter components are removed from the SRC slurry in a single vacuum column. The SRC ash slurry is sent to a Kerr-McGee Critical Solvent Deashing Unit, where it is mixed with a deashing solvent and separated into SRC and ash concentrate.

The present product slate sends one-third of the SRC to the solidifier to be solidified into a solid SRC product. Another one-third proceeds to the coker-calciner area. There molten SRC is fed to a fractionator tower where it is mixed with an appropriate amount of recycled coking solvent. The mixture is heated to about 900°F in a preheater and fed into the bottom of a delayed coking drum, where coke is formed. Vapor and gas from the drum pass back into the fractionator tower bottom where the liquid products are fractionated into heavy and light oil. Overhead vapors from the tower are compressed and sent to acid gas removal. The green coke is calcined and converted into anode grade coke in a rotary kiln. The flue gas from the calciner is scrubbed to remove SO_2 and particulates.

The sour water stream originating from the coker-calciner unit is sent to the ammonium sulfide water stripper.

The remaining one-third of the SRC product, as presently proposed, is to be fed into an LC-Finer for conversion to distillates. In the LC-Fining Process, SRC combined with internal solvent plus hydrogen are catalytically hydrogenated and hydrocracked in an expanded bed of catalyst. The expanded bed operates at isothermal temperature (750-850°F) and constant pressure. Effluents of the LC-Fining reactor are cooled and flashed in a separator. Vapor effluents are further cooled and passed through another separator where the light condensate is drawn off. The liquid is drawn off hot from the separator and let down in pressure before passing into still another separator where heavy condensate is drawn off. All liquids are then sent into a fractionator for separation into light and heavy oil cuts. The heavy SRC oils, including unconverted SRC, are then recycled to the front end for further hydrocracking.

The sour water from the LC-Fining area is again sent to the ammonium sulfide stripper unit.

The ash concentrate recovered from the Kerr-McGee deashing area, containing ash, unconverted coal, and some residual SRC, is sent to a gasification area. The gasifier serves basically two purposes. First, it converts the highly carbonaceous mineral ash residue from the deashing unit into a slag for solid waste disposal, the sulfur

compounds being converted to H_2S. Second, it generates makeup hydrogen by partial oxidation of the unconverted coal with steam and oxygen. This synthesis gas leaving the gasifier goes to a sour shift conversion reactor where the carbon monoxide and water are converted into hydrogen and carbon dioxide.

The hydrogen sulfide and carbon dioxide are removed in a Selexol Unit in the gas treatment section. The hydrogen, after carbon dioxide removal, is sent to the preheating area for makeup.

Sour water from the Selexol Unit goes to the ammonium sulfide water stripper.

Hydrogen sulfide-rich gas from the DEA acid gas removal units is combined with hydrogen sulfide from the Selexol Unit and converted to sulfur in a sulfur recovery area, which contains a Claus Unit and a Beavon Sulfur Removal Unit. The Claus Unit recovers the bulk of the sulfur from the SRC plant acid gases and the Beavon Sulfur Removal Unit provides final sulfur removal. Clean hydrocarbon gas from the DEA Unit is treated in the Stretford section of the sulfur recovery area, where the hydrogen sulfide is removed down to 4 ppm, and the gas made available for inplant fuel use.

B. PRODUCT ENVIRONMENTAL COMPLIANCE

Extensive burn tests, including a commercial-scale test, indicate that both solid and liquid solvent refined coal products can be expected to qualify as compliance fuel for new boilers under the Environmental Protection Agency's revised New Source Performance Standards (NSPS) as shown in Table 1. This conclusion applies not only to sulfur dioxide, but also to nitrogen oxide, and, with the use of appropriate control equipment, to particulates. SRC-I also complies with the emission standards for the retrofit of existing boilers and other combustors.

1. Plant Mitchell Tests

The goal of demonstrating the desirability of SRC-I as a boiler fuel was successfully achieved in a burn test at Plant Mitchell. Specific objectives of the test--to investigate the transportation, storage and handling, and burning of 3000 tons of SRC-I--were met with only minor modifications to equipment or procedures.

Shipment was accomplished in standard open coal cars; a commercially available spray coating was applied to minimize blowing losses while in transit. At the plant, the SRC-I was handled by the normal Plant Mitchell fuel conveying and storage equipment, with dust being controlled by a wetting agent during unloading operations. No

equipment modifications were required for handling or storage; no dust problems were encountered during bunker filling, storage, or feed.

The water-cooled dual register burners developed especially for the burn test performed well, delivering exceptional flame stability while firing SRC-I. Installation of these burners was the only modification made to the boiler.

Under a variety of operating conditions, there were no problems with pulverizing SRC-I. When grinding the SRC-I the pulverizers consumed 25% less power, ground finer, and had a capacity 25% greater than when grinding coal.

Boiler efficiency at full load was essentially the same when burning either SRC-I or coal. The boiler stayed much cleaner with SRC-I than with coal, totally eliminating the need for soot blowers or for deslagging the burner front during the 18-day burn test. The quantity of SRC-I fly ash was 1/7 to 1/10 that of coal fly ash, and there was no ash accumulation in any boiler section. In addition, there was almost no bottom ash accumulation from SRC-I. SRC-I ash is characteristically nonabrasive, and that fact, coupled with the very low ash loading, reduces maintenance of the ash handling systems.

Emission tests, conducted throughout the burn test using EPA and American Society of Mechanical Engineers procedures, measured particulates, sulfur dioxide (SO_2), nitrogen oxides (NOx), carbon monoxide (CO), carbon dioxide (CO_2), and oxygen (O_2). Particulate emissions leaving the secondary precipitator yielded concentrations in compliance with current EPA standards and are expected to comply with NSPS, using properly designed precipitators. Measurements indicated that SO_2 emissions were more than 20% under existing EPA standards for maximum SO_2 emissions and that NO_x emissions were also under NSPS.

The overall results from the Plant Mitchell Solvent Refined Coal Burn Test prove that the performance of SRC-I as a boiler fuel is exceptional. The fuel is clean, uncomplicated in use, and has characteristics that should substantially improve the availability and reliability of boilers and auxiliary equipment. And by meeting EPA requirements, solvent refined coal offers a clearly viable alternative to scrubber installations at both new and existing power plants.

2. Consolidated Edison Tests

Liquids from the SRC-I Demonstration Plant are expected to be better in quality than those of the SRC-II liquids. This is because the LC-Finer produces liquid products that contain more hydrogen and less nitrogen and sulfur.

Table 1 gives the results of the burn tests conducted at Consolidated Edison Co. of New York. These results showed combustion characteristics comparable to #6 fuel oil and well within EPA standards.

Table 1

New Source Performance Standards (NSPS)
For Electric Utility Boilers
Compared With SRC-I and SRC-II Solid Burn Tests

	Lb/MM Btu		
	SO_2	NO_x	Particulates
NSPS	1.2 85% reduction*	0.5	0.03
SRC-I burn test at Plant Mitchell	1.0	0.45	0.04**
SRC-II Con Ed burn test	0.3	0.35	0.02

*24-hour average. All other SO_2 and NO_x regulations are for 30-day rolling average. SO_2 emissions are set for 80% reduction for first 6,000 to 10,000 mw of commercial SRC demonstration. Reduction refers to parent coal, and credit is given for changes in heating value.

**Southern Research Institute and the Joint Venture believe that with an electrostatic precipitator, using a specific collection area of 300 ft^2 and gas velocity of 2 ft/sec, the particulate emission can be reduced to below 0.03 lb/MM Btu.

C. STATUS OF ENVIRONMENTAL REGULATIONS

Present environmental standards for coal conversion facilities are not well defined. Controlling environmental regulations for the pioneer conversion plants will probably be negotiated at the state and local level--and promulgated as data becomes available from these plants. They will be met by employing a variety of environmental control systems and options.

Controls are usually segregated into categories dealing specifically with gaseous, liquid, and solid pollutants. This follows in part from the environmental legislation, which is primarily concerned with the impact on the acceptor medium, e.g., air, water, or land. However, in evaluating a pollution control process, secondary effects on other media must be taken into consideration. It does little good to take one problem, say SO_2 emissions, and transform it into a water and land problem by the surface disposal of a hazardous scrubber sludge. Ideally, the pollution control process is fully integrated with the conversion process to take advantage of economics of energy consumption, reduced pollutant production, water reuse potential, and by-product production. The following portions of this paper discuss this concept as it applies to the SRC-I Coal Refinery.

D. AIR EMISSIONS CONTROL

Best available control technology will be employed to eliminate or minimize the air pollutants emitting from this plant. The quantities of the EPA criteria pollutants have been estimated and their impacts on ambient air quality have been assessed with an air dispersion modeling. The result of the modeling shows that there will be no significant impacts from the SRC-I Demonstration Plant. It will satisfy the EPA Prevention of Significant Deterioration (PSD) requirements for air quality and all applicable NSPS.

1. Emission Inventory and Pollution Control

Table 2 gives the emission rates of the criteria pollutants from the SRC-I facility after pollution control. The emission rates generated from a neighboring power plant are also listed in the same table for comparison.

The pollution control technology employed is highlighted for each pollutant: sulfur oxides, particulates, hydrocarbons, nitrogen oxides, and carbon monoxide.

Sulfur oxides control. Sulfur oxide control alternatives were considered for various parts of the plant. Fired heaters are potentially major sources of sulfur dioxides. But over 50% of their fire duty will be met by fuel gases produced in the process--and these

Table 2

Emission Inventory (tons per year)

Contaminants	SRC-I	Nearby power plant (with FGD)
Sulfur oxides	260	29,900
Particulates	350	2,000
Hydrocarbons	40	--
Nitrogen oxides	1,050	14,000
Carbon monoxide	550	1,250

FGD: Flue gas desulfurization

gases, after acid gas removal, contain only 4 ppm of sulfur. The rest of the fire duty will be met by using low sulfur fuel oil that has been hydro-treated, also produced in the process.

Two parallel Claus Units are incorportated in the plant design for sulfur recovery, the second unit being a 100% spare. The tailgas cleanup of the Claus Unit is accomplished by a Beavon Sulfur Removal Unit (BSRU). The vented gases from the molten sulfur storage and handling operations will be treated by small scale Stretford scrubbers to prevent release of sulfur compounds.

The flue gas from the calciner will be scrubbed with a soda ash system to minimize SO_2 and partuculates.

Hydrocarbon control. All liquid storage tanks will be equipped with fixed roofs and vented to a vapor recovery system to eliminate hydrocarbon emissions. All recovered vapors will be burned as fuel gases for the plant fuel needs or flared. In addition, pumps, valves and compressors will have double mechanical seals to minimize fugitive hydrocarbon emissions. During process upsets and emergencies the hydrocarbons will be flared prior to release. A ground flare which provides controlled combustion is being investigated for large emergency blowdowns to prevent emissions of entrained heavy hydrocarbons.

Particulates control. Fugitive emissions will be minimized by enclosing the transfer points in chutes or hoods or by spraying with a dust inhibitor. Particulates in the exhausts from the conveyors will be controlled by a baghouse.

Vent gas from coal pulverizing/drying operations will also be controlled by a baghouse. The main calciner flue gas will be scrubbed by the soda ash system, which removes SO_2 as well. All coal feed piles and open solid SRC piles will be sprayed with a polymer dusting inhibitor to control fugitive dust. The elemental sulfur from the sulfur recovery area will be stored in molten state in a closed tank to prevent emission of the fugitive sulfur dust from open sulfur piles. The anode coke from the calciner will be stored in silos, handled by a closed conveyor system with dust control, and transported in hopper cars.

Nitrogen oxides control. The principal source of nitrogen oxides will be the fired heaters. The quantity of NO_x emitted will be reduced by applying the following combustion modification techniques: flue gas recirculation, staged combustion, and minimizing excess air.

The combustor for the slurry preheater, which consumes close to half the total fuel needs, is two-stage and refractory-lined. The burner is designed to operate at low excess air but allow for complete combustion of hydrocarbons. It uses a toroidal mixing pattern in the

sub-stoichiometric first stage and a high outlet velocity in the second stage. The reducing first stage breaks down the fuel-bound nitrogen and the relatively low temperature prevents nitrogen fixation. There is vigorous internal recirculation and the high flame velocity minimizes residence time and induces jet entrainment of the combustion products. In order to cancel out the harmful effects of preheated air on NO_x formation, 25% of the flue gas will be recirculated to reduce flame temperature.

2. Air Quality Impact Assessment

The impact of the emissions from SRC-I on air quality has been assessed with air dispersion modeling.

The pollutants modeled were SO_2, total suspended particulates (TSP), NO_2, and CO. The proposed SRC-I Plant is located in an attainment area for SO_2, TSP, CO, and ozone (O_3), and in an unclassifiable area for NO_2.

Results of the air pollution dispersion modeling study--based on one-year simulations of SO_2, TSP, NO_2, and CO ambient air quality and more than one year of background air quality monitoring--support the following conclusions:

(1) SRC-I Plant emissions will have an insignificant impact on air quality in any nonattainment or unclassifiable areas for SO_2 or TSP.

(2) SRC-I Plant emissions will have an insignificant impact on air quality in any PSD Class I area.

(3) Emissions from the SRC-I Plant alone and in combination with all other definable local PSD sources will not threaten or exceed the PSD Class II concentration increments for SO_2 and TSP in the vicinity of the proposed plant site.

(4) The National Ambient Air Quality Standards (NAAQS) for SO_2, TSP, NO_2, and CO will not be exceeded in the vicinity of the SRC-I Plant site after the plant becomes operational.

E. HANDLING OF AQUEOUS WASTES

1. Major Wastewater Streams and Contaminants

The expected normal wastewater flow is 1.5 MGD which consists of the following major streams:

- Sour water
- Cooling tower blowdown
- Coal pile runoff
- Process runoff
- Weak process wastes
- Oily wastes
- Sanitary waste
- Landfill leachate

About a third of the total wastewater flow is sour water, the most heavily contaminated stream. Hydrogen sulfide, ammonia, phenolics are the major contaminants in this stream, along with some cyanide, thiocynate, and metals. Trace organics, such as polycyclic aromatic hydrocarbons, are probably present in the stream, too.

Another third of the flow wastewater is the cooling tower blowdown. Flow rate of this stream is about the same as that of the sour water. The most significant contaminant in this stream is hexavalent chromium, which is added to the cooling system for corrosion control. The common inorganic constituents originated in the makeup water to the cooling system will be concentrated and present in the blowdown.

The contamination of the cooling tower blowdown with the hexavalent chromium could be avoided if nonchromate anti-corrosion chemicals could be used in lieu of chromate. The possibility is being evaluated.

The remaining third of the wastewater comes from various sources: runoffs from raw coal and SRC piles, runoffs from the diking areas where the process equipment is located, sanitary waste, landfill leachate, oil-bearing wastes, and such lightly contaminated waters as boiler blowdown and water filter backwash.

The contaminants in the runoffs from the coal piles are mostly dissolved inorganic common solids, although trace quantities of metals may also be present. The process area runoff is contaminated with process liquids, including certain high-boiling point hydrocarbons. The landfill leachate should contain the contaminants common to the runoffs. The lightly-contaminated wastewaters contain chiefly inorganics and suspended solids.

The oil-bearing wastes, although small in quantities, deserve particular attention, because they may contain hydrocarbons that are potentially hazardous to human health, including polycyclic aromatic hydrocarbons.

The major contaminants are:

- Phenolics
- Ammonia
- Cyanide
- Thiocyanate
- Toxic metals
- Dissolved solids
- Oil and grease
- Trace organics

2. Conceptual Design of the Wastewater Treatment System

All wastewaters generated in the plant, as well as the contaminated runoff will be sent to the wastewater treatment facility. Figure 2 is a conceptual diagram for the treatment facility. The treatment processes include separation of oily wastes, precipitation/flocculation of toxic metals, two-stage aerobic biological treatment followed by filtration, and a final polishing of the effluent by activated carbon and disinfection. The system provides equalization and retention basins to promote mixing and thereby prevent upset of the biological system due to shock by toxic components.

The sour water will initially be steam-stripped to remove hydrogen sulfide and ammonia. After stripping, the stream will be combined with the landfill leachate and then fed into a first-stage precipitator for nickel removal. The optimal pH for nickel removal is about 11, considerably higher than the optimal pH, 8.5, for removing other metals.

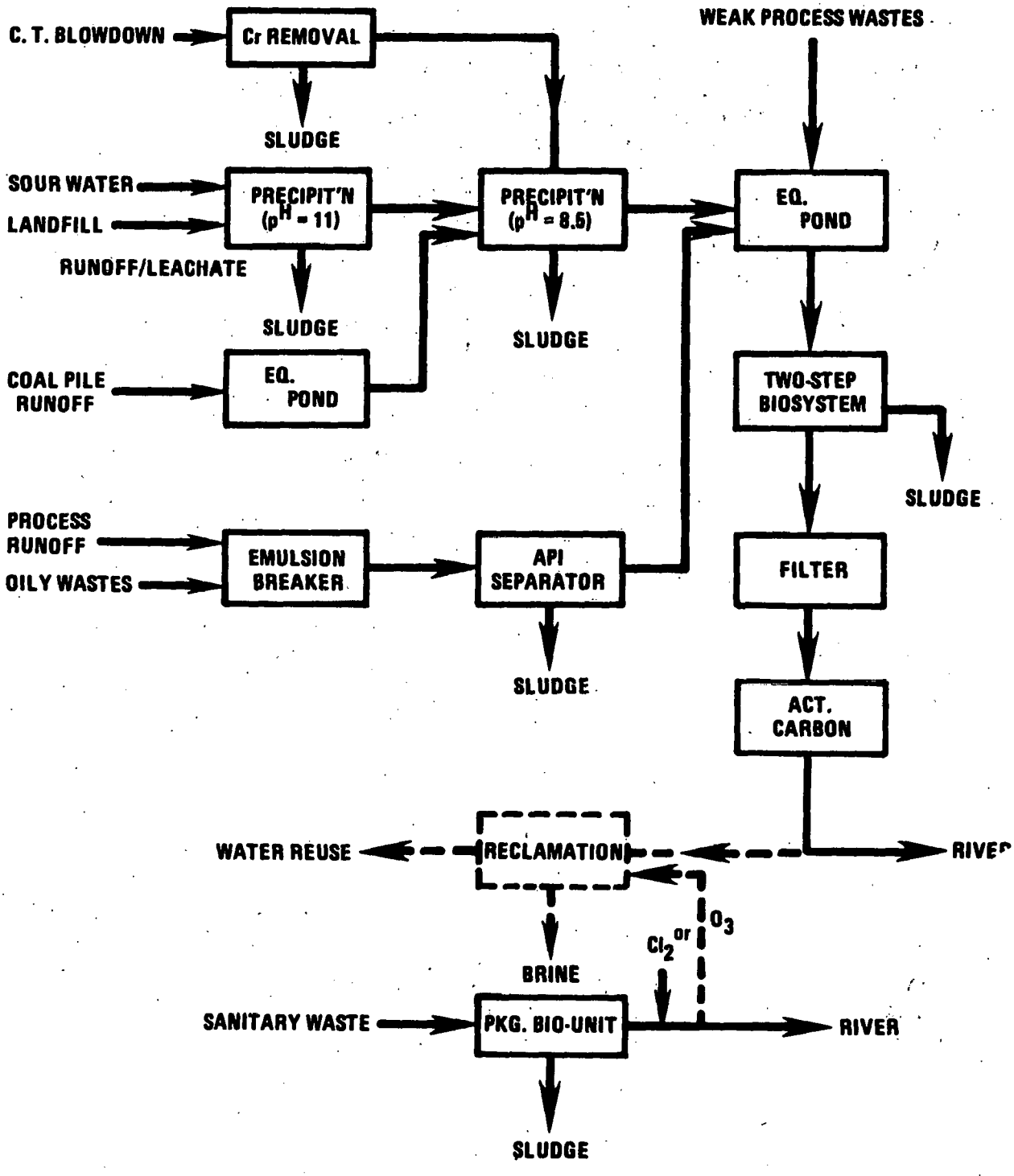
The chromate-laden cooling tower blowdown will be treated in a electrolytic reduction unit in which the soluble Cr^{+6} is reduced to trivalent chromic (Cr^{+3}) oxide precipitates. The blowdown then will flow into a second-step precipitator for solids removal.

The pH in the second-stage precipitator will be maintained at 8.5 for a maximum removal of other metals. Various chemicals will be added to facilitate the removal. For example, iron will aid in removing arsenic and vanadium and polymer or alum will enhance sedimentation. After the precipitation stage, the wastewater will flow into an equalization pond where it will commingle with other waste streams prior to biological treatment.

Also feeding into the second-stage precipitator is the coal pile runoff. Because of its high fluctuation in flow rate and concentration, it is equalized in a surge pond before feeding to the precipitator.

Process area runoff, which is likely to be contaminated with hydrocarbons, will be combined with other oily wastes for emulsion-breaking and oil removal. The treated oily waste will be introduced to

Figure 2
Conceptual Design of SRC-I Wastewater Treatment



the equalization pond upstream of the biological system. There will be an oil-skimming device in this pond to remove any floating oil that is not removed upstream.

The two-stage biological system consists of two separate biological systems. Each will have a reactor followed by a clarifier. The purpose of the first-stage biological system will be to remove mostly phenolics and other easily biodegradable materials. Removal of ammonia and thiocyanates, as well as refractory organics, should occur principally in the second-stage biological system. Since the microorganisms in the second stage are usually more sensitive to environmental changes and more susceptible to inhibitions, the first stage should provide stability for the second stage. To further protect the biological system from potential inhibition and toxicity, provisions will be made for adding powdered activated carbon.

The effluent from the biological system will be further polished by filtration and activated carbon adsorption. Filtration removes residual suspended solids and adsorption greatly reduces trace organics, particularly polycyclic aromatic hydrocarbons.

Sanitary waste will be treated separately in a package biological unit. Because of fecal coliforms, disinfection of this stream is required before discharge. Chlorination or ozonation will be employed. The decision will be made during detail engineering.

3. Expected Treated Effluent

Because a plant of this type has never been built before, the exact nature of the effluent is not known. However, anticipated effluent contaminants and their possible concentrations are given in Table 3. More study on effluent characteristics will be conducted during detailed design efforts.

4. Zero Discharge Concept

During detail engineering, we will also evaluate the zero discharge concept--which calls for eliminating or minimizing liquid effluent from the Demonstration Plant. Implementing the zero discharge concept would involve a water reclamation system (yet to be defined).

The major factors to be considered in evaluating the concept are: (1) technical feasibility, including safe disposal of highly water-soluble solid wastes; (2) economics; (3) energy consumption; and (4) overall environmental impact on multi-media.

Table 3

Anticipated Effluent Contaminants
After All Treatments[1]

Parameter	Concentration (mg/l)	
	Average	Maximum
Temp	61°F	100°F
Flow	1.5 mgd	2.88 mgd
pH (units)	6-9 units	6-9 units
BOD	20	40
COD	50	100
TOC (2.2 X BOD)	44	88
Oil and grease	10	20
TSS	20	35
TDS	TBD	TBD
Chlorides	TBD	TBD
Phenolics	0.1	0.6
Ammonia as N	5	20
Phospate as P	5	10
Nitrate	30	60
Sulfide	0.04	0.09
Arsenic	0.1	0.25
Barium	1	2
Cadmium	0.15	0.30
Chromium (total)	1	2
Chromium (Hex)	0.05	0.1
Cyanide	0.45	0.9
Fluoride	7	14
Lead	0.25	0.4
Selenium	0.35	0.7
Silver	0.1	0.2
Zinc	1	2
Nickel	0.5	1.6
Iron	2	4
Vanadium	1	5
Copper	1.0	2.0
Manganese	2	4
Mercury	0.001	0.002
Cl_2 residual (total)	1	2
Beryllium	0.005	0.01
Fecal coliform	TBD	(Below 400/100 ml)
Boron	TBD	TBD
Alkalinity	TBD	TBD
Thiocyanate	TBD	TBD
Sulfate	TBD	TBD
Polyaromatic hydrocarbons	TBD	TBD

1. Excluding waste contribution from LC-Fining

TBD: to be determined

F. SOLID WASTE DISPOSAL

1. Types and Quantities

Three major types of solid waste resulting from the SRC-I process are: (1) inert mineral residue from the gasifier; (2) metal-bearing inorganic solids mainly from wastewater treatment processes; and (3) biological solids, also from the wastewater treatment. In addition, there are minor quantities of other types of solid waste, including oily sludges, spent catalysts, and spent activated carbon. If the zero discharge concept is implemented, there will be an inorganic salt cake associated with it.

The quantities of the three major types of solid waste are estimated to be:

Gasifier slag	700 dry tons/day
Metal-bearing sludge	8 dry tons/day
Biological sludge	2 dry tons/day

2. Classification of Solid Wastes

The EPA proposed regulations for the Resource Conservation and Recovery Act (RCRA), published 18 December 1978 in the Federal Register, classify solid wastes into two categories: hazardous and nonhazardous. Much more stringent requirements are imposed for the hazardous wastes.

In the Demonstration Plant, the gasifier slag appears to be nonhazardous. High temperature, slagging, entrained flow gasifiers provide high carbon conversion, thereby precluding highly carbonaceous wastes. The slag will be low in sulfur because organic and pyritic sulfur have been preferentially converted to H_2S in liquefaction and gasification. The trace quantities of metals in the slag do not appear to present disposal problems either. Leaching tests have been conducted by the Oak Ridge National Laboratory (ORNL) for gasifier slags generated from various coal feeds and gasification technologies. Table 4 summarizes the results. Although concentrations of the trace elements vary from gasifier to gasifier, the general trend is apparent--the concentrations of the metals in the leachates are substantially below the proposed RCRA standards. Specific slag from Pilot Plant gasification of the SRC-I residue will be tested by ORNL for leachability.

Leaching data for the metal-bearing sludges are not available. Because of the metal content, it is likely that these sludges will be hazardous.

Table 4

Comparison of Leachate Concentrations (ppb)
With Proposed RCRA Criteria for Five Gasification Slags
Using the Proposed EPA Extraction Procedure

Element	Plant C	Plant E	Plant G	Plant I	Texaco	Proposed RCRA Standards
Arsenic	0.27	0.06	1	0.53	NP	500
Barium	200	500	200	500	NP	10,000
Cadmium	0.054	0.97	1	3.4	NP	100
Chromium	1.6	0.44	5	0.13	12	500
Lead	0.3	0.26	10	1.6	13	500
Mercury	0.64	0.03	1	0.192	4	20
Selenium	5	2.0	1	1.0	NP	100
Silver	0.03	0.03	2	0.07	NP	500
Copper	2.7	3.7	10	0.94	NP	*
Nickel	281	219	30	758	30	*
Zinc	63	10	13	385	23	*

*Not included in 18 December 1978 Interim Primary Drinking Water Standards of Resource Conservation and Recovery Act (RCRA).

Note: Because of proprietary agreements, the plants cannot be identified.

NP: Not published.

The classification of the biological solids will depend on the metal contents; they may or may not be hazardous.

3. Methods of Disposal

The gasifier slag will be stored onsite in ash ponds. After dewatering, the metal-bearing sludge will be stored onsite in a secure landfill. The landfill will also store the dewatered biological solids, if gasification is not feasible. Incineration or gasification will be employed to dispose of the oily sludges and the spent activated carbon.

The waste sludge landfill (Figure 3) will be constructed and maintained in accordance with U.S. Environmental Protection Agency hazardous waste guidelines and regulations (Federal Register, 1978).

Excavated material from the plant process area will be used to construct the embankment dikes for the waste sludge landfill. The landfill will be lined with a 0.91 m (3 ft) thick clay liner over a 20-mil synthetic liner. A leachate collection and removal system on top of the clay liner will collect and remove leachate generated in the landfill. The top clay liner will provide primary containment of the waste and protection for the synthetic membrane liner. The synthetic liner will provide containment of any waste that migrates or leaks through the clay liner. A leachate detection and removal system will be located beneath the synthetic bottom liner.

A ground water monitoring system will include some monitoring wells hydraulically downgradient from the facility and some upgradient from the facility.

The ash ponds will be located over an existing clay stratum, which will be exposed by stripping to topsoil overburden and compacted. The ash ponds will be lined with a 15.24 cm (6 inch) compacted clay liner (Figure 4).

The near-surface clayey soils present over the high terrace will produce an estimated coefficient of permeability (k) of about 1 x 10-7 to 1 x 10-8 cm/sec, which is normally acceptable for lining ash ponds.

The embankments that will enclose the ash ponds are planned to be only about 6.10 m (20 ft) high. The embankment slopes will be dictated primarily by maintenance or erosion control. Slopes no steeper than 2.5 (horizontal) to 1 (vertical) will be required.

G. SULFUR BALANCE

Figure 5 shows an overall sulfur balance for the 6000 TPD SRC-I Plant. Of the total 204 TPD of sulfur coming in with the coal, almost

Figure 3
Typical Section of Waste Sludge Landfill

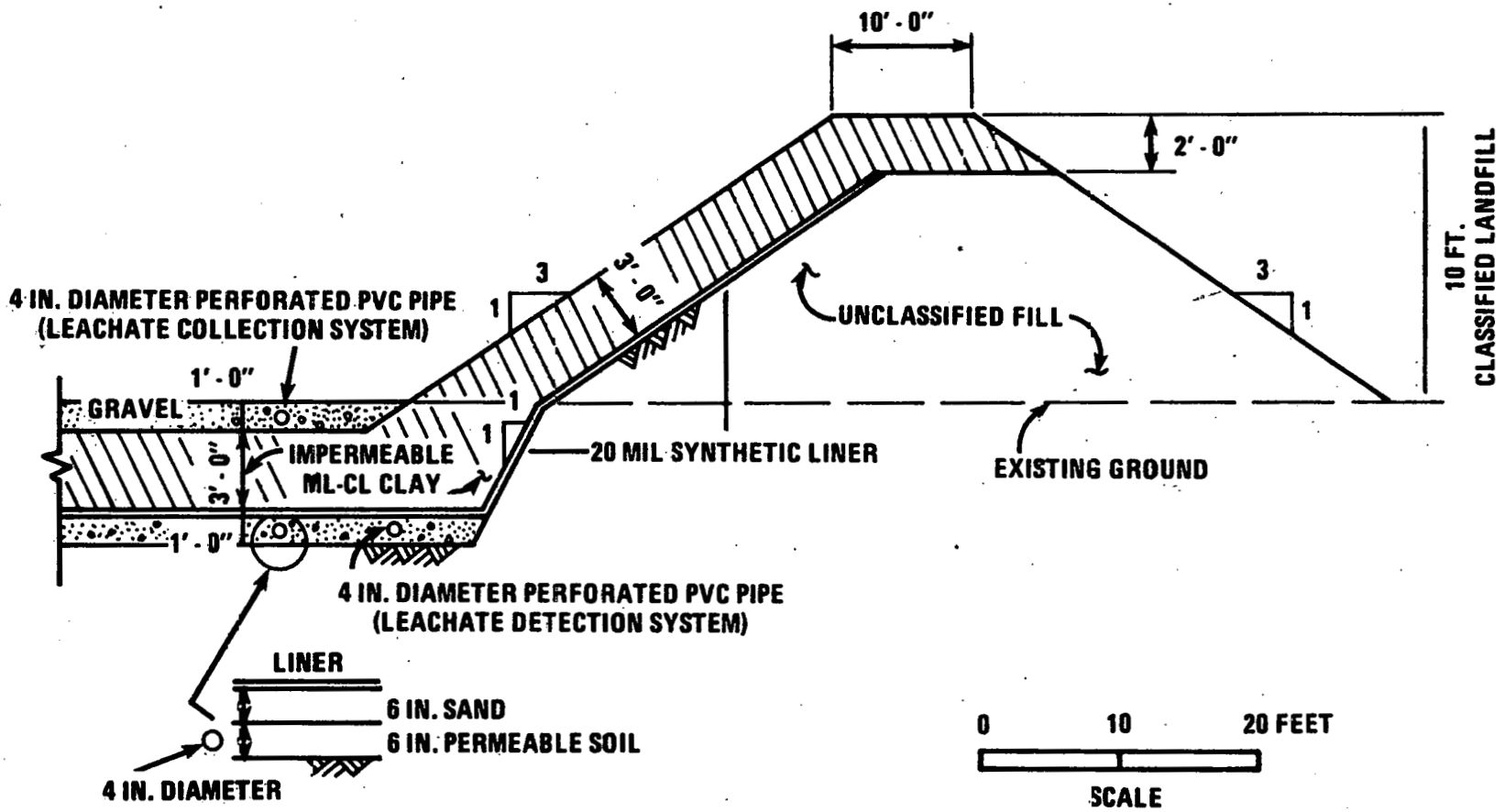


Figure 4
Typical Ash Pond Dike

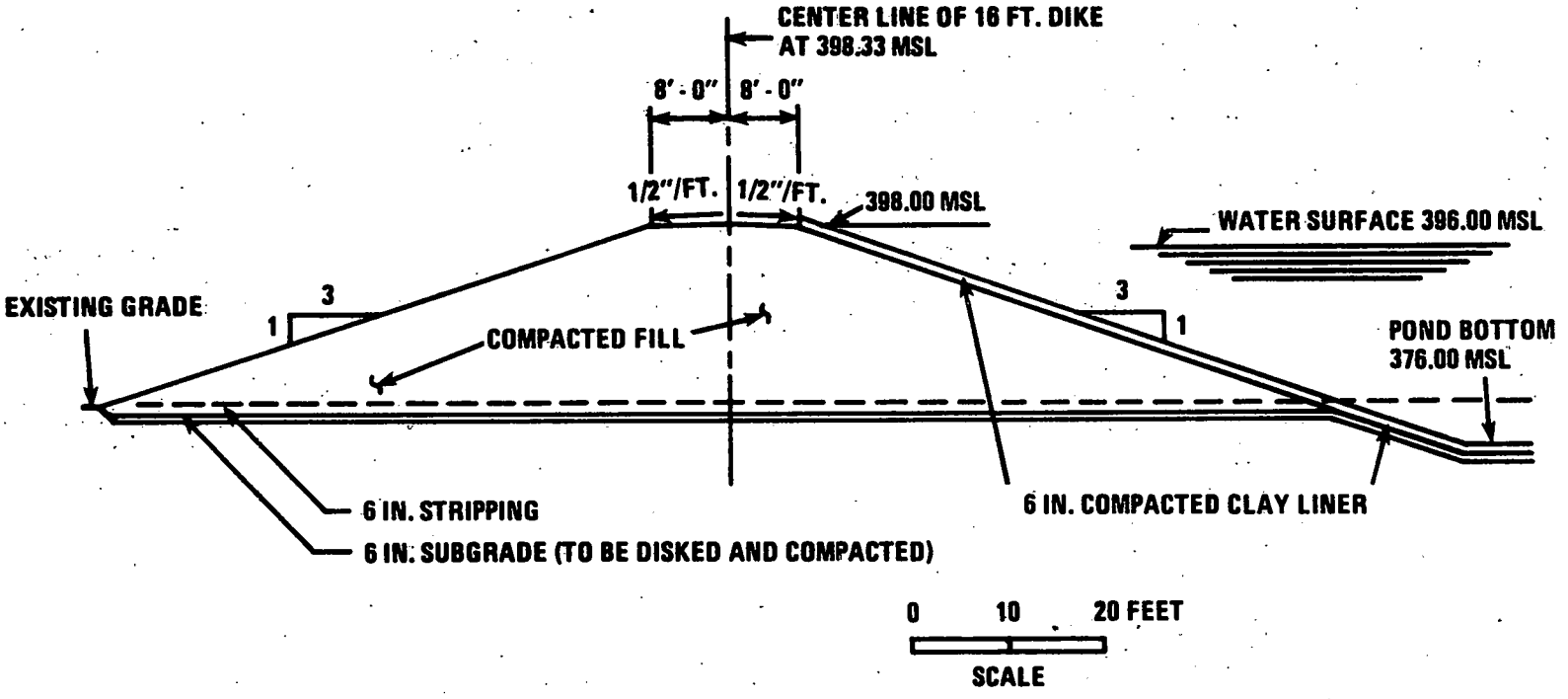
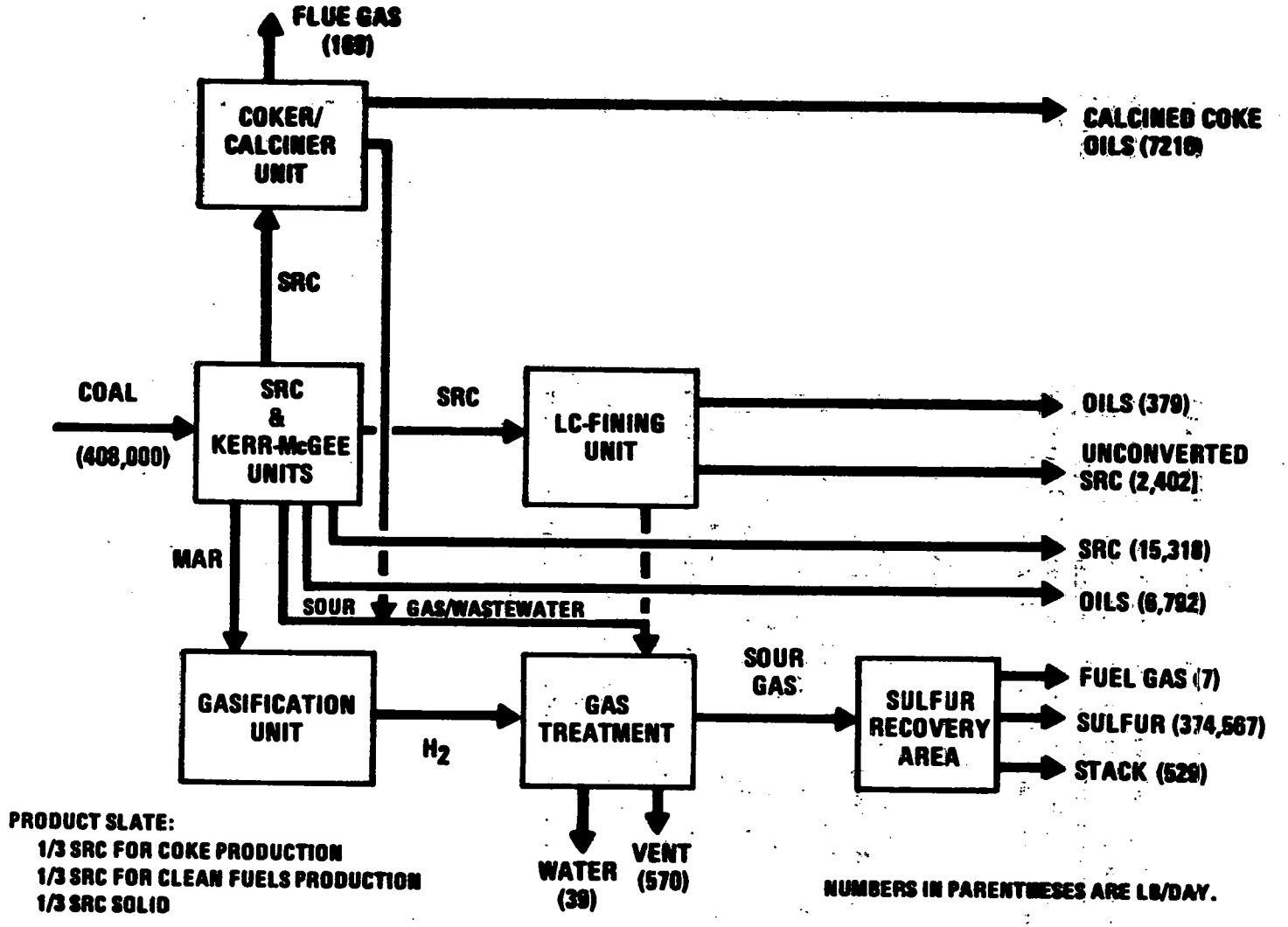


Figure 5
Sulfur Balance



92% has been converted to pure sulfur by-product, 5.8% appears in the solid SRC and coke, 2% in the oil products, and the rest in different waste streams.

H. INVESTMENT IN POLLUTION CONTROL

The pollution control equipment in the SRC-I Demonstration Plant dedicated to minimize emissions, waste effluents, and retrievement of hazardous waste will amount to 12.5% of the total plant investment. This can be broken down to: 36% Air Pollution Control; 59% for Wastewater Treatment; and 5% for Solid Waste Disposal.

CONCLUSION

For the near term, there appears to be no major environment-related constraint associated with the SRC-I Demonstration Plant. Uncertainties regarding evolving regulations under RCRA and Toxic Substance Control Act (TSCA) could present some obstacles to the design of commercial plants in the future. A need exists for intermediate-to-long-term environmental monitoring of operations at demonstration scales of development--to acquire experience in determining the best technologies to contain emissions and effluents and the ultimate disposal of solid wastes.

The SRC-I Demonstration Plant will provide the opportunity to assess the environmental impact of a coal liquefaction plant designed to use the best available pollution control technologies.

ENVIRONMENTAL CONTROL SYSTEMS FOR THE SRC-II DEMONSTRATION PLANT

D. K. Schmalzer & C. R. Moxley
The Pittsburg & Midway Coal Mining Co.

1. INTRODUCTION

In July 1978, the U.S. Department of Energy and The Pittsburg & Midway Coal Mining Co., a subsidiary of Gulf Oil Corporation, entered into a contract which has as principal objectives the design, construction, and operation of a demonstration scale SRC-II coal liquefaction plant. A basic precept in this project for both DOE and P&M is that safety, health protection, and environmental acceptability will be dominant considerations in the design and operation of the Demonstration Plant. Application of a wide variety of control technology is planned and under consideration. This paper will briefly describe these areas as well as the employee health protection programs planned.

2. PROCESS DESCRIPTION

Figure 1 shows a schematic flow diagram of the SRC-II Process. The feed, which is a typical high-sulfur Pittsburgh seam coal, is mixed with a recycle slurry produced by the process. Hydrogen enters the coal-slurry mixture and the mixture is pumped through a preheater to the reactor where the coal is dissolved and hydrocracked.

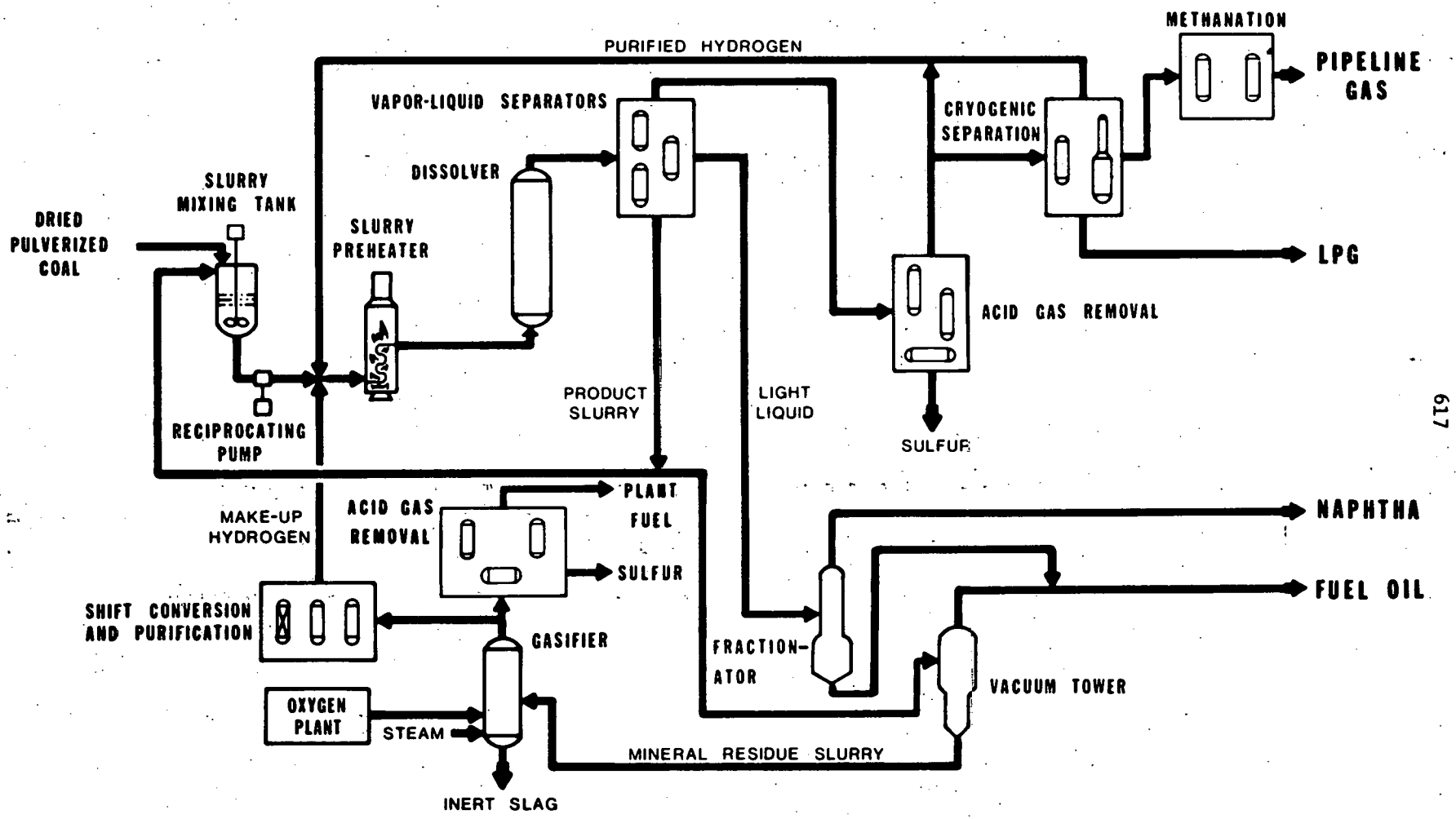
The effluent from the reactor enters a series of vapor-liquid separators. The light process gases containing hydrogen, H_2S, and CO_2 are sent through an acid gas removal system followed by a cryogenic unit to separate the hydrogen which is recycled to the process. The hydrocarbon gases are refined into methane, ethane, propane and mixed C_4 product streams.

The light liquid stream is fractionated into a naphtha product (C_5-350°F) and a middle distillate (350°F-600°F). The product slurry is split such that part is recycled to the front end to be mixed with the feed coal. The other portion is sent to vacuum distillation where a heavy distillate is produced and subsequently mixed with the middle distillate from the atmospheric tower. These two streams (heavy and middle distillates) or their blends comprise the final SRC-II fuel oil products.

The vacuum tower bottoms are sent to a high pressure slagging gasifier for production of synthesis gas, a mixture of hydrogen and carbon monoxide. Part of this gas is catalytically reacted with steam (water-gas shift) to produce hydrogen. The remainder synthesis gas is treated to remove acid gases and is used for plant fuel.

Figure 1

SRC-II PROCESS



The temperature in the gasifier is sufficient to liquefy the mineral matter in the feed. This molten ash is cooled and solidified and is sent to the slag disposal area located on site. Approximately 800 T/CD of slag will be produced by the plant.

3. CONTROL OF AIR EMISSIONS

There has been considerable speculation about the potential adverse health effects of coal and coal-derived chemicals. The present design for the SRC-II Demonstration Plant has incorporated several control techniques to protect not only the workers but also the general public from exposure to these materials.

A. Toxic Gases

The Demonstration Plant will handle large quantities of toxic gases such as H_2S and CO. In this respect, the plant is similar to petroleum refineries and many of the safety and health procedures employed at refineries will be used in the Demonstration Plant.

In the SRC-II process, the hydrogenation reaction taking place in the dissolver converts organic sulfur to H_2S. It is precisely this reaction which allows the products from the plant to be low in sulfur. A sulfur recovery plant has been designed to process all plant streams containing H_2S and CO_2. These facilities convert H_2S to elemental sulfur which is recoverable in liquid form.

The conceptual design of the sulfur recovery plant utilizes the Claus-SUPERSCOT system for sulfur removal. Acid gases not sufficiently rich in H_2S for the Claus reaction are first enriched in the SUPERSCOT unit.[2] These streams will come primarily from the Hydrogen Treating and Recovery Plant, the Hydrogen Purification and Compression Plant, and the Low Pressure Gas Compression and Treating Plant. Streams that are already sufficiently rich in H_2S, such as from the Ammonia Recovery Plant and Methanation Plant, will be sent directly to the Claus unit.

In addition, the Claus unit tail gas will be recycled to the SUPERSCOT unit in order to recover additional H_2S before incineration.

The design for the Claus unit is based on 95 wt.% sulfur recovery while an overall sulfur recovery of 98.6 wt.% is obtained with the addition of the SUPERSCOT unit. The residual H_2S is converted to SO_2 in an incinerator before release to the atmosphere.

B. Fugitive Coal Dust

The Demonstration Plant will process 6,000 TPCD of coal. Coal unloading, conveyance, crushing, and drying are integral parts of plant operations. Fugitive coal dust will be controlled through the use of bag filters, covered conveyors, and wetting agents. These techniques are not new and are in common use today.

C. Fugitive Hydrocarbons

The potential health effects of coal liquids are addressed in Section 6. Considerable attention has been given in the design of the plant to limit worker exposure to these materials. In some instances, the procedures are similar to those already being used by refineries and petrochemical plants. Examples of these are:

1) Enclosed vapor recovery systems for storage tanks

2) Extensive use of mechanical seals rather than packing on rotating shafts.

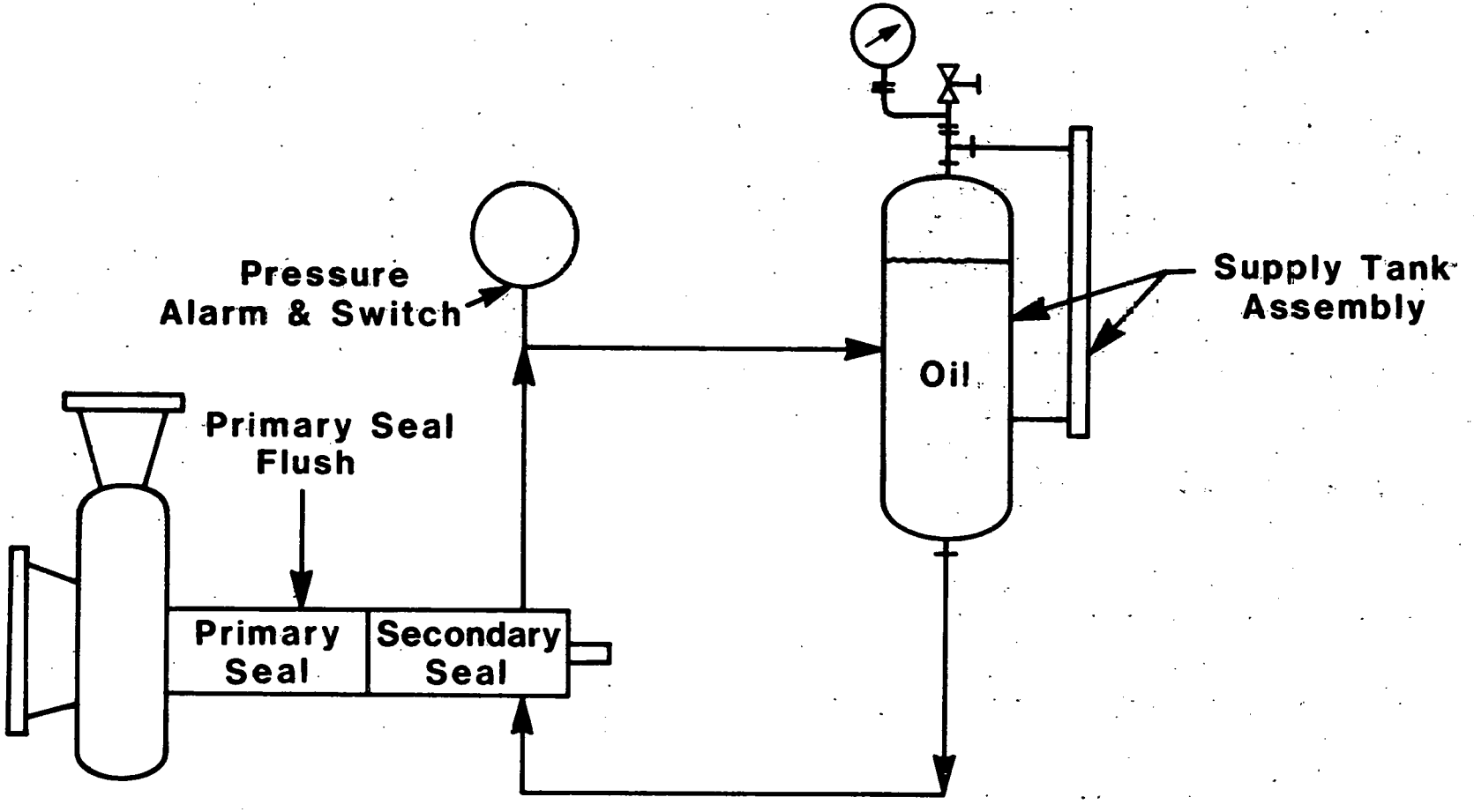
However, in addition to these standard practices, special consideration will be given to other control features to reduce potential exposure of the public and plant personnel.

(1) Pump Seals

The fact that hot coal slurries will have to be pumped presents special problems due to the abrasiveness of the materials. Several sealing systems have been investigated including tandem seals, double seals with a disaster bushing, a double seal followed by an outside tandem seal and a tandem seal with packing as a secondary seal. Detection that seal failure is imminent is of prime importance in determining the proper sealing approach. The tandem seal configuration shows the most promise of providing a reliable means of detecting that a primary seal failure is imminent. Briefly, the tandem seal consists of two mechanical seals both facing the same direction. The seal closest to the impeller, the primary, will be flushed with hot clean solvent. If the primary seal should fail, the hot solvent flush will leak into the secondary seal cavity and cause a rise in pressure. A pressure sensing switch in the secondary seal loop will detect the pressure increase and sound an alarm. The secondary seal will keep the shaft and pump sealed until the pump can be shut down and the primary seal replaced. The tandem seal arrangement is illustrated in Figure 2.

Figure 2

TANDEM PUMP SEAL SCHEMATIC



(2) Valves

Valves are a major source of hydrocarbon releases in refineries and petrochemical plants and have been estimated to cause up to 75% of the total fugitive emissions from these facilities. Due to the number of streams containing mixtures of solids (coal particles) and coal chemicals at high pressure and temperature, considerable attention is being given to the materials of construction and design of the valves used in the SRC-II Demonstration Plant. The Fort Lewis Pilot Plant has provided valuable information on valve performance and continues to test new and prototype valve designs.

(3) Product Handling

The SRC-II process produces approximately 50 MM SCF/D of gas. Pipeline shipment was selected as the only practical method of transportation and the environmental impact will be minimal since an existing pipeline system passes approximately ten miles from the plant site.

Rail shipment was chosen for the high-volume liquid products, primarily fuel oil. The tank train concept offers several positive environmental control features and is currently being considered as the method of transport. For the quantities of liquids produced at the demo plant, the tank train concept has added benefits from a product distribution and cost basis. Up to 20 cars can be loaded with a single fill connection and a single vent connection, therefore potential for spills and fugitive vapor emissions are minimized.

D. Emergency Upsets

The most frequent upsets in the Demonstration Plant that will cause a change from normal gaseous emissions are leaking relief valves, compressor shutdowns, and reduced gas treating plant capacity. These occurrences will send gases to the flare system. To ensure that these gases are fully combusted with a minimum effect on the environment, a controlled combustor system is being evaluated as a possible part of the flare system.

A controlled combustor is a highly efficient combustion system, similar to a gas fired boiler burner and firebox. It would serve two purposes. It would provide efficient destruction of a wide range of materials in the flare gases with essentially no smoke, and it would mitigate the illumination nuisance caused by frequent flaring.

For preliminary sizing evaluation of the controlled combustor, an upset condition, namely, a blockage or upset downstream of the dissolver either in the acid gas removal or cryogenic section, was used. This event may occur several times per year, especially during initial plant operation. The sulfur dioxide emission rate has been estimated to be approximately 10,200 pounds per incident.

Preliminary information from vendors indicate that two units would suffice to handle the proposed design basis. Each unit may be in the order of 25 feet in diameter and 100 feet tall. Emergency upset conditions that exceeded the design case would be diverted to the elevated flarestack.

4. LIQUID EMISSIONS

A. Water Pollution Control

Recycle, treating, incineration, and controlled site drainage are key factors in avoiding water pollution. Discharges of contaminated water into surface waters or aquifers will be eliminated during normal operation by recovery, treating, and recycle of all process water, with contaminants reduced to solids by incineration. Other alternatives will be developed if solid wastes from the incinerator will not meet disposal standards.

B. Water Treating and Discharge

It is planned that the plant process water system will have a zero discharge and the rainwater runoff collection system will be capable of holding a 10 year - 24 hour storm.

The zero process discharge system was chosen because this is a Demonstration Plant and there are unknowns in connection with the water treatment. The system used will remove organics, hydrocarbons, salts and solids using existing technology. Recovered water will be reused in the process, reducing river water requirements. The solids removed will be treated as hazardous material until such time as they are proven not to be.

Several alternates to zero process area water discharge were considered:

- The elimination of reclamation or treating of the process area water was considered to be not feasible because of the known and unknown contaminants in these streams.

- Holding of the untreated process area water for natural evaporation was considered not feasible because the natural evaporation rate is lower than the precipitation rate for the proposed plant site.

- A partial process area water discharge system was considered, one which would discharge process area water streams that would not normally be of a contaminating nature. This has been ruled out, for the present time, because of uncertainty of the risk of contamination of some of these streams.

Untreated discharge of the utility (Oxygen Plant) cooling tower blowdown is being considered. This would decrease the treatment system size by about 300 GPM.

The rainwater runoff system design is based on the EPA Impoundment Guidelines for Refineries. Holding ponds will collect runoff from the plant process area, slag disposal area, and shipping and storage area. Water so collected will be treated and reused in the process, decreasing river water requirements.

Several approaches to waste heat rejection are being explored with particular interest in utilizing dry aerial cooling to (1) reduce the consumptive use of water, and (2) to provide an additional guard against contamination of cooling tower water by process liquids. Table 1 provides a summary of cooling system options presently under consideration.

5. SOLID WASTE DISPOSAL

The major solid wastes from the Demonstration Plant Include gasifier slag and the dehydrated water soluble residues resulting from the use of a waste water incinerator.

The gasification unit will produce 800 tons per day of slag. Little information is currently available on the hazardous or non-hazardous nature of these materials as defined by the Federal Resource Conservation and Recovery Act (RCRA). In order to preclude any adverse environmental impact, the initial waste disposal plan calls for on-site burial of the material in conformance with RCRA.

The slag will be either trucked or pumped to a clay lined landfill possessing an initial capacity of 267,000 cubic yards. The disposal area will include retention dams and surface drainage diversion systems. Runoff and drainage from the storage area will be collected and pumped to the water reclamation system.

TABLE 1

SUMMARY OF BASE CASE AND ALTERNATE COOLING SYSTEMS

Note: Heat load is 1.63 billion BTU/Hr in all cases. All cases are based on the same amount of areial cooling.

CASE	BASE	ALT A	ALT B	ALT C
CASE DESCRIPTION, Tower Types:	Wet (Evaporative)	Dry Indirect	Dry Indirect Plus Wet/Dry	Dry Indirect Wet (Evaporative) Plus Wet/Dry
Water Makeup	High	Negative	Low. For Oxygen Plant cooling only.	Moderate. For all Requirements Except High Pressure Process Cooling
WATER RATES, GPM				
Circulation:	110,000	160,000	142,000	122,000
Evaporated,				
Design	3,500	0	600	2,600
Operating	3,000	0	500	2,000
Drift:	105	0	21	70
FITS WITH WATER BALANCE:	YES	NO (Negative water balance would require discharge of plant water to the river.)	NO	YES (Excessive time required to empty retention ponds.)

There have been some preliminary characterization studies done on slag produced from the gasification of vacuum tower bottoms. The results are shown in Table 2 and indicate the slag is composed primarily of aluminum, iron, and silica.

Table 3 shows the results of the analysis of the leachate from the slag.

The procedures contained in RCRA were used to obtain these data and they indicate that the slag would be classified as non-toxic.

The other major source of solid wastes are produced from treatment of process waters, and runoffs from the process area, coal piles, and slag disposal areas. Since characterization and quantification of these water soluble solid wastes are incomplete at this time, an appropriate method for handling the residues has not been defined. Because they are highly water soluble, disposal in the slag disposal area is not desirable. Depending on the final quantity of these materials, several alternatives disposal methods are being considered.

6. WORKER SAFETY AND HEALTH PROGRAM

Worker safety is a major goal in the design, construction, and operation of the SRC-II Demonstration Plant. The approach to be taken includes: designing to avoid hazards in startup, operations, maintenance, and during upsets, operating the facility in a manner that will prevent accidents, and preparing by plant design, layout, procedure development, and personnel training to deal with potential accidents.

Safety consideration, while of major importance, are substantially analogous to the provisions necessary and normal in large refining and chemical operations. In this brief paper no attempt will be made to discuss in detail the safety program.

A. Health Protection

The goal of the worker health protection program is to ensure that even a worker who spends his entire working career in an SRC facility suffers no injury to his health from occupational exposure to toxic materials or physical agents. The approach to accomplishing this at the SRC-II Demonstration Plant is to design and operate the plant so as to avoid worker exposure to potentially harmful agents and to provide a rigorous health protection program.

The plant will be designed and operated to strictly control worker exposure to toxic materials and to harmful physical agents, such as excessive noise and heat. Many of the design concepts and

TABLE 2

EMISSION SPECTROGRAPHIC ANALYSES OF GASIFIER SLAGS

	Coarse Slag (% by weight)	Fine Slag (% by weight)
Al	15	15
B	0.07	0.08
Ca	0.8	0.9
Cr	0.09	0.02
Cu	0.002	0.002
Fe	15	15
Mg	1	0.8
Mn	0.1	0.1
Ni	0.03	0.02
K	0.2	0.1
Si	20	25
Na[a]	0.07	0.1
Sr	0.05	0.03
Ti	0.8	0.9
V	0.1	0.07

([a]) by atomic absorption

TABLE 3

RESULTS OF SLAG LEACHING STUDIES

	Coarse Slag Leachable (mg/l)	Fine Slag Leachable (mg/l)	Allowable (mg/l)
Ag	<0.005	<0.005	0.50
Pb	<0.010	<0.010	0.50
Ba	<0.1	<0.1	10.0
Cr	<.010	<.010	0.50
Cd	0.015	0.013	0.10
Se	0.017	0.013	0.10
Hg	0.0004	0.0006	0.02
As	0.003	<0.002	0.50
Fe	0.04	0.1	Not listed
NH_3	0.6	1.2	Not listed
SO_4	9.8	7.5	Not listed

operating procedures used in accomplishing this will be straight forward extensions of existing refining technology and will not represent anything unique to coal liquefaction, others will be extensions of engineering controls and procedures developed in the SRC pilot plant program.

A comprehensive health protection program is planned for the Demonstration Plant and will include an employee training and hygiene program, an industrial hygiene monitoring program, and an occupational medicine and epidemiology program. This program is summarized in Table 4. Extensive toxicological studies currently underway and planned under the SRC Pilot Plant contract and by other DOE contractors will continue and will improve our understanding of the potential health and ecological impacts of SRC materials.

The employee education and hygiene program has as objectives: informing the employee of the known and potential hazards in the work environment, particularly those associated with exposure to coal-derived materials, motivating the employee to use appropriate protective measures, and providing the employees with the protective equipment, clothing, facilities, and techniques needed to minimize the potential for adverse health effects. This is summarized in Table 5. Each new employee will undergo a formal orientation and training program, and will be provided appropriate clothing and other protective gear, shower and changehouse facilities, and will be required to adhere to approved personal hygiene procedures.

The employee educational program to be utilized at the Demonstration Plant has not yet been developed in detail, but is anticipated to be structured similarly to the program presently used at the pilot plant. There the employee education program consists of new employee orientation and continuing education. The new employee orientation consists of an audio/visual slide presentation describing the plant, potential exposures in the plant, and appropriate protection techniques. After the slide presentation, the new employee is given the SRC Health Protection Manual and is required to read it. Then the employee is taken through the locker room/changehouse area and shown the proper entrances and exits within the area, proper disposition of soiled clothing, and proper storage of clean work clothing and street clothes. Periodic presentations are given to employees on various health protection and safety topics.

The industrial hygiene program will monitor the workplace for conventional toxic materials and physical agents common to refinery and chemical operations as well as to those exposures which may be unique to coal liquefaction. Development work, presently underway on techniques for monitoring dermal contamination by potentially

TABLE 4

SRC HEALTH

PROTECTION PROGRAM

MEDICAL SURVEILLANCE

EMPLOYEE TRAINING

PERSONAL HYGIENE

INDUSTRIAL HYGIENE MONITORING

EPIDEMIOLOGY

TABLE 5

EMPLOYEE TRAINING

OBJECTIVES

A. TO INFORM EMPLOYEES OF KNOWN AND/OR POTENTIAL HAZARDS ASSOCIATED WITH COAL-DERIVED MATERIALS.

B. TO EDUCATE EMPLOYEES ON THE AVAILABILITY AND USE OF PROTECTIVE EQUIPMENT, CLOTHING AND FACILITIES TO MINIMIZE THE HAZARD.

C. TO EDUCATE EMPLOYEES ON THE RECOMMENDED PERSONAL HYGIENE PRACTICES TO MINIMIZE THE HAZARD.

D. TO MOTIVATE EMPLOYEES TO USE APPROPRIATE PROTECTIVE EQUIPMENT, ETC., AND TO FOLLOW PERSONAL HYGIENE PRACTICES.

E. TO ENCOURAGE EMPLOYEES TO BE AWARE OF AND TO REPORT ANY UNUSUAL SKIN DISTURBANCES, DISCOLORATIONS, ETC.

toxic materials will, if successful, be implemented in the demonstration facility.

The occupational medical and epidemiology programs will seek to detect, at the very earliest stages, any occupationally related shifts in worker medical profiles, to reverse, to the extent possible, any untoward impact and to establish causality and preventive strategies should any occupationally related health problems be detected. The anticipated approach will be an extension of the SRC pilot plant program and will utilize pre-employment and periodic medical examinations together with intensive analysis of the findings of such examinations and the occupational and personal histories of the workers.

A major toxicological program is underway and planned for the SRC materials. Table 6 summarizes the P&M program for SRC-II materials. Major areas to be addressed in the toxicological studies are acute studies, dermal studies, reproductive toxicology studies, inhalation studies, and mutagenicity. Table 7 summarizes the complementary program under way at Battelle Pacific Northwest Laboratory.

7. ACKNOWLEDGEMENT

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TABLE 6

REVISED TOXICOLOGY PROGRAM

SRC-II

	Task 1					Task 2		Task 3			Task 4			Task 5
	Acute Studies					Dermal Studies		Reproductive Toxicology			Inhalation			Muta-genicity
								Teratology						
Materials	Oral LD50	Dermal LD50	Eye Irrit.	Guinea Pig Sens.	Aspir. Hazard	90-Day* Rabbit	18-Mo.* Mouse	Dermal* Rat/Rabbit	Inhal.* Rat/Rabbit	Dermal Multigen. Rat	Inhal. LC50	90-Day* Rat	2-Year Rat	In Vitro
Coal Slurry	X	X	X	X		X	X	X		X				X
Stripper Tower Bottoms	X	X	X	X				X						X
Product Fuel Oil	X	X	X	X	X	X	X	X	X	X	X	X	X	X
Vaccuum Bottoms	X	X	X	X			X	X						X

X = Material to be studied

* = Pilot study necessary

TABLE 7

SRC-II STUDIES BY BATTELLE PNL

ASSAYS	SRC-II MATERIALS									
	Coal Slurry	Naphtha	Middle Distillate	Heavy Distillate	SRC-II Product	Vacuum Bottoms	Stripper Tower Bottoms	Mineral Residue	Mineral Residue Leachates	Fractions from SRC Materials and Other Reference Materials
I. Cellular Studies										
A. Microbial mutagenesis	P	C	C	C	P	P	P	P	P	IP
B. Mammalian cell toxicity & transformation		IP	IP	IP	P	P	P	P	P	IP
C. Chinese hamster ovary cell mutagenesis				P	P	P				P
II. Oral Studies										
A. Acute toxicity		C	C	C	P	P	P	P	P	P
B. Subchronic toxicity		C	C	C	P	P	P	P	P	P
C. Developmental Toxicity										
1. Prenatal effects		IP	IP	IP	P					P
2. Postnatal effects			IP	IP	P					
D. Transplacental carcinogenicity				P	P					P
E. Dominant lethality				P	P					P
III. Dermal Studies										
A. LD_{50}		C	IP	C			P			IP
B. Carcinogenesis in mouse		IP	P	IP						IP
IV. Inhalation Studies										
A. Teratology								P		
B. Subchronic toxicity (90-day)								P		
C. Chronic (Carcinogenesis)								P		
D. Pulmonary function								P		
V. Other Toxicity Tests										
A. Absorption and Distribution				P						P
B. Enzyme induction			P	P	P					P
C. Metabolism of known carcinogens					P					P

P - Proposed; IP = In Progress; C = Completed

TOXICOLOGIC STUDIES OF SRC MATERIALS

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In light of the energy crisis which the U.S. faces, it is becoming imperative to develop new energy technologies in as rapid a manner as possible. In order for these new technologies to develop in the most propitious manner, it is necessary to perform studies to determine potential health and environmental effects associated with the technology. However, it is sometimes difficult to perform these studies with materials which are meaningful to the final process that is developed. Thus, a "Catch 22" situation develops. You have to have the technology before appropriate materials can be obtained; yet you need the health and environmental studies before the technology is deemed acceptable. We are going to describe an approach which has been taken in the solvent refined coal area to provide meaningful health effects data to the technology in a time-frame which permits technology changes to ameliorate potential problem areas.

We at the Pacific Northwest Laboratory have been engaged in a broadly based toxicologic program dealing with SRC materials. These studies have included 1) microbial mutagenesis, 2) in vitro mammalian cell toxicity and transformation assays, 3) epidermal carcinogenesis (skin painting), 4) acute and subchronic oral toxicity, 5) developmental toxicity, 6) dominant lethal assays, 7) inhalation toxicity, and 8) dosimetry and metabolism. We have approached the study in two concomitant modes. In the first mode we have used chemical characterization and plant operational data to select materials to be evaluated using a tier approach. In this mode, materials are first assayed using microbial systems. On the basis of the results of the microbial assays, materials are selected for study in mammalian cell culture. The results generated in the cellular systems are used as selection criteria for materials to be used in animal assays, particularly the assays for carcinogenesis. In the second mode, materials considered to be of prime importance to occupational or environmental health are entered directly into animal systems for study of acute, subchronic, mutagenic, and developmental effects. Long-term effect studies are then designed using the results from these whole-animal and cellular assays, and the chemical characterization and plant operational data. At each level of testing, we have included other materials for comparative purposes. These materials which include shale oil, petroleum crudes, other fossil-derived materials, and pure known chemical mutagens and carcinogens help us in placing results with SRC materials in a more meaningful perspective.

We have in our program attempted to establish a balance between standardized biological testing and research. The use of standard testing protocols permits us to obtain information necessary for the evaluation of the potential health hazards of a number of important materials in order to meet regulatory demands. Research, on the other hand, enables us to obtain a better understanding of the nature of potentially harmful materials as well as to obtain data which will permit a better extrapolation of the experimental data to man. The research effort also allows us to explore potential ways of ameliorating the adverse effects of such materials.

The types of materials encountered in coal liquefaction processes are generally complex mixtures which may behave quite differently in biological systems than do individual constituents. Interactions among constituents may result in both antagonistic and synergistic effects, the sum of which may or may not be predicted from the results obtained with individual constituents. Our philosophy, therefore, is to chemically characterize SRC materials (raw products, process stream materials, solid wastes, etc.) which are important in considerations of health and environmental consequences of production, storage, transport, accidental spills, and maintenance. We then characterize these mixtures biologically using cellular and animal systems and relate biologic activity to chemical composition. Further identification of the components producing biological activity is performed through iterative cycles consisting of chemical and physical fractionation accompanied by bioassay of the fractions obtained.

I would like to describe in some detail one facet of our program to: 1) illustrate a part of our approach to the toxicologic study of complex coal liquids, 2) show the benefit of interactions between biologists, chemists, and process engineers, and 3) demonstrate the necessity of evaluation and reevaluation of the relevance and representativeness of the samples being evaluated to demonstration/commercial operation. I will use our microbial mutagenesis studies since they illustrate these points in a concise way.

The materials used in these studies have been obtained from the SRC pilot plant at Ft. Lewis, Washington operated by the Pittsburgh & Midway Coal Mining Co., Inc. for the Department of Energy. Light oil (LO), wash solvent (WS), and process solvent (PS) were obtained from the SRC-I process and light, middle, and heavy distillates (LD, MD, and HD) from the SRC-II process. The boiling point ranges and specific gravity ranges for these materials are given in Table 1. The materials in all cases were obtained during equilibrium run conditions when the processes were being operated for determination of material balances. It should be noted that these materials are of pilot plant origin and may or may not represent materials to be found in demonstration or commercial applications. We will discuss this aspect later in the paper.

Table 1

Boiling Point Ranges of SRC Materials
Used in Biological Experiments

Process	Material	Boiling Range (°F)	Density
SRC-I	Light Oil	ambient to 380	0.72
	Wash Solvent	380 to 480	0.96
	Process Solvent	480 to 850	1.04
SRC-II	Light Distillate	134 to 353	0.82
	Middle Distillate	366 to 541	0.99
	Heavy Distillate	570 to 850	1.10

To illustrate how biologic evaluation can be integrated with chemical characterization and with process operations, I would like to present some data which have been obtained using the Ames Salmonella system. Briefly, the Ames assay is performed by mixing the test material with the organism in the presence or absence of mammalian liver microsomal enzymes (S9) and determining the number of organisms which revert (mutate) from dependency on histidine in the medium to nondependency. Assay in the presence of S9 detects mutagens which require metabolic activation to effect mutagenesis; assay in the absence of S9 detects mutagens which do not require metabolic activation. Use of appropriate strains of Salmonella permits determination of the nature of the mutation (frame shift or point mutation) which is a function of the biochemical properties of the test materials. The Ames assay is often used for screening large numbers of materials for biological activity because it is rapid and inexpensive and the results show a high correlation with those of carcinogenesis assays.

The mutagenic activity of a number of crude materials are shown in abbreviated form in Table 2. It can be seen that of the major process stream materials from the SRC-I and SRC-II processes, PS and HD (high boiling point materials) contain substantial mutagenic activity. The LO, WS, LD, and MD were without activity. The known chemical carcinogen, benzo(a)pyrene (BaP), shows approximately 3X the activity of heavy distillate (HD) while another well-known chemical carcinogen, 2-aminoanthracene (2-AA), is about 100 times as active. Raw shale oil shows a small degree of activity while crude petroleum showed no activity in the Ames system.

Table 2

Comparison of the Mutagenicity of Solvent Refined Coal Materials, Shale Oils, and Crude Petroleums in Salmonella Typhimurium TA98.

Materials	Revertants/μg of Material
SRC-I	
Process solvent	12.3 ± 1.9
Wash solvent	<0.01
Light oil	<0.01
SRC-II	
Heavy distillate	40.0 ± 23
Middle distillate	<0.01
Light distillate	<0.01
Shale Oil	
Paraho-16	0.60 ± 0.19
Paraho-504	0.59 ± 0.13
Livermore-L01	0.65 ± 0.22
Crude Petroleum	
Prudhoe Bay	<0.01
Wilmington	<0.01
Pure Carcinogens	
Benzo(a)pyrene	114 ± 5
2-Aminoanthracene	5430 ± 394

In order to determine the classes of materials responsible for the mutagenic activity, fractions were prepared from PS and HD using the solvent extraction procedures similar to that employed by Swain, Cooper, and Stedman(1) for fractionation of tobaccosmoke condensates, and widely used for chemical class fractionation of environmentally complex mixtures. Since PS and HD varied only in their quantitative response in the Ames system, the remainder of this report will generally use HD to illustrate the approach we have used in identifying important materials. In addition to yielding the expected acidic, basic, and neutral fractions, fractionation of HD also yielded basic and neutral tar fractions. The relative amounts of material in each fraction are shown in Figure 1. When these fractions were assayed using the Ames system, the highest specific activity (number of revertants per microgram of material) was found in the basic fraction (Table 3). Significant activity was also found in the basic and neutral tar fractions, although the specific activity was about 1/8 to 1/2 of that of the basic fraction. The total mutagenic activity in the basic and neutral tar fractions, however, was greater than that in the basic fraction due to the substantially greater mass of the tars. The acidic and neutral fractions showed essentially no mutagenic activity. Under the conditions of these experiments, the polynuclear aromatic (PNA) fraction did not demonstrate significant

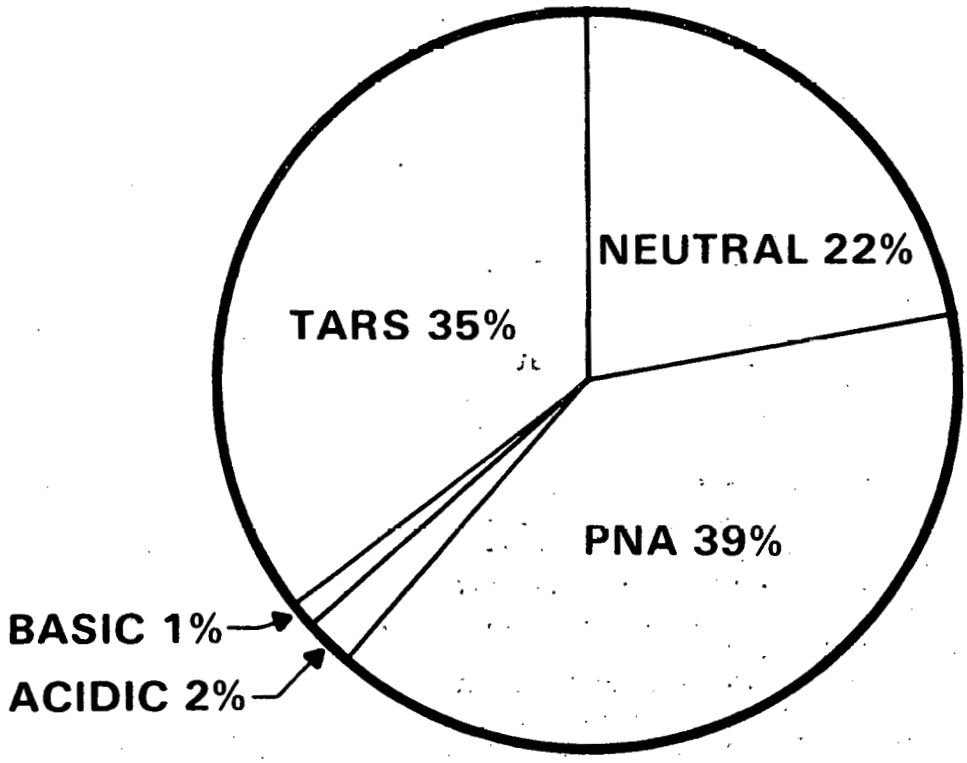


Figure 1. Percentage distribution of fractions obtained by solvent fractionation of heavy distillate.

mutagenic activity. It is important to note at this point that this occurs not because of the absence of potentially mutagenic components in the PNA fraction but is probably due to the large number of compounds in this material which prevent metabolic activation of mutagenic components.

Table 3

Mutagenic Activity in Fractions of SRC-II Heavy Distillate (HD)

Material	Revertants/μg	% of Total Activity
Heavy distillate, unfractionated	40	100
Basic fraction	400	4
Basic tar	66	16
Neutral tar	108	28
Benzo(a)pyrene	114	---
2-Aminoanthracene	4326	---

The above results led to further studies of the nature of mutagenic materials active in HD. It was felt on the basis of previous chemical analysis that polar nitrogen-containing compounds might be responsible. To test this idea the SRC-II distillates and their basic and tar fractions were analyzed by thin layer chromatography (TLC) using a solvent system designed to separate the polar nitrogen-containing compounds from less-polar constituents. Samples of pure chemicals were also chromatographed to aid in the location and identification of major compound classes known or suspected to be present in HD. Fluorescent areas corresponding to these chemicals were located by illumination with an ultraviolet light. The chromatograms were cut into strips, the strips extracted with a hexane-acetone mixture, and the extracts subjected to study for mutagenic activity.

The separation of the mutagenic constituents from the basic fraction of HD is depicted schematically in Figure 2. The major portion of the activity was found to migrate with Rf values (distance migrated by the test material/distance traveled by the solvent front on a TLC plate) between 0.07 and 0.20. These values are very close to those obtained for aromatic amines, a class of compounds suspected but not previously shown to be present in SRC-II materials. Similar results were obtained when the basic tar or neutral tar fraction of HD (or PS and PS basic and tar fractions) were chromatographed.

Extracts from the mutagenically active regions after thin layer chromatography of heavy distillate and its fractions were subjected to gas chromatographic/mass spectral (GCMS) analysis to identify specific components. Several primary aromatic amines, including aminonaphthalenes (AN), aminoanthracenes (AA), aminophenanthrene (APH), aminopyrenes (AP), and aminochrysenes (AC), were found to be associated with TLC regions which were mutagenically active. An estimate of the

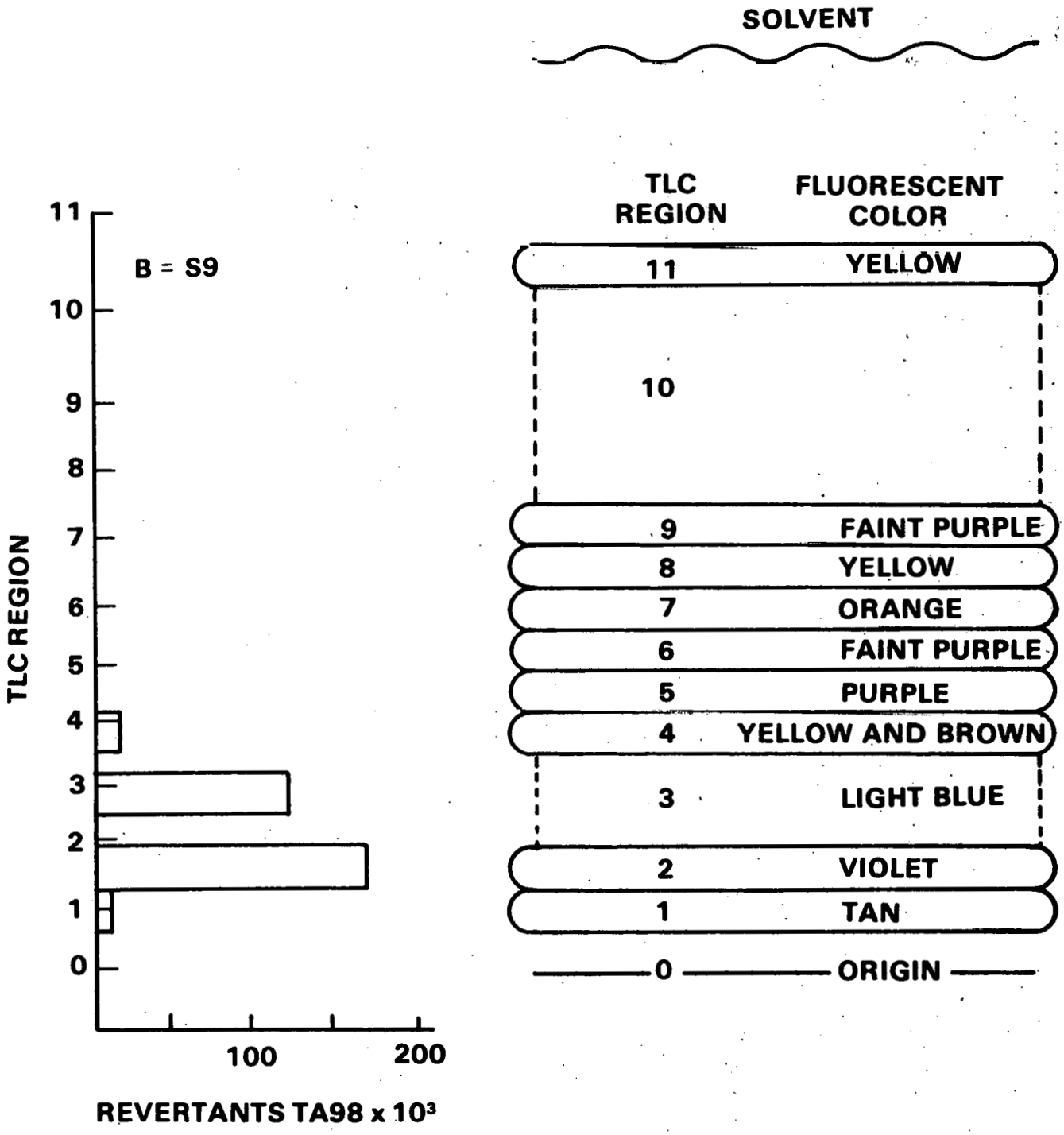


Figure 2. Thin layer chromatographic separation of mutagenic agents found in the basic fraction of heavy distillate.

aromatic amine content of the active TLC regions from the HD basic fraction is shown in Figure 3; the relative concentrations of AA, AP, APH, and AC were highest in the regions with the strongest mutagenic activity. With the exception of AN, primary aromatic amines were not found in regions that lacked mutagenic activity. Aminofluorenes (AF) and aminocarbazoles were tentatively identified in active regions from the basic fraction but higher-resolution analysis must be performed to obtain more definite identification. Qualitatively similar results were obtained when the basic or neutral tar fractions were analyzed. Analyses of these materials suggest that the 3- and 4-ring primary amines are important mutagens but that the 2-ring aminonaphthalenes contribute little to mutagenic activity.

Since GCMS analysis showed the presence of aromatic amines in the mutagenically active regions of thin layer chromatograms of the basic, basic tar, and neutral tar fractions of HD, a series of experiments were performed to determine if these amines were responsible for the mutagenic activity. One approach utilized the unique catalytic properties of a purified liver enzyme system called mixed-function amine oxidase (MFAO). This enzyme is specific for the metabolic transformation of primary aromatic amines to a mutagenically active state. The MFAO is inactive with BaP and other polycyclic aromatic hydrocarbons (PAH). Nor does it activate the 2-aminonaphthalenes, probably due to the instability of the enzyme product. Previous experiments utilized a mixture of hepatic enzymes (called S9) which activates a wide variety of PAH's; therefore, no distinction could be made between amines and other polycyclic constituents. In this experiment, the basic fraction of HD was again subjected to thin layer chromatography and the various regions tested for mutagenic activity after activation with either MFAO or S9. Again, TLC regions with Rf's of approximately 0.08 to 0.20 were found to contain the major portion of the activity when the assay was performed using S9, as had been seen previously. When activation was performed using MFAO, the same distribution of mutagenic activity among the TLC regions was found as with S9. These results thus provide further evidence that aromatic amines are both present and capable of expressing their mutagenic activity in the basic fraction of HD.

The above data were considered as presumptive for the involvement of the primary aromatic amines as causative agents in the mutagenic activity of the basic fraction and of the heavy distillate. A more direct approach was taken by treating HD and its basic fraction with nitrous acid. This procedure diazotizes aromatic amines and renders them nonmutagenic in the Ames system. Thus, disappearance of mutagenic activity in the basic fraction or in the heavy distillate after nitrous acid treatment would provide direct evidence for the importance of this class of compounds for mutagenesis. When this was done with a number of materials, as shown in Figure 4, it can be seen that the mutagenic activity of a pure aromatic amine 2-aminoanthracene was almost completely lost while the activity of benz(a)pyrene or benzacridine was not affected by the nitrous acid treatment. Moreover, treatment with nitrous acid eliminated most of the activity seen with

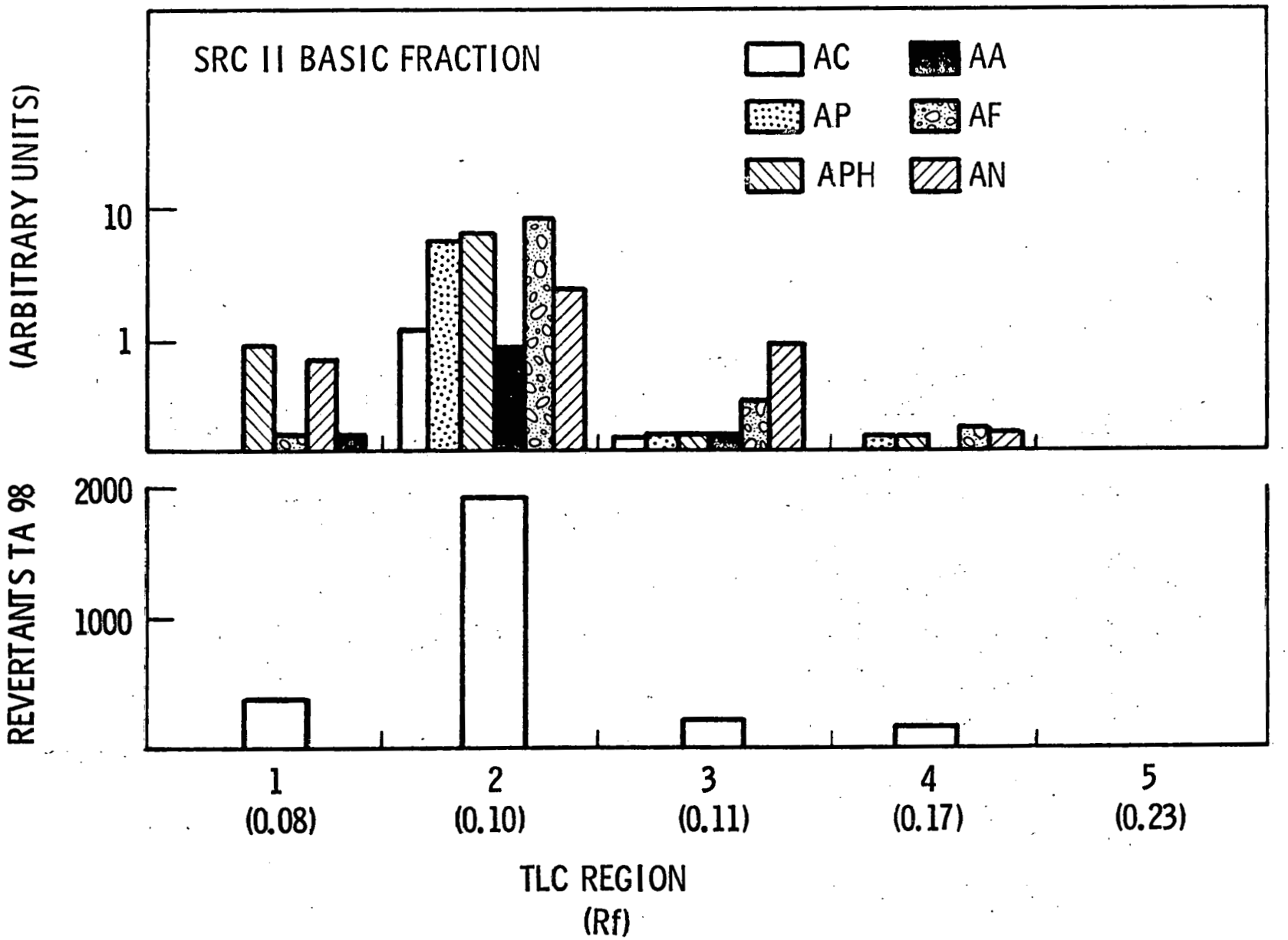


Figure 3. Relative concentrations of aromatic amines and mutagenic activity on thin layer chromatograms of the basic fraction of heavy distillate. AC, aminochrysene; AP, aminopyrene; APH, aminophenanthrene; AA, aminoanthracene; AF, aminofluorene; AN, aminonaphthalene.

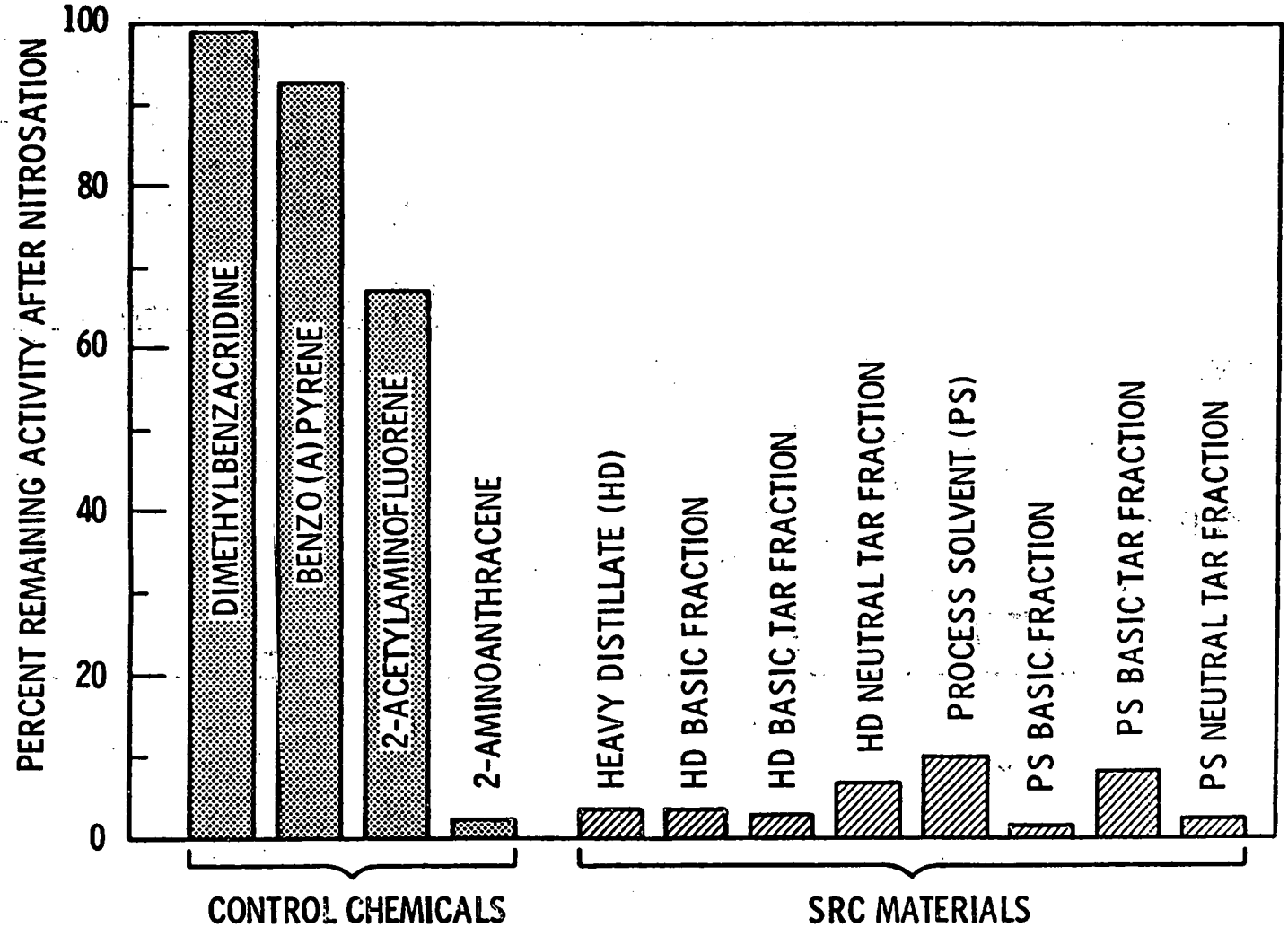


Figure 4. Effect of nitrosation on the mutagenic activity of SRC materials.

HD, PS, and their basic fractions. It thus appears that much of the mutagenic activity is probably due to the presence of primary aromatic amines in both the crude material and in the basic fractions.

The data obtained in the Ames system have been used to guide a number of other biological experiments. For example, a series of mammalian cell culture experiments have been performed using materials which are active and inactive in the Ames system. The data obtained in these experiments confirm and extend the Ames results. We also have initiated skin painting experiments with SRC materials. Since not all materials could be tested, we have utilized those which have shown substantial activity in the Ames system and have also shown transformation activity in mammalian cell culture experiments. For example, HD was initially selected as an SRC-II material to be tested in skin painting. Since light distillate has been shown to be inactive, we also used it for comparison. These comparative experiments allow us to evaluate the ability of the cellular systems to predict the carcinogenic potential of these crude materials.

Although there is not the space to present the details of the mammalian cell culture and skin painting experiments, a summary of results from the Ames assay, mammalian cell culture studies, and skin painting experiments are presented in Table 4. Examination of the results show that there is relatively good qualitative agreement between the cellular assays and the tumorigenesis data. However, there are quantitative differences. For example, mutagenic activity of 2-aminoanthracene is very high but tumorigenic activity is only moderate. On the other hand, the mutagenic activity of HD is moderate but the tumorigenic activity is high.

Table 4

Comparison of Mutagenic and Carcinogenic Activity for Several Crude Fossil-Derived Materials

Material	Ames Assay	Mammalian Cell Culture	Skin Tumorigenesis
Light distillate	----	----	----
Heavy distillate	++	++	++++
Shale oil	+	+	++
Crude petroleum	----	slight	+
Benzo(a)pyrene	++	++	+++
2-Aminoanthracene	++++	+++	++

As further separations are performed on materials derived from HD, the Ames system is used to determine their biologic activity. Those showing mutagenic activity are then subjected to further chemical characterization using, particularly, gas chromatographic mass spectrometry. Thus, this interaction between use of a simple biological system and chemical characterization will continue to be used to determine if further localization of the activity to certain specific materials can be made.

The data obtained above have also suggested that the amount of biological activity as represented by mutagenesis in the Ames system might be altered by changing process conditions or by adding other steps to the processing. For example, a sample of coal liquids was hydrotreated under either moderate or severe processing conditions. When the treated material was compared to the untreated material using the Ames system, it was found that the mutagenic activity was significantly reduced by both severe and moderate hydrotreating (Fig. 5). These biological results correlate well with changes in chemical composition produced by hydrotreating (for further discussion of the effects of hydrotreating on chemical composition, see the paper by Wilson, Pelroy, and Craun elsewhere in this volume). These data suggest that certain process treatments may be important in altering the biological activity. Thus, biological data obtained early in process development are being used in considerations of ways of altering the development of the technology to make the products more acceptable from a biological and environmental viewpoint.

The materials used in the described studies were obtained about two years ago when less information was available concerning the design of the demonstration plant. Therefore, a detailed review of the pilot plant operation when these samples were obtained has been performed. Conditions which pertained when the middle and heavy distillate samples were obtained are illustrated in Figure 6. From this sequence of operating conditions, the following factors must be considered relative to the materials used:

1) Samples were taken before fully stable operation was achieved.
2) Feed to the distillation tower at the time of MD and HD sampling included:
    a. Fresh production from 2 days of balance period operation.
    b. Seal flush HD from balance period.
    c. Seal flush HD during 30 hours of plant upset.
    d. Seal flush HD and freshly produced material during approximately 30 hours of start-up following plant upset.
3) The coal type (Blacksville) is relatively unreactive and of low priority for commercial-scale SRC feed.

This information illustrates that a number of complicating factors may be encountered during sampling of materials and that these factors must be taken into account when extrapolating the data to scaled-up operations. In the case of our studies, this evaluation shows that the materials used actually represented a cross-section of a number of conditions. Thus, the data obtained are judged to have generic significance to scaled-up operations. That is, they are probably good in a qualitative sense, but additional data are needed to ensure that the results can be applied quantitatively to demonstration/commercial operation. Thus, there must be continual interaction among the process engineers, the chemist, and the biologist to ensure

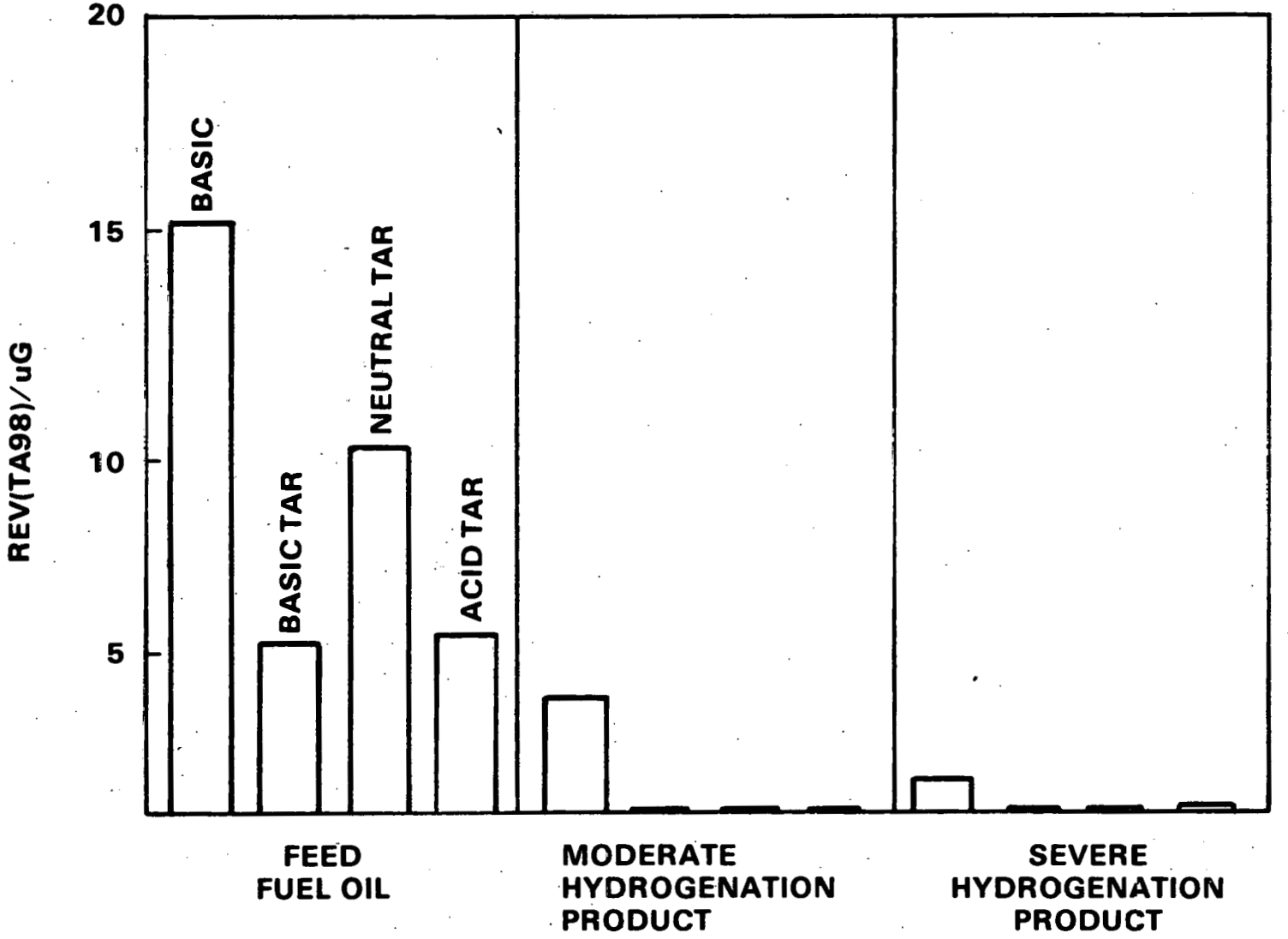


Figure 5. Effect of moderate and severe hydrotreating on the mutagenic activity of a coal-derived fuel oil.

that meaningful data are obtained in the right time-frame and that these data can be updated as more detailed knowledge of demonstration and commercial designs are obtained. We suggest the need for comparable evaluations for other technologies.

With these cautions in mind, improved sampling procedures have been devised for obtaining materials under specified operating conditions. The sampling procedures take into account elements of the process which may influence the composition of the materials to be obtained. Thus, the next set of samples should be even more closely related to those expected from demonstration/commercial operation.

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SCREENING OF HYDROTREATED COAL LIQUIDS FOR MUTAGENIC ACTIVITY

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ABSTRACT

The Ames test was used to screen coal liquids from the SRC-II process for mutagenic activity before and after hydrotreatment. The coal liquid was hydrotreated at 2,000 psig over a commercial catalyst at temperatures ranging from 310° to 400° C. This range of conditions removed more than 90 percent of the sulfur, from 30 to greater than 99 percent of the nitrogen, and from 39 to 99 percent of the oxygen. Hydrogen was increased from 8.4 to 12.4 wt-pct for these conditions. At moderate conditions for this test (325° C), mutagenic activity had been decreased to a level indistinguishable from that of the control sample which had no coal liquid present.

INTRODUCTION

Distillate coal liquids from the SRC-II process and hydrotreated products from this coal liquid were screened for mutagenic activity by the Ames test. The coal liquid was hydrotreated at several levels of severity in a bench-scale, continuous-flow hydrogenation unit at the Bartlesville Energy Technology Center. The immediate goal of this study was to survey process conditions with a commercially available catalyst to provide samples upgraded to varied degrees for investigation of biological activity and for detailed characterization analyses. Long-range goals are to contribute to a data base to evaluate raw material sources, liquefaction or other production processes, characterization of feedstocks for further refining to transportation and other end-use fuels, selection of refining processes, and estimation of type and equality of end products expected from combinations of these steps.

McFarland (5)[4] explains the potential health problems involved in handling coal liquids. However, these data still are incomplete, especially for upgraded liquids.

1/ Chemical Engineer
2/ Branch Chief now retired
3/ Chemist
4/ Underlined numbers in parenthesis refer to items in the list of references at the end of this report.

EXPERIMENTAL

Equipment

The bench-scale hydrogenation unit (figure 1) is a once-through, trickle-bed reactor with downflow of gas and liquid over a fixed-bed catalyst. The unit is designed for operation up to 3,000 psig and 450° C. Reactor temperature, pressure, and hydrogen flow and liquid level in the high-pressure product separator are controlled automatically. The catalyst was 100 ml of American Cyanamid HDS-3A, a 1.6-mm-diameter extrudate of nickel-molybdenum-alumina. The catalyst was diluted with inert, granular alpha-alumina to provide a bed depth of 46 cm in the middle section of a 2.4-cm ID vertical reactor with a 0.8-cm OD internal thermocouple well. The catalyst was progressively more dilute toward the top of the bed to minimize exothermic temperature effects. End sections were packed with alpha-alumina to provide for preheat and cooling zones.

The catalyst was presulfided and operated for about 100 hours on a petroleum gas oil (200° to 500° C boiling range, 0.8 wt-pct sulfur) to check controls and provide some catalyst aging before exposure to the coal liquid.

Sample Materials

The SRC-II liquid was obtained from the Pittsburg and Midway Coal Mining Co. The liquid was produced from Material Balance Run No. 77 SR-12 on coal from the Pittsburg seam (Consol's Blacksville No. 2 mine in West Virginia). The middle (177-288° C) and heavy (288° to 454° C) distillates were blended to the same ratio as produced by the material balance run --for example, 75.5 percent middle distillate and 24.5 percent heavy distillate. The feed contained 0.23 wt-pct sulfur, 1.06 wt-pct nitrogen, and 3.29 wt-pct oxygen and boiled between 185° and 380° C (5-95 percent) by simulated distillation.

Operating Procedures

Operating conditions selected as likely to maintain catalyst activity and provide the range of upgrading desired were 2,000 psig pressure, 310° to 400° C, and 0.5 to 1.0 volume liquid feed/volume bulk catalyst/hour (LHSV). Hydrogen flow was held constant at a rate corresponding to 10,000 scf/bbl to 0.5 LHSV or 5,000 scf/bbl at 1.0 LHSV. Variation in hydrogen flow rate in once-through operation has little effect at more than 5,000 scf/bbl. Operation at each condition was for approximately 24 hours to allow 8 to 12 hours for equilibration plus time to accumulate about 750 ml of liquid product. Table 1 shows the sequence of reactor conditions and essential process results.

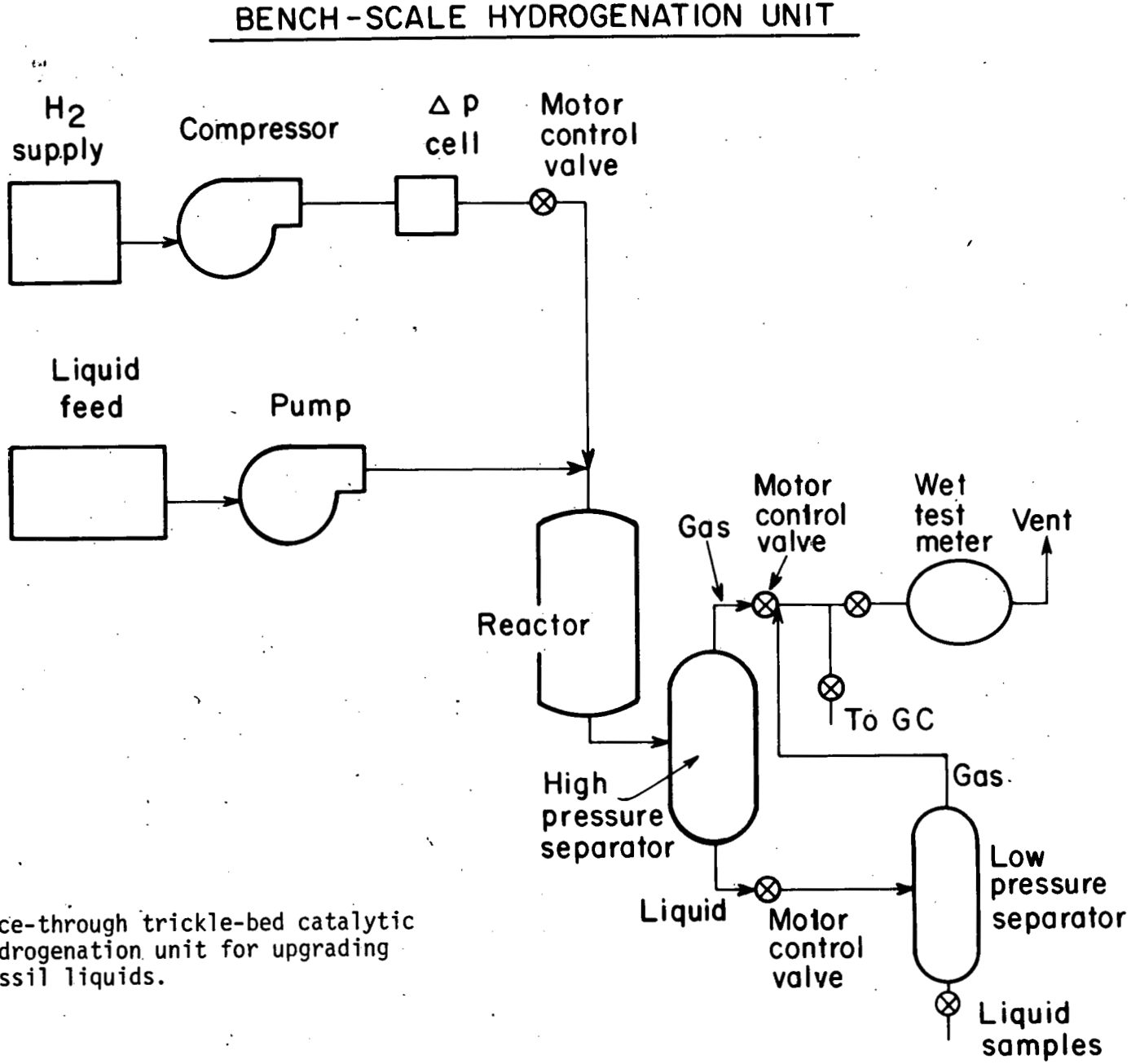


Figure 1. Once-through trickle-bed catalytic hydrogenation unit for upgrading fossil liquids.

TABLE 1. - Process conditions and results

Sample period	Liquid product					Approx. H_2 Cons., scf/bbl	Catalyst temperature, °C	Liquid feed rate, LHSV
	Sp. gr., 60°/60°F	Hydrogen, wt-pct	Nitrogen, wt-pct	Sulfur, wt-pct	Oxygen, wt-pct			
(Feed)	1.003	8.42	1.057	.25	3.29	-	-	-
1	.921	10.81	.352	.01	.59	1,930	325	0.50
2	.948	10.06	.631	.02	1.65	1,270	325	1.0
3	.902	11.54	.033	.01	.17	2,670	350	.50
4	.953	9.80	.700	.02	1.58	970	310	.50
5	.887	12.24	.001	.01	.09	2,880	375	.50
6	.877	12.39	.001	.01	.03	3,250	400	.50
7	.868	12.82	.001	.01	.06	5,010	400	.35
8	.962	9.68	.742	.01	2.00	980	325	1.0

Liquid product was withdrawn periodically from a low-pressure separator, and the combined high- and low-pressure effluent gas was sampled for analysis. The liquid feed and products were screened for chemical mutagens by the Ames assay (1,4).

Period 4 was a test of a very mild condition after a weekend shutdown. Period 7 was a test of the liquid feed pump at a low rate. Period 8 was a brief test for decline in activity from period 2, although the entire operation was too short for significant life testing. Periods in the order of 2, 1, 3, 5, and 6 were intended to cover the desired range of increasing upgrading.

RESULTS AND DISCUSSION

The results in table 1 show the expected trends as hydrotreating severity was increased with reaction temperatures in the range of 310° to 400° C. The nitrogen in the product liquid at 375° C had decreased to less than 0.001 wt-pct compared to the feed at 1.06 wt-pct. Oxygen in the 375° C product decreased to 0.09 wt-pct from 3.29 wt-pct in the feed, and specific gravity decreased from 1.00 for the feed to 0.89 in the 375° C product. Hydrogen content increased from 8.42 wt-pct in the liquid feed to 12.24 wt-pct over this same range of process conditions. Figure 2 shows the nitrogen decrease in the liquid product compared to the hydrogen increase for this sample.

Calculated hydrogen consumptions varied from 970 to 2,880 scf/bbl for the range of process conditions for 310° to 375° C which is within the ranges reported by others (2-3). Precise hydrogen content of the liquid product,

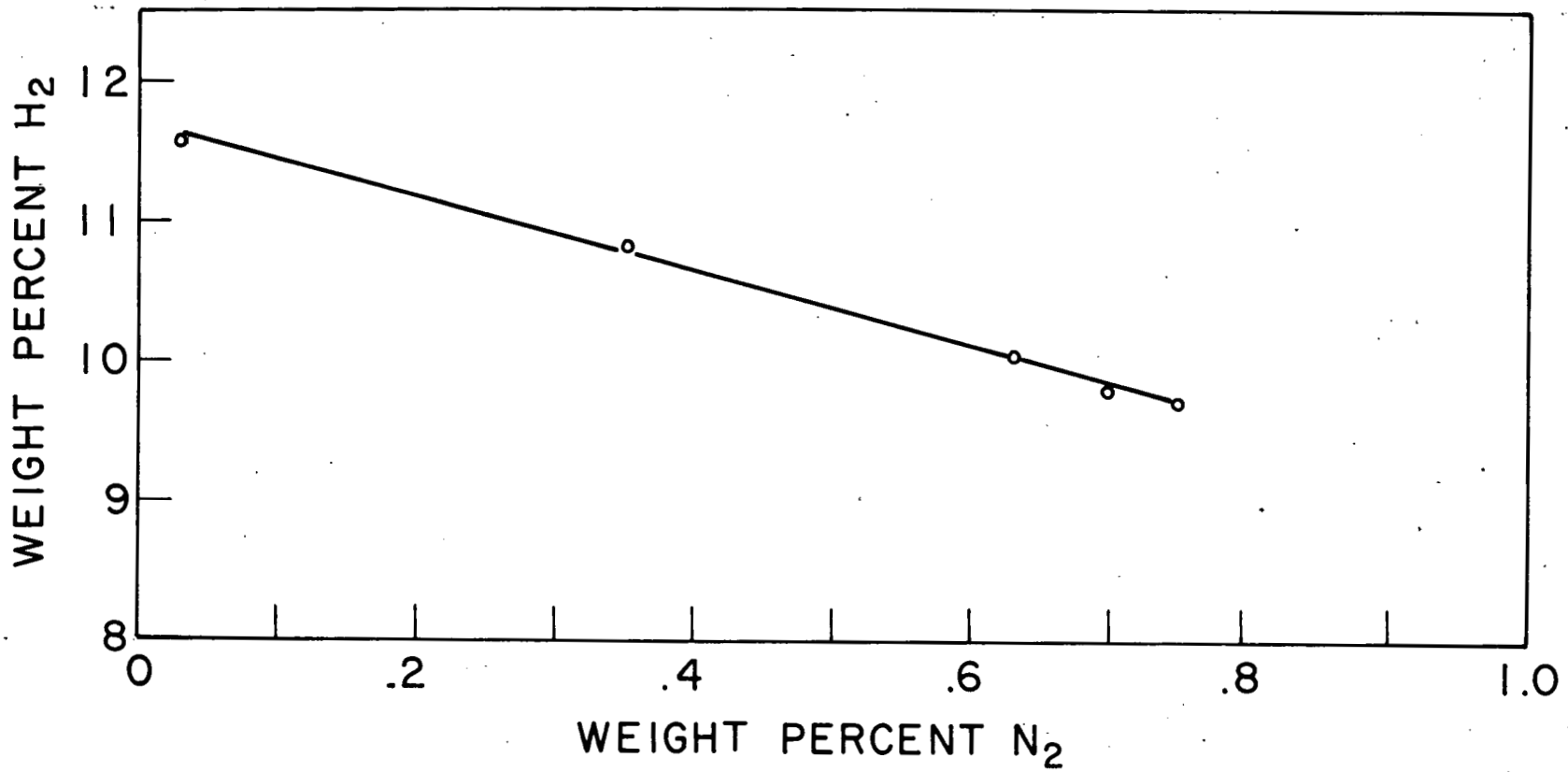


Figure 2. Correlation of hydrogen and nitrogen contents in hydrotreated SRC-II liquids.

used in calculation of hydrogen consumption, was determined by Nuclear Magnetic Resonance spectroscopy through the courtesy of Phillips Petroleum Company. Analysis of the effluent gas did not include hydrocarbons heavier than ethane. Contributions of the heavier hydrocarbons to hydrogen consumption are small for hydrotreating at conditions which cause very little cracking of hydrocarbons since most of the consumed hydrogen goes into the liquid product.

The distillation range of the liquid products was shifted downward as hydrotreating severity was increased (figure 3). A comparison of the temperatures for 5, 50, and 95 wt-pct distilled and the magnitude of the simulated distillation shifts are shown in tabular form in table 2. The last column in table 2 indicates that 8 to 22 percent of the feed is converted to material boiling below the 5 percent point of the feed.

The increase in product material boiling below 185° C results largely from saturation of aromatic rings and olefins and from removal of heteroatoms. Some hydrocarbons boiling lower than the feed would be formed by cleaving of heteroatom linkages, with scarcely any cracking of hydrocarbons expected. For example, all product liquids had initial boiling points near that of benzene/cyclohexane.

TABLE 2. - Simulated distillation of liquid feed and products

Sample period	Temp., °C., at wt-pct distilled			wt-pct converted to below 185° C
	5	50	95	
(Feed)	185	255	379	-
1	112	239	361	15
2	131	247	369	9
3	101	235	344	18
4	133	248	375	8
5	96	229	331	21
6	98	225	329	22
7	94	221	326	21
8	156	252	379	7

The results of the Salmonella/Typhimurium Mutagenicity (Ames) assay for the feed and liquid products are given in table 3. The assay was run essentially as described by Ames (1). The assay employs specially constructed strains of Salmonella Typhimurium which are reverted by a wide variety of mutagens from requiring histidine in their growth medial back to bacteria capable of synthesizing histidine.

Some chemicals require metabolic activation (addition of microsomal enzymes) prior to showing mutagenic activity; thus, data are given as number of

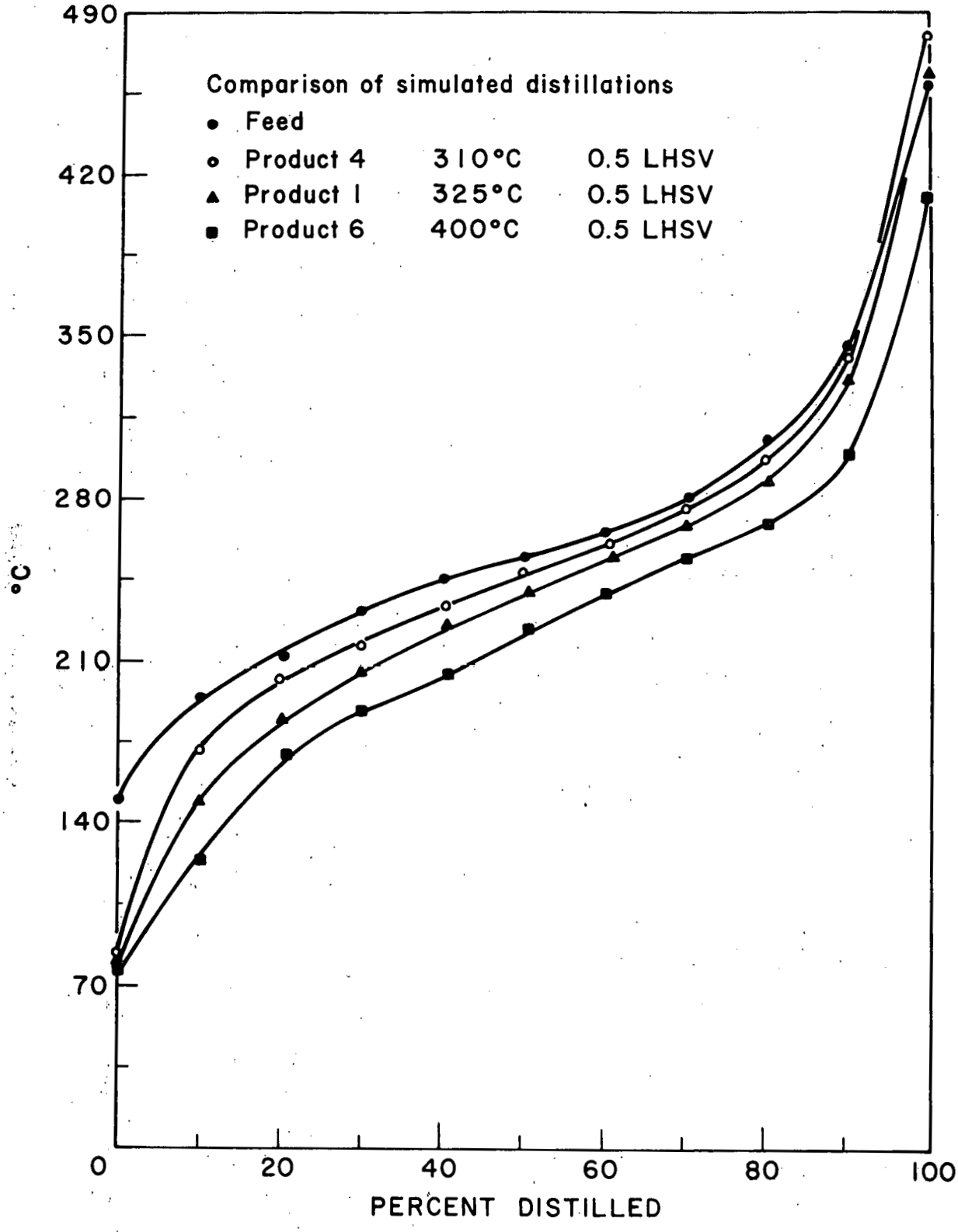


Figure 3. Simulated Distillation of SRC-II feed and hydrotreated products.

revertants without/with metabolic activation. The Ames test has thus far demonstrated a strong correlation between positive carcinogenesis in animal tests and mutagenicity in the Ames test (1,4). However, positive results from the Ames test do not conclusively show human risk.

The untreated SRC-II was tested at five concentrations with Salmonella strains TA 98 and TA 100, generally considered the most sensitive strains. In the results indicated in table 3, an increase in the number of revertants greater than two times the background (no SRC-II feed or product) is sometimes considered to indicate a definite positive (mutagenic) response. The plates which showed a positive response by this criteria are underlined.

TABLE 3. - Results of the Ames assay

Sample	Concentration, ug/plate	Number of revertants Without/With metabolic activation TA 98	TA 100
Feed	250	30/1822	144/322
Feed	100	34/1122	163/348
Feed	50	27/547	150/306
Feed	25	21/316	150/204
Feed	5	31/113	134/178
Background	0	21/60	144/142
8	100	15/131	134/257
4	100	19/111	176/232
2	100	23/178	151/226
1	100	16/64	158/218
3	100	10/40	161/194
5	100	22/64	162/194
6	100	19/70	128/186
7	100	17/65	153/218
Background	0	25/66	169/220

Activity decreased with decreasing concentration for the untreated feed but was still nearly double the activity of the background at a concentration of 5 µg per plate. A product dose of 100 micrograms was selected as a satisfactory screening test since a strong response was observed for the untreated SRC-II at this concentration and since no appreciable cytotoxicity was noted. The hydrogenation periods are listed in order of increasing severity of processing.

Activity was decreased essentially to the background level when nitrogen content was decreased to 0.35 wt-pct, oxygen content was decreased to 0.59 wt-pct, and hydrogen content was increased from 8.4 to 10.8 wt-pct. This occurred at process conditions of 325° C and 0.5 LHSV feed rate, which had originally been planned as the lowest reaction temperature expected to give substantial upgrading.

A more complete investigation will require testing of fractions of the coal liquid to identify more active components. Nitrogen and oxygen compounds and aromatic ring structures are important in this respect, with mutagenically active components likely to be in higher-boiling fractions. Tests on mammalian systems are also needed before making assessments concerning potential human risk.

SUMMARY

Hydrotreated coal liquids and distillate coal liquid from the SRC-II process with hydrogen content from 8.4 to 12.24 wt-pct were screened for mutagenic activity using the Ames test. Results of the Ames assay indicated that mutagenic activity of the liquid product decreased by an order of magnitude for 35 percent removal of nitrogen and 52 percent removal of oxygen. Mugagenic activity of liquid product with 67 percent nitrogen removal and 82 percent oxygen removal was indistinguishable from that of the background samples. The full range of effect in decreasing mutagenic activity by the Ames assay was covered by relatively mild hydrotreatment, but assessment of potential human risk must be confirmed using additional mammalian tests.

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H-COAL PILOT PLANT ENVIRONMENTAL CONTROLS

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INTRODUCTION

General

The H-Coal Pilot Plant is based on the H-Coal process developed by Hydrocarbon Research, Inc. (HRI). HRI's process converts various coals into liquids by direct hydrogenation in the presence of a catalyst. Depending on reactor space velocity either a synthetic crude or a boiler fuel can be produced.

The pilot plant in Catlettsburg, Kentucky was a cooperative venture involving the U.S. DOE, Ashland Synthetic Fuels, Inc., the State of Kentucky, Mobil, Conoco, Standard of Indiana, and Electric Power Research Institute. As of January 1980, the plant was nearing completion and commissioning is planned during the first quarter of 1980. Ashland Synthetic Fuels, Inc., has the contract to operate the pilot plant.

Plant Description

The H-Coal Plant occupies 43 acres of land bordered on the east by the Big Sandy River, the south by Ashland Oil's Catlettsburg Refinery, and on the west by C&O Railroad right-of-way. The nearest town, three miles to the north, is Catlettsburg, Kentucky.

The pilot plant is divided into sections (i.e. 100, 200, 400, 500, and 600) and is complete except for the following items. Ashland Oil's Refinery will supply hydrogen, firewater, make-up cooling water, make-up boiler feed water, plant air, utility water, instrument air, and emergency steam. The refinery will process hydrogen sulfide from the H-Coal Plant in their Claus Unit.

Section 100 - Coal Preparation

Coal is received at the pilot plant by rail or truck at the Shaker House. The coal is conveyed to a stockpiling tower where 12,000 tons can be stored. Movement of the coal continues by front-end loader and conveyor to the primary crusher (crushed to 3/4 inch coal). The

coal is then conveyed to the crushed coal bins (1,800 ton capacity). A Raymond Bowl Mill pulverizes and dries the coal (40-200 mesh and 2% moisture) after which the coal is stored in the dried coal bins (500 ton capacity) prior to entering the process.

Section 200 - Coal Hydrogenation

The dried coal is slurried with a recycle oil in order to initiate conversion and improve handling. The slurry and a portion of the hydrogen, which is fed to the reactor, is mixed and pumped to 3000 psig. The mixture is preheated to approximately 750°F and passes into the reactor. Makeup or fresh hydrogen is also heated and fed to the reactor.

The effluent from the reactor contains gases, oil, unconverted coal, and ash. These materials are separated through cooling and pressure reduction followed by distillation and fractionation.

One of the heavy oil fractions has a high percentage of the ash and unconverted coal and is sent to the vacuum stripper for additional oil recovery. The bottoms (called residuum) from the vacuum tower solidify when cooled to ambient temperatures.

Section 400 - Utilities

Utilities included in the pilot plant are:

Steam Generation	Cooling Water System
*Fuel System	*Sanitary Sewer
Nitrogen System	*Process Water Treatment
*Tank Farm	Hot Oil Tracer System
Firefighting System	*Gas Desulfurization
Instrument Air	*Foul Water Stripping
*Flare System	

Those systems with an asterisk have some relation to environmental control.

The fuel for the plant will be propane and desulfurized process fuel gas. These low sulfur fuels are required by the Kentucky Air Permit. The tank farm uses floating roof tanks for materials with a vapor pressure greater than 1.5 psia. The flare system combusts the process materials during upset conditions, preventing hydrocarbon or hydrogen sulfide emissions. The sanitary sewer system uses secondary treatment and tertiary filtration to handle the domestic wastes at H-Coal. Process wastewater is steam stripped to remove ammonia and hydrogen sulfide prior to biological treatment. Next, the process wastewater is treated (activated sludge) for removal of organics prior to discharge.

Section 500 - Antisolvent Deashing

During the Fuel Oil Mode, the heavy oil stream which normally goes to the vacuum tower is redirected to The Lummus Company's Deashing Unit. An antisolvent is used to concentrate the ash and unconverted coal into the underflow while the overflow from the unit is virtually ash free. These two streams are vacuum stripped, cooled to ambient temperature and stored as a solid.

Section 600 - Waste Oil Recovery

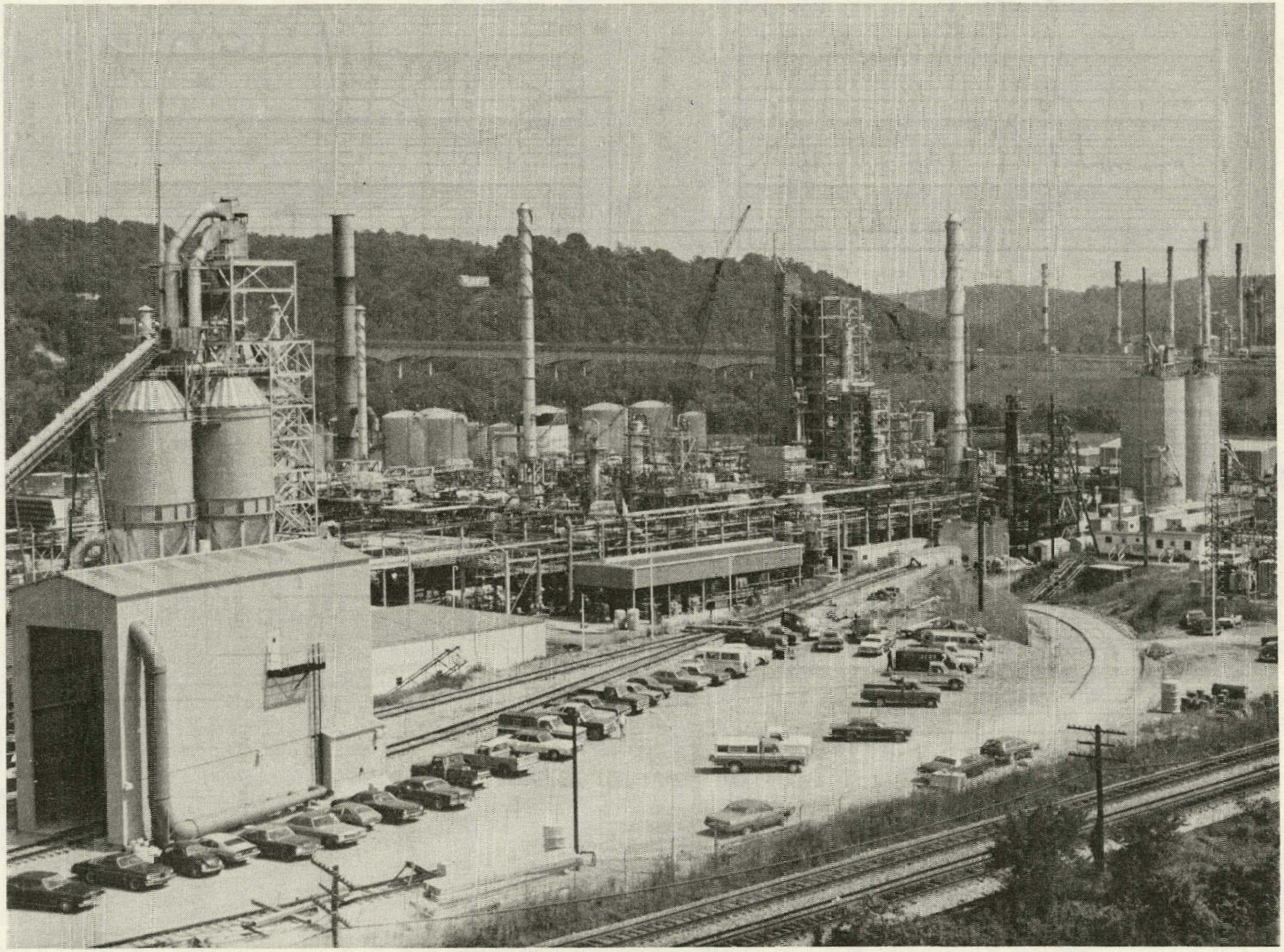
Process wastewater treatment has two units which recover oil. This oil along with other slop oils in the plant are processed by distillation to recover the oil.

Plant Photograph

Figure I is a photo taken in August 1979 of the H-Coal Plant. In the lower left is the coal unloading (shaker house) house. Just above the shaker house are the two crushed coal bins. The large concrete silos at the right are the flaked residuum silos. Ashland Oil's Refinery is in the background at the right.

In the center of the photo is Section 200, Coal Hydrogenation. The larger towers, just right of center, is Section 500, the Lummus Deashing Unit.

Figure I
H-Coal Pilot Plant



WATER POLLUTION CONTROLS

There are two distinct types of wastewater that will be generated once operation of the H-Coal Pilot Plant commences. The largest volume will be the industrial or process wastewater and there will also be domestic wastewater. Each type will be collected and treated separately using treatment methods applicable to the type of waste. The treated wastewaters will then be combined and discharged to the Big Sandy River in a single outfall pipe.

There is a source of unpolluted water and this is rain runoff from the uncontaminated areas of the plant. Of the 43 acres of land not all will be used for processing areas. The nonprocessing areas will be drained to a noncontaminated rain runoff sewer and directed to the river. The uncontaminated runoff joins the treated process and domestic wastewater before discharge to the Big Sandy River.

Process Wastewater

The H-Coal Pilot Plant processing units and ancillary facilities will produce five wastewater streams. The wastewater sources are as follows:

1) Process Water
2) Cooling Tower Blowdown
3) Boiler Blowdown
4) Oily Water Runoff
5) Coal Pile Runoff

Process Water

Within the H-Coal hydrogenation unit, there are five sources of process wastewater that are collected and treated. The five process water sources are as follows:

A) Reactor Effluent Vapor Wash Water Separator
B) High Pressure Condenser Wash Water Separator
C) Low Pressure Condenser Wash Water Separator
D) Fractionator Reflux Drum
E) Vacuum Tower Vent Condenser Collector

The main purpose of the wash water separators (A, B, and C above) is to remove ammonia (NH_3) and hydrogen sulfide (H_2S) in the overhead gases from the coal conversion process. Removal of ammonia prevents plugging of lines or exchangers due to ammonium sulfate deposition.

The purpose of the fractionator reflux drum and the vacuum tower vent condenser collector is to collect the condensed steam which has come into direct contact with the product oil streams. These process wastewaters have high concentrations (20,000 to 30,000 ppm COD) of phenols and soluble organic material.

All five process wastewaters are collected in a water degassing drum to allow any dissolved gases to be released and vented off. These vented gases are collected and sent to the vent gas desulfurization unit prior to combustion in the flare system.

Cooling Tower Blowdown

Cooling towers will be used at the H-Coal Pilot Plant for the removal of waste heat. The cooling water will be recirculated instead of a once-through cooling scheme. The heat transfer points will be non-contact heat exchangers. Preventing corrosion of the heat exchangers necessitates the use of corrosion inhibitors and the periodic blow-down of a certain volume of cooling water. This blowdown of cooling water prevents the buildup of dissolved solids in the system and helps to prevent scaling of the heat exchangers.

Since the cooling water does not come into contact with the H-Coal conversion products, there should be no organic pollutants in the wastewater stream. The water is clean except for the phosphate present in the water used for inhibiting corrosion and possibly dispersants and biocides (for algae control). The cooling water will be sent to the wastewater treatment plant for use as dilution water.

Boiler Blowdown

The water used to make steam must also be blown down to eliminate dissolved solids in the water. The water as it evaporates to make steam leaves in solution the dissolved solids it possessed. To prevent scaling on the boiler tubes, it is necessary to periodically eliminate a certain volume of water to maintain an acceptable concentration of the dissolved solids. The boiler blowdown will contain small amounts of solium sulfite (an oxygen scavenger) but will be free of organic contaminants. The blowdown will be sent to the treatment plant prior to discharge.

Oily Water Runoff

The rain that falls on or comes into contact with the processing areas will be drained into the process sewer. The rain water sometimes picks

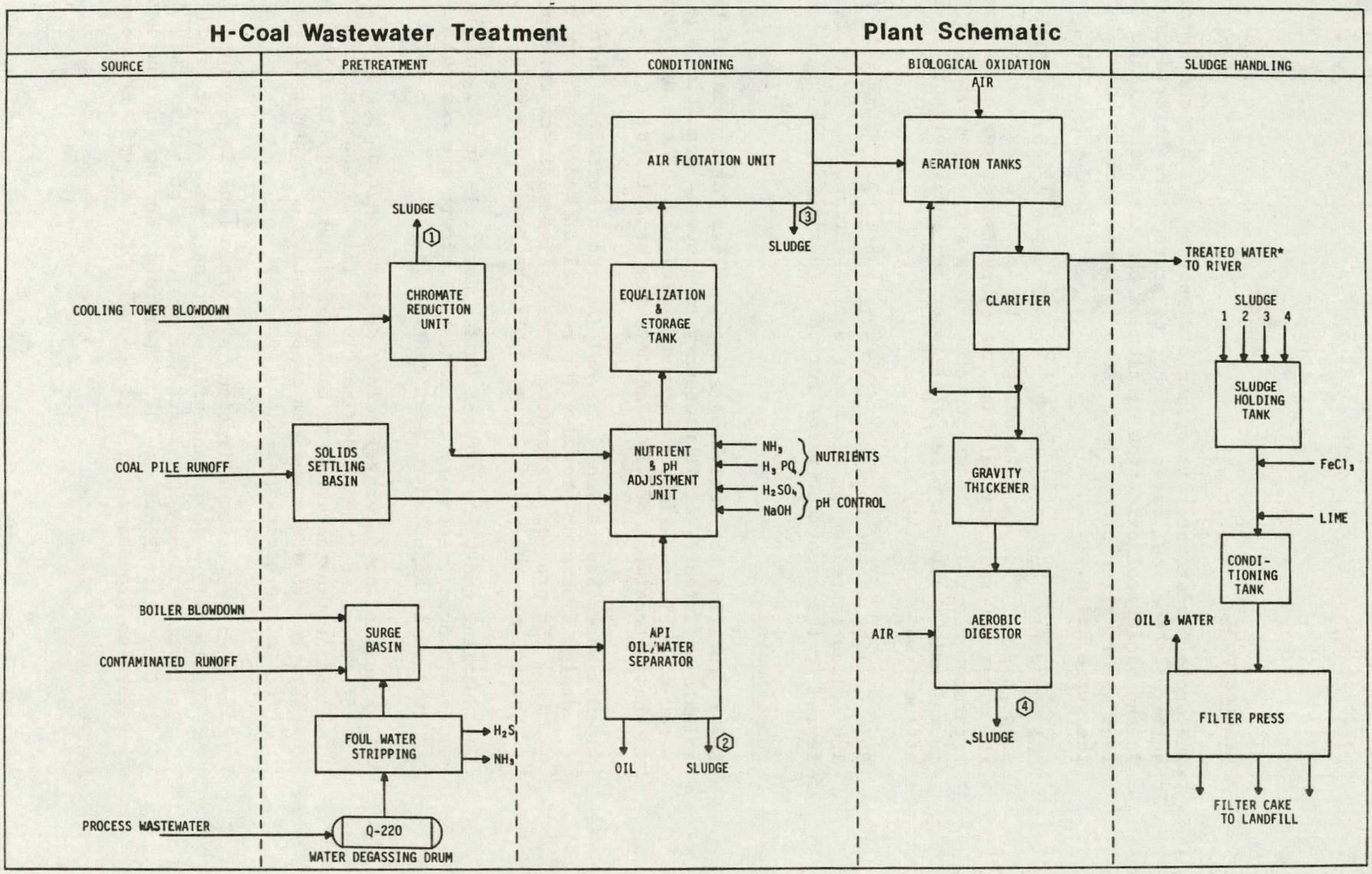
up oil and other slightly water soluble organic coal-conversion compounds and, therefore, should not be sent directly to the river. The water is treated for removal of the contaminants in the wastewater treatment plant prior to discharge.

Coal Pile Runoff

Rain that falls on the open coal storage area is drained into a coal pile runoff storage pond. The rain runoff picks up coal fines and any soluble organics found within the coal. The coal pile runoff will have a very low pH (pH of 1.0 to 2.0).

Shown in Figure II is the treatment plant schematic. The treatment plant itself is divided into three sections: 1) pretreatment, 2) conditioning, and 3) biological oxidation. Biological sludge produced via the oxidation of the pollutants is disposed of by high pressure (225 psig) filtration. One correction to the figure is that the chromate reduction unit has been deleted due to usage of a phosphate base corrosion inhibitor in the cooling tower. The cooling tower blowdown will still be processed in the treatment plant.

Figure II


H-Coal Wastewater Treatment Plant Schematic
SOURCE
PRETREATMENT
CONDITIONING
BIOLOGICAL OXIDATION
SLUDGE HANDLING
AIR
AIR FLOTATION UNIT
AERATION TANKS
SLUDGE
1
3
SLUDGE
TREATED WATER* TO RIVER
CLARIFIER
COOLING TOWER BLOWDOWN
CHROMATE REDUCTION UNIT
EQUALIZATION & STORAGE TANK
SLUDGE
1 2 3 4
SLUDGE HOLDING TANK
COAL PILE RUNOFF
SOLIDS SETTLING BASIN
NUTRIENT & pH ADJUSTMENT UNIT
NH3
H3PO4
NUTRIENTS
H2SO4
NaOH
pH CONTROL
GRAVITY THICKENER
FeCl3
LIME
CONDI-TIONING TANK
BOILER BLOWDOWN
CONTAMINATED RUNOFF
SURGE BASIN
API OIL/WATER SEPARATOR
AIR
AEROBIC DIGESTOR
OIL & WATER
FOUL WATER STRIPPING
H2S
NH3
OIL
SLUDGE
2
4
SLUDGE
FILTER PRESS
PROCESS WASTEWATER
Q-220
WATER DEGASSING DRUM
FILTER CAKE TO LANDFILL

Pretreatment

The process wastewater is stream stripped of ammonia and hydrogen sulfide in the foul water stripper to protect the bateria used in the biological oxidation section of the treatment plant. The foul water, after processing, flows into the process sewer and on to the surge basin.

All the waters collected in the process sewer discharges into the surge basin. The basin is designed to accept a maximum runoff from the plant. During dry periods, the stored water can be fed into the treatment plant at a constant rate. This surge dampening is necessary to maintain treatment plant efficiency and ensure acceptable final effluent water quality.

Rain falling on the coal pile is collected in a 1.5mm gallon basin. The solids entrained in the water settle out and the water is transferred to the treatment plant for pH adjustment.

Conditioning

Before entering the activated sludge process for removal of the soluble pollutants, it is necessary to properly condition the wastewater to achieve maximum treatment efficiency. There are four steps in the pretreatment section and they are as follows:

1) Oil/Water Separation - The API (American Petroleum Institute) design separator provides for removal of heavy sediment and oil from the process wastewater stream. The sediment settles to the bottom and the oil is skimmed off the top of the water.

2) Nutrient and pH Adjustment Unit - Nutrients (nitrogen and phosphorus) necessary for bacterial growth are controlled here and the pH is adjusted to near neutral.

3) Equalization (Storage) - The equalization tank provides 2.5 days of retention time at design flow. This allows the organic loading fluctuations to be dampened out. Equalization is necessary to provide a uniform concentration of organic matter to be fed to the biological oxidation step.

   In addition to equalization, a storage tank is provided (see Figure III). This tank will serve as a reserve of "food" for the activated sludge biomass. The projected on-stream factor for the H-Coal Pilot Plant is 50%. Therefore, during the shutdown periods, when no process water will be available, it will be necessary to

keep the bacteria alive so that when the next operation test begins, the treatment plant can quickly resume maximum treatment efficiency.

4) Air Flotation - Following equalization, the water flows by gravity from the equalization (or storage) tank to the air flotation unit. The air flotation units remove suspended solids and small oil droplets from the wastewater stream.

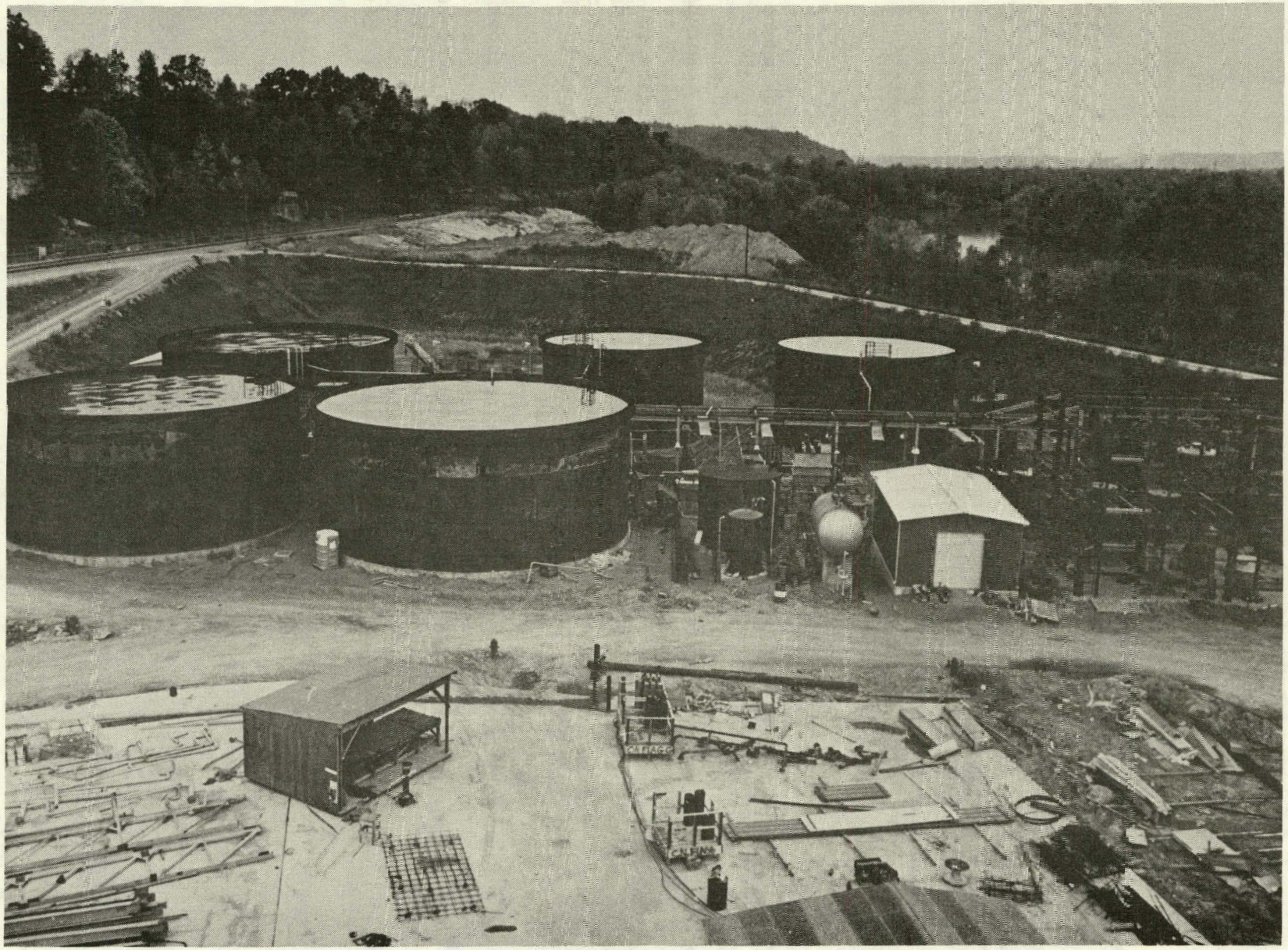
These four pretreatment steps have as their prime objective, the removal of gross contaminants and conditioning of the wastewater so that optimum biological oxidation of the remaining soluble organic matter can take place. The effluent from the air flotation unit is then pumped into the biological oxidation step.

Biological Oxidation

The process wastewater is fed continuously into an aerated tank where the microorganisms metabolize and biologically oxidize the organics. Microorganisms (activated sludge) are settled from the aerated mixed liquor under quiescent conditions in the final clarifiers and returned to the aeration tank. Clear supernatant from the final clarifiers is discharged to the river. Synthesis of the waste organics results in a buildup of the microbial mass in the system. Excess activated sludge is wasted from the system to maintain the proper foot-to-microorganism ratio to ensure optimum operation. This wasted sludge is pumped to the Sludge Holding Tank to be processed in the Filter Press System.

Figure III is a photo of the wastewater treatment plant taken October 1978. The tanks are being hydrotested. At the right is the structural steel for the filter press building. The small building (completed), located near the structural steel, is the dry chemical storage building. The group of three small tanks are phosphoric acid, sulfuric acid, and caustic. The large tank left of center is the equalization tank. Left of the equalization tank, is the storage tank. Opposite (to top of photo) from the storage tank is the No. 2 Aeration Tank. To its right, is No. 1 Aeration tank and the Aerobic digestor.

Figure III
Wastewater Treatment Plant



Domestic Wastewater

The H-Coal Pilot Plant will employ approximately 240 people and will provide sanitary facilities to accommodate the employees. The facilities will include restrooms, showers, wash basins, drinking fountains, etc. The domestic wastewater will be conveyed by a sealed sanitary sewer and three sanitary sewer lift stations which will pump the wastewater to an aerobic digestor.

The treatment plant is a 10,000 GPD prepackaged unit of the extended aeration type. The unit will be supplied with a surge tank, a comm-uniter/grinder to reduce the size of incoming waste matter, a tertiary filter, and a chlorination chamber. The plant was sized based on standard per capita usage of water in sanitary facilities in accordance with the National Plumbing Code.

AIR POLLUTION CONTROLS

Air pollution control equipment for the H-Coal Pilot Plant was designed to decrease the emissions to levels well within air quality regulations promulgated under the Clean Air Act. The overall control plan is to filter out or eliminate those pollutants which are most sensitive in this air quality region. The two pollutants which are most critical in this area are particulates and sulfur dioxide. Hydrocarbons are also controlled to minimize environmental impact.

Particulates

Particulates created during the combustion of propane and fuel gas are an intrinsic feature of the oxidation process. Every effort will be made during the operation phase of the H-Coal project to burn the fuels at their optimum efficiency. The efficient combustion of fuels minimizes the amount of particulates generated.

The coal preparation area will use four dry-media dust collectors to filter particulates. The dust collectors have at every point where dust will be generated due to transfer or crushing and drying a bag-house intake. The manufacturers guarantee for the baghouses are 99.9% removal of all particulates. A baghouse services each of the following areas: 1) coal car (or truck) unloading, 2) coal stacking and reclaim tower, 3) crushed (wet) coal bins, and 4) the bowl mill pulverizer dryer vent. Also the residuum flaking operation is equipped with two baghouses to control dust in the silos.

The H-Coal Plant has also purchased a street sweeper to operate in the coal handling area to aid in controlling fugitive particulate emissions.

Sulfur Dioxide

The potential sulfur dioxide sources are plant fuel combustion and hydrogen sulfide recovered from the process. The fuel gas used in the process heaters will be a byproduct of the H-Coal conversion process. However, the fuel gas will be desulfurized prior to burning. The design of the H-Coal Pilot Plant includes fuel gas desulfurization equipment for the recovery of H_2S formed from sulfur in the coal feed to the plant.

Additional plant fuel will be propane which is virtually sulfur free. The switch from conventional fuel oil to propane was necessary due to air permit restrictions. Certain gases within the process must be vented. There is also a vent gas desulfurization unit to remove hydrogen sulfide prior to combusting the gases in the flare system.

The largest source of sulfur is the hydrogen sulfide extracted from the fowl water stripper. The hydrogen sulfide gas (60 to 80% by volume) is sent to AOI Refinery's Claus Unit for recovery as elemental sulfur. In addition, the hydrogen sulfide from the fuel and vent gas desulfurization units are also sent to the Claus Unit.

Therefore, hydrogen sulfide is converted to sulfur and the plant fuels are extremely low sulfur. Emissions at H-Coal are expected to be less than 100 tons per year.

Hydrocarbons

A possible source of hydrocarbons is the emergency pressure relief system. However, the H-Coal Pilot Plant design incorporated a flare system by which the hydrocarbon process streams are combusted prior to entering the atmosphere. The flare converts the hydrocarbons into carbon dioxide and water.

Storage tanks are also a source of hydrocarbons; however, a review of the H-Coal product characteristics reveals that all products are of heavy fuel oil quality except for the fuel gas and naphtha. The fuel gas is consumed in the heaters and the naphtha is stored in tanks with floating roofs. A floating roof actually floats on top of the liquid surface. This eliminates the major cause of hydrocarbon emissions (working losses). The remaining H-Coal liquid products all have lower true vapor pressures than naphtha. The vapor pressures are sufficiently low so that they can be stored in fixed cone roof tanks with breather vents. These low vapor pressure hydrocarbon liquids have correspondingly low emissions. The truck loading racks are all bottom loading to minimize emissions during the transfer of the products.

SOLID WASTE

During operation of the H-Coal Pilot Plant, two principal types of solid waste will be generated, they are: 1) flaked residuum, and 2) filter cake. Flaked residuum is directly related to the operation of the H-Coal process. The filter cake is a result of the operation of the wastewater treatment plant.

Flaked Residuum

Flaked residuum is a solid byproduct generated by the H-Coal process. It contains solids (unconverted coal fines and inert matter) and the residual fraction of the H-Coal liquefaction process. The H-Coal Pilot Plant design information indicates that 42,000 tons of the flaked residuum will be produced during the two years of pilot plant operation. Its bulk density is approximately 50-55 pounds per cubic foot.

The residuum (vacuum tower bottoms) is sent to the flakers where it is cooled to ambient temperatures on a steel belt by indirect heat exchange using cooling water. The material is then flaked off the end of the belt and stored in silos prior to disposal.

The flaked residuum will have certain physical and chemical properties which research investigators may wish to study at some point in the future. Since the residuum is relatively inert, surface storage of the flaked material would allow easy recovery of the material. The residuum would be stored in segregated piles (similar to coal piles) to differentiate between modes of operation. The storage site is currently under review by the State of Kentucky.

Filter Cake

The operation of the support facilities for the H-Coal Pilot Plant will also cause waste solids to be generated. Filter cake is the term applied to the solid waste created in the high pressure sludge dewatering system in the wastewater treatment area. The filter press converts sludge (solids/water mixtures) into solid material by squeezing out the water and retaining the solids. The wastewater treatment plant will generate three waste sludge streams:

A) Biological Solids
B) API Separator Bottom Sediment
C) Air Flotation Skimmings

These three sludge streams are mixed in a holding tank and then processed in the filter press.

Biological Solids

The activated sludge process converts the soluble organic pollutants in the process wastewater into new bacterial cell mass. Maximum operating efficiency of the biological treatment process is maintained by keeping the biomass at a given concentration. Therefore, biological sludge must be routinely blown down to compensate for new bacterial growth. This excess biological sludge must be disposed of properly but the sludge can only be concentrated by gravity thickening to a maximum of 8 - 10% solids (by weight). The high pressure sludge dewatering system can remove sufficient water to turn the sludge into a solid material (approximately 45% solids).

API Separator Bottoms Sediment

The API (American Petroleum Institute) separator accomplishes the removal of oil from water and heavy sediment from water by gravity/phase separation. The API provides the quiescent conditions necessary for oil entrained in the water to coalesce, rise to the surface, and be skimmed off. There is also sufficient residence time to allow heavy sediment in the water to settle to the bottom of the separator. This bottom sediment is pumped out periodically and sent to the sludge holding tank.

Air Flotation Skimmings

The air flotation unit is part of the process wastewater scheme. The unit's purpose is (with the aid of polymers) to remove any remaining suspended solids and entrained oil from the process wastewater prior to entering the activated sludge treatment step. The polymers are added to flocculate the suspended solids and oil globules into particles large enough to be carried to the surface by the air bubbles. The foam (comprised of solids, oil, and air) is then skimmed off and sent to the sludge holding tank.

The dewatered mixture of sludges (filter cake) has the appearance of hard packed clay (45 to 55% solids) and has a bulk density of 70 to 75 pounds per cubic foot. The filter cake will be disposed of in a sanitary landfill operation. The State of Kentucky has already approved the site and disposal method used by the contractor.

ENVIRONMENTAL CONTROLS FOR THE EXXON DONOR SOLVENT COAL LIQUEFACTION PROCESS

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1. INTRODUCTION

Today I would like to describe the status of the development of environmental controls for the Exxon Donor Solvent (or EDS) Coal Liquefaction Process. As shown in Figure 1, included will be a brief description of the EDS process. Next will be a discussion of the project status, including a description of the progress in the construction of the 250 T/D Exxon Coal Liquefaction Pilot Plant, or ECLP. Then, I will cover some of the environmental effects we predict for a commercial EDS plant. Next, I will cover our strategy for developing the environmental controls. Finally, I will cover the outlook for commercialization.

The goal of the EDS Coal Liquefaction Project is to develop the process to a state of commercial readiness. This means that the technology should be available at the end of the project to design and build a full-scale, pioneer commercial plant with a reasonable and acceptable level of risk.

In the EDS process development, bench scale research, operation of small pilot units, and engineering design and technology studies are being integrated with operation of a 250 T/D Pilot Plant and likely a 70 T/D FLEXICOKING* Prototype.

2. EDS PROCESS DESCRIPTION

The process sequence shown in Figure 2 is designed to maximize liquid products. The feed coal is crushed, dried, and slurried with hydrogenated recycle solvent (the donor solvent) and fed to the liquefaction reactor in admixture with gaseous hydrogen. Reactor operating conditions are 800-900°F and about 2000 PSI total pressure. The reactor effluent is separated by distillation into a recycle solvent depleted of its donor hydrogen, light hydrocarbon gases, C_4-1000°F distillate, and a heavy vacuum bottoms stream containing 1000°F+ liquids, unconverted coal, and coal mineral matter. The recycle solvent is hydrogenated in a conventional fixed bed catalytic reactor employing "off-the-shelf" hydrotreating catalysts.

* Service Mark

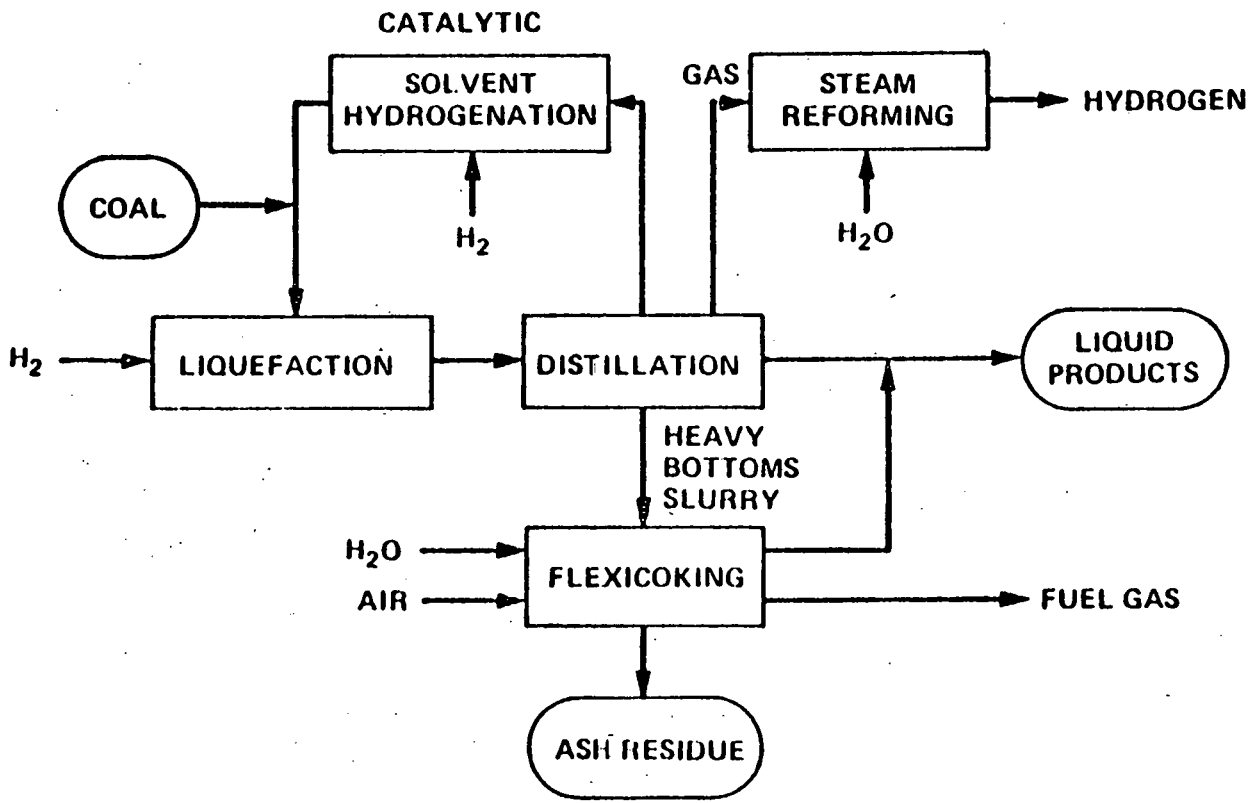
FIGURE 1

AREAS TO BE COVERED

- EDS PROCESS DESCRIPTION
- PROJECT STATUS
- 250 T/D PILOT PLANT
- ENVIRONMENTAL EFFECTS OF AN EDS PLANT
  - AIR QUALITY
  - WATER QUALITY
  - SOLIDS WASTES
  - FUEL OIL COMBUSTION
- ENVIRONMENTAL CONTROLS DEVELOPMENT STRATEGY
- OUTLOOK FOR COMMERCIALIZATION

FIGURE 2

EXXON DONOR SOLVENT PROCESS



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The heavy vacuum bottoms stream is fed to a FLEXICOKING unit with air and steam to produce additional distilled liquid products and a low BTU fuel gas for process furnaces. FLEXICOKING is a commercial petroleum process that employs an integrated coking/gasification sequence in circulating fluidized beds. This process is operated at low pressures (50 psi) and intermediate temperatures (900-1200°F in the coker and 1500-1800°F in the gasifier). Essentially all organic material in the vacuum bottoms fed to FLEXICOKING is recovered as liquid product or combustible gases. A small amount of residual carbon is rejected with the ash from the gasifier fluidized bed.

Process hydrogen is produced by steam reforming light hydrocarbon gases. An alternative method for hydrogen production which is receiving increased attention is partial oxidation of the heavy vacuum bottoms stream or of coal.

The total liquid product is a blend of streams from liquefaction and FLEXICOKING. Product utilization studies indicate that the 350°F- fraction should be used in gasoline/ petrochemical manufacture and the 350°F+ fraction in fuel oil applications. The latter fraction from Illinois #6 coal contains about 0.6 wt% sulfur and about 0.8 wt% nitrogen. These levels can be reduced further by subsequent treating, if needed, to meet emissions standards.

3. EDS PROJECT STATUS

Exxon Research and Engineering Company (ER&E) has been engaged in coal liquefaction research since 1966. The jointly funded research and development project started in 1976 and is in the fifth year of a 6-1/2 year program. The U.S. Department of Energy (DOE) is providing 50% of the funding and the remaining 50% is being provided by Exxon Company USA, Electric Power Research Institute (EPRI), Japan Coal Liquefaction Development Company, LTD., (JCLD), Phillips Petroleum Company, Arco Coal Company, and Ruhrkohle AG.

A broad technical program on the liquefaction portion of the process is being advanced essentially on schedule. The program on vacuum bottoms processing has been expanded to include planning for the operation of a 70 T/D FLEXICOKING Prototype at Baytown, Texas using the vacuum bottoms produced from the 250 T/D Liquefaction Pilot Plant. In addition, planning work for a program to test EDS vacuum bottoms in a 150 T/D Partial Oxidation unit is currently underway.

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4. 250 T/D PILOT PLANT PROGRESS

The construction of the 250 T/D Pilot Plant is proceeding. This plant is located adjacent to the Baytown, Texas Refinery of Exxon Company, U.S.A. Figure 3 shows an artist's conception of the completed plant with details of the relative position of the administration building, the coal preparation facilities, the process area and the product tankage areas. The estimated cost for the completed plant is 116M$ compared with the initial estimate of 110M$ which was prepared nearly 5 years ago.

As shown on Figure 4, construction is expected to be completed in March 1980 compared with the original schedule of January 1. An increased engineering workload and an unusually wet spring last year in the Baytown area have resulted in an extension of construction activities and slower construction progress.

Startup activities began last summer as sections of the plant were completed. Coal-in operations are expected by the end of April. A 30 month operation on 3 feed coals is then planned -- 15 months on the first coal which will be an Illinois No. 6 bituminous coal and 9 months on the second coal, which will be a sub-butuminous coal, and 6 months on the third coal. These coals have not yet been selected.

The operations of the 250 T/D Pilot Plant are designed to demonstrate the operability of the EDS liquefaction section and obtain the scaleup data required for design of a commercial facility. Key objectives are demonstration of unit operability, design data acquisition, product yield and quality confirmation, and testing and production of feeds for demonstration of environmental controls.

Certain of the facilities which may be required in a commercial EDS plant have not been included in ECLP since we do not believe that their testing on the ECLP scale is necessary. For example, no product treating is provided. The refinery will be supplying the required hydrogen and some utilities. In addition, the refinery will handle the conversion of H_2S produced at ECLP to sulfur and will process the sour water produced at ECLP.

Even though these environmental control facilities will not be onsite at ECLP, the plant emissions will meet current regulations.

5. PROJECTED EMISSIONS FROM THE EDS PROCESS

Environmental control is important within the EDS plant itself, for the surrounding community and also in the ultimate usage of the liquid products. As a part of the development program, we have sampled streams from our small pilot plants and used this information in our engineering studies to predict the plant emissions.

FIGURE 3

ARTIST'S RENDERING OF THE 250 TON-PER-DAY PILOT PLANT

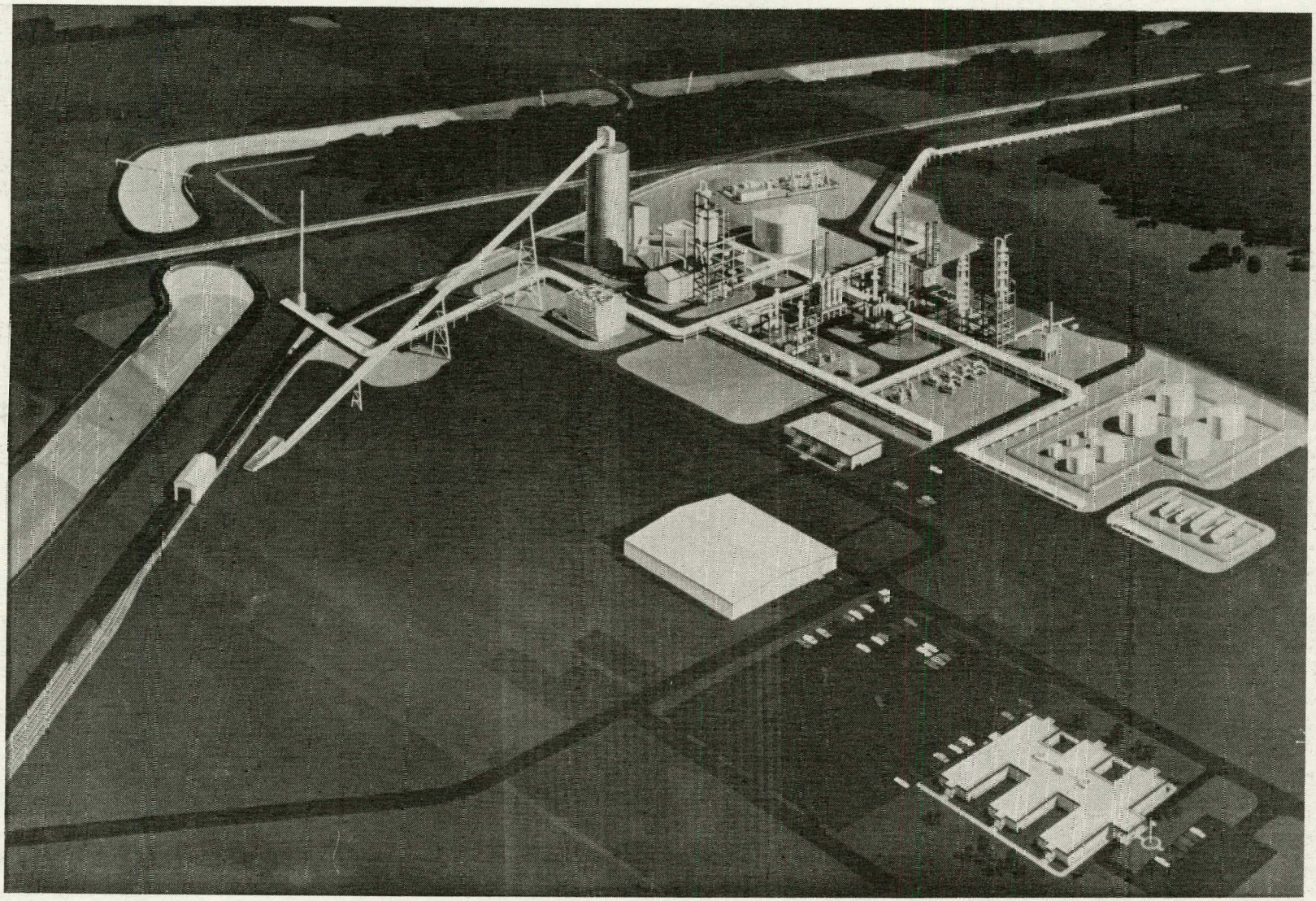
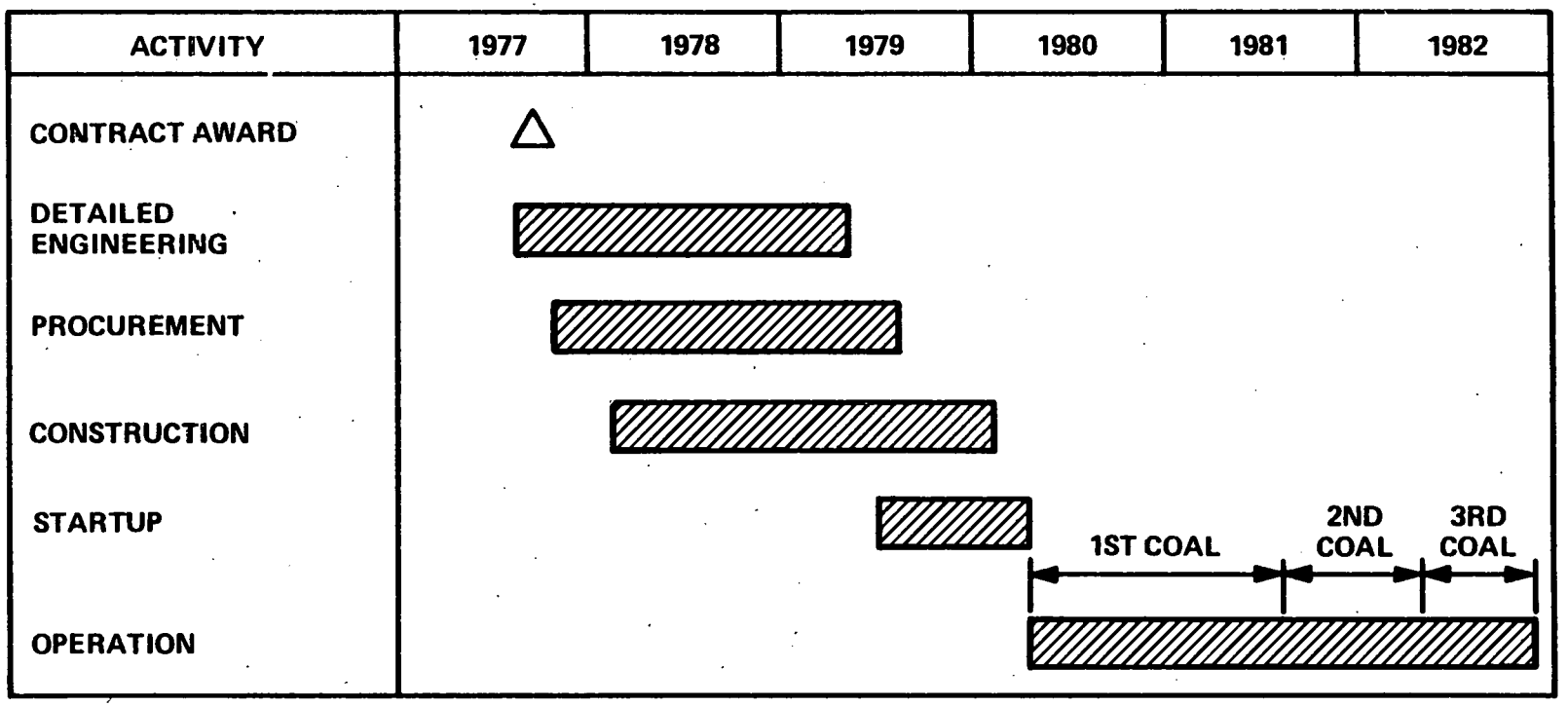


FIGURE 4

EDS 250 T/D PILOT PLANT SCHEDULE



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The EDS processing steps are extensions of existing coal and petroleum refining technology. Thus, the emission would be expected to be similar to coal-fired utility plants and petroleum refineries. Commercial design studies have indicated 10-15 percent of the commercial plant's cost would be for emission control.

The expected atmospheric emissions for a commercial EDS plant feeding 30,000 tons per day of an Illinois No. 6 coal containing 4.4% sulfur are shown in Figure 5. These values are based on a recently completed Study Design Update. Included are annual rates of about 6000 tons of sulfur oxides, 740 tons of carbon monoxide, 3200 tons of nitrogen oxides, 525 of particulate matter and 1575 tons of hydrocarbons. When stated on an annual basis these numbers appear large, but it should be noted that the sulfur oxides emission rate is less than 20 T/D.

Emission rates for all the criteria pollutants significantly exceed 100 tons/year which is the threshold to be defined as a major source. Offsetting reductions in emissions from other sources may be required to locate an EDS plant in areas classified as in nonattainment of National Air Quality Standards.

Figure 6 shows the results of dispersion model calculations of the impact on ambient air quality of an EDS plant compared to the Prevention of Significant Deterioration (or PSD) increments for a Class II area. The critical GLC's for the major pollutants from continuous sources are below these increments. Thus, an EDS plant could probably be located in a Class II attainment area having meterological conditions typical of Southern Illinois. A conservative buffer zone of 10 miles between the plant and Class I areas (national parks) would ensure that Class I Prevention of Significant Deterioration (PSD) increments would not be exceeded.

Figure 7 gives an analysis of the wastewater stream after stripping and phenol extraction but before treating from an EDS plant feeding 30 kT/D of an Illinois No. 6 Bituminous coal. The wastewater treating scheme included in the Study Design Update is shown on Figure 8. This flowplan is based on the "Best Available Technology" to control the water pollutants found in the small pilot plant water samples. Sour process waters are stripped to remove H_2S and ammonia. Slurry drier wastewater is then added and the mixture fed to phenol extraction. The non-process wastewater and oily rainwater which have passed through the API separator for oil removal are then added and the mixture fed to the steps of dissolved air floatation, activated sludge biological oxidation, dual media filtration and activated carbon treatment. Sludge from the activated sludge unit is processed in a dissolved air flotation thickener, aerobic digester and filtration. The resulting solids are disposed of in a land farm. Approximately 60% of the treated water is reused as cooling tower makeup, with the remainder being discharged. The treatment scheme proposed is predicted to meet existing Illinois effluent standards, based on laboratory simulations of the individual steps.

FIGURE 5

AIR EMISSIONS
30 KT/D EDS COMMERCIAL PLANT

POLLUTANT	TONS/YEAR
SO_2	6150
CO	740
NO_X	3200
PARTICULATES	525
HYDROCARBONS	1575

(1) ILLINOIS NO.6 COAL FEED
(4.4% SULFUR)

FIGURE 6

PREDICTED CRITICAL GROUND LEVEL CONCENTRATIONS(1,2) 30 KT/D EDS COMMERCIAL PLANT

$\mu g/m^3$

	CRITICAL GLC	CLASS II AREA PSD INCREMENTS
CONTINUOUS EMISSIONS		
SO_2(24 HR AVG)	35	91
PARTICULATE MATTER (24 HR AVG)	2	37
NO_x(1 HR AVG)	100	–(3)

(1) ILLINOIS NO. 6 COAL FEED

(2) STACK HEIGHTS
FURNACES - 150 FT
BOILERS - 120 FT
SULFUR RECOVERY - 200 FT

(3) NO INCREMENT PROMULGATED

FIGURE 7

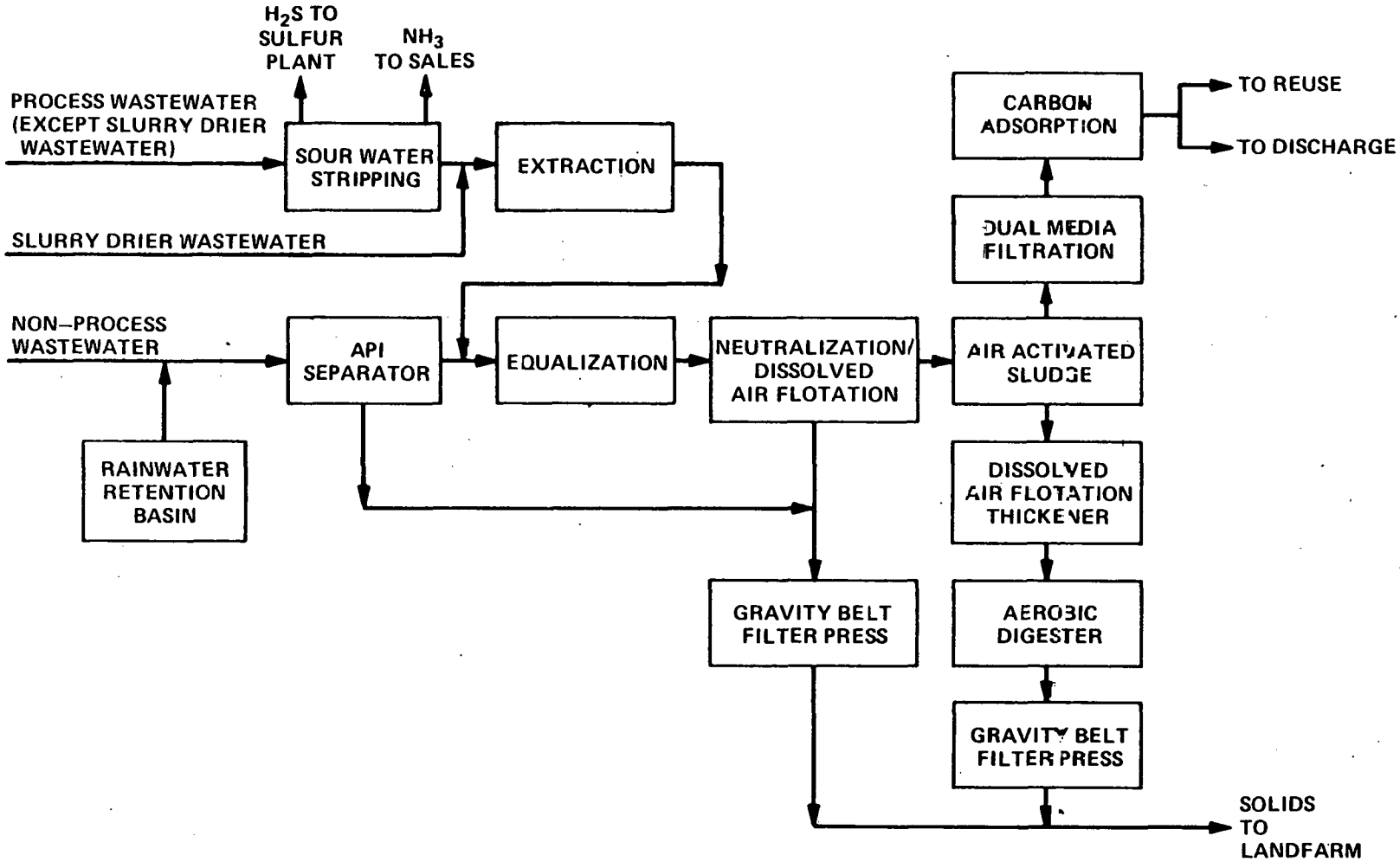
WASTEWATER CONTAMINANTS(1)
30 kT/D EDS PLANT

	WPPM	
NH_3	80	
H_2S	1	
CO_2	80	
FREE CN^-	NIL	
SCN^-	10	
CL^-	90	
Na^+	500	
Ca^{+2}, Mg^{+2} (as $CaCO_3$)	16	
$Fe^{+2,+3}$	4	
PHENOLICS	50	
ORGANIC ACIDS	1500	
OIL AND GREASE	30	
BOD_5	1410	
TOTAL SUSPENDED SOLIDS	30	
TOTAL DISSOLVED SOLIDS	2400	
RATE, GPM	2550	(MAXIMUM)

(1) AFTER STRIPPING AND PHENOLICS EXTRACTION, BUT BEFORE TREATMENT

FIGURE 8

WASTEWATER TREATING SCHEME FOR AN ILLINOIS COAL EDS PLANT



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Leaching tests have been carried out on solid wastes obtained from runs on both Illinois and Wyoming coal EDS bottoms in our small FLEXICOKING pilot plant. Figure 9 shows the results of the extraction tests using the 12/12/78 EPA Toxicant Extraction Procedure. All of the analyses are below the limit shown which is 10 times the EPA Primary Drinking Water Standard. Barium and lead are the closest values being about 60% of the standard. The "less than" values represent the limit of detection and consequently may not be significant. The FLEXICOKING solid wastes would appear to meet the non-toxic criteria specified in the 12/18/78 Draft RCRA Regulations.

Turning now to the environmental effects of the utilization of products from the EDS process, Figure 10 compares particulate and NO_X emissions for two fuel oils produced from Illinois No. 6 coal with those from low sulfur and regular sulfur petroleum fuel oils. The combustion tests were carried out in a 50 Horsepower Cleaver-Brooks firetube package boiler.

Particulate emissions are very low from either coal liquid fuel. The regular sulfur fuel oil is actually more typical of a conventional heavy fuel. You can see it gives 4-5 times as much particulate emissions as the coal liquids and is close to the current New Source Performance Standard for power generation boilers of about 0.05 wt% (0.03 lb/MBTU). NO_X emissions are higher for the EDS fuel oil reflecting the higher fuel nitrogen content. All values shown are above the Current New Source Performance Standard for coal liquids-fired utility boilers which is about 350 ppm (0.5 lb NO_X/MBTU). Some NO_X control may be required such as combustion modifications.

6. EMISSION CONTROL DEVELOPMENT STRATEGY

Our large pilot plant programs are geared to obtain the data necessary to specify emissions controls for a commercial EDS plant. Figure 11 summarizes our strategy for developing the data. In the case of air emissions, there are essentially 3 sources of pollutants - particulates from coal crushing and handling, furnace and boiler flue gases, and fugitive hydrocarbons. We will be identifying/quantifying the emissions sources from the ECLP coal crushing and handling facilities. For particulate control technology, we expect to adapt techniques used in other large coal crushing/handling facilities, such as coal fired power plants. Sulfur emissions will be controlled by scrubbing the fuel gas to furnaces and by flue gas desulfurization on coal fired offsite boilers. Hydrocarbon emissions controls will be adapted from the petroleum refining industry.

For water we will be analyzing the water produced in the Large Pilot Plants. We will then be testing water samples collected from the Large Pilot Plants in laboratory simulations of the treating scheme shown previously. Solids disposal testing will be based on leaching and other tests on products from the FLEXICOKING Prototype operation. Feed to this unit will be produced in ECLP. Noise sources will be identified/quantified in the Large Pilot Plants with control methods adapted from the electric power/petroleum refining industries.

FIGURE 9

LEACHING OF EDS FLEXICOKING TERTIARY FINES(1) VALUES IN WPPM

LEACHATE, WPPM	ILLINOIS COAL	WYOMING COAL	EPA LIMIT(2)
F	0.3 (0.9)(3)	3.3	14-24
NO_3	< 3	–	443
Ag	< .002	< .004	0.5
As	< .06	< .1	0.5
Ba	1.8	.2 (6.7)(4)	10
Cd	.04	< .01	0.1
Cr	.004	< .002 (.03)(4)	0.5
Hg	.0004	.0006	.02
Pb	[.05]	< .08 (.3)(3)	0.5
Se	< .04	< .07	0.1

(1) USING 12/12/78 EPA TOXICANT EXTRACTION PROCEDURE
(2) 10 TIMES EPA PRIMARY DRINKING WATER STANDARD
(3) GASIFIER PURGE
(4) REACTOR CHUNK

FIGURE 10

EDS FUEL OIL COMBUSTION TEST

- ILLINOIS NO. 6 COAL
- COMBUSTION WITH 10% EXCESS AIR

	EDS COAL LIQUIDS		PETROLEUM FUEL OILS	
PARTICULATE EMISSIONS	400 - 1000°F	400°F+	LSFO	RSFO
ASH CONTENT OF SAMPLE, WT%	0.027	0.03	0.02	0.08
TOTAL PARTICULATES WT% ON FUEL	0.03	0.04	0.06	0.17
NO_X EMISSIONS				
NITROGEN, WT% ON SAMPLE	0.55	0.81	0.13	0.44
FLUE GAS CONCENTRATION,(1) PPM	490	580	300	440

(1) CORRECTED TO 3% O_2

FIGURE 11

ENVIRONMENTAL CONTROLS DEVELOPMENT STRATEGY

- AIR
  - QUANTIFY ECLP COAL CRUSHING/HANDLING EMISSIONS
  - ADAPT CRUSHING/HANDLING EMISSION CONTROLS FROM ELECTRIC POWER INDUSTRY
  - BURN CLEAN FUELS IN PROCESS FURNACES
  - ADAPT FUGITIVE HYDROCARBON EMISSIONS CONTROLS FROM PETROLEUM REFINING
- WATER
  - CHARACTERIZE UNTREATED WATERS FROM LARGE PILOT PLANTS (ECLP/FLEXICOKING PROTOTYPE)
  - SIMULATE TREATING SCHEME USING WATER SAMPLES FROM ECLP/FLEXICOKING PROTOTYPE
- SOLIDS
  - PERFORM LEACHING/PROPERTIES STUDIES ON SOLIDS FROM FLEXICOKING PROTOTYPE
  - ECLP PREPARES FLEXICOKING FEED
- NOISE
  - IDENTIFY/QUANTIFY SOURCES IN LARGE PILOT PLANTS
  - ADAPT CONTROLS FROM ELECTRIC POWER/PETROLEUM REFINING
- OCCUPATIONAL HEALTH
  - MONITOR WORKPLACE IN LARGE PILOT PLANTS
  - ASSESS ADEQUACY OF HEALTH PROGRAMS
  - ANIMAL TOXICOLOGY PROGRAM BEING DEVELOPED

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A broad occupational health program is planned for ECLP patterned after one utilized for the past 14 years in our Baytown Laboratories and by other coal liquefaction pilot plant operators. The program is a seven point program combining engineering control of emissions, industrial hygiene monitoring, medical survellance, personal hygiene, operations and laboratory work practices and health education. Monitoring of this program to assess its adequacy is planned. An overall testing program to study the toxicology of EDS products, by-products, intermediates, and wastes is being developed.

7. OUTLOOK FOR COMMERCIALIZATION

Turning now to the commercialization of the EDS process, a possible schedule is shown in Figure 12. After the operation of the larger pilot plants in the 1980-82 time period, a design basis for an EDS Pioneer Plant could be available in 1982. Assuming a 3-year design and engineering effort, construction of a Pioneer Plant could start in 1985 and the start-up operations could begin in 1988 or 1989. Current estimates place the cost of such a Pioneer Plant capable of processing 13,000 tons of coal per day at around $1.5 billion (1979 dollars). Such a plant would be one train of a commercial plant and would produce 25,000 to 30,000 barrels of coal liquids per day. It would be designed for possible expansion later, to twice the size by the addition of a second process train, if and when justified.

Design of full sized commercial plants might start after the Pioneer Plant operates for a year. In the case of the illustrated development schedule for the EDS Coal Liquefaction Process, this could mean 1989, and construction could begin in 1992 with start-up in 1997.

Of course, a synthetic fuels industry will not develop in the private sector unless there is an expectation of a reasonable return on investment. Another obstacle to commercialization of coal liquids technology are current environmental and permitting difficulties which cause long delays in project implementation and create significant risks. It is hoped that the formation of the Energy Mobilization Board now being considered by the Congress will aid in reducing delay. In addition one purpose of meetings such as this is to improve communications on this problem.

Environmental concerns cannot be ignored. However, additional legislation may be required for synfuels development to allow demonstration of the technologies on a commercial scale to obtain realistic environmental data. In doing this, a greater public understanding of the need for, and impact of, synthetic fuels must be achieved.

In summary, programs for the EDS Large Liquefaction and FLEXICOKING Pilot Plants have been defined and startup of ECLP is in progress. These programs should provide the data base needed for scale up to commercial size, and help insure that commercial EDS coal liquefaction plants will be environmentally acceptable.

February 12, 1980

FIGURE 12

APPLYING COAL LIQUIDS TECHNOLOGY

