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# Proceedings of the Seventh Annual Gasification and Gas Stream Cleanup Systems Contractors Review Meeting

## Volume I

Editors
**M.R. Ghate**
**K.E. Markel, Jr.**
**L.A. Jarr**
**S.J. Bossart**

June 1987

Sponsored by
U.S. Department of Energy
Office of Fossil Energy
Morgantown Energy Technology Center
Morgantown, West Virginia

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U.S. Department of Energy
Office of Fossil Energy
Morgantown Energy Technology Center
P.O. Box 880
Morgantown, West Virginia 26507-0880

MASTER

Held at
Sheraton Lakeview Conference Center
Morgantown, West Virginia
June 16-19, 1987

August 1987

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FOREWORD

On June 16 through 19, 1987, METC sponsored the Seventh Annual Gasification and Gas Stream Cleanup Systems Contractors Review Meeting which was held at the Sheraton Lakeview Conference Center in Morgantown, West Virginia. The primary purpose of the meeting was threefold:

- To review the technical progress and current status of the gasification and gas stream cleanup projects sponsored by the Department of Energy.
- To foster technology exchange among participating researchers and other technical communities.
- To facilitate interactive dialogues which would identify research needs that would make coal-based gasification systems more attractive economically and environmentally.

More than 310 representatives of Government, academia, industry, and foreign energy research organizations attended the 4-day meeting. Fifty-three papers and thirty poster displays were presented summarizing recent developments in the gasification and gas stream cleanup programs. Scientists, engineers, and administrators discussed many of the issues facing those engaged in the research and development activities that constitute these programs. This document constitutes the proceedings of that meeting, and serves as a summary of the gasification and gas stream cleanup programs.

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This document was made possible by the efforts and expertise of many dedicated individuals who participated in the Seventh Annual Gasification and Gas Stream Cleanup Systems Contractors Review Meeting. Thanks are given to those persons who presented project status summaries, to those who made the Poster Sessions true technology exhibits, and to those who contributed to the interesting and lively discussions during the course of the meeting. A special note of thanks is tendered to Vijendra Kothari, Megan Day, Wen-Shou Liou, Suresh Jain, David Dubis, Norman Holcombe, Leland Paulson, Randall Dellefield, Hsiao-Ya Lai, Thomas Dorchak, Justin Beeson, Mark Williams and James Longanbach, each of whom served as a session chairperson. A special acknowledgment is given to A. A. Pitrolo, Director, Morgantown Energy Technology Center, for his opening remarks; Gary E. Voelker, Director of Coal Conversion Systems, Fossil Energy Headquarters for his overviews of the gasification and gas stream cleanup programs; and Dr. Sy Alpert, Technical Director, Electric Power Research Institute for a very interesting and informative keynote speech. Special recognition is also given to the following people for presenting luncheon talks which broadened the perspective of the meeting: Dr. Willam Lueckel, Vice President of Research, International Fuel Cells Corporation; Dr. James Corman, Manager, Thermochemical Processes Branch, General Electric Corporate Research and Development; and William Morse, Vice President of Research, Columbia Gas System Service Corporation. The Conference Services staff of EG&G Washington Analytical Services Center, Inc., Morgantown Operations, is also acknowledged for providing excellent coordination and support services for the meeting.

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# THE STATUS OF COAL GASIFICATION TECHNOLOGY AND ITS IMPLICATIONS FOR ELECTRIC POWER PRODUCTION

Keynote Speech, June 16, 1987
Seymour B. Alpert
for
Dr. Dwain F. Spencer
Vice President
Advanced Power Systems
Electric Power Research Institute

## INTRODUCTION

During the past 10 years or so, the Electric Power Research Institute (EPRI) has been carefully assessing and selectively developing/demonstrating a number of coal gasification technologies for use within the United States electric power industry. The initial motivation for this interest was the development of environmentally benign coal-based power generation systems which could anticipate any level of future Federal control requirements on acid rain precursors, particulary sulfur dioxide and oxides of nitrogen. In addition, particulate emissions could be controlled to extremely low levels and early studies indicated the slag from most coal gasification systems would be chemically inert under various leachate test requirements. Thus, coal gasification technology showed promise of meeting or exceeding all potential future emission and ash disposal control regulations.

In parallel, EPRI began engineering and economic analysis of alternative coal gasification technologies to determine the economic potential of coal gasification coupled to combustion turbine combined-cycle power plants. This is the integrated coal gasification combined-cycle (IGCC) concept which has begun to emerge as a leading candidate for future power generation additions utilizing high sulfur bituminous coal. Although the focus of EPRI's program was the analysis and development of high-sulfur coal gasification processes, we also had an objective to develop a range of gasification processes to utilize the full range of United States coals.

Our initial engineering and economic evaluations considered commercially available coal gasification technologies such as the dry ash Lurgi moving bed and the atmospheric pressure Koppers-Totzek entrained gasifier processes. These were not found to be economically competitive with other alternate coal-based power plants such as pulverized coal with flue gas desulfurization and atmospheric fluidized-bed combustion systems. We thus began evaluation of a number of second-generation IGCC systems, including Texaco coal gasification process (TCGP) the British gas/Lurgi slagging gasifier, the Shell coal gasification process, and others. Most of these second-generation IGCC systems, when coupled to emerging advanced air-cooled combustion turbines, had both competitive capital and bus bar electricity costs compared to conventional pulverized coal plants with flue gas desulfurization and simultaneously controlled both $SO_2$ and oxides of nitrogen to very low levels. These evaluations, performed in the mid to late 1970's, were primarily based on small pilot plant data (15 to 30 ton/day throughputs) so a major development program to obtain data from larger scale systems was necessary in order to confirm these projections.

## STATUS OF EMERGING SECOND-GENERATION COAL GASIFICATION PROCESSES

In this section, we will briefly summarize the present status of key emerging second-generation coal gasification processes which show promise of producing economically competitive power when coupled to the next generation air cooled combustion turbine combined-cycle technology. Since nearly all IGCC plants rely on the availability of this advanced combustion turbine, we will briefly review the status and performance of the next generation combustion turbine combined cycle.

Nearly all of our engineering and economic evaluations are presently based on the GE/MS7001F combustion turbine combined cycle. This unit has been under development since 1983 and the first commercial prototype is scheduled for delivery in 1988. The combustion turbine combined cycle incorporates many reliability features, as well as increased firing temperature and compression ratio, and emanates from jointly funded General Electric and EPRI projects. The characteristics of the combustion turbine are shown in Table 1 compared with the present GE/MS7000 Model E and overall efficiencies for simple cycle, combined cycle, and IGCC operation are shown in Table 2. The coupling of this advanced combustion turbine cycle to second-generation coal gasification systems should provide a range of reliable, flexible power plant additions for the United States and other electric utilities in the early to mid 1990's.

TABLE 1. Performance Improvement
GE Frame 7 Combustion Turbines

| | Model | |
|---|---|---|
| | E | F |
| Power output-Simple Cycle (MW[e]) | 75 | 135 |
| Turbine Inlet Temperature (°F) | 2,020 | 2,300 |
| Compression Ratio | 11.7:1 | 15:1 |
| Air Flow (lbs/s) | 600 | 900 |
| Specific Power (kW/lb/s) | 120 | 150 |

TABLE 2. Performance Improvement
GE Frame 7 Combustion Turbines

| | Model E | Model F |
|---|---|---|
| Heat Rate, 59°F (Btu/kWh) | | |
| • Simple Cycle HHV | 11,725 | 11,255 |
| LHV | 10,660 | 10,140 |
| • Combined Cycle HHV | 8,580 | 7,425 |
| LHV | 7,800 | 6,690 |
| • IGCC (88°F) HHV (Texaco-Based) | 9,500 | 9,000 |

The major leading emerging coal gasification systems which will be reviewed in this paper are (1) Texaco Partial Oxidation, (2) the DOW Syngas Process, (3) the British Gas-Lurgi Slagging Gasifier, (4) the Shell Coal Gasification Process, (5) the Allis-Chalmers KILnGAS Technology, and (6) the High Temperature Winkler Fluid Bed. All of these processes have been or are operating at scales of at least 200 tons/day and existing data provide us a firm basis for estimating future commercial plant performance. In our judgment, all processes integrated with power generation equipment must be operated for at least 2 to 3 years at full scale in order to provide the United States electric utility industry with adequate confidence to invest in the commercial use of these processes/power plants.

A. Texaco Coal Gasification Process (TCGP)

The Texaco coal gasification process (TCGP) is the process with the most full scale experience. In addition to the two units at southern California Edisons' cool water IGCC plant, which will be discussed in more detail later in this paper, the TCGP coal-water slurry fed process is being operated at 900 tons/day coal throughput at Tennessee Eastman in the United States to produce synthesis gas for methanol production, at 800 tons/day in the Federal Republic of Germany for oxochemical production, and at 500 tons/day in Japan to produce ammonia. Thus, the design basis for TCGP-based IGCC systems on a variety of coals is much further developed than any of the other second-generation coal gasification technologies. This paper will not discuss all of the background process development leading to the present status of TCGP for power generation, but focus on the results of the cool water IGCC power plant experience, since this is directly relevant to future commercial IGCC power systems.

As discussed above, we envision that commercial systems will be based on parallel gasification-gas turbine unit trains of approximately 200 MWe in capacity of a coal throughput of approximately 1,200 to 1,300 tons/day per coal gasifier. Therefore, the cool water IGCC demonstration plant

was designed for a single gasifier capacity of approximately 1,000 tons/day to obtain full-scale operating experience with the coal gasification/synthesis gas cooling system. At the time this system was designed, this represented a scale up by a factor of six (6) from the previous experience with TCGP coal-based systems.

A simplified block diagram of the cool water IGCC power plant is shown in Figure 1. The key characteristics of the plant include an air separation plant to produce 99.5 percent pure oxygen, a coal-water slurry preparation and pressurization system, the coal gasification, synthesis gas cooling (heat recovery) system, the gas cleaning and sulfur recovery system, and the power generation train including a GE7000E combustion turbine heat recovery steam generator-steam turbine system.

The cool water plant began operation in May 1984 and, to date, has accumulated over 15,000 hours of operation. An overall performance summary is shown in Table 3. Table 4 shows the key design requirements for the plant, as well as the actual performance on the design low-sulfur bituminous coal (SUFCO), as well as the performance on both Illinois No. 6 and Pittsburgh No. 8 high-sulfur bituminous coals. In summary, the cool water plant has exceeded all design performance requirements and met initial projected operating capacity factors. This is truly a phenomenal performance record for the first of kind facility at this scale on a new power generation technology.

In addition, Tables 5 through 8 show the actual environmental emission performance from the plant compared to both United States Federal New Source Performance Standards (NSPS) and extremely tight California air emission control requirements. In general, the cool water IGCC plant has exceeded United States EPA NSPS requirements by nearly a full order of magnitude for all key atmospheric pollutants; i.e., sulfur dioxide, oxides of nitrogen, and fine particulates. These results are based on a very extensive monitoring program and over 40,000 specific measurements. Thus, it is clear that the environmental promise of IGCC power plants has been met or exceeded at cool water.

This is not to say that we have not encountered a myriad of design and operating problems at the plant. Over the last 3 years, we have made over 5 million dollars of capital improvements in the plant compared to an initial cost of $263 million. These have included changes in the slurry feed system, redundant cooling capacity for the acid gas removal process, cross-over duct redesign, repairs to the radiant and convection section synthesis gas coolers, and major changes in the design of the liquid oxygen backup pumping and control system. However, these are precisely the reasons that a full-scale demonstration facility must be constructed and operated. Although we have experienced a few explosions in portions of the plant the overall safety record has been extraordinary with only two major lost time accidents and no fatalities. We are still continuing to learn how to enhance performance, increase on steam time, and enhance the safety of the cool water IGCC plant; however, the overall operating performance and experience is certainly adequate to provide a firm design basis for utilizing a variety of United States coal.

FIGURE 1

# BLOCK FLOW DIAGRAM
# COOL WATER COAL GASIFICATION PROGRAM

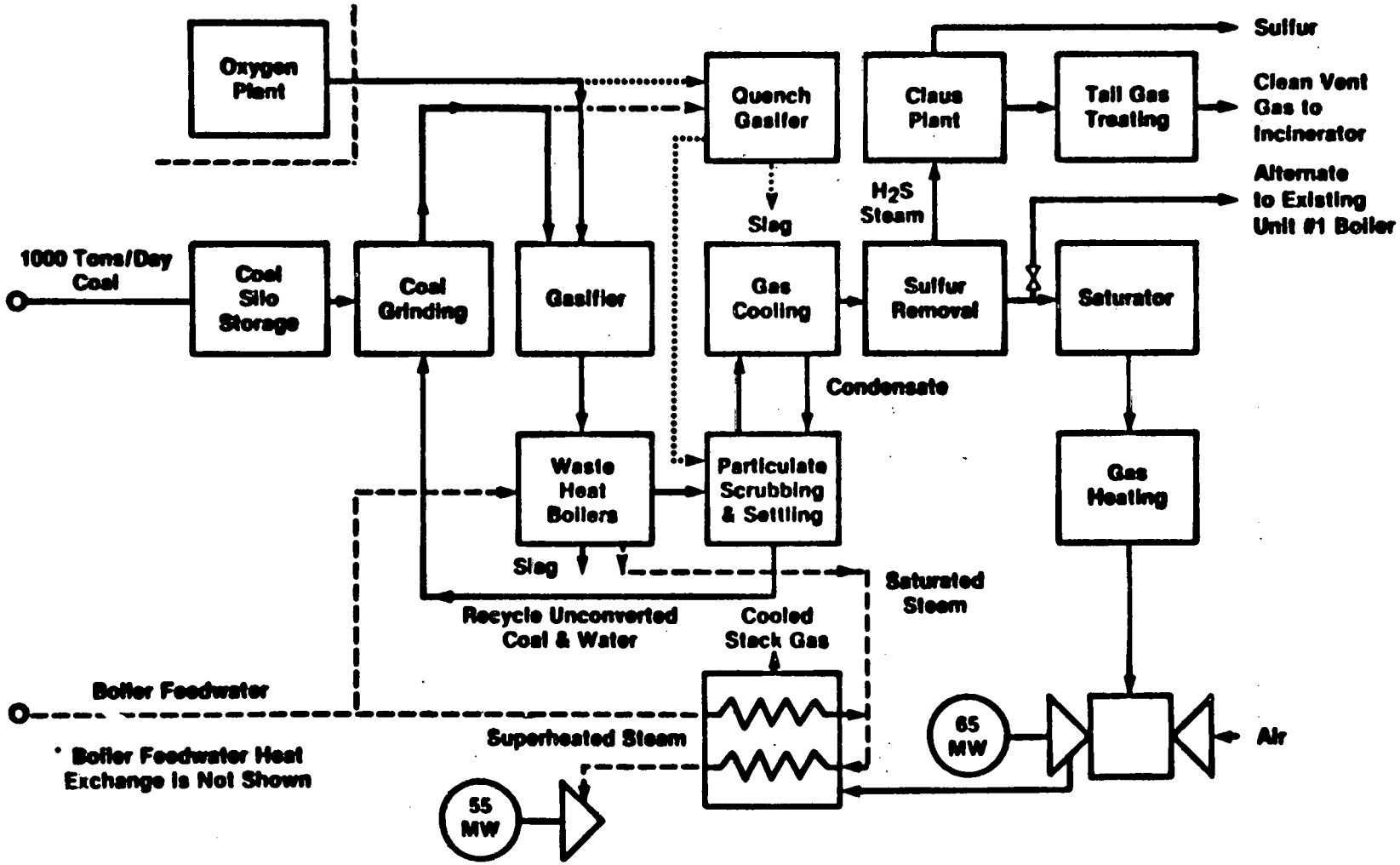


TABLE 3. Cool Water Power Plant Performance Summary

| | 6/84 Through 2/87 |
|---|---|
| Gasifier Operation (hrs.) | 14,254 |
| Coal Gasified (tons dry) | 575,071 |
| Gross Electrical Production (kWh) | 1,383,363,000 |
| On-Stream Factor (%) | 60.6 |
| Capacity Factor (%) | 50.3 |

TABLE 4. Cool Water Performance
Alternate Coals

| Coal | Design Basis SUFCo | SUFCo | Ill No. 6 | Pitts No. 8 |
|---|---|---|---|---|
| Sulfur Content (wt%) | 0.48 | 0.4 | 3.1 | 2.9 |
| Coal Feed (t/d) | 1,000 | 1,000 | 1,000 | 1,000 |
| Oxygen (t/d) | 962 | 908 | 885 | 1,004 |
| Gross Power (MW) | 114 | 116 | 120 | 129 |
| Sulfur Produced (t/d) | 4.6 | 3.8 | 30.0 | 27.0 |
| Slurry Concentration (wt%) | 60 | 60 | 64 | 62 |
| Carbon Conversion (%) | 95 | 98.3 | 97.2 | 97.8 |
| Typical Overall Heat Rate, Net (Btu/kWh) | 11,510 | 11,550 | 11,700 | 11,460 |
| Projected Refractory Life (yrs) | 1 | 4 | 2 | 2 |

TABLE 5. Cool Water Coal Gasification Program
$SO_2$: HRSG Stack Emissions (lbs/$10^6$ Btu)

| Coal Type | Federal New Source Performance Standards | California Permit Limits | Test Data |
|---|---|---|---|
| SUFCo | 0.24 | 0.033 | 0.018 |
| Illinois No. 6 | 0.60 | 0.16 | 0.076 |
| Pittsburgh No. 8 | 0.60 | 0.16 | 0.086 |

TABLE 6. Cool Water Coal Gasification Program
$NO_x$: HRSG Stack Emissions (lbs/$10^6$ Btu)

| Coal Type | Federal New Source Performance Standards | California Permit Limits | Test Data |
|---|---|---|---|
| SUFCo | 0.6 | 0.13 | 0.07 |
| Illinois No. 6 | 0.6 | 0.13 | 0.094 |
| Pittsburgh No. 8 | 0.6 | 0.13 | 0.09 |

TABLE 7. Cool Water Coal Gasification Program
Particulate: HRSG Stack Emissions (lbs/$10^6$ Btu)

| Coal Type | Federal New Source Performance Standards | California Permit Limits | Test Data |
|---|---|---|---|
| SUFCo | 0.03 | 0.01 | 0.004 |
| Illinois No. 6 | 0.03 | 0.01 | 0.009 |
| Pittsburgh No. 8 | 0.03 | 0.01 | 0.009 |

TABLE 8. Cool Water Coal Gasification Program
CO: HRSG Stack Emissions (lbs/$10^6$ Btu)

| Coal Type | California Permit Level | Test Data |
|---|---|---|
| SUFCo | 0.07 | 0.004 |
| Illinois No. 6 | 0.07 | 0.004 |
| Pittsburgh No. 8 | 0.07 | 0.004 |

B. DOW-Syngas Process

The DOW syngas technology is also a coal-water slurry fed system; however, it is a two-stage entrained system intended initially for subbituminous coal and lignite. The purpose can be designed to utilize high-sulfur bituminous coal, most probably with a single-stage configuration. The DOW process was initially an outgrowth of the TCGP technology; however, now there are fundamental design differences between the two systems. The primary differences are (1) TCGP is an entrained downflow system, DOE is a dual burner fed entrained upflow system; (2) TCGP is a single-stage gasifier, while DOW is a two-stage process, particularly with low-rank coals; (3) TCGP synthesis gas is cooled to produce saturated steam, while the DOW process uses recycle gas quench to reduce gas temperatures into a region where superheated steam can be raised; and (4) the TCGP process primarily is designed to utilize bituminous coals, whereas the DOW syngas process primarily gasifies low-rank coals.

The DOW process has been operated in two subscale units, including a 1,400-ton per day prototype reactor, and is presently being operated at Plaquemine, Louisiana at a 2,400-ton per day scale. The project at Plaquemine, similar to cool water, has obtained a price guarantee from the former United States Synthetic Fuels Corporation to defray expected operating cost shortfalls (and some profits in the case of DOW) during the first few years of operation of the plant.

We are presently working closely with DOW to evaluate the potential economics of their system on various coals and are jointly considering a high-sulfur coal demonstration project as part of the United States Clean Coal Technology program. In our judgment, the DOW process is only a few years behind our present experience base with TCGP.

C. British Gas Lurgi Slagging Gasifier

The British Gas Corporation, in cooperation with Lurgi, have been developing a slagging version of the Lurgi dry ash system for the last 30 years. Scale up to a 350-ton per day unit was accomplished in the late 1970's with support from a consortium of United States gas utilities and EPRI. EPRI sponsored a very successful set of load following tests on the unit in 1979 and 1980 on both Illinois and Pittsburgh seam coals.

An 8-foot diameter unit, capable of processing 600 tons per day of coal was commissioned in December 1984; however, a gas explosion in downstream cooling equipment delayed the planned test program to late 1986. The unit is currently operating on United Kingdom coals, with tests planned for mid-1987 on United States coals. These tests will be jointly sponsored by EPRI, the Gas Research Institute, and British Gas.

Commercial plant designs based on the process have been prepared for an SNG plant in Noble County, Ohio and for an industrial gas application for a paper company in Georgia. A site-specific design study of a 180-MWe IGCC plant was also performed for the Chesterfield Station of Virginia Power Company. Although the process shows significant promise for electric power generation, the handling of tars and utilization of fines in the gasifier remain important technical issues. There is still an aggressive effort to define an appropriate location for a North American demonstration plant being pursued by British Gas/Lurgi, with the assistance of EPRI and United States architect engineers.

D. Shell Coal Gasification Process (SCGP)

The Shell gasification process has also been under development for nearly 20 years, with the original technical effort a joint venture between Royal Dutch Shell and Krupp-Koppers. The SCGP process, as presently designed, is owned by Shell International. A 150-ton/day unit was built and operated at the Deutsche Shell Refinery in Hamburg in the early 1980's. Although a sustained 90-day run was successfully conducted at the site, a number of design improvements were identified.

EPRI also supported cycling tests on the small 6-ton/day pilot plant in the Hague, and these tests were also quite successful. Shell U.S., CE Lummus, and EPRI are now supporting the design, construction, and operation of a 200 to 400-ton/day large pilot plant (prototype) plant (SCGP-1) located at Deer Park, Texas. The plant is scheduled to begin operation in May 1987 with tests on Texas lignite and Illinois No. 5 coal planned over a 2-year period.

E. Allis-Chalmers KILnGAS Process

The Allis-Chalmers KILnGAS process uses an air-blown biflow rotating kiln gasifier to produce a low-Btu gas. A 600-ton/day unit has been operating in an integrated configuration with an Illinois Power Company boiler since late 1983; however, the unit has not yet met its design throughput and carbon conversion on bituminous coal. The best performance to date was obtained in November and December 1986 when approximately 85 percent carbon conversion was achieved at 60 percent design throughput in the biflow mode with sized coal. Carbon losses from the discharge/high-temperature/ end of the kiln still need to be recycled to achieve satisfactory carbon conversion.

Allis-Chalmers is currently seeking a venture partner to continue the development program; however, presently future operating plans for the Wood River unit are uncertain.

F. High-Temperature Winkler

A 700-ton per day high-tempearture winkler gasifier has been operating on Rheinishe brown coal since mid-1985. The synthesis gas is being utilized for methanol production near Koln, Federal Republic of Germany.

There are a number of other emerging coal gasification technologies including the Kellogg Rust Westinghouse fluidized bed, the airblown dry ash Lurgi Mark IV's, Prenflo, etc. Suffice to say that a very competitive marketplace is developing for a range of coal gasification processes capable of operating on essentially all United States and Canadian coal types. The economic performance of this broad range of alternatives will ultimately decide the preferred processes.

ECONOMIC ANALYSES OF COMPETING COAL GASIFICATION PROCESSES

EPRI has been conducting and sponsoring engineering and economic evaluations of nearly all emerging coal gasification technologies since the mid-1970's. An excellent assessment of the status (at that time) and relative economics is contained in the EPRI Coal Gasification Guide.

Based on these economic assessments, as well as information obtained from specific process developers, EPRI has identified TCGP, DOW, BG/Lurgi, and SCGP as the most likely commercial processes for electric utility application in the United States. The overall cost and performance estimates for all of these processes on bituminous coal, except DOW, are shown in Table 9. EPRI and DOW are presently collaborating on the evaluation of the DOW process on a variety of United States coals and those results should be available in late 1987. As may be seen from Table 9, all coal gasification processes when coupled with the GE/MS7001F combustion turbine are projected to be competitive with a pulverized coal-fired plant utilizing flue gas desulfurization systems. Table 10 shows a cost breakdown by major plant section for a TCGP-based IGCC plant on bituminous coal.

In addition, EPRI and utility system planning studies have shown that the IGCC plants, if phased into the utility system as simple-cycle combustion turbines and then combined-cycles firing natural gas or distillate, have an additional equivalent present worth capital savings of approximately $250 per kilowatt. Thus, there is an additional financial incentive for IGCC plants in a phased implementation mode.

During 1986 and 1987, EPRI is cosponsoring a number of site-specific engineering and economic analyses with individual utilities to further refine the generic cost and performance estimates. The specific studies underway are summarized in Table 11. By the end of this year, we should have a very well documented basis for estimating the costs of IGCC power plants in various climates utilizing a variety of coals. We believe this will further enhance the prospects for United States electric utility adoption of IGCC technology.

Table 9

Summary of Comparative Costs and Performance Estimates

Capacity - 500 MWe; Illinois #6 Coal; Constant January 1987 Dollars

| | Reference Coal-Fired Steam Plant | Texaco Partial Oxidation | Shell Coal Gasification Process | BGC Lurgi Slagging Gasifier |
|---|---|---|---|---|
| Sulfur Removal, % | 90 | 95-97 | 90/99 | 95-97 |
| $NO_x$ Emission, ppmv(1) | 150 | 50-75 | 50-75 | 50-75 |
| Heat Rate, Btu/kWh | 9,850 | 9,010 | 8,720 | 8,660 |
| Total Capital, $/kW(2) | 1,390 | 1,540 | 1,490 | 1,300 |
| Levelized Cost of Electricity at 65% C.F., Mills/kWh | 54.9 | 52.7 | 50.8 | 48.9 |



(1) 15% Excess $O_2$, Heat Rate Corrected; 2300°F Combustion Turbine for IGCC Plants

(2) Includes working capital, start-up costs, spare parts, land, royalties, and AFUDC-all IGCC plants rated at 88°F

TABLE 10. Texaco-IGCC-GE Model F Turbine -- Total Heat Recovery
88°F Design Point, Illinois No. 6 Coal

| | January 1987 Dollars $/kW |
|---|---|
| Coal Receiving, Grinding, Slurry Preparation | 60 |
| Oxidant Feed | 160 |
| Gasification, Gas Cooling, Particulate and Ash Removal | 260 |
| Low-Temperature Gas Cooling and Saturation | 30 |
| Acid Gas Removal | 30 |
| Sulfur Recovery | 20 |
| Tail Gas Treating | 10 |
| Power Generation | 430 |
| General Facilities | 190 |
| Initial Catalyst and Chemicals | 10 |
| Contingency | 180 |
| Plant Investment | 1,380 |
| Startup; Working Capital, Land, AFUDC | 160 |
| Total Capital Investment | 1,540 |

TABLE 11. Utility IGCC Site-Specific Studies

| Utility | Site | Type of Plant | Gasification Process | Coal |
|---|---|---|---|---|
| Baltimore Gas and Electric | Perryman | 4-Phase, 400-MW, IGCC | Shell | Pittsburgh No. 8 |
| Florida Power and Light | Martin/ Lauderdale | 3-Phase, 400-MW Integrated Pipeline | Shell | Pittsburgh No. 8 |
| Niagara Mohawk | Albany | Phased Repowering 200-400 MWe, Ownership by Others | Shell | Pittsburgh No. 8 |
| Northeast Utilities | Devon | Phased Repowering 600 MW | Shell | Pittsburgh No. 8 |
| Potomac Electric | Dickensen | Phased,400 MW IGCC | Shell | Maryland |
| Public Service of Indiana | Gallagher | Phased Repowering 4-150 MW Units | Texaco | Indiana/ Illinois |
| Southern Company | Wansley | 400 MW IGCC | KRW | Illinois No. 6 |
| Union Electric | Labadie | Repowering, 800 MW Model E | Texaco | Illinois No. 6 |
| Virginia Power | Chesterfield | 3-Phase, 600 MW 180 MW IGCC | Shell B&C Lurgi | Appalachian |

SUMMARY

In summary, there are a large number of emerging coal gasification processes which show promise of meeting very stringent emission control requirements and producing electricity in the United States at competitive costs. These processes are focused on the use of high-sulfur bituminous coals in order to permit continued use of this important United States domestic resource, and simultaneously meet stringent emission control limitations. Although load growth and retirement rates for present coal-fired units are both quite uncertain, we believe that IGCC systems will become a major new technology for coal-based electric power generation and make a major contribution in reducing acid rain precursors over the next 20 to 25 years. I hope by 2010 or so, there will no longer be discussion of the United States-Canada transboundary acid rain problem as the United States electric utility industry adopts this and other new clean coal technology options.

DEVELOPMENT OF A MILD GASIFICATION PROCESS

1. DOE CONTRACT NUMBER: DE-AC21-87MC23289

CONTRACTOR: UCC Research Corporation
P.O. Box 1280/Glenway Avenue
Bristol, Virginia 24203

CONTRACTOR PROGRAM MANAGER: Dr. Richard A. Wolfe

PRINCIPLE INVESTIGATORS: Dr. Charles I. C. Chu
Chang J. Im
Barry L. Gillespie

METC PROJECT MANAGER: Dr. Wen S. Liou

PERIOD OF PERFORMANCE: January 9, 1987 to January 9, 1989

2. SCHEDULE/MILESTONES:

Figure 1. depicts the schedule of the project by task.

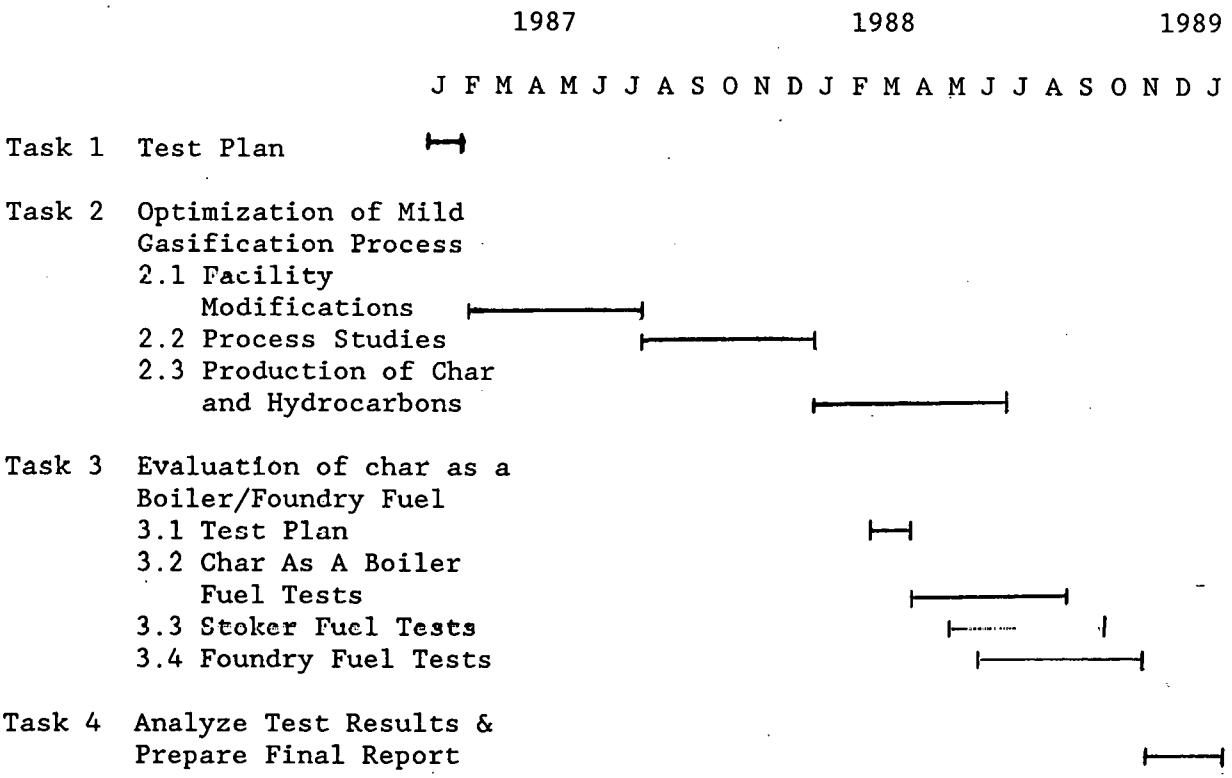



Figure 1. Project Schedule

## 3. OBJECTIVES

The objective of this research and development program is to develop a mild gasification process which produces the quantity and quality of condensibles, char, and gas that makes the process economically feasible. This project will involve : 1) modifying the existing Mild Gasification Process Development Unit (MGU) at UCC Research Corporation (UCCRC), 2) conducting extensive parametric tests with the modified MGU to obtain detailed information on the mild gasification process with a view to find the optimum operating conditions, and 3) conducting experiments to determine the suitability of char for several commercial applications. The data will be analyzed to recommend the next stage of development and to determine the best approach for commercialization.

## 4. BACKGROUND STATEMENT

The major problem currently troubling coal industry is the shrinking market share of coal in the energy field. During the past 30 years, oil has continued to erode the coal market in the transportation (locomotive and marine diesels), industrial, and utility markets. In addition, the United States has grown increasingly dependent on foreign oil supplies.

A number of new markets for coal exist, which could drastically increase coal utilization, reduce oil consumption and thus reduce the U.S.'s dependence on a foreign oil supply. For instance, the railroad industry once the largest user of coal (exceeding 75 million tons per year) now uses in excess of 2 billion gallons of diesel fuel annually. If coal could regain a portion of this market with a coal liquid fuel form, the regained market could easily use millions of tons of coal per year. Similar increases in coal usage could be realized with the development of a coal-fueled, turbine system or the development of a coal-derived, home heating fuel.

During the past 20 years or so, various kinds of new generation coal conversion processes have been proposed worldwide; however, most of them proved to be too complicated and/or uneconomical. UCCRC has taken a different approach, mild gasification. Mild gasification is a low-temperature, low pressure carbonization process which entails low-cost processing of coal. The scientific basis underlying this type of process is well-documented in the literature (1-8)*. The basic concept of the process is to remove the high quality volatile matter from the coal as condensibles and gas, and leave a high-quality char that has several potential end uses.

There is ample evidence to suggest that the condensibles from mild gasification are of high quality and are acceptable with minimal processing as transportation fuels (9-13). Nickell (9) indicates that mild gasification liquid products are significantly different from and superior to liquid products of other direct coal liquefaction processes, which are operated under more severe conditions, and many times, resort to using expensive hydrogen.

*Numbers in parentheses designate references at end of paper.

Other researchers have explored the possibility of obtaining transportation fuels from minimally processed coal liquids. Graves and Fox (12) blended mild gasification coal liquids with diesel fuel and carried out combustion tests in a variety of diesel engines. Graves and Fox stated that, "The results of the engine tests suggest that the raw pyrolysis oil has combustion qualities similar to (at least as good as) distillates from other coal conversion process, noting that the latter coal liquids have undergone considerable processing." They concluded by saying that, "A perhaps atypical, favorable conclusion has been reached regarding the commercial attractiveness of low-temperature coal pyrolysis. Evidence to support the conclusion has been derived from researching prior work and new screening experiments that revealed that sufficient yields of oils, considerably higher in quality than usually attributed to coal liquids, should be obtained if laboratory experiments can be repeated in a scaled-up process."

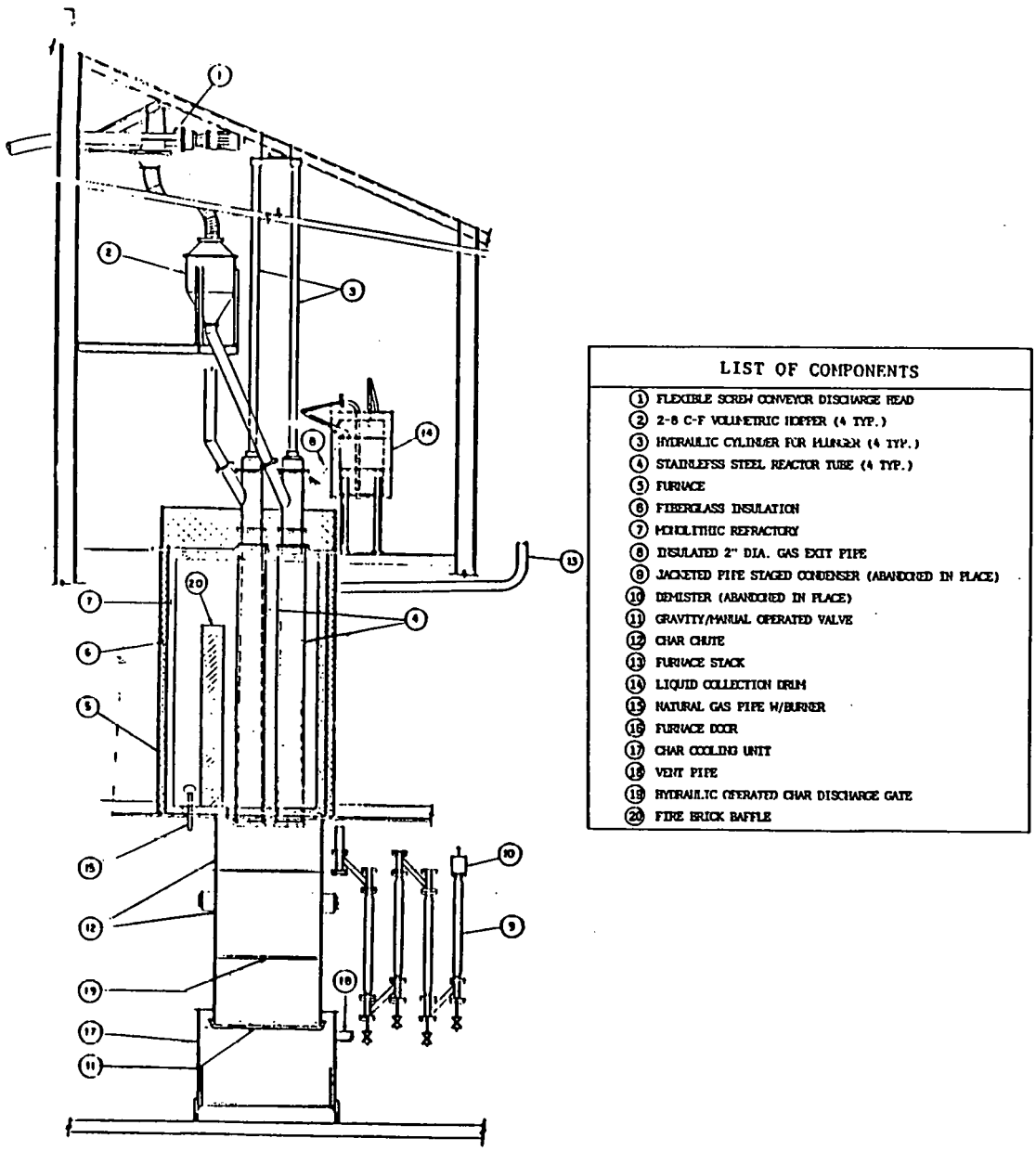
The mild gasification technology also provides a solid char fuel that is typically more environmentally acceptable than coal itself by virtue of its lower sulfur content. In many cases, depending on the process used, char has better, cleaner, handling characteristics. One of the outstanding benefits that is derived from the mild gasification technology, is that the solid char fuel produced can be handled easily within the coal industries since the infrastructure already exists for handling a solid coal product.

With these facts in mind, UCCRC, under DOE contract No. DE-AC21-84MC21108, has constructed and operated a Mild Gasification Process Development Unit (MGU) capable of handling up to 1500 lb/day of coal at temperatures up to 1500°F and atmospheric to mild vacuum pressure conditions. The MGU, shown in Figure 2, includes the following major equipment items: a one-ton coal storage bin, four volumetric hoppers, four - 8 inch diameter, 8 feet long, reactor tubes. a constant, controlled furnace, two banks of condensers, four hydraulic plungers for char removal, a char quenching chamber, and appropriate storage containers for char and condensibles produced.

Briefly, the process operates as follows: coal from the volumetric hopper, Item 2, is charged into the reactor tubes, Item 4, which are located inside a furnace, Item 5, which is heated at 1100°F to 1400°F. The coal is heated in the reactor tubes, under a slight vacuum, sealed to exclude air, for 4 to 8 hours. Devolatilized vapor is pulled through the condensing system and cooled. Condensibles are collected and non-condensible gas is sent to flare. At the end of the test run, the char is discharged into the char chamber where it is quenched with a water spray.

Tests to-date in UCCRC's MGU facility have produced good quality liquids which appear to have numerous potential applications. UCCRC has taken the raw coal liquids from the MGU and separated by distillation a <600°F boiling point fraction. Analytical work performed at Virginia Tech by Dr. Dorn and co-workers (14) show that the <600°F fraction is unique in comparison with many other fossil fuels. After analysis by LC-$^{1}$H NMR and $^{13}$C NMR techniques the following viewpoints have evolved:

Figure 2: Mild Gasification Process Development Unit



(A) The high aromaticity of this material indicates that it has a high heating value per unit volume. This quality will assure that, in jet engine application, it will enable the jet plane to achieve a long flying range with a limited fuel tank capacity.

(B) The fact that most of its aromatic constituents are 1- and 2-ring type aromatic material makes it much simpler task to hydrogenate it such that the resultant saturated product will attain a high degree of combustion efficiency.

(C) The low alkane content of this liquid sample means that it can be expected to have a very low freezing point, which is a very important quality for any jet fuels to be used in the high-flying jet planes.

The unique qualities of this <600°F B.P. sample mentioned above therefore suggests that it could be an excellent precursor for high density fuel.

Furthermore, and maybe most important, based on the experiences of Virginia Tech in analyzing a great many different types of fossil fuels using LC-$^{1}$H NMR techniques, it was felt that the <600°F B.P. liquid can be readily blended (without further pre-treatment) with various proportions of petroleum naphtha and/or methanol to make fuel products which are similar to typical petroleum diesels fuel and fuel oil, etc. One such blend tested was a mixture of methanol, petroleum naphtha, and UCC coal liquids (<600°F B.P. fraction). The ratio of the liquids was 1:1:1 on a volume basis. Another similar blend, a 1:1 mixture of KilnGas liquid/diesel oil was found to be similar to diesel fuel except for a somewhat higher fraction of aromatic hydrocarbons than is found in typical diesel fuels.

Dr. Dorn and co-workers (14) state that, "Although the 1:1:1 mixture of methanol, petroleum naphtha, and UCC liquid has an aromatic content only slightly higher than typical diesels ($f_a$ = 0.378), the methanol content probably imparts fuel properties more analogous to a gasoline range fuel. Whereas, a 50/50 mixture of UCC liquid and petroleum naphtha would probably be more analogous to a diesel fuel. Table I shows a hydrocarbon class comparison of the UCC samples with typical petroleum-derived fuels as determined at Virginia Tech.

Finally, the lump char produced during previous testing with the MGU was also of good quality; and tests and analyses to-date indicate several potential end uses. Typical char produced during MGU testing had a sulfur content of ~1%, ash content of 10-12%, and volatile matter content of 10-15%. Based on these compositions, current indications are that the char can be used directly or in a blend with coal in existing coal-fired industrial or utility boilers. The char consisted of lumps ranging in size from 1-4 inches in diameter. This size consistency along with the excellent strength characteristics of the char indicate that the char has the potential to be a coke substitute or coke blending stock. Because of the high carbon content of the char (85-90%), the char, after ash removal, could be used as a carbon feedstock for producing graphite, carbon electrodes, etc. In addition, briquetting tests have been conducted with

the char by the Samchully Co,. Ltd, in Korea. Results indicate that the briquettes made with UCC char closely resemble, in physical characteristics and combustion properties, the home-heating briquettes normally made by Samchully Co., using anthracite coal.

TABLE I. Hydrocarbon Class Comparison of Gasoline, Diesel and Coal Liquids

| | Alkanes | Monocyclic Aromatics | Dicyclic Aromatics | Tricyclic Aromatics | Methanol | Aromaticity ($f_a$) |
|---|---|---|---|---|---|---|
| Gasoline (Unleaded) | 0.086* | 0.140 | 0.010 | 0 | 0 | 0.096 |
| Diesel #10 Hudson DF2 U.S. Army | 0.550 | 0.245 | 0.159 | 0.046 | 0 | 0.285 |
| 1:1:1 Mix. of (Methanol +Naphtha+ <600°F B.P. Liquid) | 0.320 | 0.220 | 0.110 | 0.020 | 0.33 | 0.378 |
| 1:1: Mix. of (Diesel Fuel+ Kiln Gas Coal Liquid) | 0.270 | 0.147 | 0.430 | 0.154 | 0 | 0.588 |

Note: Military Aromaticity Specification ($f_a$) for JP-5 Fuel is 0.25, No specification for diesel fuels.

*Also contains 4% Alkanes.

5. Project Description

Although the results from previous work, overall speaking, are encouraging and have shown us some promising areas with great commercial/economic potential, the existing MGU facility has been found to suffer from a few major shortcomings, which prevents it from operating under optimum conditions: (A) The large, fixed-bed reactor tubes cause too solw a heating rate and low liquid yield; (B) The constant plugging problem in the coal feeding system; (C) The inefficient, in-direct condensing system; and (D) The serious leaking problem.

In light of these problems, the goals of the current project have been set to: (A) Modify existing MGU facility to eliminate or alleviate the problems mentioned above, (B) Conduct more in-depth parametric tests with a view to optimize the MGU operation, (C) Characterize the co-products and identify potential end uses, (D) Generate sufficient co-products to test char and

char/coal blends as an industrial boiler/foundry fuel and to facilitate other DOE sponsored programs for characterization and evaluation of the condensible hydrocarbons.

6. Results/Accomplishments

The following has been accomplished during the initial phase of the current project:

(i) Applied Science & Technology Company has been selected, through competitive bidding, as the design and engineering subcontractor to help carry out the task of MGU modification.

(ii) Most design changes required to facilitate the MGU modification have been figured out during technical meetings. To address the four major problem areas mentioned above, the following are the tentative solutions recommended: (A) The present eight inch diameter reactor tubes cause extremely slow heating rate (only ~ 5°F/min) in the center of the coal bed. To increase the heating rate and thus hopefully improve the liquid yield, new reactor tubes with a smaller diameter will be installed. However, since it has been said that liquid quality generally decreases with increasing heating rate, a compromise between liquid yield and liquid quality seems in order. To determine the optimum reactor tube diameter, preliminary tests will be conducted in the existing MGU using four different reactor tubes with diameters of 8, 6, 5, and 4 inches respectively. (B) To fix the plugging problem in the coal feeding system, the four existing volumetric hoppers and associated feed chutes will be removed. Four new hoppers will be installed on the third floor directly next to the reactor tube top assembly. This will eliminate the plugging of coal feed chutes and incomplete feeding of coal into the reactor tubes. In addition, a valve will be installed just below the coal feed entrance to the reactor tubes. This will separate the coal feed system from the reactor tubes and prevent condensible tars from accumulating in the coal feed system. (C) To improve the condensing system efficiency, the existing in-direct condensing system will be replaced with a two-stage, direct-quenching liquid recovery system, which is essentially comprised of a venturi scrubber followed by a tray tower. (D) To fix the leaking problems, we need to revise the reactor tube support system. Presently, the reactor tubes are supported (fixed) at the top of the furnace and are free at the bottom to allow for thermal expansion. A satisfactory seal between the char chamber and furnace was never achieved. With the slight pressure condition present at the beginning of the test run, coal gas tended to escape into the furnace chamber and was lost. With the slight vacuum condition present during the middle and end of a test run, furnace gases as well as air from the char chamber were pulled into the reactor tubes causing oxidation and other undesirable reactions, which cut down the liquid yield. The leaking problem between the furnace/char chamber and reactor tube was serious since the bottom reactor gate was not designed to form a gas-tight seal. To prevent this type of leaking from recurring, the reactor tube support system will be changed to allow the reactor tubes to float at the top (for thermal expansion) and be fastened at the bottom to the furnace floor. The exact mechanism for fastening the reactor tubes

is still to be determined, pending recommendations from the reactor tube manufacturer and design subcontractor. Preliminary design flowsheet for MGU modification is shown in Figure 3.

(iii) The test plan for carrying out the parametric testing for the modified MGU has been completed and submitted for DOE's review and approval.

(iv) The four reactor tubes with different diameters, ordered for testing the heating rate effect, have been received and installed. Hopper relocation also has been implemented. It is expected that the heating rate/reactor diameter testing will be conducted soon.

(v) A char burning test in a TAS industrial boiler system, using char produced from previous test runs has just been completed successfully, with the results to be reported shortly.

7. Future Work

For the immediate future, our task at hand is, of course, to press on with the work cut out for us in the current project scope of work, as mentioned above. However, since our ultimate goal is the commercialization of the technology, we must start also to search for the development of a truly advanced, continuous mild gasification process to take the economic advantage a continuous process usually has over a batch process. Furthermore, since it has been well received (10, 15) that mild gasification liquid could be an excellent precursor for the highly valuable high density fuel, we also need to launch the R&D effort, without undue delay, for the production of high density fuel so that the overall economy of a commercial mild gasification plant can be further enhanced.

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(2) Chemistry of Coal Utilization, Supplementary Volume, H. H. Lowry (ed.), John Wiley and Sons, New York, 1963.

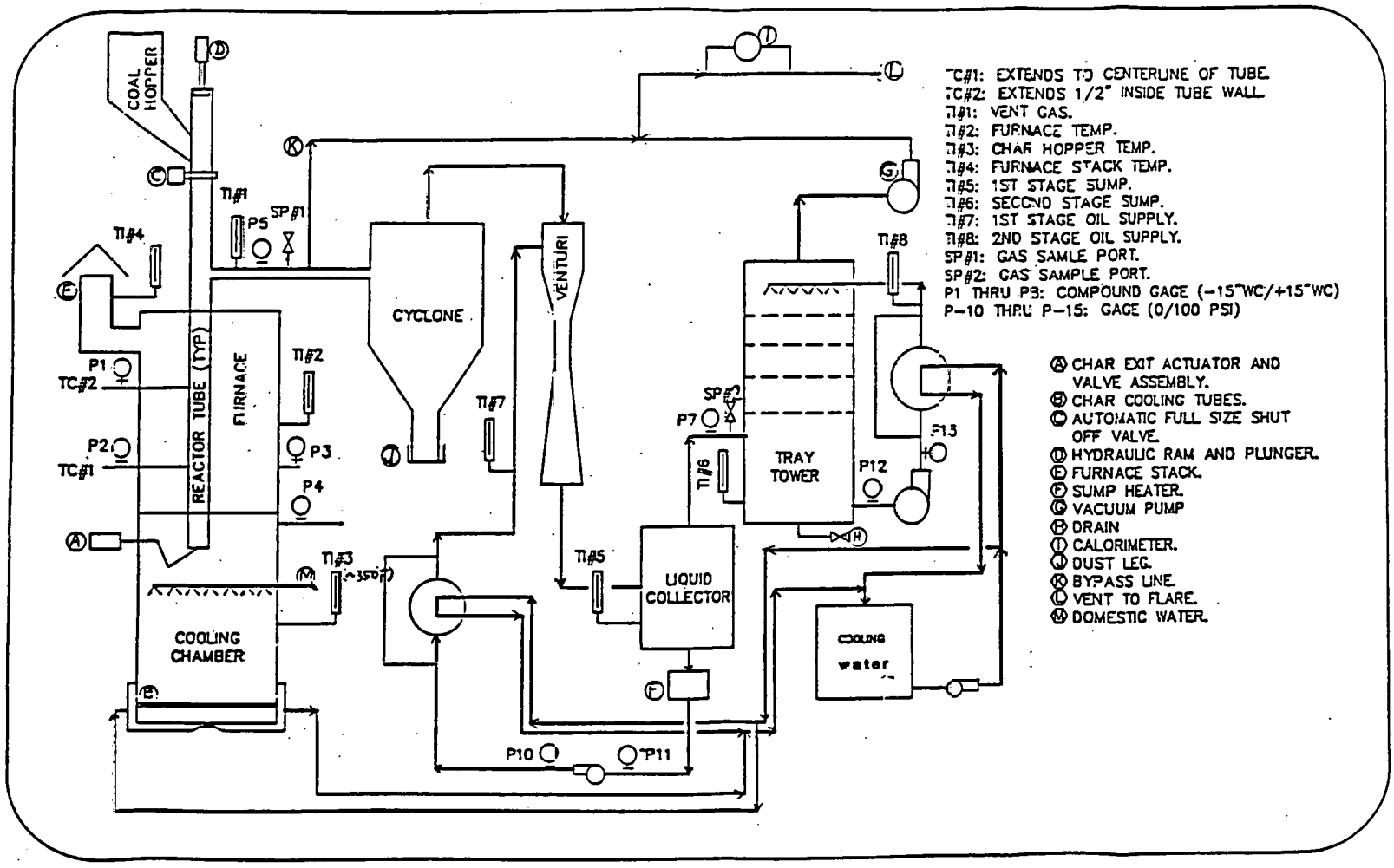
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Figure 3: Preliminary Design Flowsheet for MGU Modification



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## STEAM CONDITIONING OF COAL FOR SYNFUELS PRODUCTION

1. CONTRACT NUMBER: DE-AC21-87MC23288

CONTRACTOR: The City College CUNY
140 Street and Convent Avenue
New York, New York 10031
(212) 690-8136

CONTRACTOR PROGRAM MANAGER: Professor Robert A. Graff

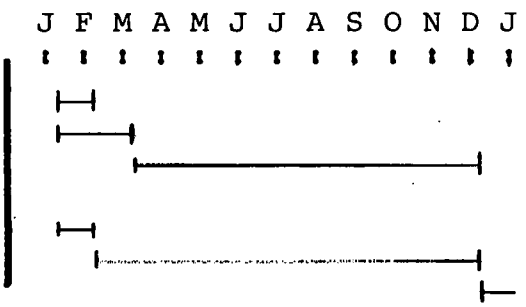
PRINCIPAL INVESTIGATOR: Professor Robert A. Graff
Coauthors: Professor Peizheng Zhou
Dr. Susan D. Brandes

METC PROJECT MANAGER: Dr. Wen-Shou Liou

PERIOD OF PERFORMANCE: January 9,1987 to August 8, 1988

2. SCHEDULE/MILESTONES:

1987 Program Schedule




3. OBJECTIVES:

The objective of this program is to examine the conditioning of coal in steam as a means for improving yield and quality of condensable hydrocarbon product in mild gasification processes. The specific objectives are to determine how product yields depend on processing conditions for both the steam conditioning step and the mild gasification step, to characterize the condensable product, and to investigate processes occurring during steam conditioning.

4. BACKGROUND STATEMENT:

Previous work has established the existence of the steam conditioning effect. Illinois No. 6 coal conditioned in 50 atm. steam at 320 to 360°C gives substantially increased yields of condensables in mild gasification and in extraction with pyridine at room temperature. Conditioning alters the coal structure in such a way as to change the

course of subsequent mild gasification reactions. However, the nature and full implications of steam conditioning remain to be determined. Neither the quality of condensable product nor optimum process conditions have yet been established.

5. PROJECT DESCRIPTION

Steam conditioning of coal and its subsequent mild gasification will be studied in bench scale equipment. Three coals will be tested in these studies: Illinois No. 6, Kentucky bituminous (Wellman blend), and lignite (Mississippi).

Initially, the effect of process conditions on product yields will be examined. In steam conditioning, pressure will be varied from one to 50 atmospheres and temperature from 300 to 400°C. Effectiveness will be evaluated by extraction of conditioned coal with pyridine at room temperature. This will be followed by a study of the effect of process conditions on yields from conditioned coal in the mild gasification step. In these tests, the semicontinuous reactor, modified to accommodate steam, will be used.

For the preparation of larger quantities of condensable product for testing and characterization, a continuous mild gasification test facility will be constructed. This will be comprised of a fluid bed reactor for the rapid heating in steam of 2.5 lbs. of coal per hour.

A variety of analytical procedures will be used to characterize conditioned coal in addition to condensables and char. This information will be interpreted in terms of physical and chemical processes occurring in coal during steam conditioning. These results will be used to project conditions for the optimum production of hydrocarbon product.

6. RESULTS/ACCOMPLISHMENTS

The following has been accomplished during the past year:

- The semicontinuous reactor has been modified for operation with steam.

- It has been established that the yield of condensables obtainable from the mild gasification in atmospheric pressure steam is increased 19% by steam conditioning.

- By means of solvent swelling and O-methylation studies, it has been established that steam conditioning increases the degree of hydrogen bond cross-linking and doubles the

number of hydroxyl groups in coal.

## REACTOR MODIFICATIONS FOR OPERATION WITH STEAM

### FEED TUBE INSULATION

In order to avoid steam condensation in the reactor, the outside surface of the feed tube must be above the steam condensation point (266°C at 750 psia, 110°C at 20 psia) while the internal feed tube is water-cooled to prevent agglomeration of the coal. Two methods of insulation were considered: a machinable ceramic insulation and a gas insulation jacket.

A problem with machinable ceramic is its relatively high thermal conductivity. Corning machinable glass ceramic, for example, has a thermal conductivity of $4 \times 10^{-3}$ cal./sec. cm. °C (at 25°C). To achieve a surface temperature of 300°C requires a minimum thickness of 6 mm. The reactor now in use is too small (1-inch i.d.) to accommodate this thickness of insulation.

Gases, on the other hand, have very low thermal conductivities. Nitrogen or air has a thermal conductivity of $6.2 \times 10^{-5}$ cal./sec. cm.°C (300°C). A 1.6 mm gas gap would provide a surface temperature of about 380°C under the above conditions.

A gas-insulated feed tube with a closed annulus (Figure 1) was designed. A possible problem with this design is that the temperature at the tip of the feed tube may either be too high (causing the coal to stick) or too low (causing steam condensation). If either occurs, the jacket could be replaced with one having an open end and supplied with a continuous flow of inert gas. This would eliminate the high conductivity bridge across the feeder tip while at the same time keeping the hot side clear of coal.

A double-jacketed feed tube with closed annulus was fabricated and installed. Preliminary tests were then conducted to check that condensation of steam would not occur on the feed tube and that the feed tube would not become blocked by coal sticking to its tip. In these tests a stable reaction temperature up to 760°C was achieved at a steam flow rate of 7 slm indicating an absence of condensation. No interruption of coal feeding occurred.

### PRODUCT COLLECTION SYSTEM

A product collection system for atmospheric pressure steam operation was designed and installed (Figure 2). It is comprised of an air cooled stainless steel tube (0.5 inch

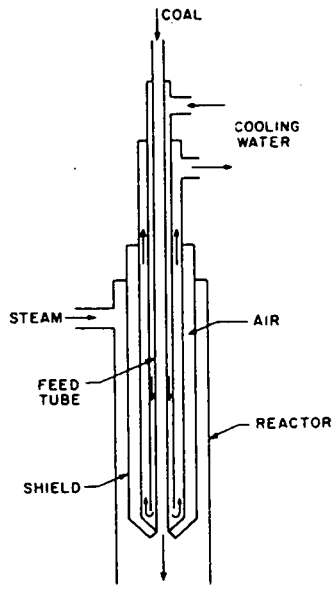



Figure 1. Gas Insulated Feed Tube.

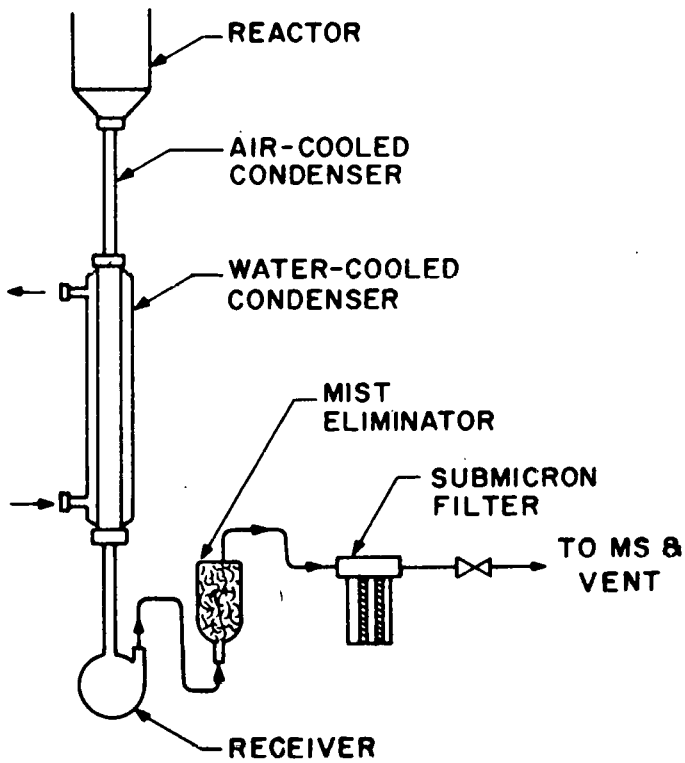



Figure 2. Collection System for Steam Operation.

o.d. X 10 inches long), a water cooled glass condenser, a glass receiver, a mist eliminator filled with quartz wool, and a submicron filter. Steam and condensable product are collected in these components. Noncondensable gases are analyzed using an on-line mass spectrometer. Condensable products are recovered after a run in two steps. The collection system is washed with pyridine and the solvent evaporated. Products in the water phase are recovered by evaporation of the water. The method was checked by extraction with methylchloride and excellent agreement was obtained.

MILD STEAM GASIFICATION

Raw and steam conditioned Illinois No. 6 coal (- 200 mesh) was mild gasified in steam at 20 psia, nominally atmospheric pressure. The quality of each sample was verified by pyridine extraction. These results are compared with yields previously obtained from mild gasification in inert gas (Graff, Zhou, and Brandes, 1986, Section 3.3.2), dashed lines in Figure 3. Since silica gel adsorbers can not be used with steam (product would be masked by water adsorption), the amount of product collected by adsorbers in helium mild gasification has been excluded. Total volatiles yields are higher in steam below about 600°C. The curve for condensables yield is shifted to lower temperatures by 100°C (the maximum is now at 550°C) and the maximum yield for raw coal is 31 wt %, 3% higher than in helium.

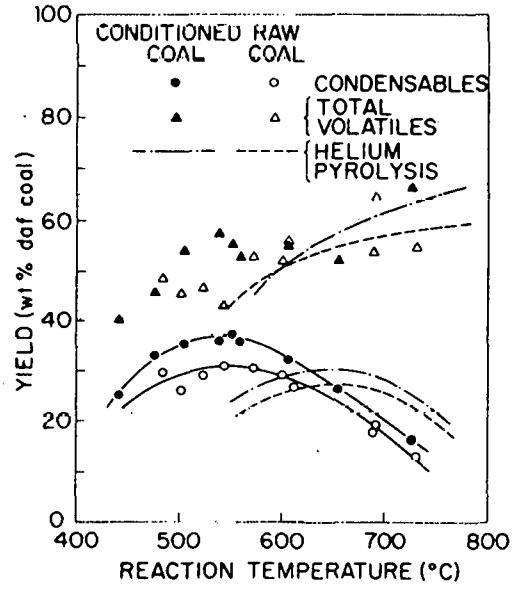



Figure 3. Mild Gasification of Illinois No. 6 Coal in Steam.

Condensable yield is increased 19% by steam conditioning. This raises the maximum condensable yield to 37 wt %, an improvement of 23% over that for an inert gas (when the amount collected in the adsorbers is excluded).

## CHARACTERIZATION OF CONDITIONED COAL

### SOLVENT SWELLING

A volumetric swelling technique, developed by Liotta (1983), was applied to steam and helium conditioned samples to gain some insight into the structure of coal modified by steam conditioning. The method has been extensively used by Larsen (1983) to obtain a direct indication of the degree of cross-linking, especially hydrogen bond cross-linking, in coal.

Swelling experiments were carried out as described in Green, et al. (1984). Samples of approximately 1g of coal were measured into 10mm X 80mm centrifuge tubes and covered with neoprene stoppers. The samples were centrifuged at 1700 rpm for approximately 10 minutes to settle the dry coal. The height of the sample was then measured by use of an external rule. Solvents were added to the tube and the tubes were capped and shaken until there was complete homogeneity. The tubes were left to stand 18 hours and then were centrifuged again until a constant height of the solid material was attained. In the case of pyridine, because of the dark color of the solution, the tube was turned upside down in order to read the height of the solids. Experiments were done under $N_2$ in a glove bag unless the sample was to be deliberately exposed to air, then no precautions were taken in handling the sample in any step of the above procedure.

Values of swelling ratios for raw and conditioned coals are given in Table 1. The measured increase in volume depends on the amount of material present in the solid phase. If during solvent swelling some of the solid is lost by extraction, the final volume is that of a reduced amount of material. An approximate correction for this loss can be made by dividing the swelling ratio by the fraction of starting material unextracted. This correction has been made to the values in Table 1 using average values obtained in room temperature extraction of the same samples (Graff and Brandes, 1987). By accounting for the amount of material in the solvent the swelling values of the solid phase are made comparable from one sample to the other.

In pyridine and in water the steam conditioned coal swells more than the raw coal or the helium conditioned coal by a considerable amount. In benzene the raw coal swells little more than helium or steam conditioned coals. Pyridine breaks

hydrogen bonds, benzene does not. The difference between the degree of swelling in pyridine and in benzene is a measure of the amount of hydrogen bond cross-linking. The smaller the difference the fewer the number of hydrogen bond cross-links. In Table 2 the difference values are listed. The amount of hydrogen bond association is high for steam conditioned coal protected under nitrogen. The helium conditioned sample shows less hydrogen bonding than raw coal.

Table 1. Swelling Ratios for Raw and Conditioned* Illinois No.6 Coal

| | Raw | | Steam Conditioned | | | Helium Conditioned | | |
|---|---|---|---|---|---|---|---|---|
| | Air | Extracted | $N_2$ | Air | Extracted | $N_2$ | Air | Extracted |
| Solvent | | | | | | | | |
| Pyridine+ | 2.80 | 1.95 | 3.01 | 2.46 | 1.88 | 2.24 | 2.24 | 1.68 |
| Benzene | 1.13 | 1.35 | 1.06 | 1.00 | 1.12 | 1.00 | 1.06 | 1.24 |
| Water | 0.98 | 1.21 | 1.83 | 1.84 | 0.98 | 1.56 | 1.41 | 1.23 |

*Conditionings in steam and helium for 15 minutes at 50 atmospheres
+Corrected for extraction losses

Table 2. Difference in Swelling Ratio (Q) of Pyridine and Benzene Swollen Samples

| | $Q_{pyr}-Q_{benz}$ |
|---|---|
| Raw | |
| In Air | 1.67 |
| Extracted | 0.60 |
| Steam Conditioned | |
| Under $N_2$ | 1.95 |
| In Air | 1.46 |
| Extracted | 0.76 |
| Helium Conditioned | |
| Under $N_2$ | 1.24 |
| In Air | 1.18 |
| Extracted | 0.44 |

Extraction in pyridine destroys essentially all of the coal's hydrogen-bond cross-links so that subsequent swelling experiments reveal the backbone structure of the coal. It is apparent from these data that there is an increase of the degree of hydrogen bonding in the conditioned coal as compared to the raw and helium conditioned samples even in the backbone of the coal after room temperature extraction. Helium conditioned coal, again, shows the least amount of hydrogen bond association.

When steam conditioned coal is exposed to air and then swelled in pyridine the swelling ratio is decreased to below that for raw coal. Exposure of helium conditioned coal to

air has no effect on the swelling ratio. The decrease in swelling indicates an increase of cross-links of any kind. For the air exposed samples the formation of oxygen cross-links is a possibility.

To wet steam conditioned coal with distilled water, 0.05% by weight Xanthum gum, a polymeric thickening agent was added. When swelling experiments were conducted in water, the increase of swelling for the conditioned sample over the raw coal was startling (Table 1). There is a twofold increase in the swelling value of the steam conditioned coal over the raw coal.

Swelling data show that it is not a reduction of hydrogen bonding in steam conditioned coal that is responsible for the steam conditioned coal's behavior. On the contrary there is an increase in hydrogen bonding in steam conditioned coal. Because of the ability of water and water miscible solvents to swell the coal and the inability of water insoluble solvent to swell the coal the following conclusions have been drawn. The steam conditioned coal is not of the same structural makeup as the raw coal, nor as the helium conditioned coal. One may postulate two different structures for the modified coal. One interpretation of the data which can be made does not include any chemical interaction of the water and the coal. Residual water not removed in the drying step of the conditioning process acts to hold open the coal structure. The water is miscible in pyridine and water and thus the coal swells. A possible alternative structure consists of newly formed phenolic groups created in the high pressure steam conditioning. The phenols may form hydrogen bonds to each other and to the coal structure. These sites readily accept the water or water miscible solvent and cause the coal to swell more than the native structure.

O-METHYLATION

O-methylation of the conditioned coal was performed following procedures described by Liotta, et al.(1981). Typically, one gram of coal was weighed into a 250 ml round bottom flask immersed in an ice bath; 2.9 mmoles of tetra-n-propylammoniumhydroxide (TnPAH) were added. This was in slight excess of the 2.5 mmoles of acidic sites that were found, by titration, to be in raw coal. For conditioned coal the amount of TnPAH added was approximately 2.5 times this amount. Freshly distilled tetrahydrofuran (50-60 ml) was added while the contents were stirred with a teflon covered magnetic stirring bar. Labeled methyl iodide ($C^{13}H_3I$),in 20% excess of the amount of TnPAH that was used, was added. Stirring was continued for 72 hours. The workup entailed removing the THF on a rotovaporizer and washing the product

with 250 ml of a hot methanol and water solution (1:1 by volume). The contents of the flask were then vacuum filtered on a 80 micron filter and washed with four liters of hot water. The coal was dried in a stream of nitrogen, transferred to a soxhlet extractor, and washed with distilled water for five days. The coal was then dried in a stream of nitrogen and in a vacuum oven at 90°C for 4 hours. Stable carbon isotope analyses were performed on these samples by Coastal Science Laboratories of Austin Texas using combustion techniques.

The values for enrichment in C-13 relative to raw O-alkylated Illinois No. 6 coal are given in Table 3 for helium conditioned coal, O-alkylated, and steam conditioned coal, O-alkylated. It is readily apparent that the steam conditioned coal after alkylation with the labeled methyl iodide is almost doubly enriched in C-13.

Table 3. Relative Ratio of C-13/C-12 In O-Alkylated Coals

| Sample | Ratio |
|---|---|
| O-methylated Raw Coal | 1.0 |
| O-methylated Steam Conditioned Coal | 1.7 |
| O-methylated Helium Conditioned Coal | 0.8 |

The increased hydrogen bonding exhibited in the conditioned coal by the swelling experiments and the presence of a shift in the hydroxyl region of the infrared spectrum (Graff, Zhou, and Brandes, 1986, Section 4.2) strongly indicate the presence of more OH functionality. The O-alkylation procedure, first described by Liotta (1979) has proven to be an excellent quantitative way to measure the relative abundance of these groups. The use of a traceable alkylating agent, in our case C-13 labeled methyl iodide, allows for an accurate count of the number of reacted groups.

The incorporation of almost twice as many labeled C-13 groups in the steam conditioned coal as the raw coal and the helium conditioned coal substantiates the speculation that steam conditioned coal contains more OH groups.

CONCLUSIONS

From these findings it is clear that steam conditioned coal has a structure altered from the raw starting coal. There is an inclusion of OH functionality in the structure which accounts for the increased hydrogen bonding and the shift in the IR spectrum. A tentative hypothesis for the increase in the extraction yields as well as the mild gasification yields (both previously reported) is that these new hydroxyl

sites are formed during the steam conditioning at places in the original coal which were covalently bound. This leaves a partially depolymerized coal, cross-linked only by relatively weaker hydrogen bonds. These bonds are highly susceptible to water and water miscible solvents.

## 7. FUTURE WORK:

A test program is presently under way to examine the effect of pressure on steam conditioning. The treatability of a lower rank coal and a second bituminous coal will also be tested. The tests will be conducted over a range of temperatures since the required temperature may be different for different coals.

This will be followed by a program to evaluate the effect of mild gasification operating parameters on yield, especially that of the condensable hydrocarbon product. Reaction pressure and temperature will be varied, and runs will be conducted with the three coals conditioned as determined in the previous test program.

Construction of a fluid bed reactor for mild gasification in steam is now under way. This continuous unit will provide larger quantities of condensable product for evaluation and testing.

Further characterization of conditioned coal samples, together with results from the above tests, will provide a clearer understanding of the physical and chemical processes occurring during steam conditioning.

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INVESTIGATION OF REACTIONS OF HETEROATOMS DURING COAL GASIFICATION

1. CONTRACT NUMBER — DE-AC21-85MC22063

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Leon M. Stock (University of Chicago)

METC PROJECT MANAGER — Dr. H. L. Lai

PERIOD OF PERFORMANCE — October 1, 1985 to September 30, 1987

2. PROJECT SCHEDULE

| | 1985 | | | | | | | | | | | | 1986 | | | | | | | | | | | | 1987 | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | O | N | D | J | F | M | A | M | J | J | A | S | O | N | D | J | F | M | A | M | J | J | A | S | O | N | D | J | F | M | A | M | J | J | A | S | O |
| Task 1. Preparation of Modified Coal Samples | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | |
| Oxygen Derivatives | xxxxxxxxxxxxxxxxxxxxxxxxx | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | |
| Sulfur Derivatives | | | | | | | | | | | | | xxxxxxxxxxxxxxxxxxxxxxxxx | | | | | | | | | | | | | | | | | | | | | | | |
| Nitrogen Derivatives | | | | | | | | | | | | | xxxxxxxxxxxxxxxxxxxxxxxxxxxxxxxxxxxxxxxxx | | | | | | | | | | | | | | | | | | | | | | | |
| Task 2. Gasification Tests | | | | | | | | | | | | | xxxxxxxxxxxxxxxxxxxxxxxxxxxxxxxxxxxxxxxxx | | | | | | | | | | | | | | | | | | | | | | | |
| Final Report | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | xxxxxx | |

3. OBJECTIVE

The principal objective of this research program is to determine the key reaction pathways that lead to the formation of the oxygen-, sulfur-, and nitrogen-containing products formed during the gasification of subbituminous and bituminous coals. The program utilizes a new approach for the assessment of the nature of the product-forming reactions occurring during pyrolysis. It involves modifying the coals in a specific way by a designed synthesis. When appropriate, isotopic labels can also be introduced into the structure. This approach enables the relationship between the structure of the coal and the product to be accurately determined. Most important, the reaction chemistry of the selected structural element can be examined in the environment of real coal molecules.

The structural elements to be studied are sulfur heterocycles, thiols, basic and non-basic nitrogen compounds, carboxylic acid derivatives, phenols, ethers and other carbonyl derivatives. The coals to be modified and subsequently gasified are Illinois No. 6 and a lower rank, oxygen-rich subbituminous coal.

Although advances in the understanding of coal pyrolysis are generally valuable in that a greater knowledge base inevitably reduces the risk of miscalculation in plant or process design, the realization of the objectives of this research should have a forseeable influence on four specific problems in gasification technology:

- The determination of the slow, rate-limiting reactions involved in coal pyrolysis is required for the development of low-cost catalysts specifically designed to enhance product-forming reactions. Such catalysts would have enormous practical cost benefits in process energy requirements and reactor construction costs.

- Once the reaction chemistry is understood, it should be possible to adjust process conditions to maximize the yields of selected products. This may allow the coupling of gasification with organic chemical concern.

- The production of tars in current commercial technology is a major concern. Therefore, it is important that the routes through which they are formed be well understood. One intent of this proposed program is to determine the impact of heteroatoms on the formation of char, tar, and gases.

- Most importantly, the research should provide new basic information on the ways in which undesirable substances such as hydrogen sulfide, carbonyl sulfide, sulfur dioxide, ammonia, hydrogen cyanide, and the nitrogen oxides are formed in the gasifier. This information may provide new clues for practical technology to suppress the formation of these materials.

## 4. BACKGROUND STATEMENT

During recent years, the emphasis in coal gasification research has been on the development of kinetic information to describe the impact of process variables on conversion (Howard 1981; Gavalas 1982; ACS 1984). Excellent work has been done on the effects of temperature, pressure, heating rate, particle size, and coal type on the reaction rates and product distributions. However, while this information is essential for the definition of the gas composition and the optimum conditions for gasifier operation, it does not yield direct chemical evidence about the fundamental pathways that control the reaction velocity or about the actual molecules responsible for the formation of the principal gasification products. The failure to gain greater perspective on this aspect of gasification chemistry considerably restricts the opportunities for a significant advance in practical technology. This research program is concerned, therefore, with remedying this deficiency by the study of the basic reactions important in the product-forming stages of coal gasification. In particular, it will focus on the role of sulfur, nitrogen- and oxygen-containing functional groups found in coal on the gasification product yields.

The observations concerning the products obtained from the sulfur compounds in coal is a good illustration of the problems to be attacked. It has been reported that when Illinois No. 6 coal is pyrolyzed there is an immediate loss of sulfur dioxide at rather low temperature, that carbonyl sulfide is the predominant sulfur-containing product at intermediate temperature, and that carbon disulfide is formed at temperatures in excess of 1000°C (Chu, Fredin, Hauge, Margrave 1984). When the tar obtained in the original pyrolysis is heated in a separate experiment, the same sulfur-containing products are observed. Prior oxidation of the coal under mild conditions leads to an increase in the yields of sulfur dioxide and carbonyl sulfide at low pyrolysis temperatures and of carbon disulfide at high temperature. Prior work in our laboratories has revealed that about 0.24% (by weight) of the Illinois No. 6 coal is converted to carbonyl sulfide during pyrolysis at 650°C. Observations of this kind imply that these heteroatom-containing compounds are produced through quite different reaction pathways. Some of these reaction pathways may be radiocaloid in character, but others may be ionic or pericyclic processes. Many basic observations suggest that heteroatoms greatly accelerate ionic and pericyclic processes. Hence the formulation of all gasification reactions as free radical processes may be greatly misleading.

## 5. PROJECT DESCRIPTION

The modified coal samples will be prepared in the Department of Chemistry Laboratories at the University of Chicago. Two coals will be used: Illinois No. 6, and a lower rank oxygen-rich subbituminous coal. The work will focus on the Illinois No. 6 coal. The reason for its choice is that IGT/UOC has obtained an extensive amount of experience with it in their ongoing study of the reactions of alkyl and aryl groups in O- and C-alkylated modified coals. The choice of the subbituminous coal will be dictated by the results from the tests with the modified Illinois No. 6 samples. The goal of the experiments with this coal will be to obtain results which may confirm those observed with the Illinois No. 6 coal.

### SAMPLE CHARACTERIZATION

The modified coals will be characterized by elemental analyses, deuterium analyses, IR analyses, NMR analyses, and chemical conversions as necessary to verify the synthesis. This will be carried out by the employment of the latest GC-FTIR, high-resolution mass spectrometry and NMR techniques.

### GASIFICATION TESTS

Although the effects of reaction parameters, such as temperature and pressure, will be evaluated, the program is not meant to be a parametric investigation. The gasification tests will be carried out in a heated wire screen reactor system which is shown in Figure 1. Although several types of reactors are available at IGT, the wire screen reactor was selected because a broad range of experimental conditions (temperature: 350° to 1200°C; pressure: vacuum to 1500 psig; heating rates: 100° to 10,000°C/s; holding time at final temperature: 0 to 30 s) can be evaluated using gases of varying composition.

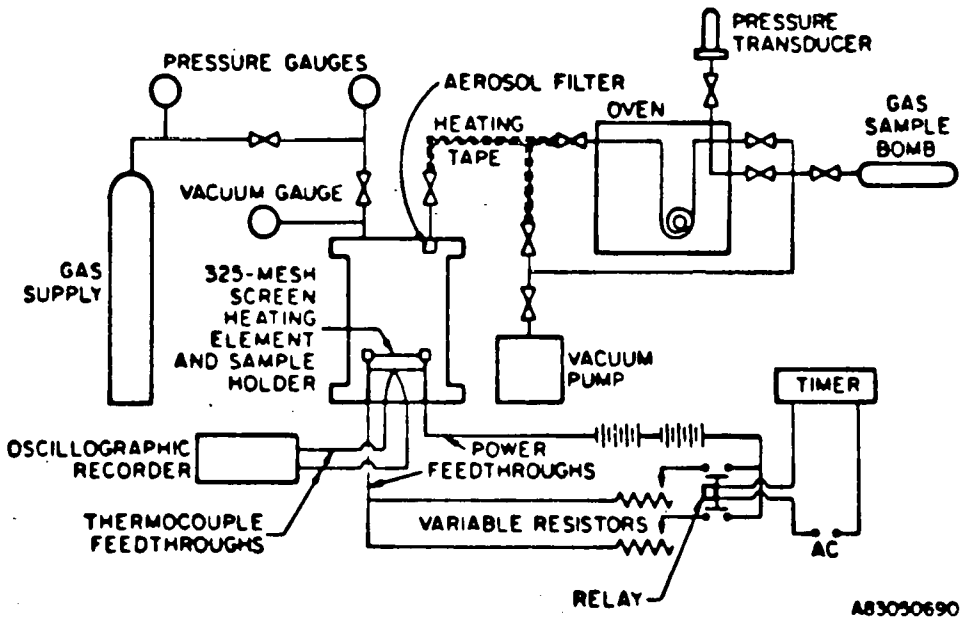



Figure 1. Wire Screen Reactor.

This equipment provides other particularly beneficial features for this investigation. The small particle sizes and loadings ensure that, insofar as possible, chemical kinetics rather than heat and mass transfer phenomena will be rate controlling. Secondary gas-phase reactions are effectively eliminated because the environment surrounding the screen and coal particles remains essentially at room temperature; hence, as the gaseous products form and diffuse away from the coal particle, they cool instantly. Although all modified coals to be prepared for this investigation are anticipated to be free-flowing, non-free-flowing samples can be pyrolyzed. In addition, the equipment is very cost-effective. A typical experiment consumes only 10 to 15 mg of material, thereby minimizing the consumption of expensive isotopically labeled coals.

For all experiments, char and tar yields are determined gravimetrically: char by weighing the screen, which serves as both a sample holder and heating element, before and after each run; and tar by weighing reactor internals and liners on which the heavier devolatilization products deposit. To ensure that the weight of the screen remains constant during each experiment, it is conditioned to at least 1000°C before each experiment. For quantitative gas analysis, the gaseous products will be collected by flushing several reactor volumes of helium through a Tenax packed column (3 inches x 0.25 inch) maintained at 77°K. The condensables are trapped while the helium is pumped away. The column is then heated to 200°C to transfer the products to a calibrated vessel for quantitative measurement. The gas is then sampled for subsequent analysis using a Finnegan Model 4510 GC-MS system.

While the equipment is capable of operating over a range of conditions, the following conditions will be used in the initial investigations:

- Temperatures: 700° to 850°C
- Pressure: 2 psig
- Environment: He
- Heat-Up Rate: 1000°C/s

Each sample will be gasified at a minimum of two temperatures. Experiments will be made at other conditions based on the results from these tests. The data to be obtained in each test will be: the yields of char, tar and gas; and a complete analysis of the gas produced, including isotopic distribution where labeled compounds are used.

In addition, char and tar analyses will be obtained for selected runs of interest. It is anticipated that the work on the tars will include analyses by FIMS, GC-FTIR and GC-MS. Should particular results with the $^{13}C$ labeled groups look interesting the char products may be analyzed by solid-state $^{13}C$-CP-MAS-NMR spectroscopy.

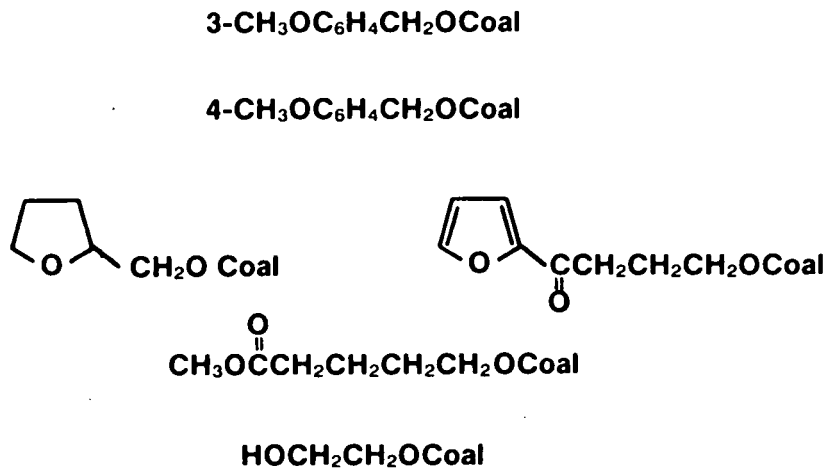
## 6. RESULTS/ACCOMPLISHMENTS

The modified Illinois No. 6 coal samples prepared by the addition of groups containing heteroatoms are shown in Figures 2 and 3. All of the samples were synthesized with Illinois No. 6 coal using the technique reported at the Sixth Annual Gasification Contractors Meeting. The oxygen derivatives prepared were 3-methyoxyphenyl, 4-methoxyphenyl, tetrahydrofuranylmethyl, furanylaceylpropyl, methyl pentanoate and hydroxymethyl. Two nitrogen derivatives were prepared, a difunctional thiomethylpyridine and a diethylamine. The sulfur derivatives prepared were designed to test the effects of the oxidation state of the sulfur within the compounds, the effect of the element bridging the sulfur group and the coal, and the effect of sulfur contained in ring compounds. The sulfur derivatives prepared were phenylsulfidemethyl, phenylsulfoxymethyl, phenylsulfonebenzyl, phenylsulfide ethyl, thiophenylmethoxy, benzothiophenylmethyl, dibenzothiophene, thiophenylbutyl and methylsulfone.

Two types of pyrolysis experiments were carried out with the samples; an in-situ high-resolution mass spec pyrolysis (HR-MS) and heated wire screen pyrolysis.

The HR-MS pyrolysis experiments were performed using the technique developed by Scott et al. These experiments are made at a relatively low heating rate (50°C/m) in contrast to the wire screen tests which were made at a heating rate of 1000°C/s, In addition, the final temperature achieved in some of the HR-MS experiments was 630°C which is considerably lower than the 700° to 850°C final temperatures achieved in the wire screen tests. Space limitations preclude the inclusion of the data tables supporting the discussion that follows; however, they can be found the January-March 1987 quarterly report for this project.

## OXYGEN DERIVATIVES PREPARED




## NITROGEN DERIVATIVES PREPARED

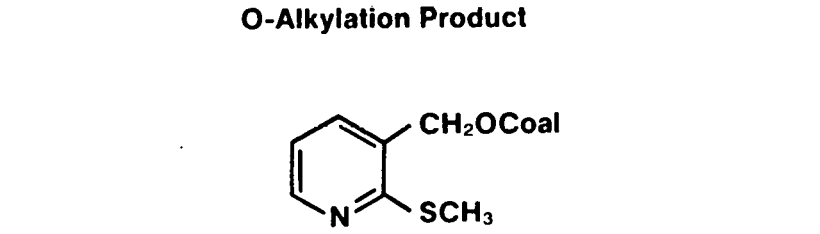



Figure 2. Illinois No. 6 Modified Coals Prepared by the Addition of Oxygen and Nitrogen Derivatives.

# ORGANOSULFUR COMPOUNDS PREPARED

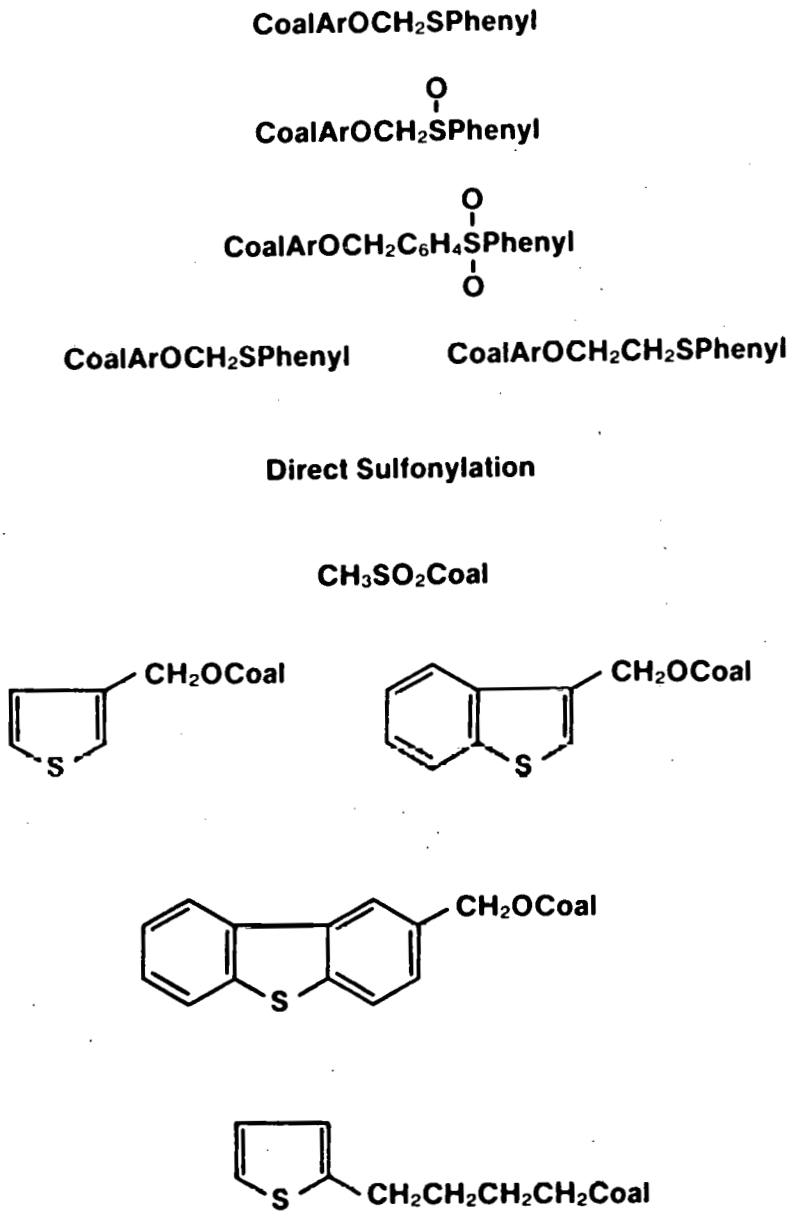



Figure 3. Illinois No. 6 Modified Coals Prepared by the Addition of Organosulfur Compounds.

The Illinois No. 6 coal samples modified by the methyl sulfonyl group produced the highest yield of carbonyl sulfide, in both the HR-MS pyrolysis and wire screen pyrolysis experiments. The greatest weight percent gas yield was produced when the O-2[(phenylsulfonyl)methyl]benzene sample was pyrolyzed in the wire screen reactor. All samples except the ones modified by the methylsulfonyl group produced extremely small amounts of carbonyl sulfide in both the HR-MS and wire screen pyrolysis experiments.

The HR-MS analysis of the sulfur group modified coal samples provided some very valuable and dramatic information concerning the fate of these groups during pyrolysis. All coal samples including the raw Illinois No. 6 coal produced methylthiophene. This observation takes on greater significance, when considered with the data obtained from the HR-MS analysis of the butylthiophene modified coal sample. In this case, all of the fragments found in significant abundance with the exception of three can be explained by homolytic cleavage, β-scission and hydrogen abstraction reactions that are probably initiated by C-O bond cleavage as an initiation point. This is in accord with the enthalpy of formation (65 Kcal/mole) for this reaction based on thermochemical kinetic calculations. The observation that is most noteworthy is the apparent conversion of the substituted thiophene into benzothiophene as indicated by the amount of benzothiophene produced. This can be an important factor in obtaining a better understanding of coal pyrolysis. Specifically, the products such as thiophene, benzothiophene, dibenzothiophene and various methylated derivatives of these molecules may have their origin, in part, in alkylated thiophenes.

This opens two questions that have to be addressed: First, does thiophene have its origin (in part) in open chain thioethers? Secondly, how does the cyclization take place? The broad data base being generated in this program will likely give information that can be used to answer these questions and explain other reaction phenomena being observed in the pyrolysis experiments with the coals modified by the addition of sulfur containing entities.

## 7. FUTURE WORK

The question of cyclization of the alkylated thiophene will be addressed by examining the behavior of thioethers. These groups are being prepared and will be used to modify Illinois No. 6 coal which will be subsequently pyrolyzed. On a broader scale work will continue with modified coals obtained by the addition of oxygen and nitrogen containing groups.

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## MEASUREMENT AND MODELING OF ADVANCED COAL CONVERSION PROCESSES

1. **CONTRACT NUMBER:** DE-AC21-86MC23075

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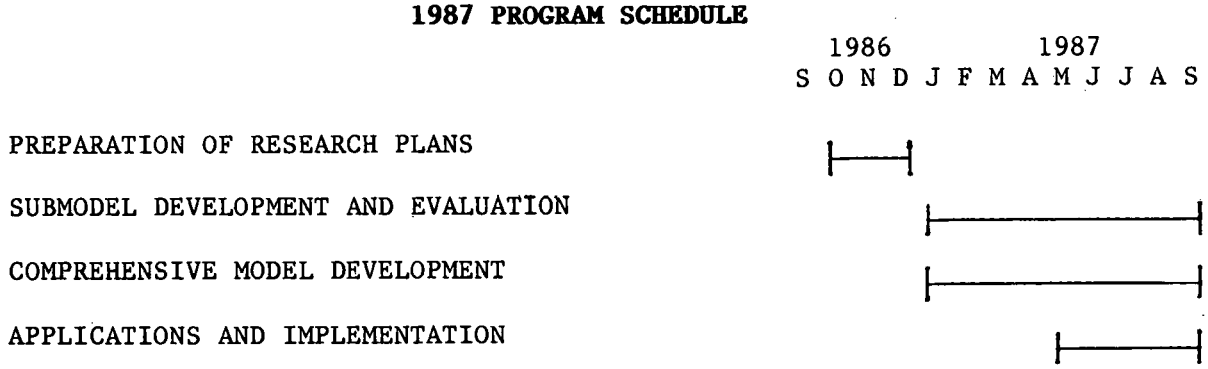
**PRINCIPAL INVESTIGATORS:**
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David G. Hamblen
D. Billy Yang
B. Scott Brewster (BYU)

**METC PROGRAM MANAGER:** Justin L. Beeson

**PERIOD OF PERFORMANCE:**
September 30, 1986 to
September 30, 1991

2. **SCHEDULE/MILESTONES:**

**1987 PROGRAM SCHEDULE**




3. **OBJECTIVES:**

The overall objective of this program is the development of computer-aided reactor engineering technology for the design, scale up, simulation, control and feedstock evaluation in advanced coal conversion devices. To accomplish this objective, the study will: establish the mechanisms and rates of basic steps in coal conversion processes, integrate and incorporate this information into comprehensive computer models for coal conversion processes and, evaluate these models and apply them to gasification, mild gasification and combustion in heat engines.

4. **BACKGROUND STATEMENT:**

The development of computer-aided reactor engineering technology, based on a systematic database and reactor simulation software, is important to

reduce the technical and economic risks inherent in utilizing coal, a feedstock whose variable and often unexpected behavior presents a significant challenge. Current computer-aided reactor engineering technology has shown significant potential, but there is a need to bring the technology to a higher level of generality, accuracy and acceptability. This program will merge significant advances made at Advanced Fuel Research, Inc. (AFR) in predicting coal conversion behavior, with technology being developed at Brigham Young University (BYU) in comprehensive computer codes for mechanistic modeling of entrained-bed gasification. Additional capabilities in predicting pollutant formation will be implemented and the technology will be expanded to fixed-bed reactors.

The foundation to describe coal-specific conversion behavior will be AFR's Functional Group (FG) and Devolatilization, Vaporization, and Crosslinking (DVC) models, developed under previous and on-going METC sponsored programs. These models have demonstrated the capability to describe the time dependent evolution of individual gas species, and the amount and characteristics of tar and char. The FG/DVC models will be integrated with BYU's comprehensive two-dimensional reactor model, PCGC-2, which is currently the most widely used reactor simulation for combustion or gasification. The program includes: i) validation of the submodels by comparison with laboratory data obtained in this program, ii) extensive validation of the modified comprehensive code by comparison of predicted results with data from bench-scale and process scale investigations of gasification, mild gasification and combustion of coal or coal-derived products in heat engines, and iii) development of well documented user friendly software applicable to a "workstation" environment.

## 5. PROJECT DESCRIPTION:

### ORGANIZATION

This program is a closely integrated, cooperative effort between AFR and BYU. The program consists of four tasks: 1) Preparation of Research Plans, 2) Submodel Development and Evaluation, 3) Comprehensive Model Development and Evaluation, and 4) Applications and Implementation. The program is outlined in Fig. 1. Task 1, the preparation of the research plan was completed during the first quarter of the program.

The objectives of Task 2 are to develop or adapt advanced physics and chemistry submodels for the reactions of coal in an entrained-bed and a fixed-bed reactor and to validate the submodels by comparison with laboratory scale experiments. The development of advanced submodels for the entrained-bed and fixed-bed reactor models will be organized into the following categories: a) Coal Chemistry (including coal pyrolysis chemistry, char formation, particle mass transfer, particle thermal properties, and particle physical behavior); b) Fundamental High-Pressure Reaction Rate Data; c) Secondary Reactions of Pyrolysis Products; d) Ash Physics and Chemistry; e) Large Coal Particle Effects; f) Large Char Particle Effects; g) $SO_x$-$NO_x$ Submodel Development; and h) $SO_x$ and $NO_x$ ModelEvaluation.

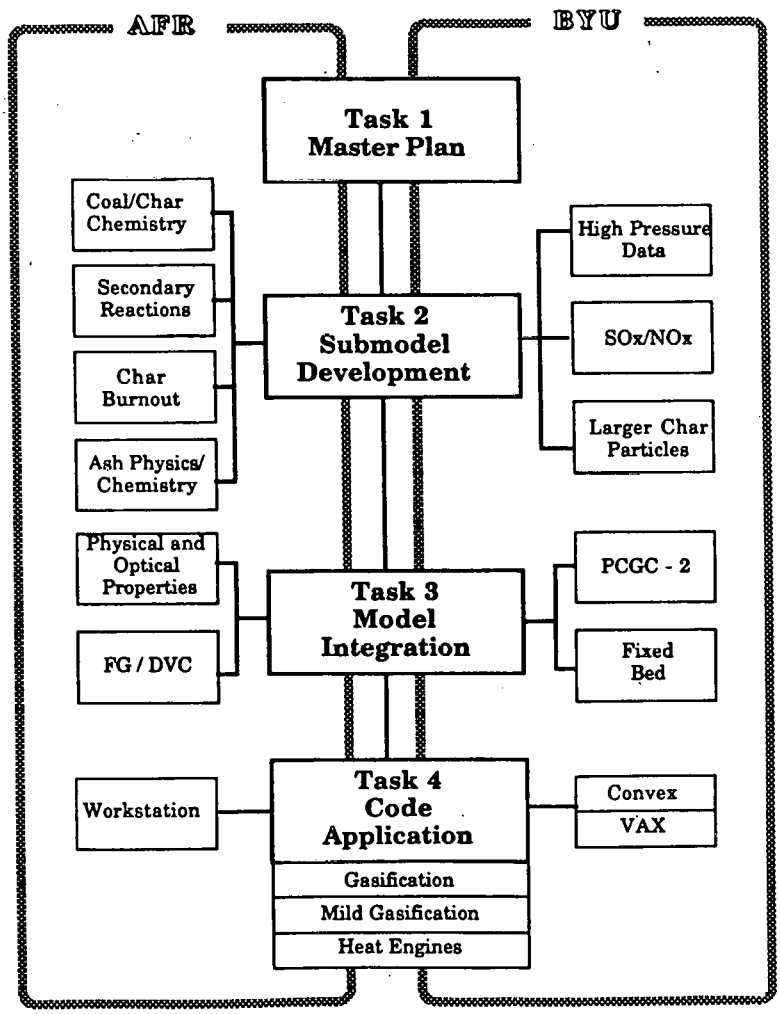



**Figure 1. Project Outline.**

The objective of Task 3 is to integrate advanced chemistry and physics submodels into a comprehensive two-dimensional model of entrained-flow reactors (PCGC-2) and to evaluate the model by comparing with data from well-documented experiments. Approaches for the comprehensive modeling of fixed-bed reactors will also be reviewed and evaluated and an initial framework for a comprehensive fixed-bed code will be employed after submission of a detailed test plan. This task will be performed in three subtasks. The first covering the full 60 months of the program will be devoted to the development of the entrained-bed code. The second subtask for fixed-bed reactors will be divided into two parts. The first part of 12 months will be devoted to reviewing the state-of-the-art in fixed-bed reactors. This will lead to the development of the research plan for fixed-bed reactors. After approval of the research plan, the code development would occupy the remaining 45 months of the program. The third subtask, to generalize the entrained-bed code to fuels other than dry pulverized coal, would be performed during the last 24 months of the program.

The objectives of Task 4 are to evaluate the integrated comprehensive codes for pulverized coal and fixed-bed reactors and to apply the codes to selected cases of interest to METC. This task will be accomplished in two subtasks, one for the entrained-bed lasting 45 months and one for the fixed-bed lasting 36 months. Each of these subtasks will consist of three components: 1) Simulation of demonstration cases on BYU computers; 2) Implementation on a work station at AFR; and 3) Simulation of demonstration cases on the workstation.

**INITIAL PROGRESS**

The discussion below highlights the progress which has been made in the following areas:

- Ignition and soot formation
- Particle optical properties
- Selection of an approach for incorporating the detailed AFR coal devolatilization model into PCGC-2.
- Review of existing fixed-bed models.

**Ignition and Soot Formation** - The study of ignition and soot formation is being performed in a Transparent Wall Reactor (TWR) using Fourier Transform Infrared (FT-IR) Emission and Transmission (E/T) spectroscopy (Best, et al., 1986; Solomon, et al., 1987, 1987a, 1987b, 1987c). For these experiments, the major advantage of the technique is its capability to determine separate temperatures and concentrations for individual gas species as well as for solid particles by employing different regions of the infrared spectrum.

The TWR facility consists of an electrically heated furnace and a heat exchanger. Gas is passed through the heat exchanger and exits the top of the furnace after passing a screen to smooth the flow. The hot gas stream, which is 10 cm in diameter, remains relatively hot and undisturbed for approximately 20 cm above the screen. Coal entrained in a cold carrier gas is injected through a co-axial 4 mm diameter tube. An octagonal glass enclosure shields the reacting stream from room air currents. The enclosure has a movable KBr window to allow access to the flame by the FT-IR spectrometer, a Nicolet 20SX FT-IR. For multi-phase reacting systems, measurements are made of the transmittance, $\tau_\nu$ , and the radiance, $R_\nu$. FT-IR measurements were made along the center of the flame at several positions above the coal injector for flames from several coals under identical conditions.

Radiance measurements are shown in Fig. 2. If the emittance, $\epsilon_\nu$ , is known, the temperature can be determined by comparing $R_\nu$ /NAL with a theoretical black-body, $R_\nu^b(T_p)$, at the particle temperature, $T_p$. Here, NAL is the intersected surface area of the particles. Figure 2a shows $R_\nu$ /NAL prior to ignition. A particle temperature (740 K) is determined from the region between 1200 and 1600 $cm^{-1}$ where for coal $\epsilon_\nu \approx 1$. Figure 2b shows $R_\nu$ /NAL in the region where a few particles have ignited. The temperature of the ignited particles (1900 K) is determined from the shape of the region above 4000 $cm^{-1}$, assuming a gray-body for char. It is

substantially higher than the unignited particles (1100 K). Figure 2c shows $R_\nu$ /NAL in the region where most of the particles are ignited. The shape of the spectrum is consistent with a temperature of 1950 K but the amplitude is only 0.31 of the black-body. This is lower than expected, assuming $\epsilon$ = 0.7 for char and will be investigated further. In Fig. 2d, the particle contributions to the radiance is very low and a particle temperature can not be accurately determined.

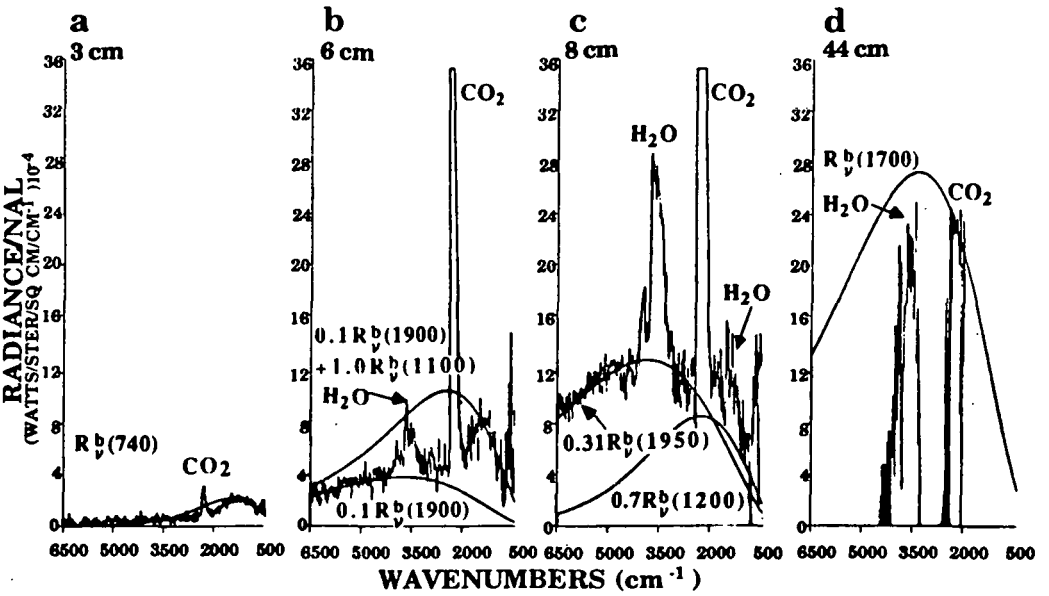



**Figure 2. Radiance Spectrum for Combustion of Zap North Dakota Lignite. Figure d is for Normalized Radiance in the $H_2O$ and $CO_2$ Regions Only.**

After the particle temperatures and attenuation contributions from particles have been determined, the $CO_2$ temperatures can be obtained from the normalized radiance. The $CO_2$ temperature of 1700 K is obtained by comparison to a theoretical black-body as shown in Fig. 2d. $CO_2$ temperatures in the flame region were as high as 2080 K.

A number of coals were run in the TWR. The ignition delay, or distance above the injection nozzle, was observed to vary from a few cm to over 30 cm. For example, a lignite ignites at 8 cm while a Pocahontas bituminous ignites at 23 cm. The ignition delay increased with increasing rank and decreasing volatile matter content. The average temperature of the coal particles prior to ignition varied from 800 to 900 K. To provide understanding of what controls the ignition delay, weight loss profiles were measured in a TGA under nitrogen and under air. There was a good correlation between the relative reactivity under nitrogen and the relative ignition distance in the TWR (i.e., the lower the temperature at which pyrolysis occurs, the smaller the ignition distance). The correlation with reactivity in air was not good. The results suggest that for the coals and conditions studied here, ignition is controlled primarily by combustion of the volatiles, not heterogeneous combustion of the coal.

The preliminary conclusions of this study have been summarized in a paper for the International Coal Combustion Symposium (Solomon, et al., 1987b).

**Optical Properties** - Knowing the spectral emittance of coal is important for three reasons: 1) The emissivity of the coal particle determines the radiative energy adsorbed by a coal particle during particle heating (the emissivity is the weighted average of the spectral emittance over the radiation spectrum of the reactor); 2) The emittance of char determines the radiation loss of the particle when it is hot and; 3) The spectral emittance needs to be known to determine particle temperatures by pyrometric techniques.

Direct measurements of coal optical properties are being made under METC Contract No. DE-AC21-85MC22050. To incorporate these measurements into a submodel, Mie theory calculations are being performed to determine how the optical properties vary with particle size and index of refraction $m = n + ik$. The imaginary part of the complex index of refraction, k, can be determined as a function of frequency from KBr pellet spectra as discussed by Solomon, et al., 1987, 1987d. For a lignite, k ranges from a value of 0.01 near 2000 $cm^{-1}$ to 0.1 in the region between 1200 and 1600 $cm^{-1}$. Taking a constant value of 1.6 for the real part of the index of refraction, n, we have used the Mie theory program in Bohren and Huffman, 1983 to calculate the emittance of particles of different size, and different k values (Fig. 3). For values of $k > 0.05$ the emissivity, $\epsilon_\nu$, will be above 0.9 for all particle sizes. For regions where $k \approx 0.01$, $\epsilon_\nu$ will vary with particle size.

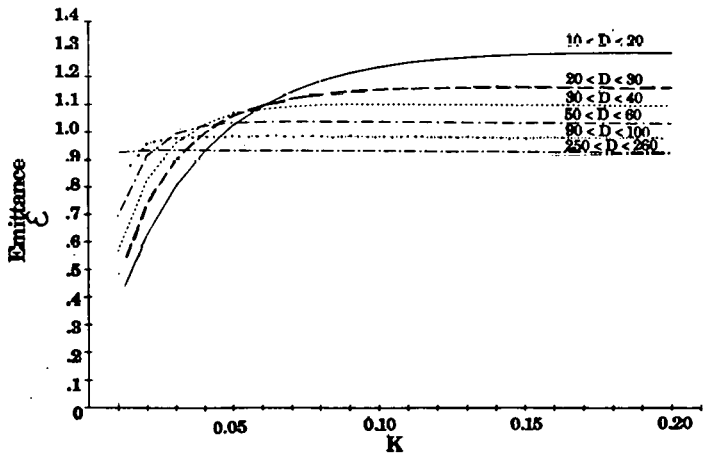



**Figure 3. Calculated Emittance as a Function of k, for Spheres of Various Diameters, with n = 1.6.**

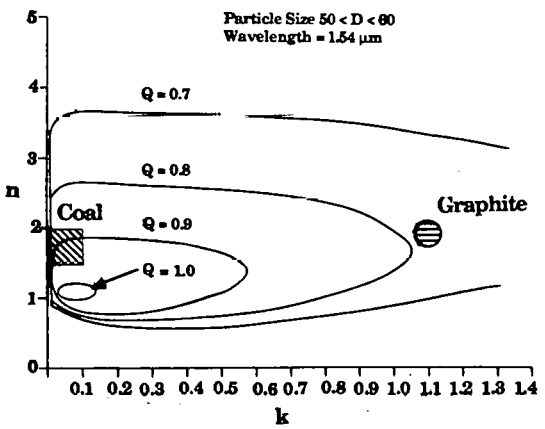



**Figure 4. Contour Plots of Constant Emittance Calculated by Mie Theory for Spheres of Various Values of n and k.**

There is a stage in pyrolysis beyond which $\epsilon_\nu$ in the 1200 to 1600 $cm^{-1}$ region starts to vary. This occurs when the coal starts to graphitize and both the real and imaginary parts of the complex index of refraction to increase. In Fig. 4 we display contour plots of emittance in the n-k plane for 55 $\mu$m diameter spheres. That part of the figure which contains the n

and k values appropriate to coals in the infrared region of the spectrum is shown shaded, on the left hand side of the figure. The region for graphite is shaded on the upper right hand side. During pyrolysis, the emittance in the 1200 to 1600 $cm^{-1}$ region (where $k \approx 0.1$) drops from a value greater than 1, towards the value for graphite. In other regions of the spectrum where $k \ll 0.1$, $\epsilon_\nu$ first increases and then decreases as k increases. Our experimental observations suggest that for residence time on the order of 1 sec, n and k increase significantly only above 1000°C, and it is above this temperature that $\epsilon_\nu$ is observed to decrease. For a highly graphitized char $\epsilon_\nu$ can be as low as 0.7.

**Incorporation of Detailed Devolatilization Model** – One of the major goals of this study is to incorporate the detailed AFR models for coal devolatilization into PCGC-2. The detailed model will extend the applicability of PCGC-2 to a wider range of coals, provide a means of accounting for variable volatiles composition, char reactivity, and heating value with burnout, more accurately predict particle properties, and allow for treatment of mild gasification. Variable volatiles composition has the potential of increasing the computational burden due to the effect of turbulent fluctuations on mean reaction rates. Composition is currently assumed to be constant for both devolatilization and oxidation. In this context, it has been shown that the influence of turbulence on chemistry can be important. The effect of variable composition has not yet been investigated. This study will investigate the relative importance of turbulence/chemistry interactions and variable volatiles composition and the extent to which each should be taken into account.

In order to better understand the effect of turbulence on chemistry, a series of calculations was initiated where fluctuations in the inlet gas mixture fraction and coal gas mixture fraction are ignored individually and simultaneously. Initial calculations have been completed for a fuel-lean (combustion) case. Ignoring fluctuations in only the inlet gas mixture fraction had little effect on the predicted values, as expected for identical composition of the inlet streams (both air) and a moderate difference in temperature. The effect of ignoring fluctuations in the coal gas mixture fraction was significant. As shown in Figure 5 for NO concentration, ignoring the fluctuations caused a significant reduction in the predicted NO levels. This effect is in direct contrast with Smoot et al. (1984), who reported that the fluctuations lowered the predicted NO levels. The discrepancy may be due to the fact that Smoot et al. ignored the fluctuations only in the calculation of pollutant species, whereas the results shown here ignored the fluctuations in the calculation of both major and pollutant species. Ignoring fluctuations also had an important effect on the temperature distribution in agreement with the results of Smith and Fletcher (1986). Also, particle conversion decreased by approximately 5 percent when the fluctuations were ignored. The investigation of turbulence effects is continuing with a fuel-rich, diffusion-flame case, where the primary and secondary gas streams are of different composition. Here, fluctuations in both mixture fractions are expected to be important.

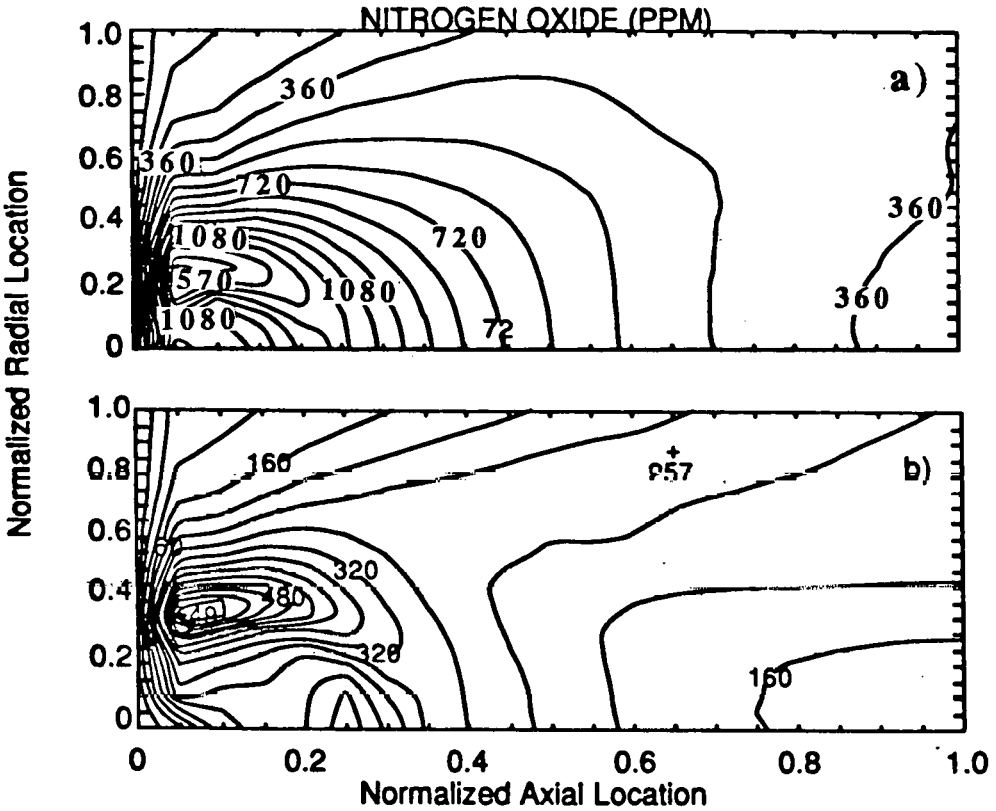



**Figure 5. Predicted NO Concentration: (a) Taking Turbulent Fluctuations in Coal Gas Mixture Fraction into Account and (b) Neglecting the Fluctuations.**

In addition to volatiles production rate, volatiles composition and heating value are required by the comprehensive code for each particle as a function of time as the particle reacts. The AFR model is capable of predicting all three, based on the functional group composition of the coal. Two approaches have been identified for integrating this model into PCGC-2. The first approach accounts for variable heating value but assumes constant elemental composition. This approach will not significantly increase the computational burden of the code. This approach has merit if the effect of heating value is the dominant effect. In the second approach, both heating value and composition are variable, significantly increasing the computational burden as explained above.

A brief investigation was conducted of several thermal effects on devolatilization in PCGC-2. These effects included coal emissivity, variable heat capacity, and volatiles heating value. Lowering the coal emissivity from 0.9 to 0.3 had little effect on the gas temperature or burnout, and code predictions seem quite insensitive to this parameter. To test the effect of variable coal heat capacity, the model of Merrick (1983) was programmed into the code. The effects of variable heat capacity were to decrease the heatup rate, thus delaying particle ignition, lowering the volatile yield, lowering the gas temperature, and decreasing particle burnout. The effects are significant, and the Merrick model is

recommended. Volatiles heating value is known to change due to changing volatiles composition, and the importance of this effect was tested by arbitrarily increasing the volatiles heating value. The effect was to increase the gas temperature, which increased the volatile yield from the coal, which increased the gas temperature even further. It is not yet known whether the heating value effect of the coal volatiles is dominant over the compositional effect. A paper summarizing these results has been prepared (Brewster, et al., 1987).

**Fixed-Bed Model Review** - Existing fixed-bed models are being reviewed to identify the best existing fixed-bed model as a starting point for the advanced model in this project. It is visualized that the fixed-bed model will be 2-dimensional, have separate gas and solids temperatures, account for radiation effects, predict pollutant concentrations, and be applicable to a wide range of conditions, including mild gasification. To date, available 2-dimensional models have been identified, including the University of Delaware model, the Washington University model, and the Lawrence Livermore Laboratories model. Computer codes for the most promising models will be obtained when available and installed at BYU for further evaluation. A plan will then be proposed for developing an advanced model during the remaining four years of the project.

## 6. RESULTS AND ACCOMPLISHMENTS:

- Completed project plans, organization and staffing.
- Obtained initial results for: ignition and soot formation; and particle optical properties.
- Identified alternative techniques for incorporating detailed submodels into PCGC-2 and installed PCGC-2 on workstation at AFR.
- Initiated work on fixed-bed modeling and identified potential model improvements.
- An investigation of turbulence/chemistry interaction effects in PCGC-2 has been initiated.
- A paper on the role of devolatilization in comprehensive coal combustion models has been prepared and submitted for presentation at the ACS Fuel Chemistry Division symposium in New Orleans next Fall (Brewster, et al., 1987).
- Parametric calculations were performed with PCGC-2 to investigate the effect of devolatilization rate, volatiles heating value, coal heat capacity, and coal emissivity.
- A literature review of existing fixed-bed models has been initiated.

## 7. FUTURE WORK:

During the next year, work will continue on developing and testing submodels for the important process in gasification. This includes: devolatilization, swelling, char reactivity, ignition, soot formation, physical properties and optical properties. Data will be taken for mineral and pollution submodels. The submodels will be integrated into PCGC-2. Special attention will be given to the importance of chemistry/turbulence interactions and the importance of variable volatiles composition and heating value. An additional progress variable will be added to the code to track coal offgas. A plan will be proposed for developing an advanced fixed-bed model. Computer codes and documentation for the selected fixed-bed models will be obtained and evaluated at BYU. The high pressure reactor will be designed and constructed. Ongoing work under independent funding on the modification of PCGC-2 to include sorbent injection will be adapted for this program. An existing cold-flow facility will be modified to simulate sorbent injection into a gasifier and obtain fluid mechanics data for model validation. Work will begin on extending an existing pollutant submodel to include sulfur reactions. The comprehensive code will be installed and tested on a workstation.

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APPLICATIONS OF ORGANO-CALCIUM CHEMISTRY TO CONTROL OF CONTAMINANT AROMATIC HYDROCARBONS IN ADVANCED COAL GASIFICATION PROCESSES

1. DOE CONTRACT NUMBER: DE-RA21-84MC-21074

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Tel.: (617) 253-3433

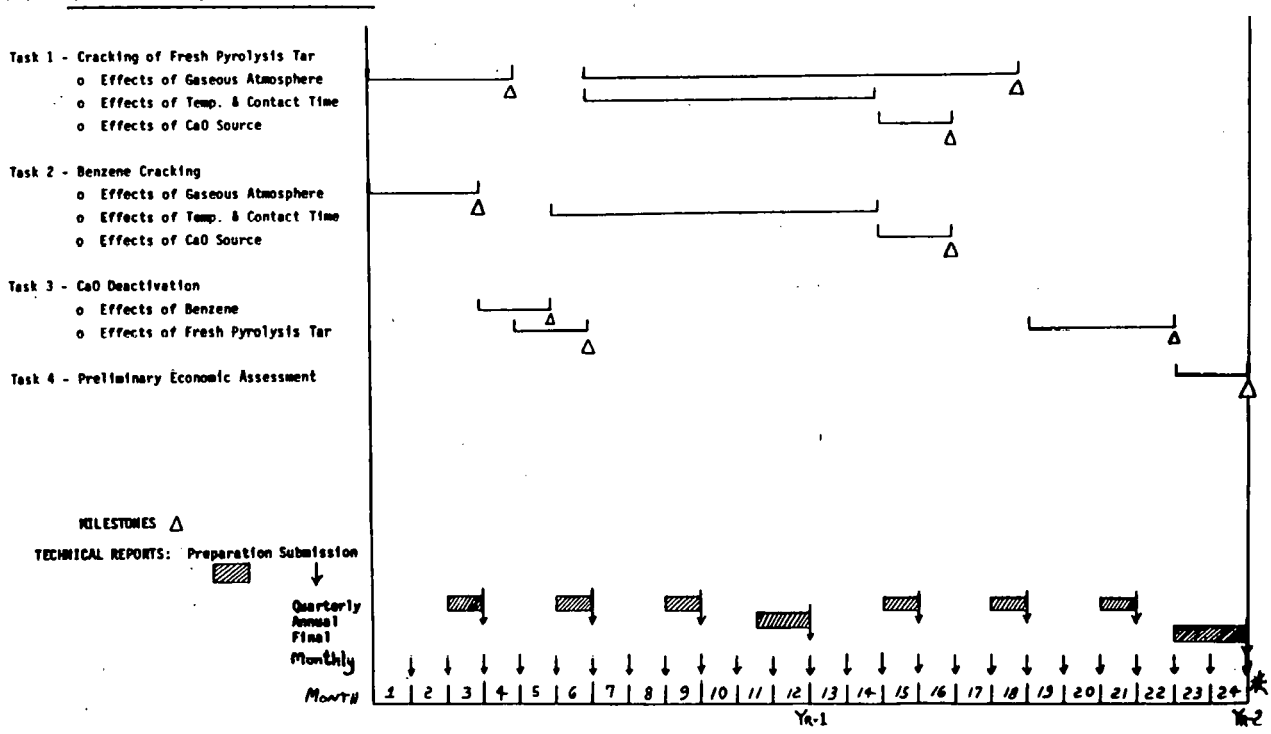
CONTRACT MANAGER: Dr. William A. Peters

PRINCIPAL INVESTIGATORS: Prof. John P. Longwell, Rm. 66-352, Dept of Chemical Engineering; Tel.: (617) 253-4534
Dr. William A. Peters, Rm. E40-483B
Energy Lab.; Tel.: (617) 253-3433
(Co-investigators: C.C.-S. Chang, C.-K. S. Lai, P. Chen, and M.R. Hajaligol)

METC PROJECT MANAGER: (Dr. Norman T. Holcombe)

CONTRACT PERIOD OF PERFORMANCE: 9/28/84 - 2/28/87

2. SCHEDULE/MILESTONES




Program Schedule and Milestone Chart.

* Extended by a no cost extension of approximately 5 months.

## 3. OBJECTIVES:

Our overall goal is to provide quantitative understanding of the thermal reactions of aromatic contaminants--with emphasis on freshly formed coal pyrolysis tars and benzene--with calcium oxide under conditions pertinent to in situ, or outboard attenuation of these contaminants from advanced coal gasification process and waste streams. Specific objectives are to:

- o Task 1 Study the cracking of fresh coal pyrolysis tar over CaO;
- o Task 2 Study benzene cracking over CaO;
- o Task 3 Determine CaO deactivation behavior; and
- o Task 4 Perform a preliminary assessment of process economic implications.

## 4. BACKGROUND STATEMENT:

Aromatic materials--such as tars, phenols, soot, and pure compounds--are impeding coal gasification technology development by contaminating product streams and increasing process costs. Cleanup equipment is costly to install and operate and often incurs a substantial energy penalty. A potentially cost-effective alternative is to develop process modifications that prevent or minimize the formation or evolution of these contaminants. For example, recent DOE-supported research at MIT has shown that calcium oxide exhibits a strong activity for thermally destroying pure polycyclic aromatic hydrocarbons (Ellig et al., 1985; Longwell et al., 1985a), and freshly formed coal pyrolysis tars (Longwell et al., 1985b). Products from the tar destruction can include gases, coke, and liquids lower in phenolic content and mutagenicity.

The present work was undertaken to investigate the applicability of the above chemistry to attaining very high extents of tar and aromatics destruction under conditions pertinent to cleanup of coal gasification process and waste streams.

## 5. PROJECT DESCRIPTION:

Experimental apparatus and procedures including reactor systems, and methods of products collection and analysis are described by Chang (1986) for freshly formed coal devolatilization tars and by Ellig et al. (1985) and Lai (1986) for pure compounds. In brief our approach involves measuring tar or pure compound conversion, quality changes, and co-product yields, as affected by thermal treatment with solid CaO at known and controlled temperatures and contact times. "Control" experiments without CaO allow effects of pure thermal treatment to be distinguished from CaO-induced phenomena. Calcium oxide deactivation was studied by measuring feed conversion over coked samples of the calcine. Calcine regeneration was studied by measuring the conversion activity of CaO recovered by $O_2$ burnoff of coked CaO, with or without follow-on hydration with liquid water and recalcination of the resulting $Ca(OH)_2$.

Much of the work during the last several months has focussed on: (1) A preliminary examination of possible economic implications (as inferred from estimated CaO replacement charges) of CaO thermal treatment for high temperature cleanup of streams containing coal tars; and (2) studies aimed at unravelling the contribution of coke and CaO to aromatics conversion over coked calcium oxide. Section 6 presents more details on the economics study. The CaO-coke work involved comparing the activity and selectivity of fresh and coked CaO for conversion of pure aromatic compounds to that of fresh and coked quartz and two carbon forms.

## 6. RESULTS AND ACCOMPLISHMENTS:

Earlier work on this and previous MIT projects (Chang 1986; Ellig 1981; Ellig et al. 1985; Lai 1986; Longwell et al. 1985a,b,1986) has shown that, compared to solids-free thermal treatment, CaO greatly accelerates rates and extents of destruction of tar (Fig. 1) and pure aromatic compounds (Table 1) including benzene (Fig. 2). Conversions of 75-100% have been realized at 600 to 860 C for contact times in the range of 0.1 to 2 s, with coke as a major product (Fig. 1). Controlled CaO thermal treatment can also reduce the

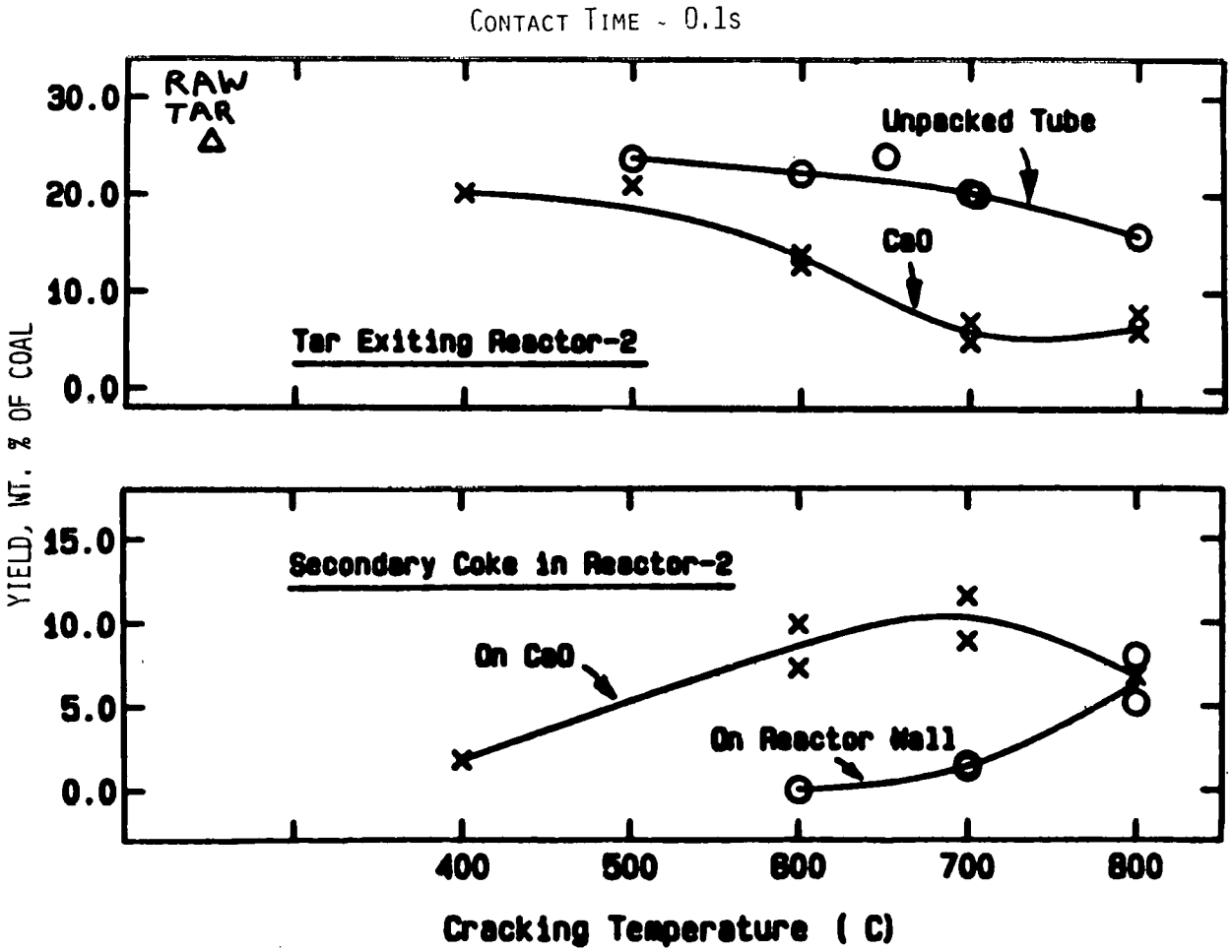



Figure 1. Tar Conversion Behavior.

TABLE 1. PYROLYSIS OF AROMATIC COMPOUNDS

| | Activation Energy (kcal/mole) | | 40 percent Conversion Temperature (°C) | | |
|---|---|---|---|---|---|
| Compound | CaO | Quartz | CaO | Quartz | ΔT |
| Benzene | 42.1 | 79.9 | 785 | 925 | 140 |
| Toluene | 46.2 | 79.5 | 710 | 850 | 140 |
| 1-Methylnaphthalene | 25.4 | 43.4 | 600 | 775 | 175 |
| 1-Methylanthracene | 12.0 | 46.0 | 490 | 730 | 240 |
| 9-Methylanthracene | 18.7 | 42.3 | 440 | 650 | 210 |
| n-Heptane | 40.6 | 48.7 | 600 | 640 | 40 |

loadings of phenolics (Chang 1986; Lai 1986; Chen, c. 1985, Lai et al. 1987), bacterial mutagens (Chang 1986; Chang et al, 1987), one-ring hetero-atom aromatics (Abrishamian, 1978, Mead 1979), and high molecular weight (MW) compounds Chang (1986). The initial CaO activity is strongly degraded by coke deposition (Chang 1986, Fig. 3; Lai 1986, Fig. 2). However, for temperatures ≥ 600 C, 50-70% of this potency can persist to higher extents of CaO utilization, and most or all of the initial activity can be recovered by appending $O_2$ burnoff of the coke by low temperature rehydration of the stone followed by calcination of the resulting $Ca(OH)_2$, (Chang 1986, Fig. 4, Lai 1986, Fig. 2).

A preliminary examination of potential economic implications of use of controlled CaO thermal treatment for high temperature tar removal was performed (Longwell et al. 1987a). Flow sheet studies and process economic analyses lie beyond the scope of this project. The following cost estimation approach was followed. Data from Chang (1986) on the decay of calcium oxide activity for thermal conversion of newly-formed coal pyrolysis tars (Fig. 3), were used to estimate CaO makeup costs for maintaining different extents of tar destruction at temperatures pertinent to hot gas cleanup. Expressing

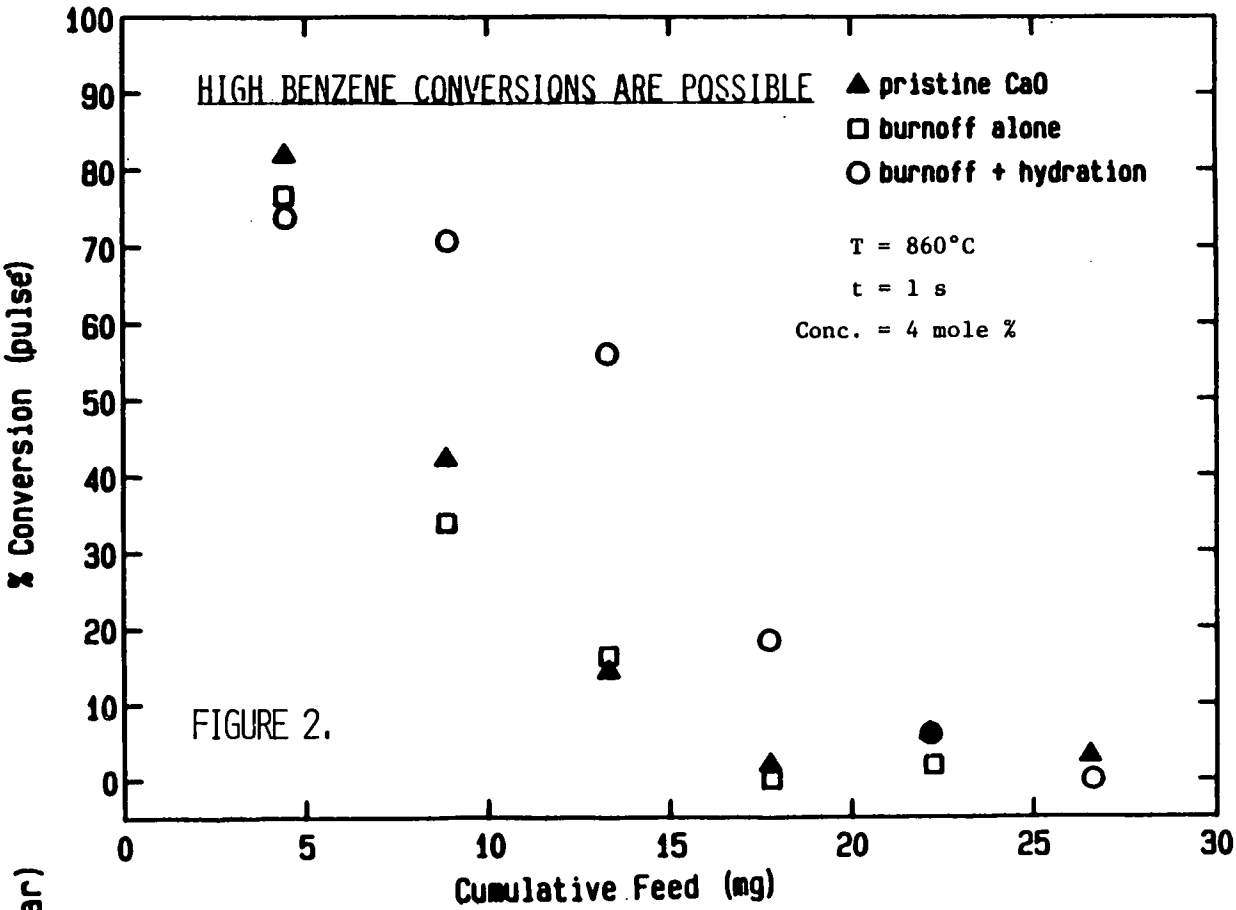



FIGURE 2.

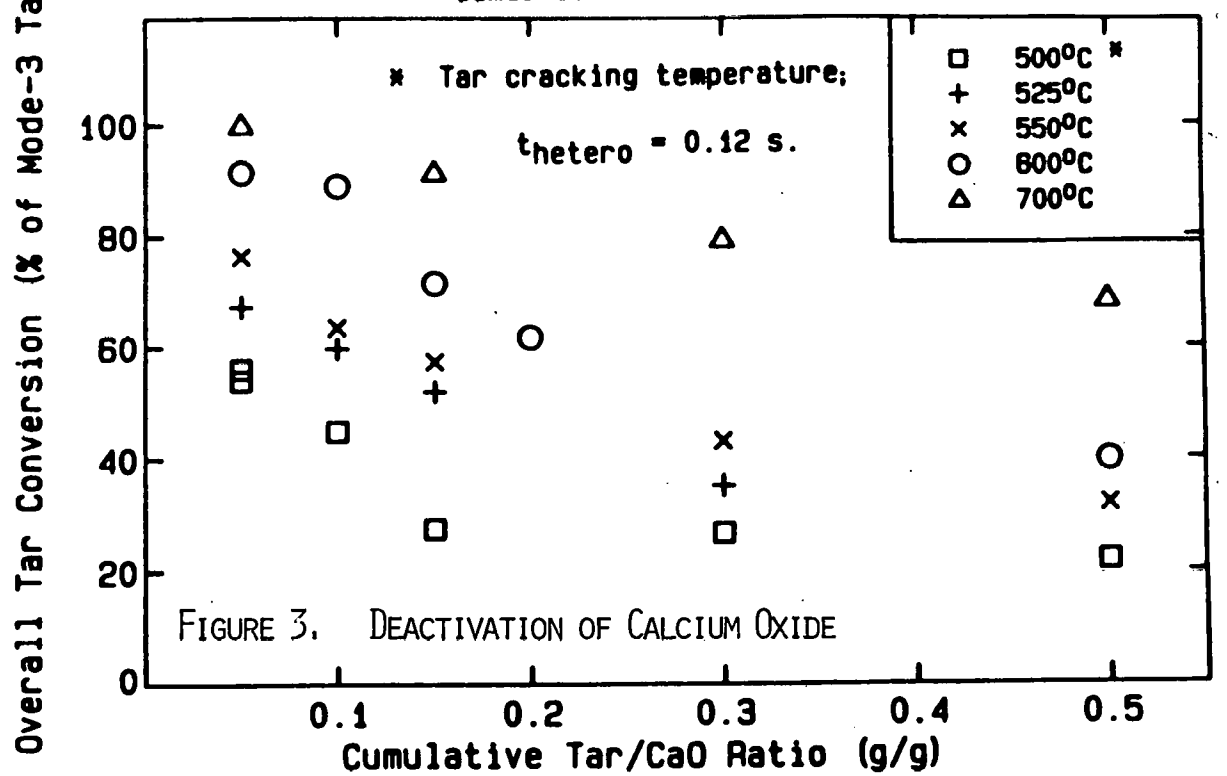
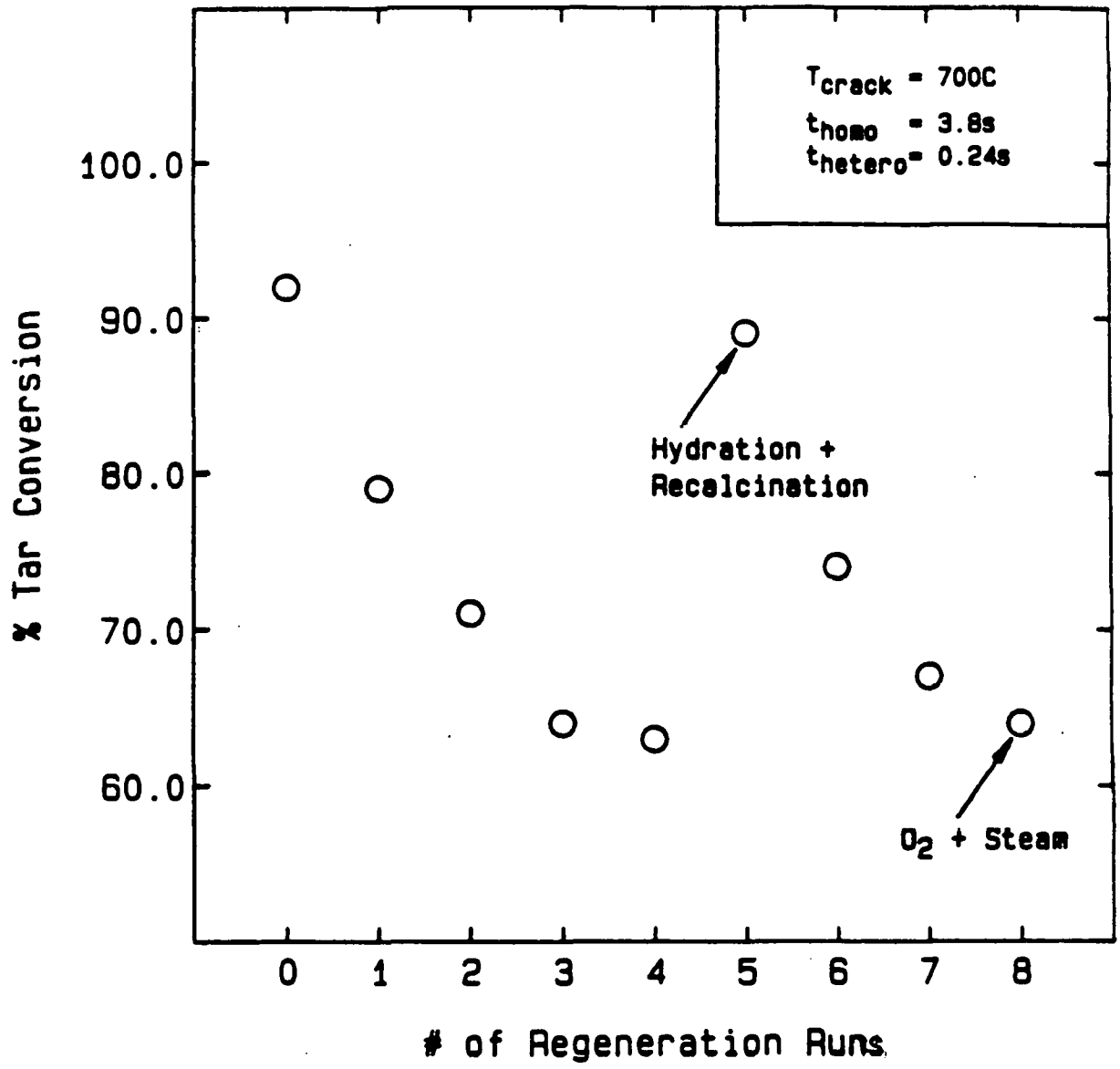



FIGURE 3. DEACTIVATION OF CALCIUM OXIDE

FIGURE 4. REGENERATION OF CaO ACTIVITY




these costs as a percentage of fuel (coal) costs (Table 2) allowed the contribution of CaO replacement charges to the final cost of electricity (COE) from selected advanced coal gasification cycles to be estimated from information provided by the U.S.D.O.E. (Moore, 1986), on the effect of fuel (coal) costs on the COE.

The analysis is very preliminary and based on several assumptions. However, the results (Table 3) show that, for reasonable extents of tar destruction (~65 wt%) under batch reactor conditions, projected CaO makeup costs would not be expected to cause prohibitive increases in the final COE. For example, while the precise costs should be directly proportional to the amount of tar requiring treatment, even for a case of 25 wt% of the feed coal being

Table 2. Relating Costs of Makeup CaO for Coal Tar Conversion to Corresponding Coal Costs

| CaO Cost, $/ton[b] | Coal Cost, $/ton[c] | CaO Cost / Coal Cost | [Makeup CaO Cost/Coal Cost][d] for Tar Conversion of: 100% | 80% | 65% |
|---|---|---|---|---|---|
| 55 | 43.20 | 1.273 | 6.366 | 1.061 | 0.318 |

[a] All costs are in 1985 U.S. dollars.

[b] Source: Chemical and Engineering News, June 24, 1985, p. 13.

[c] Assumes 24 million BTU per ton of coal, at approx. $1.80 per million BTU, a coal cost used by Moore (1986).

[d] Based on an analysis (Longwell et al. 1987a) showing that makeup CaO requirements for 100, 80, and 65% tar removal under single pass conversion conditions, would respectively amount to 5, 0.83, and 0.25 tons per ton of coal processed to yield 25 wt.% of tar requiring cleanup. Actual CaO makeup costs would be directly proportional to the quantity and reactivity of tar requiring treatment.

converted to tar needing cleanup, the CaO makeup costs are estimated to add of order 8 to 13% to the final COE under the stated conditions (Table 3). When ultra high extents of tar destruction (~100%) are desired under single pass batch CaO conditions, the projected CaO makeup charges become intractable, causing roughly 200 to 300% increases in the final COE (Table 3). However higher ( > 95%) overall levels of tar removal may still be economically attainable by process optimization, for example by series-staging three batch treatment reactors giving 65% conversion each (Table 3).

Experiments were also performed to assess the contribution of carbon deposits to the aromatics conversion activity of coked calcium oxide (Hajaligol et al. 1987). Activities of fresh (uncoked) and coked CaO for conversion of 1-methylanthracene (1-MAT) and n-heptane were measured or obtained from the literature, and compared with corresponding information for fresh and coked samples of activated carbon, spherocarb, and ground quartz. The studies showed that similar selectivity for 1-methylanthracene conversion, compared to n-heptane, was exhibited by fresh and coked CaO between 550 and 650°C, (Table 4) and by fresh CaO and fresh activated carbon between 600 and 650°C (Fig. 5). However the deactivation behavior of fresh and coked CaO due to coke deposition from aromatics conversion, is markedly different from that of these

TABLE 3. ESTIMATES OF HOW CaO MAKEUP COSTS MAY AFFECT FINAL COSTS OF ELECTRICITY (COE)

| Technology | Projected COE, mills/kwhr[a] | Percent Increase in COE from CaO Makeup for Tar Conversions of: 100%[b] | 80%[b] | 65%[b] | 95%[c] |
|---|---|---|---|---|---|
| Gasif. Island | 57 - 60 | 235 - 275 | 40 - 45 | 12 - 13 | 18 - 19 |
| Gas Turbines | 49 - 81 | 210 - 245 | 35 - 40 | 11 - 12 | 16 - 18 |
| Fuel Cells | 71 - 88 | 150 - 190 | 25 - 30 | 8 - 10 | 12 - 15 |
| KRW Gasif. Island | 61 | 230 | 40 | 11 | 16 |

[a]Data of W. Moore U.S.D.O.E. 1986

[b]Single Pass Batch CaO

[c]By Series-Staging 3 65% Conversion Reactors

Table 4. Effects of Temperature and Coke Deposition on Calcium Oxide Selectivity[a] for Conversion of Hydrocarbons[b]

| | Percent Conversion | | | | | |
|---|---|---|---|---|---|---|
| | Fresh CaO | | | Coked CaO | | |
| Temp. C | 1-MAT | n-heptane | S[a] | 1-MAT | n-heptane | S[a] |
| 550 | 53 | 18 | 2.9 | 20 | 6 | 3.3 |
| 600 | 72 | 52 | 1.4 | 42 | 30 | 1.4 |
| 650 | 92 | 83 | 1.1 | 64 | 67 | 0.96 |

[a]Selectivity is defined as (% 1-MAT Conversion/% n-Heptane conversion).
[b]Data from Figures 1 and 2.

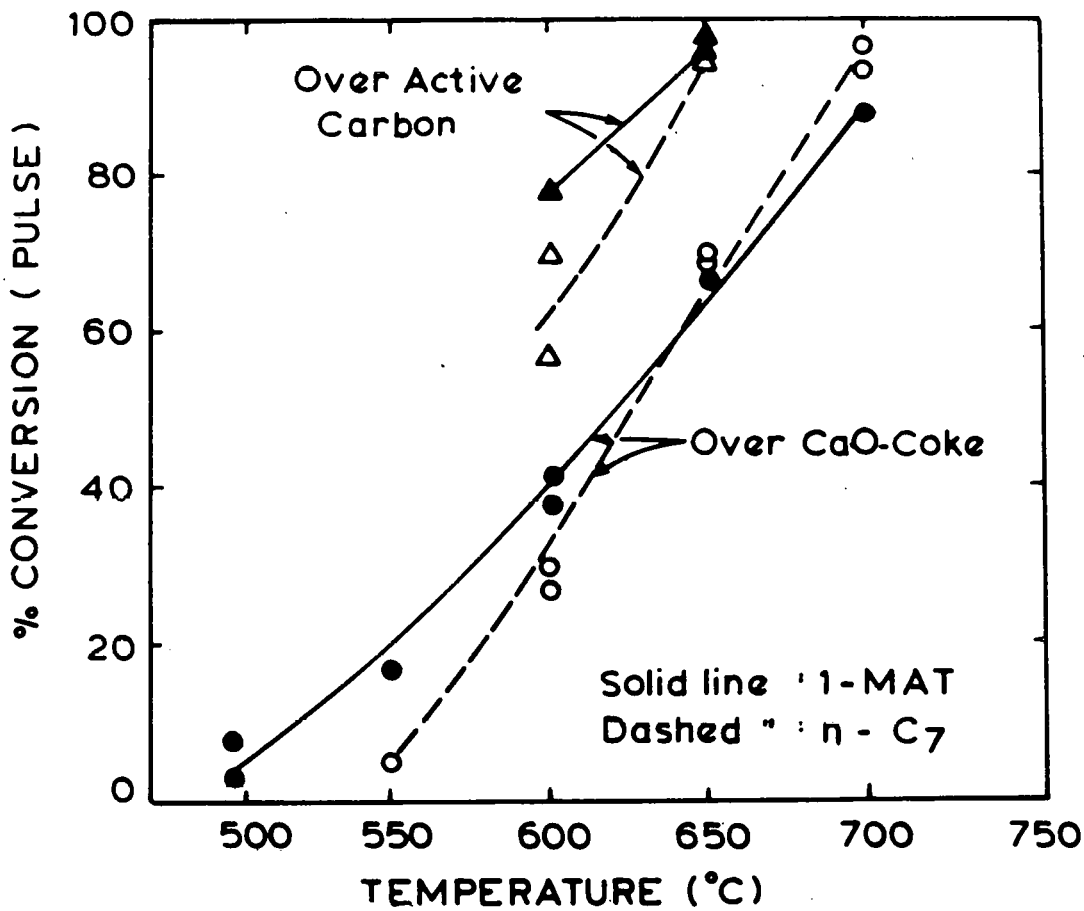



Figure 5. Conversion of 1-Methylanthracene (1-MAT) and n-Heptane Over Packed Beds of Calcium Oxide or Active Carbon.

two carbon forms (Fig. 6). At a given temperature, with increasing solids utilization, the activity of uncoked CaO initially declines quite rapidly but then remains virtually constant, whereas the activity of both carbons declines strongly and continuously until the background level of coked quartz is reached. Plugging of microporosity could account for this behavior of the carbon forms.

These and related results and literature discussed by Hajaligol et al. (1987), support the picture that the aromatics conversion activity of fresh CaO can be explained by either: (A) rapid deactivation of a limited inventory of very active sites superimposed upon enduring contributions from a less active but more abundant CaO site; or (B) rapid decommissioning of nascent CaO activity, accompanied by buildup and persistence of activity from the coke deposits at a constant level. Further work would be required to distinguish (A) and (B). One approach would be to determine the porosity of the coke deposits on CaO, and then compare the coke-induced deactivation behavior of such cokes on CaO and on non-CaO substrates.

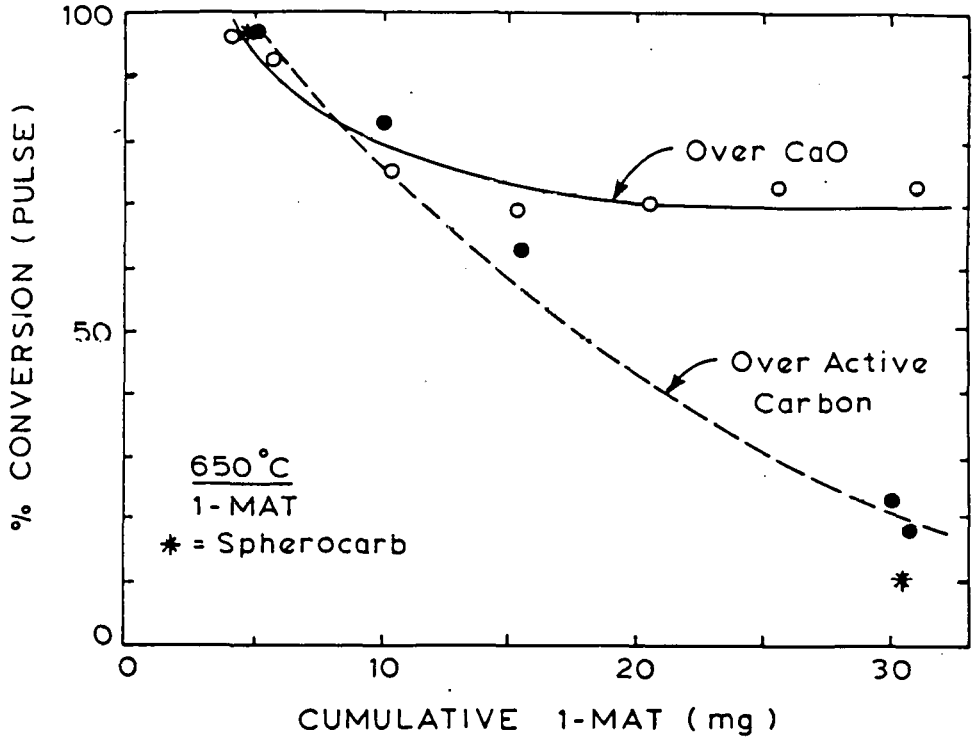



**Figure 6. Deactivation Behavior of Packed Beds of CaO and Active Carbon by Conversion of 1-Methylanthracene.**

## 7. EVALUATION OF POTENTIAL, AND FUTURE PLANS

Thermal treatment with CaO continues to show promise as a means of removing newly formed coal pyrolysis tars and pure aromatic compounds including benzene and multi-ring polycyclic aromatic hydrocarbons from coal gasification product streams. High extents of tar and pure compound conversion (75 - 100%) have been achieved, with temperature and CaO to feed ratio being the most important operating variables. Feed composition, source of calcine, and CaO regeneration procedures can also influence conversion, as can feed concentration for the pure compounds. Controlled CaO thermal treatment can also reduce the loadings of phenolics, metabolically induced bacterial mutagens, aromatics and high molecular weight constituents in newly formed coal tars, although reaction conditions optimizing liquids yield/quality relationships were not established. Preliminary estimates suggest that CaO replacement charges would not be expected to render process economics untenable if intermediate (~ 65%) extents of tar conversion in a single pass reactor can be tolerated. Series staging of three such reactors would appear to offer promise for achieving more severe (> 95%) levels of high temperature tar conversion.

Applications to the U.S. fossil energy program would include identification and development of new or improved technologies for removing aromatic contaminants--tars, phenols, mutagens, and high MW compounds--from coal gasifier product and waste streams. Beneficial effects could include minimized or diminished in situ or post-gasifier cleanup operations and reduced capital and operating charges for process stream cleanup. Another potential application would be recovery of quality-enhanced gaseous and liquid fuels via controlled CaO thermal treatment to redirect post-pyrolysis reactions of newly formed coal volatiles, as in mild gasification (Khan and Kurata, 1985) mild pyrolysis (Khan 1986, 1987) and combined fluidized bed pyrolysis fluidized bed combustion (Longwell et al. 1982; Yeboah 1980; Yeboah et al. 1980; 1982).

This contract has come to an end. Future work may focus on identifying means to use CaO thermal treatment to optimize yield quality relationships in recovering liquid, gaseous and solid fuels by mild processing of coal, and on further studies of the role of coke in determining the aromatics conversion activity of coked CaO.

### Acknowledgements

Contributions from several people including participants in the MIT Undergraduate Research Opportunities Program (U.R.O.P.) are greatfully acknowledged. Early studies by Dallabetta (1977) and Heavner (1978) are also greatly appreciated.

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NOVEL CONCEPT DEVELOPMENT OF AN INTERNAL RECIRCULATION CATALYST FOR MILD GASIFICATION

1. CONTRACT NUMBER: DE-AC21-86MC23057

CONTRACTOR: Institute of Gas Technology
3424 S. State Street
Chicago, IL 60616
(312) 567-5758

CONTRACTOR PROJECT MANAGER: Dr. Suresh P. Babu

PRINCIPAL INVESTIGATORS: Gerald L. Anderson
Dr. Bruce H. Solka

METC PROJECT MANAGER: Dr. W. S. Liou

CONTRACT PERIOD OF PERFORMANCE: August 25, 1986 to February 26, 1989

2. SCHEDULE/MILESTONES:

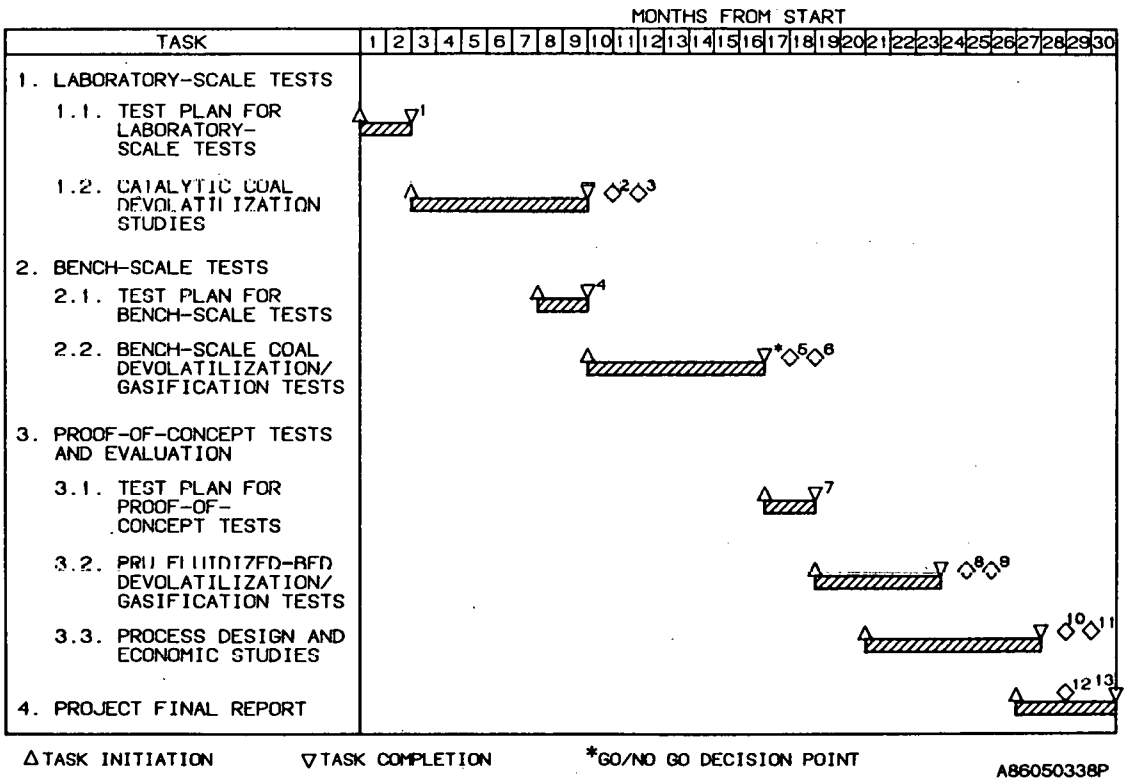



Figure 1. Project Schedule.

3. OBJECTIVES:

The primary purpose of this project is to develop and characterize a novel process concept for catalyzed mild gasification of coal using a semivolatile internal recirculation catalyst. The research is directed toward maximizing liquid product yields and improving the liquid product fuel quality.

4. BACKGROUND STATEMENT:

One of the primary economic penalties of catalytic coal gasification processes is in recovery of added catalyst from the spent char. The Institute of Gas Technology (IGT) has been exploring ways to reduce catalyst recovery costs. In the IGT process concept addressed in this work, a catalyst is used that is semivolatile under gasification conditions. That is, for a gasifier that utilizes an increasing thermal gradient from feed coal inlet to char discharge, a desirable catalyst would be sufficiently volatile at the higher temperature to be completely vaporized from the char before it is discharged. The catalyst vapor would then recirculate and condense on the cooler feed coal. Such an internal recirculation catalyst would eliminate the need for costly catalyst recovery.

Under DOE Contract No. DE-AC21-84MC21203, IGT considered various candidate catalysts on the basis of their vapor pressures at typical gasifier temperatures. Several candidates were selected for experimental testing in that program. Steam-char gasification experiments in laboratory-scale batch tests and bench-scale moving-bed tests indicated that, of the various materials with appropriate volatility, cesium hydroxide showed the highest degree of catalytic activity (Hill et al. 1986). The goal of this new project is to extend examination of these concepts to coal devolatilization while giving more attention to the detailed nature of product liquid quality and to the fate of the catalyst during coal processing. This is being done in progressive laboratory-scale, bench-scale and optional process-development-scale testing.

5. PROJECT DESCRIPTION:

The first stage of this program has been laboratory-scale examination of the effect of CsOH on volatile product nature and quantity. The reactor used for this work is illustrated in Figure 2. The sample is placed in a 1/8-inch-OD by 1-inch-long quartz tube in a flowing stream of preheated reactant or carrier gas. The tube is situated within a platinum wire coil for heating. This apparatus is directly interfaced to an analyzer for volatile product characterization. In the work reported here, analysis have been done by gas chromatography with either mass spectrometry detection (for $C_1$ to $C_{25}$ products) (Finnigan Mat. Corp. Model 4510) or chromatograph (Perkins-Elmer Corp. Sigma 1) with a thermal conductivity detector for $C_1$ to $C_3$ gases or a flame ionization detector for $C_8$-$C_{44}$ products. Tests of catalyst at heat-up rates of 210°F/sec and 390°F/sec to final temperatures of 1000°F and 1400°F have been completed for Illinois No. 6 coal in helium (50 cc/min @ 12 psig) and partially

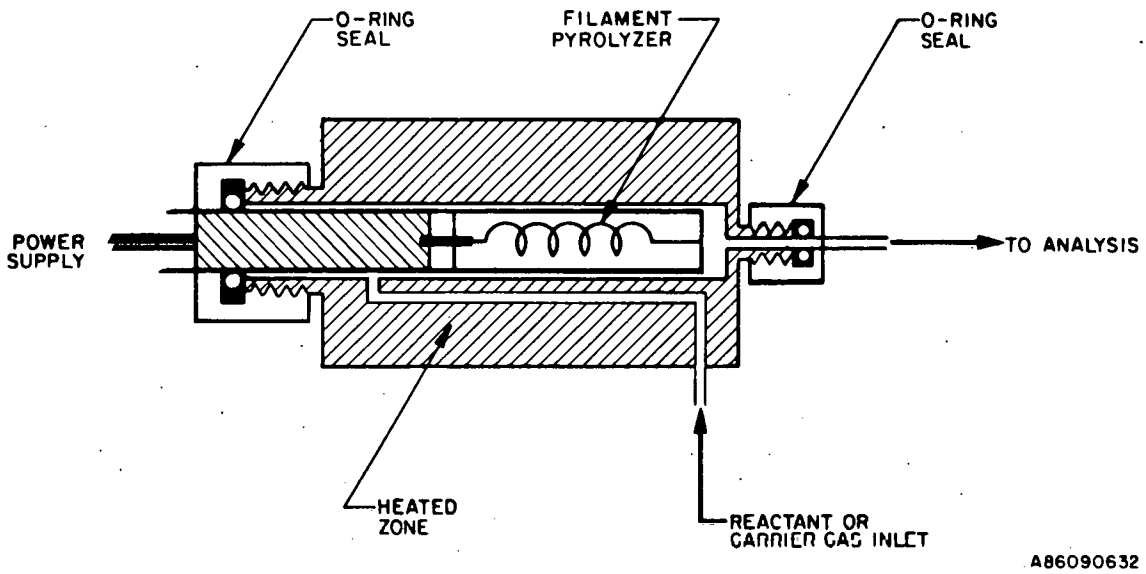



Figure 2. On-Line Reactor for Laboratory-Scale Work.

completed for Illinois No. 6 coal in 8.6% by volume of $H_2$ in He and Wyodak coal in He. Testing of North Dakota Lignite in these atmospheres and Illinois No. 6 in $He/H_2O(g)$ is planned.

Tests are being done with 2 to 3 milligram samples. Gravimetric measurements on a microscale balance permit determination of the extent of volatilization. Adequate residue remains to permit elemental micro-analysis of C, H, N, S, and Cs.

In addition to product quantities, examples of important product parameters being examined for catalyst effect are disposition of sulfur among the products and degree of aliphatic nature of condensible product liquids.

Results from these laboratory pyrolysis on-line analysis tests are being used as a guide in defining operating conditions, product collection schemes, and product analysis plans for the bench-scale tests.

6. RESULTS/ACCOMPLISHMENTS:

Extensive experiments were conducted to optimize sample time-temperature profiles in the microreactor. This is a commercially available unit (Chemical Data Systems, Inc., Oxford, PA) powered by a controller with fixed set-points. These experiments required an off-line mode (i.e., no chromatograph interface) so that a thermocouple could be inserted into the coal sample for temperature monitoring. Typical sample time-temperature profiles for various filament heat-up rates are shown in Figure 3.

It was determined that heat-transfer through the quartz sample tube severely limited sample heat-up rate. Thus, in Curve A of Figure 3, the

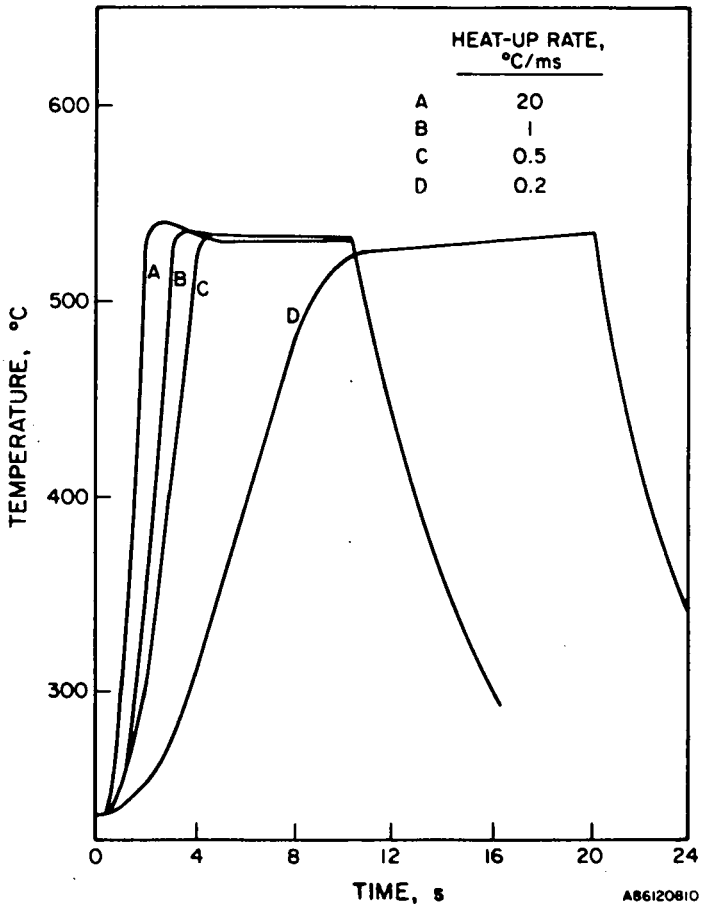



Figure 3. Sample Temperature for Heat-Up Rates to 540°C.

filament is heated at 36,000°F/sec, but average sample heat-up in the 570°F to 1000°F temperature range is only about 390°F/sec. To obtain the relatively abrupt cut-off in heat-up at the upper temperature, it was found necessary to heat the filament to a much higher temperature than that desired for the sample. After a measured time (increments of 0.5 sec) at this high temperature to maximize heat input, the filament temperature can be reduced to a value that ends the heat-up at the desired equilibrium temperature. Heat-up rates of 210°F/sec and 390°F/sec reproducible to ±50°F and final temperature of 1000°F and 1400°F reproducible to ±90°F were achievable by this approach.

Test coals were ground and sieved under nitrogen to obtain -80 + 140 mesh. Catalyzed coal was prepared by slurrying the sized coal samples in a 50% (wt) CsOH-water solution and drying for 16 to 18 hours in vacuum at 212°F. Uncatalyzed coal was prepared by the same treatment with deionized organic-free water substituted for the CsOH solution.

Overall reproducibility of measured devolatilization product yields will be a function of reproducibilities of coal sample, pyrolysis conditions, product transfer, and analysis system response. Two sets of eight tests

each were made with GC/MS analysis and smaller numbers of replicate tests were made with GC/FID and GC/TCD analysis. Results of these reproducibility tests are listed in Table 1 where the indicated uncertainties are standard deviations for the larger sets of replicates and ranges for the small sets.

Table 1. Product Distribution and Reproducibilities for Selected Tests: Illinois No. 6 Coal in Helium.

| | 210°F/sec to 1000°F | | 390°F/sec to 1400°F | |
|---|---|---|---|---|
| | GC/MS | GC/FID/TCD | GC/MS | GC/FID/TCD |
| | Wt % of Feed Coal, dry basis | | | |
| Methane | 1.3 ± 0.2 | 1.8 ± 0.3 | 4.6 ± 0.9 | 2.4 ± 0.6 |
| Carbon Monoxide | 0.99 ± 0.36 | 1.4 ± 0.1 | 3.4 ± 0.9 | 3.4 ± 0.8 |
| Carbon Dioxide | 0.58 ± 0.13 | 0.35 ± 0.11 | 1.0 ± 0.7 | 0.49 ± 0.15 |
| Ethane + Ethene | 0.9 ± 0.2 | 0.41 ± 0.06 | 1.0 ± 0.2 | 1.1 ± 0.2 |
| Hydrogen Sulfide | 0.35 ± 0.10 | 1.1 ± 0.3 | 0.29 ± 0.08 | 2.2 ± 0.7 |
| Propane + Propene | 0.42 ± 0.06 | 0.4 ± 0.1 | 0.34 ± 1.12 | 0.4 ± 0.1 |
| $C_4$ - $C_{12}$ | 4.7 ± 1.9 | 2.5 ± 0.1 | 4.5 ± 1.7 | 3.6 ± 0.1 |
| $C_{13}$ - $C_{18}$ | 2.1 ± 1.3 | 2.9 ± 0.1 | 2.7 ± 1.3 | 3.2 ± 0.1 |
| $C_{18}$ - $C_{30}$ | 0.4 ± 0.3 | 3.8 ± 0.1 | 1.5 ± 1.2 | 4.0 ± 0.1 |
| $C_{30}$ - $C_{44}$ | NA* | 4.3 ± 0.1 | NA* | 4.9 ± 0.1 |
| Residue in Tube | 69.4 ± 4.2 | 65.6 ± 4.1 | 61.6 ± 2.6 | 59.4 ± 2.4 |
| Recovery | 81.1 ± 4.8 | 84.6 ± 4.1 | 80.9 ± 3.9 | 85.0 ± 2.7 |

* NA = Not Accessible.

Several observations may be made regarding these two comparative sets of product distributions. Within the combined uncertainties, both methods of product analysis give the same results for most products and product fractions. The GC detection methods afford more precise quantitation because FID and TCD detectors are less susceptible to response drift and because for this data we used packed column methods wherein the entire product mix must flow to the analysis system. The GC/MS method is based on a high-resolution capillary column separation which affords excellent capability for measurement of individual compounds in the $C_4$ - $C_{20}$ product range but has difficulty in simultaneously quantitating the very large individual components in the $C_1$ - $C_3$ range. Difficulties have also been experienced with heavy tars causing partial plugging of the GC/MS injection system split-flow line. This introduces uncertainties in absolute yield as determined by external standard quantitation methods, but does not affect relative amounts of individual compounds in a given test run.

The results of Table 1 are typical in several respects of those obtained at the other combinations of heat-up rate and final temperature, with and without catalyst, and lead to several significant conclusions regarding this pyrolysis system:

- 30 to 40 weight percent of the coal is devolatilized, comparing favorably to the ASTM Volatile Matter test result of 38.8% for this coal.

- Product transfer from the pyrolysis zone to the capillary column analytical system clearly becomes less efficient in the $C_{18}$ - $C_{30}$ volatility range.

- Overall material balance remains at about 85% for the method of highest collection efficiency and greatest boiling range capability.

This latter point, taken in conjunction with the other experimental observations, carries strong implications for coal devolatilization studied under mild conditions. The residues include the weights of both char and a distinctly separate tarry material that has formed and left the hottest region of the reaction tube but then condensed toward the cooler ends of the tube. This cooler region is maintained at about 570° to 660°F in these tests. Experiments with pure n-tetratracontane (boiling point of 1040°F) indicate that approximately 90% of material of this boiling point range will leave the reaction tube during these tests. The tarry residue deposited by coal devolatilization is quite insoluble. A 16 hour Soxhlet extraction with pyridine fails to completely remove it from the tubes. Chromatographic analysis of a X50 concentrate of the combined Soxhlet extract of 12 tubes showed no detectable material boiling below 1040°F. The relatively flat distribution of product material between $C_4$ and $C_{44}$, the nature of these tarry residues, and the rapid devolatilization product quenching in this system implies that the 13% to 16% condensibles recovered in these tests may indeed represent only one-half of the total condensible fraction formed. The unrecovered material must mainly be material boiling above 1040°F, may extend to very high carbon numbers, and probably is relatively insoluble in common solvents. This material thus may not be recoverable or amenable to characterization in even larger scale process systems if cool regions permit it to drop out of the vapor phases before collection. Even if collected, only the most sophisticated analytical techniques specifically designed to characterize these heavy ends can be expected to generate much information on its chemical nature.

Table 2 lists product distributions for catalyst testing of Illinois No. 6 coal in helium. Only the two extremes of pyrolysis severity are shown for brevity.

Changes in product composition due to the presence of catalyst include the following:

- Decreases in methane and CO production.

Table 2. Product Distribution for Illinois No. 6 Coal Tests in Helium.

| Product | 210°F/sec to 1000°F | | 390°F/sec to 1400°F | |
|---|---|---|---|---|
| | Uncatalyzed | 8.7% CsOH | Uncatalyzed | 8.7% CsOH |
| | Wt % of dry, catalysts from coal | | | |
| Methane | 1.8 | 1.4 | 2.4 | 1.5 |
| Carbon Monoxide | 1.4 | 0.76 | 3.4 | 2.3 |
| Carbon Dioxide | 0.35 | 2.2 | 0.49 | 1.5 |
| Ethane/Ethene | 0.41 | 0.73 | 1.1 | 0.9 |
| Hydrogen Sulfide | 1.1 | 2.1 | 2.2 | 3.6 |
| Propane/Propene | 0.4 | 0.5 | 0.4 | 0.4 |
| Subtotal Gas | 5.4 | 7.8 | 9.9 | 10.2 |
| $C_4$-$C_{12}$ | 2.5 | 2.6 | 3.6 | 3.8 |
| $C_{13}$-$C_{18}$ | 2.9 | 2.4 | 3.2 | 3.0 |
| $C_{14}$-$C_{30}$ | 3.8 | 2.8 | 4.0 | 3.4 |
| $C_{30}$-$C_{44}$ | 4.3 | 3.0 | 4.9 | 3.6 |
| Subtotal Liquid | 13.5 | 10.8 | 15.7 | 13.8 |
| Residue | 65.6 | 71.5 | 59.4 | 64.5 |
| Recovery | 84.5 | 90.1 | 85.0 | 88.5 |

- Large increases in $CO_2$ production.
- Large increases in $H_2S$ production.
- Decrease in recoverable condensible liquid production, apparently caused by a leveling or broadening of the boiling point distribution of these products.
- Increase in residue, which may reflect the broadening of condensible product distribution to the extent of significantly increasing the product fraction of insufficient volatility to leave the tube.

Similar trends are observed by changing the reaction atmosphere from helium to helium containing 8.5 volume percent $H_2$. Results under these conditions are listed in Table 3.

Increasing the amount of hydrogen available during devolatilization does not appear to significantly change any catalyst effects cited above for the devolatilization in helium.

The marked increase in $H_2S$ production with the presence of a catalyst is beneficial to production of low sulfur-containing liquids and char. As

Table 3. Product Distribution for Illinois No. 6 Coal Tests in Hydrogen/Helium Mix.

| Product | 210°F/sec to 1000°F | | 390°F/sec to 1400°F | |
|---|---|---|---|---|
| | Uncatalyzed | 8.7% CsOH | Uncatalyzed | 8.7% CsOH |
| | Wt % of dry, catalysts from coal | | | |
| Methane | 0.97 | 0.91 | 1.6 | 1.0 |
| Carbon Monoxide | 0.65 | 0.39 | 2.0 | 1.6 |
| Carbon Dioxide | 0.47 | 1.7 | 0.82 | 2.6 |
| Ethane/Ethene | 0.65 | 0.61 | 1.1 | 1.3 |
| Hydrogen Sulfide | 2.36 | 2.44 | 3.5 | 4.5 |
| Propane/Propene | 0.29 | 0.28 | 0.22 | 0.32 |
| Subtotal Gas | 5.4 | 6.3 | 9.3 | 11.5 |
| $C_4$-$C_{12}$ | 3.0 | 2.1 | 2.6 | 2.9 |
| $C_{13}$-$C_{18}$ | 3.3 | 2.5 | 2.3 | 2.1 |
| $C_{18}$-$C_{30}$ | 4.0 | 2.7 | 2.7 | 2.3 |
| $C_{31}$-$C_{44}$ | 2.5 | 2.2 | 2.0 | 1.7 |
| Subtotal Liquid | 12.8 | 9.5 | 9.6 | 9.0 |
| Residue | 62.5 | 68.3 | 73.7 | 63.6 |
| Recovery | 80.7 | 84.1 | 92.6 | 84.1 |

part of the process characterization, the relative amounts of 44 selected products and groups of products are being tabulated from specific mass chromatogram data from the PY/GC/MS tests. Table 4 lists the relative amounts of specific sulfur products included in this tabulation for devolatilization of Illinois No. 6 coal in helium. The increase in production of $H_2S$ with catalyst is accompanied by a significant decrease in all major organo- sulfur compounds in the liquid product boiling range. This trend is also shown in the results (not listed here) of the other test conditions of 210°F/sec to 1400°F and 390°F/sec to 1000°F.

With the other tabulated species (such as aromatic hydrocarbons, aliphatic derivitives of aromatic hydrocarbons or aliphatic hydrocarbons) no such readily apparent trends are observed due to presence of catalyst. The CsOH does, however, have a strong effect on relative amounts of phenolics formed. Phenol and its one- and two-carbon aliphatic derivitives are the largest individual components formed in the condensible liquid product fraction. The effect of the catalyst on the relative amounts of selected phenolics is shown in Table 5.

Phenol approximately doubles in relative amount in the presence of the catalyst, while the relative amounts of phenol derivitives remain approximately the same.

Table 4. Relative Amounts of Selected Sulfur Products: Illinois No. 6 in Helium.

| Product | 210°F/sec to 1000°F | | 390°F/sec to 1400°F | |
|---|---|---|---|---|
| | Uncatalyzed | 8.7% CsOH | Uncatalyzed | 8.7% CsOH |
| | Relative Amount, arbitrary units | | | |
| Hydrogen Sulfide | 14.0 | 17.8 | 9.5 | 12.1 |
| Methyl Mercaptan | 0.7 | 1.2 | 0.33 | 0.25 |
| $C_2$-Mercaptan/Sulfide | 0.14 | 0.07 | 0.06 | 0.02 |
| Carbon Disulfide | 1.2 | 0.60 | 7.2 | 3.8 |
| Thiophene | 0.21 | 0.13 | 0.59 | 0.30 |
| $C_1$-$C_3$ Alkyl Thiophenes | 1.4 | 1.0 | 0.91 | 0.77 |
| Benzothiophene | 0.25 | 0.25 | 1.2 | 0.82 |
| Dibenzothiophene | 0.15 | 0.16 | 0.65 | 0.41 |

Table 5. Relative Amounts of Selected Phenolic Products: Illinois No. 6 in Helium.

| Product | 210°F/sec to 1000°F | | 390°F/sec to 1400°F | |
|---|---|---|---|---|
| | Uncatalyzed | 8.7% CsOH | Uncatalyzed | 8.7% CsOH |
| Phenol | 5.9 | 9.2 | 2.9 | 7.0 |
| $C_1$-$C_3$ Alkyl Phenols | 24 | 21 | 11 | 16 |
| Hydroxy Phenols | 2.3 | 0.6 | 0.4 | 0.5 |
| $C_1$-$C_2$ Hydroxyphenols | 1.4 | 1.0 | 0.55 | 0.68 |
| Hydroxy Naphthalene | 1.1 | 1.3 | 0.74 | 1.1 |

Interpretation of this type of information is still in the initial stages, but these examples serve to illustrate the power of the selected on-line analytical approach for devolatilization process characterizations.

Each test generates a char residue of only 1 to 2 milligrams. This is insufficient material to enable determination of an ash content of adequate accuracy to permit material balance calculations. It is, how-

ever, adequate to permit cesium analysis by atomic absorption spectrometry or C, H, N, and S analysis with a micro-scale elemental analyzer.

Several chars (physically separated from the tarry tube coating) were analyzed for Cs and found to account for 100% of the Cs initially added to the feed within experimental accuracies estimated at ±10%. It is on this basis that gravimetric reaction residue amounts are calculated on a catalyst-free basis. Elemental analysis results are shown in Table 6. Hydrogen in the char residue does show a decreasing trend with increased reaction severity, but the scatter in results precludes making any conclusions regarding effect of catalyst on char composition. It is felt that combinations of small sample size, slight variations in pyrolysis conditions, absorption of atmospheric water and inherent limitations of microscale instrumental analyzers are all contributing the data scatter.

Table 6. Elemental Composition of Illinois No. 6 Feeds and Chars.

| Sample | Carbon | Hydrogen | Sulfur | Nitrogen |
|---|---|---|---|---|
| | Wt % dry, catalyst-free basis | | | |
| Illinois No. 6 Coal | 64.5±3.1 | 4.45±0.09 | 4.6±0.4 | 1.3±0.3 |
| Char From 210°F to 1000°F | | | | |
| Catalyzed | 64.9±2.2 | 2.5±0.2 | 2.5±0.9 | 1.8±0.4 |
| Uncatalyzed | 71.0±2.2 | 2.8±0.4 | 2.3±1.0 | 1.9±0.9 |
| Char From 360°F to 1400°F | | | | |
| Catalyzed | 64.3±3.9 | 1.3±0.2 | 2.3±0.8 | 2.3±0.6 |
| Uncatalyzed | 65.5±5.7 | 1.1±0.3 | 2.2±0.6 | 1.5±0.4 |

## 7. FUTURE WORK:

Task 1 will be completed with testing of North Dakota Lignite, as described above, and the devolatilization of the three feeds in He-$H_2O$(g) atmosphere. The results will provide a summary of the effects of reaction atmosphere, thermal conditions, and CsOH on the detailed chemical nature of devolatilization products.

A test plan is being developed for the Task 2 bench-scale tests. From the results of Task 1, this plan will give particular attention to assuring optimum recovery of very heavy ends of liquid products to account for the elements and to account for sulfur-containing products.

## 8. REFERENCES:

Hill, A. H.; Knight, R. A.; Anderson, G. L.; Feldkirchner, H. L.; and Babu, S. P. Fundamental Research on Novel Process Alternatives for Coal Gasification. Final Report for DOE Contract No. DE-AC21-84MC21203, 1986.

## CHEMICAL AND PHYSICAL DEVELOPMENT OF CHAR PARTICLES DURING DEVOLATILIZATION

1. **CONTRACT NUMBER:** DE-AC21-85MC22050

**CONTRACTOR:**
Advanced Fuel Research, Inc.
87 Church Street
East Hartford, CT 06108
(203) 528-9806

**PROGRAM MANAGER (CONTRACTOR):** Peter R. Solomon

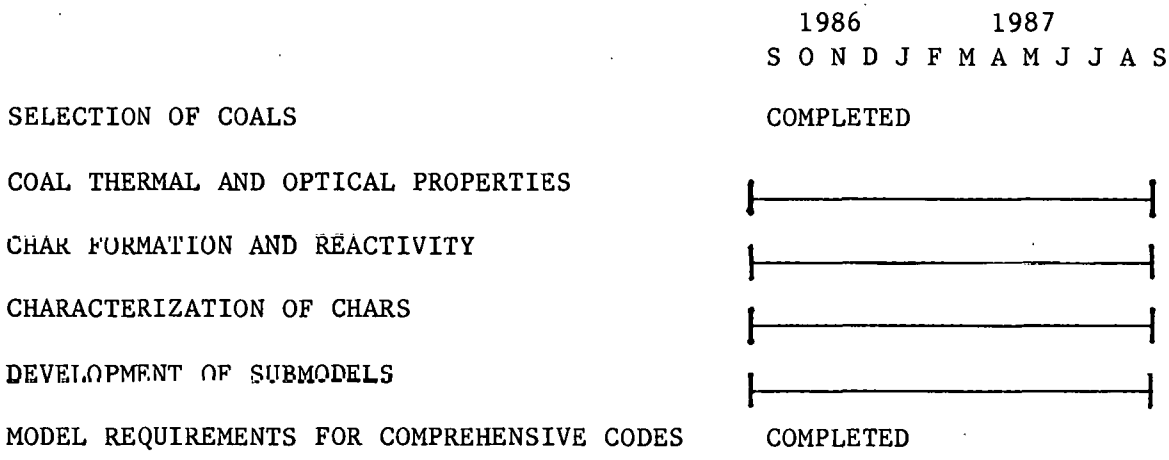
**PRINCIPAL INVESTIGATORS:** David G. Hamblen
Michael A. Serio

**METC PROGRAM MANAGER:** Justin L. Beeson

**PERIOD OF PERFORMANCE:** September 23, 1985 to
September 23, 1987

2. **SCHEDULE/MILESTONES:**

**1987 PROGRAM SCHEDULE**




3. **OBJECTIVES:**

The objective of this project is the acquisition of fundamental data and its use to develop improved predictive models for the physical and chemical behavior of coal in a gasifier. This is being accomplished through a combined theoretical and experimental program focusing on the thermal, optical, physical, and reactive properties of coal and char.

4. **BACKGROUND STATEMENT:**

An important goal of coal research has been to provide sufficient knowledge of coal's reactions so that its behavior can be predicted under process conditions. The previous program conducted by the contractor was focused on an accurate description of the devolatilization process, since it is devolatilization which is the first step in gasification and is the process which controls the amount and reactivity of the char and the amount and time of volatiles release. That program succeeded in providing an accurate

description for the time dependent yield and composition of volatiles during devolatilization based on the functional group composition of the coal. The program obtained accurate kinetic rates for devolatilization by measuring particle temperatures using a new Fourier Transform Infrared (FT-IR) Emission/Transmission (E/T) spectroscopic technique developed under the program. The rates for primary pyrolysis are the highest which have been measured below 800°C, and suggest that most previously reported rates have been too low due to over-estimation of the particle temperatures. The previous program identified two remaining areas which are important to an accurate description of coal devolatilization, for which insufficient data and models are available. These are the optical and thermal properties of the coal during devolatilization and the reactive properties of the char produced in devolatilization. It is these two areas which are the focus of the current project.

It is expected that the understanding of devolatilization processes developed in this program will permit improved control over coal's variable and sometimes unpredictable behavior, and therefore result in:

- Improved choice of feedstock
- Reduced requirements for expensive testing
- Better plant design and control
- Reduced plant shutdown
- Lower pollution levels

## 5. PROJECT DESCRIPTION:

During the past year, the project has emphasized the measurement of coal optical properties and char reactivity and the development of a general pyrolysis model. These topics are discussed below.

### COAL OPTICAL PROPERTIES

Knowing the spectral emittance of coal is important for three reasons: 1) The emissivity of the coal particle determines the radiative energy absorbed by a coal particle during particle heating, (the emissivity is the weighted average of the spectral emittance over the radiation spectrum of the reactor); 2) The emittance of char determines the radiation loss of the particle when it is hot and; 3) The spectral emittance needs to be known to determine particle temperatures by pyrometric techniques.

A new method for measuring coal emissivities has been developed by the contractor. The method, which employs FT-IR emission and transmission spectroscopy has been described in a number of publications (Best, et al., 1986; Solomon, et al., 1986, Solomon, et al., 1987 and 1987a).

Measurements were made of coal spectral emittance as a function of particle size. In the -200 mesh particle size range, characteristic of pulverized coal, the emittance is non-gray-body, and is related to the coal's particle size and composition. The results suggest that previous calculated literature values of emissivity based on measured values of the complex index of refraction for coal are in error.

The suggestion that previous results have been in error is surprising and requires careful scrutiny. Direct measurements of coal emittance have been recently made at Sandia National Laboratory (Baxter, et al., 1987). Figure 1 compares the emissivity measured for a Pittsburgh Seam coal at AFR and at Sandia. Both spectra display the chemical features of the coal and are in fair quantitative agreement over most of the spectrum. The Sandia spectrum cuts off above 3500 $cm^{-1}$ due to noise in the spectrum. The agreement of the Sandia results support the conclusion that previous index of refraction values were in error by more than a factor of 10.

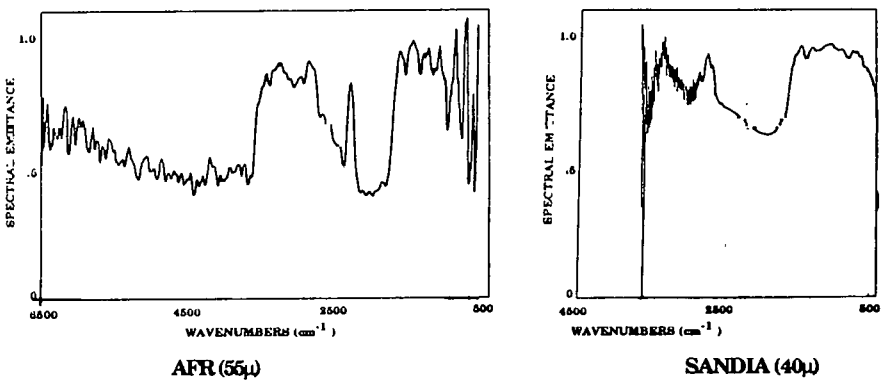



**Figure 1. Spectral Emittance of Pittsburgh Seam Bituminous From Two Laboratories reprinted with Permission from the authors.**

## CHAR REACTIVITY

Recent studies of char reactivity (Mahajan and Walker, 1978; Essenhigh, 1981; Smith, 1982; Wells, et al., 1982; Ashu, et al., 1978; Essenhigh and Farzar, 1982; and Nsakala, et al., 1982) demonstrate that there is a wide variation in observed reactivities with rank and char formation conditions. This section reports on a study of the reactivity of a set of chars from a variety of different coals prepared by pyrolysis at heating rates between 0.5 and 20,000°C/sec to temperatures between 400 and 1600°C. A new technique was developed in which the weight loss was measured while the sample was heated at a constant heating rate in the presence of air. The technique, which has been presented previously (Solomon, et al., 1986a) determines a critical temperature, $T_{cr}$, to achieve a common reaction rate for each sample. This section presents data for the variation of reactivity with char formation conditions and char properties (including surface area, hydrogen concentration, mineral concentration, and molecular order).

Chars for this study were prepared from the 200 x 325 mesh sieved fractions of Zap, North Dakota lignite, Montana Rosebud subbituminous, Illinois No. 6, Kentucky No. 9, and Pittsburgh No. 8 bituminous coals. Sample properties are given in Serio, et al., 1987 and Solomon, et al., 1986a. The chars were prepared by pyrolysis in an inert atmosphere in one of four reactors as discussed in Solomon, et al., 1986a. Samples of coals were demineralized according to the technique of Bishop and Ward, 1958.

Figure 2 summarizes the results for chars from the five coals tested. The critical temperature ($T_{cr}$), which varies inversely with reactivity, is plotted as a function of the (daf) hydrogen content, which is used as a measure of the extent of pyrolysis. For each char type, there is a trend for increasing $T_{cr}$ (decreasing reactivity) with decreasing hydrogen. Most of the change occurs below 2 1/2% hydrogen, after the evolution of aliphatic hydrogen is complete. $T_{cr}$ appears to vary primarily with the concentration of aromatic hydrogen. This could be due to a variation in the active site concentration, correlated with ring condensation accompanying the elimination of aromatic hydrogen. There does not appear to be any drastic effects due to heating rate for low rank coals which contain minerals, as chars for a wide range of conditions all fell along the same curve. However, the reactivity of these coals is dominated by mineral catalysis. The results for bituminous coals and demineralized low rank coals do not exhibit the same degree of heating rate independence.

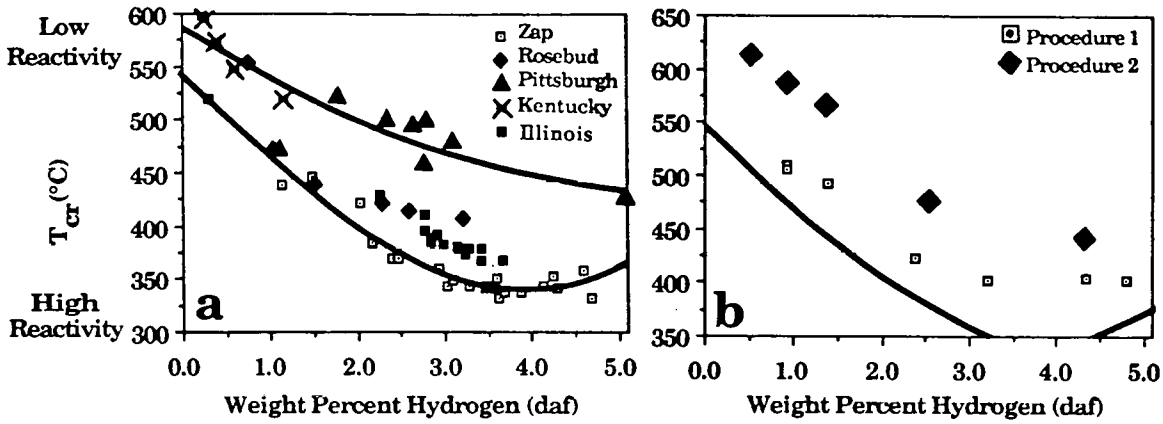



**Figure 2. Comparison of Reactivity as a Function of Hydrogen Concentration. $T_{cr}$ Varies Inversely with Reactivity. a) Chars from Five Coals. b) Chars from Demineralized Zap Lignite (data), Chars from Raw Zap Lignite (line from Fig. a). Procedure 1 was a Modification of the Bishop and Ward, 1958 Technique with a Lower HF Strength. Procedure 2 was the standard Bishop and Ward Technique.**

The upper solid line in Fig. 2a is a "best fit" line drawn through the data for Kentucky No. 9 and Pittsburgh Seam bituminous chars. The lower solid line is a best fit line drawn through the Zap lignite chars. It is known that the vertical displacement of the curves is at least partly due to the variations in catalytic activity of minerals. The most reactive chars are for the Zap lignite which are known to have a high Na and Ca content. The results for $T_{cr}$ versus daf hydrogen content for Zap chars demineralized by two procedures are shown in Fig. 2b. In both procedures, the Bishop and Ward, 1958, technique was used, except that in procedure 1 the HF was used at one-fifth normal strength. It is apparent that this produced a lower extent of demineralization, which was verified by XPES analysis. Both data sets are compared to the "best fit" line drawn through the Zap data in Fig. 2a. It is evident that reactivity results for the Zap demineralized by procedure 2 are similar to chars from bituminous coals (see Fig. 2a). Samples of Pittsburgh Seam and Illinois No. 6 bituminous coals were also subjected to demineralization but did not exhibit as dramatic an effect.

A systematic study of the variations of reactivity with coal rank has been performed. Figure 3 presents a correlation between the oxygen content in the parent coal and the reactivity of char produced in the TGA by heating in nitrogen at 30°C/min to 900°C. The open squares are results obtained for raw coals, the solid squares show the results for demineralized coals. The results suggest that the decrease in reactivity with decreasing rank is a property of the organic matter at high rank (less than 8% oxygen) and a property of mineral matter at low rank (greater than 8% oxygen).

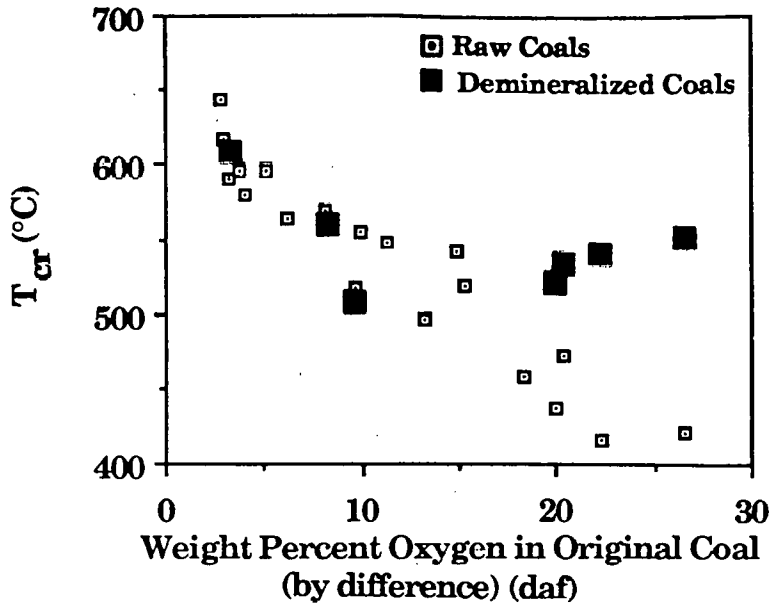



**Figure 3. Variation of Reactivity with Coal Rank for Chars Prepared by Heating in Nitrogen at 30°C/min to 900°C.**

Chars have been studied by x-ray diffraction to examine the dependence of reactivity on the molecular order in the char. For chars prepared at a constant heating rate, it is observed that molecular order (determined from the area under the **(10)** line) is proportional to $T_{cr}$ (i.e., increasing order, decreasing reactivity).

**MODELING COAL PYROLYSIS**

A major goal of this program has been the development of accurate models for coal devolatilization which treat heat transfer, mass transfer, and chemical kinetics. In accordance with this goal, extensive work has been done to develop a Functional Group (FG) model for chemical kinetics as well as models of heat and mass transfer. A summary of pyrolysis results for several coals in several reactors with comparisons to predictions of the Functional Group (FG) model was assembled for the new ACS Journal of Energy and Fuels (Serio, et al., 1987). The FG model provides accurate prediction of pyrolysis yields for heating rates of 0.5°C/sec to 20,000°C/sec, temperatures of 300°C to 1600°C and coal ranks from lignite to bituminous.

A second publication, Solomon and Serio, 1986, prepared for the NATO Workshop of "Fundamentals of Physical-Chemistry of Pulverized Combustion" reviewed the coal pyrolysis literature to draw conclusions about the rates of heat transfer, mass transfer and chemical kinetics in pyrolysis. The paper concluded that variation in heat transfer rates coupled with imprecise knowledge of coal particle temperature is responsible for much of the variation in pyrolysis rates reported in the literature.

The major work on modeling during the past year was an experimental and theoretical effort to develop a general model of coal pyrolysis applicable to all ranks. The model combines two previously developed models, a Functional Group (FG) model (Solomon, et al., 1982; Solomon and Hamblen, 1985; Serio, et al., 1987) and a Devolatilization-Vaporization-Crosslinking (DVC) model (Solomon and King, 1984; Squire, et al., 1986; Solomon, et al., 1985; Solomon, et al., 1987b; Solomon, et al., 1987c). The FG model describes the formation of gas species and the DVC model, the formation of tar. The major rank dependent phenomenon is the amount and rate of crosslinking. Crosslinking controls the yield of tar and molecular weight distribution in the tar and char. In principal, the amount and molecular weight distributions of molecular fragments in the char determines the char's viscosity (van Krevelen, 1976), which in turn controls the transport of volatiles within the particle. A major simplification of the combined model is that the crosslinking is correlated with the evolution of $CO_2$ and $CH_4$ (one crosslink is formed for each molecule evolved) (Solomon, et al., 1987b) and these gas evolutions are predicted by the FG model.

In the DVC model, the parent coal is represented as a two-dimensional network of monomers linked by strong and weak bridges as shown in Fig. 4a. The network consists of condensed ring clusters (monomers) linked to form an oligomer of length "n" by breakable and non-breakable bridges. The clusters are represented by circles with molecular weights shown in each circle. The breakable bridges (assumed to be ethylene) are represented by single lines, the unbreakable bridges by double lines. "m" unbreakable crosslinks are added randomly so that the molecular weight between crosslinks corresponds to the values reported in the literature.

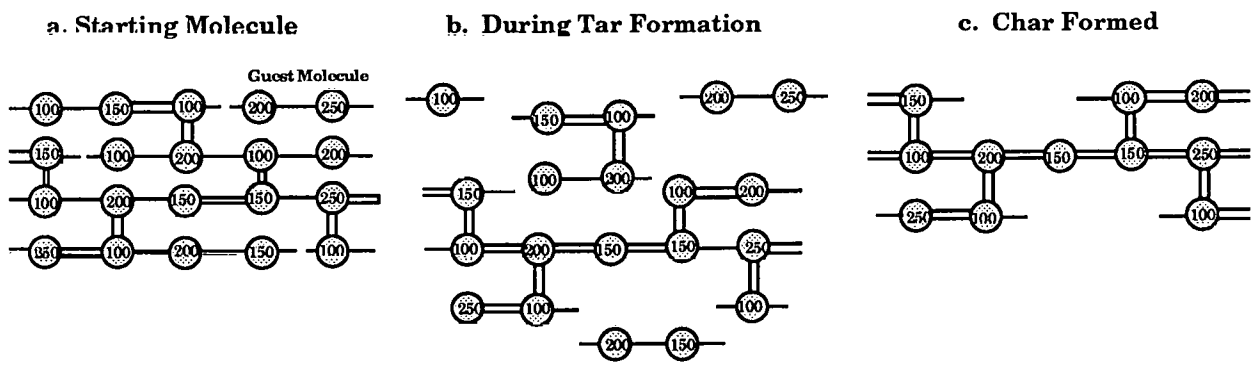



**Figure 4. Representation of Coal Molecule in the DVC Simulation. The Circles Represent the Monomers (ring clusters and peripheral groups). The Molecular Weight Shown by the Numbers is the Molecular Weight of the Monomer Including the Attached Bridges. The Single Line Bridges are Breakable and can Donate Hydrogen. The Double Line Bridges are Unbreakable and do not Donate Hydrogen.**

Unconnected "guest" molecules (the extract yield) are obtained by choosing the value of n. The ratio of ethylene bridges (two donatable hydrogens per bridge) to non-breakable bridges (no donatable hydrogens), which determines the value for total donatable hydrogen, is employed as an adjustable parameter. The model employs a Monte Carlo technique to simulate the combined depolymerization, transport and crosslinking events.

Figure 4b shows the molecule during pyrolysis. Some bonds have broken, other bonds have been converted to unbreakable bonds by the abstraction of hydrogen to stabilize the free radicals and new crosslinks have been formed. Char formation in the DVC model can occur by crosslinking at any monomer to produce a two-dimensional crosslinked network.

Figure 4c shows the final char which is highly crosslinked with unbreakable bonds and has no remaining donatable hydrogen.

Work has been performed to define the reactions which cause crosslinking (Solomon, et al., 1987b). Under the assumption that the crosslinking reactions may also release gas species, the molecular weight between crosslinks or crosslink density (estimated using the volumetric swelling technique developed Green, et al., 1984) was correlated with the observed evolution of certain gas species during pyrolysis. Likely candidates are $CO_2$ formation from carboxyl groups and methane formation from methyl groups. Both reactions leave behind free radicals which can be stabilized by crosslinking. Condensation of hydroxyl groups to form water and an ether link is also a possible reaction.

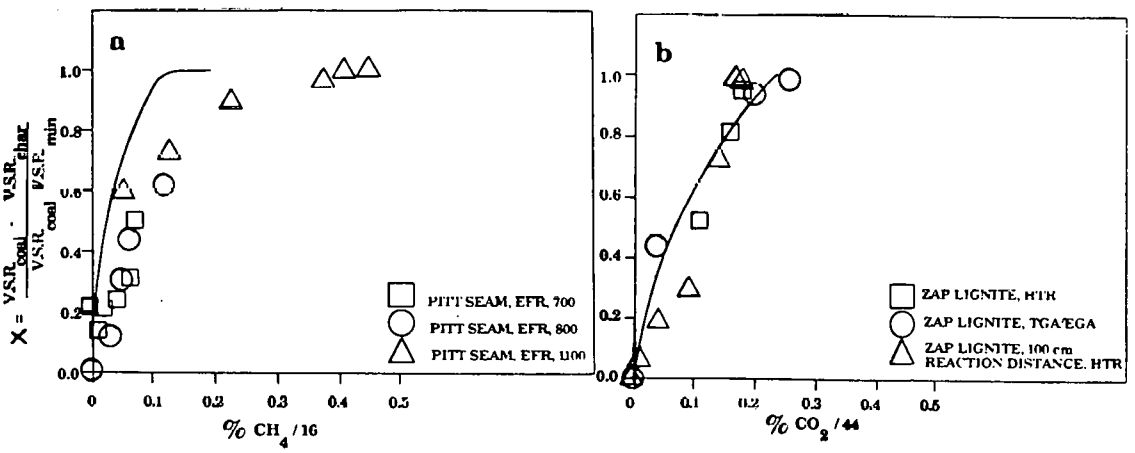



**Figure 5. Measured and Calculated Volumetric Swelling Ratios for Coal and Chars. a. Pittsburgh Seam Bituminous Plotted Against the Methane Yield and b) Zap North Dakota Lignite Plotted Against $CO_2$ Yield. $V.S.R._{min}$ is the Value Achieved when Crosslinking is Complete.**

Figure 5, from Solomon, et al., 1987b, presents the loss of swelling in pyridine plotted against $CO_2$ evolution for a Zap, North Dakota lignite and against $CH_4$ evolution for a Pittsburgh Seam bituminous coal. The abscissa is a parameter X which is the change in volumetric swelling ratio (VSR) between coal and char divided by the maximum change. X = 0 for coal and 1

for fully crosslinked char. On a molar basis, the evolution of $CO_2$ from the lignite and $CH_4$ from the bituminous coal appear to have similar effects on the VSR. No correlation was observed between the VSR and tar yield for either coal.

The combined FG and DVC model was used to predict the data of Fig. 5. The Functional Group parameters, kinetic rates, and molecular structure constants for the two coals were published (Serio, et al., 1987 and Solomon, et al., 1987b).

The swelling ratio is predicted using the Flory-Rehner equation discussed by Nelson, 1983 from the molecular weight between crosslinks, $M_c$ determined in the model. The agreement between theory and experiment is good for the $CO_2$. For the $CH_4$, the model predicts a more rapid decrease in the swelling ratio than is observed. Here, the crosslinking occurs during tar formation and the model does not include the effect of bond breaking which would increase $M_c$ and hence the swelling ratio.

A second prediction made by Solomon, et al., 1987b, with the combined model is for the data of Fong, et al., 1986 for pyrolysis of a Pittsburgh Seam bituminous coal. Figure 6 compares the data (squares) of Fong's Fig. 2 with the predictions of the model. The extractable material is assumed to be all molecules in the char with molecular weight less than 2500. The agreement is excellent. The agreement is also excellent for the data presented in Fong's Fig. 1d (holding temperature = 745°C). Agreement at lower holding temperatures of 540°C (Fig. 1a) and 585°C (Fig. 1b) was only fair, with overprediction of the ultimate tar yield. The lack of agreement appears to be due to the lack of transport model for tar molecules within the particle. The addition of internal transport is being considered under METC contract No. DE-AC21-86MC23075.

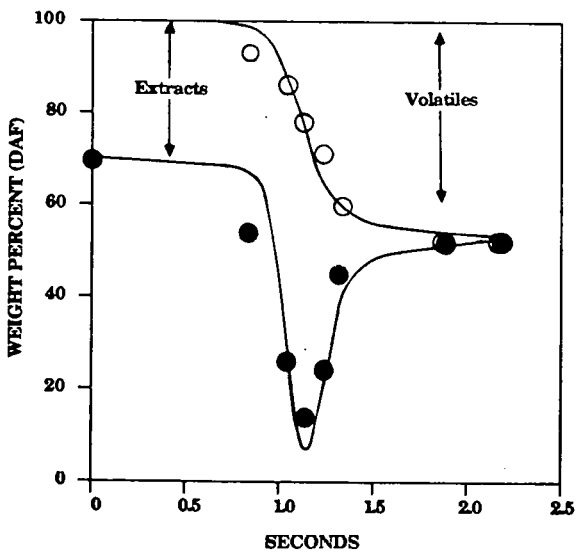



**Figure 6. Comparison of FG-DVC Model Predictions to the Data of Fong, et al. 1986.**

## 6. RESULTS/ACCOMPLISHMENTS:

- Applied the FT-IR E/T method developed by AFR to measure coal emittance as a function of particle size. The results suggest that previous calculated coal emissivities have been in error.
- Developed a new method of measuring char reactivity and determined char reactivity for a wide variety of chars.
- Established general correlations between reactivity and coal rank, extent of pyrolysis, and molecular order.
- Developed an accurate general model of coal pyrolysis.

## 7. FUTURE WORK:

- Measurements of pyrolysis in a transparent wall reactor.
- Measurements of coal emissivity as a function of particle size and rank.
- Modeling of heat transfer and pyrolysis in the entrained flow, transparent wall and heated tube reactors.
- Improvements and validation of thermal and optical properties submodels.
- Measurements of $CO_2$ reactivity, and reactivities of demineralized and preoxidized coal.
- Correlation of reactivities with the order in the crystal structure as determined from x-ray diffraction.

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**STUDY OF THE EFFECTS OF SOOT, PARTICULATE AND OTHER CONTAMINANTS ON MOLTEN CARBONATE FUEL CELLS FUELED BY COAL GAS**

1. CONTRACT NUMBER: DE-AC21-84MC21154

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CONTRACTOR PROJECT MANAGER: A. Pigeaud

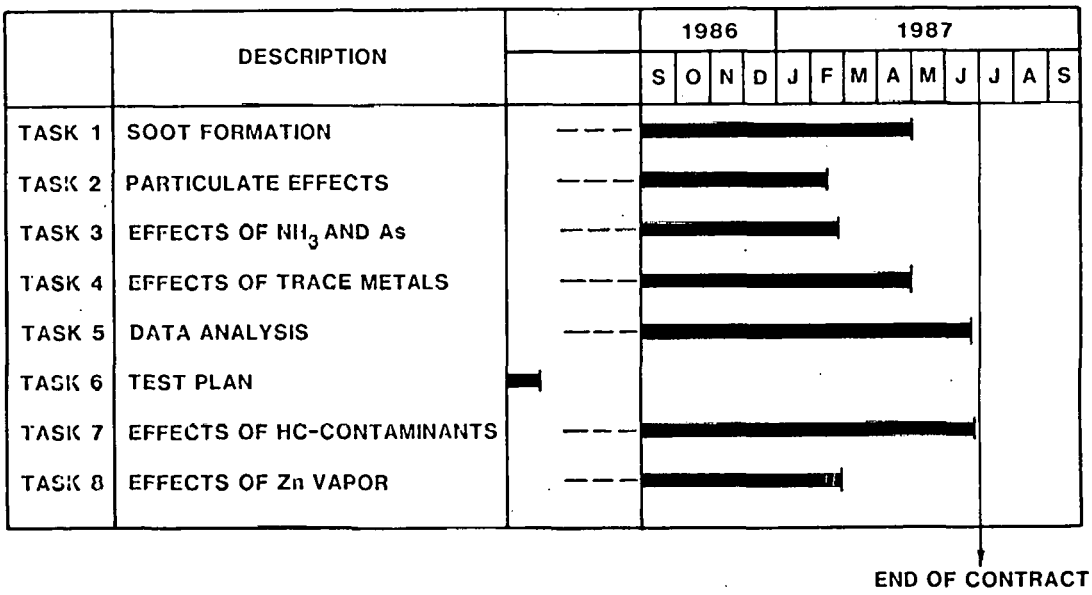
PRINCIPAL INVESTIGATORS: J. Klinger
H. Kennedy

METC PROJECT MANAGER: S.C. Jain, COTR

PERIOD OF PERFORMANCE: August 28, 1984 to June 30, 1987

2. SCHEDULE/MILESTONES:

1987 SOOT AND PARTICULATES PROGRAM SCHEDULE




3. OBJECTIVES:

The objective of the 34-month program at Energy Research Corporation (ERC) now being terminated was to study the effects of coal-gas derived contaminants on the performance and endurance of the Molten Carbonate Fuel Cell (MCFC). Additional goals were to evaluate soot deposition due to unstable fuel compositions at typical MCFC temperatures, as well as tar and soot

formation due to small amounts of unsaturated and cyclic hydrocarbon contaminants. The goals of this study with respect to contaminant effects were to evaluate, set limits, and suggest clean-up methods for particulates, arsenic, ammonia and trace amounts of volatile metal compounds, including zinc, mercury and Pb-vapor. The present study is one of the first integrated projects to look at the entire spectrum of soot, particulates and contaminant effects both from a short-term fundamental, as well as a longer-term experimental, in-cell, perspective.

4. BACKGROUND STATEMENT:

The Molten Carbonate Fuel Cell (MCFC) System represents a highly efficient alternative mode of power generation from both coal-derived and natural gas. However, there is a concern that the molten carbonate fuel cell components basically consisting of anode, cathode and electrolyte matrix may react with contaminants present in coal-derived fuels (TRW 1981). The historical development and technical progress made in improving the molten carbonate fuel cell over the last two decades have been discussed in several recent review articles (Selman and Maru 1983, Baker 1984, Maru et al. 1984). To be economically competitive and commercially viable, endurance of the individual fuel cells as well as the stack structures must be relatively long. Hence, both the immediate and the cumulative effects of contaminants that may be present in fuel need to be understood.

A lifetime of approximately 40,000 hours or five years has been considered desirable for economic operation of the MCFC using coal-derived gases, whereas a life of 25,000 to 30,000 hours appears reasonable for internal reforming cells operating at considerably higher efficiency and usually on natural gas sources. Considerations of pollution of the environment due to the presence of contaminants, and the cost factors involved in gas cleanup are also concerns that must be addressed. This has therefore entailed determining, by both out-of-cell studies (usually TGA) and in-cell testing, the tolerance limits for soot formation, or the presence of dust, or various contaminants in standard MCFC gas compositions. Table 1 illustrates the levels of some of the more serious contaminants that can result from a variety of coal types when combined with different gasifier systems, and what remains after a first stage of hot-gas cleanup when using the zinc ferrite system. A preliminary comparison with tolerance levels estimated from this program is provided in the last column of this table.

5. PROJECT DESCRIPTION:

SOOT FORMATION

Carbon deposition in isothermal, thermogravimetric experiments from unstable fuel gas mixtures using a TGA apparatus were presented at the previous Contractor's Conference (No. 6). Significant progress was reported at that time in identifying the various parameters affecting soot formation. One important condition which strongly affects the kinetics of 'free carbon' deposition due to the Boudouard reaction, $2CO \rightarrow CO_2 + \underline{C}$ , is the condition of the available catalyst surface, which is usually a porous nickel plaque (commonly used as the anode) or the stainless steel of the

Table 1. Contaminants in Coal Gases Related to MCFC Tolerance Levels.

| | HYGAS FLUIDIZED BED | Koppers-Totzek ENTRAINED BED | LURGI FIXED BED | METC (raw gas) FIXED BED | (Cleaned Gas) $ZnFe_2O_4$ BED | MCFC - Non IR† TOLERANCE |
|---|---|---|---|---|---|---|
| Max. Prod. Temp., °C | 940 | 1900 | 750 | 1300 | <600 | 650 |
| Pressure, psi | O2-blown, 1165 | O2-blown, 15 | O2-blown, 435 | Air-blown, 220 | Regenerative, 150 | 15 psi |
| Product. Gas, °C | ---- | 1500 | 600 | 650 | <700 | Feed at >600 |
| Methane, Vol. % | 18.6 | 0.1 | 11 | 3.5 | 3.5 | <15 |
| Coal Type | Pittsburgh #8 | Bituminous, Eastern | Sub-Bituminous Navajo | Sub-Bituminous New Mexico | Humidified Output) | Cleaned Coal-gas |
| **Sulfur, ppm** (Total $H_2S$, COS, $CS_2$, mercaptans) | 12,000 | 3,500 | 2,000 | 5,300 | <10 | ~1 ($H_2S$) |
| **Halogens, ppm** | 300-4000 | 366 | 200 | 700 | 500 | <10 est. |
| **Trace Metals, ppm** | | | | | | |
| - As | 0.8 | 5 | 2.0 | | | <1 |
| - Pb †† | 5.0 | 2 | 0.8 | 2 | 1.7 | <1 |
| - Hg †† | 0.1 | | 0.4 | | | Tolerant |
| - Zn | 13. | | 0.4 | | 140 | <20 @ 30% fuel utilization |
| **$NH_3$, Vol%** | 0.5 | 0.11 | 0.4 | 0.44 | 0.25 | <0.5 |
| **Hydrocarbons, Vol %,††** | | | | | | |
| - $C_2H_6$ | 0.7-1.6 | | 1.0 | 0.3 | | Tolerant |
| - $C_2H_4$ | | | | | | <0.25 |
| - $C_2H_2$ | | | | | | <0.2 |
| - Benzene | | | | | | <0.5 |
| - Tar Oil | | | 0.09 | | | - |
| - Aromatics, e.g., $C_{10}H_8$ | | | | | | <0.5 |
| - Crude Phenols | | | 0.014 | | | TBD |
| **Particulates, g/l** | | 0.015 | 0.016 | 0.058 | 0.01 est. | <0.1 *for large particles (>3 μm) |

† - Present studies are not addressing the internal reforming (IR) type of MCFC system. MTO478

* - A high tolerance is allowable, because large dust particles do not appear to reach fuel gas distribution passages or anode pores.

†† - Based on contaminant interaction with electrolyte-free surfaces. More tolerance expected in presence of carbonate wetting.

MCFC hardware. Two critical regions of soot formation were established depending on the state of surface wetting of these catalytic materials with molten carbonate electrolyte. Figure 1 illustrates the critical regions or zones on a C-H-O diagram, showing how they relate to each other under carbonate-wet and carbonate-dry conditions. This figure also shows that the regions are located above and below the theoretical (i.e. thermodynamic) line for equilibrium soot formation as determined by the combined

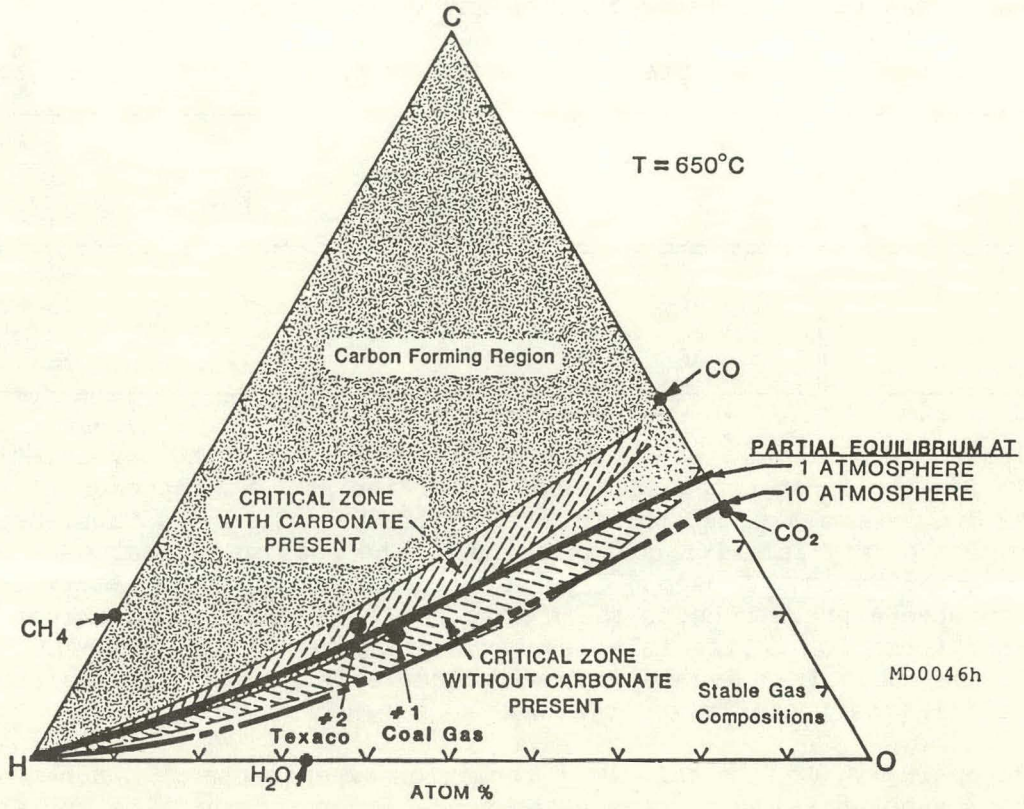



Figure 1. Carbon Formation Boundaries With And Without Carbonate Melt Present. Also Shown Are Partial Equilibrium Lines For Boudouard And Water Gas Shift Equilibrium At 1 And 10 Atm..

Water-Gas and Boudouard reactions at 1 atmosphere gas pressure. It is seen that soot formation from gas compositions that lie nominally in the carbon forming region are suppressed when carbonate surface wetting occurs. And that carbon deposition is accentuated even when gas compositions lie nominally in the stable region below the partial equilibrium line but are in contact with dry, highly active, catalyst surface. The distance that these zones should be shifted downwards when a total gas pressure of 10 atmospheres instead of 1 atm. occurs may be estimated from the difference between the solid and dot-dash, theoretical equilibrium lines at 1 and at 10 atm. pressure.

In-cell soot depostion experiments have been performed in 300 $cm^2$ bench-scale fuel cells to verify these empirically determined relationships both

at 1 and 5 atmosphere pressure. Carbon deposition (and removal) during cell operation was monitored using a system of 5 differential pressure transducers strategically located so as to detect flow restrictions in the innermost fuel cell passages. Two fuel gas mixtures were selected for these tests, (as shown in Table 2) illustrating the typical ranges of composition which simulate approximately a Texaco, oxygen-blown, coal-gas. Figure 1 shows the location of these fuels with respect to the atom % of carbon, hydrogen and oxygen present in the mixtures and compares them to the zones where carbon formation may be expected.

Table 2. Texaco Type Coal Gas Compositions (Water-Gas Shifted).

| | mole % | | | |
|---|---|---|---|---|
| Gas # | $H_2$ | $CO_2$ | $H_2O$ | CO |
| 1 | 37 | 22 | 21 | 20 |
| 2 | 46 | 14 | 12 | 28 |

Indeed, Coal Gas #1 did not form soot deposits in the dry inlet system or inside the first bench-scale cell operated at 1 atmosphere. But Coal Gas #2 did severely plugg the inlet port of the cell and without depositing carbon on any interior channels inside the fuel cell that were wet with carbonate melt. A second bench-scale cell is now being operated at 5 atmosphere pressure with these same fuels. Initial indications are that soot formation in the inlet port and preheater system external to the cell is presently less severe following some enlargements and modifications made in the heater/mixer system.

Accordingly, the in-cell soot formation experiments in bench-scale MCFC's have substantially confirmed the correlations and critical zones established by our initial TGA work. Using the C-H-O plotting technique and a computer method for rapid calculation of composition points and equilibrium lines, good estimates and predictions of soot formation can now be made over a large range of gas compositions and for a wide variety of fuel cell temperature, pressure and wetting conditions.

PARTICULATE EFFECTS

Particulates settling out of fuel gas as a function of particle size, gas velocity, and dust loading involves several mechanisms of deposition that require the knowledge of a considerable number of parameters. Calculations for particulate deposition from laminar gas flow were first performed, making allowance for both gravitational settling and Brownian diffusion motion. The computer code for these calculations was developed at ITT (Gidaspow, 1986) and is based on a generalized hydrodynamic flow model. Specifically, it was shown that the deposition rate inside small anode passages of particles <1 μm in diameter depends mainly on Brownian diffusion, while gravitational settling primarily is a force which affects particles >3 μm in diameter which settle out well before the smallest

particles deposit. This has been shown to be consistent with, and closely compares to, our experience with in-cell testing described below.

Therefore, it is suggested that to simulate deposition of very fine particles, which are the main concern in anode channel and pore clogging, a greatly simplified flow kinetic approach be used instead of the complete hydrodynamic flow model which covers all particle sizes. The simple flow kinetic or continuum approach assumes that particles move approximately the way large gas molecules do; only motion perpendicular to the gas flow direction (random walk diffusion) and along the direction of plug flow should affect the very smallest of particles in a gas stream. As illustrated in Figure 2, with such lateral diffusion in the y-direction and forward motion in the x-direction (depending on the overall gas velocity), only a portion of submicron-sized particles will contact the channel walls inside a fuel cell and consequently have a chance to deposit.

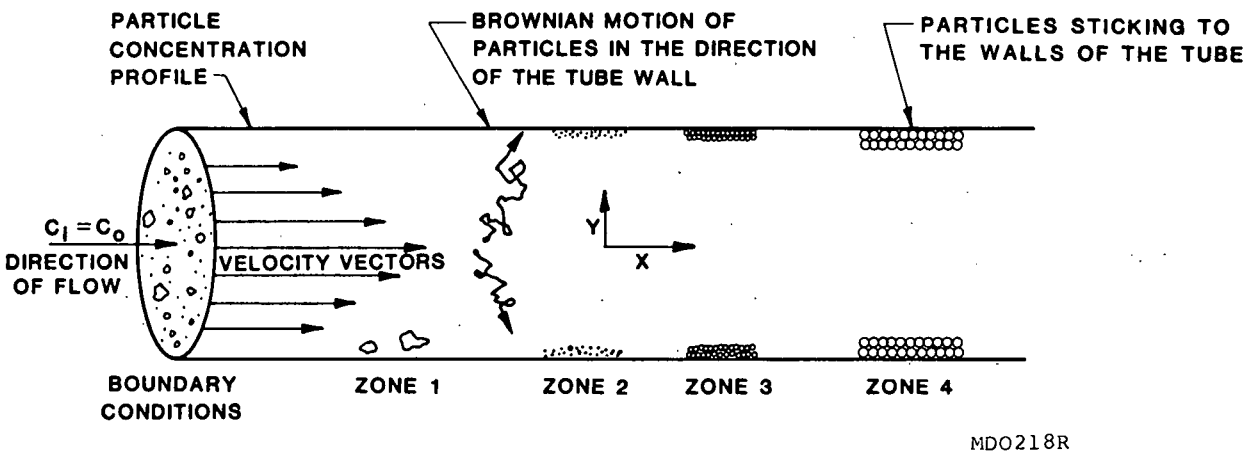



Figure 2. Schematic of Particle Deposition In Hot Flow Tube.

Boundary condition along the anode channel walls, expressed in terms of an empirically determined sticking coefficient, may be used to determine the number and size of the small particles that remain when they come into contact with the channel walls. Large particles (>1 μm) however, are expected to settle out much earlier (e.g. Zone 1) in the gas conduits or manifolds of a stack, primarily as a result of gravitational forces. Therefore, the larger particles are not expected to even reach really sensitive, internal fuel cell passages and anode channels which are our main concern. When particles deposit on cell hardware or on the electrolyte films present, chemical or dissolution reactions may also occur which then will clearly predominate over any momentary physical sticking or deposition; hence much more severe plugging behavior can result inside a cell when particles are reactive instead of inert.

The effect on the performance of a 300 $cm^2$ bench-scale MCFC caused by lithium aluminate particles injected in the fuel supply was investigated. In contrast to previously described experiments with very fine, reactive, ZnO dust, this represented a test with chemically 'inert' particles of approximately the same size range as previously used. Particle feed rate

of the $LiAlO_2$ dust (4 μm mean particle diameter) was set at 0.5 mg/ℓ into a simulated METC-type coal gas flowing at an average of 2.3 ℓ/min. Hence, rate of dust addition to the cell during periods of contaminated gas flow was at about 1.2 mg/min.. A total of 4.4 gram of $LiAlO_2$ dust was fed to the cell which during initial short injection periods (1.5 g) hardly affected its performance. When major quantities of dust were injected later on over longer, continuous periods of addition, cell performance was strongly affected although the cell resistance and open circuit voltage remained relatively unchanged. Pressure drop across the cell, however, did steadily increase during the later dust injection periods and plugs of deposits could occasionally be cleared by probing the intake port section of the cell where the majority of dust particles appeared to accumulate.

Thus, performance decay without any changes in OCV, resistance, wet seal or cross-over could not be explained except by fuel starvation of the anode due to this plugging as was also indicated by the increasing pressure drop across the cell. Upon disassembly, after 3700 life hours, it became abundantly clear that most of the particles fed to the cell had settled out in the deep gas distribution groove in front of the anode channels which themselves were quite clean and unaffected. The conclusion could therefore be drawn that blockage primarily occurred before the gas could enter the anode passages and hence this was the cause of the cell decay. This is entirely consistent with previous theoretical conclusion that dust with a particle distribution from 1 to 8 μm can not reach the internal passages of a fuel cell or be able to cause actual anode pore clogging. However, experimental investigations and flow kinetic modeling should be continued to determine the effects of extremely fine, submicron, particle contaminants that might still be present in fuel gas.

EFFECTS OF AMMONIA

After the initial investigations of arsenic effects reported last year, the consequences of ammonia as a contaminant on fuel cell performance have also been studied. It was quickly established from equilibrium thermodynamics that more than 99% of this gas should decompose to nitrogen and hydrogen at 650°C provided the reaction $2NH_3 \rightarrow N_2 + 3H_2$, with an equilibrium constant of $K(650^\circ) = 7.2 \times 10^5$, is rapid. Namely, in an exit gas stream from a low Btu fuel (50% $N_2$) with 20% hydrogen remaining, the equilibrium concentration for an initial 1 vol.% $NH_3$ containing fuel should rapidly decline to <75 ppm ammonia. However, experimentally this was not found to be the case. G.C. analysis of the entry and exit gas showed that, on the average, only 5% of the ammonia being added to the fuel either was being absorbed in the cell or decomposed to $N_2$ and $H_2$. Namely, G.C. sampling of the anode exit gas was able to detect an average of 4500 ppm unreacted $NH_3$ in the effluent gas while 0.5 vol% $NH_3$ was being added. Although it was originally thought, as the literature indicated, that ammonia would decompose inside the cell in the presence of such a major amount of catalytic nickel surface (Roy et al. 1975), it is now believed that this bimolecular decomposition reaction does not readily occur, 1) because of the very dilute $NH_3$ concentrations being considered, and 2) because of the lessened catalytic activity of nickel surface as a result of carbonate wetting. The fact that not all the ammonia decomposed

is evident from the cell resistance increases as shown in Figure 3 which indicate that an interaction must be occurring during periods of ammonia addition.

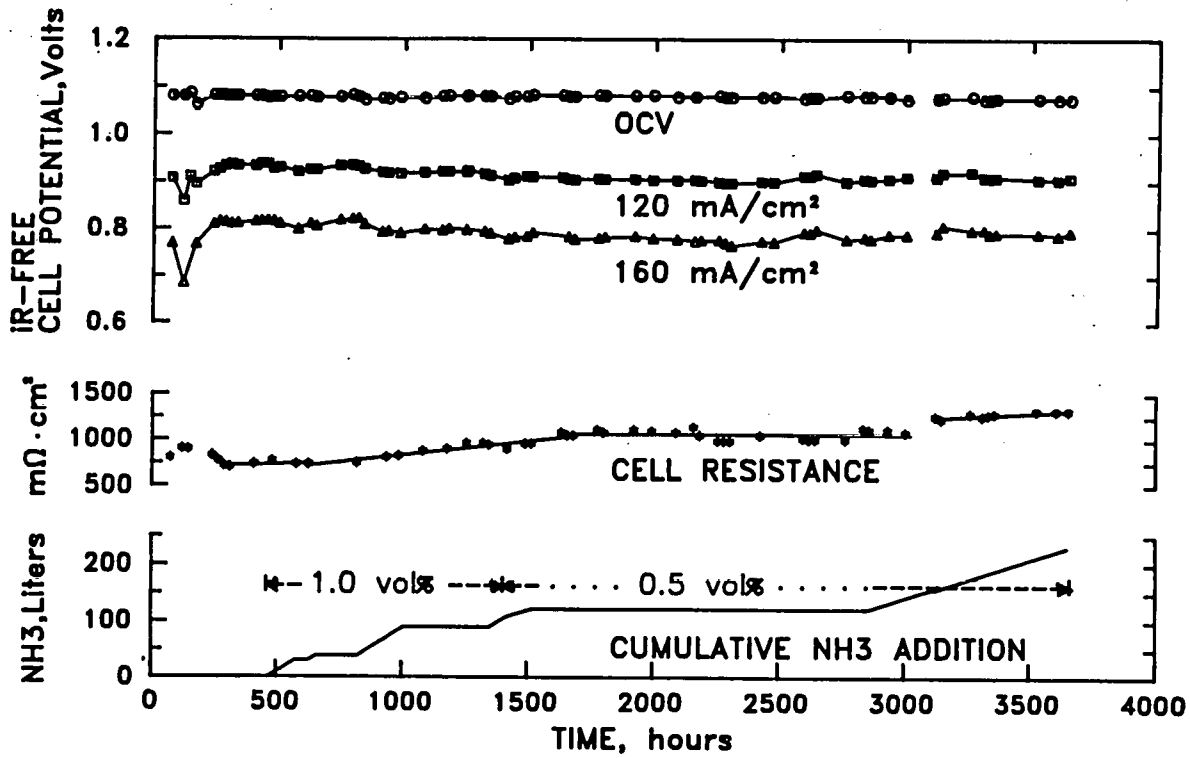



Figure 3. Lifegraph Of Fuel Cell With Ammonia Addition.

Even though in the early stages of $NH_3$ addition the cell resistance appeared to recover during several contaminant-free periods, this was not the case due to the cumulative effects later on in its life. Anode polarization as indicated by iR-free performance did not seem to be affected by the presence of ammonia. After disassembly upon termination, the cell looked extremely clean and did not show any visual signs of either reaction with the anode, or corrosion of the plenum surfaces. But post-test analyses have now indicated that much of the ammonia which did not exit the cell, was indeed absorbed in the electrolyte; 2150 ppm as nitrogen was analyzed in the carbonate portion of the electrolyte matrix. It is suggested that this unusually high elemental nitrogen content in the electrolyte may consist of a form of $NH_3$/salt-complex or simply as a free ammonium ion in melt solution. Nitrogen gas as such in electrolyte is usually not detected as a dissolved species when medium or low Btu gases containing much larger amounts of nitrogen (e.g. from air-blown gasifiers) are passed through a fuel cell.

The tolerance limit for ammonia can thus be suggested as <0.5 vol.% following these preliminary experimental results which indicate that overall cell performance can decay in a relatively short period when this contaminant is present in fuel gas. Coal-gas can on occasion contain up to 0.5 vol.% ammonia.

EFFECTS OF TRACE METALS

The objective of this task was to investigate the effect on fuel cell components of a few trace metal impurities that may be present to a fair extent in coal gas. Based on a critical review of the published literature, three contaminants viz. lead, mercury and tin, were considered to be of concern (Park and O'Brien 1980, TRW 1979-81, Vidt et al. 1982). Two of these contaminants, mercury and lead, were selected for critical screening by the TGA analytical technique at 650°C and at atmospheric pressure because of the possibly higher reactivities of these elements with fuel cell components.

Isothermal (650°C) TGA experiments with lead as the contaminant at two concentrations in various gas mixtures were performed with the weight changes of the nickel anode sample being continuously monitored. Effects were first investigated on a dry nickel coupon with Pb vapor at 1 and 2 ppm concentration in high and medium Btu fuel. Experimental results are summarized in Table 3, showing that the Pb vapor contaminant in these fuels did increase nickel sample weight. The weight increases when normalized for the run duration and Ni-coupon weight, appear to be roughly

Table 3. Coal Gas Compositions Used In Trace Metal Contaminant Studies With Observed Ni Sample Weight Gains.

| Gas Composition (Water-Gas Equilibrated) mole % | | | | Pb vapor concentration (ppm) | Weight gain (mg of Pb/g of sample/hr) | Run Time (hours) | Fraction of Total Pb |
|---|---|---|---|---|---|---|---|
| $H_2$ | $CO_2$ | $H_2O$ | CO | | | | |
| 21 | 31 | 39 | 9 | 1.0 | 0.026 | 40 | 0.30 |
| 25 | 33 | 25 | 17 | 1.0 | 0.030 | 66 | 0.29 |
| 25 | 33 | 25 | 17 | 1.0 | 0.053 | 30 | 0.51 |
| 62 | 7 | 20 | 11 | 2.0 | 0.108 | 32 | 0.75 |
| 62 | 7 | 20 | 11 | 2.0 | 0.105 | 29 | 0.73 |

proportional to the Pb vapor concentration in the fuel. Thus it seems plausible that lead dissolves directly from the vapor phase into Ni metal as a function of Pb-vapor activity at 650°C. It may possibly be forming a surface alloy on the nickel which then increases the coupon weight.

TGA studies with mercury as the trace metal contaminant were also performed by adding 2 ppm Hg vapor concentration to standard HBtu fuel. Whereas mercury is known to form analgams with many metals, including nickel, addition of mercury vapor at 2 ppm concentration to fuel gas at 650°C caused no weight gain or reaction with the dry nickel anode sample. Even at a very high mercury vapor concentration (35 ppm) which is higher than what could be found in coal-gas mixtures, no weight gain of the nickel coupon was noted. TGA experiments with both lead and mercury contaminants relative to electrolyte-wetted nickel anode samples are in progress.

Based on the experimental results obtained so far, tolerance limits for Pb and Hg vapor in fuel gas mixtures were established. The results have shown that fuel should contain <1 ppm of Pb vapor to avoid any alloy formation with a dry nickel electrode. It was also established that the MCFC may have a high tolerance for mercury vapor at levels much higher than is ever found in coal gas, at least with respect again to a non-wetted nickel electrode.

EFFECTS OF HYDROCARBON CONTAMINANTS

An extensive literature search of a number of data bases was performed concerning hydrocarbon contaminants present in coal-gas. These were surveyed as reported last year in connection with their soot, tar and coke forming tendencies in the molten carbonate fuel cell. Based on these sources, it was evident that the unsaturation characteristic of any trace hydrocarbons present in fuel gas is the major cause for soot formation. Unsaturated and also aromatic and polycyclic hydrocarbons can form soot, tar or coke deposits which are in addition to any Boudouard-type carbon formation which can occur as a result of borderline stability of the fuel itself ($CO/CO_2$ equilibrium ratio).

Several hydrocarbon contaminants that are frequently present at varying concentrations, as shown in Table 4, were selected for thermogravimetric testing (i.e. isothermal TGA) on a porous nickel substrate such as the usual anode plaque employed in MCFCs. This is also the most active catalytic surface generally used for these type disproportionation and soot formation reactions.

Table 4. Soot Formation Tolerance Limits Of Hydrocarbon Contaminants.

| HC Contaminant | Vol % HC-Contaminant in Coal-Gas | | Type of Coal Gas Used |
|---|---|---|---|
| | Carbon Depositing | Carbon Removing | |
| Methane | - | 12.0 | B |
| Acetylene | 0.2 | 0.1 | B |
| | - | 0.6 | A |
| Ethylene | 0.25 | 0.12 | B |
| Benzene | 1.0 | 0.2 | B |

Two fuel gas compositions were used as the base fuel, as shown in Table 5; one was a low Btu, relatively stable gas (A) and the other a medium Btu, but slightly less stable gas (B) when compared in terms of their Water-Gas/Boudouard reactivities.

The TGA experimental results presented in Table 4 were all obtained on a dry, non-carbonate-wetted, nickel plaque, the surface of which was always prepared in advance with a good amount of carbon deposited on it by using an unstable fuel; this is done to reduce the soot induction period which always occurs with fresh coupons. Results with the different contaminant

Table 5. Simulated Coal-Gas Compositions Used In HC-Contaminant Studies.

| Type of Gas | Water Gas Shifted Mole % | | | |
|---|---|---|---|---|
| | $H_2$ | $CO_2$ | $H_2O$ | CO |
| low Btu (Gas A) | 12.5 | 50 | 25 | 12.5 |
| medium Btu (Gas B) | 25 | 33 | 25 | 17 |

concentrations are expressed in terms of 'carbon depositing' conditions, meaning that continuous weight gain was noted, and 'carbon removing' conditions which implies weight loss of the initial preformed soot deposit by carbon reoxidation. Between these measurements lies a concentration region for approximate equilibrium conditions, where the forward and reverse carbon (and/or tar) forming reactions are in balance.

An addition even of 12 vol.% methane to the less stable Fuel B did not succeed in changing gas, B's tendency to continue oxidizing the weight of the preinduced carbon deposit. However, with the other contaminants, carbon deposits can either be formed or reoxidized depending on the concentration of the contaminant in Fuel B. In the case where the more stable Gas A was used, no carbon could be formed even when using large amounts of acetylene impurity. But a pre-existing soot deposit which can be removed with the stable Gas A (i.e. 0% $C_2H_2$), remains constant in the presence of acetylene at a concentration of 0.6 vol.%. Bench-scale MCFC experiments to verify these contaminant effects are in progress.

EFFECTS OF ZINC VAPOR

Previous TGA transpiration experiments and a bench-scale cell test with ZnO dust added to the fuel have shown that zinc vapor and solid zinc oxide (or $ZnFe_2O_4$ pellets) between 600° and 700°C in a humidified reducing atmosphere are in equilibrium with each other according to the reaction: $ZnO(s) + H_2(g) \xrightarrow{K} Zn(g) + H_2O(g)$ with a $K(650^\circ C) \cong 2 \times 10^{-5}$. From this relationship it is seen that from 100 to 10 ppm of Zn-vapor can be present in fuel gas with ratios of $H_2O/H_2$ of approximately 1/4 to 2 respectively. These are ranges of the $H_2O/H_2$ ratio commonly seen from inlet to exit gas when operating at high fuel conversion.

An MCFC laboratory-scale test has recently been operated for about 3000 hours with Zn-vapor contaminant to determine the effect of the above mentioned low concentrations possible after a hot-gas $ZnFe_2O_4$ desulfurization cleanup system. Figure 4 illustrates the life graph of this cell which was operated under a variety of fuel utilizations and Zn-vapor contaminant additions. It is seen that the OCV and IR-free performance of the cell were not seriously affected during this relatively long-term test, meaning that zinc apparently does not affect electrode polarization of the cell or causes cross leakage. It was noted, however, that cell resistance increased periodically as more severe ZnO depositing conditions - examplified by high contaminant levels with high fuel utilization - were

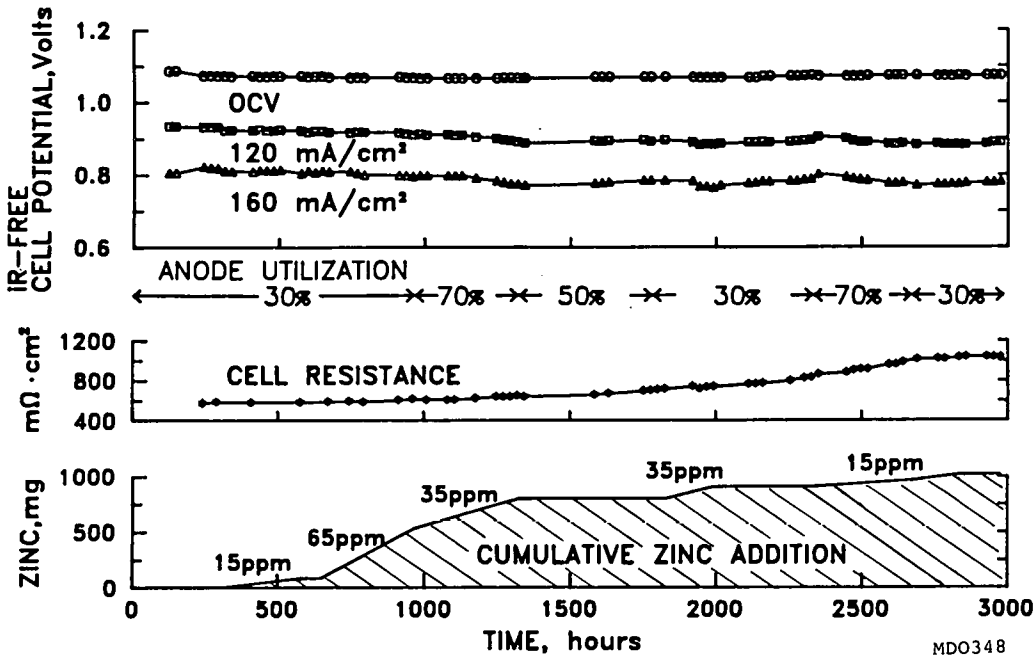



Figure 4. Lifegraph Of MCFC Laboratory Cell Operated Under Zinc Contaminant Conditions.

imposed. The effects on resistance of more ZnO(s) precipitating inside the cell due to the early increases in $H_2O/H_2$ ratio when high fuel conversion is used, are apparently somewhat offset or delayed. And the differences in magnitude of the effects are probably also the result of operating periods at very low utilization (i.e. high gas flow) when only small amounts of ZnO(s) form and the dust can remain suspended in the gas and be rapidly blown out of the cell without being deposited; this has, in fact, been observed.

When precipitation of ZnO(s) does occur inside the cell and it deposits on carbonate wetted surfaces, zinc oxide appears to dissolve in the electrolyte under fuel gas conditions thus providing Zn ions which may migrate throughout the cell. This has been confirmed in both this cell and in an earlier bench-scale cell which was operated with ZnO dust as a chemically active particulate contaminant. Zinc impurity has been analyzed in fair concentrations wherever carbonate electrolyte exists in the cell, e.g. in the anode,in the matrix, at the wet seals and in any electrolyte creepage outside the cell. Therefore, it appears from all evidence that momentary as well as continuous contamination with zinc can accumulate in the MCFC which may cause deleterious resistance increases. A zinc tolerance level of <30 ppm is estimated from the present data when operating at 30% fuel conversion. However, this tolerance level would have to be lowered if cells or stacks are operated under continuous and much higher utilization conditions.

6. RESULTS/ACCOMPLISHMENTS:

A wide range of sophisticated test procedures have been developed for adding and detecting the various contaminants and for simulating borderline stable feed gases to be used in our thermogravimetric (TGA) experiments, by isothermal analysis, and in the in-cell MCFC studies. Especially, the bench-scale cell modifications necessary for introducing contaminants that are only gaseous or stable at elevated temperature was quite challenging. Altogether nine bench-scale and lab-scale (single cell) molten carbonate fuel cells were operated providing a total of 30,000 hours cumulatively acquired experience. The most significant results achieved during this last year are as follows:

- Confirmed that soot forming tendency in MCFCs is comparable to the previous TGA-derived corrlations which show that three different zones are applicable for stable, borderline and unstable fuels when plotted on a C-H-O diagram.

- Determined that only submicron particles can reach as far as the anode passages in a typical single cell configuration. Large particles >1 μm will deposit well before entering the anode channels.

- Determined that 0.5 vol.% ammonia in fuel begins to affect MCFC electrolyte resistance even though only 5% of this $NH_3$ gas is being absorbed in the cell.

- Established that 0.2 vol.% acetylene, the most unstable of unsaturated hydrocarbon contaminants, can cause soot formation on dry nickel anode surfaces in a MBtu fuel. Other unsaturates and aromatic contaminants may also deposit carbon.

- Estimate that the MCFC can tolerate somewhat less than 15 ppm zinc vapor presence in fuel when operating continuously on 70% fuel utilization; <30 ppm with 30% utilization.

7. FUTURE WORK:

The present study is now being finalized, with the last two conference reports containing essentially all that has been learned in this first complete review of the effects that coal-gas contaminants may have on the molten carbonate fuel cell. Out-of-cell and in-cell effects of many of the most critical contaminants were studied and their initial behavior and reaction trends have been identified.

Soot formation in a pressurized (5 to 10 atmosphere) bench-scale MCFC is currently still being studied. Similarly, behavior of different aromatic hydrocarbon contaminants in a bench-scale fuel cell is also still under evaluation. Besides these cell tests, a number of post test analyses are still being processed which will all be included in a soon to be issued final report.

While a good beginning has been made in gaining an overall perspective on MCFC sensitivity to coal-gas impurities, some of the most important

contaminants should be further evaluated in longer term tests. This is needed to verify any extrapolated cumulative effects that may be implied from the present data. Moreover attempts should be made to enhance our mechanistic understanding of the various measured effects. This will be an important step for further effectively dealing with the various contaminants that have been studied.

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# MILD GASIFICATION OF COAL

1. CONTRACT NUMBER: AS-116-PSD

CONTRACTOR:

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CONTRACTOR PROGRAM MANAGER: Meyer Steinberg

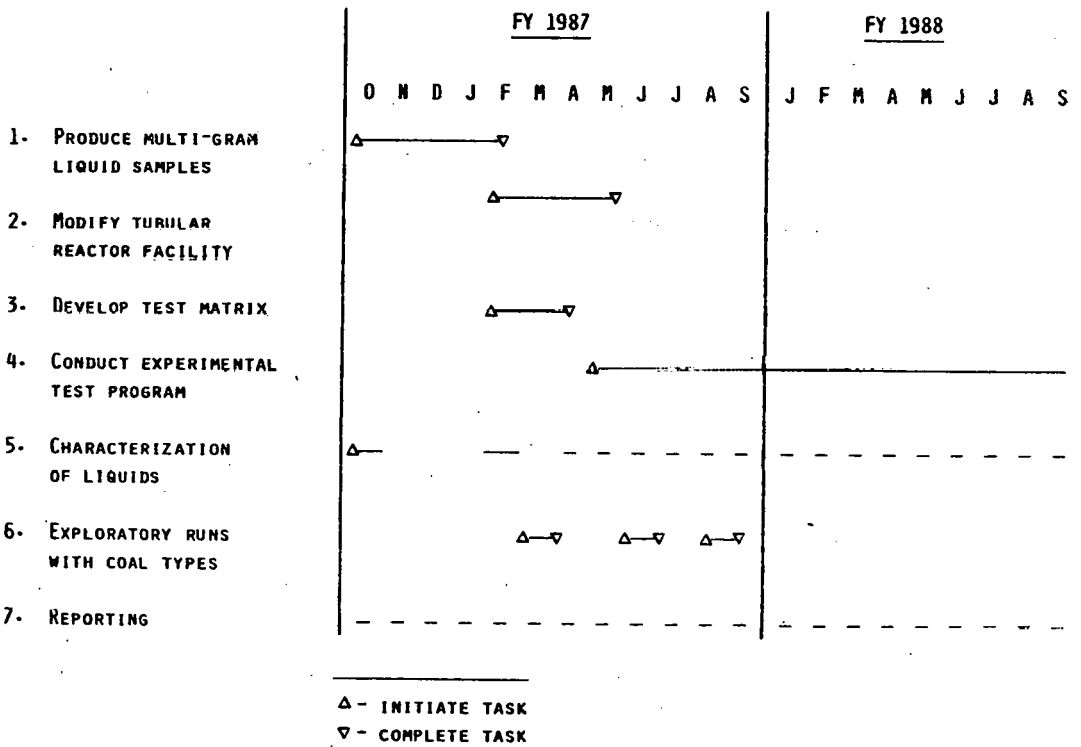
PRINCIPAL INVESTIGATORS: Peter T. Fallon
Muthu S. Sundaram

METC PROJECT MANAGER: Lisa Baker-Jarr

CONTRACT PERIOD OF PERFORMANCE: October 1, 1986 to September 30, 1987

2. SCHEDULE/MILESTONES:

SCHEDULE/MILESTONES




(1-2)

3. OBJECTIVES:

The objective of this program is to conduct research and development on the mild gasification concept for Eastern coals for the purpose of determining (1) the process chemistry, (2) the yield of liquid, gas, and solid co-products, and (3) the quality of liquid product.

4. BACKGROUND STATEMENT:

Mild gasification of coal is defined as processing coal at relatively mild conditions to produce a suite of valuable products. Mild conditions are usually considered in terms of process conditions of temperatures below approximately 750°C, pressures below approximately 50 psig, and coal residence times up to a number of minutes. Under these conditions, the capital investment and operating costs for processing large quantities of coal are reduced, compared to processes which require high severity (high pressure, high temperature, and long residence time) conditions. Another factor in conventional coal conversion processes is that there is a need to add hydrogen from an outside source which increases the cost of the process and reduces the overall conversion of coal to a usable fuel. In mild gasification, the internal stoichiometry of the coal provides the needed hydrogen. Earlier data from Germany and Great Britain in batch reactors indicate that usable oils and tars can indeed be produced from coal in this manner. Recent data at METC (Khan 1986), United Coal Corporation (Wolfe 1986), and Brookhaven National Laboratory (BNL)(Steinberg 1986) indicate process and product potential for mild gasification. However, the conditions were not optimized and process data are not available so that they could be applied to the design of a continuous reactor and a process system. Furthermore, the quality of the products have not been sufficiently characterized. The economic potential of a mild gasification process depends on the yield of condensibles, gas, and char co-products, the quality of condensibles in terms of their usefulness as either boiler or transportation fuels, and the value of the char as a boiler fuel or for other useful purposes. From the exploratory tests and depending on the stoichiometry of the coal, the maximum realizable yield of liquid to be expected ranges up to about 20%. This liquid may have to be upgraded, for example, by a mild hydrogenation with hydrogen generated from the light gases obtained during mild gasification. The char, which contains the residual ash and sulfur, may require upgrading. However, the primary problem at present is to determine the yields and quality of products as a function of the process conditions in a system that would be amenable to scale up to a full-scale continuous process. It is, thus, the purpose of this program to run a bench scale unit of sufficient capacity to obtain product yield and product quality data as a function of process conditions.

This task contributes to a team effort of the METC program on gasification-based systems for coal conversion and production of co-products. It is a mission-oriented multi-year program leading to industrial implementation.

5. PROJECT DESCRIPTION:

At BNL, an entrained flow reactor has been successfully operated for the rapid devolatilization of coal. The unit has a capacity of up to about 2 lbs/hr of coal. This equipment, however, requires modification so that mild gasification experiments can be adequately run over a range of conditions. The advantage of this tubular reactor facility is that it can produce multi-gram quantities of products at controlled conditions at a relatively low experimental cost. The data obtained is useful for evaluating the product quality and for designing larger scale fluidized and moving bed reactors which will eventually be needed for industrial scale mild gasification plants. The modification of the reactor deals with converting the batch receiver at the bottom of the tubular reactor to a flow-through type. The unit will operate at various temperatures and residence time conditions. The receivers for collecting quantities of products are to be modified to operate at increased capacities. The entrained tubular reactor is to be operated to obtain multi-gram quantities of co-products for characterization and test.

The experimental work is to be conducted in accordance with a systematic test plan designed to cover a range of eight process variables, as shown in Table 1.

Table 1. Experimental Test Parameters.

| Variable | Range |
|---|---|
| Coal Type | Kentucky No. 8, Bit., Pittsburgh No. 8 Bit. Mississippi Lignite |
| Coal Flow Rate | 0.5 to 1.5 lb/hr |
| Coal Particle Size | 50$\mu$ to 500$\mu$ |
| Temperature | 500° to 750°C |
| Pressure | 15 psig to 45 psig |
| Coal Heat-up Rate | 50°C/sec to $\sim 10^5$ °C/sec |
| Coal Particle Residence Time | 10 sec to 50 min. |
| Sweep Gas | $N_2$ and 50% Steam/50% $N_2$ |
| Coal Conditions | Hydrated Lime, Silica Flour, Recycled Char, and Ash |

The co-products are to be collected and a mass balance made. The yields will be determined and correlated. The characterization of the liquids include (1) elemental analyses (C,H,N,S,O), (2) boiling point range determined by DTGA, (3) solvent extraction, (4) viscosity, (5) density, (6) aromaticity, (7) mol-wt distribution and (8) Btu value.

6. RESULTS/ACCOMPLISHMENTS:

Prior to completing the modification of the tubular reactor facility, two sets of runs were made for the purpose of collecting approximately 500 to 600 gm of liquid product for characterization. The Wellmore Kentucky No. 8 bituminous coal was used. One set was run without hydrated lime and one with hydrated lime addition to coal at 650°C, 30 psig, a heat-up rate of $2 \times 10^4$ °C/sec and accumulated coal particle residence time ranging from 25 min to 96 min. Nitrogen was used as a sweep gas. Table 2 gives a summary of the conditions and the product yields. The yields of total hydrocarbon liquid obtained including BTX was 12.6% (carbon conversion basis) without lime and 14.5% with 20% hydrated lime addition. The carbon balances were fairly good, totaling 92.4% and 94.0% respectively.

Table 3 gives the characteristics of the co-products, liquid and char. Water which condenses with the liquid product presents a problem in separation and analysis, however, this has been taken into account in Table 3. It is noted that the aromaticity and viscosity are lower in the liquid derived from the run with the addition of hydrated lime. DTGA measurements of the liquids were similar as shown in Figure 1, indicating 50% boil-off at temperatures between 150° to 160°C and 85% to 90% boil-off up to 400°C. However, the liquid formed with lime addition showed more boil-off at lower temperatures indicating lighter materials present than that obtained without lime addition. It is also noted that the sulfur in the liquid in the lime addition experiment is considerably low (0.4%) than in the coal alone experiment (0.9%). Approximately 67% of the sulfur and 81% of the nitrogen in the feed coal remains in the char with no addition of lime. Also the fact that there is residual oxygen present in the liquid indicates that the liquids contained 10 to 12% phenolic compounds.

The modification of the tubular reactor facility has been completed, as shown in Figure 2 and is being test run. The modification included extending the heated zone to include the coal receiver, fitting a drive motor drive from the receiver to the char pot collector, improving the liquid product condensers and collector, and adding an effluent gas scrubber. The heat-up rate of coal particles is controlled by the sweep gas preheat temperature, and the tubular reactor heated wall. Secondary variables include particle size, gas velocity, and reactor pressure. The equations controlling the coal particle heat-up rate is given in Table 4. The coal particle residence time is the sum of the residence time of the particle in the tubular reactor and the coal receiver. The coal residence time in the coal receiver is controlled continuously by the drive motor mechanism and can be extended up to 50 min.

Table 2. Process Conditions and Average Product Yields from the Mild Gasification of Wellmore Kentucky No. 8 Bituminous Coal
Coal Particle Size Range - 50 to 150 microns.

| | Coal Alone | 20% Lime Added |
|---|---|---|
| Run Set | 2 | 3 |
| System Pressure (psi) | 30 | 30 |
| Temperature to Receiver (°C) | 400 | 400 |
| Receiver Temperature (°C) | 650 | 650 |
| Coal Flow Rate (lb/hr) | 1.01 | 1.00 |
| $N_2$ Flow Rate (lb/hr) | 1.26 | 1.26 |
| (lb moles/hr) | 0.045 | 0.045 |
| $N_2$/Coal Ratio (lb/lb) | 1.25 | 1.26 |
| (lb moles/lb) | 0.045 | 0.045 |
| Avg. Coal Particle Heat-Up Rate (°C/sec) | $2x10^4$ | $2x10^4$ |
| Time for Coal to Reach 400°C (sec) | 0.02 | 0.02 |
| Coal Residence Time in Heated Receiver-Range from Beginning to End of Run (min.) | 80-20 | 96-20 |
| Average Product Yields (%C Converted) | | |
| $CH_4$ | 1.4 | 2.2 |
| $C_2H_4$ | 0.6 | 0.1 |
| Total Gas H. C. | 2.0 | 2.3 |
| BTX | 4.5 | 6.8 |
| Heavy Liquids | 8.1 | 7.7 |
| Total Liquids | 12.6 | 14.5 |
| Total H. C. | 14.6 | 16.8 |
| CO | 0.7 | 0.5 |
| $CO_2$ | 0.2 | 0.1 |
| Total $CO_x$ | 0.9 | 0.6 |
| Char | 76.9 | 76.6 |
| Total | 92.4 | 94.0 |
| Total Gms of Heavy Liquid Collected/100 gms of Coal Feed (water contaminated) | 9.8 | 8.7 |

## MILD GASIFICATION OF WELLMORE KENTUCKY NO. 8 COAL

## TGA CURVE OF HEAVY LIQUIDS PRODUCED AT 650°C AND 30 PSI

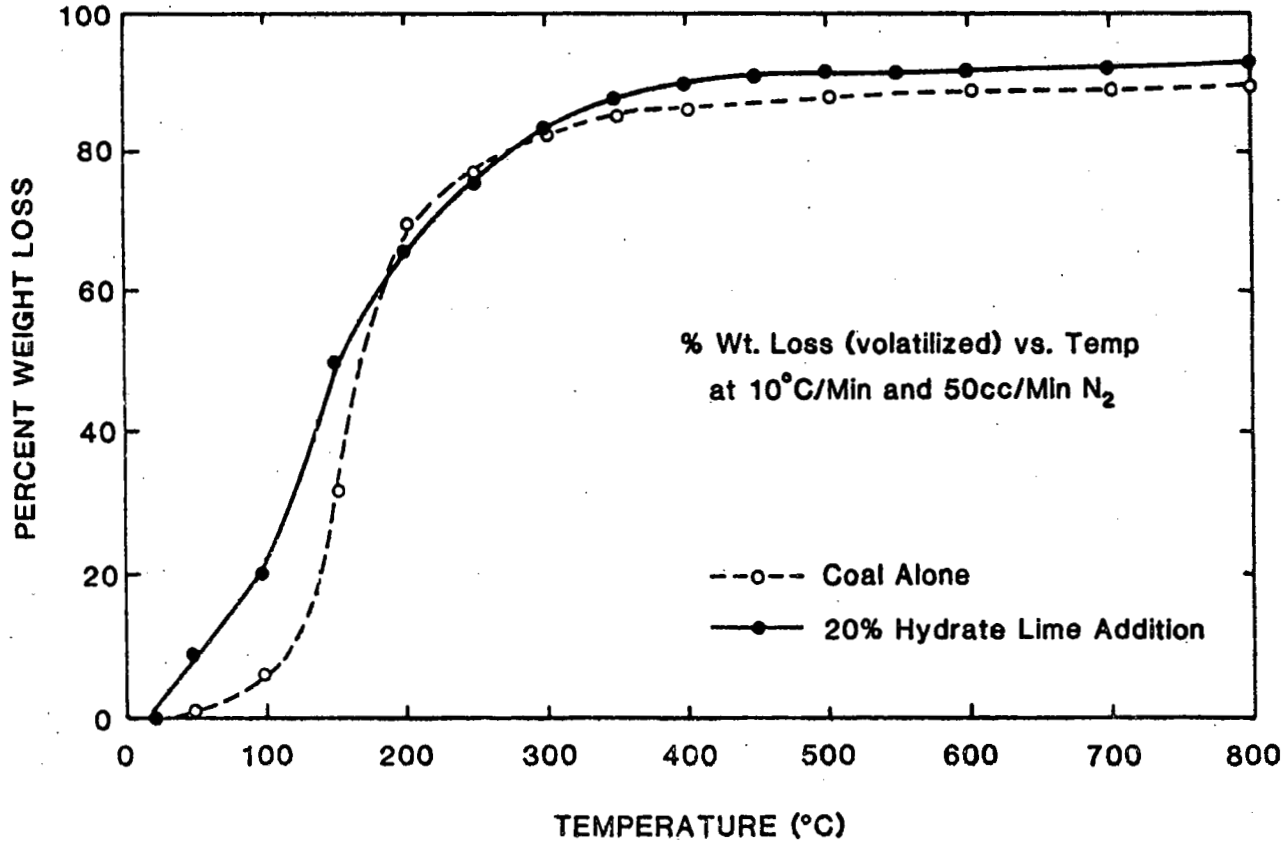



Fig. 1

Table 3. Characteristics of Co-Products
Mild Gasification of Wellmore Kentucky No. 8 Bituminous Coal
Coal Particle Size Range - 50 to 150 microns - $N_2$ Sweep Gas
Reactor Conditions - 650°C and 30 psig.

| Run Set | Kentucky No. 8 Coal Feed | Co-Products Set 1-Coal Alone | | Co-Product-Set 3 with 20% Hydrated Lime | |
|---|---|---|---|---|---|
| | | Liquid[1] | Char | Liquid[1] | Char |
| Elemental Analysis (wt% dry) | | | | | |
| C | 77.2 | 79.4 | 80.8 | 79.4 | 58.3 |
| H | 4.9 | 8.4 | 2.2 | 7.5 | 1.7 |
| N | 1.6 | 1.2 | 1.7 | 1.1 | 1.1 |
| S | 1.3 | 0.9 | 1.2 | 0.4 | 1.1 |
| O | 6.4 | 10.0[2] | 1.5 | 11.6 | ND |
| Ash | 8.7 | 0.0 | 12.6 | 0.0 | ND |
| Ratio H/C | 0.8 | 1.3 | 0.3 | 1.1 | 0.3 |
| Liquid Yield (%C) | | 12.6 | | 14.5 | |
| Heating Value (Btu/lb) | 13,790 | 15,740 | | 15,390 | |
| Viscosity (Cps) | | 33,000 | | 3,200 | |
| Aromaticity (%) | | 79.1 | | 71.1 | |

1) Corrected for water contamination.
2) Estimated.
ND Not determined.

A complete test matrix using a statistical factorial box method has been designed to take into account the eight variables mentioned above. In Phase I using a nitrogen sweep gas - Group 1 consisting of 12 runs, will first determine the behavior of three types of coal. This will be followed by a Group 2 consisting of 40 runs with one selected coal to investigate the other variables. Phase II will then be made with a 50% steam/50% $N_2$ sweep gas and will consist of another 40 runs to determine the statistical behavior of all the other variables.

7. FUTURE WORK:

Having completed the preliminary multi-gram liquid runs, the modification of the equipment and the design of the test matrix, the experimental runs will be conducted according to plan. The co-product yield data and co-product quality will be correlated with the conditions of the runs. In this manner, a firm data base will be established for eventual industrial application.

Table 4. Coal Particle Heat-Up Rate

Coal Particles Heated by Sweep Gas:

$$t = \frac{M\ C_{ps}}{H_g\ A_s} \cdot \text{Ln}\ \frac{T_g - T_i}{T_g - T_s}$$

$H_g$ = gas film to coal particle heat transfer coefficient
$C_{ps}$ = heat capacity of coal
$M$ = mass of coal particle
$A_s$ = area of coal particle
$T_g$ = temperature of gas
$T_s$ = temperature of coal particle
$T_i$ = initial temperature of coal particle
$t$ = time to raise the particle temperature from $T_i$ to $T_s$

where,
$$H_g = \frac{2.06\ K_g}{D_p} \cdot N_{re}^{0.425} \cdot N_{pr}^{0.333}$$

$K_g$ = thermal conductivity of gas
$D_p$ = diameter of coal particle
$N_{re}$ = reynolds number = $\frac{D_p\ V\ \rho_g}{\mu_g}$
$N_{pr}$ = prandtl number = $\frac{C_{pg}\ \mu_g}{K_g}$
$V$ = free fall velocity of coal particle (stokes law)
$\rho_g$ = density of gas
$\mu_g$ = viscosity of gas
$C_{pg}$ = heat capacity of gas

Coal Particle Heated by Wall:

$$m_g\ C_{pg}\ \frac{\partial T_g}{\partial Z} + m_s\ C_{ps}\ \frac{\partial T_g}{\partial Z} + 2\pi R H_w\ (T_w - T_g) =$$

$$2\pi R^2 \left(\rho_{vg}\ C_{pg}\ \frac{\partial T_g}{\partial t} + \rho_{vs}\ C_{ps}\ \frac{\partial T_s}{\partial t}\right)$$

$m_g$ = mass flow rate of gas
$m_s$ = mass flow rate of coal
$Z$ = distance along length of reactor
$R$ = inside radius of reactor
$H_w$ = reactor wall to gas heat transfer coefficient
$T_w$ = temperature of reactor wall
$\rho_{vg}$ = volumetric apparent density of gas
$\rho_{vs}$ = volumetric apparent density of coal

SCHEMATIC FLOWSHEET OF

MILD GASIFICATION TUBULAR REACTOR EXPERIMENT

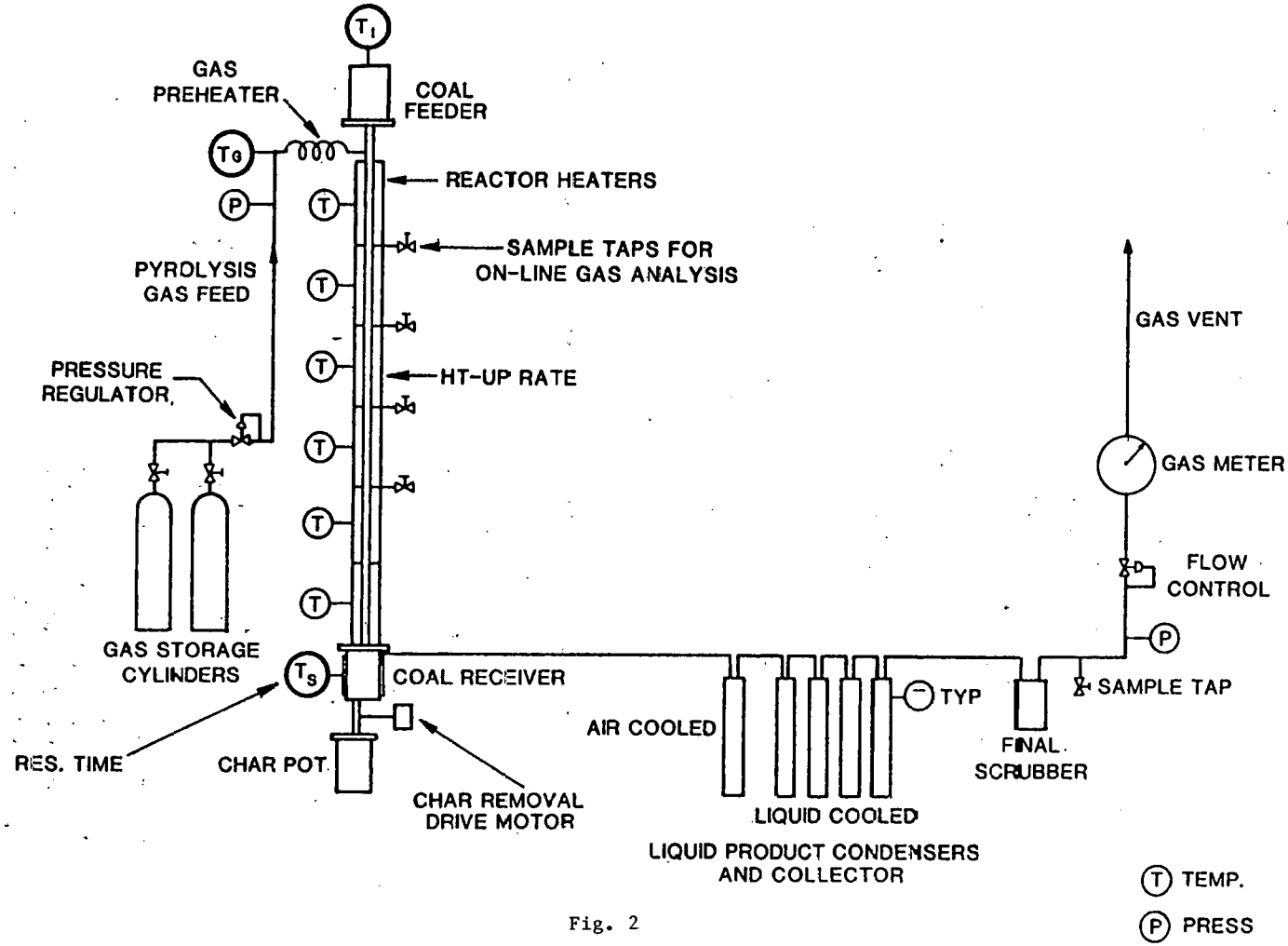



Fig. 2

8. REFERENCES:

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Steinberg, M., Fallon, P. T., and Sundaram, M. S., 1986. Mild gasification of coal - exploratory experiments, BNL 38309, Brookhaven National Laboratory, Upton, NY.

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(Co-investigators: T. P. Griffin, G. H. Ko, and W. S. Fong)

METC Project Manager: Mr. Justin Beeson

Contract Period of Performance: 9/30/85 - 9/29/88

2. Schedule/Milestones

| | No. of Months Into Project | Key Milestone |
|---|---|---|
| **Task 1. Intra-particle Secondary Reactions** | | |
| Preliminary Runs-1 Coal | 6 | |
| Systematic Studies-1 Coal | 12 | Δ |
| Tar Characterization | 24 | |
| Math. Modeling | 18 | Δ |
| Studies of Other Coals | 36 | Δ |
| **Task 2. Effects of Coal Type** | | |
| Tar Yield Correlations | 8 | Δ |
| Reactor Modifications | 10 | |
| Study of 3 Coals | 18 | |
| Study of Remaining 3 Coals | 30 | Δ |
| Light Gas Yields Correlations | 18 | Δ |
| Math. Modeling | 36 | Δ |
| **Task 3. Integrated Devolatization Model for Gasification** | | |
| o Identify & Assemble Existing Models + Input Parameters | 12 | Δ |
| o Identify Critical Information + Modeling Voids | 12 | Δ |
| o Integrate Models, Data & Input Parameters Including Information Being Generated in This Program | 24 | Δ |
| o Perform Predictions of Devolatilization Behavior Using Integrated Model and Compare to Existing Measurements | 30 | |
| o Refine Model + Predictions | 36 | Δ |

3. OBJECTIVES:

Our overall objective is to advance current understanding of coal physics and chemistry to allow improved, quantitative predictions of coal devolatilization behavior under gasification conditions. Our specific objectives are to:

(1) Study the role of intra-particle chemical kinetic and transport rate phenomena in coal devolatilization.

(2) Experimentally determine how coal type influences coal devolatilization behavior including the following phenomena: product yields, compositions and evolution kinetics; intra-particle secondary reactions of tar; extra-particle secondary reaction of tar; and the plasticity of softening coals.

(3) To develop an integrated mathematical model of coal devolatilization under coal gasification conditions.

4. BACKGROUND STATEMENT:

Previous MIT studies (Anthony 1974; Suuberg, 1977; Oh, 1985; Fong 1986) have provided quantitative data on effects of temperature-time history, particle size, and pressure on total weight loss, and yields, compositions and rates of formation of products from rapid pyrolysis of a highly softening Pittsburgh No. 8 bituminous coal and a non-softening Montana lignite. Extra-particle secondary reactions of newly formed tars from devolatilization of Pittsburgh No. 8 seam bituminous coal have also been studied systematically (Serio, 1984). However, there remains need for systematic study of effects of coal type and intra-particle secondary reactions on coal devolatilization behavior, and for development of an integrated coal devolatilization model applicable to gasification. Such research is timely because:

o Devolatilization is an important step in coal gasification processes that, depending on conditions and coal type, may influence not only the performance of the gasifier itself, but also the design and operating specifications of processes and equipment for coal preparation and feeding, and for post-gasifier product and waste stream processing and cleanup.

o It would provide improved data, and mathematical correlations for treating devolatilization in computer-simulation models of coal gasifiers.

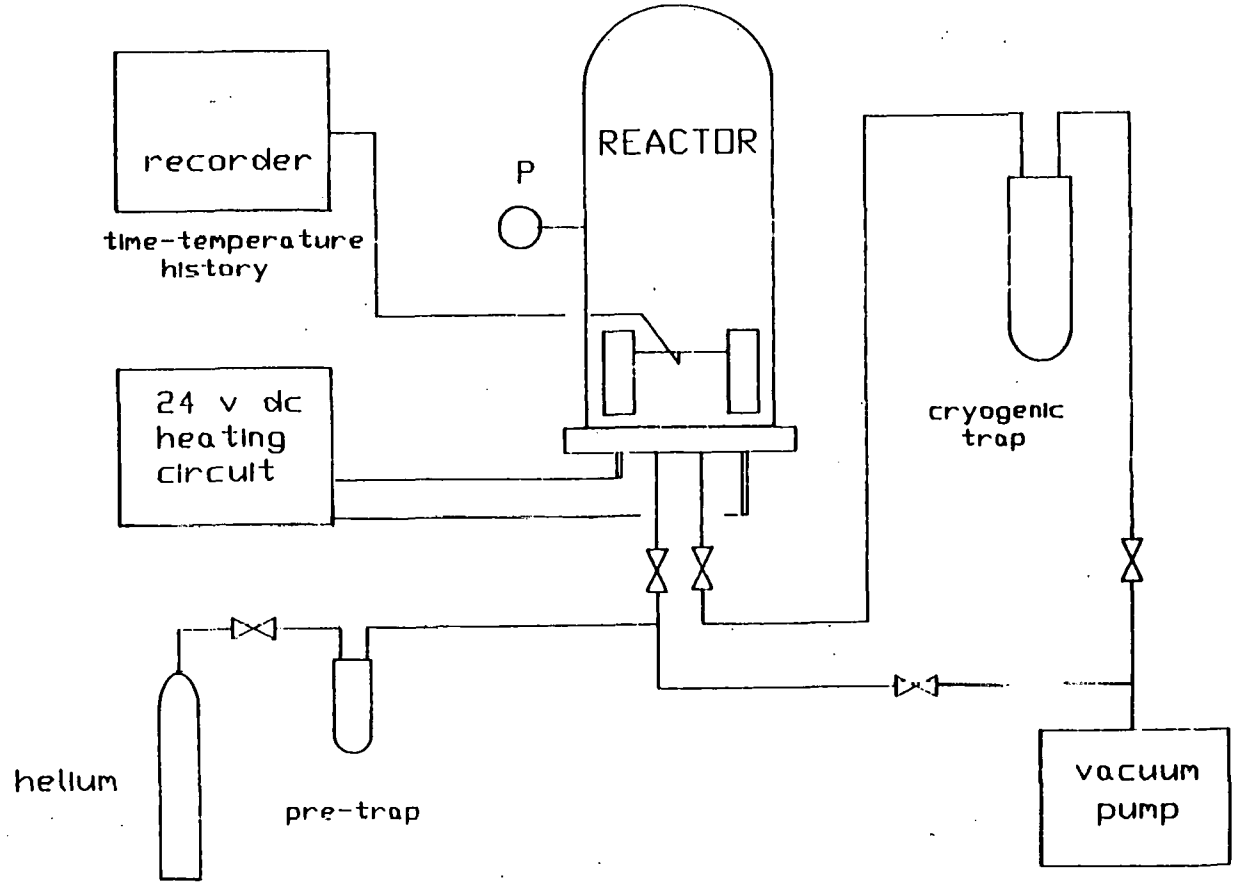
o It would contribute to improved understanding of generic questions in coal devolatilization kinetics including the relative importance of physical transport and coal-specific rate phenomena.

5. PROJECT DESCRIPTION:

Our approach involves experimental measurements of coal devolatilization products yields and production rates. The apparatus provides for manipulation of physical and chemical rate processes and allows study of independent effects of coal type and reaction conditions of practical interest such as

temperature, heating rate, holding time, pressure, and particle size. To this end, heavy reliance is placed on various versions of the electrical screen heater reactor (Fig. 1) which provides for the above measurement requirements, while offering good material balances and amenability to kinetic interpretation. The work also involves developing mathematical correlations and models of devolatilization kinetics.

Fig. 1. Electrical Screen Heater Reactor With Accessories




## 6. RESULTS/ACCOMPLISHMENTS:

Work under Task 1, intra-particle secondary reactions, has focussed on theoretical and experimental preparation for systematic data acquisition and mathematical modeling. A literature review of experimental and theoretical investigations pertinent to intra-particle secondary reactions was completed. A detailed research plan for experimental and modeling studies of intra-particle secondary reactions, including runs to independently examine effects of total pressure, particle size, and heating rate, was prepared. As part of this work potentially dominant modes of intra- and extra-particle mass

transfer were conceptualized for incorporation in theoretical analyses to separate kinetic effects of primary pyrolysis, secondary reactions, and physical transport. Experimental preparation included modifications to a screen heater pyrolysis reactor to allow for improved precision in product collection at pressures above atmospheric, and adaptation of a gas chromatograph for use with a cryogenic (total gas) trapping procedure. Mass balances of (100 $\pm$ 5%) have been achieved in preliminary experiments to refine operating and analytical techniques.

Our goal in tar characterization is to identify analytical techniques offering global or molecular information useful in correlating tar thermal reactivity. Tar analytical methods investigated include gel permeation chromatography (for determining molecular weight distributions), NMR spectroscopy (aromaticity), sequential elution chromatography (polarity), and high performance liquid chromatography (various chemical chromophores and identification of individual compounds or compound classes).

Work under Task 2, studies of coal type, has included considerable effort to refine and validate experimental methods for accelerated recovery of volatiles from the screen heater reactor for quantitative yield measurements. These steps were motivated by the need to expedite acquisition of kinetic data on volatiles products, in light of the large number of runs expected to be necessary to meet the goals of this Task. Systematic measurements of weight loss and volatiles yields and compositions for peak temperature runs up to 1000°C at 1 atm for the six coals chosen for this study are in progress. Runs to date have concentrated on temperatures below 600°C. Mass balances are satisfactory (90 - 110%, as received basis).

A literature survey was performed to determine what is known about coal chemical structure and how it is affected by coal type. This information will be used to predict global chemical structural features of the six coals chosen for this study, and may establish a basis for relating yields of gaseous volatiles to coal-specific structural parameters.

A correlation to quantitatively relate maximum tar yields (from rapid ($\gtrsim$ 100°C/s heating rate) devolatilization to coal type and total pressure was presented at the 1986 METC Gasification Contractors' meeting. Tar yields from different coals representing a wide range of ranks and three countries, and pressures from "vacuum" ($10^{-3}$ to $10^{-4}$ atm) to 90 atm, were correlated with coal type via a coal-specific parameter derived from a hypothesized mechanism of tar formation, using only information on the elemental analysis of the raw (unreacted) coal. Because of errors in converting from as received to dmmf basis for several coals, the correlation coefficients have been revised. The numerical values changed by < 1%, and the overall reliability of the revised correlation remains satisfying, with measured tar yields generally being reproduced to within $\pm$ 5% (Fig. 2). The revised correlation also gives satisfying correlations of observed changes in tar yield with total pressure (Fig. 3). A description of this work, with the revised correlation coefficients, is expected to soon be published in the journal Fuel (Ko *et al.* *c*. 1987).

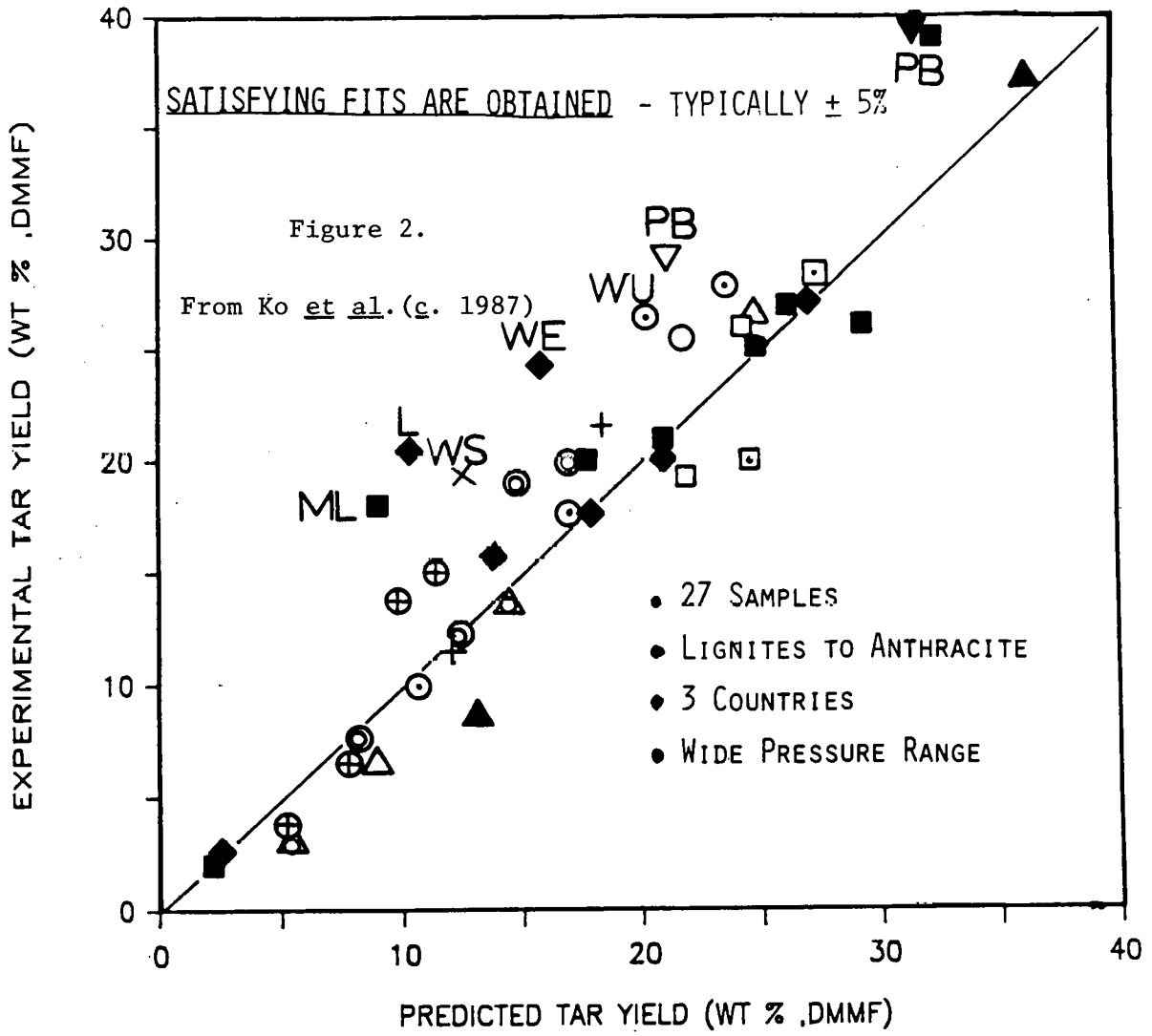



Figure 2.

From Ko et al. (c. 1987)

Work under Task 3, development of a unifying model of coal devolatilization under conditions pertinent to gasification, is still in its early stages. Modeling efforts under Tasks 1 and 2 will contribute to progress under this task.

## 7. EVALUATION OF POTENTIAL AND FUTURE PLANS:

This research will provide improved understanding of how to account, quantitatively, for devolatilization in modeling or predicting the gasification behavior of different coals, including data and mathematical correlations appliable in computerized coal gasification simulation models. The project will also furnish methods, data, and interpretive models useful for inferring pyrolysis product yields, and evolution rates in other coal conversion process options such as mild gasification, liquefaction, and pyrolysis (carbonization). It will also contribute to improved quantitative understanding of generic questions in coal devolatilization kinetics including the relative importance of physical transport and coal-specific rate processes.

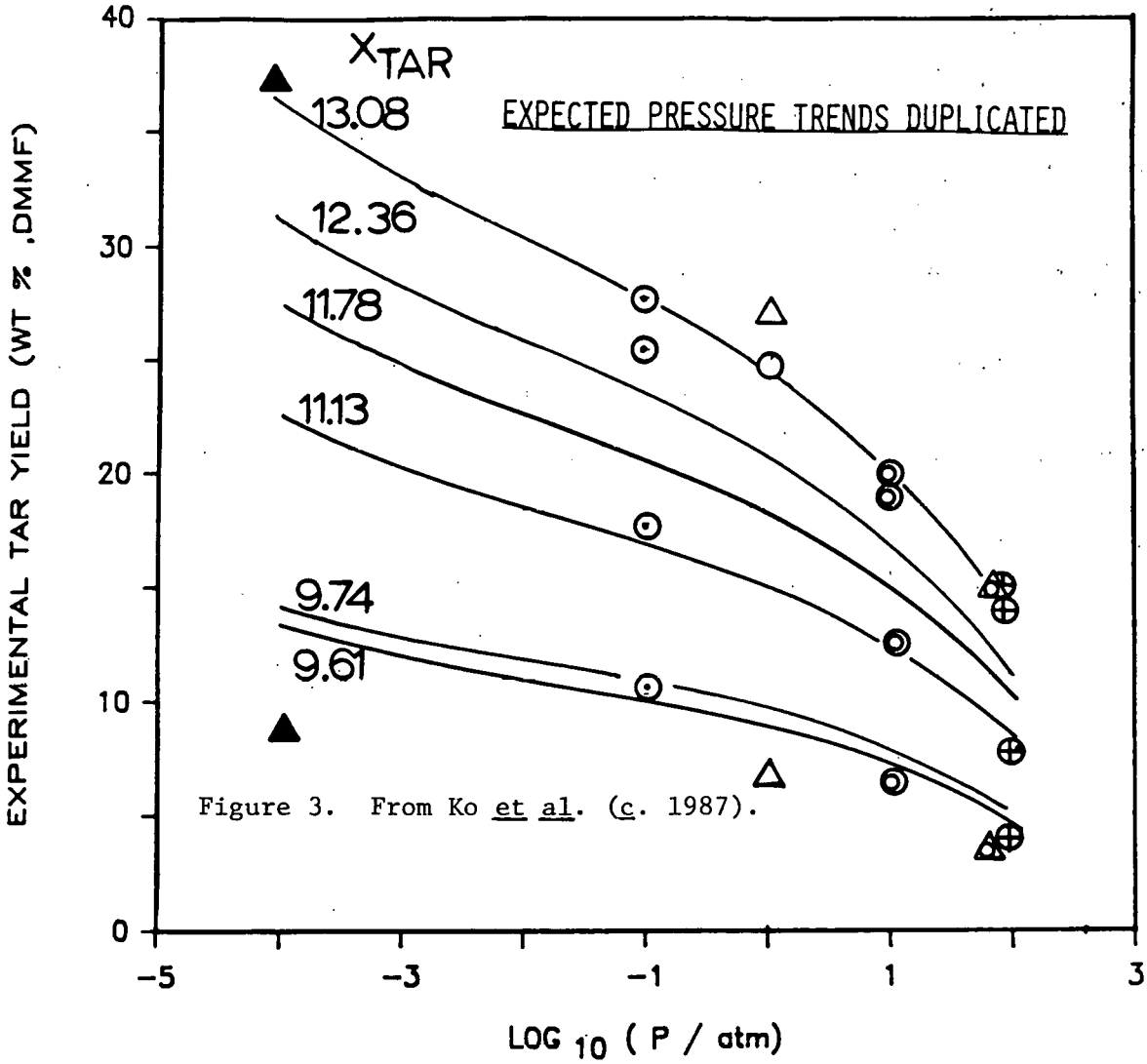



Figure 3. From Ko et al. (c. 1987).

Future work will focus on

o Systematic experimental and modeling studies of intra-particle secondary reactions.

o Measurements of effects of coal type on rapid devolatilization product yields and evolution kinetics, and development of correlations for the results.

o Development of a unifying coal devolatilization model for eaction conditions pertinent to coal gasification.

Acknowledgements

Contributions from several people including Ms. Debra Sanchez and other MIT students including participants in the MIT Undergraduate Research Opportunities Program (U.R.O.P.), are greatfully acknowledged.

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# UPGRADING OF CONDENSIBLES FROM COAL DEVOLATILIZATION

1. FTP/A NUMBER: 00323

CONTRACTOR: Oak Ridge National Laboratory
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CONTRACTOR PROJECT MANAGER: R. A. Bradley

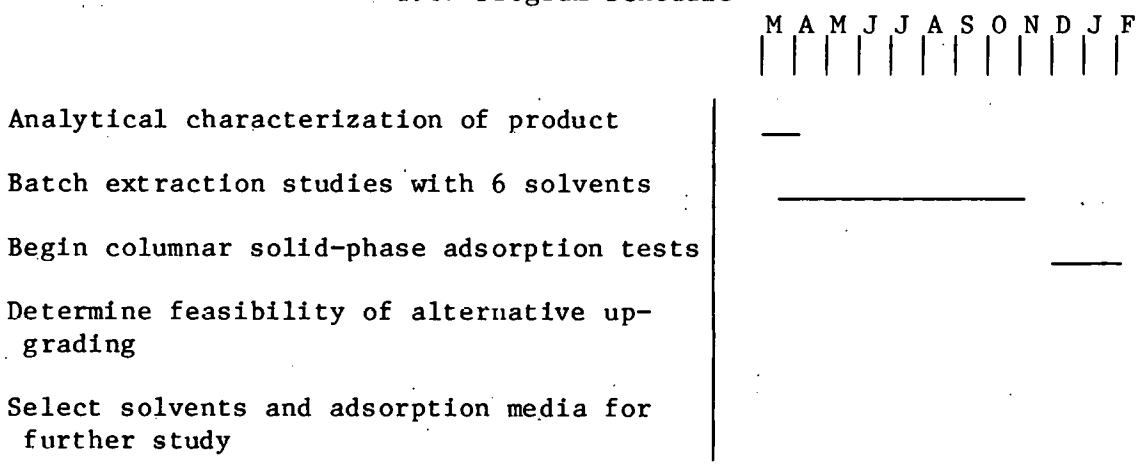
PRINCIPAL INVESTIGATORS: John E. Mrochek
Charles D. Scott

METC PROJECT MANAGER: Madhav R. Ghate

PERIOD OF PERFORMANCE: March 17, 1987 to September 30, 1987

2. SCHEDULE/MILESTONES:

1987 Program Schedule




3. OBJECTIVES:

The primary purpose of this project is to develop alternative or adjunct technologies to hydrotreating for upgrading condensible products derived from low-temperature devolatilization of coal. Hydrotreatment in a packed-bed catalytic reactor will continue to be an important processing tool for coal-derived liquids to minimize concentrations of heteroatom-containing and polynuclear aromatic hydrocarbons which may be hazardous to human health. However, chemical separations to remove these undesirable heteroatom-containing (N, S, and O) "contaminants" could reduce catalyst poisoning and hydrogen demand in a cost-effective manner. Hydrotreatment could even be eliminated, depending upon the effectiveness and cost of the separations process.

4. BACKGROUND STATEMENT:

The condensible products obtained from devolatilization of coal at temperatures in the range of 1100 to 1300°F are complex mixtures containing saturated and aromatic hydrocarbons together with contaminant heteroatoms such as nitrogen, oxygen, sulfur, and with minor quantities of high molecular weight multi-ring (polynuclear) aromatic hydrocarbons and water. This product may have direct utility as a boiler fuel without significant additional processing, but it would be significantly increased in value if some of these "contaminants" were removed and some upgrading were performed.

Removal of the residual water is relatively easy using either decantation or drying agents such as molecular sieves. However, the removal of compounds containing heteroatoms and potentially carcinogonic agents such as polynuclear and certain substituted polynuclear aromatics is a a more difficult task. The development of innovative energy efficient separations techniques to remove such contaminants would do much to demonstrate the potential economic viability of these coal-derived synthetic fuels.

Hydrotreating is the conventional technology used in the petroleum industry for heteroatom removal and product upgrading. It has also been employed to upgrade liquids derived from several different coal liquefaction and shale oil processes. In a previous DOE-sponsored program designed to study the upgrading of coal- and oil shale-derived liquids, fixed-bed hydrotreating at three different severity levels was used to produce gasoline, jet and diesel fuels from SRC II, EDS, and H-Coal liquids. Satistactory fuels were obtained, although high hydrogen consumption was observed. It was found that the upgrading process was very sensitive to asphalteen-like impurities in the feed liquid. Removal of these impurities enabled significant reduction (factors of 1.5- to 3-fold) in the size of the hydrotreater reactor for jet fuel production and reduced their detrimental effect on catalyst performance (Sullivan 1981).

Three approaches to separating contaminants from coal-derived condensibles provide potential opportunities for application to the upgrading of coal-derived condensibles. These processes include solvent extraction, solid phase adsorption, and liquid membrane permeation. Primary emphasis during the course of this project will be on solvent extraction and solid phase adsorption technologies. Solvent extraction was selected for initial evaluation because of the existence of a wealth of operating experience in the petrochemical, chemical, and nuclear industries. Based on the existence of extensive knowledge about this process, its extension to the cleanup of coal-derived condensibles should be technically and economically feasible.

A number of solvent extraction processes have been employed for the removal of aromatics from petroleum-based liquids. They include the NMP-(N-methyl-pyrrolidone) process, the TETRA (tetraethylene glycol)

process, and the SULFOLANE (Tetrahydro-thiophene-1,1-dioxide) process; all three are used primarily for the recovery of high purity BTX (benzene, toluene, xylene)(Kosters 1983, Muller 1983, and Vidueira 1983). Other solvents, perhaps more suited to the complex coal condensibles separation, include liquid sulfur dioxide-benzene, phenol, furfural, and a dual solvent system employing propane and "selecto" (a brand of cresol and phenol)(Albright 1935, Kenny 1941, and Miller 1947).

Basic nitrogen-containing impurities present in raw shale oils were substantially removed by a solvent extraction process employing formic acid. The shale oil raffinate from this process was hydrotreated under mild severity conditions at substantially lower hydrogen consumption compared to hydrotreating raw shale oil (Madgavkar 1983).

Another approach to separating contaminants from coal-derived condensibles utilizes solid phase adsorption. This technique has been widely used in analytical separations to aid in the identification of individual components of complex mixtures. Silica gel and alumina (fully activated and/or partially deactivated with water) have been employed to separate saturates, aromatics, and polar, heteroatom-containing compounds from complex, coal-derived products. Ferric chloride supported on attapulgite clay has been used to sorb neutral nitrogen-containing compounds by complexation (Altgelt 1975, Dooley 1974).

5. PROJECT DESCRIPTION:

This project has only been underway a very short time and initial efforts have been concerned with upgrading studies on the condensibles from the United Coal Company's mild gasification process. Ultimate analysis of the raw condensible product has been performed together with more detailed characterizations employing gas chromatography (GC) using flame ionization and nitrogen-specific detectors. In addition, gel permeation (GPC) and high-performance liquid chromatography (HPLC) using refractive index and ultraviolet detectors were performed to determine molecular weight distribution and aromatic and polar molecules in the heavy oil product. Initial upgrading studies were performed by solvent extraction using aqueous formic acid to investigate the removal of basic nitrogen-containing compounds.

The project plan calls for solvent extraction studies with at least six solvents -- most of which will be directed at extraction of heteroatom-containing compounds. However, some studies will be directed toward recovery of purified aromatic fractions from the raw condensible product. Solid phase adsorption using a relatively cheap and readily obtainable medium such as attapulgite clay saturated with various metal salts will also be tested for its efficacy in heteroatom removal. Multi-stage extractions will be performed with promising solvents using highly efficient mixer-settlers under controlled temperature conditions as the project progresses and time permits.

6. RESULTS/ACCOMPLISHMENTS:

Ultimate analysis of a sample of the condensible product from the Mild Gasification Process Demonstration Unit operated by the UCC Research Corporation is shown in Table 1. The data, with a hydrogen/carbon (H/C) atom ratio of 0.73, suggested the product to be highly aromatic in nature. The H/C ratio for 3-ring aromatics such as anthracene or phenanthrene is 0.71 whereas for a mixed aromatic-cyclic aliphatic such as tetralin this ratio is 1.2 and for a strictly linear aliphatic, the H/C ratio ranges from 4 to about 2.1 depending upon the length of the chain.

Table 1. Ultimate Analysis of UCC Condensibles[1]

| Element | (wt %) |
|---|---|
| C | 87.06 |
| H | 5.31 |
| O[2] | 5.67 |
| N | 1.50 |
| S | 0.73 |
| Total | 100.27 |

Notes: [1] Sample from UCC Test Run BC-108, dated 3/14/86.
[2] Analyzed by neutron activation.

The UCC condensible product was analyzed by capillary column GC using two detectors, flame ionization (FID) and nitrogen/phosphorus (NPD). The chromatogram contained peaks ranging from about $C_8$ (linear n-alkane, $C_8H_{18}$) to beyond $C_{28}$ (linear n-alkane, $C_{28}H_{58}$). Here the designation $C_8$ to $C_{28}$ refers to an approximation of a boiling range encompassing these linear alkanes. Nitrogen-containing components were observed over the range $< C_8$ to about $C_{25}$ with about 14 constituents containing nitrogen observed. This product was also characterized by HPLC using a series of three columns designed to separate components by number of aromatic rings and polarity. Major components observed were 3-, 4-, and 5-ring aromatics with lesser quantities of 6- and higher-ring compounds. Numerous peaks were observed in the polar region of the chromatogram; however, a five-fold increase in optical sensitivity was required to detect them. Separation of the condensibles according to size by GPC showed the major fraction of this heavy oil to be within the molecular weight (MW) range of < 150 to approximately 310 with a small fraction above 85,000 MW.

Initial solvent extraction studies were aimed at the removal of basic nitrogen-containing heterocyclics using formic acid. Aqueous formic acid (5 and 25 v/v %) was contacted with the condensible product in a separatory funnel at 1:1 volume ratio. The results of this single-

contact extraction shown in Table 2 are somewhat disappointing with only about 10% of the nitrogen-containing material being removed. An unexpected result was the nearly 41% removal of oxygen functionality shown for extraction with 25 v/v % formic acid.

Table 2. Ultimate Analysis of UCC Condensibles after Contact with Aqueous Formic Acid

| | Ultimate Composition, Wt % | | |
|---|---|---|---|
| | | After Extraction[1] | |
| Element | Original | 5 (v/v %) | 25 (v/v %) |
| C | 87.06 | 88.14 | 88.56 |
| H | 5.31 | 5.07 | 5.05 |
| O | 5.67[2] | 5.52[2] | 3.36[2] |
| N | 1.50 | 1.36 | 1.33 |
| S | 0.73 | NA[3] | NA[3] |

Notes: [1]Single extraction with indicated aqueous (v/v %) concentration.
[2]Determined by neutron activation analysis.
[3]Not analyzed.

These extraction studies were then expanded to include multiple contacts (3) and higher concentrations of formic acid (50 and 75 v/v %). The results shown in Table 3 demonstrate the need for higher concentrations of formic acid with nearly 50% removal using the highest concconcentration (75%) formic acid. Oxygen analyses are in progress and will be reported at the contractor's meeting in Morgantown.

Table 3. Extraction of Nitrogen-containing Compounds from UCC Condensibles with Aqueous Formic Acid[1]

| Nitrogen Content, Wt % | | | | |
|---|---|---|---|---|
| Original | 5[2] | 25[2] | 50[2] | 75[2] |
| 1.50 | 1.24 | 1.12 | 1.17 | 0.76 |

Notes: [1]Three extractions using fresh formic acid.
[2]Concentration of formic acid in water, (v/v %).

## 7. FUTURE WORK:

This project has just begun and judgement regarding its potential for achieving an efficient and cost-effective adjunct/alternative process to hydrotreating for the upgrading of coal devolatilization products is not possible at this time. Initial results have shown some promise

concerning removal of the basic nitrogen content of the heavy oil condensate from the UCC process. In addition, results showing a decrease in oxygen content, while unexpected and not yet verified, do look interesting. The concentration of aqueous formic acid extractant will be increased to at least 90 v/v % and the effect of pKa on nitrogen distribution will be investigated using a series of halogenated acetic acids.

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ASSESSMENT OF INSTRUMENTATION NEEDS FOR

ADVANCED COAL CONVERSION POWER PLANTS

1. CONTRACT NUMBER: DE-AC21-86MC23088

CONTRACTOR: Gilbert/Commonwealth, Inc.
Box 1498
Reading, PA 19603
(215) 775-2600

CONTRACTOR PROJECT MANAGER: Eric T. Nelson

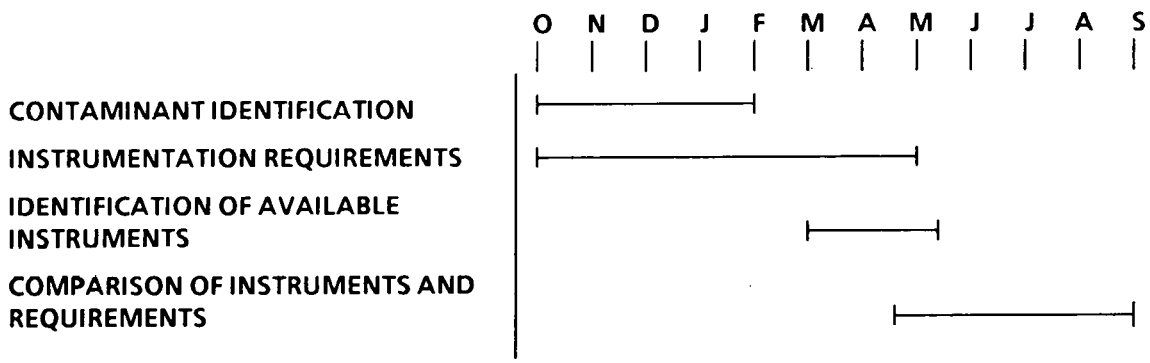
PRINCIPLE INVESTIGATOR: Eric T. Nelson

METC PROJECT MANAGER: Vijay P. Kothari

CONTRACT PERIOD OF PERFORMANCE: July 3, 1986 to September 2, 1987

2. SCHEDULE/MILESTONES:

1987 Project Schedule




A Topical Report describing the results of the contaminant identification and instrument requirements work (tasks 1 and 2) is in the process of being finalized.

3. OBJECTIVES:

The purpose of this study is to provide an assessment of instrumentation needs for advanced coal conversion process applications. Integrated Gasification Combined Cycle (IGCC), Pressurized Fluidized Bed Combustion (PFBC), and Molten Carbonate Fuel Cell (MCFC) power systems are considered. The study involves

identifying contaminants and their control levels in power system gas streams, assessing available instrumentation for measuring and monitoring these contaminants, and identifying deficiencies in the types of instruments available.

4. BACKGROUND STATEMENT:

In 1981, a study was completed by TRW (Energy Engineering Division) which was similar to this study, but was limited to molten carbonate fuel cell power plants. Subsequently, gas cleanup and molten carbonate fuel cell technologies have advanced, as have gas cleanup technologies for use with other coal conversion processes. In addition, instrumentation availabilities have changed.

A large amount of information documenting this activity exists in the form of reports on various instrument and gas cleanup system development studies. There exists a need to evaluate this information so that more advanced technologies will be considered by the electric utilities as they search for more efficient means of using coal.

5. PROJECT DESCRIPTION:

IGCC, PFBC and MCFC power systems offer excellent potential for reduced pollution and high efficiencies, but they require complex process control and composition analyzer systems. These analyzer systems must be capable of extracting and conditioning gas samples from dusty gas streams at high temperatures and pressures, or else they must use in situ methods which are still under development. To achieve utility company acceptance, improved contaminant control methods must be developed. In addition, load-following capabilities of the new analyzer and gas cleanup systems must meet typical utility operational requirements.

To establish instrumentation needs for the three types of power systems, published conceptual designs of IGCC (Parsons Company 1985), PFBC (General Electric 1978), and MCFC (General Electric 1982) power systems were studied. It was beyond the scope of this study to generate optimized conceptual designs for the IGCC and MCFC power plants based on the hot-gas cleanup option. However, having established a set of base case instrumentation requirements for the cold-gas cleanup options, our instrumentation needs assessment work was then directed toward the following three hot gas cleanup options:

- The METC Zinc Ferrite Process - based upon the use of zinc ferrite, $ZnFe_2O_4$, which tends to combine the high sulfur affinity of zinc oxide with the good regenerability of iron oxide. The zinc ferrite is regenerated by roasting with air or oxygen.

- The Battelle Solid-Supported Molten Salt (SSMS) Process - based on the reversible reaction of $H_2S$ with molten lithium, sodium, potassium or calcium carbonates. Regeneration with a carbon

dioxide and steam-rich stream releases $H_2S$ at a high concentration which is converted to elemental sulfur.

- The IGT Mixed Metal Oxide Process - based on the use of an elemental sulfur producing metal oxide sorbent combined with a high sulfur affinity metal oxide. After the metal oxide is fully loaded, it is regenerated using a mixture of oxygen and tail gas.

In a cold gas cleanup option, load changes are normally handled by adjusting the flow of the lean solution. Gas composition is generally monitored at the absorber outlet and the setpoint of the flow controller is adjusted accordingly.

In hot gas cleanup processes, the contaminant undergoing sorption is removed continuously from the fuel gas stream, and is accumulated in a solid (or solid-supported liquid) phase. A sorption wave moves through the bed until a break through point is reached. Either a forward or reverse flow of regenerant gas is used to pass a desorption wave through the bed. Most gas-solid contaminant removal systems are not difficult to control because rapid load changes do not lead to the existence of outlet concentration transients.

Flow diagrams were developed for each power system and gas cleanup option, and then instrumentation needs were assessed based on contaminant level and process control considerations. However, not all contaminants are measured for process control purposes. Many are measured in the plant laboratory for quality control or environmental control purposes. Also, in the case of demonstration plants, many process and/or plant laboratory analyzers are required for research or process optimization purposes.

Contaminants in coal conversion system process streams are often grouped as sulfur compounds, nitrogen compounds, halogen compounds, trace elements hydrocarbons, oils, tars and particulates. The oils and tars are condensed mixtures of aromatics, polycyclic aromatics, phenols and organic sulfur compounds. Various other heterocyclic compounds also contain sulfur and trace metals. The particulates contain ash, char, and solid compounds of volatile metals and halides. Many of these substances may cause trouble in the power train if they are not removed by the gas cleanup systems. Many others are contained in cleanup system effluent streams which must be monitored using plant laboratory instrumentation.

6. RESULTS/ACCOMPLISHMENTS:

Results and accomplishments to date include a review of published designs for IGCC, PFBC, MCFC power systems, the identification of their gas stream contaminants, and the development of appropriate gas stream contaminant control strategies. A preliminary instrumentation requirements and availabilities assessment methodology has been developed and used to list instrument requirements and availabilities.

## 6.1 METHODOLOGY:

The following approach was adopted:

- Based on published information, describe a basic configuration and some typical configuration variations for each power plant type.
- Generate process flow diagrams for the various configurations using numbered flow streams.
- Review each stream (primarily each gas stream) for contaminant control requirements based on operational, research and environmental needs.
- Determine operational needs based on power system dynamic response considerations.
- Exclude most streams for which satisfactory instruments exist based on current commercial practice.
- Generate a list of quantitative factors related to each operational need, and reference notes on less quantifiable factors.
- Identify the process and laboratory instrument types which are capable of satisfying the defined requirements.
- Identify the process instruments which are available.
- Compare process instrument needs with availabilities.

## 6.2 CONTAMINANT IDENTIFICATION

### Contaminant Release

Table 1 shows some of the contaminant concentrations to be expected from gasifiers and PFBC's. These concentrations may have to be reduced before the gas or its combustion products are admitted to the various power trains. The reduction required will depend on the power train being considered. In any system, the stack emissions must comply with environmental regulations, but these may be less stringent than the power train requirements.

Table 1. Ranges Of Gas Compositions From Illinois No. 6 Coal (volume percent).

| SPECIES | GASIFIERS FIXED BED | FLUIDIZED BED | ENTRAINED BED | COMBUSTOR PFB |
|---|---|---|---|---|
| $H_2S$ | 0.6-1.5 | 0.4-1.2 | 0.7-1.4 | |
| COS | 0.001-0.06 | 0.02-0.05 | 0.06-0.3 | |
| $CS_2$ | | | <0.1 ppm | |
| $SO_2$ | | | ~0.003 | 10-1000 ppm |
| $SO_3$ | | | | 2-300 ppm |
| $NO_x$ | | | | 80-350 ppm |
| $NH_3$ (ppm) | 4000-9000 | 300-400 | 200-1100 | |
| HCN (ppb) | | | ~20 | |
| HCl (ppm) | ~700 | 200-700 | ~4000 | 30-60 |
| HF (ppm) | | | | 1.5-25 |
| NaCl | 28-35 ppb | 0.8-23 ppm | 8-46 ppm | 0.1-40 ppm |
| KCl | 13-16 ppb | 2-12 ppm | 4-1000 ppm | 0.06-15.5 ppm |
| Pb (ppm) | ~2 | ~2 | ~2 | |
| As (ppm) | | ~9 | ~5 | |
| Tar & oil (ppm) | 300-7000 | | | |
| Particulate (gr/scf) | 1.5-5 | 3.5-7 | 10-50 | 4-14 |
| Pressure (psia) | 15-400 | 15-250 | 15-1000 | 90-300 |
| Temperature (°F) | ~1000 | ~1700 | ~2400 | ~1650 |

Contaminants Detrimental to Components

Although there is little actual experience available on using gas turbines in IGCC configurations, a substantial amount of experience has been obtained with gas turbines operating on low Btu gas from blast furnaces. This gas is normally cooled and scrubbed with a two-stage wet scrubber prior to combustion. Many plants using this method have operated for long periods without problems.

The gas turbine manufacturers publish different contaminant tolerance limits, but they are in the neighborhood of 20,000 ppm $H_2S$, 0.3 ppm vanadium, 0.5 ppm sodium and potassium, with calcium, lead and copper each in the low or sub-ppm regions. In general, sulfur specifications for the turbine are less stringent than environmental requirements and emission standards. Early particulate tolerance levels preferred by gas turbine manufacturers were very low and did not discriminate with respect to size distribution. Current limits in the low hundreds ppm range are higher and have been developed with more concern given to size distribution. These limits are less stringent than environmental

limits which will set the requirements for particulates. In the case of PFBC power systems, gas turbines are the major components subject to damage.

The molten carbonate fuel cell power plant requires the purest fuel gas of the plants considered here. Practically all the naturally occurring elements occur in coal, and may appear in the raw fuel gas. Cell damage in the form of degraded output or structural failure can result from their presence if they are not removed to sufficiently low levels. While the damage mechanisms of some contaminants such as sulfur and halogen compounds are known, very little is known about other contaminants such as metals.

Sulfur compounds ($H_2S$, COS, $CS_2$ and $SO_2$) greater than 1 ppm lead to anode deactivation by chemisorption, sulfation of carbonates and sulfidation of cell hardware. Halogen compounds ($Cl_2$, HCl and the alkali halides) lead to performance loss at the cathode, hardware corrosion and the formation of chlorides. Small amounts of iron, copper and arsenic cause deactivation and plugging, and the heavy metals cause corrosion, alloying and structural damage. Hydrocarbons greater than 1 mole percent lead to carbon formation. Tar and oil in extremely small quantities cause deactivation and mechanical problems, and more than 0.005 $gr/ft^3$ of particulates (50% less than 2 μm) block flow passages in the electrodes.

## 6.3 PROCESS CONTROL STRATEGY

Low temperature gas cleanup systems were developed primarily for steady state operation in petroleum industry applications, and electric utility load-following objectives have yet to be established for power systems which use hot gas cleanup processes. In the absence of better input information, the process control requirements for this study were based on the assumption that many utilities would like to bring about a 40% change in load at a rate of 2% per minute.

In the case of low temperature cleanup, the lean solution flow rate to the absorber would be controlled to accommodate this load change. In the case of hot gas cleanup, the packed bed absorber will have the capability to retain whatever $H_2S$ may be present up to the point that breakthrough occurs. A three to five minute response time should be satisfactory for any reasonably long sorption/regeneration cycle.

## 6.4 PROCESS INSTRUMENTATION REQUIREMENTS

Most of the instrumentation requirements listed in this section pertain to the hot gas cleanup processes. Some low temperature gas cleanup needs and some requirements not directly related to gas cleanup have also been included.

Today's process analyzer systems feature integrated sampling systems, user friendly I/O devices, self-contained diagnostics and built-in data highway ports. Optical spectrometers are making increased use of fiber

optics, many instruments use solid state sensors, and all are being integrated with microprocessor based monitors. These features have not been included in the requirements tables (Tables 2 and 3), but they were factored into the selection process which was used to develop the availability table (Table 4). Most of the requirements listed in Table 2 are related to $H_2S$ absorption. In the case of the MCFC power system, instruments have been included for the on-line monitoring of $H_2S$, COS, $CS_2$, $SO_2$, chlorine, halogen acids and the alkali halides. The requirement indices shown in Tables 2 and 3 were assigned in the order that the various power systems and gas cleanup systems were studied. They have been used in Table 4 to identify suitable analyzers. In some cases, more than one requirement can be satisfied by the same analyzer. In such cases, the analyzer system (which includes the analyzer and sampling system) may be different. Tables 2 and 4 are included at the end of the paper and Table 3 follows.

Table 3. Summary of Other Power System Instrumentation Requirements.

| Requirement Indices | | | Upstream/ | |
|---|---|---|---|---|
| IGCC | PFBC | MCFC | Actual Unit | Requirements |
| 41 | | 48 | Gasifier | Bed temperature |
| 42 | | 49 | Gasifier | Operator assistance |
| 43 | | 50 | Incinerator Stack | Stack emissions |
| | 44 | | Combustor | Bed level |
| | 45 | | Coal Hopper | Coal feed rate |
| | 46 | | Dolomite Hopper | Dolomite feed rate |
| | 47 | | -- | Power system control |
| | | 57 | Water Treatment System | Water analyses |

## 6.5 LABORATORY INSTRUMENTATION REQUIREMENTS

The plant laboratory is primarily a quality control laboratory. As such, it contains the off-line instruments needed to determine whether the products and raw materials meet their specifications, and whether all of the waste streams meet the criteria set by the applicable local, federal, and state regulations. In the case of pilot or demonstration plant facilities, the laboratory will also contain the instruments needed to satisfy the research and development objectives of the project. Most plant laboratories contain general purpose instruments. Primarily, they are used to implement or replace analytical procedures which have been approved as standard methods. In practice, an analytical chemist or chemist team selects needed instruments from

those commercially available. Some typical instruments are referenced in Section 6.8. Each selection will be site-specific and will reflect the problems, needs and preferences associated with the plant under consideration.

## 6.6 PROCESS INSTRUMENTATION AVAILABILITY

In this study, emphasis has been placed on process analyzers which are needed to control or participate in the control of gas cleanup systems. No process analyzer can provide continuous, specific, low cost, on-stream, maintenance free, high sensitivity readings without drift or need of a sampling system. Analyzer selection always involves compromise.

As a first step in determining instrument availability, the primary measurement species listed in Table 2 were used to retrieve measurement method information from in-house data and available publications (Measurementation Inc. 1987). This method information was then screened on the basis of range limits and response times and then further screened on the basis of the coded factors shown in Table 4 which summarizes the results of this screening activity. Following the completion of this activity, various vendors were contacted for additional information. The vendor names listed in Table 4 were included as a means of describing a type of instrument. No attempt has been made to recommend a specific vendor. In most cases, competitive instruments are available from a numerous vendors. The availabilities which are more directly related to power system control will be discussed in the final report.

## 6.8 LABORATORY INSTRUMENTATION AVAILABILITY

Laboratory instrumental methods are widely used for quality and pollutant control purposes. For regulatory purposes, almost any instrumental method is permitted provided that the results obtained are checked periodically against an approved standard method. As a consequence of this freedom of choice, a large number of instrumental methods are available, some of which are listed below.

Selective ion electrodes are useful for measuring ammonia, cadmium, copper, lead, potassium, sodium, total cations, bromide, chloride, cyanide, fluoride, idodide, nitrate and sulfide ions, and numerous commercial probes are available for measuring dissolved oxygen, pH, and conductivity. Ion chromatography is frequently used to determine anions or cations using ion exchange and conductimetric, ampometric or colormetric detectors. Also potentiometric methods are useful for making titrimetric determinations. Atomic absorption spectrometers, flame or flameless, are used to determine metals. Inductively coupled plasma and related methods are well suited for scanning waste streams for various metal ions.

Gas chromatograph and gas chromatograph/mass spectrometry techniques are widely used for phenols, halogenated hydrocarbons and various taste

and odor-causing compounds. High performance liquid chromatography is useful for performing effluent water analyses.

## 7. EVALUATION OF POTENTIAL FUTURE WORK

The instrument availabilities shown in Table 4 have been subjected to a more exhaustive review based on discussions with vendors. The final results of this availability work will be included in the final report. After reviewing all vendor-supplied specifications, they will be evaluated to determine the extent to which the available instruments satisfy the identified performance requirements.

Commercial acceptance of the advanced power systems may be affected by deficiencies which are related to the following preliminary observations. These observations and deficiencies will be subjected to further review throughout the remainder of the program. Also, some existing and/or developmental analytical methods will be discussed relative to improvements which are needed to ensure the commercial readiness of contaminant control instrumentation for advanced power systems.

A list of preliminary observations follows:

- The problem of defining and quantifying instrumentation needs for the various gas cleanup processes should be studied in more detail. The development of an expert system for this purpose should be considered.

- The existing low temperature gas cleanup processes were developed for steady state operation. Their suitability for utility load-following should be investigated.

- Dynamic analysis studies as they pertain to the requirements of the electric power generation industry should be conducted prior to completion of the process engineering, materials and component studies which are presently being performed for the emerging hot gas cleanup processes.

- Process control systems, process analyzer systems and plant laboratories tend to emphasize different technologies. Greater attention should be paid to their integration.

- Sampling systems tend to resemble miniature high maintenance chemical plants which are difficult to operate. Chemical processes of any type which are integrated with power generation systems should be reliable, as maintenance free as possible and easy to operate, otherwise they will not be readily accepted by the power generation community.

- Although a general preference exists for in situ analyzers, a majority of instrument vendors and analyzer engineers believe that sampling systems will be unavoidable over the next decade. During

this period, the trend will probably be toward fully integrated and automated vendor-supplied measurement systems.

## 8. REFERENCES


General Electric Co. "CFCC Development Program - Commercial Plant Stacked Combustor/Steam Generator Design Evaluation" (Task 2.1). FE-2357-32, NTIS, June 1978.

General Electric Co. "Development of Molten Carbonate Fuel Cell Power Plant." Contract No. AC02-80ET17019, NITS, September 1982.

Measurementation Inc. Anadata Process Measurement Encyclopedia.

Ralph M. Parsons Company. "Evaluation of the British Gas Corporation/Lurgi Slagging Gasifier in Gasification-Combined-Cycle Power Generation." EPRI Report AP-3980, Research Projects 2029-5 and 20296, March 1985.

TRW Energy Engineering Division. "Monitoring Contaminants in Coal Derived Gas for Molten Carbonate Fuel Cells." May 1981, DOE/METC/82-44."

Westinghouse Electric Corp. "Evaluation of Gasification and Gas Cleanup Processes for Use in Molten Carbonate Fuel Cell Power Plants." Westinghouse R&D Center. DOE/MC/16220-1306, 1983

Table 2. Summary of Gas Cleanup System Instrumentation Requirements.

| Instrument Requirement Indices | | | | |
|---|---|---|---|---|
| IGCC | PFBC | MCFC | Upstream /Actual Unit | Primary Measurement(s) |
| 1 | | | Sulfur Absorber (Lurgi) | $H_2S$ |
| 2if | | 25if | Gasifier (KRW) | $H_2S$ |
| 3, 6f | | 26, 29f | Sulfur Absorber (METC) | $H_2S$ |
| 4, 7f | | 27, 30f | Regenerator (METC) | $SO_2$ |
| 5, 8f | | 28,31f | Reductive Regenerator (METC) | $H_2S$ |
| 9 | | 32f | Fluidized Bed Absorber (METC) | Particulates |
| 10 | | | Alkali Absorber (METC) | Alkali Metal Compounds |
| 11 | | 35 | Sulfur Absorber (SSMS) | $H_2S$ |
| 12 | | 36 | Regenerator (SSMS) | $H_2S$ |
| 13 | | | Alkali Absorber (SSMS) | Alkali Metal Compounds |
| 14 | | 38 | Sulfur Absorber (IGT) | $H_2S$ |
| 15 | | 39 | Regenerator (IGT) | $SO_2$ |
| 16 | | | Sulfur Condenser (IGT) | $N_2$ |
| | 17f | | Combustor | $SO_2$ |
| | 18f | | Cyclones | Particulates |
| | 19f | | Fine Particle Cleanup | Particulates |
| | 20f | | Alkali Absorber | Alkali Metal Compounds |
| | | 21 | Tar Cracker | Total Hydrocarbons |
| | | 22 | Ammonia Scrubber | $NH_3$ |
| | | 23 | Sulfur Absorber (Selexol) | $H_2S$ |
| | | 24 | Sulfur Absorber (Zinc Oxide) | $H_2S$ |
| | | 33, 34f | Sulfur Polisher (METC) | $H_2S$ |
| | | 37 | Sulfur Polisher (SSMS) | $H_2S$ |
| | | 40 | Sulfur Polisher (IGI) | $H_2S$ |

NOTES:

i denotes in-bed desulfurization and
f denotes fluidized bed unit

Table 2. Summary of Gas Cleanup System Instrumentation Requirements (Cont'd).

| Upstream /Actual Unit | Maximum Response (min) | Overall Range | Low Range Accuracy | Stream Conditions (°F) | Stream Conditions (psia) |
|---|---|---|---|---|---|
| Sulfur Absorber (Lurgi) | 3 | 0-5000 ppm | ± 5 ppm | 246 | 295 |
| Gasifier (KRW) | 5 | 0-15000 ppm | ± 5 ppm | 1000 | 250 |
| Sulfur Absorber (METC) | 5 | 0-5000 ppm | ± 5 ppm | 1000 | 250 |
| Regenerator (METC) | 5 | 0-100% | ± 5 ppm | 1200-1400 | 233 |
| Reductive Regenerator (METC) | 3 | 0-1000 ppm | ± 10% | 1000 | 233 |
| Fluidized Bed Absorber (METC) | (>200 ppm, mean size <10 μ m) | (>200 ppm, mean size <10 μ m) | | 1000 | 250 |
| Alkali Absorber (METC) | 10 | 0-10 ppm | ± 10% | 1000 | 250 |
| Sulfur Absorber (SSMS) | 5 | 0-5000 ppm | ± 5 ppm | 1470 | 255 |
| Regenerator (SSMS) | 3 | 0-5% | ± 10% | 1000 | 230 |
| Alkali Absorber (SSMS) | 10 | 0-10 ppm | ± 10% | 1470 | 255 |
| Sulfur Absorber (IGT) | 5 | 0-5000 ppm | ± 5 ppm | 1300 | 250 |
| Regenerator (IGT) | 3 | 0-5% | ± 10% | 800 | 35 |
| Sulfur Condenser (IGT) | 10 | 0-100% | ± 10% | 200 | 15 |
| Combustor | 5 | 0-500 ppm | ± 10% | 1650 | 150 |
| Cyclones | | (Size Range 50% <30 μ m, Loading <1 gr/scf) | | 1650 | 150 |
| Fine Particle Cleanup | | (Size Range 50% <2 μ m, Loading <.015 gr/scf) | | 1600 | 150 |
| Alkali Absorber | 10 | 0-10 ppm | ± 10% | 1600 | 150 |
| Tar Cracker | 10 | 0-10 ppm | ± 10% | 1472 | 225 |
| Ammonia Scrubber | 5 | 0-10% | ± 10% | 100 | 555 |
| Sulfur Absorber (Selexol) | 3 | 0-5000 ppm | ± 5 ppm | 120 | 22 |
| Sulfur Absorber (Zinc Oxide) | 3 | 0-1 ppm | ± 10% | 750 | 515 |
| Sulfur Polisher (METC) | 3 | 0-1 ppm | ± 10% | 1000 | 250 |
| Sulfur Polisher (SSMS) | 3 | 0-1 ppm | ± 10% | 1400 | 170 |
| Sulfur Polisher (IGI) | 5 | 0-1 ppm | ± 10% | 1300 | 170 |

Table 4. Summary of Process Analyzer Availabilities.

| Upstream Unit (Process) | Req. ndices (See Table 2) | See Note 6 | | | | | | | | | Component(s) |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | I | E | S | M | G | O | R | C | F | |
| $H_2S$ Sorption/Regen. | See Note 7 | | X | X | | | X | | | | $H_2S$ |
| Sulfur Polisher | 24 | | X | X | | | X | | | | $H_2S$ |
| $H_2S$ Sorption/Regen. | See Note 7 | | X | X | | | | X | | | $H_2S$ |
| Regenerator (IGT) | 15, 39 | X | | X | | | X | | | | $SO_2$ |
| Regenerator (METC) | 4, 7, 27, 30 | | X | X | | | X | | | | $SO_2$ |
| PFBC Combustor | 17 | | X | X | | | X | | | | $SO_2$ |
| Alkali Absorber | 10, 13, 20 | X | | | X | | | X | | | Alkali Metals |
| Sulfur Condenser (IGT) | 16 | | X | | X | | X | | | | $N_2$, $SO_2$ |
| Ammonia Scrubber | 22 | | X | X | | | X | | | | $NH_3$ |
| Sulfur Polisher | 33, 34, 37, 40 | | X | | | | X | | | | $H_2S$ |
| Sulfur Polisher | 33, 34, 37, 40 | | X | | | | X | | | | $C1_2$ |
| Sulfur Polisher | 33, 34, 37, 40 | | X | | | X | | X | | | See Note 1 |
| Gasifier | 2, 25 | | X | | | | X | | | | $H_2S$ |
| Gasifier | 2, 25 | | X | | | | X | | | | $H_2$ |
| Gasifier | 2, 25 | | X | | X | | X | | | | CO, $CO_2$, $CH_4$ |
| Tar Cracker | 21 | | X | | | | X | | | | Hydrocarbons |
| Incinerator Stack | 43, 50 | X | | | | X | X | | X | | See Note 2 |
| Incinerator Stack | 43, 50 | | X | | | X | | X | | | See Note 2 |
| Water Treatment | 51 | | X | | | | X | | X | | BOD |
| Water Treatment | 51 | | X | | | | X | | X | | Dissolved $0_2$ |
| Water Treatment | 51 | | X | | | X | | X | | | See Note 3 |

NOTES:
1. $H_2S$, COS, $CS_2$, $SO_2$, $C1_2$, HC1, alkali halides.
2. Using an IR instrument, up to six components can be selected (e.g. CO, $CO_2$, $SO_2$, NO, HC1, hydrocarbons). Using a GCsimilar measurements would be made but with better resolution and higher accuracy.
3. Numerous organic and inorganic wastewater pollutants.
4. Cycle time or response time (percentage of response).
5. A general purpose analyzer such as the Siemens P101 Gas Chromatograph may be preferred for research purposes.
6. I - in situ, E - extractive, S - single parameter, M - multi-parameter, G - general purpose instrument, O - operational, R - research, C - current environmental regulations, F - future environmental regulations.
7. Absorbers: 1, 3, 6, 11, 14, 23, 26, 29, 35, 38, Regenerators: 12, 36, Reductive Regenerators: 5, 8, 28, 31.

Table 4. Summary of Process Analyzer Availabilities (Cont'd).

| Upstream Unit (Process) | Response (sec) (See Note 4) | Range Limits | Manufacturer | Model No. | Method |
|---|---|---|---|---|---|
| $H_2S$ Sorption/Regen. | 150 | 0-20 ppb, 0-100% | Houston Atlas | 722R | Paper Tape |
| Sulfur Polisher | 75 (90) | 0-0.5 ppm, 0.5-50 ppm | Thermo Electron | 45-1 | Pulsed UV |
| $H_2S$ Sorption/Regen. | 75 (90) | 0-50 ppm, 0-5000 ppm | Thermo Electron | 45-2 | Pulsed UV (See Note 5) |
| Regenerator (IGT) | <60 | 0-1000 ppm, 0.25-25% | Westinghouse | 260 | $K_2SO_4$ Probe |
| Regenerator (METC) | 5 (90) | 0-50 ppm, 0-100% | Anarad | AR-30SM | NDUV |
| PFBC Combustor | 5 (90) | 0-50 ppm, 0-100% | Anarad | AR-30SM | NDUV |
| Alkali Absorber | | (comm. prototype under development) | | | Atomic Emission Spectrometer |
| Sulfur Condenser (IGT) | 24 (90) | 0-10%, 0-50% ($SO_2$) | Leeds & Northrup | 7866 | Thermal Conductivity |
| Ammonia Scrubber | 18 (95) | 0-10 ppm, 0-100% | Foxboro | 973 | IR |
| Sulfur Polisher | 75 (90) | 0-0.5 ppm, 0.5-50 ppm | Thermo Electron | 45-1 | Pulsed UV |
| Sulfur Polisher | 5 (90) | 0-100 ppm | Anarad | AR-300R | NDUV |
| Sulfur Polisher | Approx. 5 Min. | ppb/ppm | Siemens | P101 | GC |
| Gasifier | 150 | 0 - 100% | Houston Atlas | 722R | Paper Tape |
| Gasifier | 24 (90) | 0 - 100% | Leeds & Northrup | 7866 | Thermal Conductivity |
| Gasifier | 5 (95) | 0 - 100% | Syconex | 6000 | IR |
| Tar Cracker | Approx. 10 Min. | ppb/ppm | Siemens | P101 | GC |
| Incinerator Stack | 5 (95) | ppm/percent | Syconex | 6000 | IR |
| Incinerator Stack | Approx. 10 Min. | ppm/percent | Siemens | P101 | GC |
| Water Treatment | 150 | 0-10, 0-20000 ppm C | Ionics | M82 | Total Oxygen Demand |
| Water Treatment | | 0-150% sat'n | Siemens A.G. | M54345 | Polagraphic Electrode |
| Water Treatment | Approx. 10 Min. | ppb/percent | Waters Promonix | | HPLC |

NOTES:
4. Cycle time or response time (percentage of response).
5. A general purpose analyzer such as the Siemens P101 Gas Chromatograph may be preferred for research purposes.

# REDUCED ENTRAINMENT PRECIPITATOR (REP) FOR HIGH-TEMPERATURE & HIGH-PRESSURE (PHASE I)

1. CONTRACT NUMBER: DE-AC01-86ER80343

CONTRACTOR: ETS, Inc.
3140 Chaparral Drive SW
Suite C-103
Roanoke, VA 24108

CONTRACTOR PROJECT MANAGER: Mr. John Mycock

PRINCIPAL INVESTIGATOR: Mr. Dale Furlong

METC PROJECT MANAGER: Mr. Thomas P. Dorchak

PERIOD OF PERFORMANCE: July 15, 1986 to January 31, 1987

2. SCHEDULE/MILESTONES:

| | |
|---|---|
| Design & Fabricate Bench-Scale Model | 9/15/86 |
| Complete Parametric Tests | 11/28/86 |
| Submit Phase I Final Report | 1/26/87 |

3. OBJECTIVES:

The overall technical objective of Phase I was to demonstrate the particulate removal capability of the REP and to determine the technical feasibility of applying the REP to HTHP processes.

4. BACKGROUND STATEMENT:

A concept which has potential application for particulate control in advanced combustion systems such as pressurized fluidized beds is the reduced entrainment precipitator (REP). In an electrostatic precipitator, particles once captured, do not necessarily remain captured. Solid particles, especially those with low resistivity properties, are only lightly held to the collecting plate and can be easily dislodged by the gas flowing by the plates. The REP limits this re-entrainment by the use of porous collecting plates, allowing a bleed stream of clean gas to flow through and thus exerting an aerodynamic force on the collected particulate.

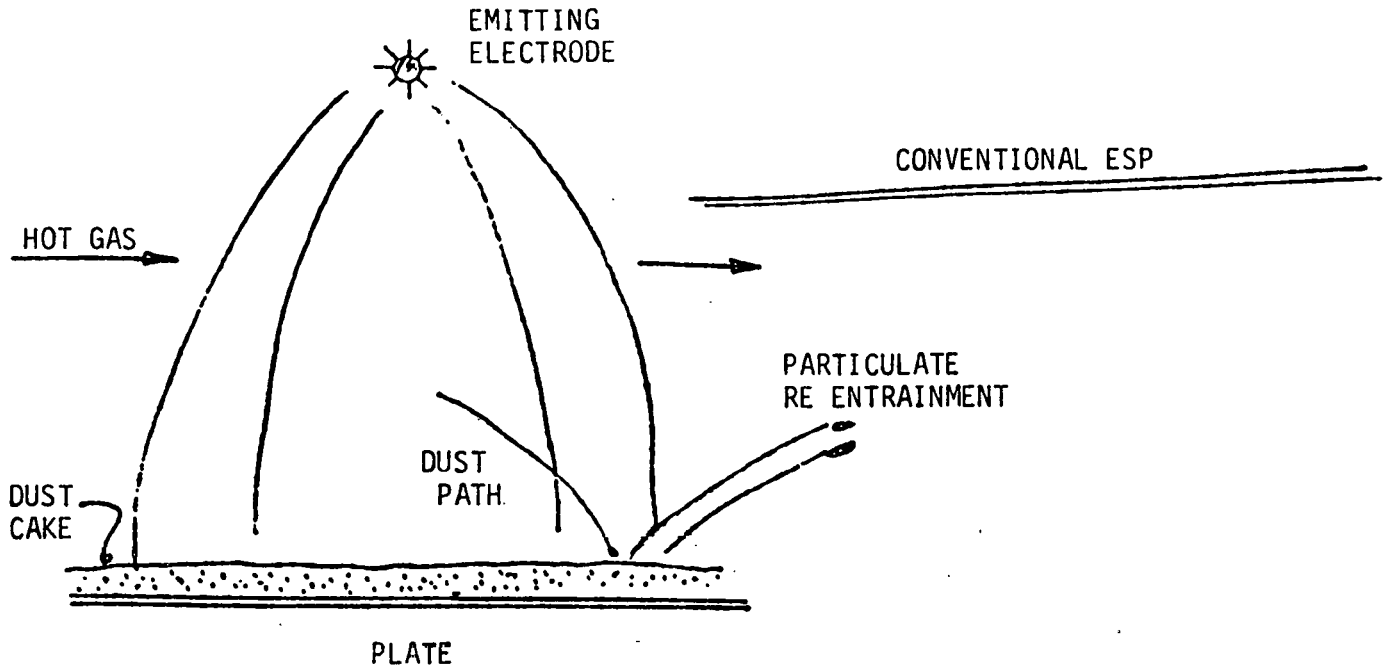
5. PROJECT DESCRIPTION:

Five specific tasks were identified for Phase I:

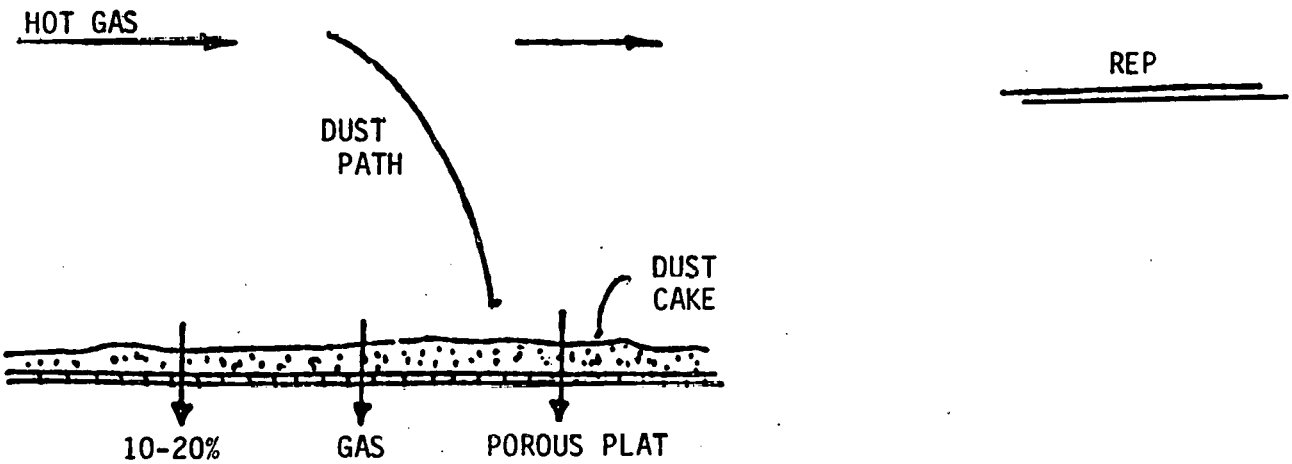
1) Demonstrate the REP's capability of collecting high or low resistivity ash.

2) Demonstrate that high or low resistivity ash can be collected and held on the plates during the REP precipitation mode and this ash can be dislodged from the plate during the cleaning mode.

3) Determine the specific parameters required for application of the REP for HTHP conditions.




NON-EMITTING
ELECTRODE




BASIC APPROACH

Comparison of Basic Approach used in the REP to a Conventional Precipitator

4) Provide a preliminary design basis for larger scale testing of the REP under HTHP conditions.

5) Develop preliminary economics of the HTHP REP system.

6. RESULTS/ACCOMPLISHMENTS:

A series of tests was carried out to evaluate the technical feasibility of a Reduced Entrainment Precipitator (REP) for particulate removal from high temperature and high pressure (HTHP) gas streams. The REP consists of a combination of two well understood technologies, the electrostatic precipitator and the fabric filter. The combination of technologies represented by the REP have not been previously used. Hence the real significance of this test series was to evaluate, at ambient conditions, the basic concept of the REP.

- Test results apparently show that the REP can provide significant improvements in the particulate removal efficiency of an ESP. In-depth analysis of the data, beyond the scope of the present effort, would be necessary to confirm this. The improved efficiency was not found to depend on the particulate resistivity. Hence it is predicted that similar improvements should also occur at HTHP conditions.

- A very preliminary economic analysis suggests that the REP should be less costly than either a HTHP ESP or a HRHP fabric filter.

7. FUTURE WORK:

It is proposed that the REP development be carried forward into Phase II. Prime objectives of Phase II would include:

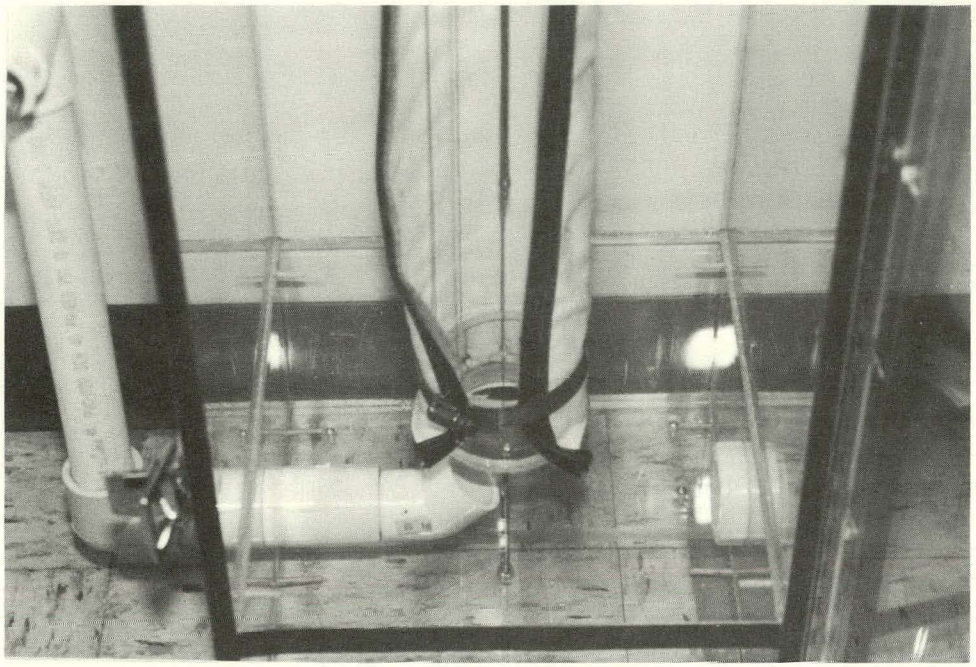
- Evaluate the particulate removal performance of first a 4-inch and second as 8-inch diameter tubular REP at the HTHP conditions of 1600$^{o}$F and 150 psi and for inlet velocities of 4 to 8 ft/sec.

- Evaluate the ability of a plenum pulse type cleaning technique to maintain the particulate removal performance of the HTHP REP configuration.

8. REFERENCES:

Furlong, D. A., Shevlin, T. S., "Fabric Filtration at High Temperature," Chemical Engineering Process, January 1981.

ETS
REDUCED
ENTRAINMENT
PRECIPITATOR
TEST RIG



PHASE I
REP TEST
EQUIPMENT

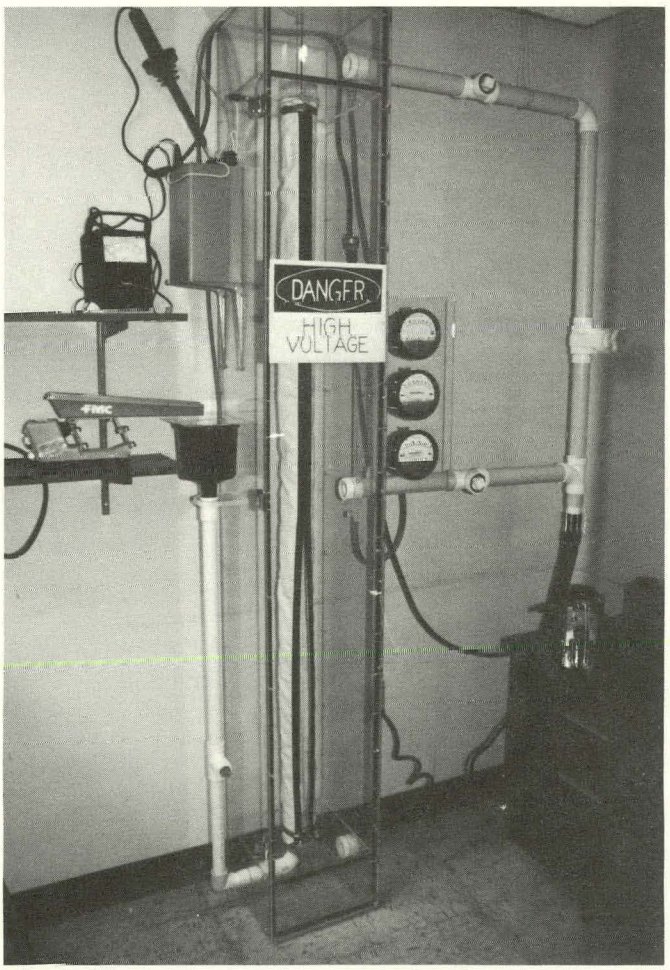


Table 1. Summary of Data from Test Series 1

REP DATA SUMMARY
9/24 - 9/30/86

| RUN NO. | INLET FLOW ACFM | PERCENT SIDE | VOLTAGE kV | CONFIGURATION | FEED RATE gm/min | EFFICIENCY % |
|---|---|---|---|---|---|---|
| 1 | 17.67 | 20 | 21 | 1 | 5.90 | 82.6 |
| 2 | 17.67 | 20 | 20 | 1 | 9.10 | 69.0 |
| 3 | 17.67 | 20 | 20 | 1 | 5.00 | 62.9 |
| 4 | 17.67 | 20 | 0 | 1 | 5.13 | 77.7 |
| 5 | 17.67 | 20 | 10 | 1 | 3.51 | 70.2 |
| 6 | 10.00 | 20 | 20 | 1 | 3.01 | 71.8 |
| 7 | 30.00 | 20 | 20 | 1 | 3.66 | 41.7 |
| 8 | 17.67 | 22 | 22 | 1 | 3.45 | 62.9 |
| 9 | 17.67 | 22 | 0 | 1 | 3.10 | 75.3 |
| 10 | 17.67 | 25 | 19.5 | 2 | 2.89 | 76.7 |
| 11 | 17.67 | 30 | 19 | 2 | 4.90 | 88.4 |
| 12 | 17.67 | 35 | 19 | 2 | 5.86 | 82.4 |
| 13 | 17.67 | 25 | 20 | 3 | 5.14 | 96.6 |
| 14 | 17.67 | 25 | 20 | 3 | 3.86 | 93.4 |
| 15 | 17.67 | 30 | 20 | 3 | 4.71 | 97.1 |
| 16 | 17.67 | 25 | 22 | 4 | 4.33 | 68.8 |
| 17 | 17.67 | 20 | 25 | 5 | 8.13 | 100 |
| 18 | 17.67 | 20 | 25 | 6 | 10.75 | 99.2 |

NOTES - Glass beads used for all runs.

- CONFIGURATIONS:

1 - Electrode - 0.125" diam. mild steel except bottom 8 inches which was 0.032" diam.
Ground - 10 equally spaced 0.020" diam. copper wire.

2 - Electrode - 0.032" diam. mild steel wire, total length of bag.
Ground - Same as No. 1.

3 - Electrode - 0.040" diam. copper wire, full length.
Ground - Same as No. 1.

4 - Electrode - Bottom 2 ft. used 0.032" diam. steel, remainder was o.125" steel.
Ground - Same as No. 1.

5 - Electrode - 0.040" copper wire, full length.
Ground - Window screen, no bag.

6 - Electrode - Same as No. 5.
Ground - 1/2"x1/2"x0.042" diam. wire mesh; mesh inside bag.

Table 2. Summary of Data from Test Series 2

REP DATA SUMMARY
10/6 - 11/3/86

| RUN NO. | INLET FLOW ACFM | SIDE % | VOLTAGE kV | CONFIG. | DUST TYPE | FEED RATE gm/min | DUST LOST grams | EFFICIENCY % |
|---|---|---|---|---|---|---|---|---|
| 19 | 17.67 | 20 | 26/30 | 7 | GB | 16.6 | 7.2 | 99.1 |
| 20 | 17.61 | 20 | 24 | 8 | GB | 8.5 | 25.1 | 97.3 |
| 21 | 17.61 | 20 | 24 | 9 | GB | 4.6 | 10.5 | 98.6 |
| 22 | 17.61 | 20 | 24 | 9 | GB | 11.0 | 5.0 | 99.2 |
| 23 | 17.61 | 20 | 24 | 10 | GB | 9.3 | 27.8 | 95.2 |
| 24 | 17.61 | 20 | 24 | 8 | GB | 12.1 | -1.19 | 98.5 |
| 25 | 17.61 | 20 | 25 | 10 | GB | 12.2 | 34.6 | 96.5 |
| 26 | 17.61 | 20 | 0 | 8 | GB | 7.6 | 6.3 | 62.6 |
| 27 | 17.61 | 20 | 0 | 7 | GB | 8.3 | 2.9 | 99.7 |
| 28 | 17.61 | 20 | 10 | 8 | GB | 7.5 | 11.7 | 97.6 |
| 30 | 17.61 | 10 | 20 | 11 | GB | 11.4 | 15.8 | 93.7 |
| 31 | 17.61 | 0 | 15/22 | 11 | GB | 11.7 | 14.4 | 89.2 |
| 32 | 17.61 | 30 | 25 | 11 | GB | 10.3 | 13.6 | 93.8 |
| 33 | 35.34 | 15 | 23 | 11 | GB | 16.6 | -14.1 | 82.7 |
| 35 | 16.35 | 22 | 20 | 12 | GB | 11.0 | 26.3 | 54.8 |
| 36 | 16.35 | 22 | 20 | 12 | GB | 11.1 | 14.5 | 40.6 |
| 37 | 16.35 | 22 | 20 | 12 | FA | 8.8 | 50.0 | 96.8 |
| 38 | 16.35 | 22 | 20 | 12 | GB | 14.3 | 17.8 | 33.3 |
| 39 | 16.35 | 22 | 20 | 12 | GB | 14.3 | 11.4 | 22.9 |
| 40 | 16.35 | 22 | 0 | 12 | GB | 11.1 | 7.3 | 22.9 |
| 41 | 16.35 | 22 | 0 | 12 | FA | 6.7 | 50.7 | 68.5 |
| 42 | 16.35 | 22 | 20 | 12 | FA | 10.0 | 39.0 | 96.1 |
| 43 | 16.35 | 22 | 20 | 12 | GD | 8.33 | 47.5 | 97.5 |
| 44 | 16.35 | 22 | 0 | 12 | GD | 10.0 | 37.4 | 67.0 |
| 45 | 16.35 | 22 | 20 | 13 | GD | 12.5 | 40.1 | 93.3 |

CONFIGURATIONS:

ELECTRODE : Bottom 2 feet made of 0.040" diam. mild steel wire, remainder of 0.125" diam. mild steel.

GROUND PLANE :

7 - 1/2" Wire mesh cage; No bag.
8 - 1/2" Wire mesh cage; Bag on inside of screen.
9 - Fine mesh cage; No bag.
10 - Fine mesh cage; Bag on inside of screen.
11 - 1/2" Wire mesh cage; Bag on inside; Funnel at bottom of bag.
12 - 1/2" Wire mesh cage; Bag outside of screen; Funnel at bottom.
13 - No Cage; Bag only.

DUST TYPE:

GB - glass beads
FA - fly-ash
GD - gassifier dust

Table 3. Summary of Data from Test Series 3

(11/24 - 12/3/86)

| Run # | % Side | Duration min. | Efficiency % | Penetration % | Max P in.W.G. | Accum.Dust grams |
|---|---|---|---|---|---|---|
| 101 | 50 | 60 | 98 | 1.97 | 0.9 | ~ 0 |
| 101-A | 50 | 10 | - | - | 1.0 | 359 |
| 102 | 50 | 60 | 100 | 0.02 | 0.95 | 337 |
| 103 | 50 | 60 | 99.9 | 0.06 | 0.85 | 714 |
| 104 | 50 | 60 | 99.8 | 0.15 | 1.95 | 1043 |
| 105 | 0 | 5 | - | - | - | 1365 |
| 106 | 0 | 35 | 94.3 | 5.69 | - | 1206 |
| 107 | 0 | 25 | 89.6 | 10.43 | - | 1293 |
| 108 | 0 | 17 | 78.6 | 21.43 | - | 1382 |
| 109 | 50 | 60 | 99.7 | 0.35 | 1.68 | 1356 |
| 110 | 25 | 58 | 95.7 | 4.34 | 1.9 | 1626 |
| 111 | 25 | 5 | - | - | 1.3 | 1945 |
| 112 | 25 | 60 | 96.6 | 3.44 | 1.2 | 1404 |
| 113 | 25 | 60 | 97.0 | 3.02 | > 2 | 1680 |
| 114 | 37.5 | 60 | 97.6 | 2.37 | 5.0 | 1990 |
| 115 | 37.5 | 60 | 94.9 | 5.08 | 8.0 | 2297 |
| 116 | 37.5 | 32 | 90.6 | 9.38 | 9.0 | 2594 |
| 117 | 37.5 | 57 | 90.7 | 9.30 | 10.0 | 2408 |
| 118 | - | - | - | - | - | 2623 |
| 119 | 37.5 | 60 | 99.7 | 0.26 | 0.5 | 294 |
| 120 | 37.5 | 60 | 100 | 0.05 | 0.3 | 345 |
| 121 | 25 | 60 | 100 | 0.04 | 0.2 | 342 |
| 122 | 0 | 60 | 99.5 | 0.54 | - | 388 |
| 201 | 0 | 29 | 97 | 3.01 | - | 394 |
| 202 | 25 | 60 | 98.6 | 1.41 | 1.0 | 348 |
| 203 | 15 | 60 | 99.8 | 0.22 | 0.15 | 444 |
| 204 | 25 | 60 | 99.7 | 0.32 | 0.35 | 583 |
| 205 | 7.5 | 31 | 93.1 | 6.87 | 0.5 | 671 |
| 301 | 25 | 53 | 96.2 | 3.85 | > 2 | 402 * |

NOTES - Inlet flow rates: 26.5 ACFM (Runs 101-122)
35.4 ACFM (Runs 201 - 301)
- Inlet dust rates: 7 gm/min. (Runs 101-122)
9.3 gm/min (Runs 201 - 301)
- Accum. Dust = Total amount of dust in bag before run.
- * Bottom half of bag covered with plastic for run 301.

Table 5. Preliminary Economics of the HTHP REP Systems

DESIGN ASSUMPTION:

System Size = 110 MW
System Flow = 85,000 ACFM
Temp. = 1650°F
Pressure = 139 PSIA
Six separate modules each with outlet poppet, hopper and high voltage power supply.
Module Diameter = 11 feet
Module Height = 24 feet
Number of tubes/module = 91
Tube Size = 8" dia. x 96" length

MODULE COSTING:

| | | |
|---|---|---|
| Fabricated Metal @ $1.50/lb. | = | $ 31,635 |
| Insulation (25% of metal cost) | = | 7,909 |
| Internal Metal Parts @ $7.50/lb | = | 46,350 |
| Ceramic Fabric Tubes @ $500/tube | = | 45,500 |
| High Voltage Power Supplies | = | 50,000 |
| Poppet Valve Actuator | = | 5,000 |
| | | $ 186,394 |

INSTALLED SYSTEM COSTING

| | | |
|---|---|---|
| Six Modules | = | $1,118,364 |
| Manufacturer's Profit @ 40% | = | 447,346 |
| Manufacturer's Selling Price (Q) | = | $1,565,710 |
| Installation Materials @ .27 Q | = | $ 442,742 |
| Installation Labor @ .77 Q | = | 1,205,597 |
| Engineering @ .10 Q | = | 156,571 |
| Contractors Fee @ .15 Q | = | 234,857 |
| Taxes @ .03 Q | = | 46,971 |
| Sub-Total | = | $3,632,447 |
| 20% Contingency | = | 726,489 |
| TOTAL CAPITAL COST | = | $4,358,937 |
| UNIT CAPITAL COST | = | $ 39.63/KW |
| COMPARABLE ESP UNIT CAPITAL COST (REF. 5) | = | $ 77.90/KW |

## VAPORIZATION OF TRACE INORGANIC SPECIES FROM COAL UNDER COMBUSTION AND GASIFICATION CONDITIONS

1. CONTRACT NUMBER: DE-AC21-86MC23261

CONTRACTOR:
SRI International
333 Ravenswood Avenue
Menlo Park, CA 94025
(415) 859-2019

CONTRACTOR PROJECT MANAGER: Dr. Robert D. Brittain

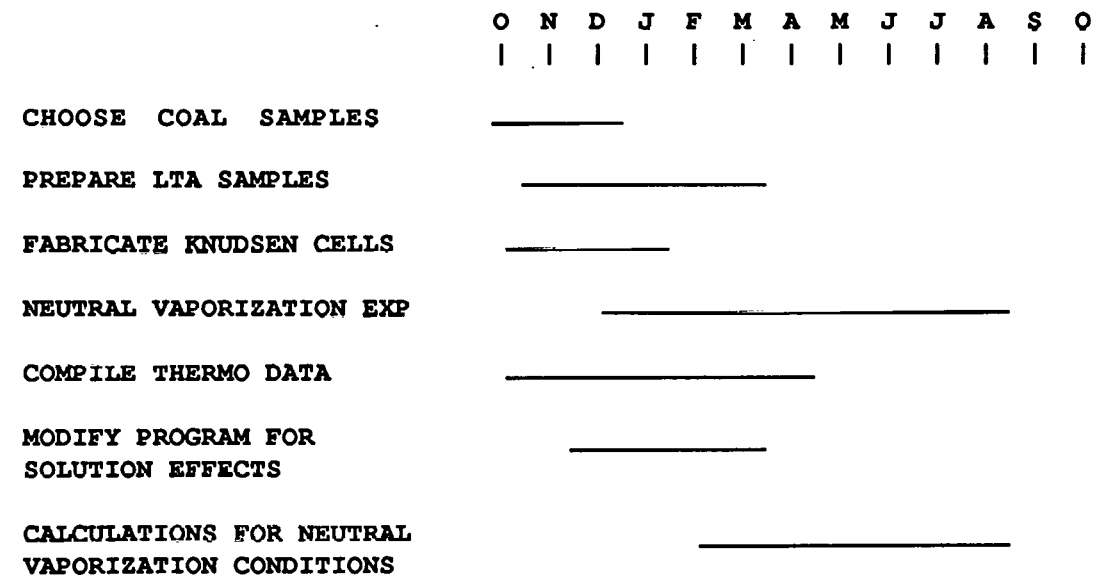
PRINCIPAL INVESTIGATORS:
Dr. D. L. Hildenbrand
Dr. K. H. Lau
Dr. R. H. Lamoreaux
Dr. G. N. Krishnan
Dr. R. D. Brittain

METC PROJECT MANAGER: Dr. Norman Holcombe

PERIOD OF PERFORMANCE: September 24, 1986 to September 23, 1988

2. SCHEDULE/MILESTONES:

1986-87 Program Schedule



3. OBJECTIVES:

The objective of this project is to establish the chemical forms and relative abundances of trace inorganic species in coal during combustion and gasification. Knowledge of the chemical species involved in trace element transport will be useful in designing strategies for removal of species with negative impacts on various coal use technologies.

4. BACKGROUND STATEMENT:

Whereas some trace element volatilized from coal during combustion or gasification have negative technological or environmental effects, the chemical species involved in vapor transport of most of these elements have not been directly identified. This program is designed to identify the chemical forms and relative abundances of trace element vapor species by an interactive experimental and calculational approach.

5. PROJECT DESCRIPTION:

Knudsen cell mass spectrometry and Gibbs energy minimization calculations are being used to study the vaporization of two representative U. S. coals: Illinois No. 6 bituminous and Wyodak subbituminous. Experimental studies are performed by Knudsen cell mass spectrometry on samples of each coal which have been ashed at low temperature by an oxygen plasma. This low temperature ashing process retains inorganic species in the product ash. To more closely simulate actual coal, some samples are only partially ashed to retain some of the original organic components. Vapor species are identified, and their abundances measured, over the temperature range 300 - 1700 K. In the first year of the program, vaporization from the coal ash alone is being studied; in the second year, the influence of added oxidizing and reducing gas mixtures on trace element vaporization will be investigated.

Coincident with experimental studies, trace element vaporization behavior is being evaluated by Gibbs energy minimization calculations. A data base including both solution and pure condensed and gaseous components has been compiled. Nearly three hundred species are considered in the calculations. During the first year of the project, calculations are being performed to simulate the conditions of the mass spectrometry experiments. The approach is interactive: species seen in mass spectrometry experiments are added to the data base for calculations, and predicted species from calculations are searched for in the experiments. After reasonable agreement has been reached between the results of the two approaches, calculations during the second year of the program will be extended to the higher pressure conditions existing during actual coal gasification and combustion. The results of the latter calculations will be used to evaluate proposed strategies for the removal of trace elements which have deleterious technological or environmental effects.

6. RESULTS/ACCOMPLISHMENTS:

- Selected and obtained samples of Illinois No. 6 and Wyodak coals; prepared samples for mass spectrometric analysis by low-temperature oxygen plasma ashing (LTA).

- Identified vapor species above both Illinois No. 6 and Wyodak LTA samples. The samples chosen were ashed to constant weight, or to within 90% of constant weight (to retain more hydrocarbons in the ash). Over 50 vapor species of over 25 elements have been identified in the temperature range 300 - 1700 K. Two new vapor species were observed above both of the coal samples: $NaBS_2$ and $KBS_2$.

- Measured dynamic pressures of the vapor species above Illinois No. 6 LTA samples as functions of time and temperature over the range 300 - 1700 K (See Tables 1 and 2).

- Modified an existing SRI computer code for Gibbs energy minimization calculations to allow inclusion of solution effects. The new program, CEQSOL can be used with up to 250 species of 30 elements.

- Compiled a data base of major and trace element vapor and condensed phase species for initial calculations. Thermodynamic data for oxide solution phases of major mineral phases were estimated.

- Completed initial calculations to establish the vaporization behavior of major mineral species from Illinois No. 6 coal.

7. FUTURE PLANS:

During the next year of the project, the experimental studies will be extended to address the effects of added gases ($H_2/H_2O$, $CO/CO_2$, and $O_2$) on the chemical identities of trace element species above the LTA coal samples. Calculations will be carried out to model the vaporization of trace species from LTA coal under neutral conditions (no added gases) and in the presence of added gases. When satisfactory agreement has been reached between the results of experiments and calculations, the calculations will be extended to the higher pressure regime of coal gasification and combustion. We will then evaluate the implications of the results for proposed trace element removal strategies (e.g. for removal of certain trace elements from hot coal gas before entry to molten carbonate fuel cells).

Table 1. Mass Spectrometry Results for Illinois No. 6 - 90% Ashed

| Element | Conc (ppm) | Species | T (max, K) | P (max, atm) [a] |
|---|---|---|---|---|
| Li | 140 | Li | 1681 | $3.2 \times 10^{-10}$ |
| Na | 900 | Na | 1459 | $7.0 \times 10^{-5}$ |
| | (B 160) | $NaBS_2$ | 1382 | $3.5 \times 10^{-7}$ |
| K | MC [b] | K | 1591 | $1.5 \times 10^{-4}$ |
| | | $KBS_2$ | 1268 | $1.8 \times 10^{-7}$ |
| Rb | 30 | Rb | 1591 | $3.7 \times 10^{-7}$ |
| Cs | 5 | Cs | 1681 | $1.4 \times 10^{-8}$ |
| Mg | MC | Mg | 1681 | $3.1 \times 10^{-4}$ |
| Ca | MC | Ca | 1681 | $2.2 \times 10^{-5}$ |
| Sr | 140 | Sr | 1681 | $5.0 \times 10^{-8}$ |
| Ba | 420 | Ba | 1681 | $1.2 \times 10^{-8}$ |
| Mn | 120 | Mn | 1681 | $3.8 \times 10^{-6}$ |
| Fe | MC | Fe | 1681 | $2.2 \times 10^{-6}$ |
| Co | 12 | Co | 1681 | $8.4 \times 10^{-8}$ |
| Zn | 470 | Zn | 1138 | $2.7 \times 10^{-5}$ |
| Cd | 3 | Cd | 1138 | $2.1 \times 10^{-7}$ |
| Al | MC | Al | 1681 | $4.3 \times 10^{-5}$ |
| | | AlF | 1459 | $2.8 \times 10^{-6}$ |
| | | $Al_2O$ | 1681 | $1.3 \times 10^{-5}$ |
| | | $Al_2S$ | 1681 | $3.2 \times 10^{-8}$ |
| Ge | 20 | GeS | 1268 | $3.5 \times 10^{-7}$ |
| Pb | 160 | Pb | 1138 | $9.5 \times 10^{-7}$ |
| | | PbS | 1138 | $2.5 \times 10^{-7}$ |
| As | 32 | As | 1591 | $4.9 \times 10^{-8}$ |
| | | $As_2$ | 1459 | $1.8 \times 10^{-8}$ |
| | | AsS | 1382 | $2.0 \times 10^{-7}$ |
| Sb | 3 | Sb | 1268 | $3.0 \times 10^{-9}$ |
| F | 490 | HF | 1037 | $2.3 \times 10^{-7}$ |
| | | AlF | 1459 | $2.8 \times 10^{-6}$ |

a - dynamic pressures (measured values may be kinetically limited)

b - MC - major component (>1000 ppm)

Table 2. Elements Observed In Other Mass Spectrometry Experiments

| Element | Conc (ppm) | Species | T (K) | Coal |
|---|---|---|---|---|
| Cl | 170 | NaCl | 1073-1273 | Wyodak |
| | | KCl | 1173-1373 | Wyodak |
| | | HCl | 773 | Both |
| I | 2 | HI | 773 | Both |
| Ga | 29 | GaF | 1173-1373 | Wyodak |
| Se | 47 | SeS | 873 | Wyodak |
| Sn | 3 | SnS | 1073-1373 | Both |
| Sb | 3 | Sb | 1268 | Ill. No. 6 |
| | | SbS | 1173-1373 | Both |
| Bi | <1 | Bi | 1038-1138 | Both |
| | | BiS | 1038-1138 | Ill. No. 6 |

HOT GAS CLEANUP SYSTEMS ANALYSIS

Kevin R. Craig and Robert W. Koch
Morgantown Energy Technology Center

The use of high-temperature, high-pressure cleanup processes hold potential for significantly reducing capital and operating costs and increasing efficiencies in coal-based energy production systems. The goal of the hot gas cleanup systems analysis effort at METC is to determine the interaction of novel cleanup processes on the remainder of these energy systems and identify areas where further research could improve efficiency, reduce costs, or increase a processes chances for development and implementation by the commercial sector. These interactions are determined through engineering analyses conducted using a variety of tools including computerized process models, engineering calculations, and literature studies. Figures 1 and 2 outline the objectives and expected products from the hot gas systems analysis activities.

## Objectives

**Assess the system implications of high temperature, high pressure processes for removal of contaminants on the overall performance of coal based systems.**

- **Assess the ability of proposed control schemes to meet environmental and technical performance requirements**
- **Develop system level models of contaminant control schemes and incorporate them into overall system simulations**
- **Use experimental results to improve accuracy and predictive ability of existing models**
- **Assess scale-up potential to commercial units**
- **Assess economics of cleanup systems and their impact on overall system economics**

METC 86-487-1 BE5

FIGURE 1

## Products of Systems Analyses

- Assess understanding of controlling physical and chemical phenomena
- Determine relative economic benefits
- Determine systems implications of various cleanup processes
- Identify technical uncertainties and data needs
- Identify synergisms among related technologies
- Suggest changes which may improve performance, economics, or performance

METC 86-487-6 BE5

FIGURE 2

Figure 3 lists the more significant accomplishments achieved during fiscal year 1987 under the hot gas cleanup systems analysis activity at METC. Most of these are discussed in the following figures and accompanying descriptions.

## Significant Accomplishments

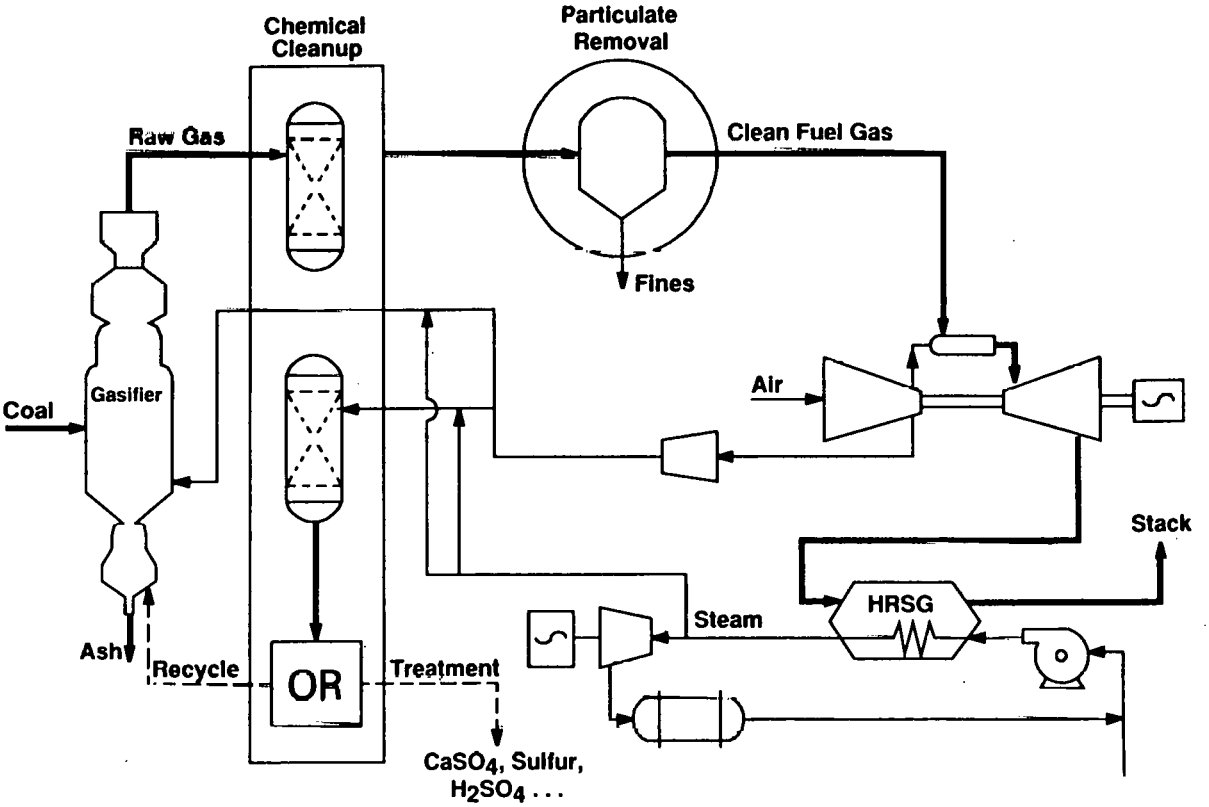
- Assessment of systems and economic issues for in-bed desulfurization in fixed-bed gasifiers
- Analysis of performance aspects of tail-gas treatment options in gasification island systems
- Determination of sulfuric acid industry capacity and production
- Update of estimated zinc ferrite capital and operating costs
- Assessment of existing zinc ferrite modeling tools
- Determination of applicability of hot gas cleanup for methanol production

METC C87-1294-1 TS9

FIGURE 3

The gasification island concept (Figure 4) is a second generation power production option for satisfying the anticipated electric power needs of the 1990's and beyond. The concept features air-blown gasification, high temperature removal of pollutants and pollutant precursors, modular construction, and is applicable for incremental capacity additions. As part of a recent study, METC evaluated options for treatment of the sulfur dioxide containing stream produced when zinc ferrite sorbent is regenerated as well as options for high-temperature, high-pressure removal of particles.

## Gasification Island Concept



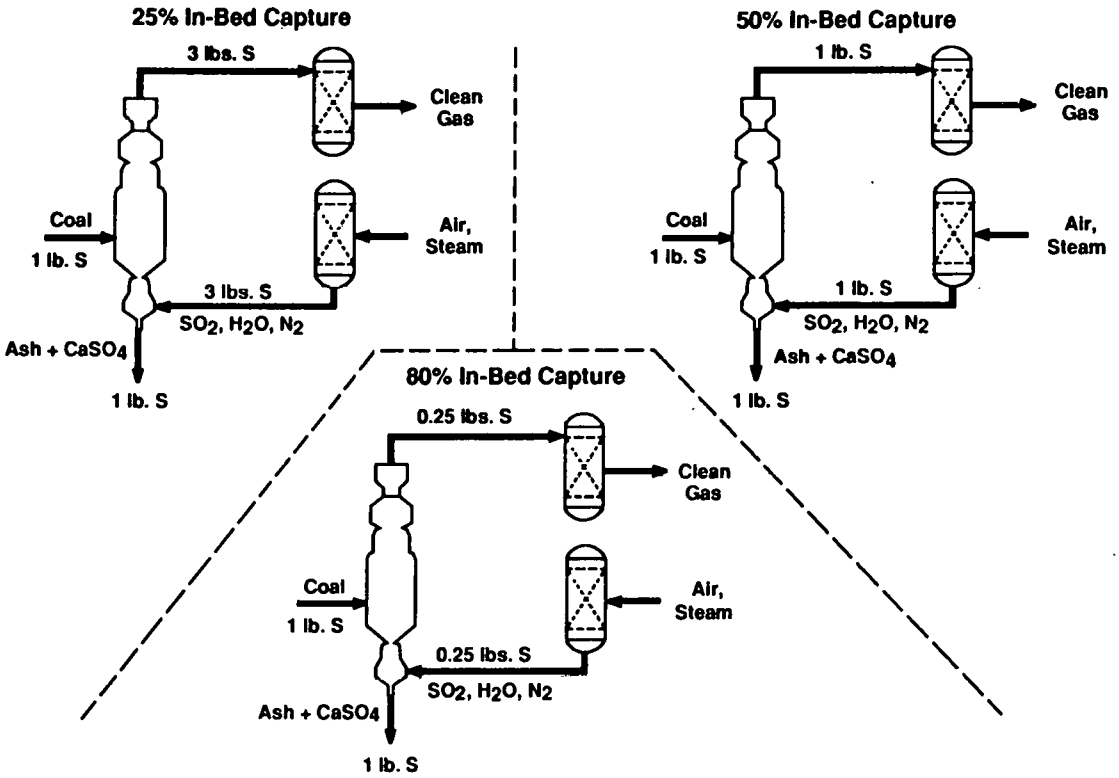

METC 187-1294-B TS9

FIGURE 4

A number of options exist for treating the regeneration tail-gas stream generated during the regeneration of metal oxide desulfurization sorbents. One possibility is recycling the regeneration tail-gas back to the gasifier where sulfur dioxide is captured by a calcium sorbent (e.g. limestone, lime, or dolomite) that is added with the coal. High levels of in-gasifier sulfur capture have been demonstrated in fluidized-bed gasifiers, but the lower capture expected in fixed-beds can significantly affect system viability. One impact of gasifier sulfur capture is the absorption "duty" of the zinc ferrite unit. Figure 5 shows this effect; the lower in-gasifier sulfur capture, the more sulfur is passed on to the zinc ferrite system (potentially even more than contained in the coal). This higher duty results in higher zinc ferrite operating costs. The capital cost of the zinc ferrite units is not likely to be affected since the units are sized on a space velocity and linear gas velocity basis.

# Effect of In-Bed Capture on Absorber Duty

## -- Feed: 25 lbs. of 4% Sulfur Coal --

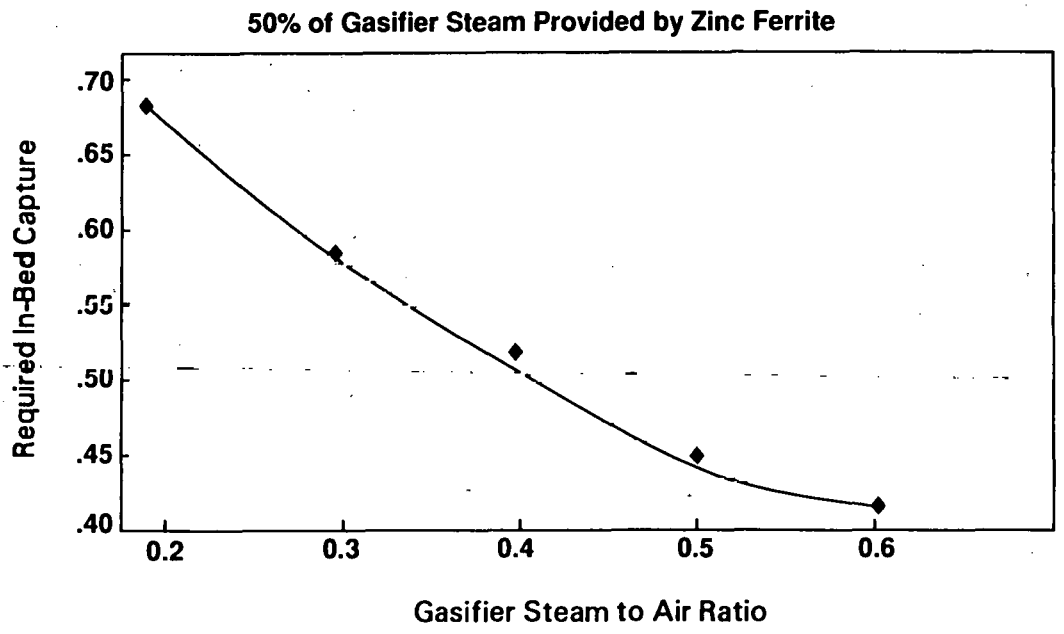



METC I87-1294-J TS9

FIGURE 5

Since steam is used as the diluent in regeneration, increased absorber duty also ultimately results in more steam being fed to the gasifier via the regeneration tail-gas recycle stream. Figure 6 shows the level of in-gasifier sulfur capture required if the recycle stream provides half of the steam required for gasifier operation for a number of gasifier steam/air ratios (the air/coal ratio is fixed). Important parameters affecting this steam balance and the required level of in-gasifier sulfur capture are: gasifier steam/air and air/coal ratios; coal sulfur content; regeneration gas composition (typically 15% air, 85% steam); and the quantity of independent steam desired.

## Required In-Bed Capture: Steam Balance Constraints

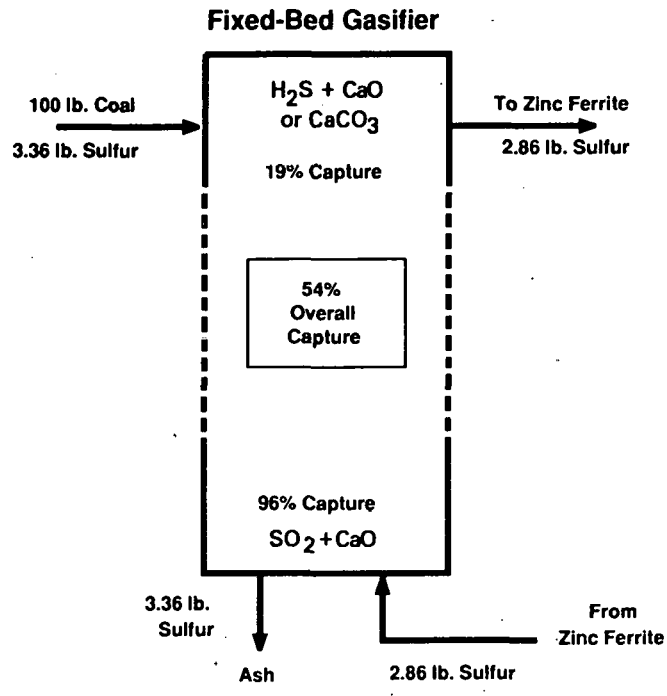



METC C87-1294-E TS9

FIGURE 6

Figure 7 shows, in an idealized representation, how the overall required capture indicated in the previous figure might be obtained. The amount of sulfur capture in the top of a fixed-bed to which limestone has been added is not expected to be large due to the unsuitable form of the sorbent at that point. However, capture in lower bed sections is expected to be quite good since the sorbent will have completed calcination. These separate capture mechanisms average out to provide the overall level indicated in the figure. Of course, in a real gasifier, a number of other reactions can also occur, and the various sulfur capture mechanisms and regions will not be so clearly separated.

# Overall and Individual Capture Mechanisms




METC C87-1294-F TS9

FIGURE 7

Another option that has been evaluated for treatment of the regeneration tail-gas stream is the dual alkali process. This is one of the few (perhaps the only) conventional FGD (Flue Gas Desulfurization) processes expected to be capable of treating the relatively high (in excess of 2.0 percent) sulfur dioxide content of the regeneration tail-gas stream. Operating information for this process as used for flue gas desulfurization was incorporated in an ASPEN (Advanced System for Process ENgineering) model (Figure 8) so that the system effects of this treatment option could be evaluated. Use of the dual alkali process instead of tail-gas recycle to the gasifier decreased the efficiency of a gasification island system by two percentage points. The system studied included a fluidized-bed gasifier, zinc ferrite desulfurization, and a combined cycle for power generation. This decrease results primarily from loss of the steam contained in the regeneration tail-gas stream which would otherwise be returned to the gasifier in a recycle system. Performance predictions will be updated when data from the experimental work being performed (under DOE contract) on the dual alkali process under gasification island conditions by Arthur D. Little Inc. becomes available.

# Tail Gas Treatment Modeling

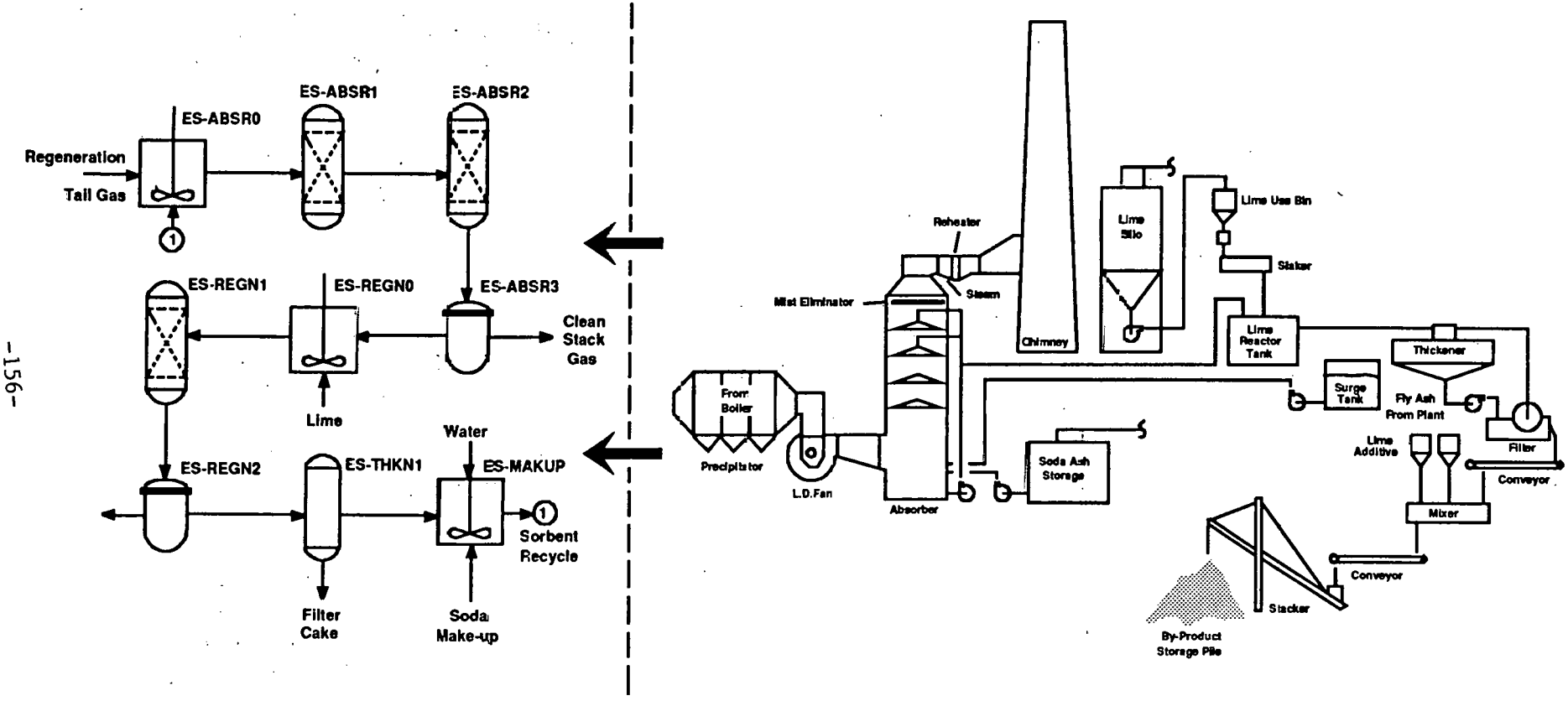







FIGURE 8

A third option for treatment of the regeneration tail-gas stream is the production of sulfuric acid. This option produces a marketable by-product rather than one which must be disposed of. It is necessary, however to consider the market for such a potential product especially if this technology is deployed on a large-scale basis (Figure 9). At present, the fertilizer market, which utilizes sulfuric acid in the production of phosphoric acid, is depressed due to the present problems of U. S. agriculture. There are indications however that prospects are good for modest long-term growth in the sulfuric acid industry. Also, as sulfur from current stockpiles are depleted, there will be a need for new sources of sulfur for sulfuric acid production. No imminent danger exists of sulfuric acid over-supply in the U.S. through the first part of the twenty-first century as a result of new coal burning power plants.

## U.S. Sulfuric Acid Industry

- **Production of sulfuric acid from the $SO_2$ produced in a zinc ferrite unit is a viable alternative to disposal as calcium sulfate**
- **U.S. output of sulfuric acid in 1986 was 38.2 million tons**
- **70% of sulfuric acid is used to make phosphate fertilizers**
- **Sulfuric acid production has declined due to decreased use of fertilizers**
- **1700 (100 MWe) IGCC plants required to produce enough sulfuric acid to meet the total U.S. demand**

METC I87-1294-2 TS9

FIGURE 9

Figure 10 compares the relative economics of the two regeneration tail-gas treatment options discussed above. The added capital and operating costs incurred by the dual alkali process are "chargeable" to additional zinc ferrite sorbent replacement necessitated by recycle of the sulfur dioxide containing stream to the gasifier (see Figure 5). This additional sorbent cost can then be translated (using process operating conditions, sorbent cost and capacity, etc.) into a level of overall in-gasifier sulfur capture. This is the level of capture where the cost for the two options is equal. Any greater level of capture will favor the recycle system. When comparing this level (24%) with the level required for system steam balance (Figure 6), it is clear that, for this set of assumptions and using a fixed-bed gasifier, the operability constraint dominates. Recent experimental work at METC indicates that the required levels of capture may be achievable in fixed-bed gasifiers. The numbers contained in the cost and process analysis are are specific to the case studied, and are affected by a number of process parameters (e.g. sorbent cost and capacity, coal sulfur level, gasifier operating conditions, and calcium to sulfur ratios).

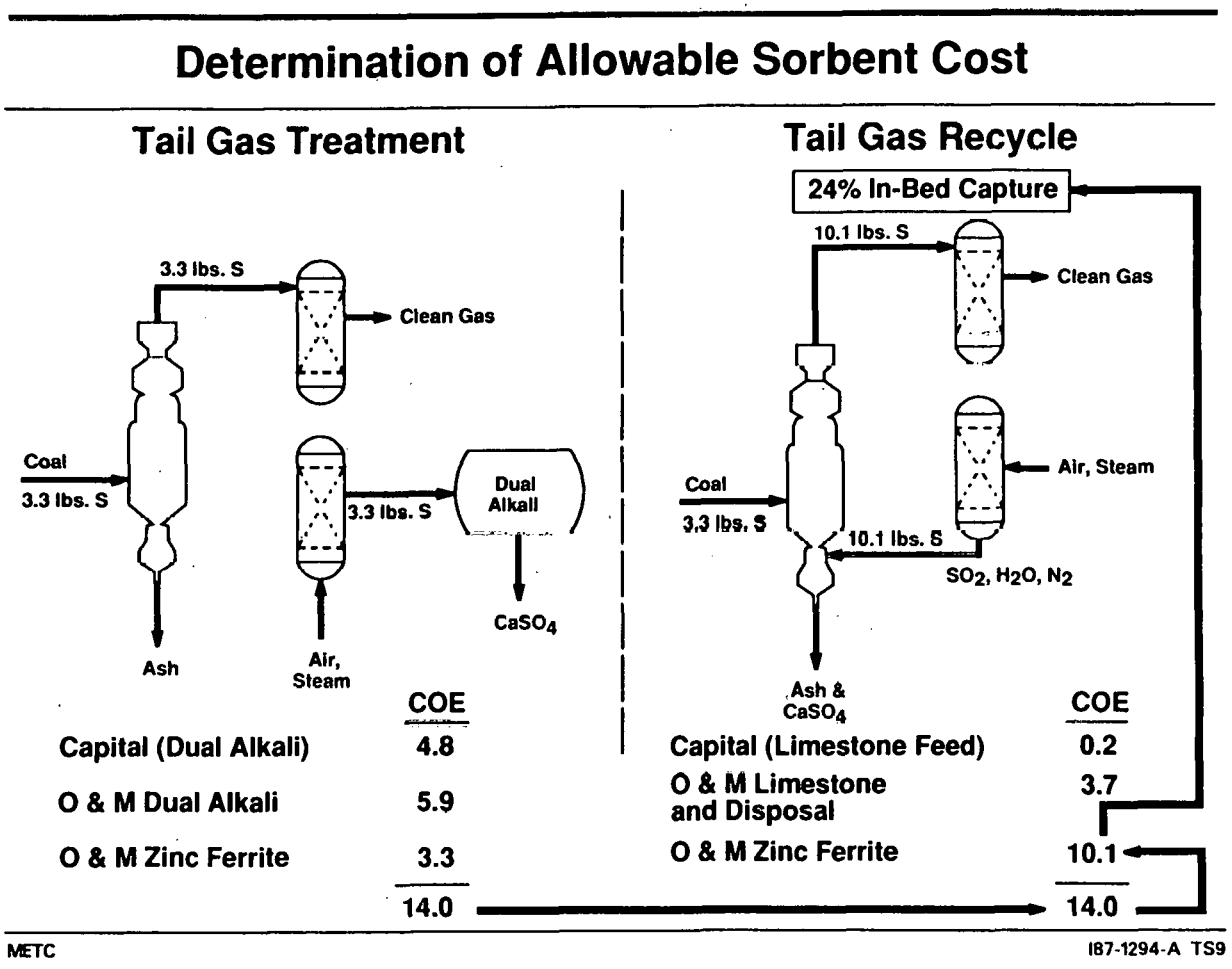



FIGURE 10

As part of METC's continuing effort to assess the critical factors affecting development and commercialization of promising technologies, cost projections are updated based on the most recent experimental findings and economic conditions. Figure 11, an earlier version of which appeared in the proceedings of the Sixth Annual Contractors Meeting on Contaminant Control in Coal-Derived Gas Streams, shows the effect of zinc ferrite sorbent life on the overall cost of sulfur removal. Figure 11 shows that additional cost for zinc ferrite replacement rapidly decreases above a sorbent life of approximately forty cycles, and levels off at a negligible amount at a sorbent life of around sixty cycles (particularly for systems using in-gasifier sulfur capture). These levels of sorbent durability have already been demonstrated (with minimal sorbent deterioration) in small-scale experimental work conducted by AMAX Extractive R&D Inc. under DOE contract. However, even for the lower sorbent durability levels, zinc ferrite retains cost advantage over retrofit LIMB (Limestone-Injection Multi-staged Burner) and FGD technologies. Research is continuing in order to produce sorbents with greater physical strength, sulfur absorption capacity, reactivity, and durability.

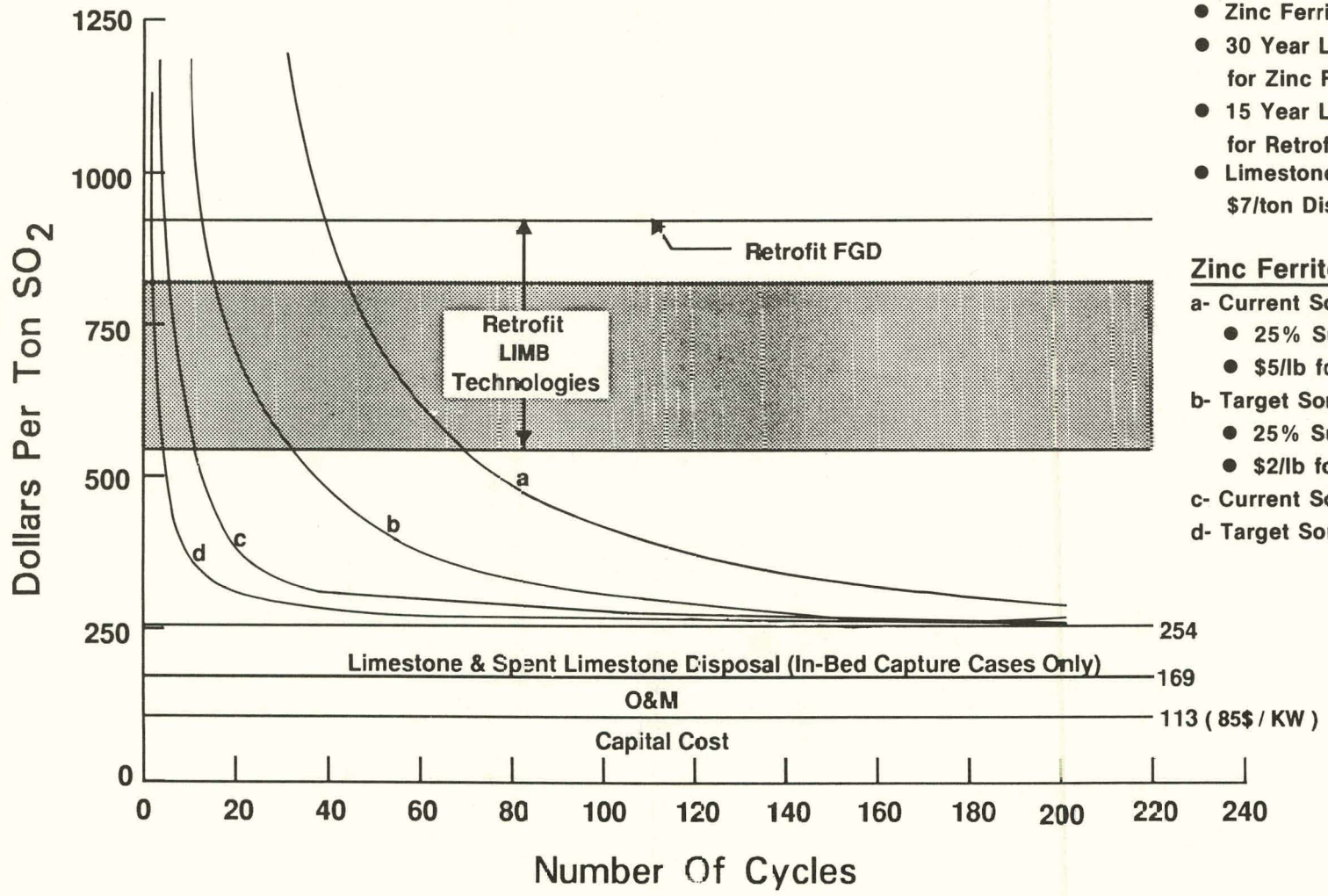
Raw gas from a coal gasifier can be contacted with desulfurization sorbent in a number of ways. Two potential process configurations are the fixed-bed and moving-bed absorbers. Figures 12 and 13 depict these processes and point out the major advantages and concerns of each. A fluidized-bed absorption process would further simplify such aspects as bed temperature control and sorbent transport and replacement, but would require an even stronger, attrition-resistant sorbent particle. The areas of concern noted in the figures are being addressed by on-going DOE research efforts.

Most of the large particles leaving a coal gasifier can be removed from the fuel gas stream using one or more stages of cyclones. In order to protect down-stream components and the environment, however, additional particle removal may be necessary following the desulfurization unit. The particle levels required are less than 1200 ppm for gas turbine protection, and less than 200 ppm to meet projected environmental regulations. Several high-temperature, high-pressure particulate removal devices developed for fluidized-bed combustion applications show promise for gasification systems (Figure 14). Two of these, the ceramic cross-flow filter and the ceramic bag filter, have demonstrated removal efficiencies of over 99 percent in short runs conducted using fuel gas from the METC fluidized-bed gasifier. An electrostatic precipitator was also tested, but encountered difficulties related to equipment design. Research on these devices in gasification applications is continuing in order to improve durability, resolve remaining technical difficulties (e.g., delamination, seam weakness) and to test them on a longer term basis.

Studies have also been undertaken to determine whether other coal-based processes could benefit from application of hot gas cleanup technology. One such investigation involved coal syngas to methanol systems. Depicted in Figure 15 is a representation of one possible process for converting coal to methanol. Also studied was a process employing fluidized-bed gasification and zinc ferrite desulfurization. The latter process was determined to be more feasible from an economic perspective. Further studies are planned to assess the economics and market potential for production of other chemicals from coal.

# Zinc Ferrite Costs

## — 3.8% Sulfur Coal —




**Basis:**

- 3.8% Sulfur Coal
- Zinc Ferrite From GE Systems Study
- 30 Year Levelized Cost for Zinc Ferrite System
- 15 Year Levelized Cost for Retrofit Technologies
- Limestone $16/ton// Ca/S = 2/1 $7/ton Disposal

**Zinc Ferrite Curves**

a- Current Sorbent/No In-Bed Capture
- 25% Sulfur Loading
- $5/lb for Sorbent

b- Target Sorbent/No In-Bed Capture
- 25% Sulfur Loading
- $2/lb for Sorbent

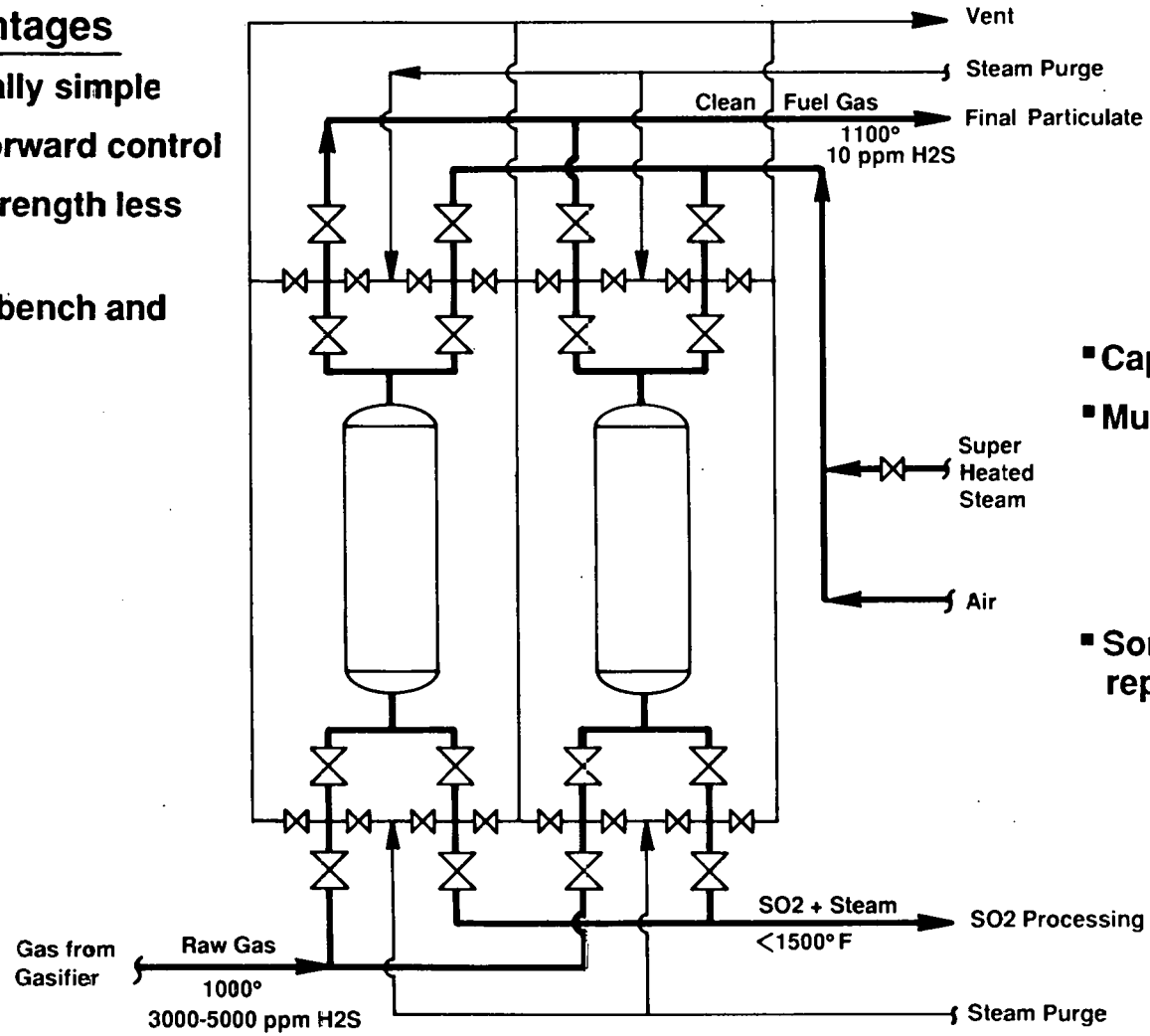
c- Current Sorbent/90% In-Bed Capture

d- Target Sorbent/90% In-Bed Capture

# Dual Fixed-Bed Zinc Ferrite Process

## Advantages

- Mechanically simple
- Straight-forward control
- Sorbent strength less critical
- Proven at bench and PDU scale




## Concerns

- Capital cost (16 major valves)
- Multi-step regeneration
  - Oxidative
  - Purge
  - Reductive (sulfate elimination)
- Sorbent more difficult to replace



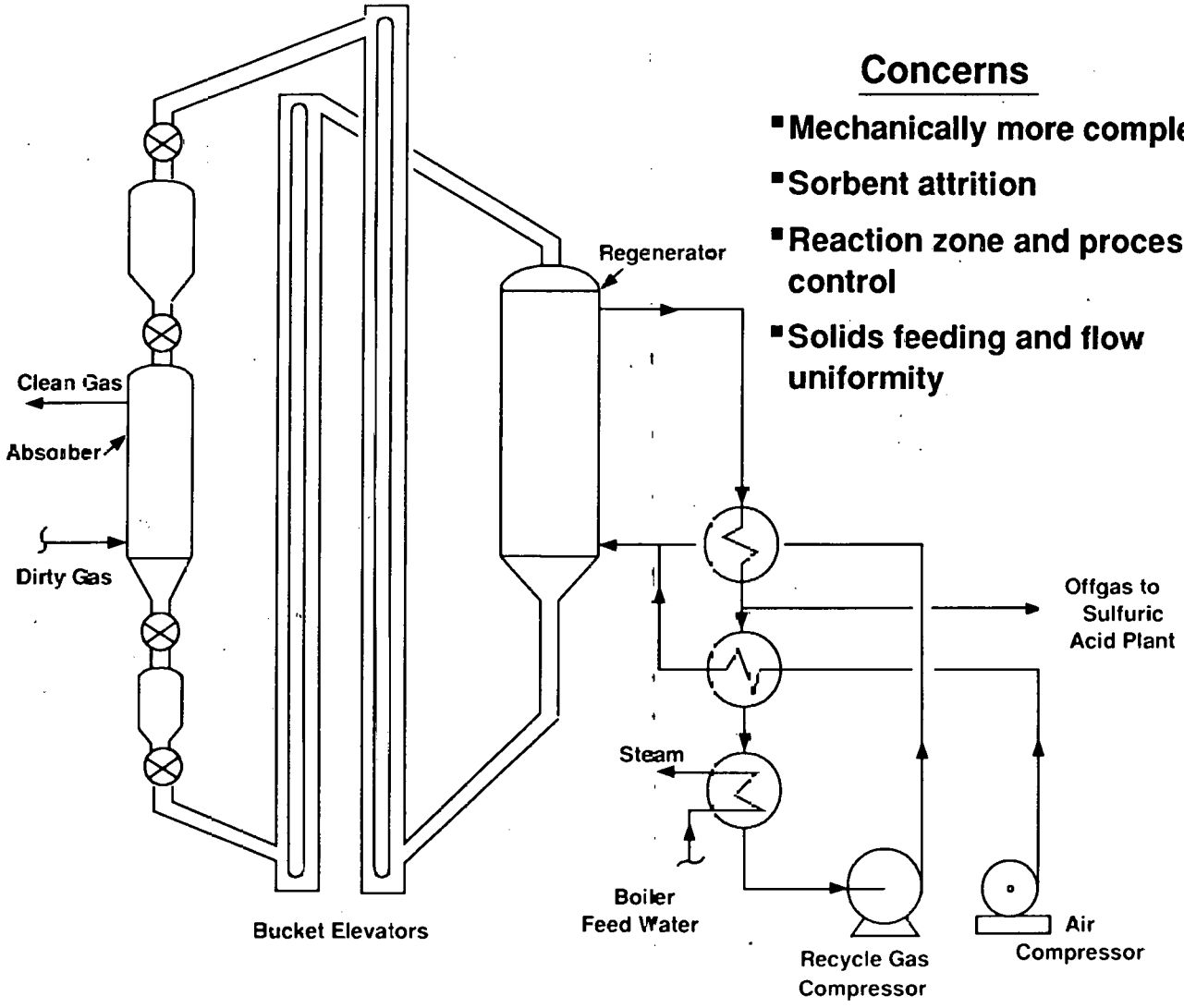


FIGURE 12

# Moving Bed Zinc Ferrite Process

## Advantages

- Utilizes off-gas recycle in place of steam as regeneration diluent
- Oxidative and reducing environments isolated
- Effective integration with off-gas treatment schemes
- Easy sorbent replacement
- Only absorber need be pressurized




## Concerns

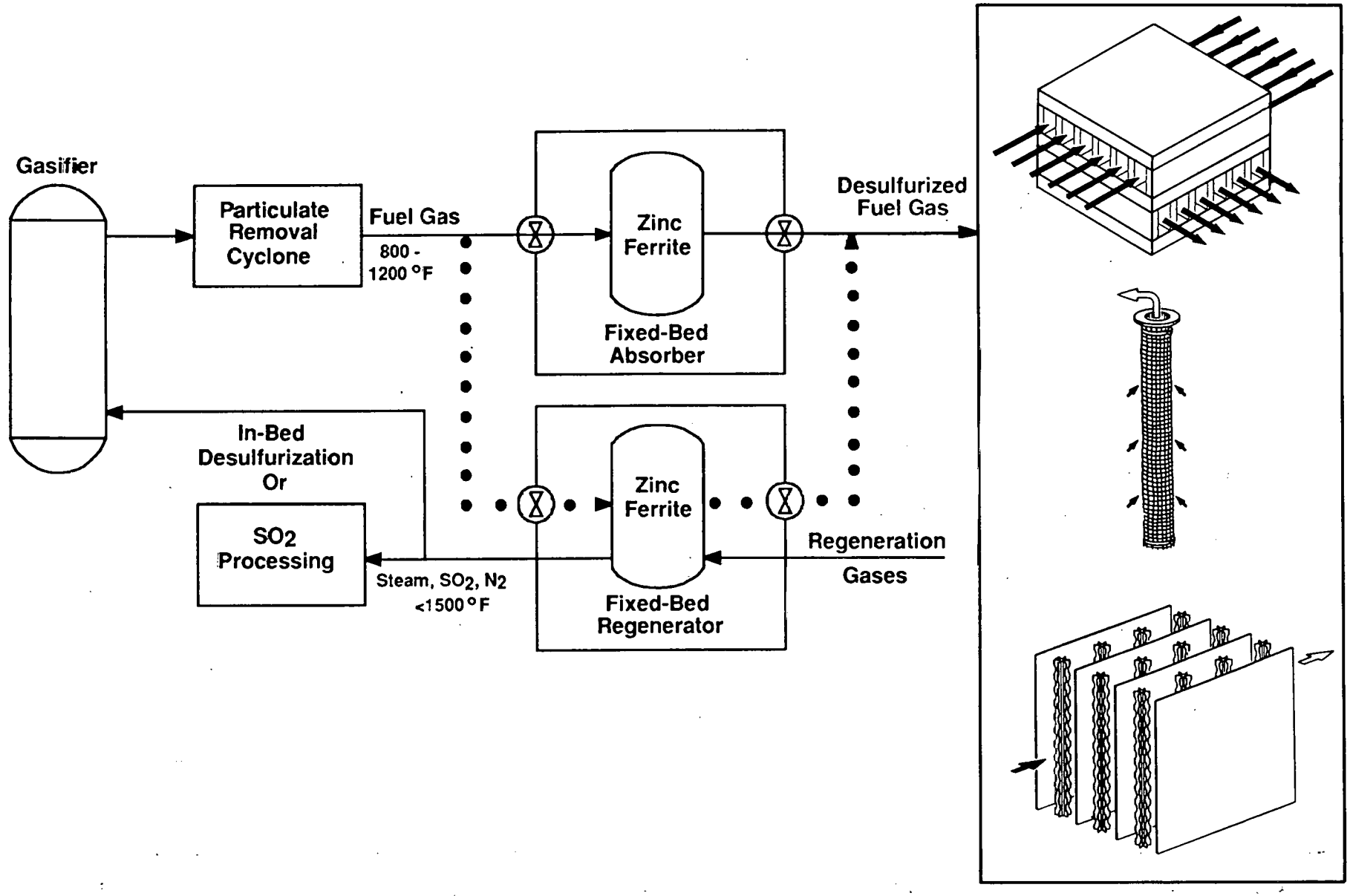
- Mechanically more complex
- Sorbent attrition
- Reaction zone and process control
- Solids feeding and flow uniformity





FIGURE 13

# Particulate Removal Options






METC

I87-1294-K TS9

FIGURE 14

# Proposed Coal to Methanol System Using Hot Gas Cleanup

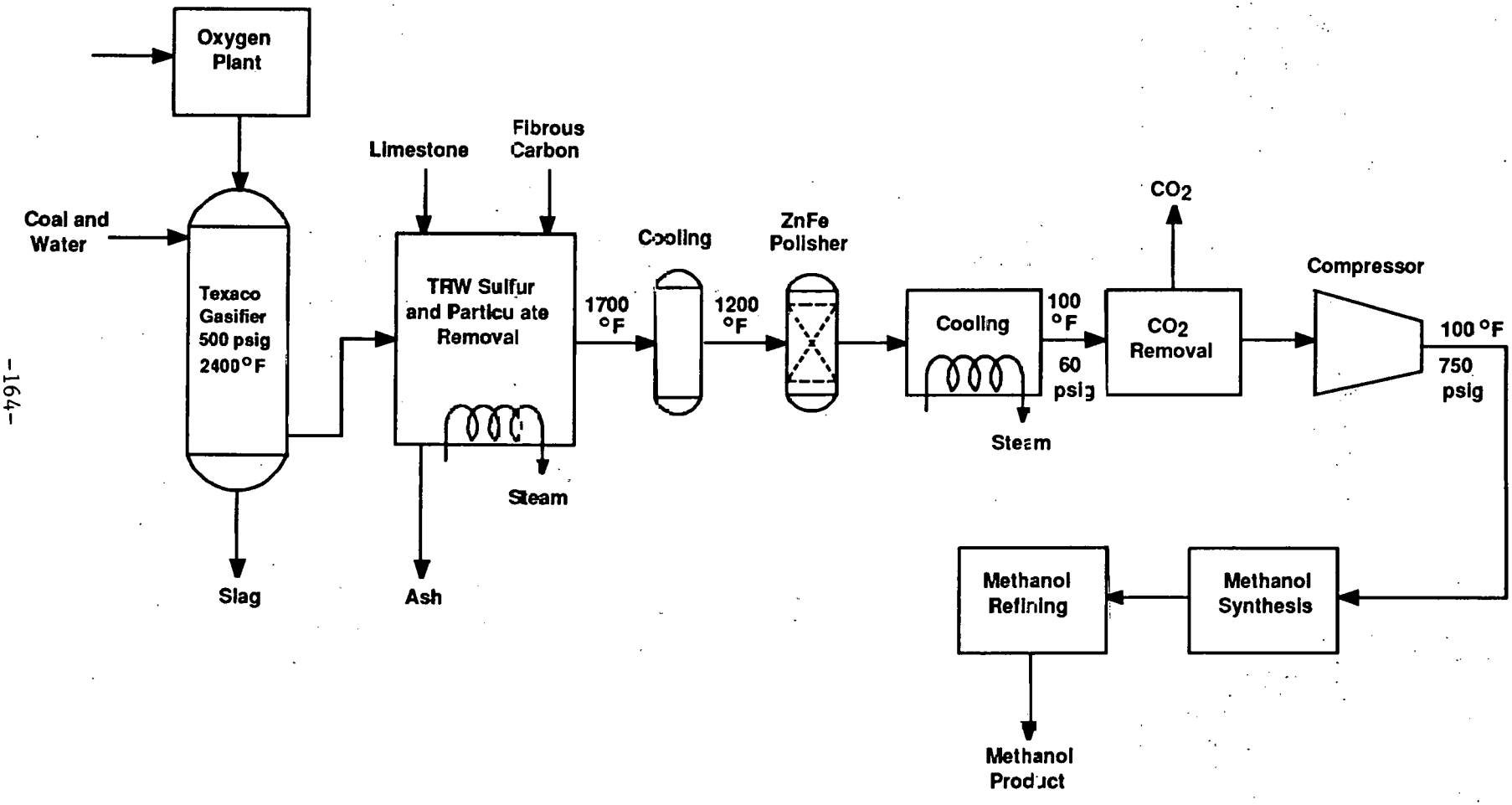







FIGURE 15

# EXPERIMENTAL DEVELOPMENT OF A MULTI-SOLID FLUIDIZED-BED REACTOR CONCEPT

1. CONTRACT NUMBER: DE-AC21-87MC23293

CONTRACTOR: Battelle Columbus Division
505 King Avenue
Columbus, Ohio 43201-2693
614/424-6424

CONTRACTOR PROJECT MANAGER: Mr. Robert D. Litt

PRINCIPAL INVESTIGATOR: Mr. William G. Steedman

METC PROJECT MANAGER: Lisa A. Jarr

PERIOD OF PERFORMANCE: June 1987 to June 1989

2. SCHEDULE/MILESTONES:

The Project Schedule is illustrated in Figure 1. A major milestone and decision point precedes Task 4 which includes pilot plant testing.

3. OBJECTIVE:

The objective of the proposed experimental program is to prove the feasibility and quantify the performance of the MSFB gasification system. Development of this advanced coal gasification system is directed toward meeting the needs of the utility industry for an economical, environmentally acceptable and flexible technology. A series of progressive experiments are planned to provide performance data to be used in a process technical and economic evaluation.

4. BACKGROUND STATEMENT:

Battelle's two-stage Multi-Solid Fluidized Bed (MSFB) Gasification process represents an advanced combined cycle power generation system (see Figure 2). The MSFB is a high-throughput gasifier which produces a medium-Btu gas without requiring an oxygen plant. Elimination of an oxygen plant is a major process simplification and cost reduction. The product gas is of sufficient quality that it can replace natural gas without extensive modifications to existing combustion equipment.

Coal is fed into a MSFB gasifier which operates at 10-30 feet per second superficial velocity. The product gas is separated from circulating solids in a cyclone and then goes to product gas cleanup. The circulating solids go to a MSFB combustor which burns the unreacted char to provide heat for the gasifier. Circulating solids are returned to the gasifier to control temperature and heat balance between the two vessels. The combustor flue gas goes to a heat recovery system without diluting the product gas. Therefore, air can be used in the combustor with significant savings over systems which require oxygen and/or dilute the product gas stream.

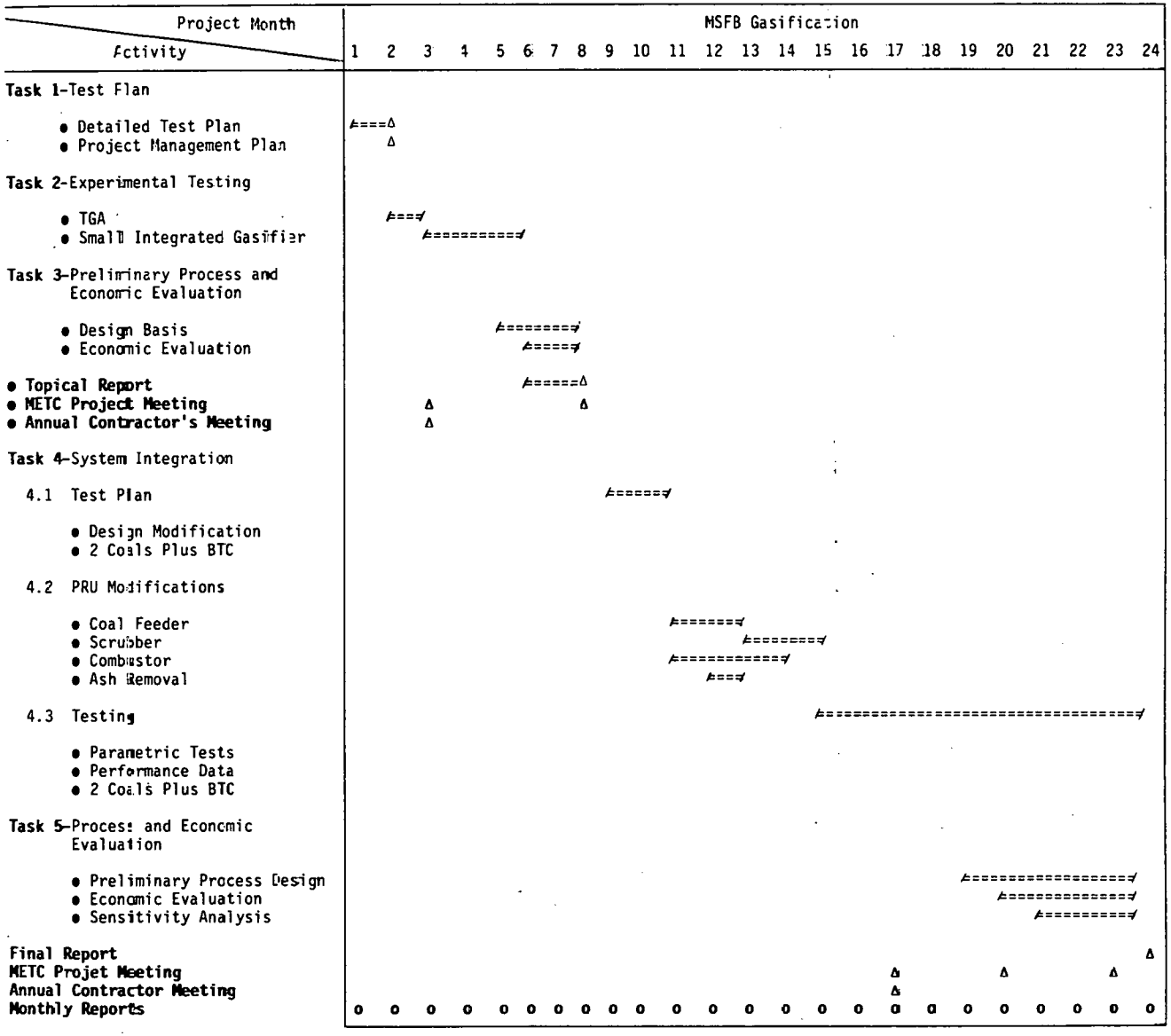



Figure 1. Project Schedule

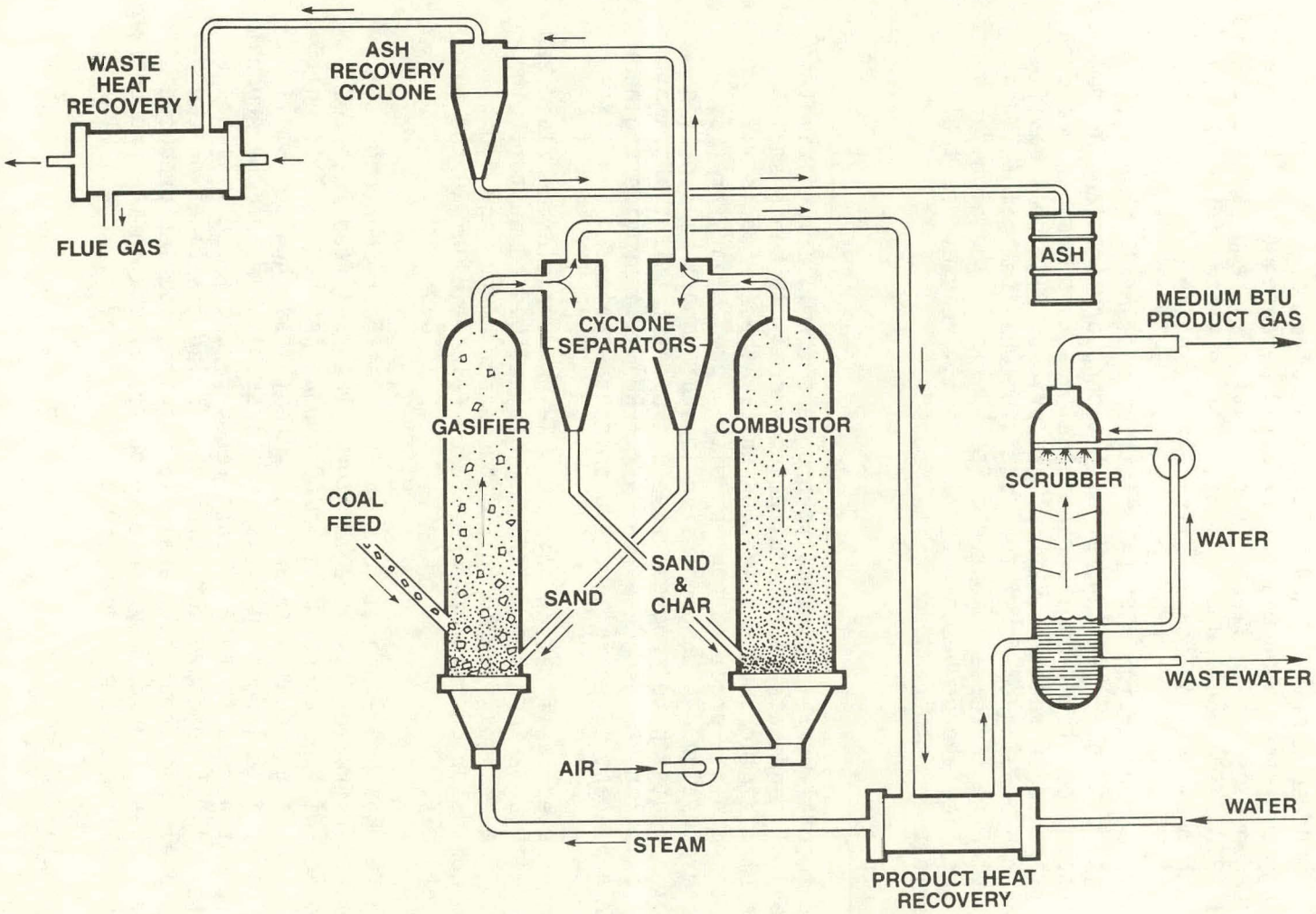



Figure 2. Two-Stage MSFB Gasification.

Fuel flexibility is provided by the turbulent mixing in the MSFB dense bed. Coal particle sizes ranging from 2-inch including fines can be fed into the MSFB reducing rejected material and fuel preparation costs. Reduced ash agglomeration problems are expected because of the turbulent mixing in the dense bed; experimental verification is required. Battelle Treated Coal (BTC), impregnated with lime, will be tested for enhanced reactivity, ash modification and in-situ sulfur capture.

Successful development of the MSFB Gasification system will benefit electric utility companies seeking retrofit technology or planning modular plants with phased construction. Conventional gas turbines can be purchased to take advantage of current low natural gas prices. The coal gasification plant can be planned for future addition when the natural gas price is expected to increase compared to coal price. The high-throughtput of the MSFB gasifier and combustor result in small reactors suitable for shop fabrication with reduced capital cost.

5. PROJECT DESCRIPTION:

Project experimental work is planned to progress from Thermogravimetric Analysis (TGA) of candidate eastern bituminous coals to bench scale testing in a small integrated gasfication unit. These efforts will establish the technical proof of concept with a preliminary process and economic evaluation. A comprehensive Topical Report will provide the basis for a decision to progress to pilot plant testing. Parametric tests in the existing Process Research Unit (PRU) will provide engineering data for a process technical and economic evaluation.

The small integrated gasification unit is a 2-inch circulating fluidized bed gasifier with a 12-inch conventional fluidized bed combustor. The gasifier coal feed ranges from 10 to 20 pounds per hour. The fluidized gasifier and combustor operate at superficial velocities of 20 fps and 2 fps, respectively.

The existing PRU has a 10-inch circulating-bed gasifier connected to a 40-inch (I.D.) refractory lined combustor. The coal feed rate to this pilot plant will be approximately 100 pounds per hour. This unit can operate with larger coal size and lower heat loss than the small bench-scale unit. The larger unit also has less dilution of the product gas by instrument purges so that product recovery and yield will be more accurate. Any liquid products produced during gasification can be more completely and accurately analyzed with the samples produced from the PRU. These liquids may prove to be too dilute in the product gas from the small bench-scale unit, to be quantified.

6. RESULTS/ACCOMPLISHMENTS:

Project work is expected to begin in June 1987.

## 7. FUTURE WORK:

Interaction with interested utility representatives is planned to guide this project and future work toward meaningful scale-up and application.

## 8. REFERENCES:

Feldmann, H. F., Paisley, M. A., and Ball, D. A., "Industrial Co-generation Through Use of a Medium-Btu Gas from Biomass Produced in a High-Throughput Reactor", ASME 83-Pet-7, 1983.

Litt, R. D. and Sirois, R. H., "Advanced Fluidized Bed Technology Applied to Coals and Other Fuels," 22nd Annual Kentucky Industrial Coal Conference, April 1983.

# MECHANISMS OF MILD GASIFICATION AND LOW SEVERITY COAL DEVOLATILIZATION

M. Rashid Khan
Morgantown Energy Technology Center

ABSTRACT

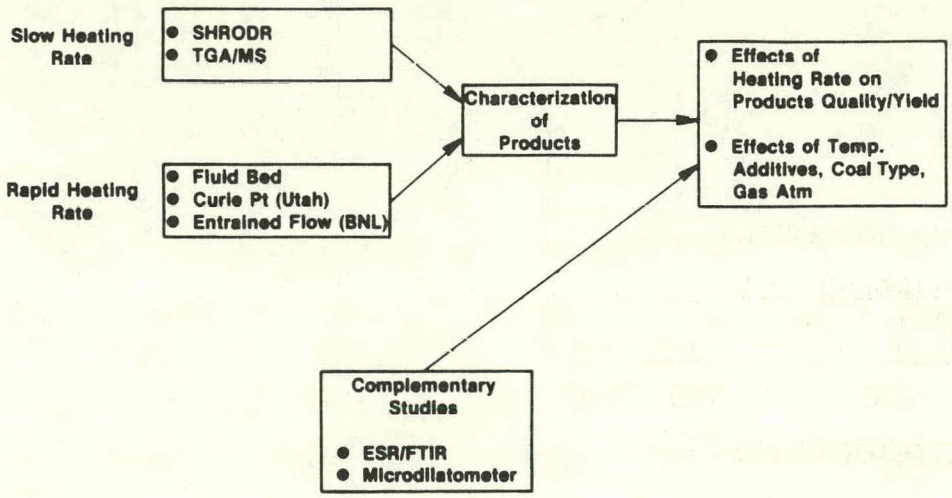
Contemporary coal devolatilization studies have emphasized optimizing the yield of the liquids by operating at severe conditions of temperature, pressure, and heating rate. The objective of this study is to investigate the influences of relatively mild operating conditions (e.g., heating rate) on products quality/yield by comparing devolatilized products obtained at a range of temperatures and heating rates. A slow heating rate organic devolatilization reactor (SHRODR) was used to obtain liquid and solid products at a mild heating rate to a range of final temperatures. The rapid rate liquid products were obtained using either a fluid-bed reactor or an entrained-flow system. The liquids generated at mild and severe conditions are being characterized by a number of techniques (Field Ionization Mass Spectroscopy [FIMS], Sequential Elution Solvent Chromatography, Fourier Transform Infrared Spectroscopy [FTIR], Elemental Analysis, etc.). At a rapid heating rate, the yields of heavier polyfunctional groups are markedly greater compared to that obtained at a slow rate. The liquids generated at a slow heating rate are of lower molecular weight, viscosity, sulfur content, but of higher H/C atomic ratios compared to the liquids obtained at a rapid rate. The effect of increasing the maximum devolatilization temperatures (at a constant slow heating rate) was to increase the yield of light gases (mainly $H_2$) at the expense of char hydrogen content. The tar yield is not markedly influenced when the peak devolatilization temperature is increased. However, the quality of the liquids or the reactivity (in air) of the product char was reduced when the peak pyrolysis temperatures were increased. It is proposed that at a rapid rate, the primary products, representative fragments of the parent coal structure, are devolatilized and, therefore, are of poorer quality. At a slow heat-up rate, however, the primary coal fragments undergo additional cracking reactions forming low molecular weight hydrocarbons of relatively higher quality.

## Characteristics of Mild Gasification

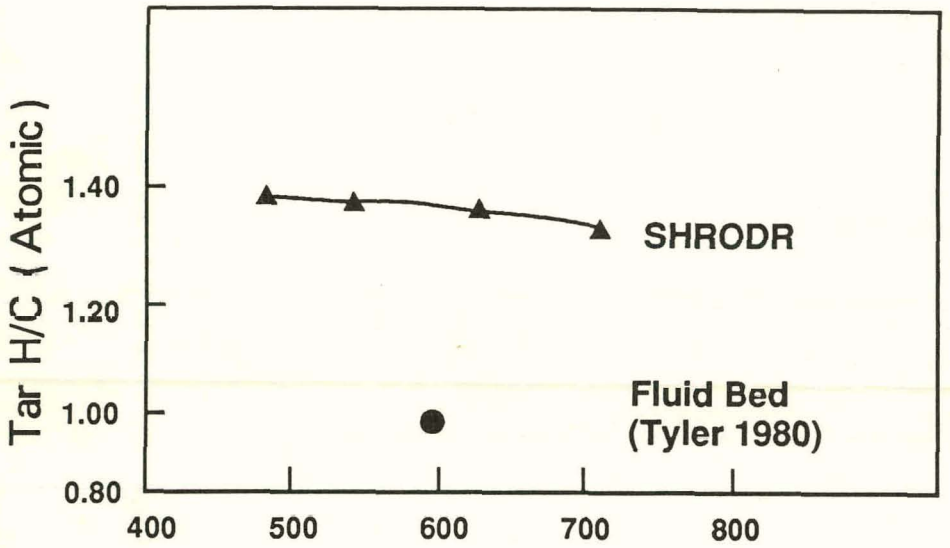
- Devolatilization under mild conditions (temperature and pressure)
- Potential to produce clean liquid, solid, and gaseous fuels
- Quality and yield improved by:
  - Additives
  - Pre/post treatment
  - Gaseous atmospheres
- Implications to a wide range of gasification processes



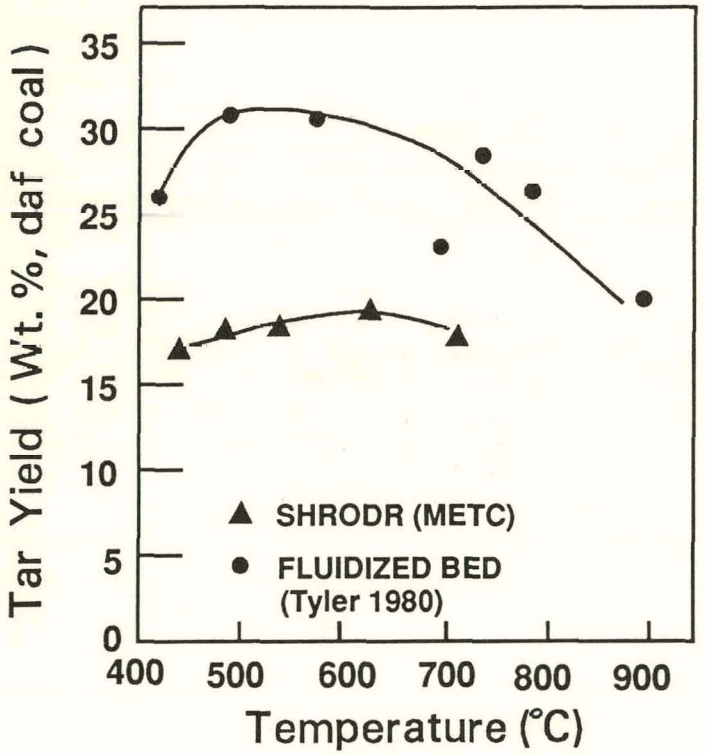
## Strategy of Devolatilization Studies



# Influence Of Peak Heat Treatment Temperature on Yield and the H/C (atomic) Ratio of Pyrolysis Liquids (Pit 8 Coal)



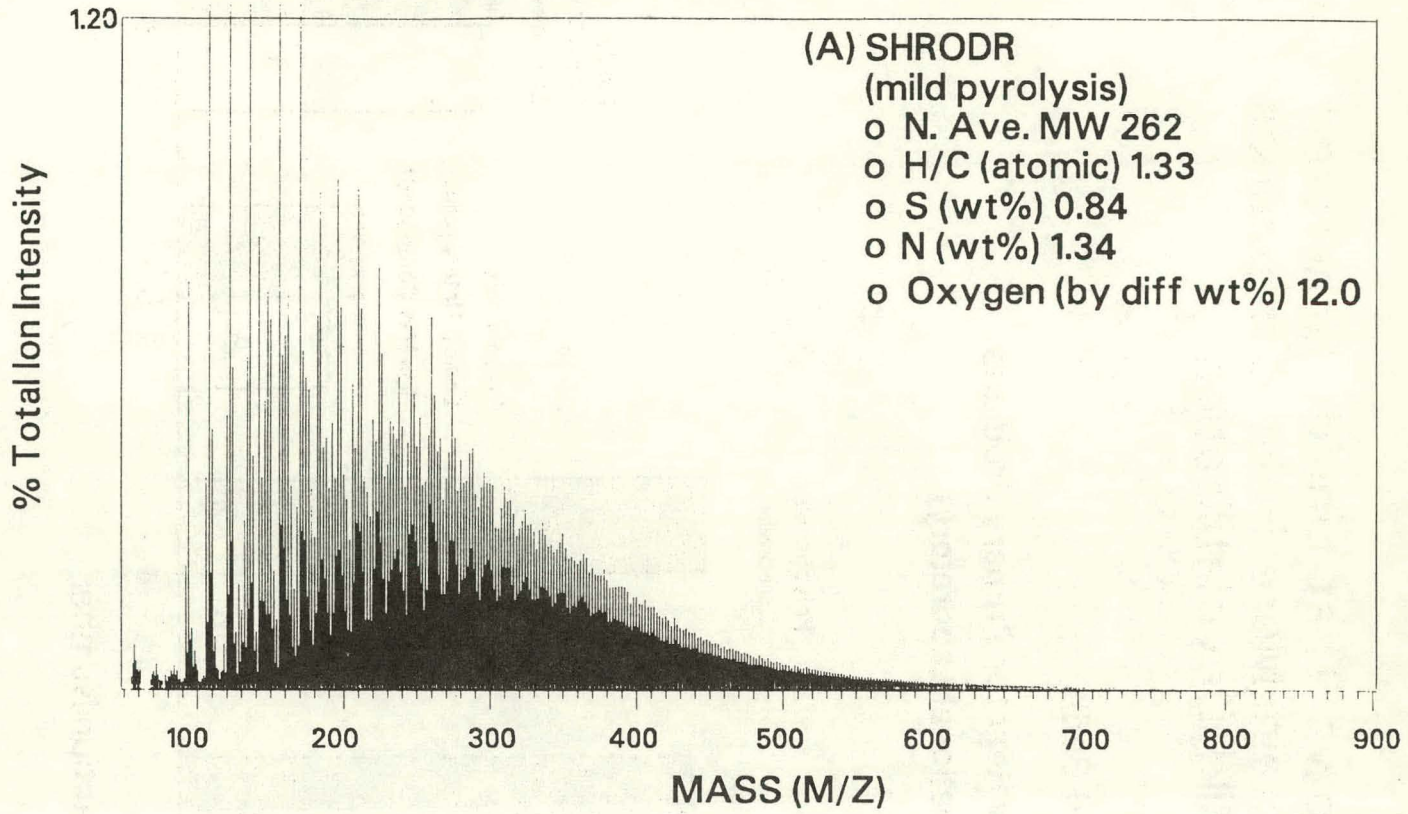

- Fluid Bed Shows Higher Yield But Lower H/C (at 600°C)
- In Mild Pyrolysis, Increasing Peak Temperature Increases Yield But Does Not Affect H/C

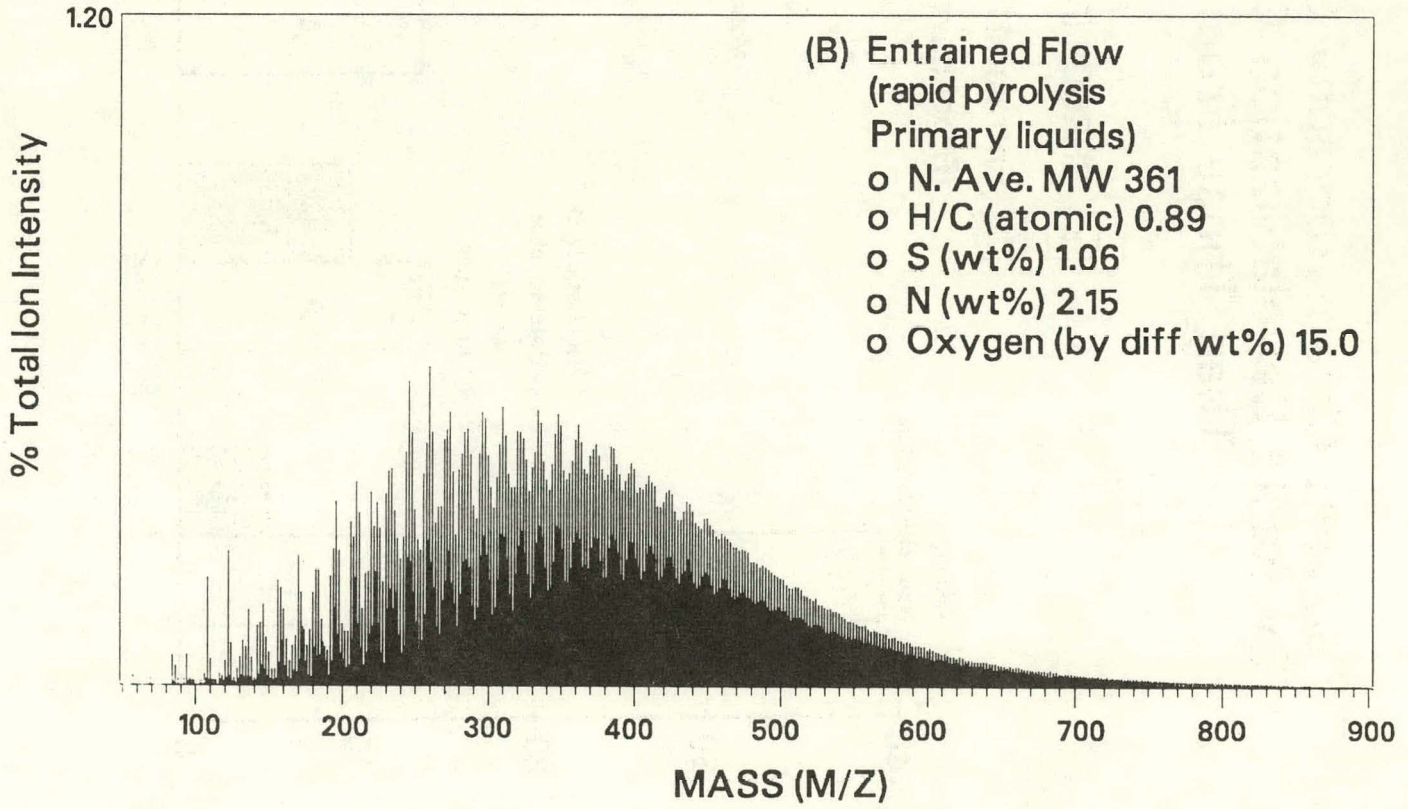



I87-1212-B BP8

# Mass Spectral Data Show That Liquids From Rapid Pyrolysis Are Heavier Than Those From Mild Pyrolysis

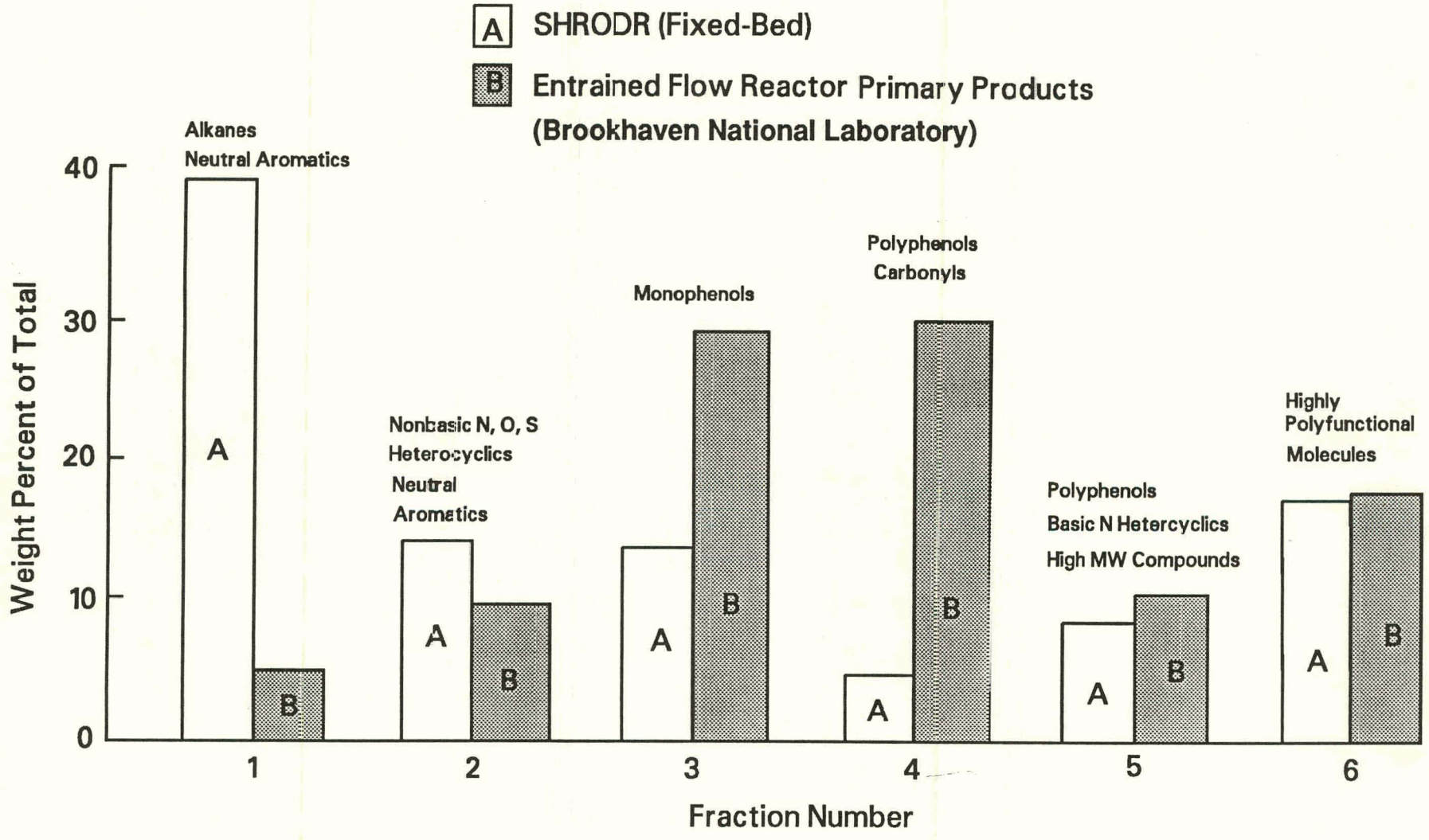
## (Pittsburgh No. 8 Coal, 650°C)



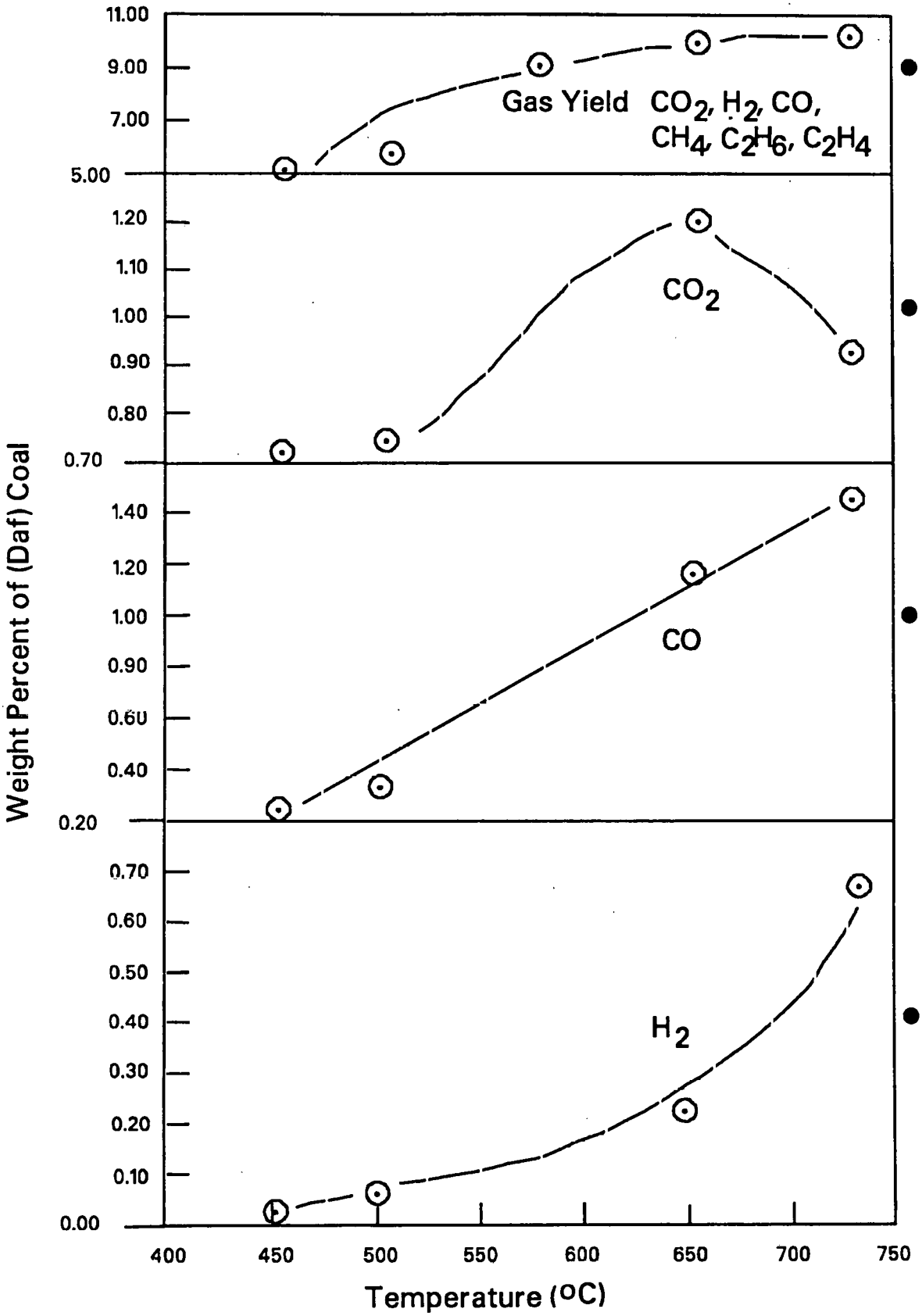

**Rapid Pyrolysis Liquids Supplied by Brookhaven National Lab**

# Solvent Chromatography Shows That Liquids Generated By Rapid Devolatilization Contain More Polar Compounds Than Those From Mild Devolatilization




C87-1126-F BP7

# Influence of Peak Heat Treatment Temperature on SHRODR Yield and Composition (Pit 8 Coal)

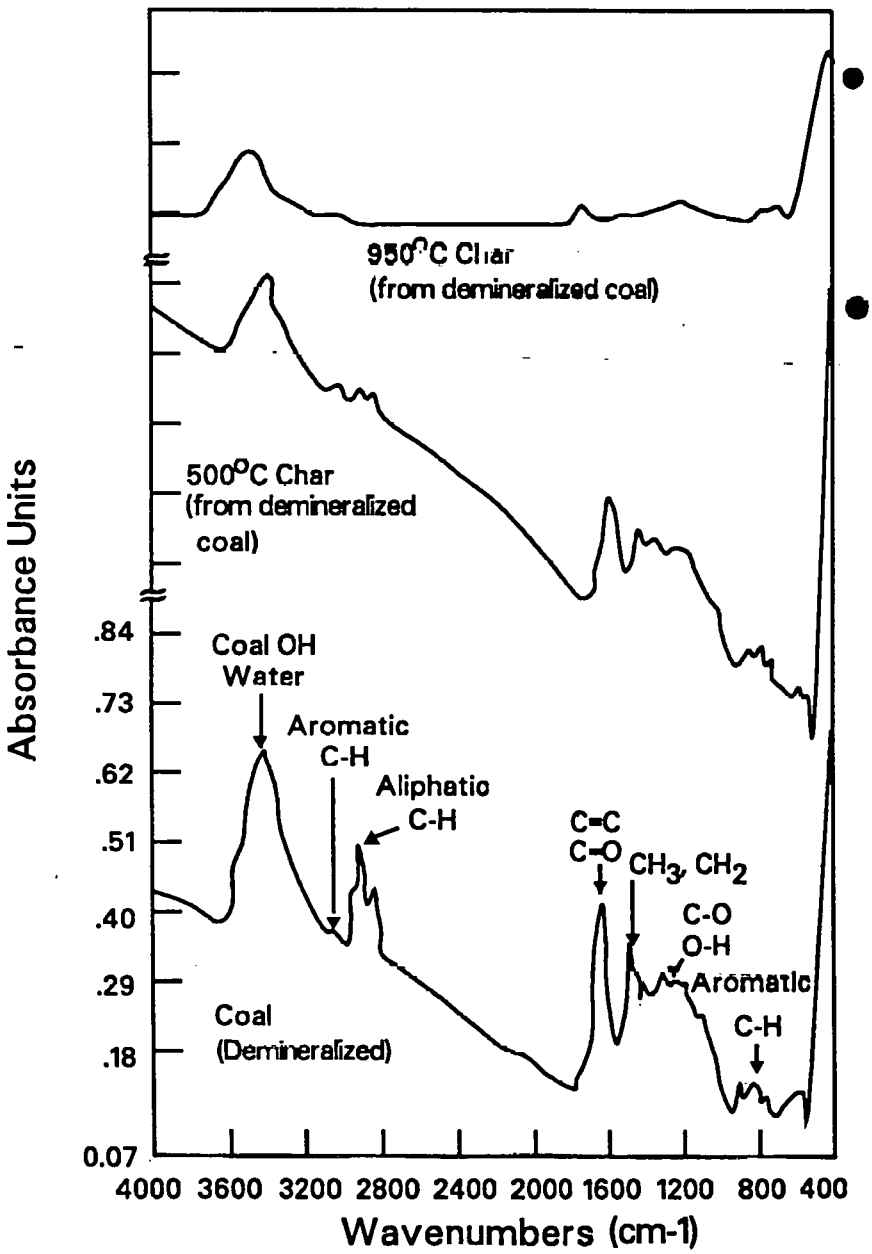



- Total Gas Yield Increases With The Increase In Temperature
- $CO_2$ Yield Goes Through A Maximum
- CO Increases With The Increase In Temperature
- $H_2$ Shows Rapid Increase Above 650°C



I87-1126-C BP7

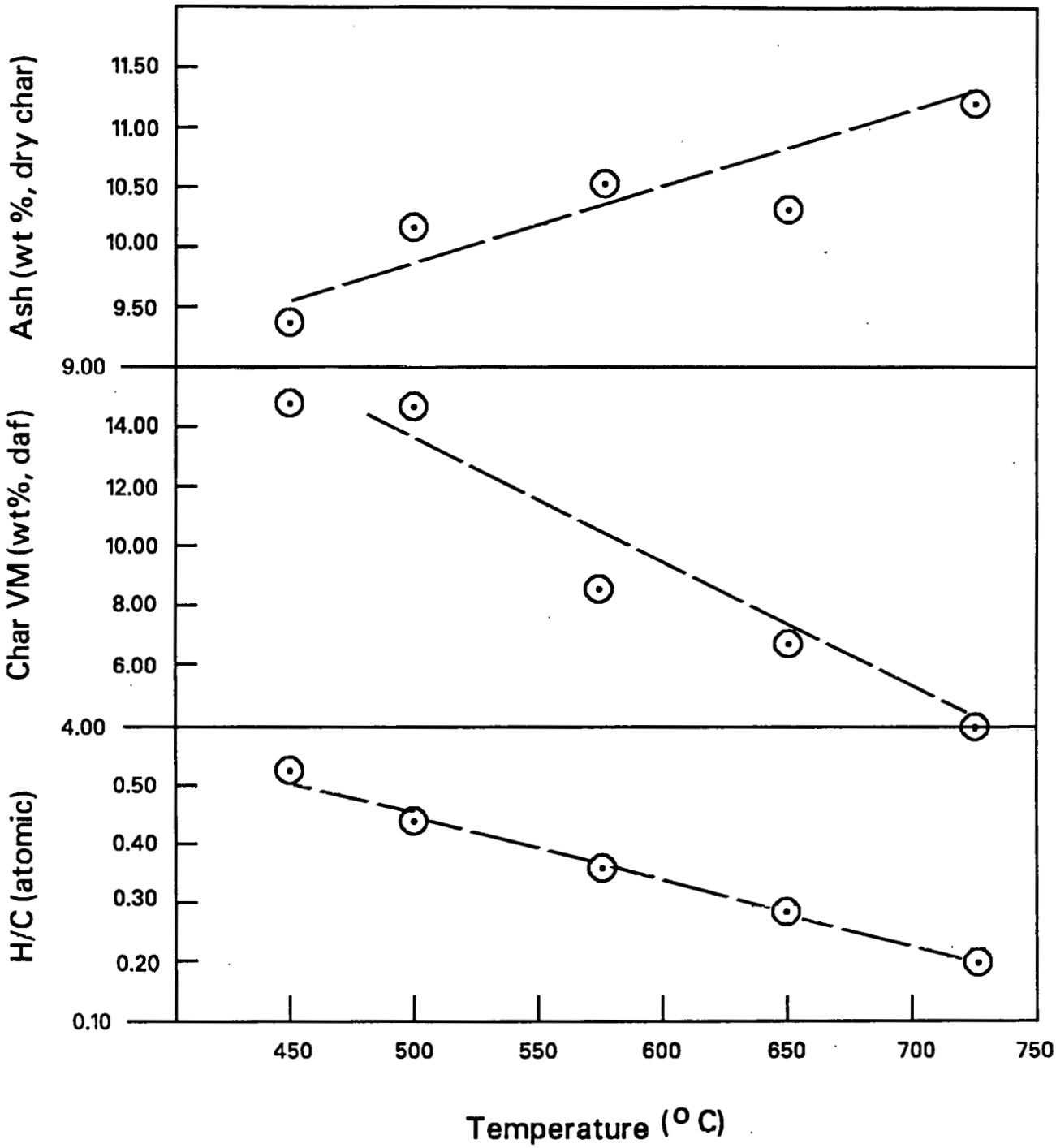
# Influence of Heat Treatment Temperature on Char Structure as Determined by Fourier Transform Infrared Spectra (FTIR)




- Low Temperature Chars Show Characteristics of Original Coal
- High Temperature Chars are Highly Graphitic

C87-1126-M BP7

- Increase In Heat Temperature Treatment Increases The Ash Content But Decreases The VM Or H/C Of Chars




## Influence of Peak Heat Treatment Temperature on Char Composition (SHRODR, Pit 8 Coal)

C87-1126-8 BP7

## Summary

**Influence of Heating Rate and Peak Pyrolysis Temperature on Product Composition**

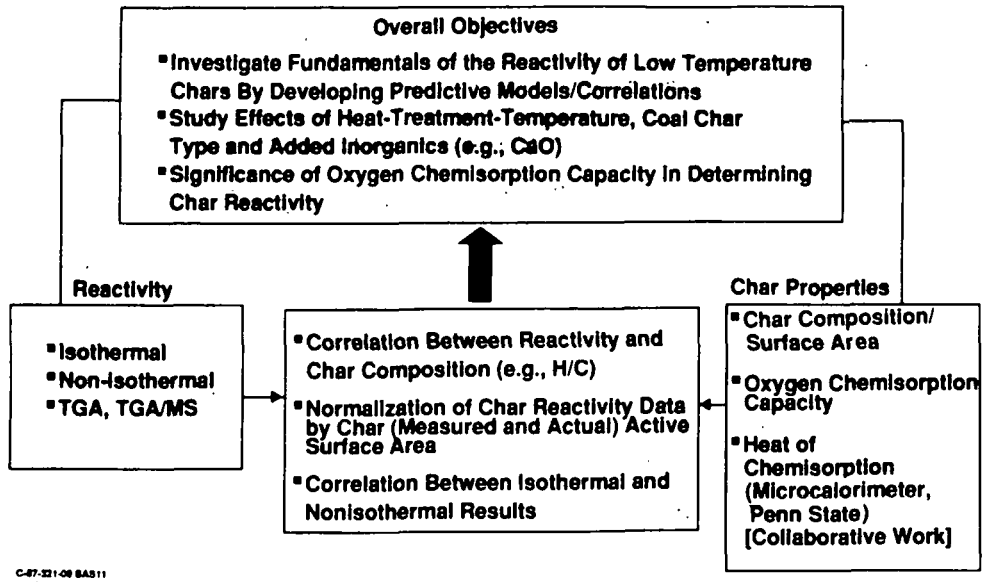
- Rapid rate coal pyrolysis optimizes liquid yield at the expense of liquid quality
- With the increase in peak pyrolysis temperature (at a const. heating rate), light gas yield (especially $H_2$) increases at the expense of char hydrogen and VM contents
- These data improve our understanding of product yield/quality trade-offs
- It is proposed that the primary products (of low H/C) are formed in rapid rate systems. At slow heating rate, the primary products undergo cracking reactions forming lighter oil



## Rationale for Char Reactivity Studies

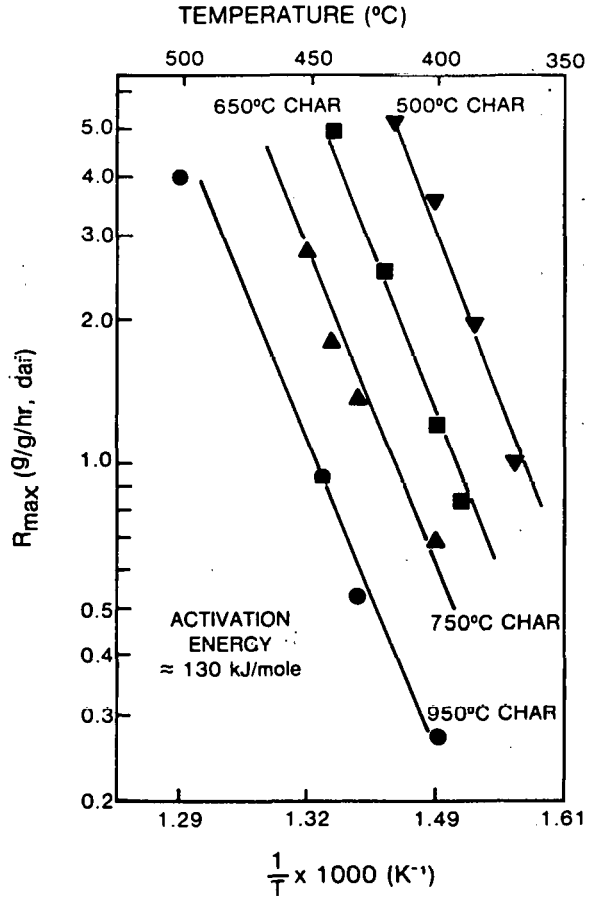
- Char is the major product from any devolatilization process
- Char utilization is a key to overall process economics
- Usability of fuel requires good reactivity and fuel value
- Lab reactivity tests can be used to predict char utilization behavior

## Reactivity of Low and High Temperature Chars




C-87-321-09 SA511

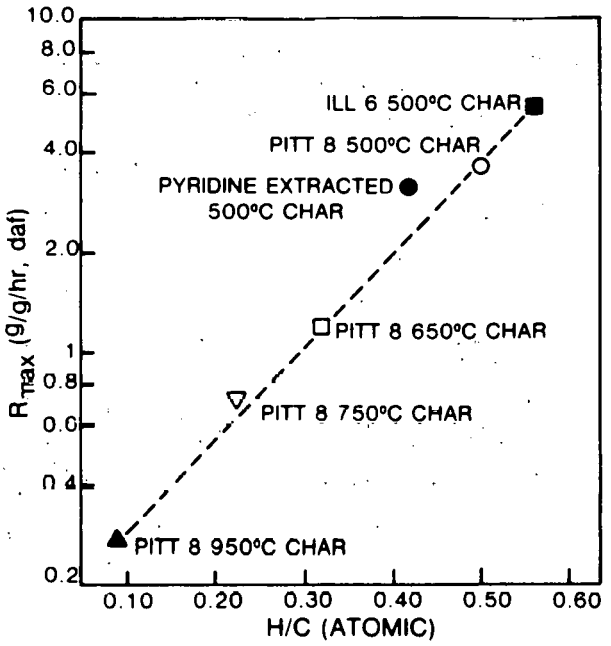
## Arrhenius Relationship Between Chars Prepared at Various Conditions




- Low Temperature Chars Are Highly Reactive Compared To The High Temperature Chars
- For Char Oxidation, The Activation Energy Of 130 KJ/mole Is The Same For Both Low And High Temperature Chars

I87-430-F BP3

## The Correlation Between Char Reactivity at 400 Degrees C with Char H/C (Atomic)




C87-430-6 BP3

## Can We Develop a Better Fundamental Parameter to Predict Char Reactivity?

**Isothermal reactivity of carbonaceous materials is given by:**

$$R = -\frac{1}{Mc}\frac{dMc}{dt};$$

$\frac{dMc}{dt}$ = instantaneous slope of burn-off curve

Mc = daf char wt at time, t

$$\frac{dMc}{dt} = -k\, Mc P_{O_2}\, (ASA);$$

$P_{O_2}$ = Partical P of oxygen
n = true order
ASA = Active surface area

$R = k\, P_{O_2}^{n}\, ASA$

$R \propto k\,(ASA)$, if $P_{O_2}$ is constant

$R/(ASA)$ = Constant

METC

T87-1212-3 BP6

# Isothermal Char Reactivity (Rm) Correlates Well With Char Active Surface Area

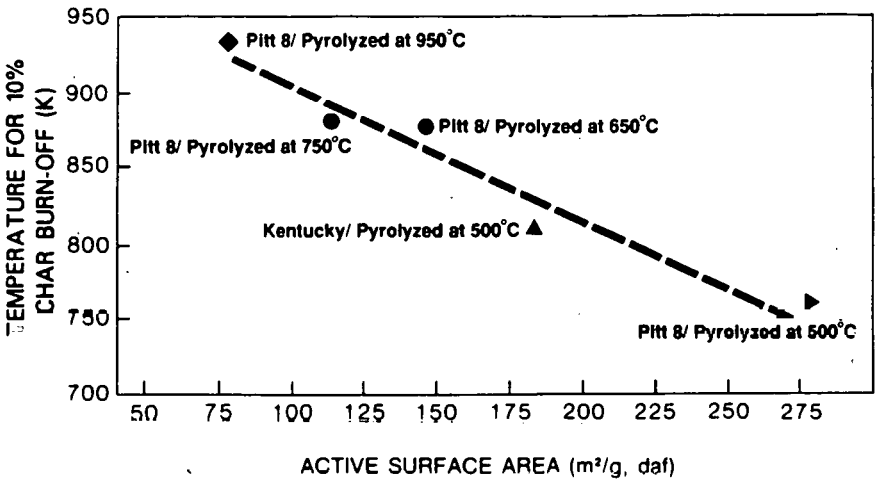
## A Comparison of Reactivities and Active Surface Areas for Various Coal Chars

| Sample/ Preparation Condition | H/C (Atomic) | ASAm* (at 200°C) ($m^2/g$) | ASAa** | Rm (400°C) (g/g/h, daf) | | k, x $10^3$ ($g/m^2$ASAm.h) | | $k^1$, x $10^3$ ($g/m^2$ASAa.h) | |
|---|---|---|---|---|---|---|---|---|---|
| Pittsburgh No. 8/TGA 500°C | 0.45 | 253.5 | 461 | 3.3 | (highest) | 13.0 | (highest) | 7.2 | (highest) |
| Pittsburgh No. 8/TGA/650°C | 0.28 | 150 | 208 | 1.2 | | 8.0 | | 5.8 | |
| Pittsburgh No. 8/TGA 750°C | 0.17 | 103 | 124 | 0.73 | | 7.0 | | 5.8 | |
| Pittsburgh No. 8/TGA 950°C | 0.07 | 70 | 75 | 0.26 | (lowest) | 3.7 | (lowest) | 3.5 | (lowest) |
| Illinois No. 6/SHRODR 500°C | 0.41 | 157.5 | 257 | 1.26 | | 8.0 | | 4.7 | |
| Kentucky No. 8/SHRODR 500°C | 0.22 | 170.4 | 218 | 1.32 | | 7.8 | | 6.1 | |
| L. Kittanning/TGA 500°C | 0.43 | 158.7 | 278 | 1.14 | | 7.2 | | 4.1 | |

* ASAm: Experimentally measured ASA.

** ASAa: Actual char active surface area determined, $ASA = \frac{ASAm}{(1-H/C)}$

Non-Isothermal Reactivity Parameter (Temperature For 10% Burn-off) Correlates Well With Char Active Surface Area




I87-430-E 6P3

## Summary and Conclusions
## Reactivity of Low and High Temperature Chars

- For char oxidation, the activation energy of 130 kJ/mole is the same for both low- and high-temperature chars
- The char active surface area is a relevant reactivity parameter for both low- and high-temperature chars
- Developed a new approach to calculate char ASA by incorporating char hydrogen content
- Low-temperature (500°C) chars appear to be more reactive (TGA) compared to the parent coals
- At low conversion, non-isothermal reactivity parameter can be correlated with char ASA

# MILD GASIFICATION OF COAL

1. CONTRACT NUMBER: DE-FC21-86MC10637

CONTRACTOR: University of North Dakota
Energy Research Center
Box 8213, University Station
Grand Forks, ND 58202
(701) 777-5000

CONTRACTOR PROJECT MANAGER: Robert O. Ness, Jr.

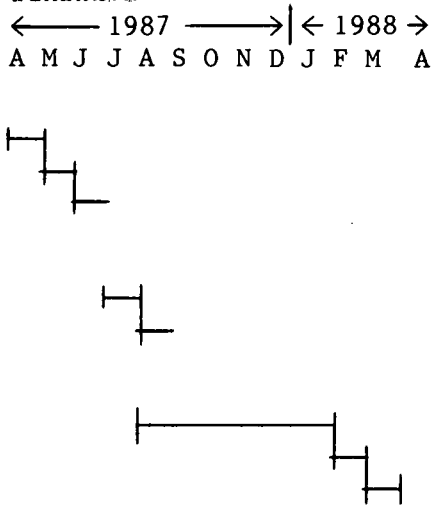
PRINCIPAL INVESTIGATORS: Robert O. Ness, Jr.
Dr. Warrack G. Willson

METC PROJECT MANAGER: Leland E. Paulson

PERIOD OF PERFORMANCE: April 1, 1987, to April 1, 1988

2. SCHEDULE/MILESTONES:

1987/1988 Program Schedule




3. OBJECTIVES:

- Auxiliary equipment for handling char and condensables will be designed and fabricated. An upgraded hot cyclone and quench system will be constructed and retrofitted on the pressurized fluid-bed gasifier (PFBG). This is necessary because the operating temperatures are lower than the original design. The equipment will be designed and built during the first three months of the project.

- The PFBG will be used to perform a preliminary process evaluation. The screening will evaluate yields versus residence times (seconds to 20 minutes), temperatures (1000° to 1350°F), pressures (atm. to 50 psi), steam-to-carbon ratio (1:1 to 4:1), and coal variability (lignites and bituminous).

- An extensive analytical test program will evaluate the mild gasification products. The analysis will include testing for use as activated carbon, feedstock for hydrogen production, diesel fuel blends, aviation fuel, liquid feedstock additives, and gaseous fuels.

4. BACKGROUND STATEMENT:

For coal to become more marketable, specific areas need to be targeted in which coal products, such as char and coal-derived liquids, are not in direct competition with oil or natural gas. These areas, in the case of mild gasification, can be grouped into three areas: 1) solids; 2) condensables; and 3) gases.

Several mild gasification solid products have shown promise in the energy and non-energy related areas. One product is activated carbon, which is widely used for removal of trace organics from secondary effluents. Economic evaluations of activated carbon adsorption processes used for wastewater treatment indicates that sometimes more than 50% of the treatment cost is attributed to the cost of make-up carbon. Activated carbon has also shown potential as a catalyst support in lower-temperature systems (below 425°C). Production of a good-quality, low-cost activated carbon from char may be one alternative that would provide an end use for char, which in turn would make mild gasification an economically viable operation.

Another option for the char produced from mild gasification is in the production of hydrogen via the catalytic steam gasification of the char. Mild gasification would separate the high volatile materials into their respective gas and condensable streams. Exact stream fractions could be adjusted by changing process operating parameters. The remaining char would then be used to produce hydrogen. This process allows the flexibility of producing a number of products depending on market prices and demands.

Mild gasification also produces a slate of condensable materials which may be directly fired, blended with petroleum-refined fuels, or blended with solid coal. These fuels also have potential uses in gas turbines, aviation applications, diesel engines, as chemical precursors, and as petroleum substitutes. Liquid condensables produced by mild gasification do not match existing specifications for No. 2 diesel fuel, but research groups have demonstrated that off-specification fuels can perform adequately in diesel engines and turbines. Such blends could be used as feedstocks for the Gasification Island System. While these products are in direct competition with petroleum products, the mild gasification liquid products may provide characteristics that are not available from petroleum due to the aromatic nature of the coal such as a high-density fuel.

A blend of the solid char and liquid products could play an important role in the transportation industry as coal had done in the past. Because of the escalation of fuel costs, the railroad industry has again

looked at coal as an energy source. Diesel costs rose from approximately $0.10 per gallon to over $1.00 in 1972 and, even with the current oil crunch, remain at around $0.50. This represents a significant change in fuels cost and is now responsible for about 75% of the operating costs of a locomotive. Coal, coal products, and coal-petroleum blended products offer a chance for a reduction in these costs. Fuel costs for these diesel engines, amounting to 4 billion dollars a year, are more than three times those of a coal-fired, steam-generating locomotive.

As mild gasification may provide fuels for several areas, the key to successful economic viability will lie in product and operation optimization. In order to maximize processing flexibility, a fluidized-bed reactor system was selected. The fluidized-bed offers efficient mass transfer rates and a high rate of heat transfer. In addition, because fluid-bed systems allow coal devolatilization, gasification, and ash removal with a single vessel, they are likely to be used in system scaleup. The uniform temperature and solids distribution, and high heat transfer coefficients characteristic of fluid-bed operation are also important. Further, the use of smaller particles in a fluid-bed system results in less diffusional resistance than a fixed-bed system, more efficient waste heat recovery, and smaller pressure drops.

In tests conducted at UNDERC, selected low-rank and high-volatile bituminous coals will be tested. The use of low-rank coals may offer several advantages due to their enhanced reactivity relative to coals of higher rank. This increase in reactivity is caused by higher concentrations of active sites, higher porosity, and a more uniform dispersion of alkali impurities that act as inherent catalysts. In steam gasification tests conducted at the University of North Dakota using bench-scale, thermogravimetric analysis, low-rank coal char reactivities were found to be nearly ten times higher than those of a bituminous coal char gasified at the same conditions. The higher reactivities enable lower-cost production of hydrogen by catalytic steam gasification of the char, or the char--due to its high porosity--may be an excellent source of activated carbon.

5. PROJECT DESCRIPTION:

Figure 1 shows a schematic of the mild gasification process. With the two-stage process approach, char, condensables, and gas production yields can be individually optimized. Also, a wider variety of products can be produced and evaluated. The coal will be fed to the pressurized fluid bed gasifier (PFBG) at a rate of 25 lbs/hour. Steam and/or nitrogen will be fed to the PFBG at a rate of 25 to 100 lbs/hour. The char will be evaluated for use as activated carbon or hydrogen production use. A large condensable analysis lab will evaluate the liquids produced for use as fuels or fuel blends.

The char will be evaluated in the second stage for hydrogen production or for activated carbon production.

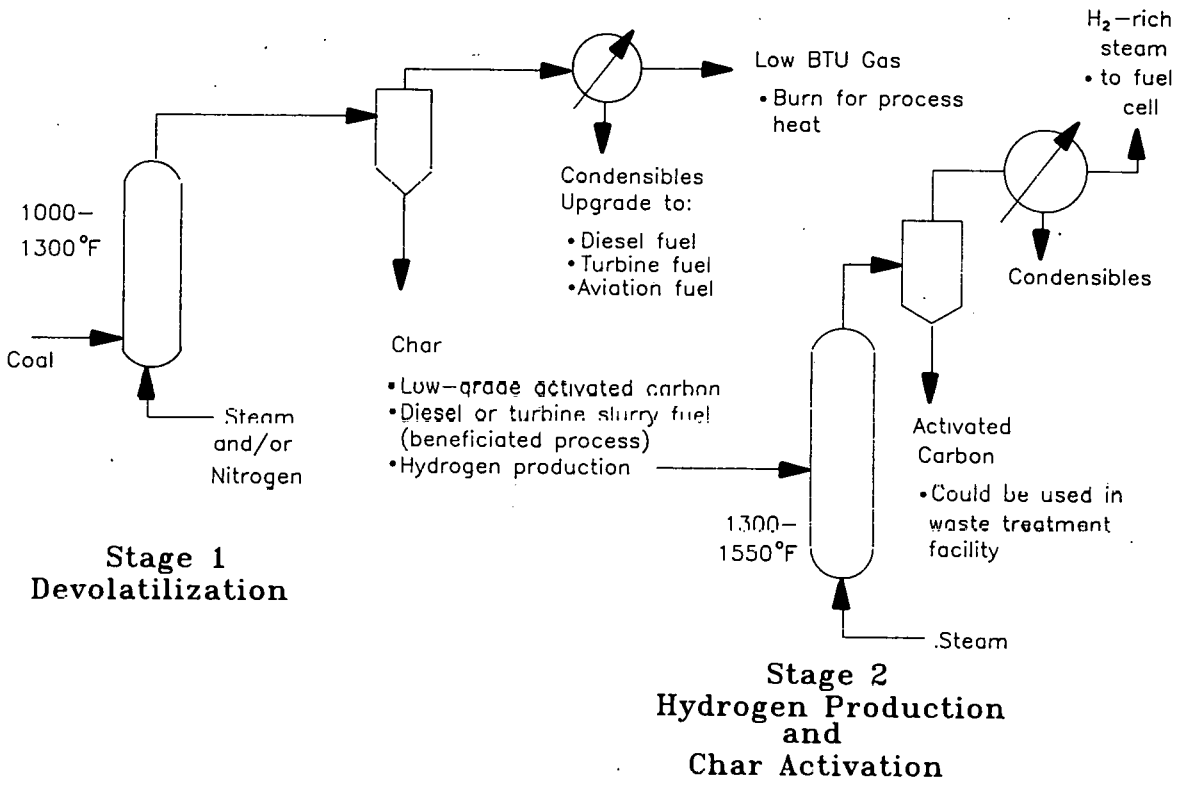



Figure 1. Mild Gasification Process Scheme.

6. RESULTS/ACCOMPLISHMENTS:

Results from preliminary TGA data have indicated lignite chars that were reacted with steam are approximately eight times more reactive for hydrogen production than higher-rank coal chars. BET analysis also indicated a surface are of 350 $m^2/g$ at reaction temperature of only 650°C. At present the PFBG is undergoing shakedown testing for hydrogen production and will not be available for experimental testing at the lower temperatures (1000° to 1350°F) until August.

7. EVALUATION OF POTENTIAL FUTURE PLANS:

Several analytical techniques are being evaluated for use for determining the characteristics of the char for use as activated carbon. Experiments may be done to evaluate these carbons for use at municipal waste treatment facilities. Combustion testing of the condensables may be possible in the UNDERC gas turbine simulator in the fall. These tests would provide data on erosion, deposition, and combustion efficiency in reference to other coal slurries and coal-derived products.

GASIFICATION SYSTEMS ANALYSIS

J.M. Klara, A.W. Gessner, and
T.J. Hand
Morgantown Energy Technology Center

ABSTRACT

The major objective of the Gasification Systems and Analysis project at the Morgantown Energy Technology Center (METC) is to identify feasible gasification systems by providing in-house, computer-based systems analysis expertise. As a continuing effort, this project is investigating various process alternatives for a commercial-scale mild gasification process which produces a suite of solid, liquid, and gaseous fuels from a devolatilization system operating at relatively low temperature (1000-1200 degrees F) and pressure (1-2 atm). As a new effort in this project, several alternate configurations for the production of hydrogen fuel from a coal gasification-based system are being evaluated. These configurations focus on the utilization of novel processes for gasification, water-gas shift catalysis, gas separation, and gas purification. Using the Advanced System for Process ENgineering (ASPEN) process simulator to determine mass and energy balances and by performing capital and operating cost estimates, these gasification-based systems are being evaluated for their technical and economic merit.

In the search for technically and economically viable gasification processes, the systems analysis engineer makes use of various types of information and computer models. The tools depicted in Figure 1 are used to establish base case process configurations, to investigate alternate configurations, to assess the applicability of recent developments, and to perform sensitivity studies.

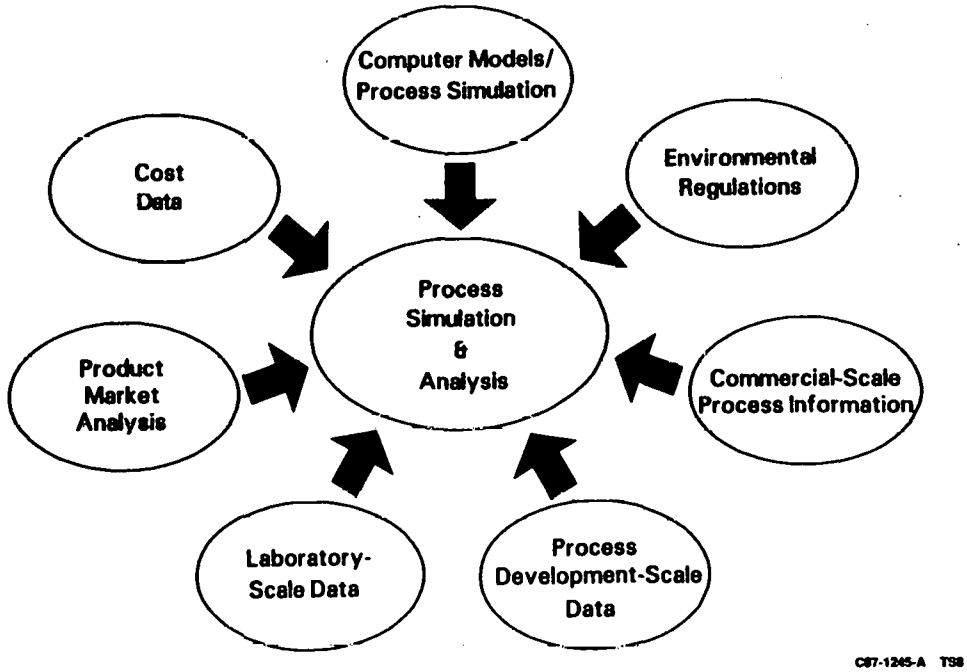



FIGURE 1. THE ROLE OF SYSTEMS ANALYSIS

In the effort to identify a feasible commercial-scale process for mild gasification, a configuration which utilizes vertical retort tubes similar to those used in the COALITE process, was studied during the last fiscal year. COALITE, a batch operated process which has been operating in the United Kingdom for over 50 years, produces a smokeless solid fuel for domestic heating and coal-derived liquids for chemical feedstock and industrial and transportation fuels. The vertical tube mild gasification process investigated (Figure 2) operates in a batch mode in which the coal is heated indirectly by hot gas circulating around the outside of the vertical tubes. This process configuration was evaluated not only because of its conceptual simplicity, but because it is believed that the long residence time and slow heating rate employed may optimize liquid product quality. However, because this process is operated in the batch mode, it provides product streams of varying quality and has high labor requirements.

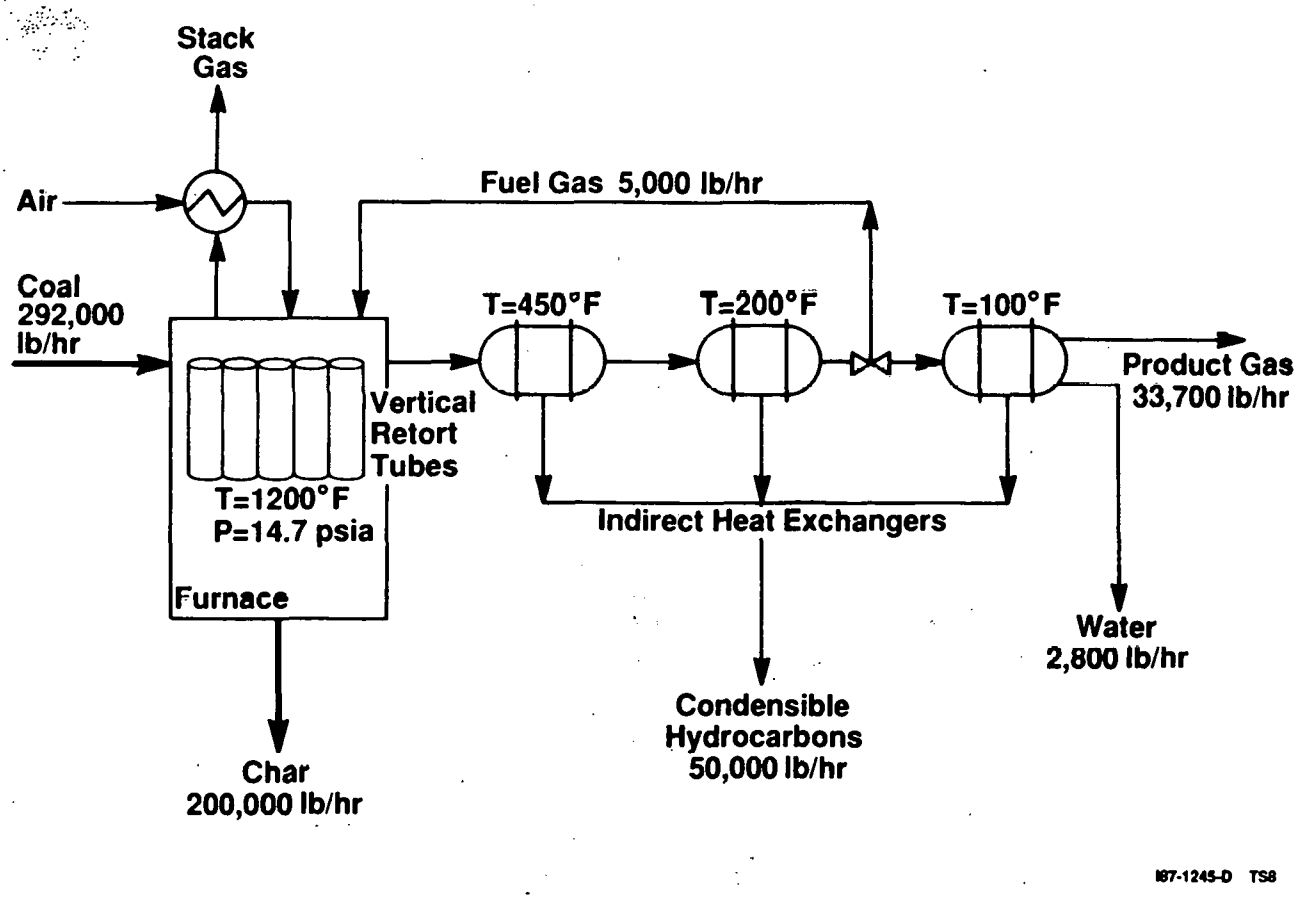



FIGURE 2. VERTICAL TUBE MILD GASIFICATION PROCESS

Another system assessed during last fiscal year utilizes a screw feeder to transfer coal through the system (Figure 3). This process possesses a long residence time and slow heating rate just as in the vertical tube configuration. Furthermore, this process has the advantage of operating continuously. The screw feeder design uses indirect heat by circulation of hot gases in the first zone where coal devolatilization occurs. In the second zone, the char is cooled indirectly with air. Unfortunately, the screw feeders may plug when coal becomes sticky making the system susceptible to operating upsets. And like the vertical tube process, this process is very wasteful of energy.

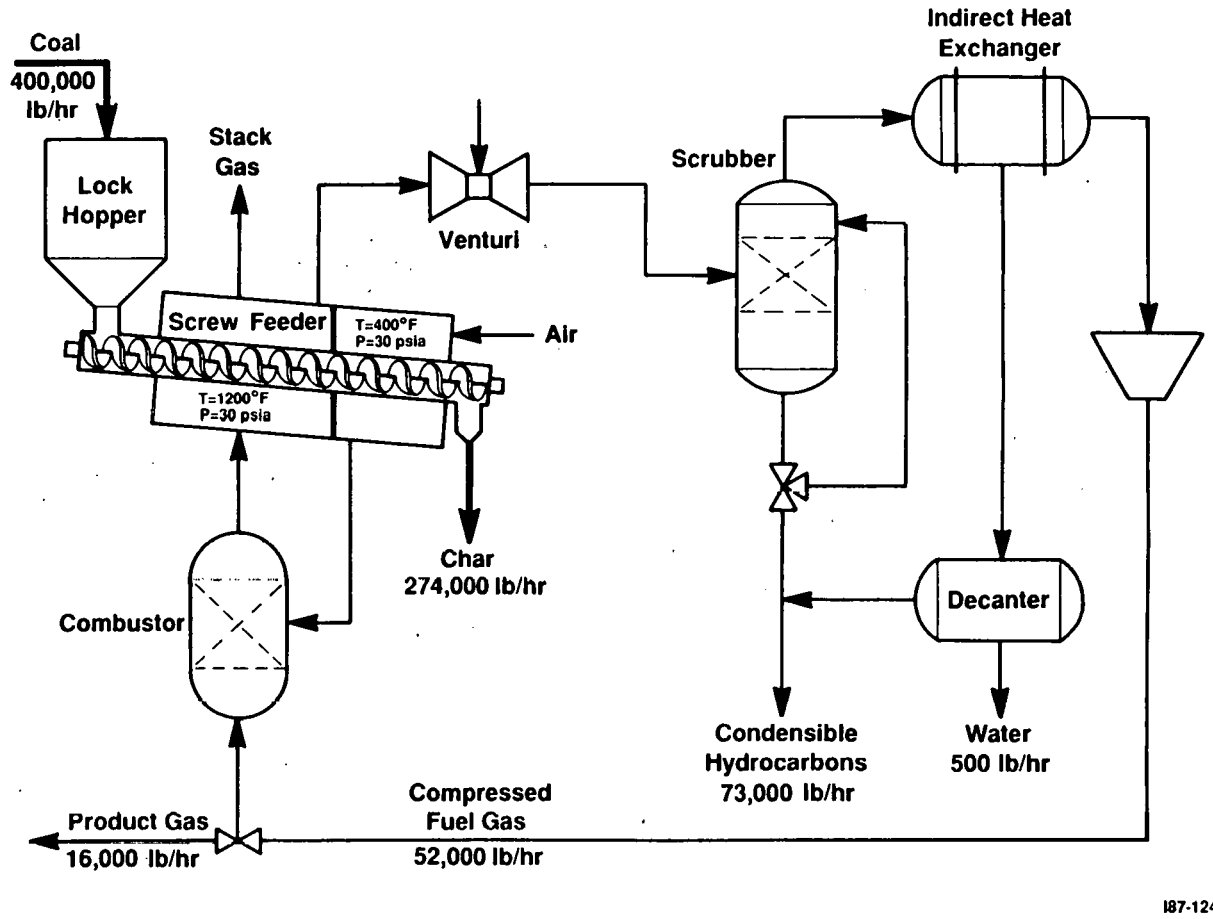



FIGURE 3. SCREW FEEDER MILD GASIFICATION PROCESS

During the current fiscal year, processes using more efficient direct heat exchange for devolatilization are being analyzed. One such process uses a fluidized-bed reactor for mild gasification and recycles hot char to this vessel to provide the necessary heat (Figure 4). Coal is fed from lockhoppers into the hot recycle char stream such that the coal and char are transported by steam in a dilute phase to avoid agglomeration. Gas produced during devolatilization is used both for fluidizing gas in the mild gasification vessel and for fuel gas to heat the recycle char and to produce steam. This process has the advantages of operating continuously and with better energy efficiency, and it may be able to handle caking coals. The residence time in the fluidized-bed reactor is shorter and the heating rate is faster than those of the processes studied previously in this project. These conditions may lead to a higher liquid yield, although possibly at the expense of product quality. Additionally, particulate carry over is of concern.

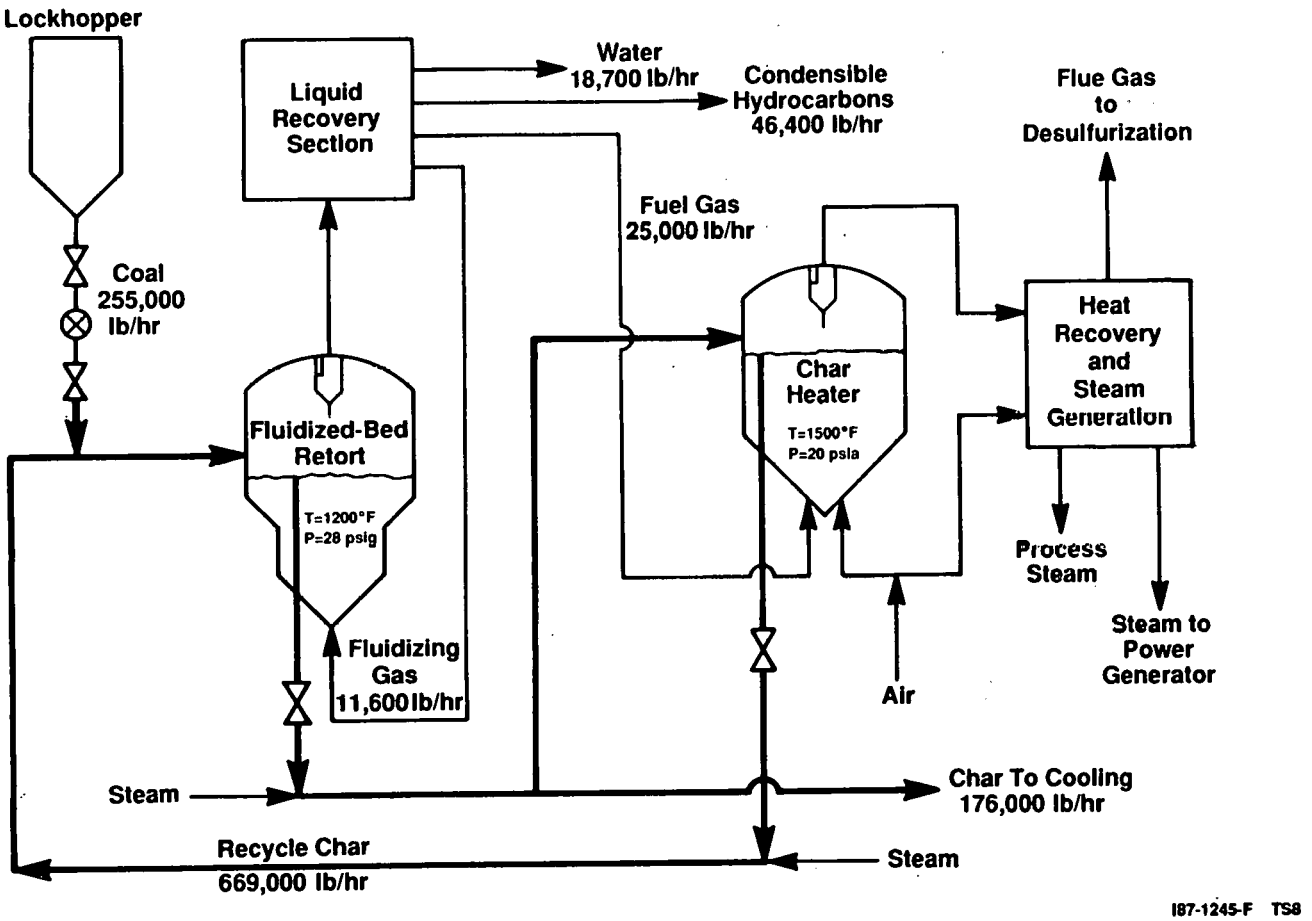



FIGURE 4. FLUIDIZED-BED MILD GASIFICATION PROCESS

In an attempt to maximize the yield and quality of condensible hydrocarbons, another fluidized-bed retort configuration which uses steam conditioned coal is being investigated. In this process (Figure 5), the coal is conditioned in steam before it enters the mild gasification vessel. Experimental data from the City College of New York indicate that liquid yields may be significantly improved if the coal is first steam conditioned. Char is recycled in this process to provide heat to both the steam conditioning and the mild gasification fluidized-bed vessels. As in the more conventional fluidized-bed process, this process may suffer from reduced product quality due to the high liquid yield, and the quantity of waste water produced is higher than in the other cases due to the use of steam throughout the process.

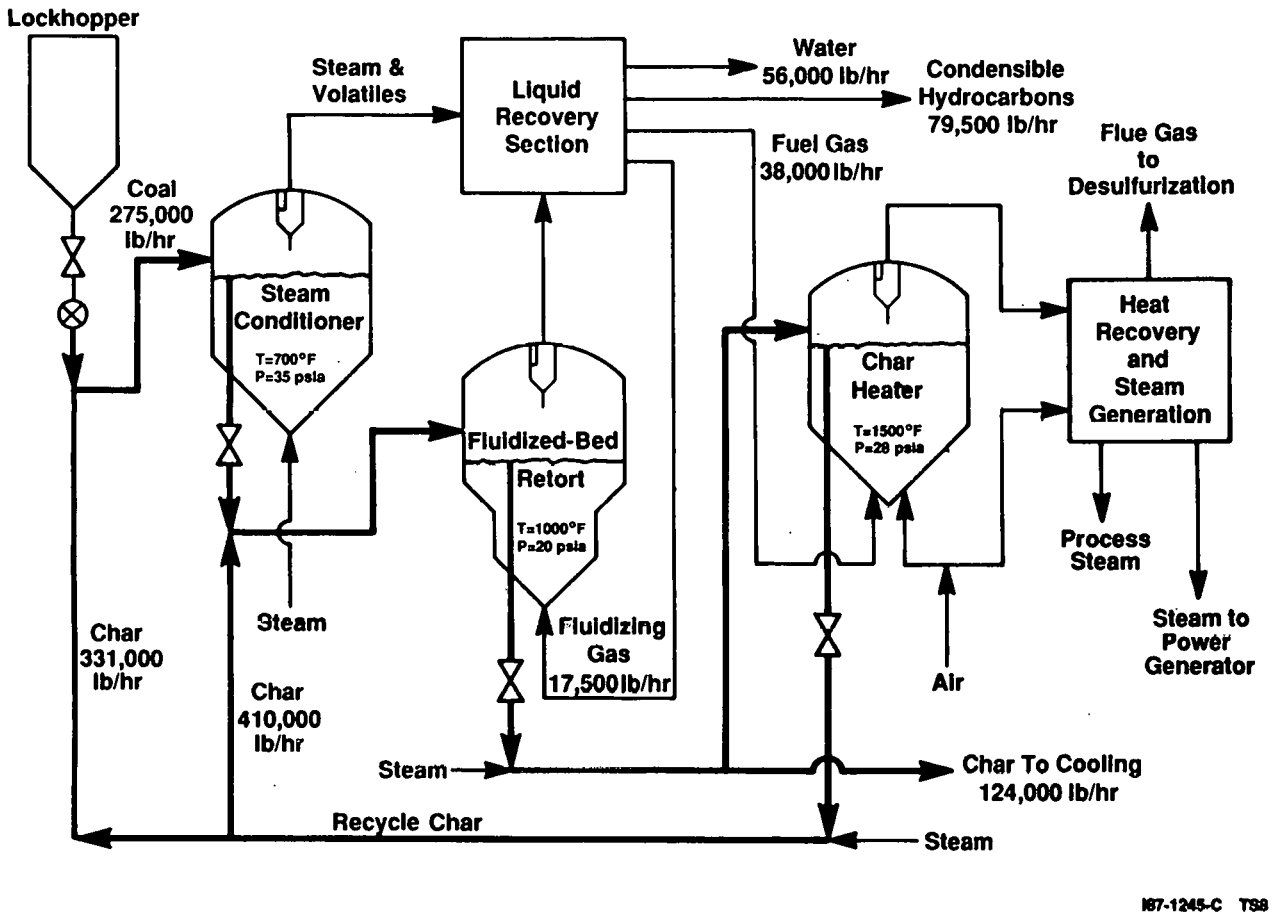



FIGURE 5. FLUIDIZED-BED MILD GASIFICATION WITH TREATED COAL

To determine the economic feasibility of mild gasification processes and to identify how these systems might be improved to make them more competitive, comparisons are being made with other similar processes such as conventional coal gasification and oil shale retorting processes (Figure 6). Material and energy balances for the mild gasification configurations have been determined with the aid of the ASPEN process simulator. These simulations, although non-predictive, allow scoping-level sensitivity studies to be performed which evaluate the technical, environmental, and economic merits of these processes. Since capital cost appears to be a major driver in the economics of mild gasification processes, detailed cost estimates for the fluidized-bed configurations are being prepared to obtain realistic investment costs.

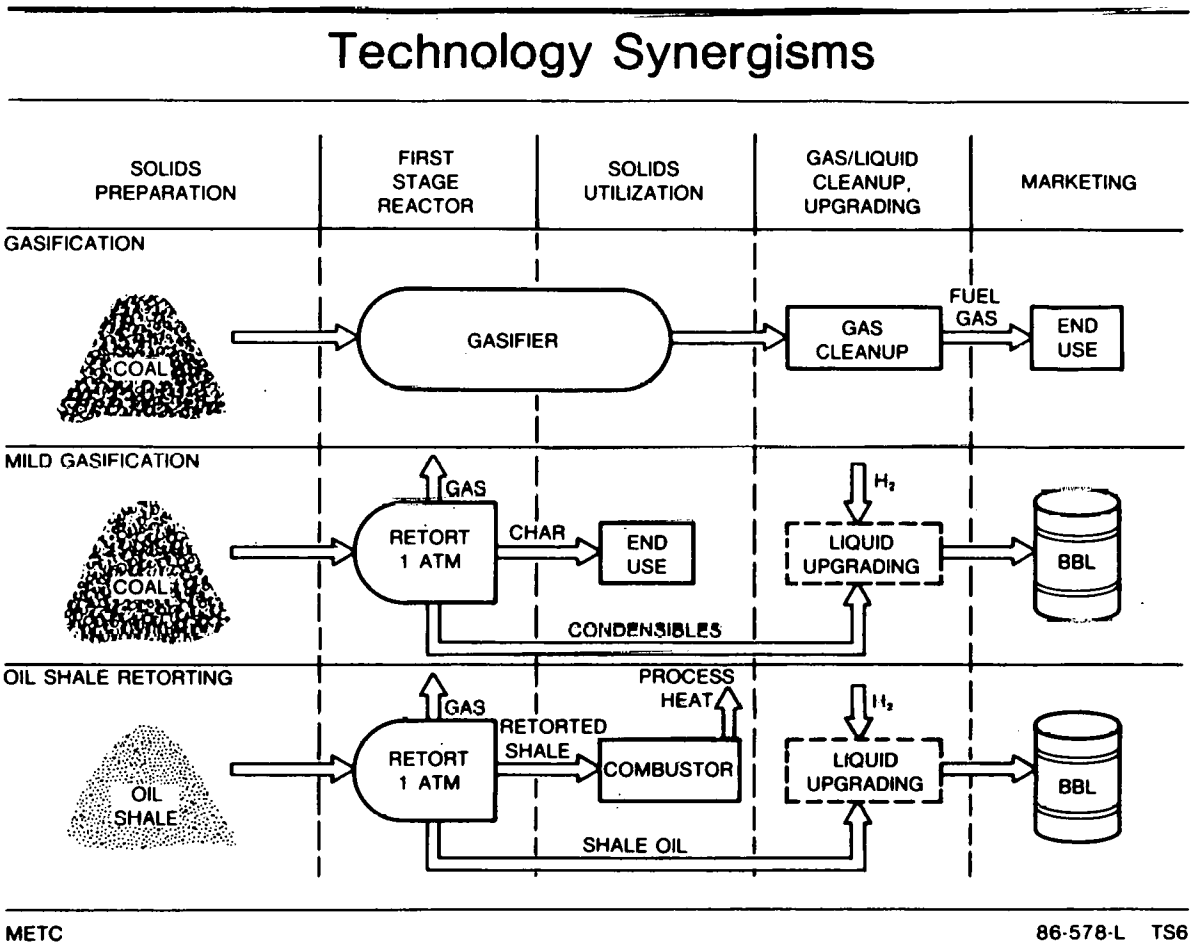
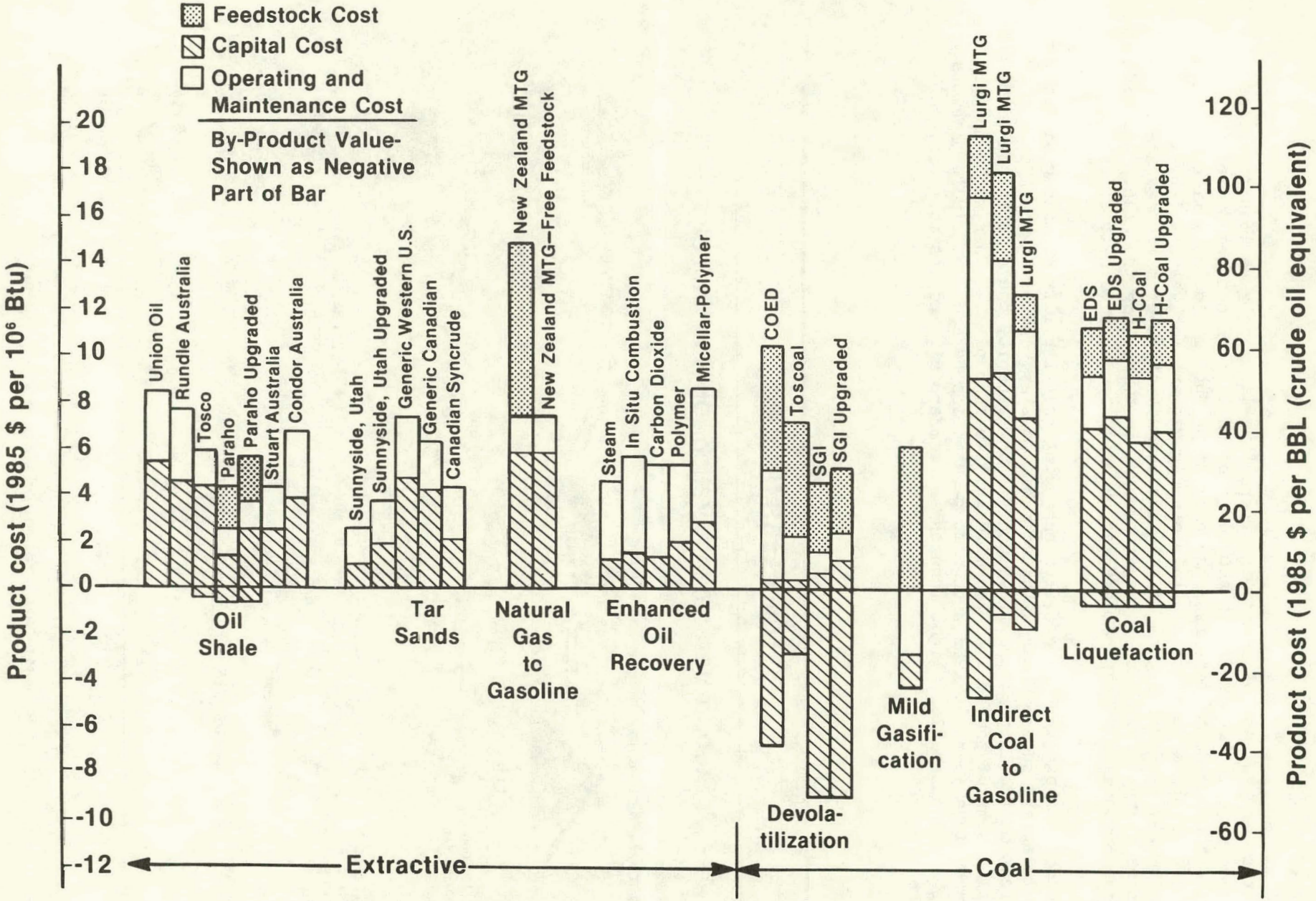



FIGURE 6. TECHNOLOGY SYNERGISMS




NOTE: Product cost is the sum of feedstock and operating costs plus 10% DCF rate of return on capital

FIGURE 7. COST OF VARIOUS ALTERNATIVE LIQUIDS

Estimates for the cost of producing alternative liquids by various processes have been made in Figure 7. It should be noted that an estimated capital investment was used to determine the cost of producing liquid by mild gasification since detailed capital cost figures are not yet available. It can be seen in this figure that a distinct advantage of mild gasification processes is the additional revenues brought in by selling the char. Most of the other processes do not receive any by-product credit to help offset costs.

One concept, shown in Figure 8, for enhancing the viability of mild gasification is to integrate this process with the coal industry. By siting a mild gasification facility at the minemouth, mining capacity could be increased by diverting some of the coal to the mild gasification plant. Char would be sold in conventional coal markets with some penetration by char and liquid products into the transportation, light industrial, commercial, and institutional sectors.

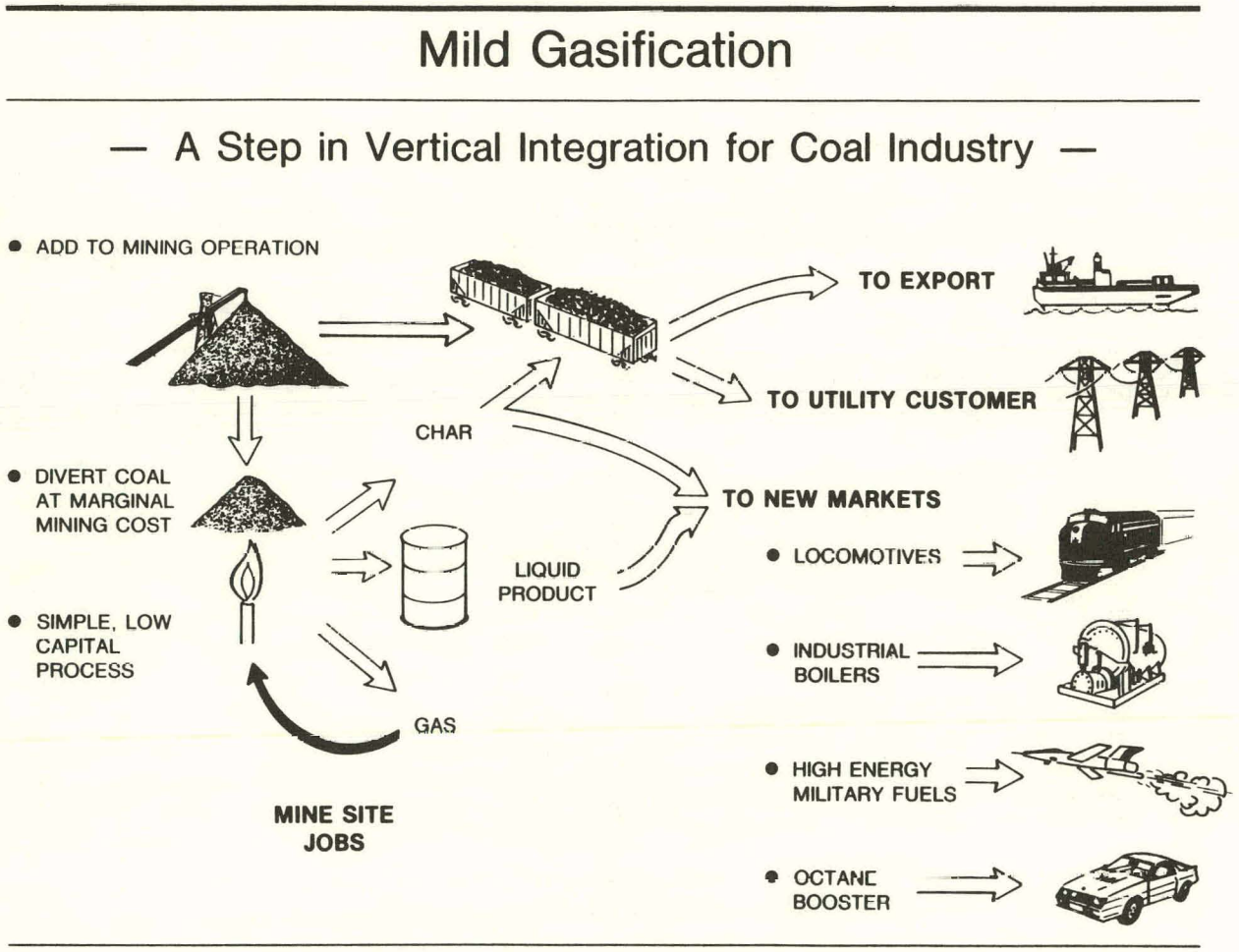



FIGURE 8. VERTICAL INTEGRATION FOR COAL INDUSTRY

In addition to the mild gasification studies being conducted, several alternate configurations for the production of hydrogen fuel from a coal gasification-based system are being evaluated. A base case was established (Figure 9) using the Texaco entrained coal gasification process, high-temperature sulfur tolerant CO-shift, Selexol and Claus processes for removal and recovery of sulfur, and molecular sieve pressure swing adsorption for hydrogen purification. A model for this base case is being developed using the ASPEN process simulator.

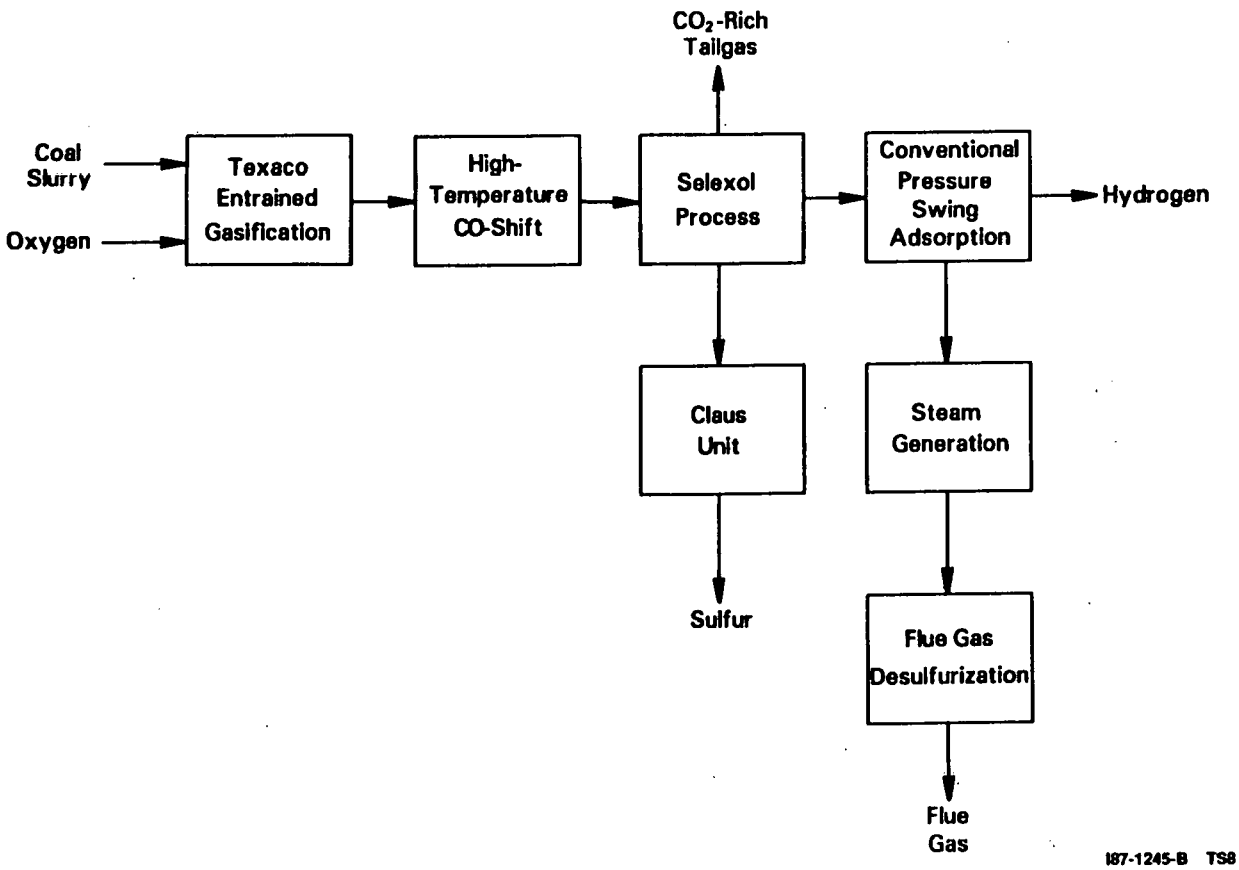



FIGURE 9. CONVENTIONAL COAL-TO-HYDROGEN PROCESS

Models for novel processes will be developed and substituted into the base case to determine if they can perform appropriately and are economically viable for producing low-cost hydrogen fuel from coal. Processes which have been identified for evaluation are shown in Figures 10 - 15 and include Shell dry-feed entrained gasification, Lawrence Berkeley Laboratory (LBL) catalytic gasification, SRI International low-temperature sulfur tolerant CO-shift catalysis, University of California at Berkeley (UCB) acid gas removal process, State University of New York (SUNY) bulk pressure swing adsorption, Membrane Technology and Research (MTR) polymeric membranes, and National Bureau of Standards (NBS) facilitated transport membranes.

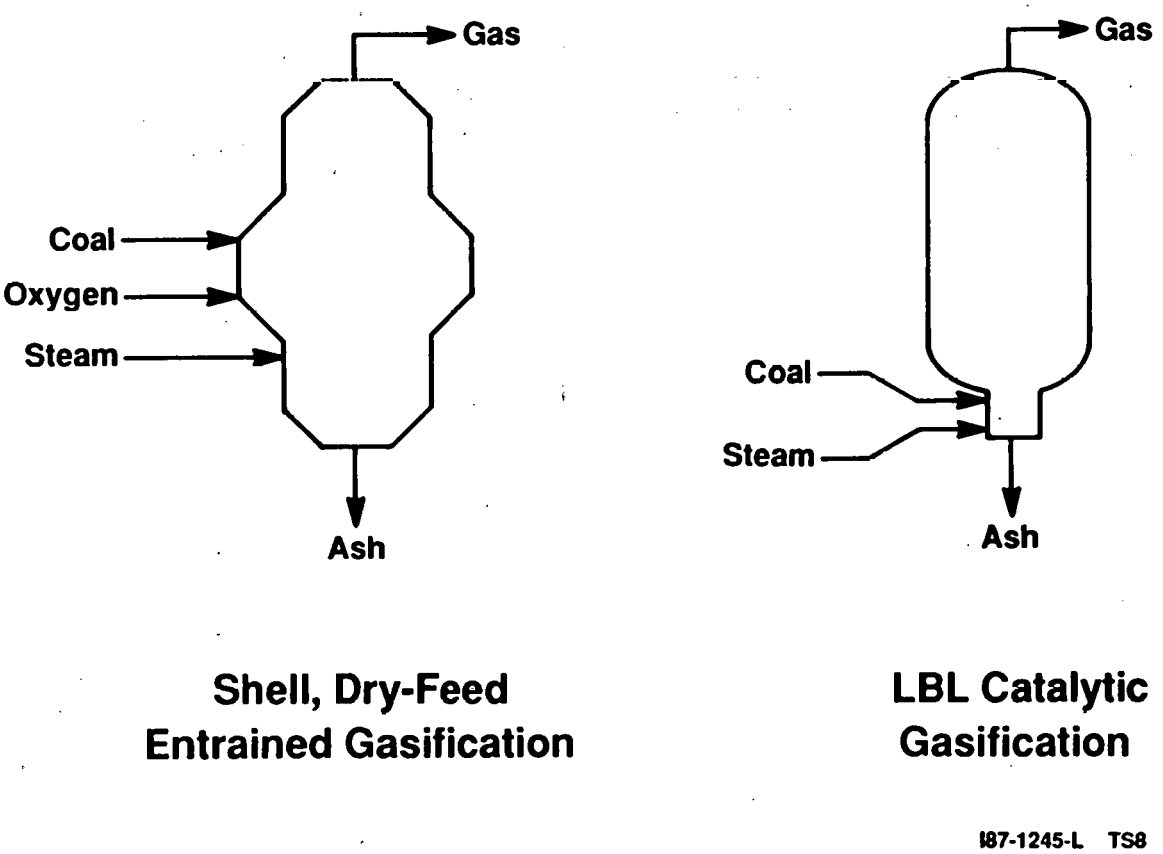



FIGURE 10. NOVEL GASIFICATION CONCEPTS

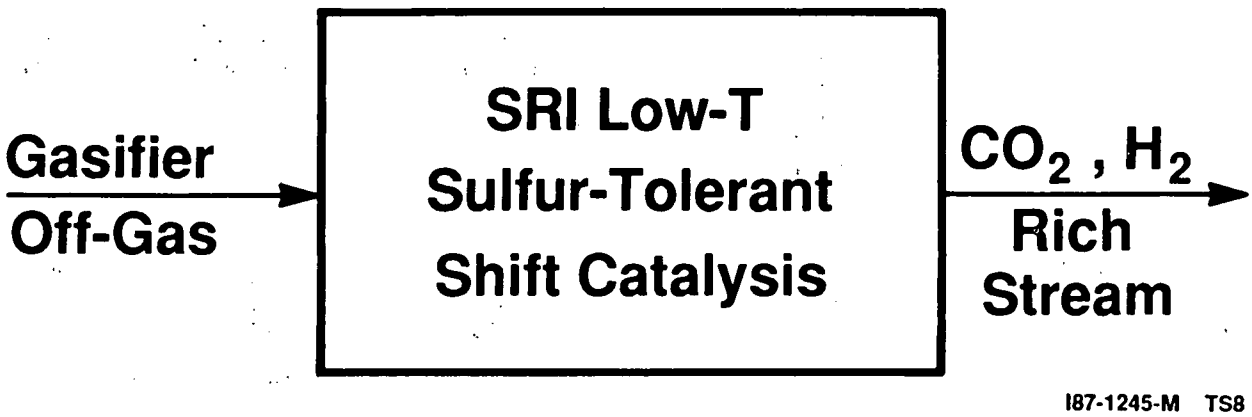



FIGURE 11. SRI LOW-T CO-SHIFT

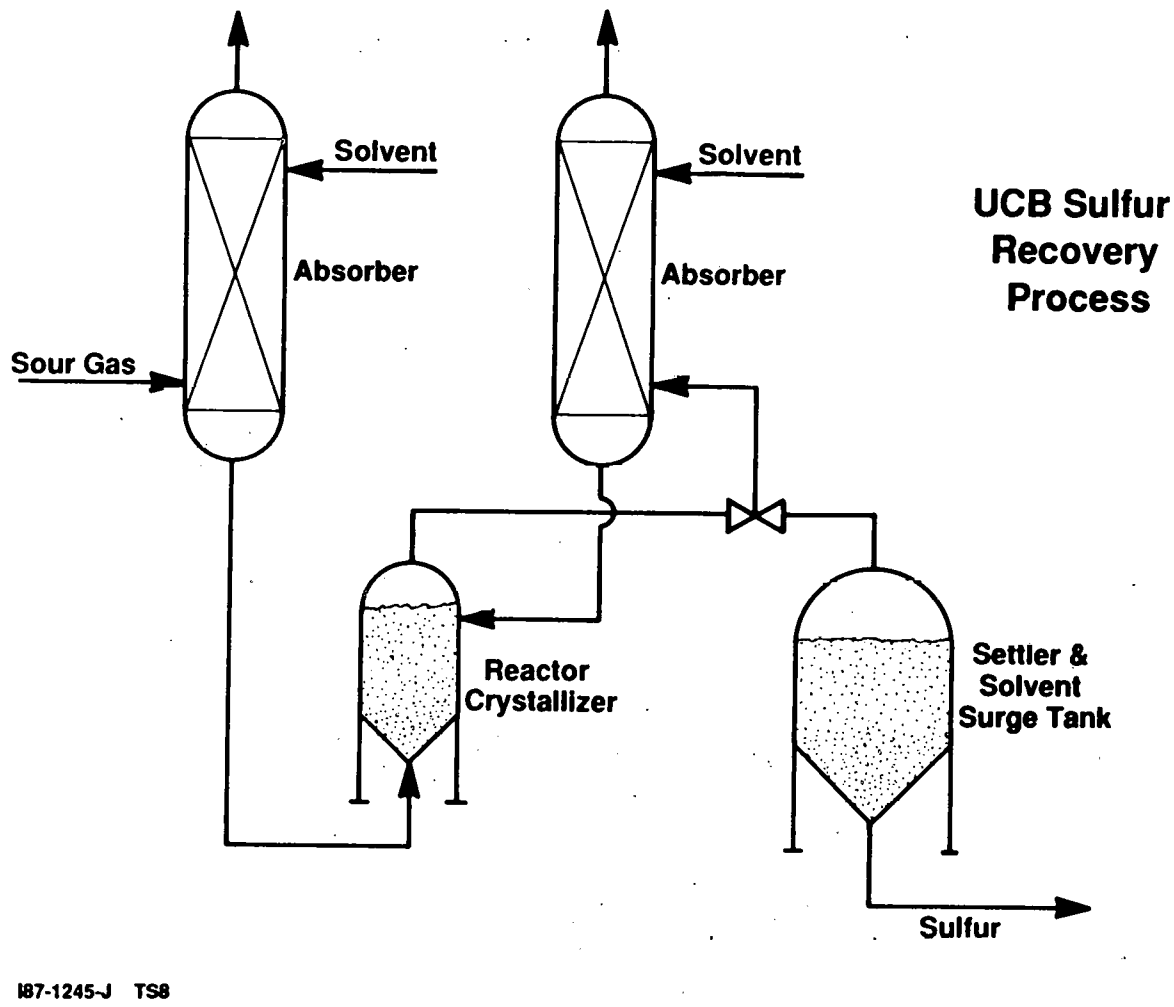



FIGURE 12. UCB ACID GAS REMOVAL/SULFUR RECOVERY

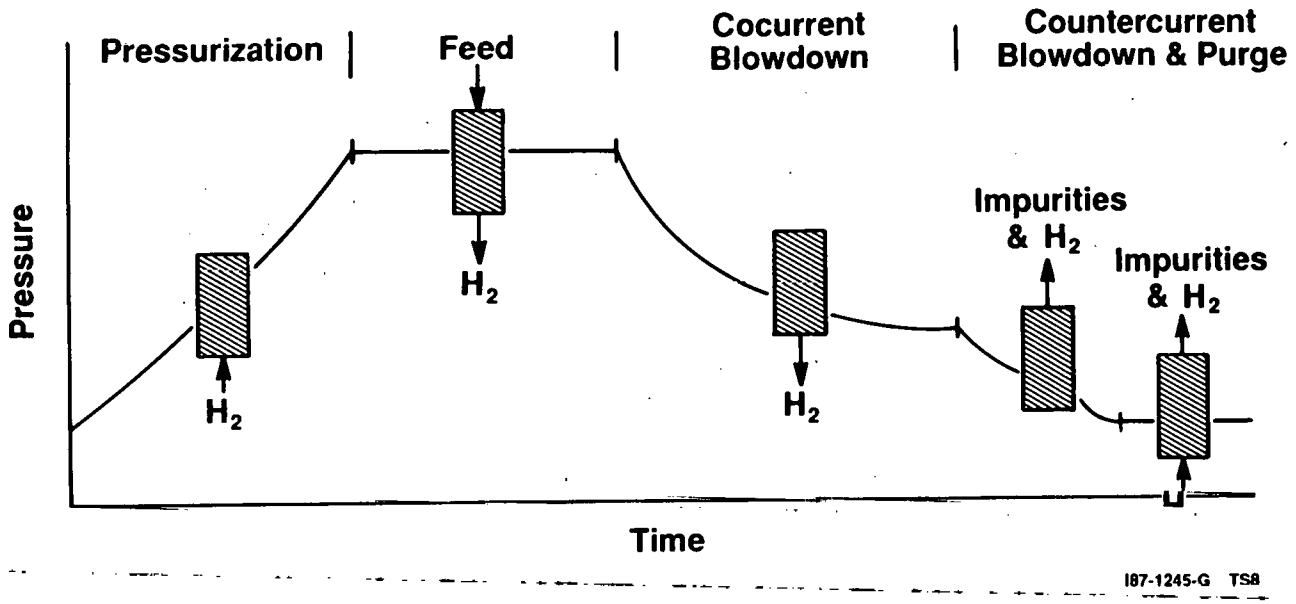



FIGURE 13. SUNY PRESSURE SWING ADSORPTION

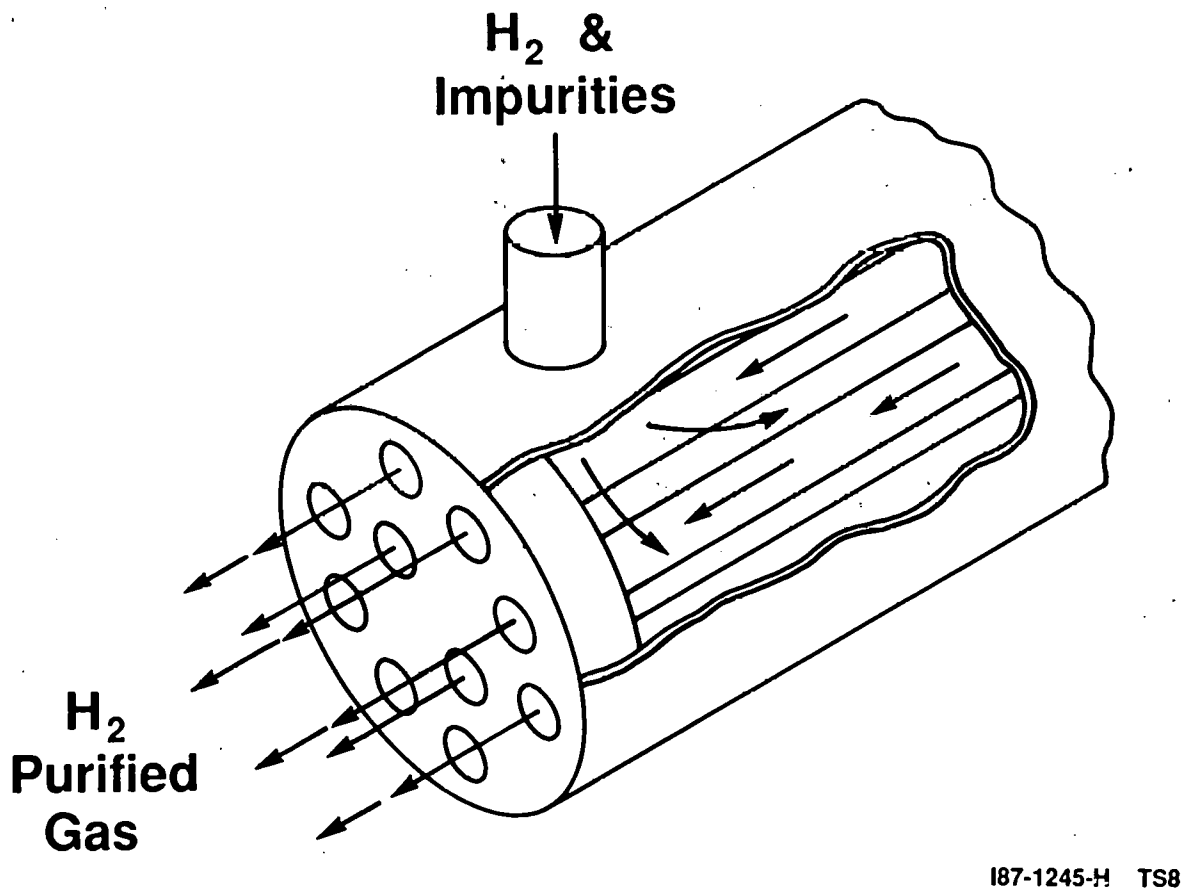



FIGURE 14. MTR POLYMERIC MEMBRANES

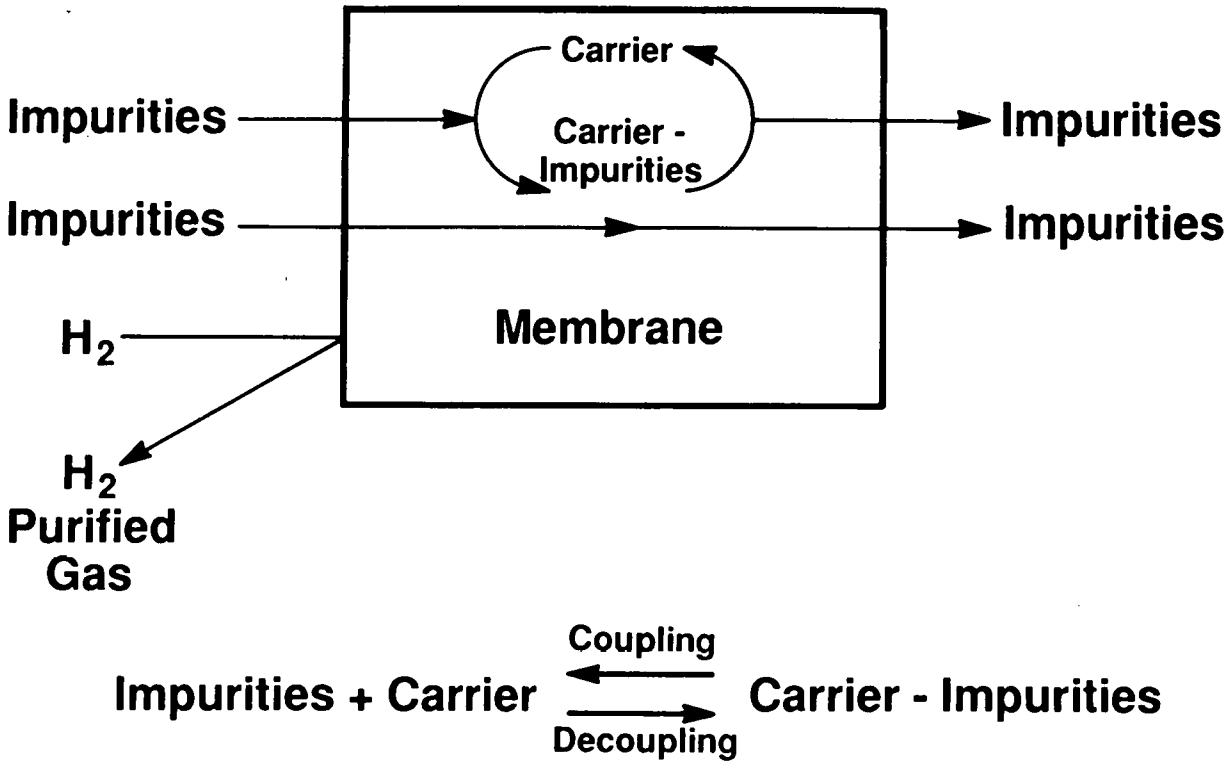



FIGURE 15. NBS FACILITATED TRANSPORT MEMBRANE

FUNDAMENTAL RESEARCH ON MILD GASIFICATION CHAR FUEL DEVELOPMENT

1. DOE CONTRACT NUMBER: DE-AC21-87MC23290

CONTRACTOR: UCC Research Corporation
P.O. Box 1280/Glenway Avenue
Bristol, Virginia 24203

CONTRACTOR PROGRAM MANAGER: Dr. Richard A. Wolfe

PRINCIPLE INVESTIGATORS: Dr. Charles I. C. Chu
Chang J. Im
Barry L. Gillespie

METC PROJECT MANAGER: Dr. Wen S. Liou

PERIOD OF PERFORMANCE: March 20, 1987 to March 20, 1989

2. SCHEDULE/MILESTONES:

Figure 1. depicts the schedule of the project by task.

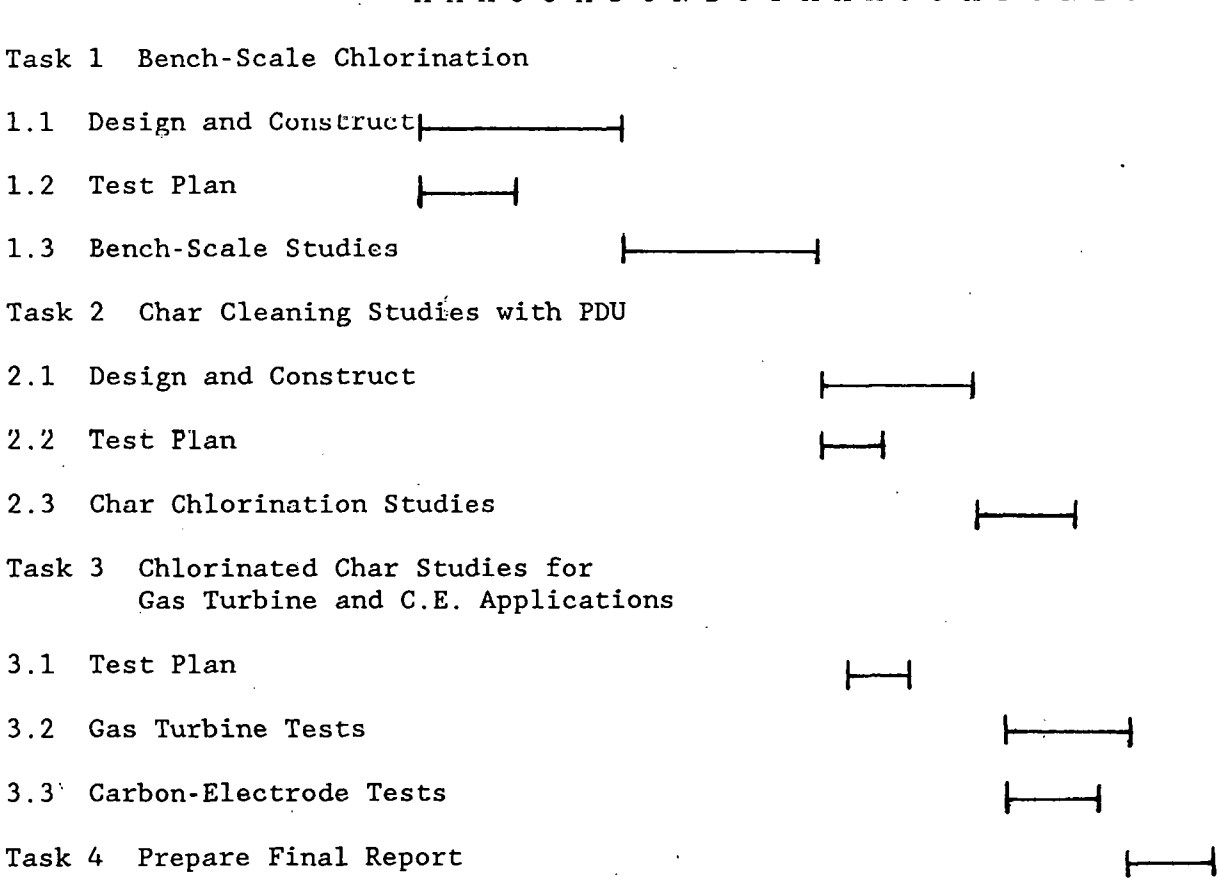



Figure 1. Project Schedule

## 3. OBJECTIVES

The primary objective of this project is to develop a novel process for upgrading the char produced in the mild gasification process in order to enhance the economic advantages of mild gasification. The project will involve: (A) designing, constructing, and testing a bench-scale char chlorination unit, (B) if bench-scale tests are successful, designing, constructing and testing a char chlorination process development unit (PDU),and (C) conducting gas turbine and carbon electrode application studies with the cleaned (chlorinated) char from the PDU.

## 4. BACKGROUND STATEMENT

During the past 20 years or so, various kinds of new generation coal conversion processes have been proposed worldwide; however, most of them proved to be too complicated and/or uneconomical. UCC Research Corporation (UCCRC) has taken a different approach, mild gasification. Mild gasification is a low temperature, low pressure, carbonization process which entails low cost processing of coal. The basic concept of mild gasification is to remove the high quality volatile matter as condensibles and gas, leaving behind a char which has several potential end uses. Due to the fact that the char produced by this process is by far the largest co-product (typically 60-75% by weight of the original coal feedstock), upgrading the quality of the char and identifying potential new markets and applications would make the mild gasification process more economically viable.

UCCRC has investigated various means of reducing the sulfur and ash content of mild gasification char. Recent work has indicated that among the various physical and chemical methods for cleaning the char, only treatment of the char with chlorine at elevated temperatures reduced the ash and sulfur levels to nearly zero (1)*. Tests were conducted in a stationary graphitizer using char ground to 60 mesh x 0. The char was heated under a nitrogen purge to reaction temperature and then chlorine gas was passed over the char for a pre-determined length of time. At the end of the test run, the reactor was purged with nitrogen and the char allowed to cool. Results of these tests are shown in Table I.

* Numbers in parentheses designate references at end of paper.

Table I. Data from Preliminary Char Chlorination Tests

| Sample I.D. | Chlorination Temp °C | Ash, % | Sulfur, % | Sodium, % | Potassium, % |
|---|---|---|---|---|---|
| Low Ash Char | (Untreated) | 2.00 | 1.05 | 0.28 | 0.023 |
| Treated Low Ash Char | 600 | 1.84 | 0.70 | 0.06 | 0.022 |
| Treated Low Ash Char | 1200 | 0.65 | 0.50 | <0.050 | 0.007 |
| Treated Low Ash Char | 1800 | 0.24 | 0.10 | <0.050 | 0.005 |
| High Ash Char | (Untreated) | 11.15 | 1.50 | 0.36 | 0.382 |
| Treated High Ash Char | 600 | 6.39 | 0.90 | 0.072 | 0.210 |
| Treated High Ash Char | 1200 | 0.66 | 0.60 | <0.050 | 0.010 |
| Treated High Ash Char | 1800 | 0.00 | 0.06 | <0.050 | 0.005 |

Notes:

(i) All percentages shown are dry weight percent of the whole char sample.

(ii) The Sodium content of <0.050% for char at 1200°C and 1800°C indicates a result below the detection limit of the analytical procedures used.

5. Project Description

The initial char chlorination tests conducted by UCCRC are very encouraging and warrant further investigation. Therefore, it is the purpose of this project to develop the char chlorination process for upgrading the mild gasification char. Task 1 will involve the design, construction, and testing of a bench-scale char chlorination unit. It is planned to conduct a number of preliminary tests with a rotating tube graphitizer to obtain the fundamental information needed to finalize the design parameters for the bench-scale unit. If testing with the bench-scale unit is successful in removing ash and sulfur, Task 2 will be carried out to design, construct, and test a larger scale process development unit. Char from the PDU will be used in Task 3 to conduct gas turbine and carbon electrode application studies.

6. Results/Accomplishments

The contract began in late March, 1987 and preliminary testing in the rotating tube graphitizer has only been initiated recently.

7. Future Work

For the immediate future, our plans are to complete the current project. Future plans beyond the current project are dependent on the technical and economic data derived from the char chlorination studies.

8. References

(1) Topical Report, A feasibility Study on Liquid Coal Preparation and Coal Char Demineralization, June, 1985, DOE/PETC Contract Order No. DE-AC22-86PC60773.

# EFFECTS OF HALIDES ON THE PERFORMANCE OF COAL GAS-FUELED MOLTEN CARBONATE FUEL CELL

1. **CONTRACT NUMBER:** DE-AC21-86MC23136

**CONTRACTOR:** International Fuel Cells
195 Governors Highway
South Windsor, CT 06074

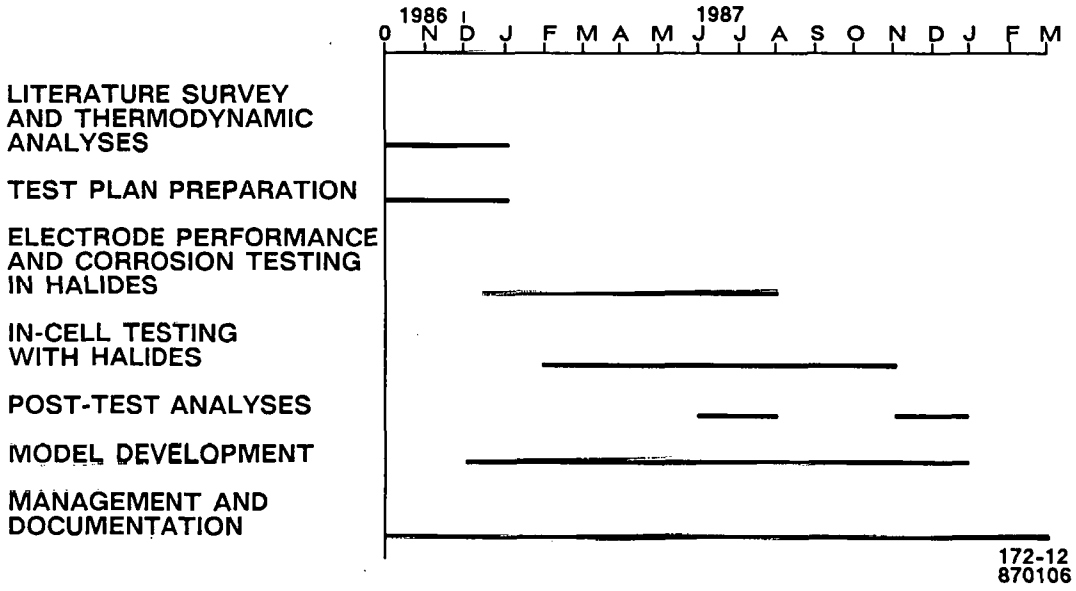
**CONTRACT PROJECT MANAGER:** Fred S. Kemp

**PRINCIPAL INVESTIGATORS:** H. Russell Kunz
Thomas P. Magee

**METC PROJECT MANAGER:** Suresh C. Jain

**PERIOD OF PERFORMANCE:** September 30, 1986 to February 29, 1988

2. **SCHEDULE/MILESTONES:**




3. **OBJECTIVES:**

The objectives of this contract are to develop a model and determine the probable limits of halides in fuel and oxidant streams to achieve a desired coal-gas-fueled molten carbonate fuel cell life between 25,000 and 40,000 hours. The information will be useful in the development of the coal gasifier/molten carbonate fuel cell power plant since it will define the gas cleanup and cell tolerance requirements that enable the mating of the coal gasifier with the fuel cell.

## 4. BACKGROUND STATEMENT:

Chlorides and fluorides are known trace components in gasified coal. Previous short-term bench-scale cell tests performed by the General Electric Company and United Technologies Corporation indicate that chloride can be harmful to molten carbonate fuel cells. Several contracts have been sponsored by the Department of Energy to develop hot-gas-cleanup systems for the removal of impurities including chloride. In order to allow the successful mating of the cleanup system and molten carbonate fuel cell, to result in the desired 25,000 to 40,000-hour fuel cell life, the tolerance limits of the fuel cell to chloride and fluoride must be defined. A model of the decay mechanisms should be developed so the factors controlling the cell tolerance limits are clarified.

## 5. PROJECT DESCRIPTION:

The program consists of several tasks. First, a literature survey and thermodynamic analyses were performed to determine the anticipated effects of halides. These results were used to formulate a test plan. The tests consist of laboratory out-of-cell measurement of the performance of anodes and cathodes with halides present in the electrolyte and corrosion measurements on materials of construction. In-cell tests will be performed and all the data modeled to enable the prediction of the effects of halides on cell performance.

## 6. RESULTS/ACCOMPLISHMENTS:

A literature survey and thermodynamic analyses were performed to investigate the effects that halides might have on molten carbonate fuel cells. The survey included previous operating experience of molten carbonate fuel cells with chloride added to the reactants, the effects on the electrolyte properties of converting part of the anions to chloride or fluoride, and the effects on corrosion of cell components. Thermodynamic calculations were performed to determine the equilibrium composition of cell materials for which thermodynamic data were available. The combination of the survey and analyses provided considerable information concerning the anticipated effects of chloride and fluoride.

Previous cell experience and thermodynamic calculations indicate that the nickel components on the anode-side of the cell should not corrode in the presence of less than 100 ppm chloride in the fuel. Poisoning of the anode reaction may occur. Accelerated attack of cathode-side components is expected, especially corrosion of the stainless steel current collector and separator plate. Some attack of the nickel oxide cathode and the lithium aluminate matrix material may occur.

A major effect is the change in properties of the electrolyte. Any hydrogen chloride or fluoride entering the cell in the fuel or oxidant should react completely with the electrolyte to form lithium and potassium chloride and fluoride. These salts are more volatile than the unconverted electrolyte and can result in an accelerated loss of electrolyte by evaporation. Therefore, vapor pressures of the electrolyte were calculated as a function of the anion fraction of chloride and fluoride. The results of these calculations are shown in Figures 1 and 2 where the calculated values are compared with the measured vapor pressures of the pure halides. Where data were not available for the pure halides, the calculated values were compared to extrapolations of the data to fuel cell operating conditions.

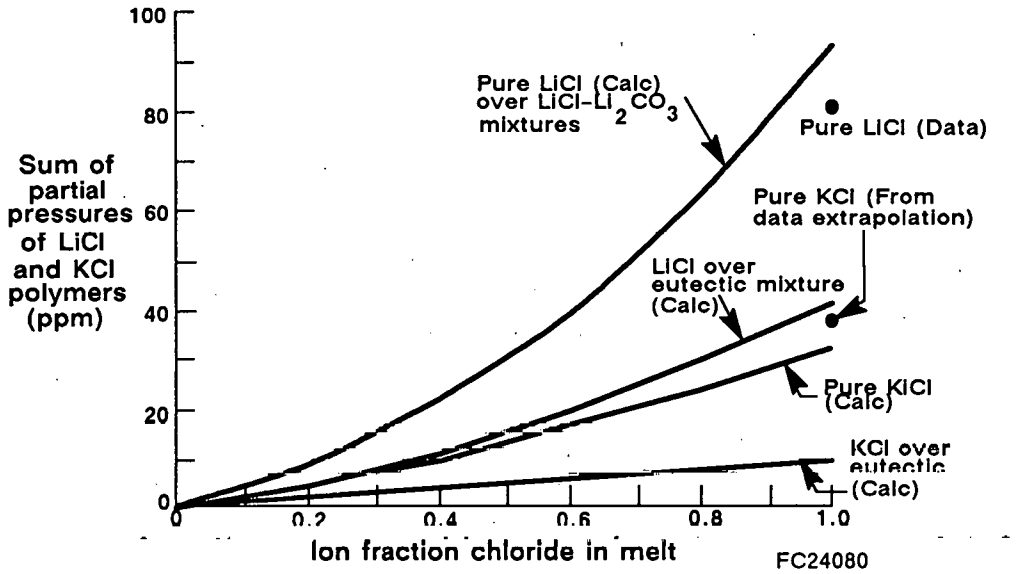



Figure 1. Calculated Chloride Vapor Pressures

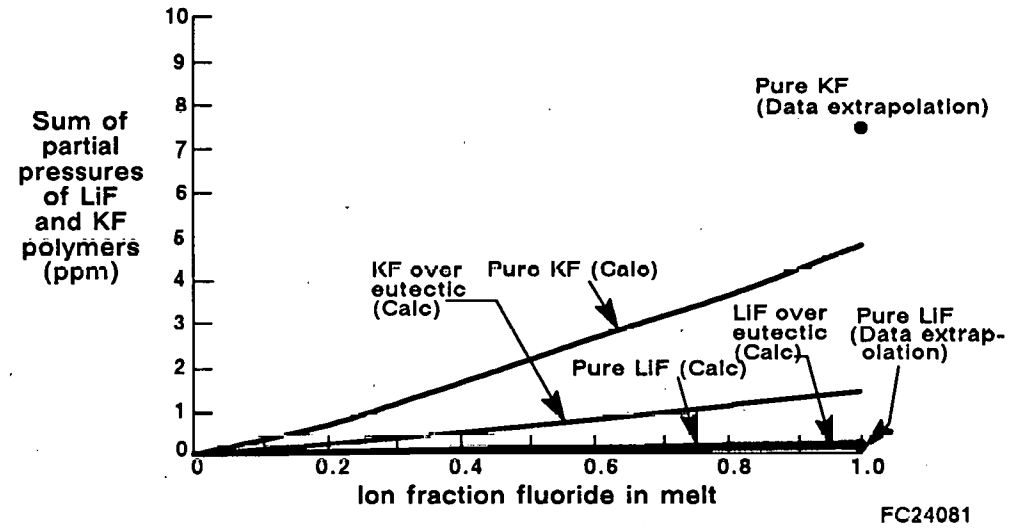



Figure 2. Calculated Fluoride Vapor Pressures

Another major effect on the electrolyte properties is a reduction in the carbonate ion activity. Since carbonate ions are the product of the cathode half-cell reaction and are consumed in the anode half-cell reaction, a reduction in the carbonate ion activity can affect the electrode polarizations. If different carbonate ion activities are present at the anode and cathode, a concentration polarization and a performance loss due to a liquid junction potential can occur.

Because of these anticipated effects, out-of-cell tests were begun to determine the effects of chloride and fluoride in the electrolyte on the corrosion of cathode-side components, to determine the short-term effects of halides on the performance in half-cell tests of both anode and cathode-side components, and to determine the importance of electrolyte concentration polarization. These last tests were performed first because data are needed to determine the effect of halide in the electrolyte on electrode open circuit potential. Concentration polarization data were obtained by performing a series of open circuit voltage measurements between electrodes in halide-free and halide-containing electrolytes. For both chloride and fluoride, the open circuit voltages were found to be increased due to the presence of halides, as would be expected, accounting for the reduced carbonate ion activity in the Nernst equation.

Four chloride concentrations (23, 50, 78, and 92 anion percent chloride) and two fluoride (23 and 44 anion percent fluoride) concentrations were tested. One sulfate data point was available from a previous study. Results are plotted in Figure 3.

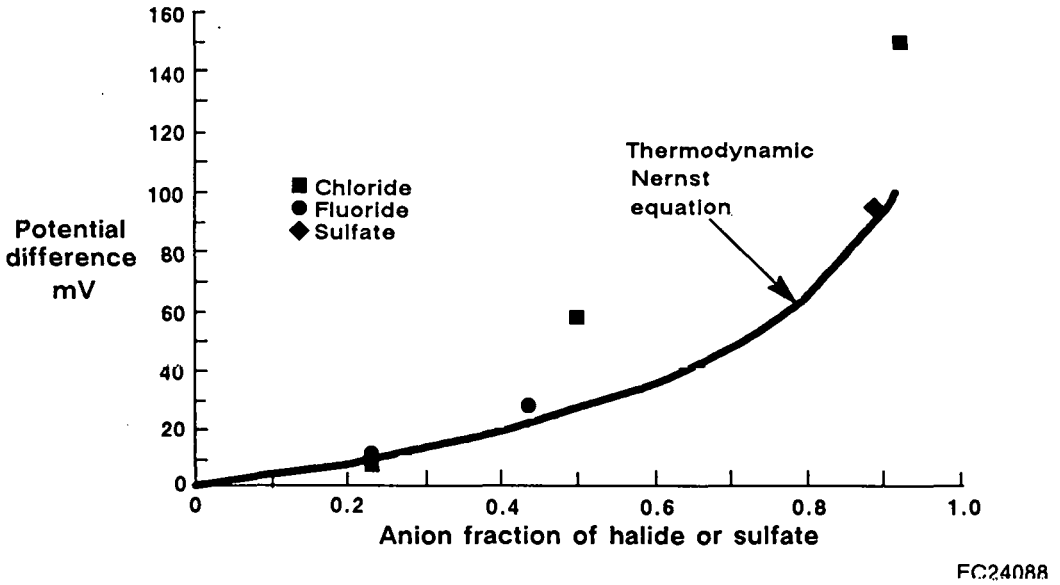



Figure 3. Electrolyte Concentration Polarization

The cause for the data differing from the Nernst equation is not known. Possible reasons are that a liquid junction potential effect is significant, that an unknown reaction is taking place, that a complex is forming or that the carbonate ion is partially dissociating (Kruglov 1968). The data seem to follow the Nernst equation for anion fractions of halide less than 0.23.

Nine half-cell performance tests were then run using cathodes in which electrolyte content was varied. The content was varied in each test because electrolyte loss is considered to be a major decay mode cause by halides. Six of these tests were performed using 72 mole percent $Li_2CO_3$, 28 mole percent $K_2CO_3$ electrolyte containing no halide, one using the same electrolyte with 3.1 anion percent

chloride, one with 23 anion percent chloride and one using 23 anion percent fluoride.

The tests on halide-free electrolyte were performed to develop a baseline performance level and to improve the reproducibility of the data using present cell components. A summary of the cathode data is shown in Figure 4. Although fluoride has little effect on cathode performance, the effect of chloride is significant.

Corrosion testing was begun on samples of structural materials (AISI 310 stainless steel, AISI 316 stainless steel, and Inconel 825) in electrolyte containing 3.1 anion percent chloride in a cathode environment. Samples were removed after 500 hours for post-test analyses.

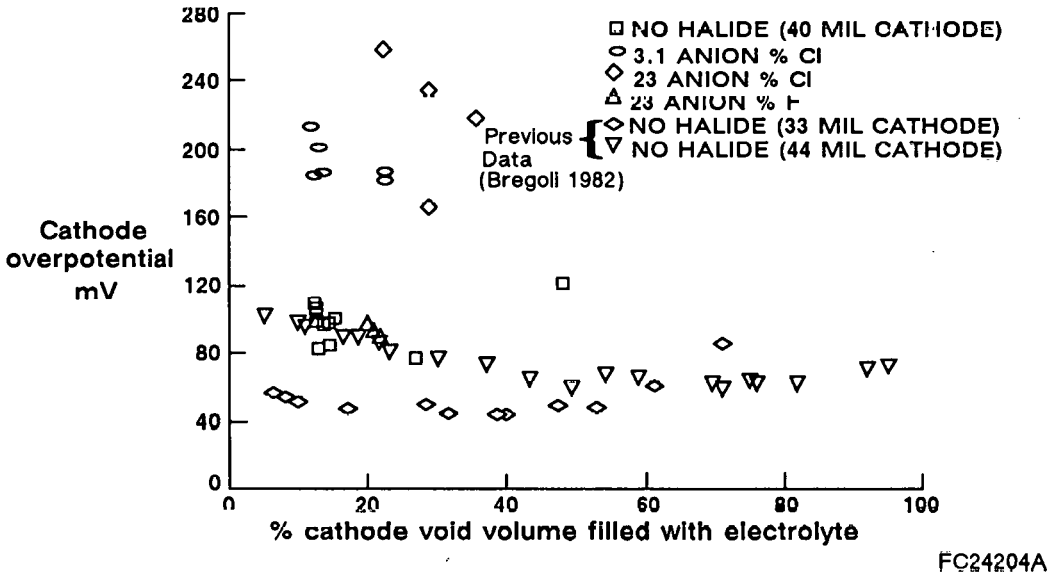



Figure 4. Effect of Halide on Cathode Half-Cell Performance

## 7. FUTURE WORK:

Further half-cell performance tests and corrosion experiments will be performed to investigate the effect of chloride and fluoride in the electrolyte. The half-cell performance tests will consist of anode-side tests in electrolyte containing 23 anion percent chloride, 23 anion percent fluoride and halide-free electrolyte. The corrosion experiments using electrolyte containing 3.1 anion percent chloride will be continued to 1000 hours. A similar 1000-hour test using 3.1 anion percent fluoride will also be run on AISI 310 stainless steel, AISI 316 stainless steel, and Inconel 825.

The future in-cell experiments include two 1500-hour-long bench-scale tests that will determine the effects of either 10 ppm KCl or 10 ppm HF in the fuel and oxidant gases at 1 and 10 atm operating pressure and one 4500-hour test at 1 atm to verify halide tolerance levels determined by the 1500-hour tests and the model.

The model and computer code will be developed to explain and predict the effect of halides on the performance behavior, and materials of construction of the molten carbonate fuel cell. The model will be structured as an aid to halides removal subsystem designers.

## 8. REFERENCES:

Kruglov A.N., V.P. Kochergin, and V.V. Yakovleva. 1968. Thermal Dissociation of Sodium and Potassium Carbonates in the Presence of Univalent Metal Chlorides and Fluorides. *Russ. J. Inorg. Chem., 13 (7)*:921–23.

Bregoli L.J. and H.R. Kunz. 1982. The Effect of Thickness on the Performance of Molten Carbonate Fuel Cell Cathodes. *Jl. of the Electrochem. Soc. 129*:2711–15.

COMPONENT SYSTEMS ENHANCEMENT

REDUCED GIRTH SEAM WELDMENTS FOR HEAVY-WALLED VESSELS*

1. CONTRACT NUMBER: DE-AC21-86MC22068

CONTRACTOR: CBI Na-Con, Inc.
800 Jorie Boulevard
Oak Brook, IL 60522
(312) 572-7976

PROGRAM MANAGER (CONTRACTOR): Samuel C. Leventry

PRINCIPAL INVESTIGATORS: Don R. Horacek
Steve W. Peters

METC PROJECT MANAGER: Dave Dubis

CONTRACT PERIOD OF PERFORMANCE: February 25, 1986 through June 25, 1987

2. SCHEDULE/MILESTONES:

- Typical vessel determination: February, 1986 through April, 1986.
- Scale model design and detailing: April, 1986 through October, 1986.
  Model ADINA analysis
  Model manufacture
- Model testing: September, 1986 through February, 1987.
- Test Evaluation: February, 1987 through April, 1987.
- Final design recommendations: April, 1987
- Cost analysis: April, 1987 - June, 1987
- Video Tape: May, 1987 - June, 1987
- Final Report: April, 1987 through June, 1987

* Patent applied for.

## 3. OBJECTIVES:

The objective of this contract is to evaluate by design, analysis and testing three different configurations for the reduced thickness area. The detail that has proven to be the most technically merited has been evaluated to determine the vessel cost savings for implementing the design details. This concept results in an overall vessel cost reduction of 9.5% for a typical gasification vessel. Construction schedule savings will also be estimated and resulting finance cost savings for a gasification plant will be estimated. A qualitative estimate for the overall plant cost savings for a plant using larger vessels (as made practical by this research) and therefore, fewer process trains will be made. The specific objectives of this research are:

- o Demonstrate that a local reduction in thickness for a heavy-wall vessel can be designed to meet the Appendix 4 rules of ASME Section VIII Division 2.

- o By analysis and testing determine which of three different configurations provides a pressure-load capacity most like that of a vessel without areas of reduced thickness. Develop cost estimates for vessel savings and overall plant savings as a result of this concept.

- o Provide information to the public domain so that the component enhancement developed by this research can be used in planning future coal gasification projects.

## 4. BACKGROUND:

The concept of reduced thickness girth seam weldments can most easily be explained by a simplified review of the pressure load on a cylindrical shell. The required thickness for the cylinder in the circumferential direction can be approximated as $t_C = PR/S$ where;

P = design pressure
R = vessel radius
S = allowable design stress

The required thickness for the longitudinal direction is approximately by $t_l = PR/2S$. Therefore the nominal thickness for a cylindrical shell is controlled by the stress in the circumferential direction and is twice the required thickness for the longitudinal direction. Providing a local area of reduced thickness to 2/3's the nominal thickness will still provide excess thickness for longitudinal stress.

The reduced thickness area will create higher stress locally in the circumferential direction. However, since the total amount of material removed is small when compared to the remaining material, the ultimate capacity will not be significantly reduced. As the thinned area tries to stretch due to the higher stress it will be restrained by the thicker material on either side of it. Therefore, some of the pressure loading in the thin area will be shifted to the thicker material. Bursting for ductile materials will not occur until all the material has fully yielded and is at the ultimate capacity of the material.

5. PROJECT DESCRIPTION:

Fuels from synfuel plants are not currently cost-competitive with naturally occurring hydrocarbon fuels due, in part, to high plant construction costs including financing costs due to long construction schedules. The subject of this research will make synfuels more competitive by reducing the cost of individual components (heavy-wall pressure vessels) as well as reducing the overall cost of the plant due to fewer process trains and reduced construction schedules. All studies done to date for coal gasification plants have used heavy-wall vessels that are constant thickness for a given diameter. Some of the complications with field erection of heavy-wall vessels are:

- Eight inches (8") is a practical limit for isotope radiation sources for radiographic examination of weldments. Therefore, when the welds are thicker than 8", a linear accelerator must be used for radiography which will require extensive shielding of the area during radiography. This will complicate the completion of these welds making the costs higher and requiring longer schedules.

- SA-387 Grade 22 Class 2 material is one of the commonly referenced vessel materials due to its proven success in similar process conditions in the petroleum refining industry. As the weld gets thicker more PWHT time is required and it is more difficult to provide material that can withstand these long PWHT times and still maintain the specified strength properties after PWHT. Therefore, for very thick vessels, the materials are more expensive per unit weight and are also available from fewer sources.

- For large site-erected heavy wall vessels, individual cylindrical sections of the shell are assembled on the ground or at a shop manufacturing facility and then shipped to the site. These rings are then lifted into place and the girth seams welded together. The time required to complete these girth seam weldments has a very direct relationship to the construction schedule for heavy-wall vessels. The time and labor to complete the girth seam weldment increases as a quadratic function of the weld thickness.

The reseach has addressed all three of the above problems. Heavy wall vessels can be designed such that the girth seam weldments need only be 2/3's of the nominal vessel thickness. Therefore, a thick vessel can be erected in about the same time and cost as a vessel that is the same size but ony 2/3's as thick.

The goal of the research is to demonstrate to the synfuels industry that larger and thicker heavy-wall vessels can be economically site-erected. This will provide greater overall flexibility in plant design as well as lower plant costs. The goal has been accomplished by meeting the following objectives:

- o Verification of design procedures for evaluating reduced girth seam weldments per the analysis provisions of ASME Section VIII, Division 2.

- o By nonlinear analysis of each configuration, predicting the theoretical burst pressure for vessels using each configuration.

- o Verification of the design work by strain gauging and pressurizing the model vessels to the design pressures.

- o Verification of the predicted burst pressures by testing model vessels to failure.

This research has shown by analysis and model testing that the concept can be utilized for heavy-wall vessels to significantly reduce the cost of the vessels.

## 6. RESULTS

The following portions of the research have been completed:

- o ADINA nonlinear analysis of the three models to predict failure pressures

- o Fabrication and testing to failure of all models

- o Comparison of analysis predictions vs actual test results. The models with the enhancement failed within 2% of a "standard" vessel.

- o Estimated cost savings of 9.5% for heavy-wall vessels utilizing this concept

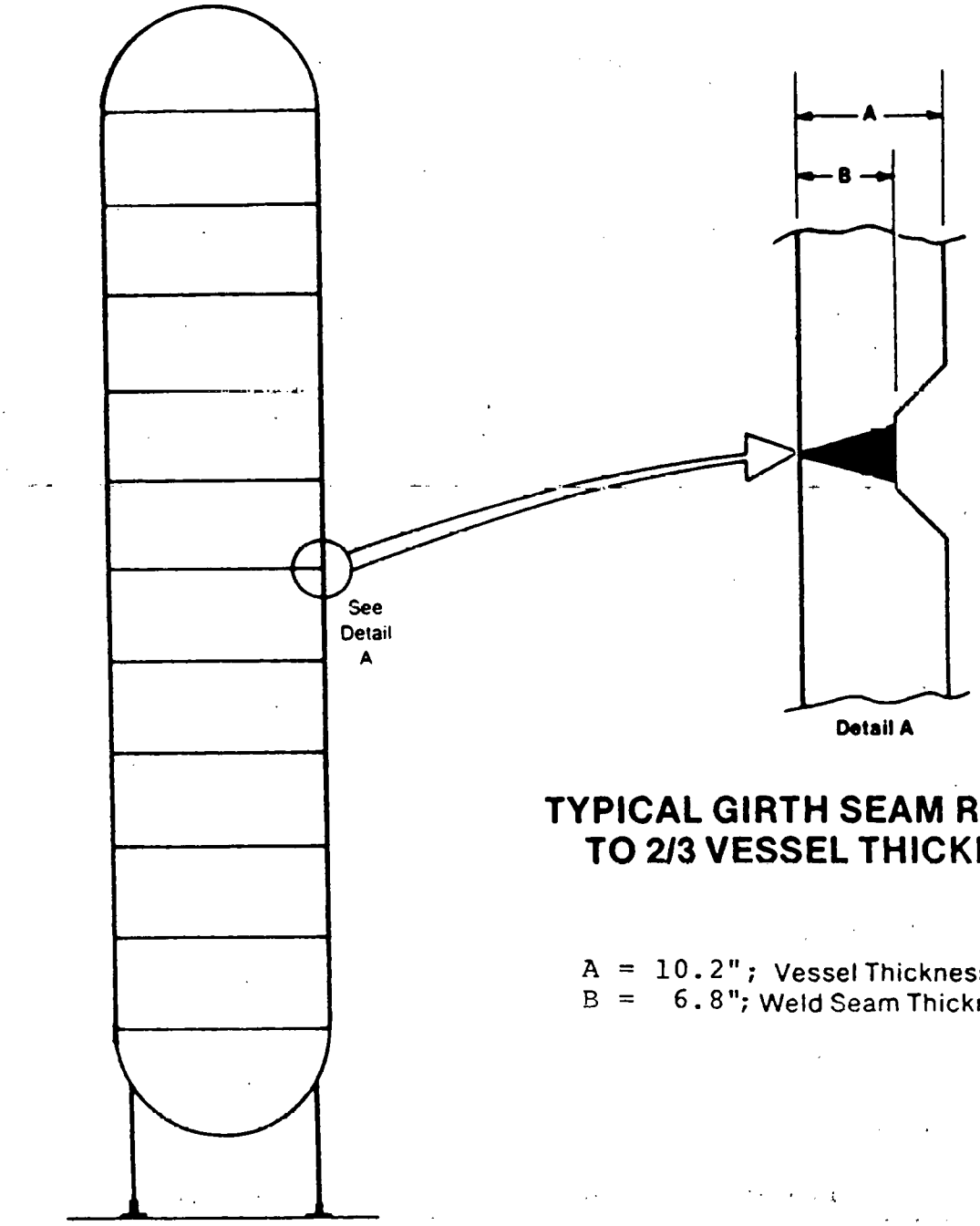
The following tasks remain to be completed:

- o Qualitative estimate for the overall plant cost savings for a plant using larger vessels (as made practical by this research) and therefore, fewer process trains.

## 7. FUTURE PLANS

The current research used machined specimens to model the reduced thickness area. (i.e. a weld was not made in the reduced thickness area.)

Larger scale models using the same materials as used for the actual gasification vessels should be used during the future research program. These models should also have girth seam welds at the location of the reduced thickness. This final testing program would very closely model a full size gasification vessel and would then provide a basis for design of production gasification vessels.




**TYPICAL GIRTH SEAM REDUCED TO 2/3 VESSEL THICKNESS**

A = 10.2"; Vessel Thickness
B = 6.8"; Weld Seam Thickness

**TYPICAL GASIFICATION VESSEL**

Figure 1 - Reduced Girth Seam Detail

# COAL SLURRY LETDOWN DEVICE

1. CONTRACT NUMBER: DE-AI21-81MC16512

CONTRACTOR: Jet Propulsion Laboratory
California Institute of Technology
4800 Oak Grove Drive
Pasadena, CA 91109
(818) 354-7020

CONTRACTOR PROJECT MANAGER: W. J. Marner

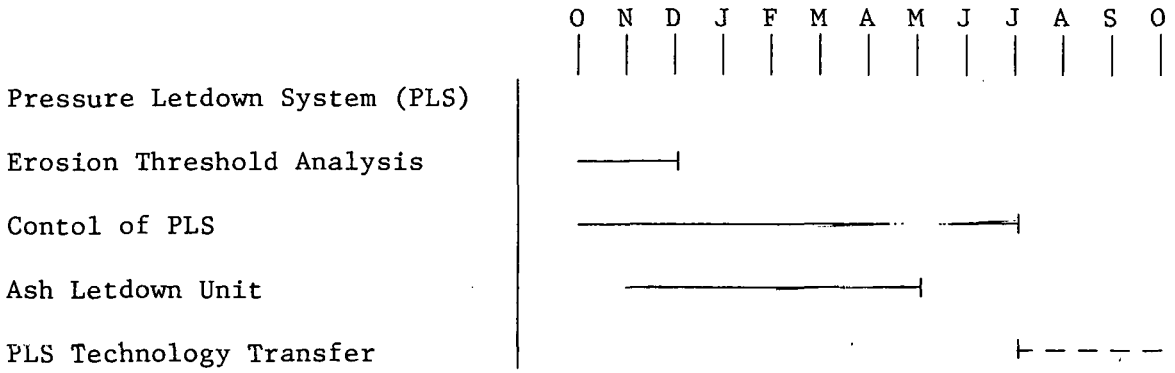
PRINCIPAL INVESTIGATORS: W. J. Marner
Earl R. Collins
Naresh K. Rohatgi

METC PROJECT MANAGER: David Dubis

CONTRACT PERIOD OF PERFORMANCE: November 1, 1982 to June 30, 1987

2. SCHEDULE/MILESTONES:

1987 Program Schedule




3. OBJECTIVES:

The objectives of this project are:

- Develop and demonstrate the performance of a pressure letdown system (PLS) and formulate a PLS design methodology.
- Determine parameters for minimum erosion in three-phase flow.
- Develop a controllable pressure letdown device using a vortex control element.
- Determine suitability of the pressure letdown device as an ash letdown unit.

4. BACKGROUND STATEMENT:

A problem common to most coal gasification and liquefaction processes is the lack of reliable, long-life pressure letdown systems. Such systems must accommodate three-phase, solid-liquid-gas mixtures at temperatures up to 1600 F and pressures up to 3000 psia. Commercial development of these advanced fuel processes requires reliable, low-maintenance letdown systems. The standard approach to pressure letdown is to throttle the flow by reducing the flow area in a throated control valve. Unfortunately, high velocities in the valve throat combine with the abrasive solids content of typical coal-derived slurries resulting in excessive valve wear, lack of controllability, and short lifetimes. Attempts to use advanced materials which are more durable under such conditions have met with limited success.

An alternative approach, developed at the Jet Propulsion Laboratory, California Institute of Technology (JPL), is to reduce the throat velocities by using the concept of the porous plug (Kendall 1983). In this technique the pressure is reduced by means of a throttling process through a series of successive stages. Each stage consists of a perforated plate and a plenum chamber as shown in Figure 1. The number and size of the orifice holes are chosen to be large enough to pass entrained particles while maintaining low velocities through the orifices in the latter stages to accommodate volumetric flowrate increases resulting from liquid flashing to vapor as the pressure is reduced.

The four major tasks in this effort include: (a) Development and testing of the PLS, (b) Experimental erosion studies and analysis, (c) Control of the PLS, and (d) Development of an ash letdown unit based on the PLS technology. In this paper attention is focused on Items (c) and (d) since these tasks have received most of the attention in the current fiscal year. Details on the earlier work may be found in (Collins and Suitor 1984; Suitor, et al 1985; and Marner, et al 1987).

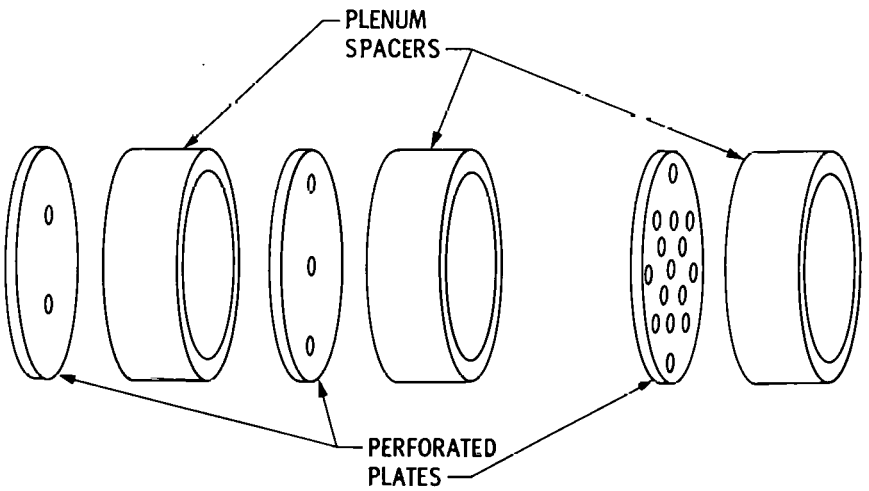



Figure 1. Pressure Letdown System Plate Arrangement

5. PROJECT DESCRIPTION:

Owing to space limitations, only a very brief description of Tasks (c) and (d) listed above will be given.

CONTROL OF THE PRESSURE LETDOWN SYSTEM

The objective of this task was to develop a means of controlling the supply fluid flowrate in the PLS. A vortex flow control element, based on fluidic principles, was developed for this purpose and tested in a small JPL Test Loop and at the JPL Edwards Facility (EF). The most recent version of the control element, which has two supply and two control ports, is shown in Figure 2. The supply fluid enters the supply ports in the control element and spirals inward, leaving the outlet port as shown. The control fluid enters the control ports and, by providing a centrifugal force against the entering supply fluid, regulates the supply flowrate through the device. The effectiveness of the control element may be quantified through the turndown ratio, TR, defined as

$$TR = \frac{\text{Uncontrolled Supply Fluid Flowrate}}{\text{Controlled Supply Fluid Flowrate} + \text{Control Fluid Flowrate}} \quad (1)$$

ASH LETDOWN UNIT

This task is concerned with the application of the PLS technology to a solids-gas application, namely the removal of hot ash from a reactor vessel while minimizing the loss of hot gases from the reactor. A bench scale unit was designed and constructed, and tests were carried out using sand and nitrogen to simulate the ash and gas in the reactor with air as the control fluid.

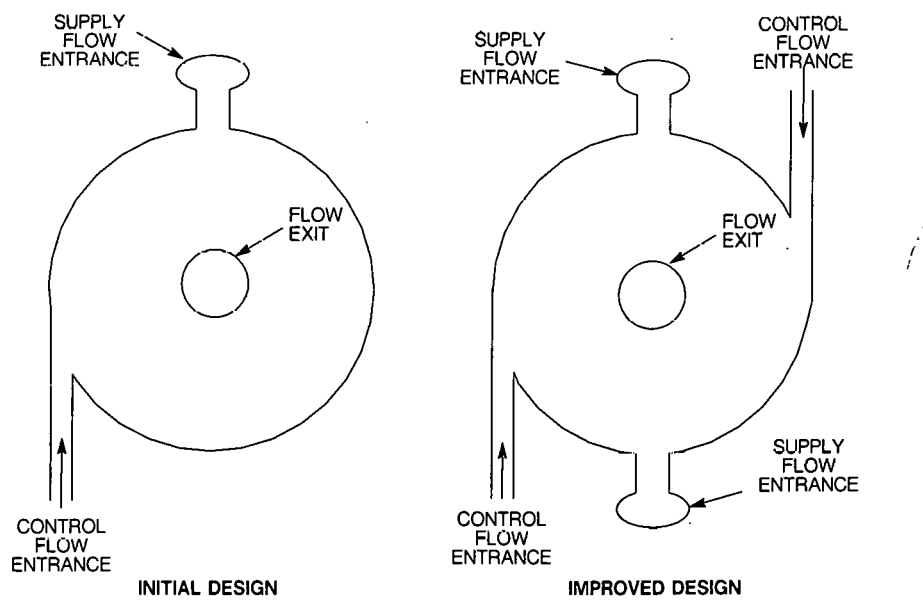



Figure 2. Initial and Improved Control Element Designs

6. RESULTS/ACCOMPLISHMENTS:

The major results and accomplishments for the "Control of the Pressure Letdown System" and "Ash Letdown Unit" tasks during the current fiscal year are included in this section.

CONTROL OF THE PRESSURE LETDOWN SYSTEM

Tests in the JPL Test Loop confirmed that control of liquid flow could be achieved using the initial control element design (one supply and one control port), but only with a very high control-to-supply flow pressure ratio, $P_c/P_s$. To overcome this problem, a modified control element was developed as described in Figure 2. Subsequent tests with water showed considerably improved performance with a turndown ratio, TR, of 2.82, achieved with $P_c/P_s = 1.28$. The modified control element was then subjected to a much more severe test in the 20-stage PLS at EF using a simulated SRC-II slurry consisting of 75 percent No. 2 Diesel fuel, 22 percent pulverized coal, and 3 percent n-Pentane, by weight. The results proved quite successful in that cutoff of the supply flow at 200 psig was achieved with $P_c/P_s = 1.25$ and TR = 3.09.

ASH LETDOWN UNIT

Based on proof-of-concept testing in a Plexiglas model, a bench scale unit was designed and constructed. A schematic drawing of this device is shown in Figure 3. The supply tank was made of 2-in. pipe and was about 24 in. long. A 5-stage PLS, preceded by a vortex control element with one supply and one control port, was installed to letdown the pressure in the device to atmospheric conditions. Tests were carried out using sand and nitrogen to simulate the ash and gas in the reactor, and air as the control fluid. Experiments were conducted at supply pressures up to 300 psig and sand temperatures up to 740 F. The results showed that cutoff of the supply flow could be achieved with a maximum value of $P_c/P_s = 1.25$. There was some erosion in the control element resulting from the interaction of the control flow and the sand in the control element. However, it is felt that a 2-control, 2-supply port control element should be able to overcome this problem.

7. FUTURE WORK:

The results of the threshold erosion, control of the letdown device, and ash letdown unit studies are currently being summarized in an intermediate final report. The final task of this project will then be concerned with the transfer of letdown device technology to industry for commercialization. This phase of the work, which will begin about July 1987, will include a PLS industrial survey and industrial testing.

8. REFERENCES:

Collins, E.R., Jr., and Suitor, J.W., Coal Slurry Letdown Valve -- Concept Test Phase, Publication D-1367, Jet Propulsion Laboratory, California Institute of Technology, Pasadena, California, January 1984.

Kendall, J., U. S. Patent No. 4,418,722, National Aeronautics and Space Administration, December 6, 1983.

Marner, W.J., Collins, E.R., and Rohatgi, N.K., Coal Slurry Letdown Valve, Proceedings of the Instrumentation, Components, and Materials Contractors Meeting, Hobday, J.M. (Editor), DOE/METC-86-6069, Morgantown Energy Technology Center, Morgantown, WV, January 1987, pp. 146-155.

Suitor, J.W., Collins, E.R., Jr., Glazer, C.R., and Dubis, D., The Development of a Coal Slurry Letdown Valve, Presented at the ASME-ASCE Joint Applied Mechanics Conference, Albuquerque, NM, June 1985.

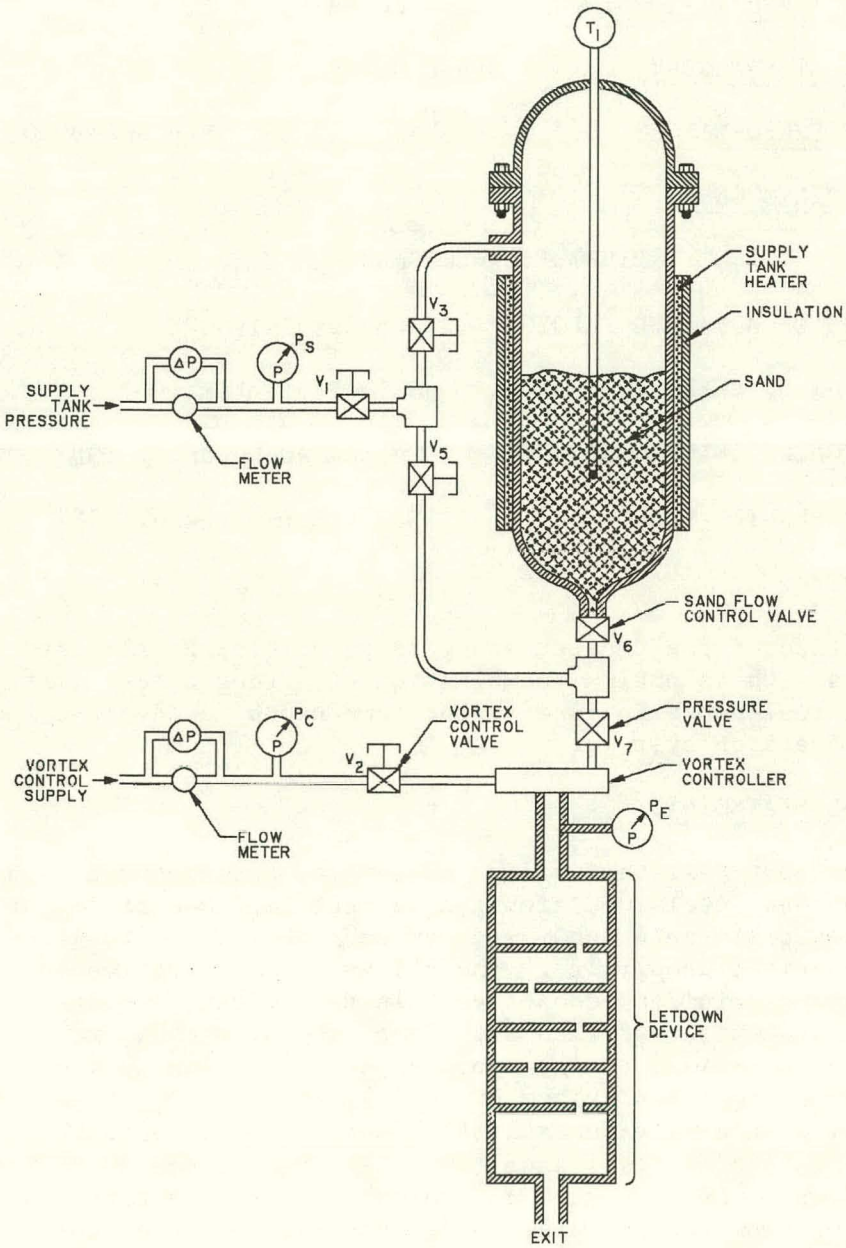



Figure 3. Schematic of Ash Letdown Test Unit

DEVELOPMENT OF IRON ALUMINIDES FOR COAL GASIFICATION SYSTEMS

1. FTPA NUMBER: 00218

CONTRACTOR: Martin Marietta Energy Systems, Inc.
Oak Ridge National Laboratory
P. O. Box X
Oak Ridge, TN 37831

CONTRACTOR PROGRAM MANAGER: Roddie R. Judkins

PRINCIPAL INVESTIGATORS: C. G. McKamey and C. T. Liu

METC PROJECT MANAGER: David Dubis

PERIOD OF PERFORMANCE: October 1, 1985 — September 30, 1989

2. SCHEDULE/MILESTONES:

1987 Program Schedule

| | |
|---|---|
| EVALUATION OF ADVANCED ALLOYS | January—July 1987 |
| FABRICATION OF SELECTED SHAPES | July—September 1987 |
| PREPARATION OF INTERIM REPORT | September—December 1987 |
| SELECT COMMERCIAL VENDOR | September—December 1987 |

3. OBJECTIVES:

The objective of the present study is to develop $Fe_3Al$-based aluminides with an optimum combination of strength, ductility, and corrosion resistance for use as hot components in advanced fossil energy conversion systems.

4. BACKGROUND STATEMENT:

Currently, heat-resistant alloys are either nickel-based or high-nickel-content steels containing a delicate balance of one or more of the strategic elements such as chromium, cobalt, and tungsten to produce the desired properties. The alloys under investigation in this study (iron aluminides) do not contain significant amounts of strategic elements, and they also have properties that make them attractive for fossil energy applications. Because of their ability to form a protective aluminum oxide film at very low oxygen partial pressures, iron aluminides near the $Fe_3Al$ composition exhibit excellent corrosion resistance (including resistance to sulfidation) at high-temperatures in such environments. Other advantages are high strength at room temperature, lower density, and lower cost. Although

the usefulness of the binary alloys is limited by low room-temperature ductility (1-2%) and poor hot strength above 550°C, studies of several advanced (with minor alloy additions) iron-aluminum alloys based on the $Fe_3Al$ composition indicate dramatic improvements in properties (McKamey and Liu 1986, McKamey et al. 1987). This report describes recent progress in characterizing the effects of additions of other elements (<10 at. %) on the metallurgical and mechanical properties of our selected base alloy, Fe-28 at. % Al.

5. PROJECT DESCRIPTION:

Alloys of the desired compositions were prepared by standard melting, casting, and rolling techniques. Specimens were prepared for tensile, creep, oxidation resistance, and weldability tests. Standard test procedures were used to confirm the acceptability of these alloys for their intended application.

6. RESULTS/ACCOMPLISHMENTS:

From our study of the properties of Fe-Al binary alloys with compositions between 24 and 30 at. % Al (McKamey and Liu 1986, McKamey et al. 1987), we have chosen the Fe-28 at. % Al alloy as our base material for further development. Table 1 lists the alloys which are presently being studied.

Table 1. Alloys Presently Being Studied

| Alloy designation FA- | $TiB_2$ added[a] | Alloying element |
|---|---|---|
| 37,61 | Y,N | Base alloys |
| 52,53,56 | Y,Y,Y | Mo |
| 62 | N | Mo |
| 69,70 | Y,Y | Mn |
| 71 | N | Mn |
| 63,64,65 | Y,Y,Y | Cr |
| 77,72,78 | N,N,N | Cr |
| 59,66 | Y,Y | Nb |
| 79 | N | Nb |
| 57,58 | Y,Y | Ce |
| 67,68 | Y,Y | Y |
| 60 | Y | B |
| 54 | Y | Zr |
| 55 | Y | Ti |
| 73,74,75 | N,N,N | Combinations of |
| 80,81,82[b] | N,N,N | the above |
| 83 | N | " |

[a] $TiB_2$ was added to some alloys as precipitates to refine grain size (Y=yes, N=no).

[b] Aluminum concentration was varied from 24 to 28%.

## TENSILE PROPERTIES

Figures 1(a) and (b) show the room temperature yield strength ($\sigma_y$) and ductility for the iron-aluminum alloys tested. The alloy designated FA-37 is the base alloy, with 1 at. % $TiB_2$ (0.5 wt %) added for grain refinement. Compared to this base alloy, improvements in tensile properties were seen in those alloys with additions of Mo, Cr, or Nb, and in alloys containing combinations of these and other elements. Some of the alloys were comparable to or stronger than modified 9Cr-1Mo alloy. In terms of room temperature ductility, only alloys containing chromium showed real promise. With the appropriate heat treatment, the elongations of two of the chromium-containing alloys (FA-77 and -72) were above 10%.

Figure 1(c) shows $\sigma_y$ for alloys tested at 600°C. Values in excess of 300 MPa were seen for all alloys tested, with a maximum of 516 MPa for a niobium-containing alloy (FA-66). These strengths are much higher than either the modified 9Cr-1Mo alloy or type 316 stainless steel. Elongations at this temperature were in excess of 30% for most of the alloys.

## CREEP PROPERTIES

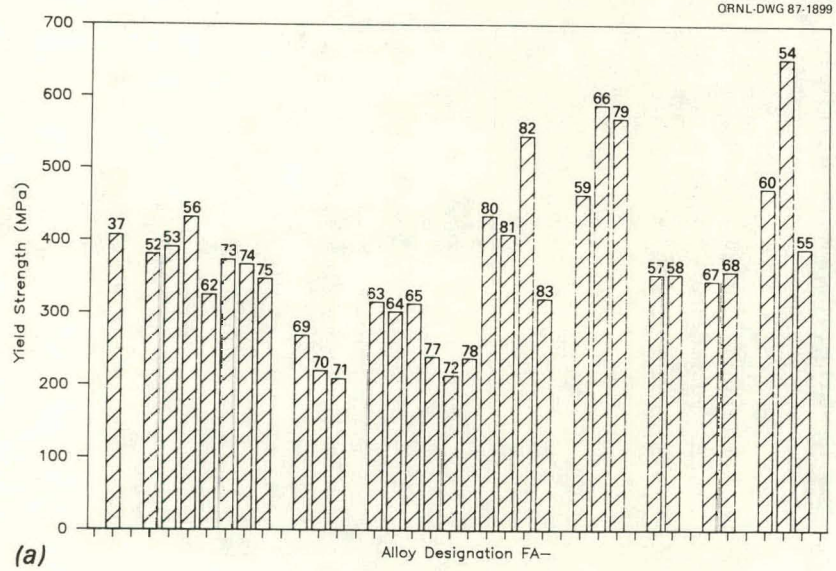
In preliminary studies of the creep resistance the base alloy was determined to be weak; however, creep properties can be improved by alloying additions. The creep resistance of one of the alloys (FA-73) was found to be comparable to type 304 austenitic stainless steel at the same test condition. All the alloys showed excellent ductilities (>20%) in creep.

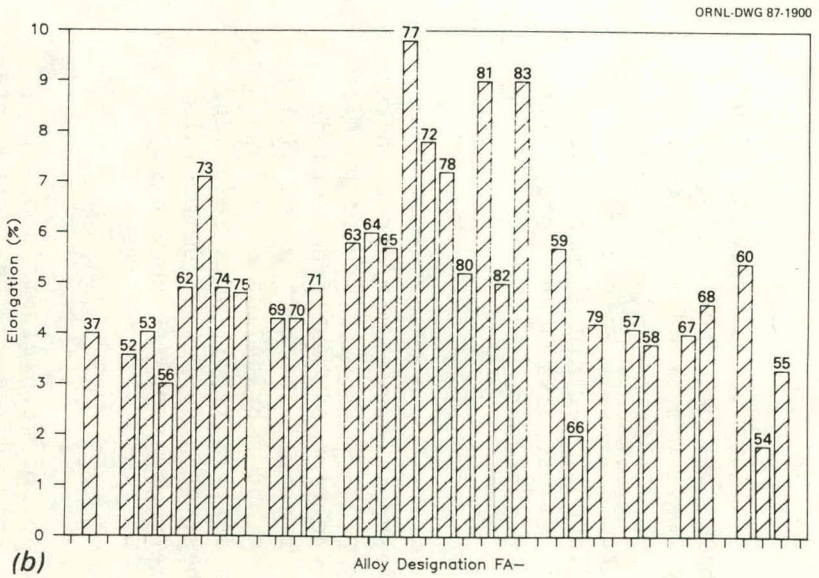
## OXIDATION STUDIES

Studies are just beginning of the oxidation resistance of some of the more promising alloys (FA-72, -79, -81, and -83). After 500 h, all of these alloys showed excellent resistance to oxidation, with no alloy gaining more than 7 $mg/cm^2$. Although some spalling of the $Al_2O_3$ film was observed from alloy FA-72, this problem was corrected by alloying additions. Alloy FA-81 exhibits the best oxidation resistance ($<1$ $mg/cm^2$).

## WELDABILITY

The weldability has been studied using both EB and GTA welding. The addition of a $TiB_2$ dispersion, which was originally added for grain refinement, was found to be deleterious to the weldability, producing hot cracks along the fusion line (McKamey et al. 1987). The weldability is improved by additions of chromium or niobium. Thus, our current weldability studies include alloys with chromium or niobium additions but without the $TiB_2$ dispersions.



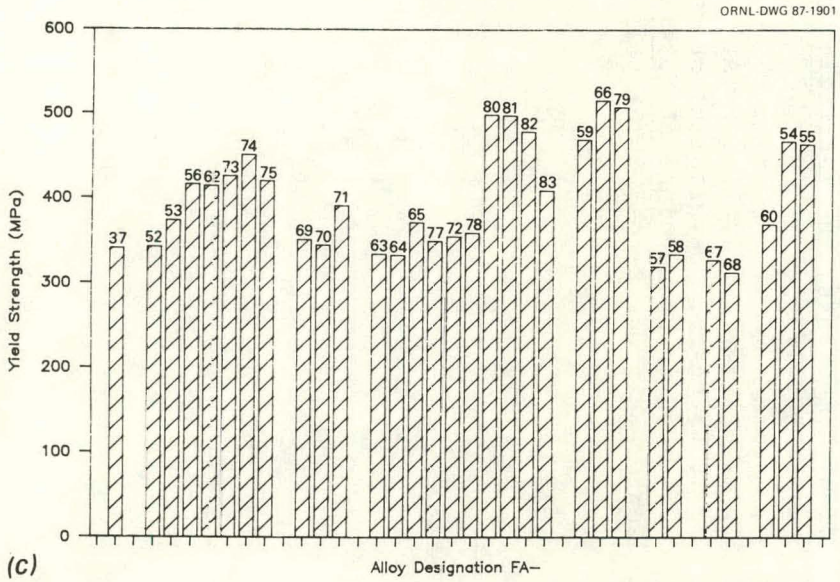




Figure 1. Tensile Properties of Iron-Aluminum Alloys. (a) Room Temperature Yield Strength. (b) Room Temperature Ductility. (c) Yield Strength at 600°C.

ACCOMPLISHMENTS

We have produced ternary and quaternary alloys based on $Fe_3Al$ with molybdenum, manganese, chromium, niobium, cerium, yttrium, boron, zirconium, and titanium. These alloys were prepared by conventional (and less costly) melting, casting, and rolling techniques. These alloys have excellent corrosion resistance in both oxidizing and sulfidizing atmospheres. Minor additions of certain elements were shown to substantially improve mechanical properties and weldability without measurably reducing oxidation resistance.

7. FUTURE WORK:

Future work will include producing advanced iron aluminides with compositions based on the results of the present study. The properties of these alloys will be studied as a function of heat treatment in order to find the optimum condition for each. The best alloy will be used for heat-to-heat variation studies and fabrication of alloys with selected shapes. In December 1987 an interim report will be issued describing the results of our small heat studies and a commercial vendor will be engaged to prepare a large heat of the best alloy.

8. REFERENCES:

C. G. McKamey and C. T. Liu, "Development of Iron Aluminides for Gasification Systems," pp. 207–217 in Proceedings of the Instrumentation, Components, and Materials Contractors Meeting, DOE/METC-86/6069 (September 1986).

C. G. McKamey, C. T. Liu, S. A. David, J. A. Horton, and J. V. Cathcart, "Development of $Fe_3Al$-Based Aluminides," to be published in Proceedings of Fossil Energy Materials Program Conference, Oak Ridge, TN, May 19-21, 1987.

PROTECTIVE COATINGS AND CLADDINGS: APPLICATION/EVALUATION

1. CONTRACT NUMBER: FTP/A 49678

CONTRACTOR: Argonne National Laboratory
9700 South Cass Avenue
Argonne, IL 60439
(312) 972-2000

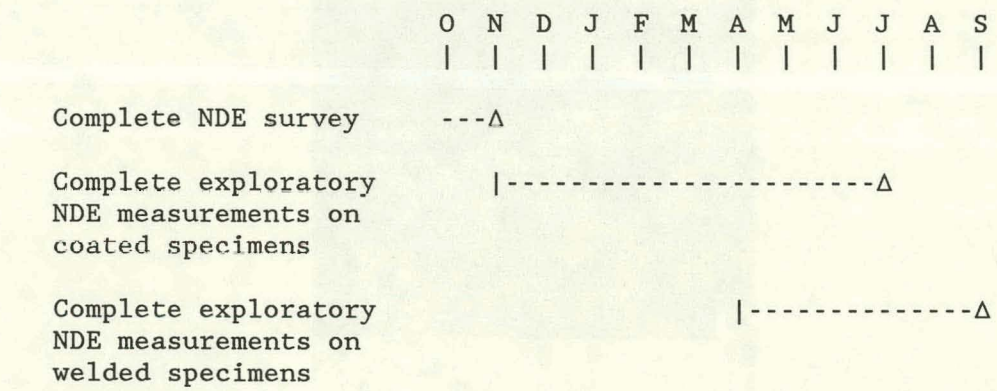
CONTRACTOR PROJECT MANAGER: W. A. Ellingson

PRINCIPAL INVESTIGATORS: W. A. Ellingson
N. Gopalsami
D. Y. Wang

METC PROJECT MANAGER: D. R. Dubis

PERIOD OF PERFORMANCE: October 1, 1981 - open

2. SCHEDULE/MILESTONES: Nondestructive Evaluation




3. OBJECTIVES:

The primary objective of this program is to develop corrosion-resistant coatings on low-alloy steels for application in downstream waste heat recovery systems of coal gasifiers. A further objective is to develop nondestructive evaluation (NDE) methods for inspection of the coatings that are developed in this program. The NDE work should play an integral role in formulating the eventual coating specifications.

4. BACKGROUND STATEMENT:

The previous work on this program[1] included microstructural examination of as-received coated materials and the investigation of the corrosion behavior of these materials in two different gaseous environments under both isothermal and thermal-cycling conditions. One of the conclusions/recommendations arising from this work was that methods must be

developed to characterize coating defects and to establish a relationship between the nature of the defects (e.g., type, size, shape and orientation) and the observed corrosion behavior. Consequently, efforts in this fiscal year were directed toward development of NDE techniques for coatings.

5. PROJECT DESCRIPTION:

The NDE part of this project consists of (i) determining the NDE requirements, (ii) reviewing potential NDE techniques in the literature, and (iii) testing the performance of selected techniques. The nature and size of defects that one must be able to characterize in pack-diffusion coatings by NDE techniques can be seen from micrographs of coated specimens. Figure 1, for example, shows a cross section of an as-received aluminized carbon steel specimen and the corresponding Al concentration profile.[1] The presence of discrete Al oxide particles and oxide colonies has been observed in the outer Al-rich region of several coatings, along with fine cracks extending mainly perpendicularly from the surface.

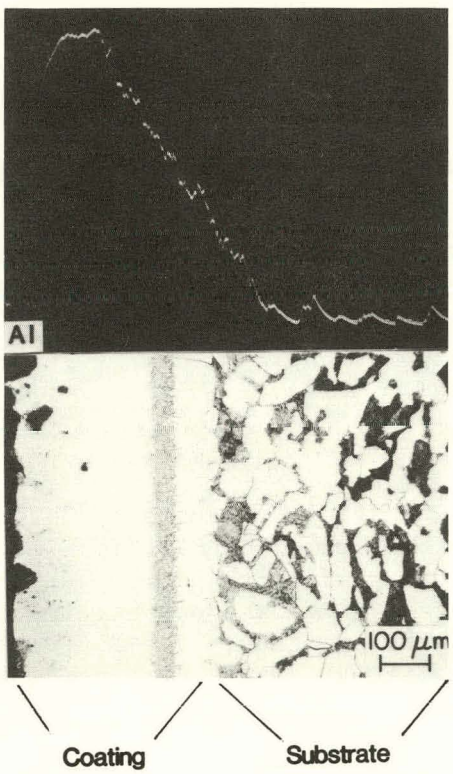



Fig. 1. Cross Section of an As-received Aluminized Carbon Steel Specimen Showing Internal Oxide Particles, Acicular (Fe,Al) Carbide Phase, and Al Concentration Profile. From Ref. 1.

The above and other microstructural observations suggest that an NDE technique for coatings should ideally be capable of detecting fine cracks, inclusions, voids, and Al/Cr concentration profiles. The defect sizes are on the order of tens of micrometers, and therefore require a high spatial resolution. The NDE system must be adaptable to complex (particularly tubular) surfaces and varying surface conditions (a coating surface roughness of up to several tens of micrometers is estimated from visual examination).

6. RESULTS/ACCOMPLISHMENTS:

NDE techniques that hold promise for the present application are reviewed, followed by a discussion of preliminary experimental results on a selected technique.

THERMAL-WAVE IMAGING

Thermal-wave imaging is receiving increased attention as a technique for NDE of surface and subsurface features of opaque solids.[2,3] In this technique, an intensity-modulated, finely focused laser or particle (electron or ion) beam is used to produce a periodic, localized heating in the specimen. This periodic localized heating generates thermal waves, which propagate from the heated region. In the same way as conventional waves are reflected and scattered at discontinuities, thermal waves are reflected and scattered by surface and subsurface thermal features. The reflected or scattered thermal waves may be detected by a variety of means: optical beam deflection, reflective optical beam deflection, photothermal radiometry, piezoelectric detection, and gas-cell detection.

Thermal-wave imaging is capable of mapping surface and subsurface features with micron-scale resolution. With a wide range of sources and detection methods available, it is possible to image most types of defects. The imaging system can be totally noncontacting and can be adapted to complex surfaces. A major limitation of current thermal-wave imaging systems appears to be the slow speed of imaging. More theoretical development is needed to permit quantitative interpretation of thermal-wave imaging features.

SCANNING ACOUSTIC MICROSCOPY

The scanning acoustic microscope (SAM) is becoming increasingly important in materials research because it offers the possibility of imaging the structural features of materials with high spatial resolution.[4,5] In a reflection-mode SAM, which is appropriate for the present application, a transducer on the top of an acoustic lens launches a pulsed ultrasonic beam and the lens then focuses this beam into a diffraction-limited spot on or below the object surface. The geometry of the lens system is such that it generates Rayleigh waves on the object surface and the leaky Rayleigh waves carrying the object-related information are mode converted and reflected back to the same lens system.

A reasonable imaging speed is possible with the SAM (one commercial vendor quotes approximately 10 seconds per image). The variation of transducer output signal V with respect to the distance z of the object surface from the focal plane, called the V(z) curve, may bear some relevance to the coating composition of the outer layer. However, features lying deep inside the sample are not imaged with adequate sensitivity and resolution. Also, surface roughness and complex shape may affect the output voltage because of their varying reflection characteristics.

## BACKSCATTERED SURFACE WAVES

Like the SAM method, the backscattered surface-wave technique employs leaky Rayleigh waves for imaging near-surface flaws in materials.[6] A focused transducer produces a pulse of longitudinal waves focused at the water-sample interface at an average angle of incidence near the Rayleigh critical angle. A pulse of propagating Rayleigh waves is thereby generated in a small volume below the focal spot. The surface waves, when incident on a flaw near the focal spot, are reflected or backscattered. The backscattered pulse carrying the flaw information, because of its leaky nature, will be received by the transducer. A delay time-gate is used to image a narrow region/volume near the focal spot.

This method may be well suited for detecting a vertical surface-breaking crack because of the normal incidence of the waves on the crack. It is also suited for fast imaging of large inclusions and voids near the surface. The resolution and sensitivity afforded by this method are generally low, compared to SAM or thermal-wave imaging. Surface roughness may be a problem since the coupling of energy to surface waves will be affected by surface scattering.

## EXPERIMENTAL INVESTIGATION

Based on the review of potential applicability of the various techniques and the availability of experimental facilities, backscattered surface waves and thermal-wave imaging were chosen for experimentation. Preliminary experiments on the use of backscattered surface waves were conducted with a simultaneously aluminized/chromized sample of tubular geometry and a 25-MHz focused transducer. A rectangular slot 70 $\mu$m wide, 8 mm long, and 800 $\mu$m deep at the center was made on the sample surface in the transverse direction, and ultrasonic scans were made in the axial direction (perpendicular to the slot orientation). Distinct surface wave echoes were observed when the ultrasonic beam approached the slot as well as the edge of the sample. The peak amplitude of the signal from a narrow-time gate set behind the direct backscattered signal with a delay of about 1 $\mu$s was digitized and mapped with respect to x-y movements. Figure 2 gives such a digitized image with a resolution of 100 $\mu$m per pixel; both the slot and the end of the sample are seen clearly. The analysis of the data is continuing in an effort to correlate other observable image features with the coating nonuniformities.

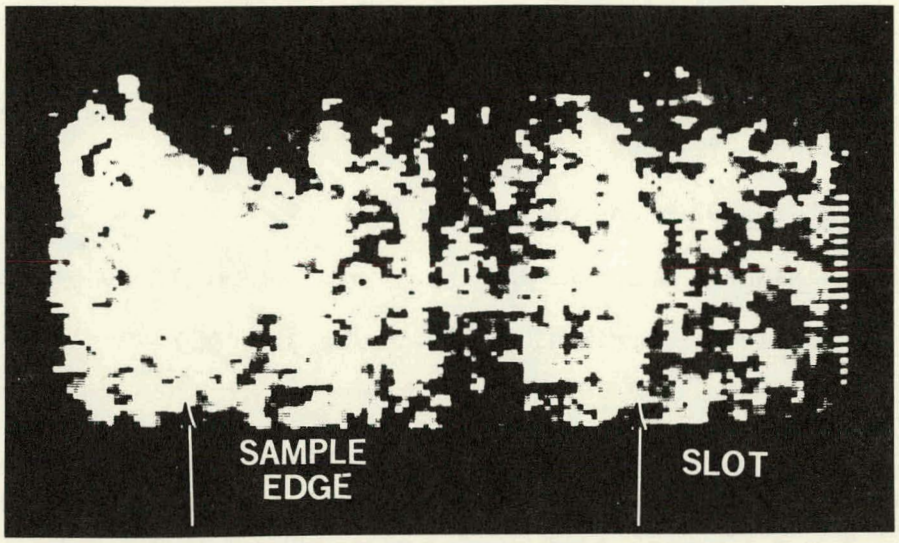



Fig. 2. Backscattered Surface-Wave Image of a Slot in an Aluminized/ Chromized Sample.

## 7. EVALUATION OF POTENTIAL FUTURE PLANS

Further testing of the backscattered-surface-wave technique will be carried out with an emphasis on determining the type and size of coating defects that can be imaged. Preliminary experiments on thermal-wave imaging of coated samples will be conducted at outside facility (in collaboration with Dr. Doug Rose, U.S. Army Tank-Automotive Command, Warren, MI). In close coordination with coating vendors, coatings with well-defined defects will be produced to enable efficient testing of the NDE techniques.

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[2]R. L. Thomas, L. D. Favro, and P. K. Kuo, Thermal-Wave Imaging for Nondestructive Evaluation, Can. J. Phys., Vol. 64, pp. 1234-1237 (1986).

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[4]C. F. Quate, A. Atalar, and H. K. Wickramasinghe, Acoustic Microscopy with Mechanical Scanning, Proc. IEEE, Vol. 67, pp. 1092-1114 (1979).

[5]J. M. R. Weaver et al., Applications of the Scanning Reflection Acoustic Microscope to the Study of Materials Science, IEEE Trans. Sonics Ultrason., Vol. SU-32, pp. 302-312 (1985).

[6]R. A. Roberts, Focused Ultrasonic Backscatter Technique for Near-Surface Flaw Detection in Structural Ceramics, presented at the 16th Symposium on Nondestructive Evaluation, San Antonio, Texas, April 21-23, 1987.

## ASH AND SLAG CHARACTERIZATION

1. CONTRACT NUMBER: DE-FC21-86MC10637

CONTRACTOR: University of North Dakota
Energy Research Center
Box 8213, University Station
Grand Forks, ND 58202
(701) 777-5000

PRINCIPAL INVESTIGATOR: Sharon Falcone

METC PROJECT MANAGER: Dr. H.L. Lai

PERIOD OF PERFORMANCE: April 1, 1986 - March 31, 1989

2. SCHEDULE/MILESTONES:

The schedule of planned milestones for the contract year April 1986 through March 1987 is shown in Table 1 according to Tasks A through E.

3. OBJECTIVES:

The objective of this ongoing research project at the University of North Dakota Energy Research Center (UNDERC) is the development of a unified picture of chemical and mineralogical changes occurring during ashing and slagging of low- and high-rank coals and the associated changes in certain slag physical properties during gasification. Specific tasks to be addressed include: 1) the mechanisms operating on the inorganic portion of the coal resulting in mineral transformations affecting ash and slag formation, 2) the nature of the volatile inorganic species released from the coal, and 3) the formation of slag and its composition and physical behavior (i.e. viscosity and surface tension) as related to slag flow and ash agglomeration.

The stated project objectives directly support and complement the current gasification research as summarized at the Sixth Annual Gasification Project Contractors' Meeting. The specific areas of operational problems to benefit from this research include slag flow maintenance, ash agglomeration, and the nature of the inorganic volatiles generated during heating.

4. BACKGROUND STATEMENT:

The initial phase of the research project was the establishment of a viscosity data base and an understanding of the mechanisms responsible for the interaction of specific inorganic components present in low- and high-rank coals. The ash and the slag phases produced at high temperatures were studied to determine their composition and physical behavior (i.e. viscosity and surface tension). The mechanisms forming new inorganic species during the ashing of high-rank coals are not entirely the same in coals of lower rank. The increased mineral and organically-bound cation content of low-rank coals can affect the rates of gasification, as well as the amount, composition, and physical character of the gasification ash or

## TABLE 1

SCHEDULE FOR PLANNED MILESTONES

A. Characterization and Identification of Mineral Transformations During Gasification and Their Effects on Gasification Rates

- a.1 Ashing of five low-rank coals under reducing conditions
- a.2 Identification of mineral transformations and compositional changes

B. Vaporization of Inorganics During the Gasification Process

- b.1 Evaluation of cooled-probe
- b.2 Preliminary theoretical phase diagram work using modified SOLGASMIX
- b.3 Vaporization test runs on five ash and char samples

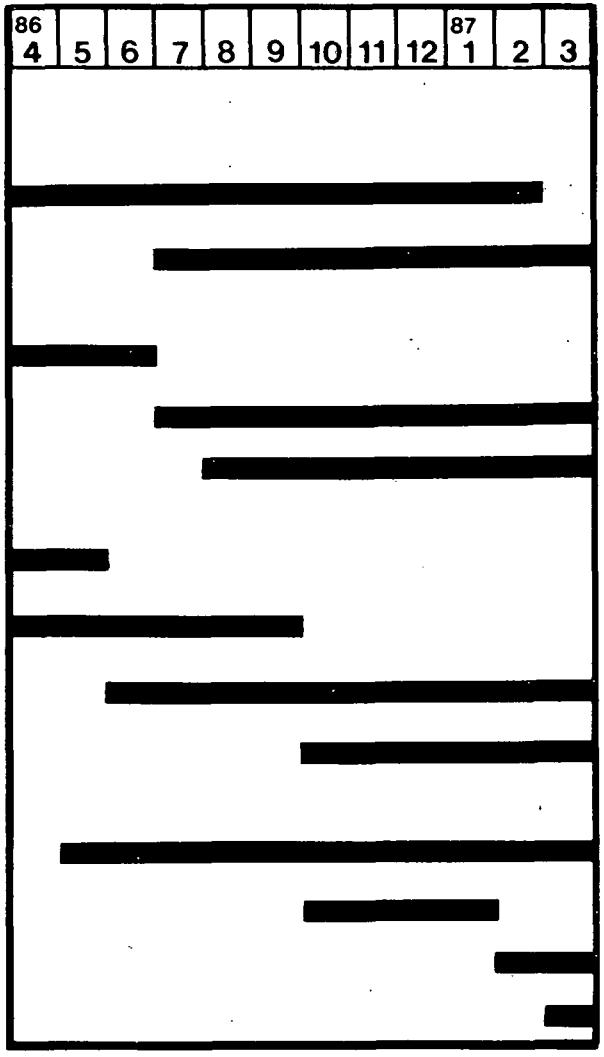
C. Slag Viscosity Behavior Under Gasification Conditions

- c.1 Viscometer Recalibration
- c.2 Set up computer data base for existing viscosity and compositional data
- c.3 Conduct five viscosity tests under gasification atmospheres and analyze samples
- c.4 Application of viscosity data to modified Urbain equation

D. Slag Surface Tension Studies Under Gasification Conditions

- d.1 Completion of three surface tension runs of coal slags on vitreous carbon
- d.2 Preliminary investigation of alternate methods for determining surface tension of slags
- d.3 Correlation of surface tension and composition

E. Annual Report for Tasks A through D



slag by-products. Therefore, research into this area, is warranted, especially as low-rank coals are becoming increasingly important in fuel conversion processes as in the case of the first commercial gasification plant at Beulah, North Dakota.

Another area of concern is ash agglomeration in dry bottom systems. With agglomeration, clinkers of unacceptable size for proper removal through the ash grate may form or adhere to the side wall corroding the wall refractory. Four mechanisms of sintering by which particles bond to one another outlined by Kuczynski (1) are viscous flow, vapor condensation, diffusion, and surface tension. The principal physical parameters of concern in this study are surface tension and viscosity. In both cases, surface tension and viscosity are related through the Fenkel sintering model (2):

$$x^2 = \frac{3r\gamma t}{2\eta} \qquad (1)$$

where; $x$ is the radius of the interface assumed to be circular, $r$ is the radius of the spherical particles, $\gamma$ is the surface tension, $t$ is time, and $\eta$ is viscosity.

With increasing temperature both viscosity and surface tension decrease while sintering increases (Figure 1). Based on the Frenkel equation it is obvious that the change in surface tension relative to viscosity determines the potential for sintering or agglomeration of a particular ash. In turn, changes in ash composition and atmosphere will effect both of these physical properties thereby changing the ash agglomeration and slag flow behavior. While these relationships were developed for combustion environments their application to gasification environments is reasonable.

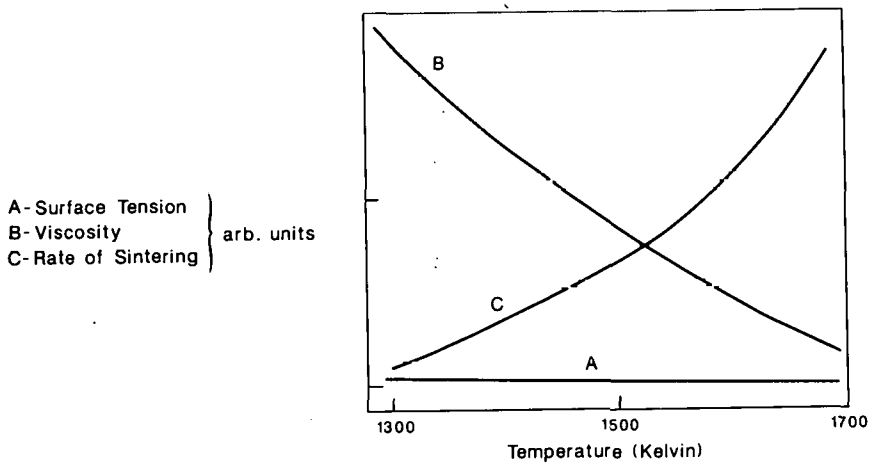



Figure 1. Relation of Viscosity, Surface Tension and Sintering to Temperature (Frenkel Equation).

Another aspect of this project is the development of empirical equations which enable the prediction of slag viscosity as a function of composition. The viscosity of a slag is directly influenced by its composition; therefore, the difference in the range and occurrence of inorganics of various coal ranks likely precludes the development of a universal viscosity equation. To evaluate equations useful for low- and high-rank coal slags, a data base of experimentally derived viscosities related to low- and high-rank coals, synthetic stags, ceramics, and glasses was also established.

5. PROJECT DESCRIPTION:

This project consists of two parts. The first is a study of the effects of ashing and slagging conditions on the mineralogical and bulk chemical compositions of ashes or slags derived from a series of low- to high-rank coals. The second, is a study of surface tension and viscosity of coal slags under reducing and oxidizing conditions as they relate to composition and temperature.

Task A is the characterization and identification of mechanisms responsible for mineral transformations during gasification. This work will initially involve generating ashes in both oxidizing and reducing atmospheres up to 1000°C and working with pilot-scale fluidized bed gasifier ashes and commercially-generated ash.

Task B involves the study of vaporization of inorganics during gasification. Both theoretical and experimental work will be conducted. SOLGASMIX (3), a computer software program, will be used to determine those thermodynamically favored phases present in different ashes and slags under various atmospheric and pressure conditions. Chars will also be produced using a pressure pyrolysis unit and analyzed for changes in inorganic composition with changes in pressure and the addition of steam. Chars are produced at temperatures up to 850°C at 400-450 psi.

Task C evaluates slag viscosity behavior under reducing and oxidizing conditions as related to gasifier operability. The specific areas of application are in ash agglomeration and slag flow maintenance. Studies will concentrate on developing a viscosity data base, evaluating predictive viscosity equations of the Newtonian flow regime, and relating slag composition to viscosity and surface tension as a reflection of sintering potential and flow maintenance. Comparisons of viscosity data obtained using low- and high-rank coal slags under oxidizing and reducing conditions with and without steam will be made at temperatures up to 1500°C.

Task D investigates slag surface tension as it relates to composition and viscosity. The surface tension of slags on an inert substrate (vitreous carbon) under reducing and oxidizing atmospheres with and without steam are studied. The sessile drop technique is used to measure the slag bead geometry at temperatures up to 1500°C. A technique developed by Maze and Burnet (4) is used to actually calculate the slag surface tension.

6. RESULTS/ACCOMPLISHMENTS:

The key accomplishments over the last year have been in the area of viscosity and surface tension studies of bulk low- and high-rank coal slags. The specific accomplishments deal with the preparation of a viscosity data base, the evaluation of predictive viscosity equations, comparison of commercially-generated agglomerated versus non-agglomerated ash samples, the effect of atmosphere on viscosity and surface tension, and the relation of surface tension, slag composition, and viscosity to sintering.

VISCOSITY DATA BASE

The compiled data base includes data from a total of 361 low- and high-rank coal slags, synthetic slags, and glasses run under oxidizing and reducing atmospheres. An additional twenty-four coal slags evaluated during the last year at UNDERC have also been added to the data base. This data base will serve to statistically evaluate various predictive equations.

EVALUATION OF PREDICTIVE VISCOSITY EQUATIONS

The Urbain (5) and the modified Urbain equations (6) were used to calculate the viscosities of thirty-one coal slags ranging in rank from lignite to bituminous. Each coal slag had experimentally measured viscosities for a range of temperatures under reducing and oxidizing conditions. Twenty of the thirty-one slag viscosity curves were better predicted by the Urbain equation than the modified Urbain equation (VISCALRE, VISCALOX). At this time the statistical significance of the measured versus calculated viscosities for each equation has not been determined but is slated for Year 2.

VISCOSITY STUDY OF COMMERCIALLY-GENERATED AGGLOMERATED VERSYS NON-AGGLOMERATED ASH SAMPLES (GREAT PLAINS GASIFICATION PROJECT)

A comparison of two commercially-generated ashes, one agglomerating and one non-agglomerating, was made to better understand the relation of ash and slag chemistry to agglomeration potential. The two samples came from the Great Plains Gasification Project in North Dakota which uses lignite from the Freedom Mine in North Dakota. The one sample represents a non-agglomerated ash easily removed from the gasifier through the ash grate as it was designed. The other sample represents clinker of unacceptable size for proper removal from the system. These clinkers may slag to the point of adhering to the wall refractory or may agglomerate and be too large to pass through the ash grate. Ash agglomeration periodically results in a reduction in load capacity.

The chemistries of the two samples reveal the clinker to contain less silicon dioxide but greater amounts of calcium oxide than the non-agglomerated ash. The differences in composition determines the potential of the ash to agglomerate in the gasifier system. By using the Urbain equation, the theoretical viscosity of the ash, if melted, an be

calculated. The viscosity values are approximations since the bulk composition is used to calculate the viscosities, however, a relative comparison of the viscosities can be made. The viscosities for both samples are shown in Figure 2. The calculated viscosity of the ash clinker is significantly lower than that of the ash. The presence of a substantial amount of an alkali (CaO) in the clinker is probably the cause for the reduced viscosities. In fact, studies of the Freedom Mine show the presence of a calcite seam associated with the coal. Within the context of the Raask sintering model (2), the results are consistent with the explanation that reduced viscosity results in increased sintering and agglomeration.

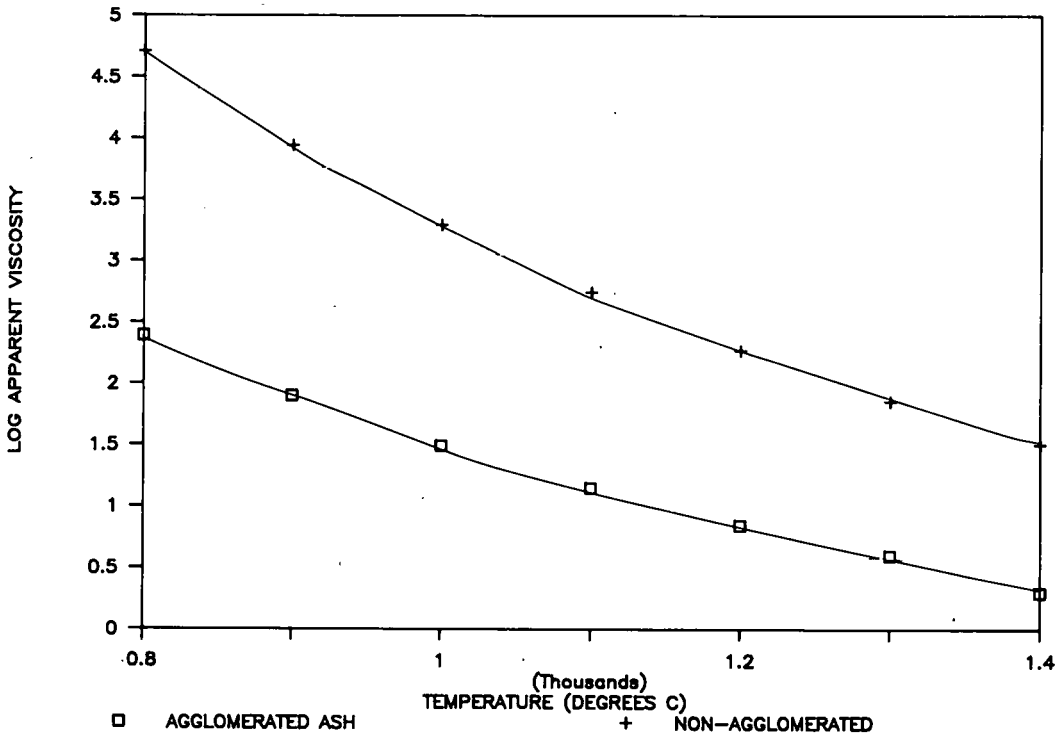



Figure 2. Calculated Viscosity Curves of Agglomerated and Non-Agglomerated Great Plains Gasifier Ash Slag.

## THE EFFECT OF ATMOSPHERE AND COMPOSITION ON VISCOSITY AND SURFACE TENSION, AND SINTERING

The concept of a sintering model in studying ash agglomeration is a useful tool in that it relates the physical properties of viscosity and surface tension. Viscosity is shown to be inversely proportional to sintering while surface tension is shown to be directly proportional to sintering. Both properties are effected by composition and, in turn, the composition effected by atmosphere. The results show that under a reducing atmosphere viscosity decreases while surface tension increases given a constant ash composition.

To verify that the surface tension of a slag is greater in a reducing atmosphere, a plot of temperature versus surface tension for four different coal slags in air (oxidizing), nitrogen, and eight percent hydrogen in nitrogen is shown in Figure 3. Given the above statement, it follows that the potential for sintering and or slag formation is greater under reducing conditions than oxidizing conditions.

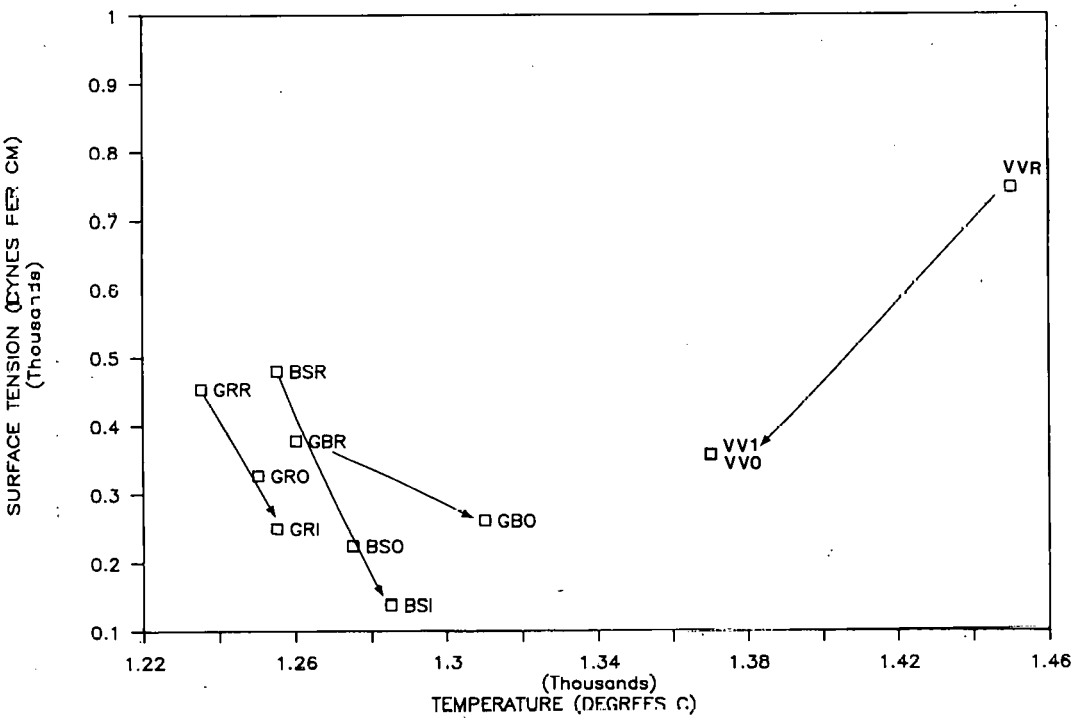



Figure 3. Temperature Versus Surface Tension (Measure) for Coal Slags Under Oxidizing Reducing and Inert Atmospheres.

In an effort to relate bulk composition to surface tension, a series of plots relating individual slag oxide content to slag surface tension were constructed. In Figure 4 the ratio of sil,icon dioxide to sodium oxide versus surface tension shows clustering of data points. Each data point shown is also labeled as to the tendency of the ash to sinter based on previous ash fouling work with that coal. Ashes which tend to agglomerate are designated with an "H" or "M" for high or moderate agglomerating tendency, respectively. Ashes which tend to have a low tendency to agglomerate or sinter are designated with a "L". In Figure 4 there is consistent clustering between those ashes which tend to have a lower tendency to sinter and those ashes which tend to sinter. Compared to the single component graphs where clustering was not apparent, the definite clustering of data points by graphing oxide ratios versus surface tension verify that a combination of elements are important in effecting surface tension. These results in combination with viscosity test results suggest the following:

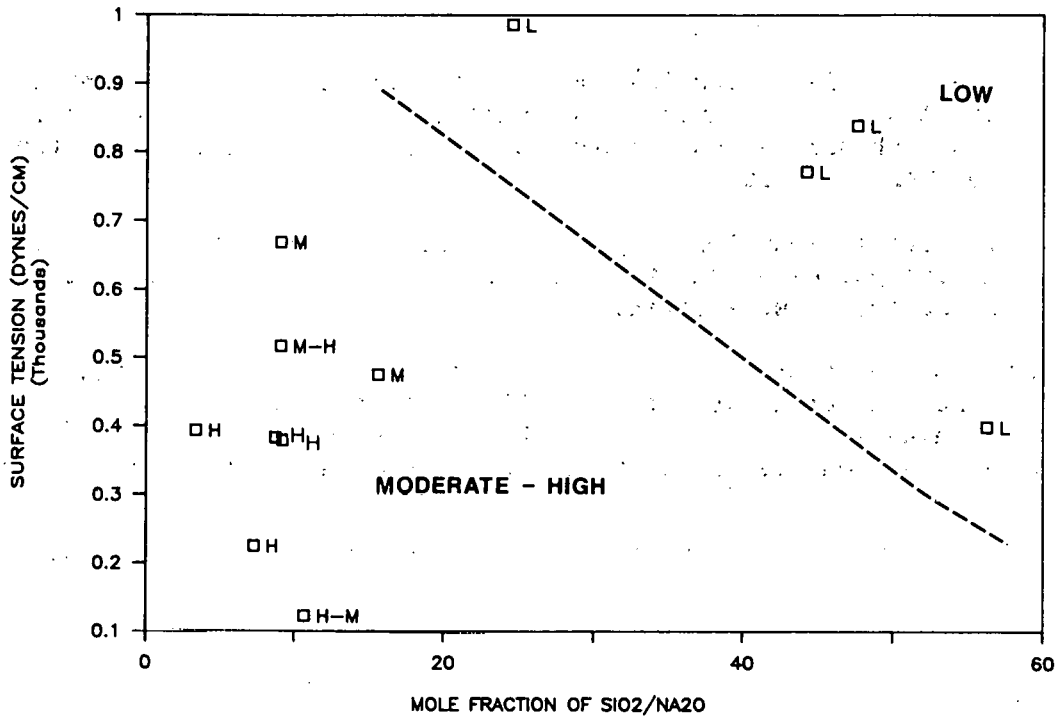



Figure 4. $SiO_2$:$Na_2O$ Ratio Versus Measure Surface Tension. (L = Low Agglomeration, M = Moderate Agglomeration, H = High Agglomeration).

- increased silicon dioxide content increases both the viscosity and surface tension of a slag.
- increased sodium oxide content (or total alkali content) decreases both the viscosity and surface tension of a slag.

Given the relation by Raask that surface tension is directly related to sintering while viscosity is inversely related, it is difficult to determine what the compositional effects are on sintering when both parameters are simultaneously increasing or decreasing. Both surface tension and viscosity decrease with temperature while the rate of sintering increases. According to Raask (2), the coefficient of surface tension is small and is proportional to the inverse of the square root of temperature. On the other hand, viscosity changes exponentially with temperature. Consequently, the rate of ash sintering will show an inverse relationship with viscosity and increase rapidly as the temperature of the coalescing particles is raised. So, if both temperature and composition change, then it is quite difficult to determine the relationship between them and viscosity and surface tension.

To better understand the relation of composition to surface tension and viscosity, combination of experimental surface tension data and calculated viscosity values were used to improve the clustering of data points. The following methodology was used:

- the particle radius (r) and time (t) variables in the Fenkel equation were assumed to be constant, therefore $x^2$ (the radius of the neck bridge between particles) is proportional to $\gamma/\eta$ (surface tension/viscosity).

- the Urbain equation was used to calculate the viscosity of the molten phases at the temperature at which the surface tension measurements were taken.

In Figure 5 a plot of the log 10 viscosity versus surface tension is shown. The clustering is not as distinct as in other plots, however, a trend is revealed which relates to the assumption listed above. The ratio of surface tension (measured) to viscosity (calculated) is related to

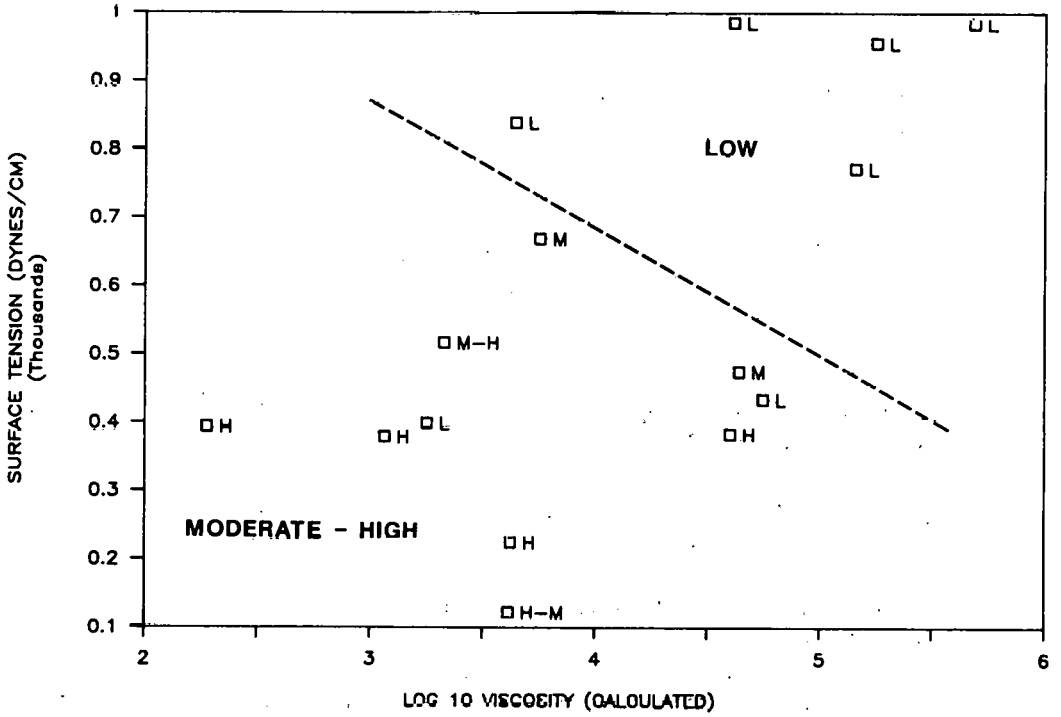



Figure 5. Log 10 Viscosity (Calculated) Versus Surface Tension (Measured). (L = Low Agglomeration, M = Moderate Agglomeration, H = High Agglomeration).

sintering ($x^2 \alpha \gamma/\eta$). Those ashes observed to have exhibited low sintering have surface tension to viscosity ratios of .024 or less. Those ashes displaying sintering or slagging at combustion temperatures have ratios on the order of 0.110 through 2.080. The results suggest:

- ashes which tend not to sinter or agglomerate from molten phases have higher viscosities relative to their surface tension at a given temperature, and

- ashes which tend to agglomerate form molten phases which have lower viscosities relative to their surface tension at a given temperature.

The mole fraction ratio of silicon dioxide to sodium oxide content versus viscosity (calculated) was plotted (Figure 6). The purpose of such a comparison was to tie a compositional parameter to viscosity via surface tension. The result reveals a much tighter clustering of ash types related to viscosity than surface tension. The results suggest that the viscosity factor is considerably more sensitive to compositional parameters (i.e. silicon dioxide and sodium oxide) than surface tension. Therefore one can conclude:

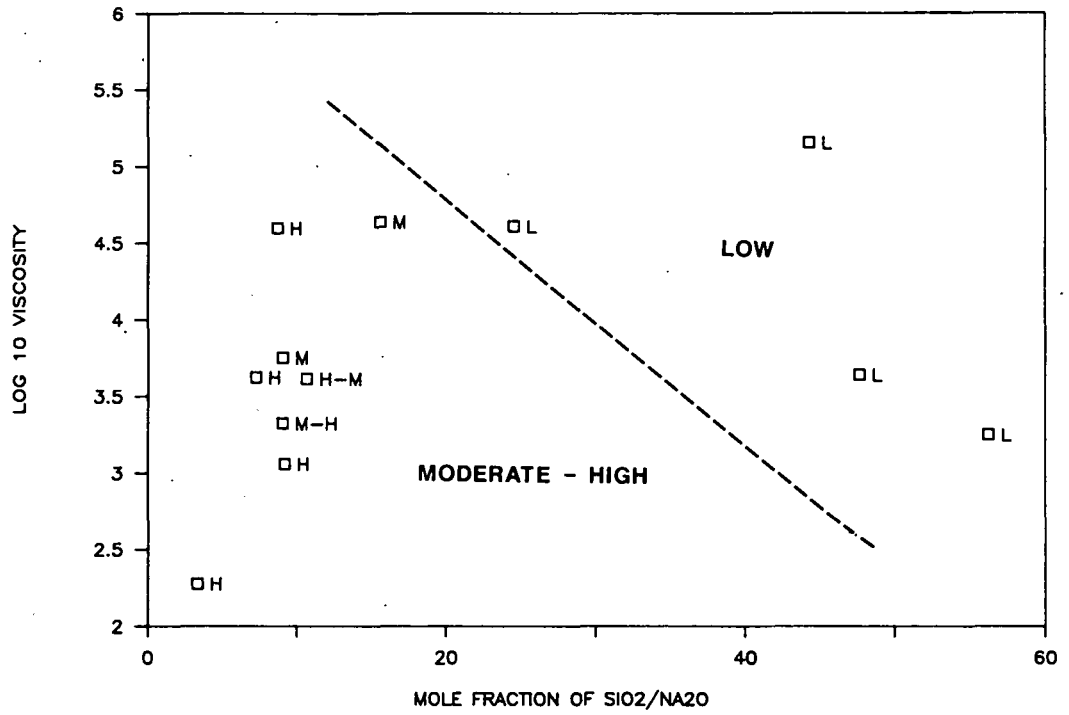



Figure 6. $SiO_2/Na_2O$ Versus Log 10 Viscosity (Calculated). (L = Low Agglomerating, M = Moderate Agglomerating, H = High Agglomerating).

- Even though surface tension is elevated by increased silicon dioxide content, ashes which have higher silicon dioxide to sodium oxide ratios at a given temperature tend to have higher viscosities relative to their surface tension. As a result these ashes tend to exhibit reduced sintering and agglomeration. While sodium oxide tends to decrease surface tension, it tends to decrease viscosity at a greater rate resulting in increased viscous flow sintering.

## 7. FUTURE WORK:

The future work plan of this project is to pursue the study of the effect of ash and slag chemical composition as it relates to ash agglomeration and slag flow behavior. Additional ashes to be used in the surface tension and viscosity studies will include the following: ashes generated in a drop-tube furnace, pilot-plant ashes generated in a fluidized bed gasifier, and ashes produced under static conditions with and without the addition of steam. Also included is the use of synthetic slags for modeling purposes.

The scale of the project to date has considered bulk ash and slag chemistry, bulk physical properties, and vaporization. In a study of slag flow initiation and maintenance this approach is quite acceptable. The use of a bulk slag approach is acceptable in the early stage of studying agglomeration phenomena, however, detailed particle to particle interactions must be investigated. The intent of the surface tension and viscosity work in Year 2 is to evaluate the detailed particle to particle aspects of sintering under various atmospheres. In this way the specific components which are more important in effecting various physical parameters can be isolated. Additional detailed work to expand the SOLGASMIX data base will be compared to actual experimental data to test the data base system. The viscosity data base will be used to statistically evaluate and refine predictive equations.

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# EXPERIMENTAL AND THEORETICAL INVESTIGATION OF THE FORMATION AND GROWTH OF ASH AGGLOMERATES

1. CONTRACT NUMBER: DE-AC21-87MC23283

CONTRACTOR: Institute of Gas Technology
3424 S. State Street
Chicago, IL 60616
(312) 567-3751

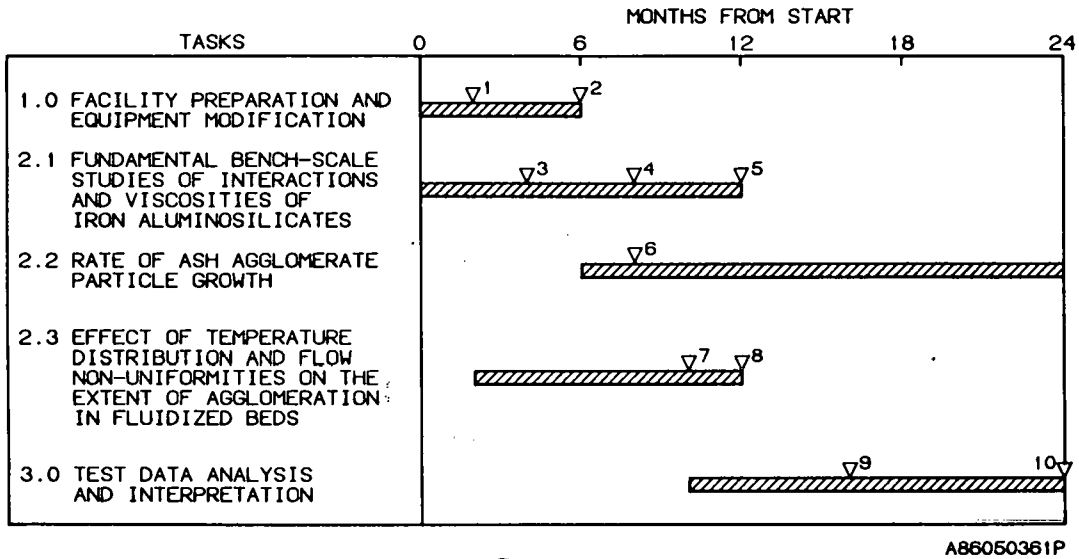
CONTRACTOR PROJECT MANAGER: Ronald H. Carty

PRINCIPAL INVESTIGATORS: Ronald H. Carty
Amir Rehmat

METC PROJECT MANAGER: Dr. Hsiao-Ya L. Lai

CONTRACT PERIOD OF PERFORMANCE: March 25, 1987 to March 24, 1989

2. SCHEDULE/MILESTONES:




Milestones:

1. Complete modification of the 6-inch-diameter glass fluidized-bed agglomerator.
2. Complete modification of the 2-inch-ID fluidized-bed agglomerator.
3. Prepare synthetic slags.
4. Complete wire-screen reactor studies.
5. Complete viscosity measurements.
6. Complete shakedown tests and begin studies on the rate of ash agglomerate growth.
7. Complete batch operation tests.
8. Complete continuous steady-state tests.
9. Complete data analysis of Subtask 2.3.
10. Complete formulation of the mathematical description of agglomerate growth.

Figure 1. Project Schedule.

3. OBJECTIVES:

The objectives of this work are to obtain the experimental data and perform the data analysis required to correlate the formation of ash agglomerates in an agglomerating fluidized-bed coal gasifier with the gasifier configuration and operating conditions and the physical and chemical characteristics of the mineral constituents. In addition, a theoretical investigation of the agglomeration mechanism from first principles will be used to develop the governing mathematical relationships. The specific objectives of this investigation are —

- Investigation of the effects on ash agglomeration of in-bed sulfur sorbents and recycle of the regeneration gas from a hot-gas sulfur removal unit.

- Bench-scale experimental measurement of the rate of agglomerate growth as a function of temperature, viscosity, and chemical composition using well-characterized synthetic slags.

- Exploration of the development of an optimum design basis and operating procedure for fluidized-bed coal gasification processes based on the analysis of bench-scale experimental data. These data will measure the effect of temperature distribution, flow patterns, and particle-size distribution on the rate and extent of agglomeration in a fluidized bed.

- Development of mathematical relationships based on fundamentals of fluid mechanics, heat transfer, and the previously developed Institute of Gas Technology (IGT) description of the agglomeration phenomenon in a fluidized-bed gasification system.

4. BACKGROUND STATEMENT:

The behavior of the mineral matter of coal and its reaction product, ash, is of concern in gasification processes because it governs deposition on gasifier internal and hot-cyclone surfaces, agglomeration in ash-agglomerating gasifiers, and slag removal in slagging gasifiers. The ultimate aim of the IGT research program in ash chemistry is to be able to predict the behavior of the mineral matter in a fluidized-bed gasifier based on a minimum analysis of the characteristics of the mineral matter present in the coal feed and the operating conditions. The current program that began in April 1987 will use experimental studies and a theoretical analysis to accomplish this objective.

In the experimental studies, iron aluminosilicates of compositions similar to those of the matrix material of ash agglomerates will be prepared and used to measure the rate of agglomerate growth in a 2-inch-ID fluidized bed. By measuring the rate of agglomerate growth and examination of the type of agglomerates formed over a range of temperatures, the viscosity range of molten coal mineral matter required for agglomeration will be determined.

In the theoretical analysis, a series of both batch and continuous agglomeration tests using plastic particles will be performed in a 6-inch-ID glass fluidized bed with a heated center jet to measure the effects of jet temperature, particle size, and fluidizing and jet velocities on the extent of agglomeration. These data will be used to extend and verify the mathematical expressions that were previously developed in an IGT project. These mathematical relationships will also be applied to the data obtained in the experiments using the iron aluminosilicate agglomerate material.

As the current program is in the initial phase of equipment modification, the major emphasis of this paper will be on the results of the ash chemistry studies completed in 1986 (Carty 1987).

## 5. PROJECT DESCRIPTION:

In the ash chemistry studies completed in 1986, the research program addressed the key issues of ash particle contact, conditions and rates of reaction of mineral matter, and agglomeration conditions in fluidized-bed gasification. The specific objectives of the investigation were to determine —

- The effect of coal mineral matter variation on the behavior of ash and to correlate this behavior with a detailed analysis of the mineral matter present in the coal.
- The reaction rates of individual clays and silica with the pyrite and carbonates of coal.
- The feasibility of employing the dielectrophoretic manipulation technique (DEM) to identify the conditions under which colliding ash particles coalesce, shatter, or deposit.

Five eastern and two western coals were tested under this project. The choice of the eastern coals was limited to washed products in order to concentrate better on the initial phases of ash reactions — those of the ash brought into juxtaposition for reaction by the gasification of the carbon of individual particles.

Coals were sought whose ash composition would reflect the full range of the most important variable for agglomeration, the average concentration of pyrite relative to the siliceous minerals. The concentration of calcium minerals — typically calcite — is probably the next most important. Accordingly, we selected four coals covering a wide range of iron oxide and only small amounts of calcium oxide in the ash. It was also desired to test a coal with low iron oxide in combination with a high calcium oxide concentration. Total sulfur, silica-to-alumina ratio, and $Fe_2O_3$ and CaO content of the ash of the selected coals are presented in Table 1.

In addition to Mossbauer and computer-assisted scanning electron microscopy (SEM) analyses, another method of characterizing the mineral matter

of coal was developed. Of greatest interest here was a practical method of determining how much of the ash of the coal will be of relatively low-melting composition as the char of single particles become completely gasified. Iron and calcium oxide contents of the ash in relation to silica plus alumina are most important. For this investigation, the ash compositions of 32 single particles (-10+12 mesh) of the coals were determined chemically. This size furnishes enough ash for the chemical analysis and is about the average size, by weight, of the coal feed to a pilot plant or commercial fluidized-bed gasifier. Particle weight, ash content, iron oxide, and calcium oxide in the ash were determined and the content of basic constituents was estimated (Mason 1987).

Table 1. Mineral Matter Characteristics of Coals Tested.

| | KY 9 | Pitt | KY 13 | IL 6 | IN VI | York | Rosebud |
|---|---|---|---|---|---|---|---|
| Total Sulfur | 3.1 | 3.2 | 1.4 | 3.1 | 2.6 | 0.5 | 1.3 |
| $SiO_2/Al_2O_3$ | 3.1 | 2.0 | 2.2 | 3.2 | 2.3 | 1.8 | 2.1 |
| $Fe_2O_3$ | 19.9 | 31.7 | 8.1 | 10.7 | 15.7 | 9.0 | 7.0 |
| CaO | 2.29 | 1.14 | 0.90 | 8.34 | 2.48 | 8.15 | 7.16 |

A comparison of the bulk analyses and the averages for the particle analyses obtained on all of the coals except the York Canyon are presented in Table 2. The York Canyon coal was supplied in a size consist too fine for the test (-20 mesh).

Table 2. Comparison of Bulk and Single Particle Analyses.

| | Ash Content* | | $Fe_2O_3$ in Ash | | CaO in Ash | |
|---|---|---|---|---|---|---|
| Coal | Particle Avg | Bulk Avg | Particle Avg | Bulk Avg | Particle Avg | Bulk Avg |
| KY 9 | 6.3 | 7.6 | 22.3 | 19.9 | 1.10 | 2.29 |
| Pitt 8 | 10.9 | 7.5 | 34.2 | 31.7 | 1.14 | 0.90 |
| KY 13 | 8.2 | 7.3 | 8.6 | 8.1 | 0.69 | 0.90 |
| IL 6 | 10.3 | 11.9 | 12.1 | 10.7 | 0.83 | 8.34 |
| IN VI | 16.4 | 13.4 | 6.9 | 15.7 | 0.36 | 2.48 |
| Rosebud | 10.3 | 11.3 | 0.55 | 7.0 | 9.4 | 7.2 |

* Moist Basis.

Although the average iron oxide in the ash of the 32 particles of Kentucky No. 9 coal agrees well with the conventional analysis, less than

half as much calcium oxide was present in the -10+12 mesh particles as in the conventional analysis. IGT believes that the missing calcium oxide occurs as calcite in the cleat of the coal and that attrition of the calcite occurs in crushing and sieving, resulting in its concentration in the finer sieve fractions.

Similar loss of calcium oxide is also evident with the Indiana VI coal, while 90% of the average 8.34 weight percent of calcium oxide in the ash of the Illinois No. 6 coal has been lost. No loss, or only a marginal one, is evident from the Pittsburgh No. 8 or Kentucky No. 13 coals. Neither did it occur with a subbituminous B Rosebud coal in which the calcium occurs dispersed in the organic matter, partly as carboxylate and (probably) partly as calcite from decomposition of calcium carboxylates. However, about 90% of the average amount of iron oxide is absent from the -10+12 mesh particles of this coal. This is in accord with observations by other investigators that the pyrite of this coal occurs in the cleat.

The distributions of calcium oxide, iron oxide ($Fe_2O_3$), and basic constituents in the ash of the 32 particles of three of the coals are presented graphically in Figures 2 to 4. To prepare a plot, the particle analyses were arranged in the order of increasing amount of the component, such as iron oxide, and the cumulative amount of ash for that order was calculated.

A summary of the distribution of iron oxide in the ash of the -10+12 mesh particles is presented in Table 3 for the eastern bituminous coals, together with the average iron oxide content. The particle analyses of this coal show 59% of the ash to have 0 to 20 weight percent $Fe_2O_3$ and 38% to have 20 to 80 weight percent $Fe_2O_3$. Although the ash of the Pittsburgh No. 8 coal has an average $Fe_2O_3$ content of 31.7 weight percent, much higher than that of the ash of the Kentucky No. 9, its fraction of ash in the 20 to 80 weight percent $Fe_2O_3$ range is much lower, only 10%. This indicates that the ash of the Pittsburgh coal should agglomerate more slowly. The same is true of the Indiana VI coal, whose ash has overall sufficient iron, 15.7 weight percent $Fe_2O_3$, for agglomeration, although very little falls in the 20 to 80 weight percent range.

Table 3. Summary of Distribution of $Fe_2O_3$ in -10+12 Mesh Particles of Eastern Bituminous Coals.

| Coal | Average $Fe_2O_3$ Content, wt % | $Fe_2O_3$ Distribution in Particles | | |
|---|---|---|---|---|
| | | 0-20% $Fe_2O_3$ | 20-80% $Fe_2O_3$ | 80-100% $Fe_2O_3$ |
| Kentucky No. 9 | 19.9 | 59 | 38 | 3 |
| Pittsburgh No. 8 | 31.7 | 61 | 10 | 29 |
| Kentucky No. 13 | 8.1 | 95 | 5 | 0 |
| Illinois No. 6 | 10.7 | 93 | 5 | 2 |
| Indiana VI | 15.7 | 96 | 4 | 0 |

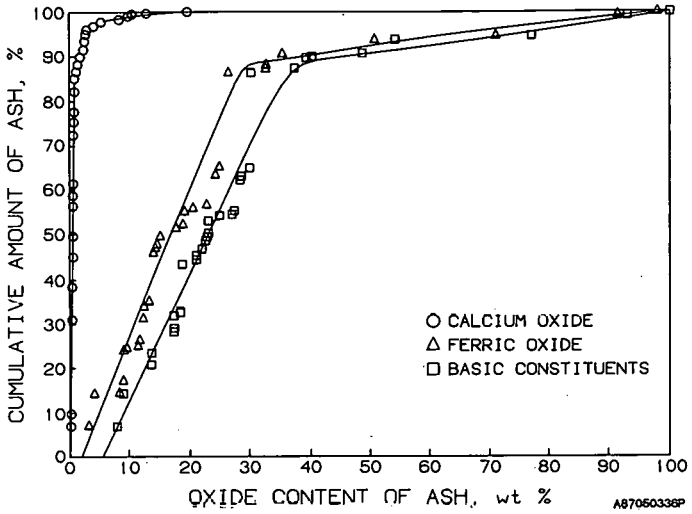



Figure 2. Distribution of Basic Oxides in Particles of Kentucky No. 9 Coal.

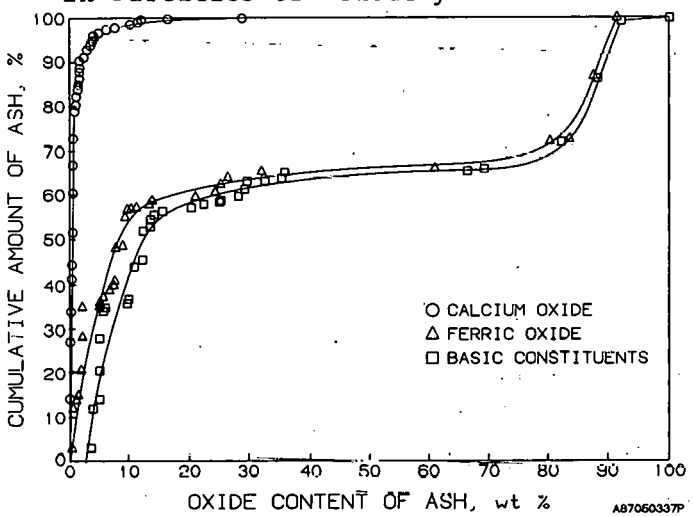



Figure 3. Distribution of Basic Oxides in Particles of Pittsburgh No. 8 Coal.

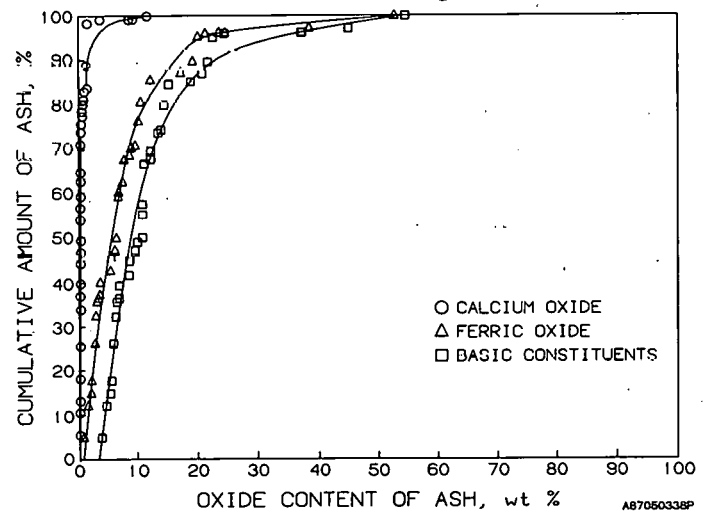



Figure 4. Distribution of Basic Oxides in Particles of Kentucky No. 13 Coal.

For the ash agglomeration tests of these coals, a 2-inch-diameter fluidized-bed gasifier with a center jet was used. The major effect of using a center jet to introduce the oxygen into the gasifier is to produce a hot region in the fluidized bed where the temperature may be as much as 300°F higher than the bed temperature. This higher temperature is necessary to foster the production of the iron aluminosilicate, which is the principal component of the ash agglomerate matrix material.

The tests were conducted at a superficial velocity of 2.0 ft/s and a flow of nitrogen through an annulus around the center air jet was used to cool the jet and to diminish the formation of clinkers. The testing was standardized at a steam-to-oxygen ratio of 2:1 and a bed temperature of 1950°F.

The mineral matter was isolated from the unreacted char of the reactor residues by ashing the residue at 900° to 1100°F for at least 20 hours. This temperature is high enough to combust the carbon but low enough to avoid further reactions of the mineral matter other than oxidation of the ferrous sulfide. The agglomerates, free ash, and pieces of clinker that are isolated by the combustion of the carbon in the reactor residue are then sieved and each sieve fraction is examined visually. The particles larger than 325 mesh are then mixed and mounted for petrographic examination. Two briquettes of each residue are prepared for each residue, and two particle counts are made on each briquette (a total of 1200 counts). The results of these particle counts are averaged, and an average of the particle count and sieve analysis methods are presented in Table 4.

Table 4. Percent of Agglomerates in Ash Freed of Char.

| Coal | wt % Agglomerates |
|---|---|
| Kentucky No. 9 | 59 |
| Kentucky No. 9 (fine ground) | 93 |
| Pittsburgh No. 8 | 61 |
| Kentucky No. 13 | 24 |
| Illinois No. 6 | 51 |
| Indiana VI | 94 |
| York | 34 |
| Rosebud | 32 |

The Kentucky No. 9 that was fine ground showed a suprising improvement in agglomeration properties indicating that a more uniform distribution of the iron, even at overall concentrations of less than 20%, improves agglomeration. The large amount of both low and high concentrations of iron in the particles of Pittsburgh No. 8 coal caused less agglomeration than would be expected from a coal with such a large bulk concentration

of iron. York Canyon coal, which has approximately the same amount of basic constituents as both the Illinois No. 6 and the Indiana VI coals, showed less ash agglomeration due to the iron being uniformly distributed in the clay. The Indiana VI coal showed a degree of ash agglomeration that is not consistent with either the amount or distribution of the iron and calcium species.

Eight synthetic slags representative of the mineral matter that occurs in eastern bituminous coals were prepared and measured for viscosity as a function of temperature using a pentrometer viscometer. The slags had the following range of compositions:

- $SiO_2/Al_2O_3$ ratio = 2.0 to 3.0.
- $Fe_2O_3$ content = 10 to 60 weight percent.
- CaO content = 2.5 to 20 weight percent.
- Silica ratio = 27 to 72.

These viscosity measurements, together with those made previously, form a data bank of viscosity versus temperature relationships of slag compositions that are important in the formation of ash agglomerates. These measurements show that the Watt-Fereday correlation that was developed for much lower viscosities shows a surprisingly good agreement with the measured viscosities in the homogeneous region.

Studies of the reaction rates of the siliceous minerals with the basic oxides present in coal mineral matter were conducted in this program. Initial tests to determine the most appropriate type of reactor to use in these studies were conducted using a hot-stage microscope. As a result of the hot-stage microscope studies, a wire-screen type of reactor was chosen to conduct the reaction rate studies. These reactor tests using a solid titanium metal filament instead of a wire screen at ~2300°F for 6 seconds, kaolinite and siderite reacted to form a small amount of iron aluminosilicate, amounting to less than 10% of the total observed product. The bulk of the product was individual grains of decomposition products from the clay and siderite. In a similar test at 2400° to 2500°F and 5 seconds duration, most of the reaction product was iron aluminosilicate. Thus, these two tests bracket the temperature for substantial reaction of these two minerals.

The feasibility of constructing an apparatus for the observation and measurement of the outcome of the particle/particle and particle/wall collisions of molten ash based on the principles of dielectrophoretic manipulation was investigated. Our efforts to utilize this method have led to the conclusion that the perfection of this method would require significantly more time and money than was available in this project. Since this was an exploratory task to determine the feasibility of using the DEM to study particle-to-particle collisions, we have concluded that the DEM particle acceleration is not an appropriate technique for this purpose.

6. RESULTS/ACCOMPLISHMENTS:

In summary, several significant insights into the mechanisms and chemistry of the formation of ash agglomerates have been made. The accomplishments of this program and the resulting clarifications of the mechanisms of ash behavior include —

- The reaction of iron- and calcium-containing components of coal ash with the siliceous components is critical for the formation of relatively low-melting aluminosilicates that make it possible to form ash agglomerates in a fluidized-bed coal gasifier.

- The results of this investigation indicate that the association of the calcium and/or iron components with the siliceous components in single particles differs greatly from one coal to another in addition to differences in the total or average amounts of the component.

- One result of the variation in the association of the ash components is that the availability of low-melting agglomerative product from the initial complete gasification of single particles also varies from coal to coal. Another result of this variation in association of components is that it is likely that the ease of agglomeration of the whole of the ash by collision with low-melting material will also vary.

- The viscosity-temperature relationship, including a range of viscosities higher than is usually measured, of the ash reaction products is their most important property affecting the rate of agglomeration among reaction products and of the reaction products with unreacted ash. Under this program, viscosities from about $10^2$ to $10^8$ poises have been determined on a number of slags typical of the coal ash compositions at temperatures covering the range encountered in fluidized-bed gasification.

- In reactivity tests, ferrous oxide showed essentially no reaction with kaolinite after 24 seconds at about 2000°F, but did react nearly completely in 24 seconds at about 2250°F. Ferrous oxide is probably the most reactive iron species formed from ferrous sulfide by oxidation in the jet region. The results indicate that the high temperature of the jet region, as well as its oxidizing atmosphere, is necessary for formation of the low-melting agglomerative reaction product.

7. FUTURE PLANS:

The investigation of the formation of ash agglomerates will be furthered in the coming year by —

- Completion of equipment modifications.

- Preparation of synthetic ash agglomerate material and measurement of its physical properties.

- Initiation of tests to determine the viscosity at which agglomeration is initiated in the synthetic slags.

- Investigation of the effects of in-bed sorbents and $SO_2$ injection on the formation of ash agglomerates.

- Completion of modeling tests using plastic particles and initiation of the data analysis.

At the completion of the present program in 1989, it is expected that basic mathematical relationships that describe the formation of ash agglomerates as a function of temperature, gas distributor configuration, viscosity, and particle velocity will be formulated. These relationships can be used both in the design and scale-up of new gasifiers and the establishment of operating conditions for improved gasifier performance.

8. REFERENCES:

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Mason, D. M., and Chao, S. Determination of the Distribution of Ash, Pyrite, and Basic Constituents in Coal Particles. Paper for presentation at the meeting of the ACS Fuel Chemistry Division at New Orleans, August 30-September 7, 1987.

# PERFORMANCE EVALUATION OF A SCREENLESS (COUNTER-CURRENT) GRANULAR BED FILTER ON A SUBPILOT-SCALE PFBC

1. CONTRACT NUMBER: DE-AC1-84MC21335

CONTRACTOR:
Combustion Power Company
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(415) 324-4744

CONTRACTOR PROJECT MANAGER: Keith B. Wilson

PRINCIPAL INVESTICATORS:
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Jerry Cooper
Fernando Placer

METC PROJECT MANAGER: Mr. Randall J. Dellefield

PERIOD OF PERFORMANCE: September 28, 1984 to June 30, 1987

2. SCHEDULE/MILESTONES:

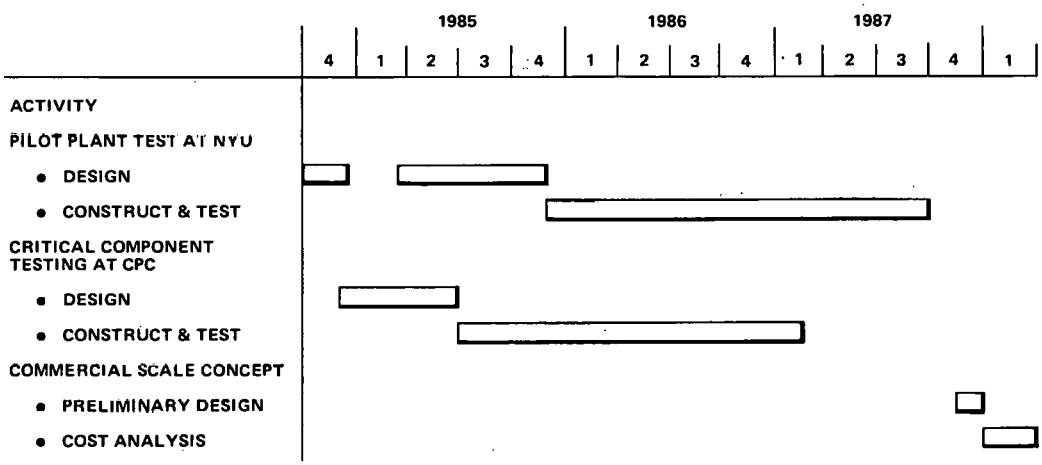



Figure 1. Program Schedule

3. OBJECTIVES:

The objectives of this investigation are: 1) to augment information on the feasibility of a Granular Bed Filter (GBF) for controlling particulate in a Pressurized Fluidized-Bed Combustor (PFBC) power generating system, 2) to assess the design and life of critical components in the filter system, and 3) to estimate costs of a commercial-scale design based on tested concepts.

## 4. BACKGROUND STATEMENT

Efforts to operate coal-fired gas turbines have been conducted in recent years. These attempts, like the one at Combustion Power Company (CPC) in the early 1970's, have been plagued by turbine problems due to ash-laden combustion gases. It was at this time that CPC began experimentation with a method of cleaning exhaust gases or process streams of particulate using granular media. This experimentation was in conjunction with the PFBC development work for power production and actually utilized a gas turbine. The filter media used was 2 mm alumina spheres making the gas cleaning process reminiscent of filtering suspended solids from waste-water through a sand bed.

The early work at CPC took two paths. For low to medium temperature gas cleanup a filter was commercialized, (Reese 1975) (Grace, 1979). Numerous of these filters are used in industry today. For high-temperature gas cleanup (over 1000°F) a development effort began.

### HOT GAS CLEANUP

Initial high temperature gas cleanup testing utilized the same technology developed for low to medium temperature applications; that is, 2 mm granular media was contained in the space between two concentric louvered screens (Vander Molen, 1984). Performance with this configuration was quite good, but continued difficulty was encountered with screen pluggage at gas temperatures above 1400°F. The design eventually evolved away from the screened configuration, hence the label "screenless". Figure 2 shows a schematic of the present screenless configuration (Guillory, 1983), and Figure 3 shows the filter essentials installed in a pressure vessel. Three zones of gas-cleaning are identified. A very high amount of ash is collected in the parallel-flow zone and the final ash collection/gas polishing takes place in the counterflow zone. Additional layers of media in the counter-flow zone can increase gas cleanup effectiveness. Furthermore, although 2 mm media has been used in all testing to date, it can be shown that a more compact filter will result by utilizing 3 mm filter media (Rubow, 1984).

Tests of the pilot-scale filter element shown in Figure 2 at atmospheric pressure and at a temperature of about 1600°F demonstrated successful operation over a 1500-hour test period. Collection efficiencies of 99 percent were obtained at a pressure drop at about 25 in. $H_2O$, and degradation of the collection media did not occur. The filter also operated successfully under upset conditions (inlet loadings 10 times normal and inlet flow rates 25 percent higher than

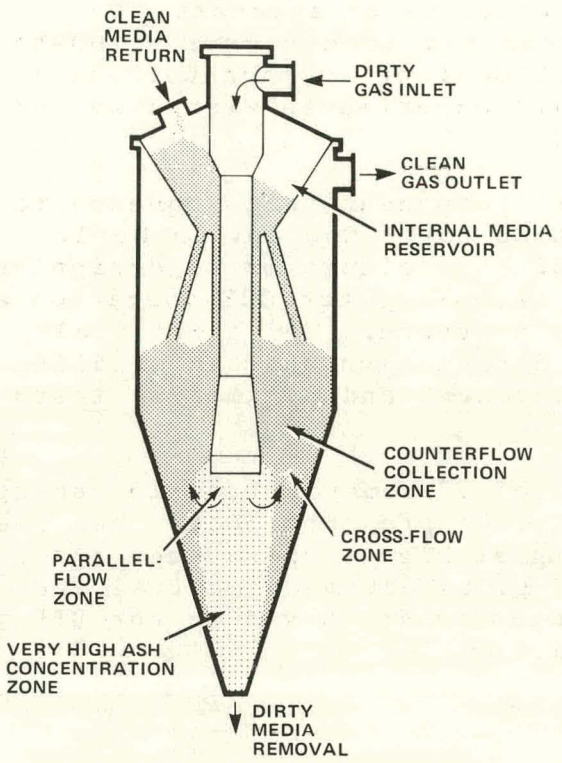



Figure 2. Screenless Counter-Flow Granular Filter Bed

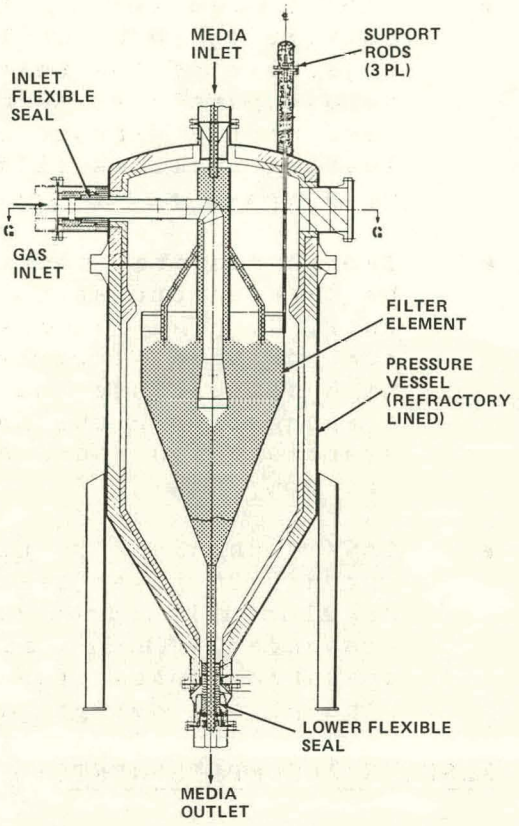



Figure 3. Granular Bed Filter Installation

normal). Analytical studies showed that similar operating characteristics could be maintained at high temperature and high pressure. It is projected that with the proper selection of design parameters, new source performance standards (NSPS) can be met while providing a gas turbine with economic blade life.

## 5. PROJECT DESCRIPTION:

### PLANNED HIGH-TEMPERATURE, HIGH-PRESSURE DESIGN AND TESTING

The purpose of this program is to obtain information on the operational and economic feasibility of the moving granular bed filter (GBF) in a PFBC power generating system. Information generated will consist of (1) operational data carried out on the pilot-plant scale, (2) experimental data generated on critical GBF system components, and (3) an update of the commercial-scale design based upon the experimental data.

To meet the stated purpose, the contract is divided into three tasks as follows:

- TASK 1 requires a pilot plant test sequence at New York University (NYU) utilizing actual PFBC exhaust. The objective of the test sequence is to successfully remove particles to the required levels over a 200-hour test period without operational or component failure. Testing includes filtration experiments with 2 mm and 3 mm alumina media spheres.

- TASK 2 requires a critical component test sequence to be carried out at Combustion Power Company in Menlo Park, CA The objective of this effort is to design and test critical components necessary for GBF operation at high temperature and high pressure. These critical components are the media circulation and ash handling systems. 500 hours of component and parametric tests are completed.

- TASK 3 requires an update of a commercial scale concept for a PFBC power station. The present concept has been developed based on testing at high temperatures and low pressures. The objective is to estimate capital and operating costs of a cleanup train, based on the GBF concept and design principles.

6. RESULTS/ACCOMPLISHMENTS:

GBF EQUIPMENT FOR NEW YORK UNIVERSITY TESTING

The GBF gas cleanup schematic is shown on Figure 4. PFBC flue gas flows through the moving granular bed and gives up particulate. 2 mm or 3 mm filter media, laden with ash, flows downward towards the bottom apex of the filter cone to be collected for cleaning and recirculation.

The filter media will be recirculated at a rate of 15-40 lb/min using nominally 11 lb/min of lift gas by a 2-inch pneumatic lift pipe. The transport gas will be flue gas that is being recirculated through the closed transport gas system. As the particulate-laden filter media is transported vertically through the lift-pipe, the media is cleaned. At the top of the lift-pipe, a de-entrainment vessel separates the cleaned filter media from the now particulate-laden transport gas. The cleaned filter media then flows by gravity to a media reservoir located above the filter pressure vessel.

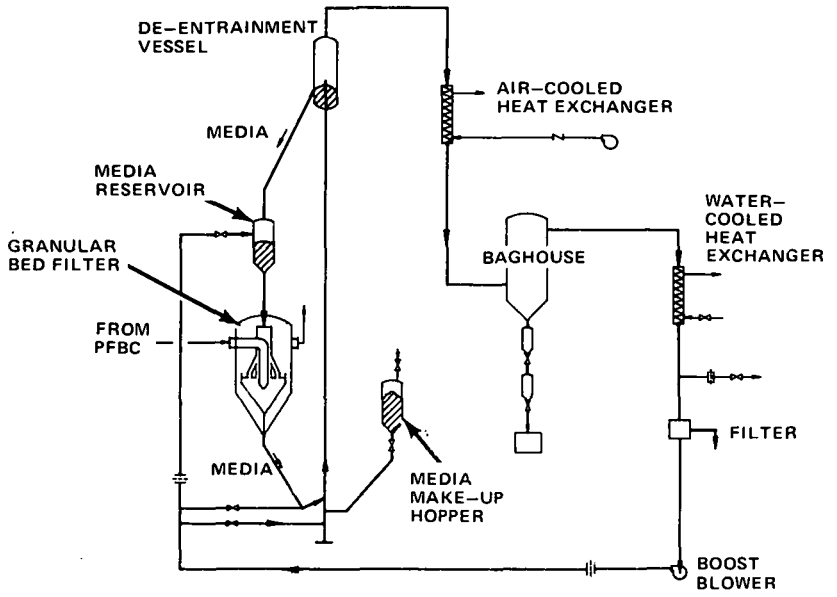



Figure 4. Granular Bed Filter Installation

The hot, particulate-laden transport gas leaving the de-entrainment vessel will be cooled and sent to a pressurized baghouse for removal. Note that in a commercial-scale unit, heat recovery can be considered. (Rubow, 1984) The collected dust from the baghouse will be transported to a disposal bin by a double lock-hopper arrangement. The cleaned transport gas will be recompressed and circulated back to the media transport system.

The arrangement of the filter element within the pressure vessel is shown on Figure 3. In comparing this configuration with the filter element that underwent 1000 hours of low-pressure, high temperature testing (Figure 2) one recognizes that the critical relationship between the physical components within the filtering regime has remained the same. The intent is to preserve the gas flow distribution through the parallel-flow, cross-flow, and counterflow collection zones.

Media distribution to the filter body has been altered significantly as can be seen by comparing Figures 2 and 3. Moving the media reservoir out of the filter has advantages in the commercial-scale design because it saves valuable space in a pressure containment vessel. Furthermore, the media feed pipe from the remote reservoir creates a low-leakage seal between the filter element and the media circulation system. Minor pressure differences between these two zones can exist without upsetting media flow or particulate capture.

EQUIPMENT FOR CPC TESTING

Figure 5 shows a schematic of the system developed and tested at CPC prior to the NYU test sequence. This system includes the actual media circulation and ash handling components to be utilized at NYU. The equipment, operation and flexibility of the system is much like that described for installation at NYU with the following exceptions:

- The GBF is replaced by a small surge hopper with arrangements to inject ash.
- The heat source to bring the NYU filter system up to temperature is for the PFBC. A separate heat source is needed for critical component testing at CPC.

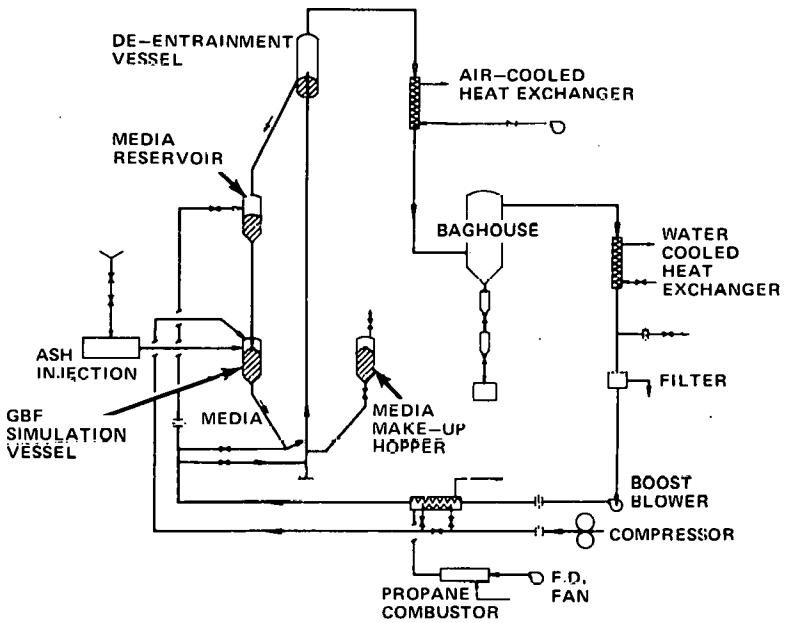



Figure 5. Schematic for Critical Component Testing at CPC

Figure 6 shows an elevation view of both the CPC critical component test system and the NYU pilot-scale filter. These views are unfolded for clarity, but are depicted somewhat to scale, vertically, to give an idea of the physical differences. The 10 foot height difference between the NYU and CPC test facilities saves cost in the support structure at CPC and in the GBF simulation vessel. Operational differences due to this change are not significant.

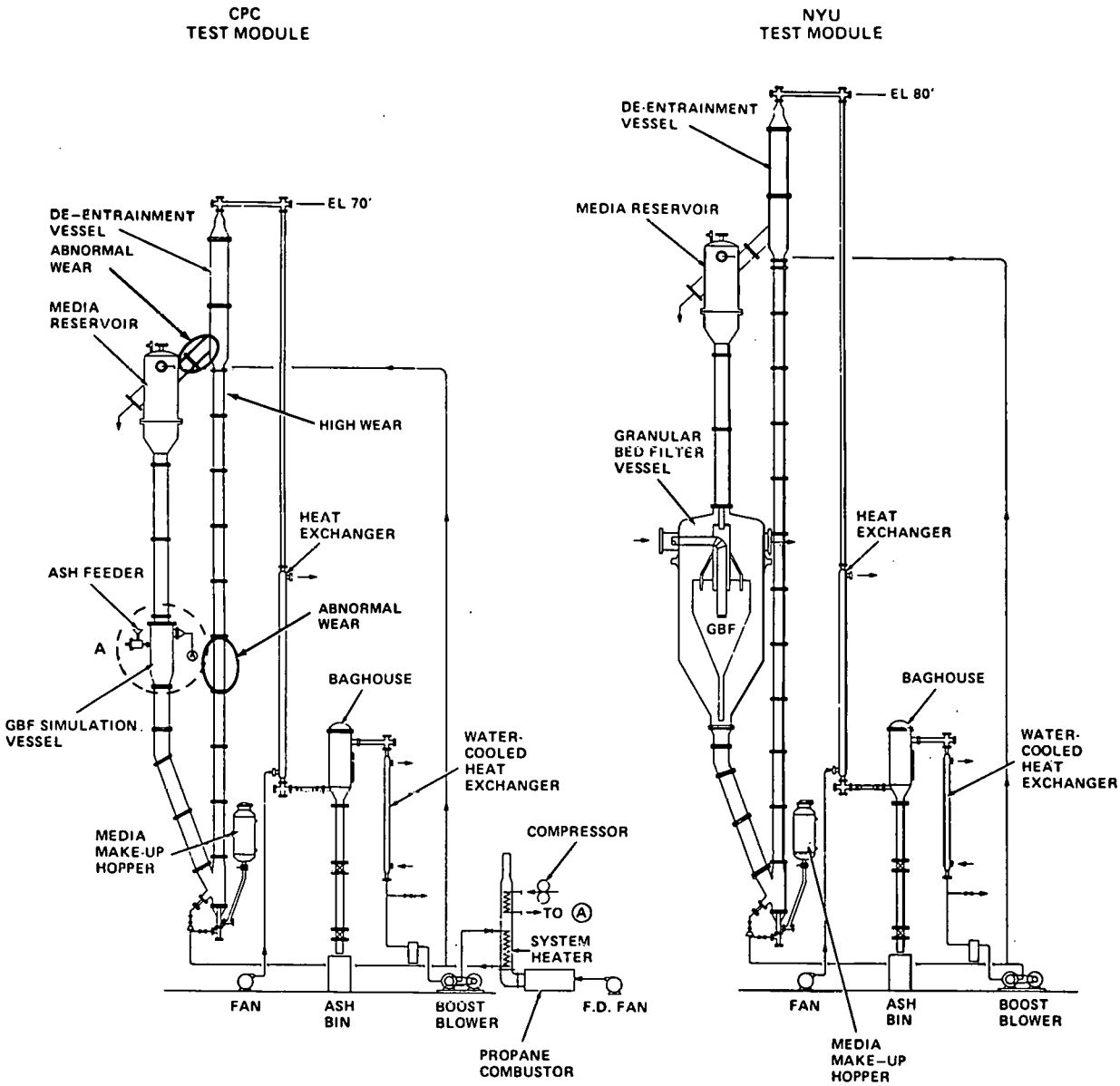



Figure 6. Test Facilities at CPC and NYU.

## TEST RESULTS

Parametric tests were completed at CPC that compared measured and theoretical media circulation rates. These tests were run at different combinations of temperature, pressure, transport air flow, and media circulation rates. Other tests were run to observe the ash carrying capability of the media, the operation of the ash discharge system, and the characteristics of operation with larger (3 mm vs. 2 mm) media. Results were:

- Early parametric tests showed remarkable agreement between measured and theoretical circulating rates. Some disparity was noted at lower airflows. See Figure 7.

- Continued parametric tests showed increased divergence between measured and theoretical circulation rates. Refractory wear in the lift pipe was suspected. Disassembly and inspection of the lift pipe showed abnormal wear in two unrelated areas identified in Figure 6. Because refractory wear was significantly diminished in adjacent areas, defective materials or installation was suspected. Refractory was repaired prior to delivery of equipment to NYU.

- Tests showed that a very small amount of air could be bled from the circulation loop at the baghouse and result in a pressure profile favorable to moving ash and media in the same direction out of the filter. This technique is called "artificial pressure balancing" and may be useful for operation at NYU.

- Ash was loaded and circulated with the media to the 5-6% range (ash-to-media by weight). This coincides with expected results. These same ash loading tests suggested ash could easily bridge in the baghouse and double airlock discharge system. Steps will be taken to insure reliable ash discharge at NYU.

- Media circulation, as evidenced by lift-pipe pressure drop, started and stopped in a reliable and controllable fashion. It was smooth and steady in the desired ranges.

- The de-entrainment vessel design was insensitive to all imposed changes in pressure, temperature and flow rates. Ash separation from media was achieved. Media carryover towards the baghouse was not detected even though occasional operator error resulted in velocities above design.

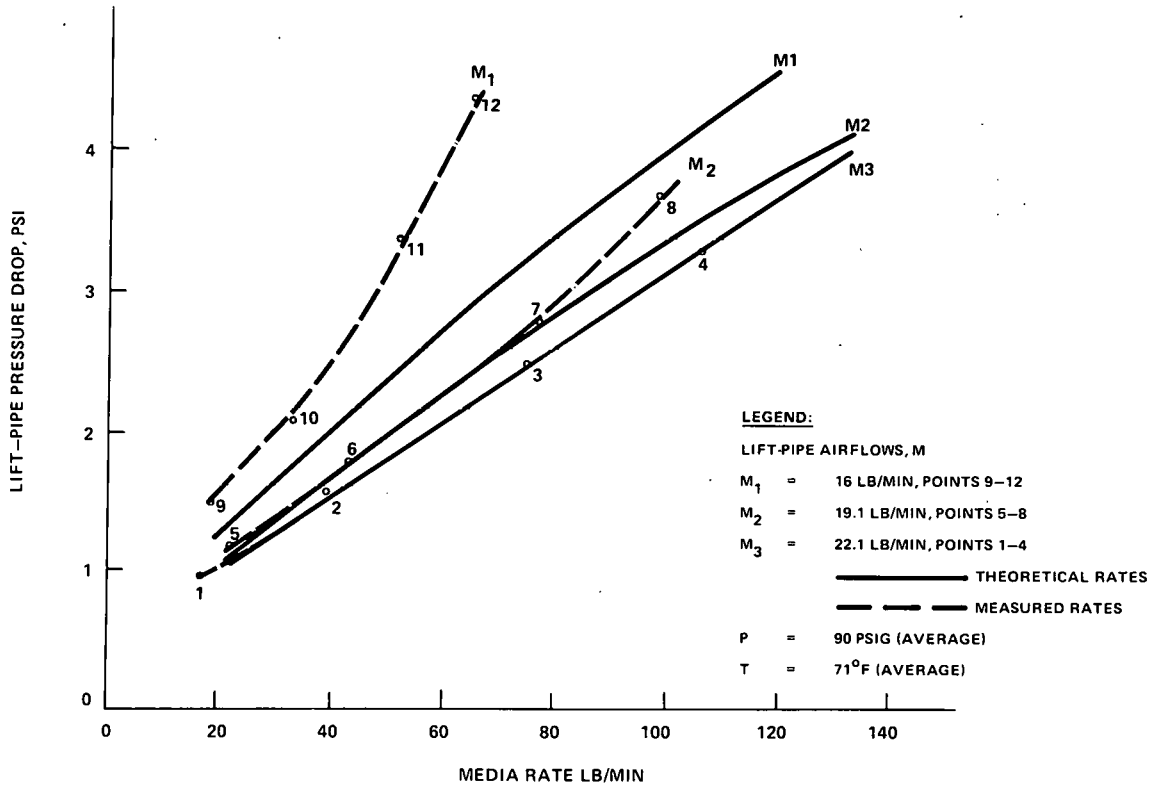



Figure 7. Media Rates in 2" I.D. Litt-Pipe, Data Set 3

- Heat exchangers performed fine during this test series but were not really challenged to operate at capacity. We do not have adequate heat input capability at CPC to assess the performance of the air-cooled and water-cooled heat exchangers. This was expected; also, it does not concern CPC because these heat exchangers are of standard design.

- Baghouse operation and pulsing had no adverse affect on the circulation system. Pressure drop across the coalescing filter downstream of the baghouse was to warn of baghouse failure. A steady pressure drop across this auxiliary filter, responsive only to changes in air flow rates, indicated efficient baghouse operation.

- The ash pressure letdown system (sequencing the Kamyr ball valves) did not affect circulation system. There was no fugitive dust problem at the ash collection barrel as all leakage gases were exhausted through a standard air filter.

- The boost blower is a sliding vane compressor, It provided a reliable and steady source of media transport air at a pressure rise of 6-10 psi. It is a positive displacement type machine so it automatically adjusted for pressure changes. It was run during periods of both stable and changing system pressures with no difficulties. The blower was attached to a mechanical type variable speed drive. Speeds were infinitely variable between about 725 rpm to 1700 rpm. Furthermore the combinations of temperature, pressure, and media lift requirements all required blower speeds in a fairly narrow range. Only circulation at atmospheric conditions required a large change in blower speed to achieve.

- At each unique level of temperature and pressure there appears to be a range of optimum lift-pipe air flows as opposed to a single point. Choking (media collapse in the lift pipe) occurs at 50-75% of typical lift-pipe air flows. In practicc, this is quite a safe gap.

- Operation with 3 mm media produced results expected in that only about 5% more circulation air flow was necessary to transport the media. Otherwise 3 mm media behaves much the same as the 2 mm media.

## 7. EVALUATION OF POTENTIAL FUTURE PLANS:

Equipment and operating data from critical component testing at CPC will be used in the 200-hour, NYU test sequence. Tests at NYU will concentrate on assessing the particulate removal efficiency of the GBF in the environment of an actual PFBC exhaust. Parametric tests will be conducted over a pressure range of 7 to 10 atm at different process gas flows and media circulation rates. A single operating point will be chosen for a long term (100-hour) steady state test.

Based on results from both test sequences, the commercial-scale approach will be updated and cost estimated.

CPC's goal is to demonstrate the GBF concept to be an operationally and economically feasible means to remove particulate from a PFBC off gas. We expect the GBF to meet both turbine tolerance limits the federal pollution control standards.

## 8. REFERENCES:


Grace, D.S. et al, Electrostatic Enhancement of Moving-Bed Granular Filtration, 2nd Symposium on the Transfer and Utilization of Particulate Control Technology (July 1979)

Guillory, J. L., High Temperature Particulate Removal by Moving Bed Granular Filtration, 25th Int. Gas Turbine Conference (March 1980)

Guillory, J. L., et al, Granular Bed Filter Development Program, Phase II, DOE Report DOE/ED/10373-T10 (Combustion Power Company, Menlo Park, California) (May 1983)

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Rubow, L. N., Technical and Economic Evaluation of Ten High Temperature, High Pressure Particulate Cleanup Systems for Pressurized Fluidized Bed Combustion, Gilbert/Commonwealth, Reading, PA DOE Contract No. DE-AM21-84MC19196 (July 1984)

Vander Molen, Robert, Moving Bed Granular Filters for PFB Hot Gas Cleanup, EPRI Pressurized Fluidized-Bed Combustion Power Plant Utility Conference (June 1984)

# TESTING OF ELECTROSTATIC PRECIPITATOR AT NEW YORK UNIVERSITY

1. CONTRACT NUMBER: DE-AC21-84MC21094

CONTRACTOR: Cottrell Environmental Sciences
PO Box 1500
Somerville, New Jersey 08876

CONTRACTOR PROJECT MANAGER: K. S. Kumar

PRINCIPAL INVESTIGATORS: K. S. Kumar
P. L. Feldman

METC PROJECT MANAGER: Randall J. Dellefield

CONTRACT PERIOD OF PERFORMANCE: September 1, 1984 to September 1, 1987

2. SCHEDULE/MILESTONES:

| | 1986 | | | | | | 1987 | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | J | J | A | S | O | N | D | J | F | M | A | M | J | J | A | S |
| Debug Precipitator | | | | | | | | | | | | | | | | |
| Conduct ESP Tests | | | | | | | | | | | | | | | | |
| Submit Preliminary Report with Recommendations | | | | | | | | | | | | | | | | |

3. OBJECTIVES

Test and evaluate the performance of sub-pilot scale electrostatic precipitator following the pressurized fluidized bed combustor located in Westbury, New York.

4. BACKGROUND

The electrostatic precipitator testing and evaluation program at New York University's PFBC test facility was initiated in November 1986. The objective was to determine its particulate collection efficiency at the combined cycle PFBC exhaust conditions of 1650$^{o}$F and 10 atmospheres. The nominal gas flow to ESP at these conditions was typically 1200 acfm. The electrostatic precipitator was of the horizontal flow plate type such as that used in conventional utility power plants. Though previous sub-pilot scale tests were performed with tubular ESP geometry, both engineering design and economic analysis pointed towards horizontal flow plate type geometry for the 100 MW commercial size modules for utility application. However, the concept of packaging plate type ESP's in horizontal flow pressure vessels was new for this application and needed engineering development. Figure 1 is a conceptual description of the ESP being tested at NYU.

The design philosophy for the New York University's precipitator has been described in previous papers on the subject[1,2]. In summary,

the most salient features were (a) the use of single point suspension of the high voltage frame using a single insulator for both support and feedthrough, (b) location of the insulator at the top of pressure vessel, (c) use of two independent electrical sections in series as opposed to one section in the previous programs, (d) use of multiple, horizontally located pneumatically operated piston rapping systems, (e) use of melamine rapper insulators outside of the gas stream, (f) the contoured panel collection plates and (g) rigid discharge electrodes.

5. PROJECT DESCRIPTION:

November 1986 Tests

The test program was conducted initially in November 1986. After about 5 hours of PFBC operation using Pittsburg coal, the precipitator showed abnormal operation, manifesting very low operating voltage levels. Though voltage levels up to 100 kilovolts (KV) were obtained during start-up at ESP inlet temperatures up to 1300$^{o}$F using kerosene pre-heat, the depowering of ESP was noted soon after the coal feed. Both the high voltage insulators (one in each section) were found upon inspection to have suffered brittle failure. Each was split into two pieces upon disassembly. There were no indications of electrically induced failure.

The inspection of ceramic insulators suggested severe thermal shock. Since it was thought that PFBC operation could have presented a major source of thermal shock to alumina insulators, procedures were developed jointly by Stone and Webster, NYU and CES to ensure acceptable rate of rise of ESP inlet temperature during the next start-up. Also, CES recommended a few design modifications to improve HV insulator assembly design. These were (a) improve thermal shields on the high tension frame, (b) use water instead of air for the indirect cooling of high voltage insulators, (c) use a dedicated nitrogen source for the forced convection, direct cooling of insulators, (d) the sparger loop for nitrogen feed was also to be improved to distribute the flow more evenly and (e) add thermocouples to better characterize the temperatures inside ESP.

CES had proposed an alternate approach in December to DOE - that of using an outrigger section to house the insulators. This design was successfully utilized at Curtis-Wright. However, due to budgetary and schedule constraints, in December, the improvisary approach suggested above was followed for the 50-hour run in March '87.

March Test

The testing in March produced insulator failures similar to the November tests. Both the HV insulators failed on approach to 1600$^{o}$F at the ESP inlet as noted by the symptoms of extreme underpowering. Upon dismantling, it was found that the insulators had cracked at

locations identical to the November tests. Again, there were no indications of electrically induced failure.

## Overall Observations

In both cases during November and March, ceramic fracture destroyed the electrical function of the insulators and the ESP was unable to perform at desired voltage. The inspection of ESP internals showed that in both instances the collecting plates and discharge electrodes were in excellent condition. There were no signs of misalignment or dust buildup that could have caused the precipitator to result in underpowering. The only failures were of the high voltage bushings. These were confirmed by the concentration of sparking occurances at the bushing flange location observed both during PFBC operation after the depowering, and during the inspection following system shutdown.

## Description of Bushing Assembly

Figure 2 shows the high voltage insulator assembly for one electrical section of the electrostatic precipitator at NYU. The high voltage assembly comprising the discharge electrodes is hung from the bottom of the high voltage insulator. The high voltage insulator has an overall length of 34" and a nominal O.D. of 8". As seen from Figure 2, the high voltage bushing has a two-inch collar located at 10 1/2" from the bottom of the bushing. The bottom portion of this bushing has grooves, which were primarily introduced to provide additional electrical 'creep' paths and thus improve electrical reliability. This bottom portion was located inside the pressure vessel and a gasket at the bottom provided the pressure isolation between high tension frames and atmosphere through the central, hollow path of the insulator.

The weight of high tension frame assembly, 1500 lbs, was supported by the high voltage bushing collar, which has a $30^{0}$ bevel. The bushing is held at its location at the pressure vessel flange by means of bushing flange circumferentially clamped at this portion. The gas tight seal at the bottom of the high voltage bushing is made possible by the frameweight and spring loading of the 3" diameter pipe shaft at the top of the bushing.

## OBSERVATIONS OF FAILED HIGH VOLTAGE BUSHINGS

After each of the tests of November and March, the insulators were removed for observations. Figures 3 shows the failed insulators after November tests. It is seen that the breakage has been from the high pressure side at the bottom in both these insulators. Also, many of the grooves at the bushing exterior had shown remarkable and numerous crack failures while the inside of bushing was relatively crack free. The separation of the insulators into two pieces coincides with the theoretically estimated location at both these points. The absence of stress cracks on the inside of bushings indicates that the

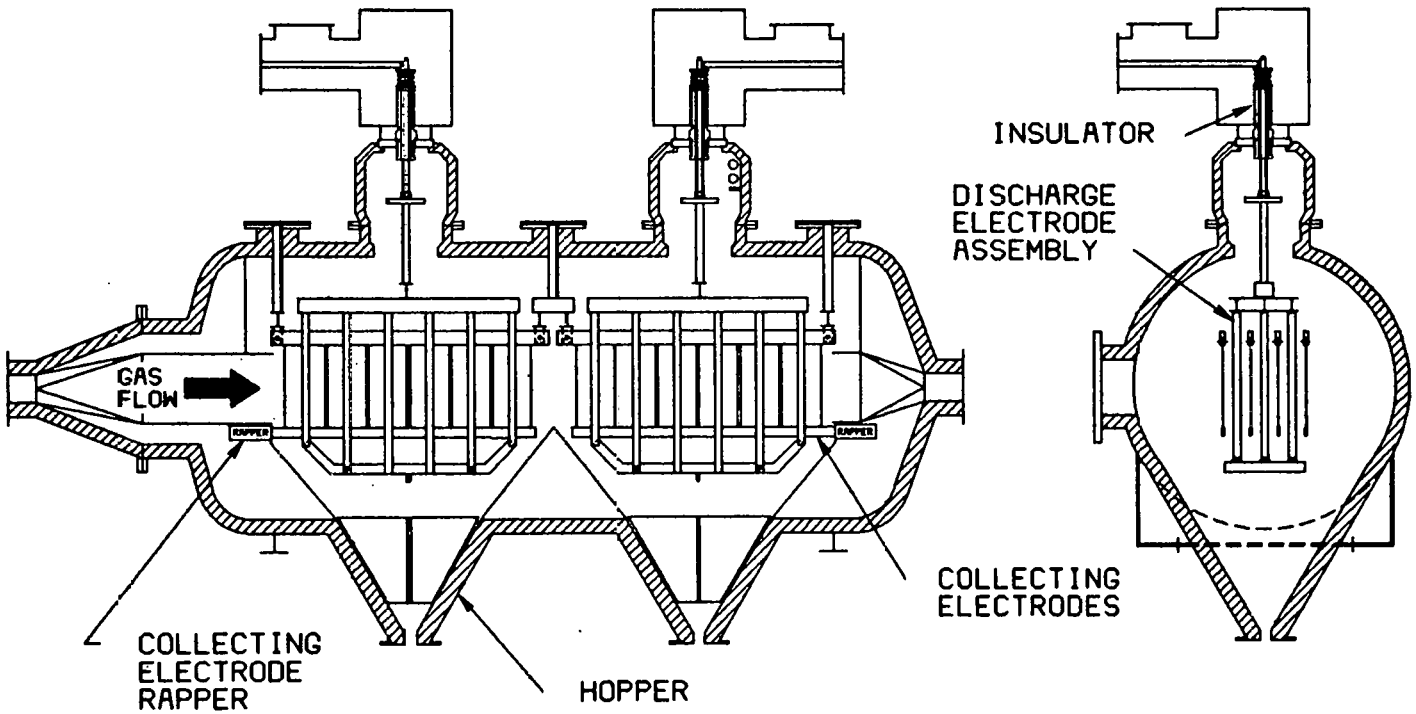



Figure 1: Conceptual Schematic of Precipitator at NYU

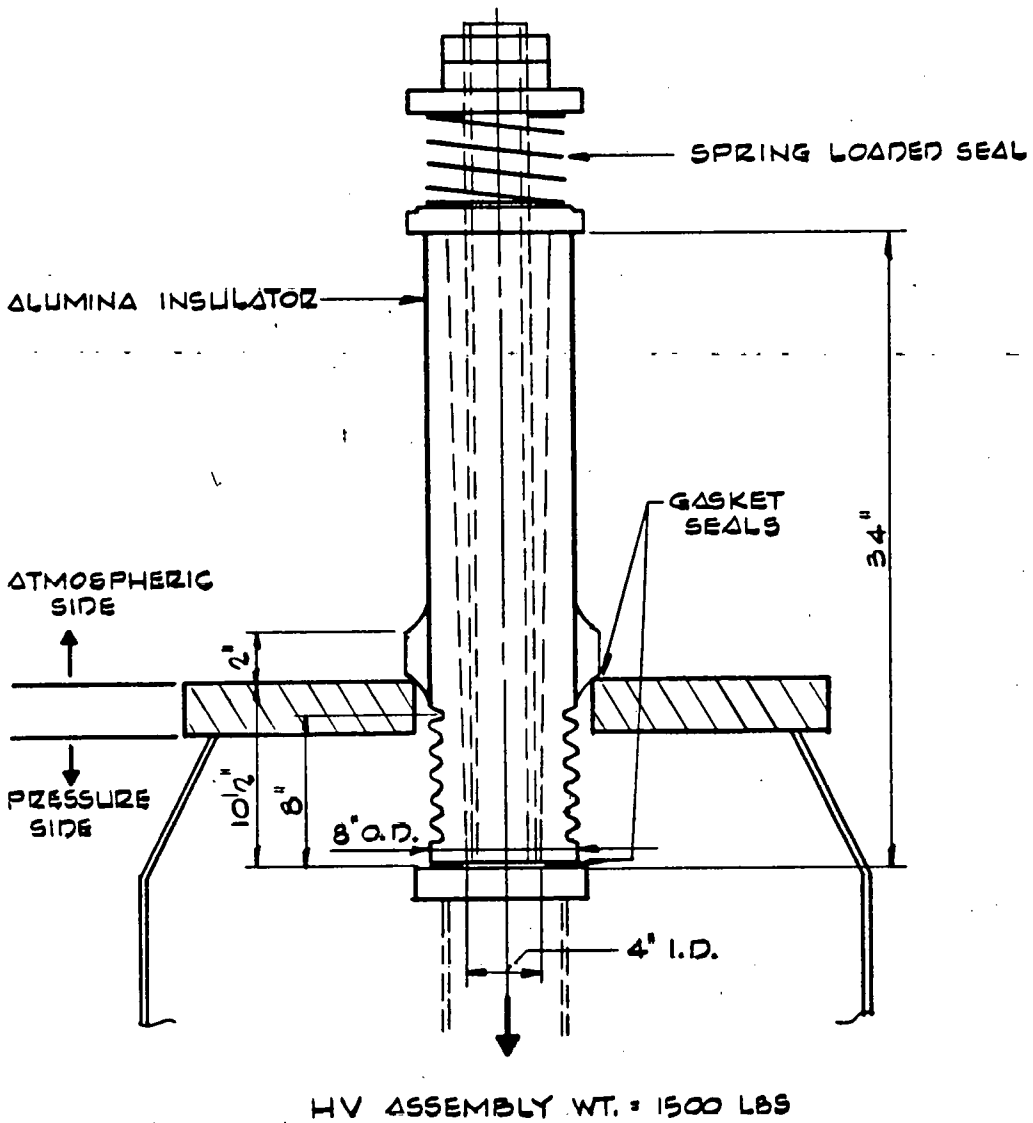



Figure 2: High Voltage Insulator Assembly at NYU

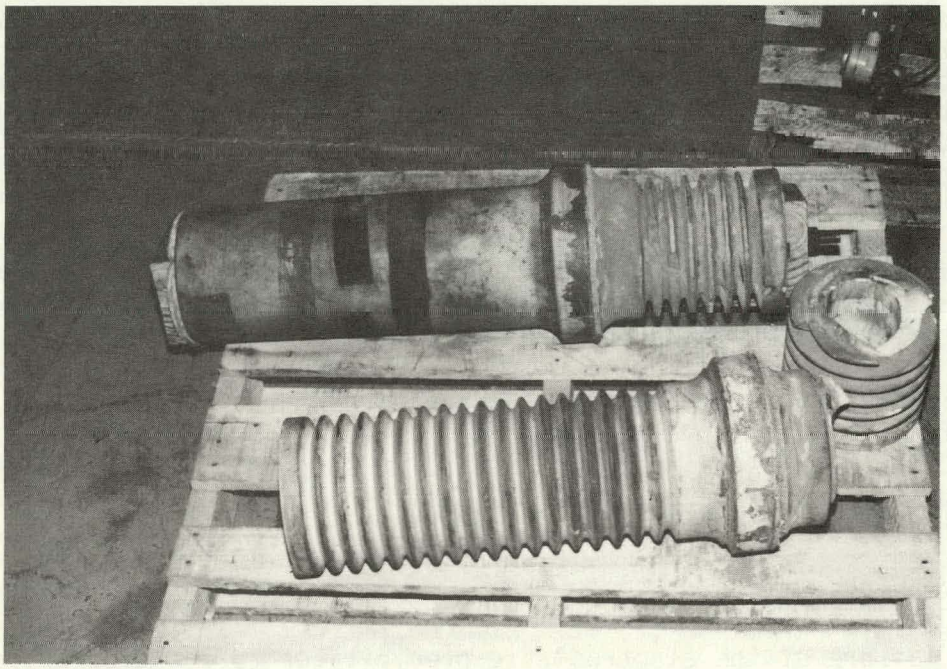


Figure 3: Failed Insulators After Testing in November

temperatures were relatively higher on the inside hollow portion when compared to the outside. Also, the location of bushings was such that heat conduction from the precipitator high tension frame could reach the inner hollow portion while retaining relatively high temperatures. The uneven cooling of the outside insulator surfaces by the jet could create a condition of thermal gradients in both axial and circumferential directions.

It is also felt that air jets aimed at the lower section of insulator could have created hot air currents to flow to the top of insulator and thus create a temperature gradient in the axial direction, hot at the collar and colder at the bottom of bushings. This flow profile needs verification by flow visualization studies. Multiple cracks on the grooves coincide approximately with the air flow path.

In addition, intermittent mode of air sparger operation was present many times during the November and March tests a) due to the brief non-availability of sparger flow following NYU's air compressor failure, b) the brief stoppage of Nitrogen source, and c) due to the operator's well intentioned efforts to keep the bushings clean by intermittent bursts of sparger flow. Further, unscheduled combustor upsets created unsteady thermal environments in the HV insulator compartment.

All things considered, it is felt that the inability to maintain a thermally benign environment for the bushing was the nemesis of ESP operation. The failed bushings show "thermal shock" effects and the failure seems explainable.

During March tests the combustor could run for a longer period prior to failure. It is felt that the concerted efforts of improved cooling (within the constraints of single point suspension) allowed for cooler insulator temperatures, but not sufficiently low or uniform to avoid ultimate failure.

## 6. PROGRAM RESULTS

- The failure of the electrostatic precipitator to energize properly during the middle of combustor runs was a result of the structural failure of high voltage insulators during the November and March PFBC runs. The broken pieces and post-inspection current-voltage tests with failed insulators attest to this observation.

- No sign of electrically induced insulator failure (such as from overheating) was observed. The failure was also not attributed to any misalignment problems. The precipitator appeared free from misalignment and dust build-up problems.

- The behavior of failed insulators follows the theoretical expectations resulting from a) the discontinuity introduced in the design by the grooves to promote electrical function, b) thermal gradients resulting from the thermal environment of the insulator, c) thermal transients caused by the air sparger, d) thermal transients due to the combustor

operation and e) the nature of horizontal loads resulting from bevels at the bushing collar.

7. EVALUATION OF POTENTIAL FUTURE PLANS:

- o The recommendations to improve the insulator design are as follows: Develop alternate designs that can avoid the detrimental stresses induced both by structural design and operating thermal environment.
- o Develop a bench-scale testing concept that can validate by experiments the integrity of proposed insulator assembly design.
- o Recommend the most promising insulator design for sub-pilot scale testing, based on the results of validation tests.

8. REFERENCE

Testing and Evaluation of ESP at New York University, Proceedings of the Fifth Contaminant Control Conference, Morgantown, WV, (Kumar 1985)

Testing and Evaluation of ESP at New York University, Proceedings of the Sixth Contaminant Control Conference, Morgantown, WV, (Kumar 1986)

STATUS REPORT ON
KILnGAS COMMERCIAL MODULE

1. CONTRACT INFORMATION:

AGREEMENT TITLE: KILnGAS Commercial Module

AGREEMENT NUMBER: DE-FC21-85MC22146

CONTRACTOR: Allis-Chalmers Coal Gas Corporation
P. O. Box 512
Milwaukee, WI 53201-0512
(414) 475-2000

PROGRAM MANAGER: Daniel D. Spanaus

PRINCIPAL INVESTIGATORS: Francis J. Enright
Peter G. Garside
Barry T. Johnson

METC PROJECT MANAGER: Daniel C. Cicero

PERIOD OF PERFORMANCE: September 15, 1985 to March 14, 1988

2. SCHEDULE/MILESTONES:

A multi-phased Reliability, Availability, Maintainability (RAM) program is being conducted at the KILnGAS Commercial Module (KCM). The first phase (RAM I) was completed early in 1986. The second phase (RAM IIA), the subject of this paper, was completed at the beginning of 1987. The third phase (RAM IIB) is now in progress and will be completed by the end of 1987. A fourth phase (RAM IIC) is scheduled to begin in 1988, with completion scheduled for 1989. RAM I, IIA and IIC include plant test preparation, test operation, and results evaluation. RAM IIB focuses on extended results evaluation and long-lead engineering for the RAM IIC program.

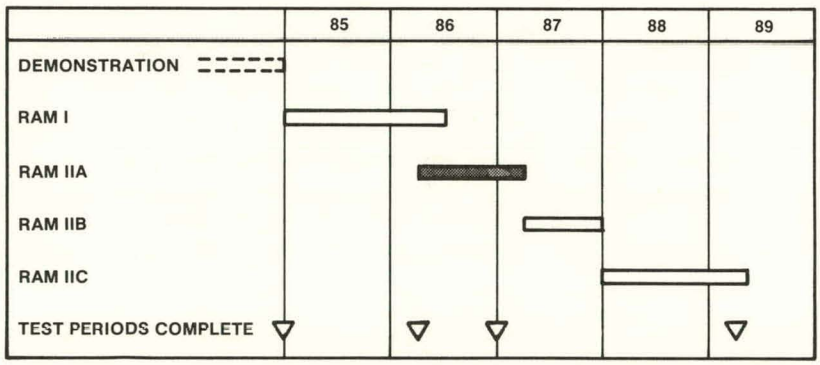



Figure 1. KILnGAS RAM Program Schedule

3. OBJECTIVES:

The overall RAM program objective is to operate the KILnGAS Commercial Module to obtain sufficient data and experience to verify process performance expectations and to provide a basis for commercial offering. Specific objectives for RAM IIA were as follows:

- Improve plant availability.
- Operate at 30 percent carbon in gasifier ash while in the biflow mode of operation.
- Determine plant carbon losses.
- Operate at 75 percent of design production rate.
- Determine constraints that limit gas production rates.

4. BACKGROUND STATEMENT:

The KILnGAS process uses a ported and pressurized rotary kiln to produce fuel gas from coal, suitable for use in combined-cycle power generation plants.

Development of the process began at Allis-Chalmers in 1971. Demonstration and testing is being performed in a 600 ton-per-day plant (KILnGAS Commercial Module) located on the site of the Wood River Station of Illinois Power Company in East Alton, Illinois. (Refer to Figure 2.)

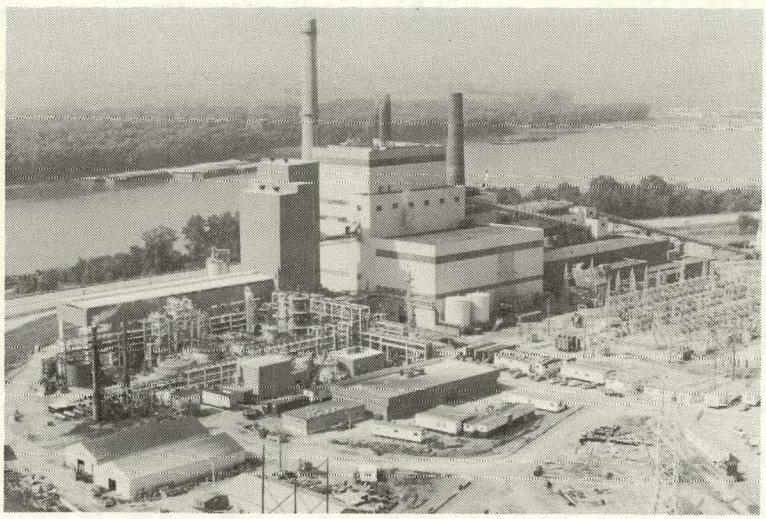


Figure 2. KILnGAS Commercial Module

Construction of the KILnGAS Commercial Module was completed in 1983 and initial demonstration, using Illinois coal, was completed in 1984. Results of the work completed in 1984 are discussed in one reference (Garside, March 1986), and the results of RAM I are discussed in the other (Garside, October 1986). The RAM IIA program was funded by the following:

U.S. Department of Energy
State of Illinois
Central Illinois Light Company
Illinois Power Company
Monongahela Power Company
Ohio Edison Company
Potomac Edison Company
Union Electric Company
West Penn Power Company

The KILnGAS process was conceived to produce fuel gas from coal in large-capacity units suitable for utility-scale operation. In a commercial application, the KILnGAS system would be the fuel source in an integrated combined-cycle power plant. Studies were recently conducted with Utility Power Corporation and Kraftwerk Union to evaluate both a first commercial and a mature KILnGAS-based combined-cycle power plant using low-temperature gas cleaning technology. Results of these evaluations, based on the use of Kraftwerk Union's gas turbines, show that a mature KILnGAS-based IGCC plant in the late 1990's will use one gasifier and two gas turbines, will produce over 400 MW of electric power, and will have heat rates in the low 8000 Btu(HHV)/kWh range. Further work has shown that a first KILnGAS-based combined-cycle power plant could approach 400 MW, and would have one gasifier and two gas turbines, with a heat rate under 9000 Btu(HHV)/kWh.

The gasifier (Figure 3) is a ported and pressurized rotary-kiln. Coal is introduced into the uphill end of the gasifier (from the left in the illustration). As the coal moves through the gasifier it is progressively dried, heated, devolatilized, and gasified. Ports in the shell allow controlled injection of steam and air under the tumbling bed of coal and char. Description of the KILnGAS reactor and the KILnGAS Commercial Module can be found in the references (Garside, March 1986).

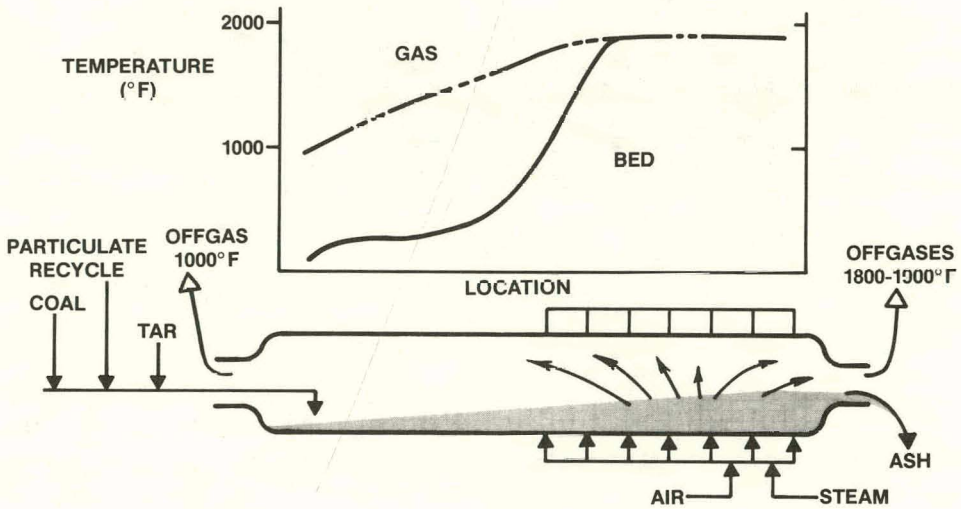



Figure 3. Gasifier Schematic

The earlier Demonstration and RAM I programs provided a significant basis for proceeding with the RAM IIA program. The following are highlights of the findings and accomplishments which formed that basis:

- The gasifier biflow function was demonstrated.
- Tar and particulate recycle were a routine part of plant and process operation.
- Agglomerated ash is produced in the form of ash balls at higher carbon conversion levels.
- Ash ball production can be controlled.
- The plant operated at 30 percent carbon in the gasifier ash in the counterflow mode while meeting other operating parameter goals of 270 lbs air/million Btu gas, 3.8 to 1 air:steam ratio, and 150 Btu/scf gas heating value.
- Gas production at 60 percent of plant design rate was achieved, although gas production capacity was limited by the capability to deliver sufficient air and steam to the gasifier.
- Gasifier seal integrity was demonstrated and operation was routinely carried out at rated gasifier pressure.
- The rotary-lock coal feed routinely supported operation.
- Dust entrainment was higher than desirable in the coal-feed buffer-gas exhaust.
- The continuous ash pressure letdown system performed well and did not contribute to operating delays.
- The ash-discharge system did not adequately handle agglomerates, and was the greatest source of operation delays.
- The gasifier air and steam port, using the trap configuration, was demonstrated.
- Discharge-end gas heat recovery was demonstrated; however, corrosion was produced during down times.
- Quality of recovered tar was inconsistent due to contamination with particulates.
- Wastewater quality was inconsistent due to contamination with tar.
- Sulfur removal at design efficiency was routinely achieved with the Stretford process.
- Liquor was entrained into the product gas from sulfur removal.
- Operation during the Winter season was achieved.

5. PROJECT DESCRIPTION:

The RAM IIA phase of the program included both preparations for and execution of the RAM IIA test, which transpired in the Fall of 1986.

To meet RAM IIA objectives and to overcome shortcomings observed during earlier operations, inspections, repairs, and modifications were carried out on select equipment. Highlights of this preparation work were as follows:

- Coal-feed locks were refurbished and modified to control dust carryout.

- Gasifier brick lining was replaced with castable refractory in ported zones to correct weaknesses in the brick keying.
- Gasifier seals were inspected, and the buffer steam supply was upgraded to improve reliability.
- Sixty additional ports were activated on the gasifier to increase capacity. Various port valve tests were added.
- Particulate recycle leg was modified to correct dust carryover into gas quench, which had produced inconsistent tar quality.
- Ash-discharge grinders were modified to improve reliability.
- Heat-recovery tubing was repaired and tube heating was added to control downtime corrosion.
- Mist eliminator was added to control carryover from the Stretford absorber.
- Piping and vessel internals were modified to improve wastewater quality.
- Test equipment was added to evaluate gasification of plant maintenance residuals.

RAM IIA testing was performed from October to December of 1986, in accordance with the test plan. Following a shakedown period, the plant was operated under three conditions to evaluate conversion and capacity performance.

## 6. RESULTS AND ACCOMPLISHMENTS:

The RAM IIA test was completed with a cumulative on-stream factor of 59 percent for the entire 70-day test period. By comparison, RAM I had an on-stream factor of only 30 percent. The specific goal for the test was 60 percent. The ash agglomerate crushing equipment, located under the discharge end of the gasifier, accounted for over 80 percent of the total outage during the test period. Equipment durability and accessibility for maintenance were the primary sources of total downtime. The configuration of the crushing equipment handled agglomerates produced. (Refer to Figure 4.) However, the equipment was not sufficiently durable to continually handle ash agglomerates for an extended period.

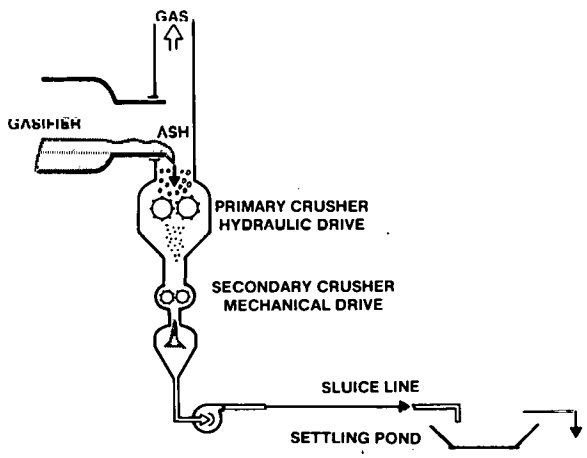



Figure 4. KCM Gasifier Ash Discharge

To compensate for this equipment limitation, gasifier operating conditions were adjusted to minimize ash ball production. This was done by maintaining the gasifier ash carbon content at about 30 percent rather than down at 15-10 percent, and by decreasing the air-to-steam ratio and lowering the upper operating temperature limit in the two ported zones nearest the ash discharge of the gasifier. The process control achieved its needed results and the final 26 days of the test were carried out at an 80 percent on-stream factor. However, the down side of this operating control was an expected slightly poorer measured gasification performance, and necessary deferral of process testing at highest conversion levels and best performance conditions.

The gasifier was operated at three conditions, which provided process data as shown in Table 1.

Table 1. RAM IIA Test Operating Condition

| | R2.5 | R2.6 | R2.7 |
|---|---|---|---|
| Coal (lb/hr) Ill. No. 6 | 32,000 | 22,500 | 40,300 |
| Air (lb/hr) | 68,200 | 54,800 | 85,000 |
| Steam (lb/hr) | 24,200 | 15,500 | 28,700 |
| Gas (MM Btu/hr) | 239 (59%) | 192 (47%) | 323 (79%) |
| Air:Steam Ratio | 2.8 | 2.3 | 2.96 |
| Air:Gas Ratio (lb/MM Btu) | 285 | 285 | 323 |
| Carbon in Gasifier Ash (%) | 32 | 29 | 44 |
| Heat & Mass Balance Period | 72-hour | 32-hour | 35-hour |

Operating experience during the earlier RAM I phase, as well as our process forecasts, indicate optimum air-to-steam ratios of 4-to-1 and air utilization of 270 lb per million Btu of gas. The RAM IIA operation was slightly poorer for reasons discussed above. However, the second test objective was met; i.e., operation at 30-percent carbon in the gasifier ash while in the biflow mode of operation.

The third test objective was to quantify process and plant carbon losses. In particular, the carbon loss due to solids entrainment out with the gas on the discharge end was to be determined. Table 2 summarizes carbon loss data.

Table 2. RAM IIA Test Carbon Loss Summary

| | |
|---|---|
| 7.0% | Gasifier Ash |
| 5.0% | Discharge-End Particulates |
| 1.5% | Vent Gases |
| 1.5% | Wastewater |
| 5.0% | Unaccounted For |

The particulates entrained from the discharge end are collected in the cyclone, heat-recovery boiler, and a venturi scrubber. (Refer to Figure 5.)

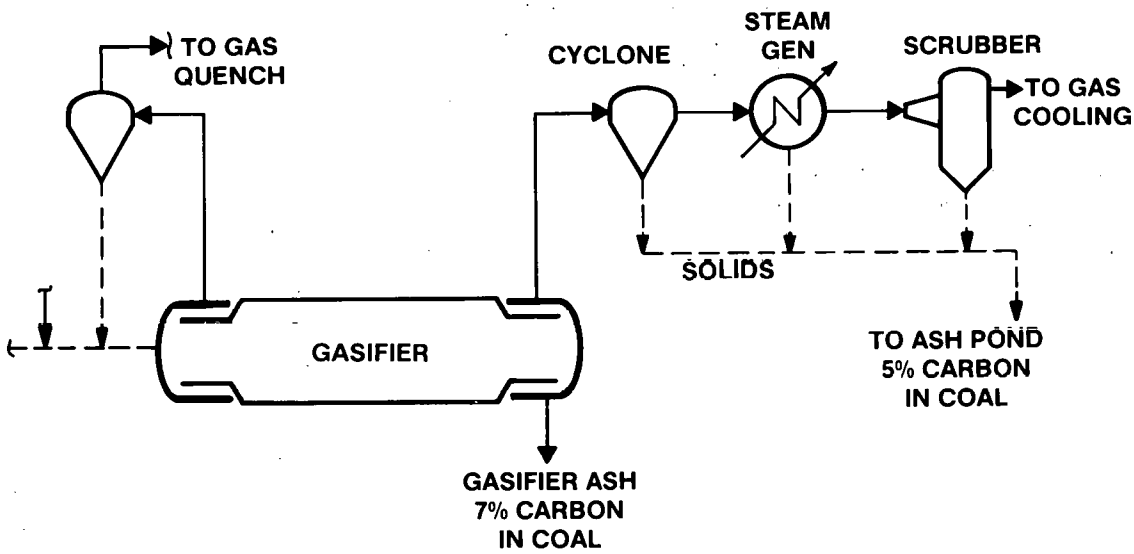



Figure 5. Gasifier and Discharge-End Solids Discharges

Overall data collected during the test indicate that discharge-end particulate carbon losses, at full capacity, may go as high as 7 percent of the carbon in the coal.

At present, overall carbon balances are showing a general bias of 5 percent less carbon out than entering the plant. Further evaluation of data and test methods is in progress.

The fourth objective was to increase plant gas production to at least 75 percent of design capacity. One test (Condition R2.7) was run at 79 percent of design capacity. Various equipment limitations prevented good steady-state operation; however, equipment and control improvements made during the test allowed the plant to achieve over 90 percent of design capacity prior to final test shutdown.

The primary capacity constraint concerned the gasifier port valves, which turn off and on to control air and steam flow underbed to the coal/char bed. These solenoid-actuated valves tended to intermittently stall in a closed position at high capacities, which limited the total flow of air and steam to the gasifier. Figure 6 schematically shows the position of the port valve within the porting system on board the gasifier.

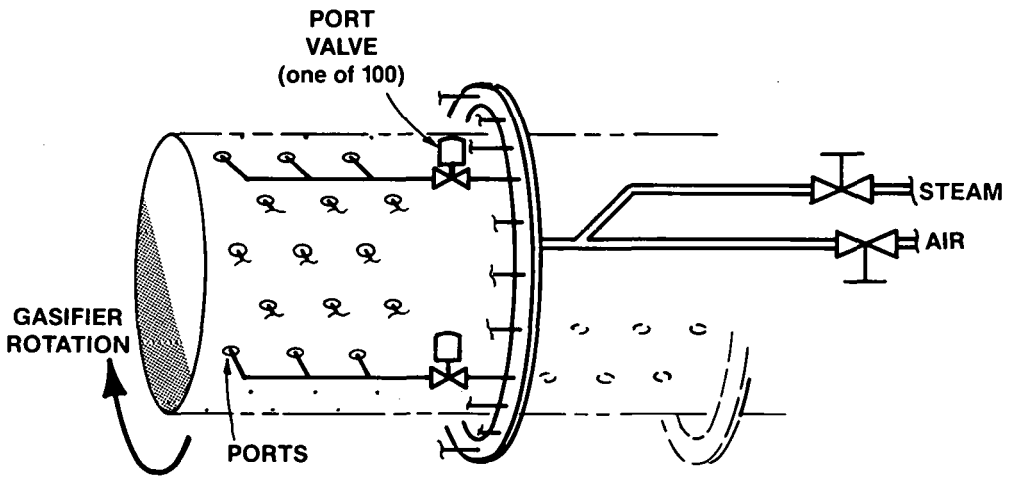



Figure 6. Gasifier Air and Steam Porting

The second most significant capacity constraint involved the gas-cooling system. Below 75 percent of design capacity, gas cooling was satisfactory. However, above that, gas cooling decreased.

In addition, the ash-discharge grinding operation must be considered a capacity constraint, although a process workaround temporarily prevented it from being a constraint.

Modifications to the coal-feed locks and the buffer-gas system worked well, and coal dust carryout measured in the buffer-gas exhaust was within original design specification.

The particulate recycle modifications also were successful, and tar quality was stabilized at the desired low-quantity of particulates. Wastewater modifications successfully controlled the intermittent contamination of wastewater with tar.

The gasifier seals continued to perform to expectations and the buffer steam supply was brought to the desired level of reliability.

The heat-recovery tube heating controlled corrosion during down times, as indicated by a corrosion test meter. Minor piping modifications are needed, however, to simplify operation.

The mist eliminator, added to control liquor carryout from the Stretford absorber, functioned as intended. However, inadequate temperature control of gas entering Stretford resulted in intermittent unacceptable foaming and additional carryout.

7. EVALUATION OF FUTURE POTENTIAL PLANS:

The RAM IIA test showed:

- Ash agglomerate crushing equipment durability is not adequate; redesign of the system is planned.
- The number of air/steam ports on the gasifier (290 ports active versus 580 originally installed) is adequate to achieve full design capacity. However, further port valve modifications are planned to allow proper process operation at full design capacity.
- Discharge-end particulate carbon losses are forecast at 7 percent of carbon in the coal at full capacity. It is planned to recover and recycle those particulates.
- Final gas cooling is not adequate at high capacity. Improvements in contacting performance and the liquor cooler for low-temperature operation are also planned.

The primary activities for the current RAM IIB program include evaluation and reporting of RAM IIA test results, long-lead engineering associated with items discussed above, evaluation of commercial forecasts, and redefinition of demonstration needs based on current status. A follow-on RAM IIC program is planned to begin at the end of this year, with a three-month operating program planned for the beginning of 1989.

8. REFERENCES:

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J. S. Deacon and R. M. Thomas, 5-15-85, The Application of KILnGAS Technology to the Gasification of Petroleum Coke, Publication No. 820-00030.

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# EVALUATION OF A CERAMIC CROSS-FLOW FILTER IN A BENCH-SCALE GASIFIER

1. CONTRACT NUMBER: DE-AC21-84MC21338

CONTRACTOR: Westinghouse Electric Corporation
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CONTRACTOR PROJECT MANAGER: David F. Ciliberti

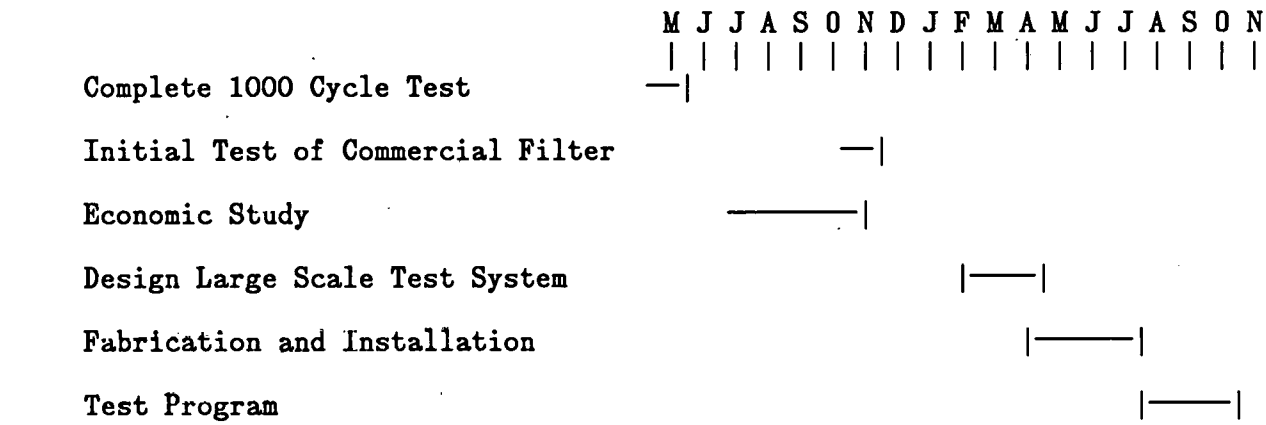
PRINCIPAL INVESTIGATORS: John H. Meyer
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METC PROJECT MANAGER: Randall J. Dellefield

CONTRACT PERIOD OF PERFORMANCE: April 1984 - November 1987

SCHEDULE/MILESTONES:

86-87 Program Schedule




3. OBJECTIVES:

The Department of Energy is currently supporting a program that will aid in the development of cross flow filtration technology as applied to combined cycle power generation with coal gasification. The stated overall goal is to gain information on both the operational and economic feasibility of the implementation of cross flow filtration in various gasifier options. Most recently the focus has been on demonstration of reliable operations of newly developed "commercial" scale filter elements in single and multiple element tests at elevated temperatures and pressure.

4. BACKGROUND STATEMENT:

In previous DOE sponsored programs the cross flow filter has been demonstrated to be a superior hot gas filter in both pressurized fluid bed combustion and coal gasification applications (Ciliberti 83, 86). Efforts described in this paper include the results of an economic study in which implementation of cross flow filter technology was shown to give mid 1986 first year Costs of Electricity (COE) in the range of 116 to 121 mills/kwh for a range of gasifier technologies. Also included in this report are experimental results of a 1000 cycle test program in which recent modifications in filter fabrication techniques were shown to improve the mechanical properties of a 6x6x2 inch filter. Subsequent testing of a single large element fabricated in the same manner demonstrated excellent filter properties but failed mechanically after about 42 hours of operation. Finally, we discuss current efforts to conduct HTHP testing on eight large elements simultaneously in order to generate more meaningful statistics on the mechanical properties of the elements.

5. PROJECT DESCRIPTION:

This DOE cross flow filter development program being carried out by Westinghouse is intended to obtain information on the operational and economic feasibility of applying the cross flow filter to coal gasification power generating systems. The program in place calls for three general areas of effort to reach these goals. The first area of work is to conduct a small, bench-scale test program at METC where the cross flow filter was operated in an actual gasification system. This relatively short duration test program was intended to offer "proof of concept" in the application rather than a detailed data base of operating experience. The second area of effort involves experimental and theoretical efforts aimed at the development of design principles and data that are thought to be lacking, but needed for scale up calculations. For the cross flow filter this task primarily dealt with the development of sound methods for scaling up the blowback system from single element data to the multi-element designs. The third area of effort was directed at using scale-up algorithms to arrive at conceptual designs and costs for full size filter systems for various gasification technologies.

While the majority of these goals have been met and are reported (Ciliberti, 86), the project has recently been modified in order to allow the test and development of larger and more reliable filter units. This effort includes a longer term test of recently improved small filters, initial testing of a single large element and a large scale test of a multi element - multi module system.

6. RESULTS/ACCOMPLISHMENTS:

The following section provides a brief summary of results and accomplishments from this program's recently active elements: the economic study, the 1000 cycle test, and the first test of a single large filter element.

The third technical task comprising the original program was an economic analysis that originally included estimates of capital and operating costs for the following systems using the cross flow filter: air blown Lurgi fixed bed, the oxygen blown KRW fluid bed gasifier and the oxygen blown Texaco entrained bed gasifier. Later in the task a fourth option was analyzed. It consisted of an air blown KRW gasifier.

The three contractors participating in this family of programs and DOE came to a consensus for a consistent design basis upon which the study was carried out. Plant size was set at a net 100-MWe combined-cycle gasification system with hot gas desulfurization and a heat rate of 9,000 Btu/kWh.

Using standard EPRI costing procedures the appropriate costs were developed on a consistent basis. The major results of this effort are summarized below in Table 1.

Table 1
Gasification/Cross-flow Filter System Cost Summary

| Gasification System | LURGI | KRW/$O_2$ | TEXACO | KRW/Air |
|---|---|---|---|---|
| Mid '81 Capital, $1000 | 198,226 | 201,342 | 201,185 | 191,273 |
| Mid '81 1st. yr. COE, Mills/kWh | 94.7 | 94.2 | 94.2 | 90.8 |
| Mid '81 Capital, $1000, Texaco Cool Water/Selexol | | | 239,194 | |
| Mid '81 1st. yr. COE, Mills/kWh, Texaco Cool Water/Selexol | | | 110.4 | |
| Mid '86 Capital, $1000 | 210,912 | 214,228 | 214,061 | 203,514 |
| Mid '86 1st. yr. COE, Mills/kWh | 121.6 | 120.8 | 120.6 | 116.2 |

Several points of major importance emerged from the economic analysis.

- Hot gas cleaning with the cross flow filter offers a very large economic incentive for all systems studied. Compared with cold gas cleaning systems such as the Texaco Cool Water Selexol case cited, this advantage was on the order of 15% for both capital costs and COE.

- The cross flow filter hot gas cleaning system applied to each gasifier system gave rise to filter designs that were very compact, manageable, reasonable and consequently economically attractive. The units were typically housed in pressure vessels 7 ft in diameter and 20-25 ft long.

- Differences among the cases studied were negligible with the exception that the KRW air blown case appeared 4 to 5% better.

- Because the gas filtration is carried out on high pressure fuel gas, rather than flue gas (as with PFBC), the hot gas cleaning system costs are a small fraction of the COE so that considerable uncertainty can exist in the gas cleaning costs and it can still be concluded that it is economically attractive to pursue the technology.

The costing effort included a sensitivity analysis of two important parameters, the filter operating face velocity and the assumed plant availability. Filter face velocity was varied from 6 to 12 ft/min about the design basis of 10 ft/min and was found to impact COE in a minor way resulting in COE changes of only plus or minus 0.1 mills/kWh. Availability, on the other hand resulted in roughly a 20% change in COE when varied from 65 to 85%.

1000 CLEANING CYCLE TEST:

Two significant issues have remained unresolved throughout previous developments with the filter. the first of these is the tendency of the filter element delaminate in service. This form of mechanical failure typically results in a small, but detectable, increase in dust penetration. The second issue arises from the fact that virtually all testing to date has been relatively short in duration leaving unanswered questions about the long term pressure drop stability of the filter.

The goal of the test segment, therefore, was to determine the effectiveness of recently improved filter fabrication techniques in preventing filter failure by delamination, and to carry out a large number of cleaning cycles to determine the long term pressure drop behavior of the filter during its conditioning period.

The test program carried out was quite simple in design and consisted of testing a single 6 x 6 x 2 inch flanged cross flow filter fabricated by the Coors Porcelain Company. This element had been fired at high temperature, machined, slip coated and refired at high temperature. The slip coating had been applied to the flange and back wall of the element in an attempt to prevent the initiation of cracks thought to evolve into delamination. The element tested had an effective filter area of approximately 1.1 $ft^2$. The testing was carried out in the Westinghouse HTHP simulator rig at temperatures ranging from 1400-1450°F and at a pressure of 150 psig. Filter velocity during the first third of the program was maintained at 13 ft/min and was lowered slightly to 11 ft/min during the remainder of the test. The dust fed to the system was a

redispersed PFBC ash from the Curtiss Wright plant and had a mass mean diameter of about 10 $\mu$ and a standard deviation of 2.03. The dust loading presented to the filter was relatively constant throughout the test at a level of about 3000 ppm. The pulse jet cleaning parameters utilized throughout the vast majority of the testing consisted of 0.2 second pulses from a reservoir charged to 400 psig. The average pulse nozzle flow at these conditions was approximately 0.75 lbm/sec, and typically gave rise to internal filter element pressure rises of 4 to 6 psi over ambient.

SUMMARY OF TEST RESULTS:

During the test period, which ranged from 3/13/86 to 5/14/86, 1012 cleaning cycles and 1100 pulses were obtained on the test filter with no sign of mechanical failure in the test element. During this time there were 29 actual test days during which we accumulated about 250 hours of dust feeding/filtration time at pressure and temperature. The typically 12 hour test day format was chosen for both facility manning convenience and to expose the test element to a large number of start up/shut down thermal cycles.

The actual test data are summarized in Figure 1 which presents a plot of the filter baseline pressure drop as a function of cleaning cycle number.

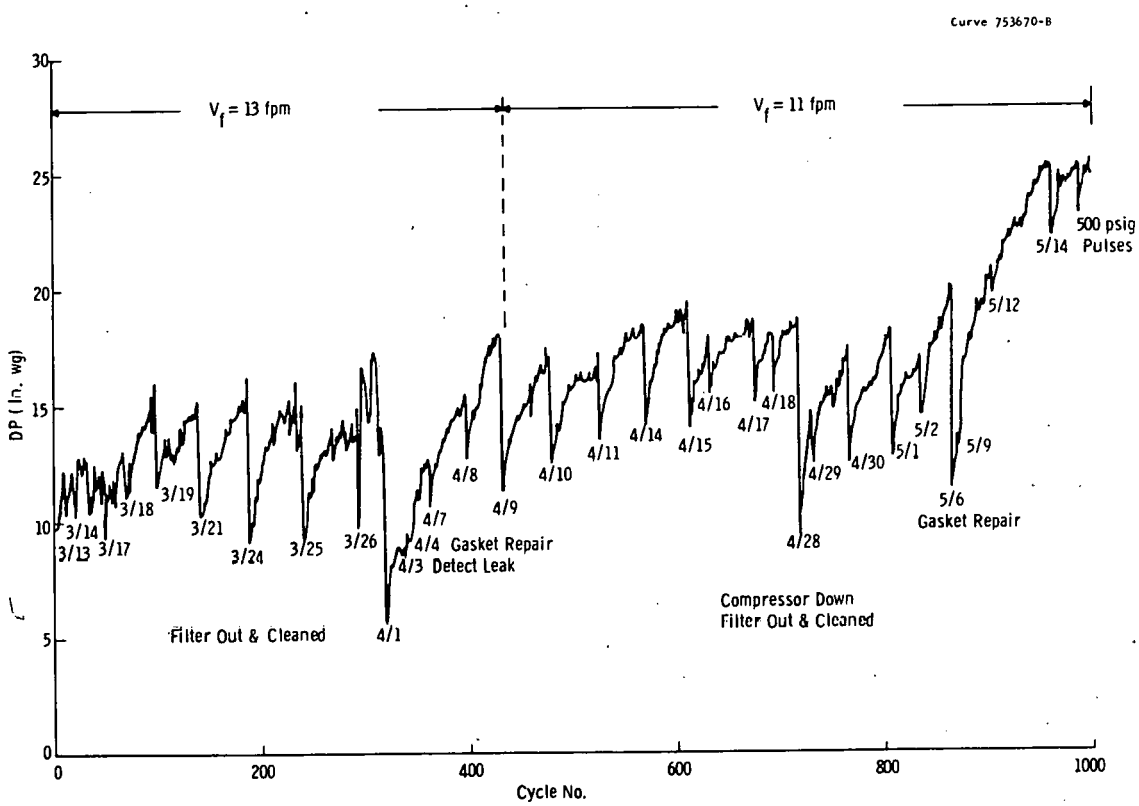



**Figure 1 - Baseline Pressure Drop as Function of Cleaning Cycle**

The baseline pressure drop (or residual filter pressure drop) is the observed filter pressure drop measured immediately after a cleaning pulse has been administered to the element. As can be seen in Figure 1, there was a pronounced diurnal variation of the baseline pressure drop in which gradual increases were observed to occur throughout the test day, but which would virtually disappear upon restart of the test on the succeeding day. This effect is not specific to the cross flow filter and has been observed on several other types of filters tested in the facility. We do not, however, have a satisfactory explanation for the behavior.

CONCLUSIONS:

The entire test segment was completed with no mechanical failure of the improved filter element and based on this highly successful test campaign we have drawn the following important conclusions regarding the cross flow filter and its performance.

- Demonstrated the ability of the twice fired, slip coated (2XC) filter element to withstand a large number of cleaning cycles (1012) which included 1100 pulse jet cleaning puffs.

- The element was capable of withstanding pulse jet cleaning internal pressure rises to 10 psig without failure.

- Demonstrated the ability of the element to withstand more than 30 start up/shut down thermal cycles with no damage. This is quite remarkable given that the start up heating rate is very high going from ambient to 800°F in a matter of a few minutes.

- Filter efficiencies for PFBC dust are 99.9+%, except when seal leaks occurred. The two seal leaks experienced are believed to be related to a fault in the specific test jig being used and was made worse by a rounded corner surface on the filter mounting flange.

- It appears that even after 1000+ cycles the filter is not completely conditioned and stable. We believe that this situation is somewhat confused by the fact that the element was removed and externally cleaned at points throughout the test.

LARGE SINGLE ELEMENT TEST PROGRAM:

In conjunction with a closely related DOE sponsored program, both Coors and GTE made several large (12 x 12 x 4 inch) Cross Flow Filters available for testing. It was decided that a delay in the schedule of the associated project could be beneficial, as it allowed the HTHP proof test of a single large element in the bench scale test facility at the Westinghouse R&D Center. To carry out this testing some relatively minor modification to the test rig had to be carried out, and the pressure housing previously used in this project at the METC test site had to be retrieved and installed in the R&D Center's system.

Over the next month a total of 43 hours of actual "dust feed" test time was accumulated at operating conditions of T = 1500°F, P = 150 psig, filter velocity = 3.2 ft/min and a dust loading of 4400 ppm. Throughout the test period pulse jet cleaning was accomplished using a 500 psig source pressure with a 1/2 inch tube pulse nozzle that gave pulse flows of about 2.5 lbm/sec and generated internal filter pressure rises of 2 to 4 psi.

After a relatively short initial conditioning period the filter operation became quite stable. Figure 2 presents a typical pressure drop trace for the test period. Typical pressure drop cycles as for the test period are summarized follows:

at hr 10 -------7 to 20 in wg in 35 min
at hr 20 -------6.5 to 20 in wg in 28 min
at hr 30 -------8 to 20 in wg in 23 min
at hr 40 -------9.5 to 20 in wg in 17 min.

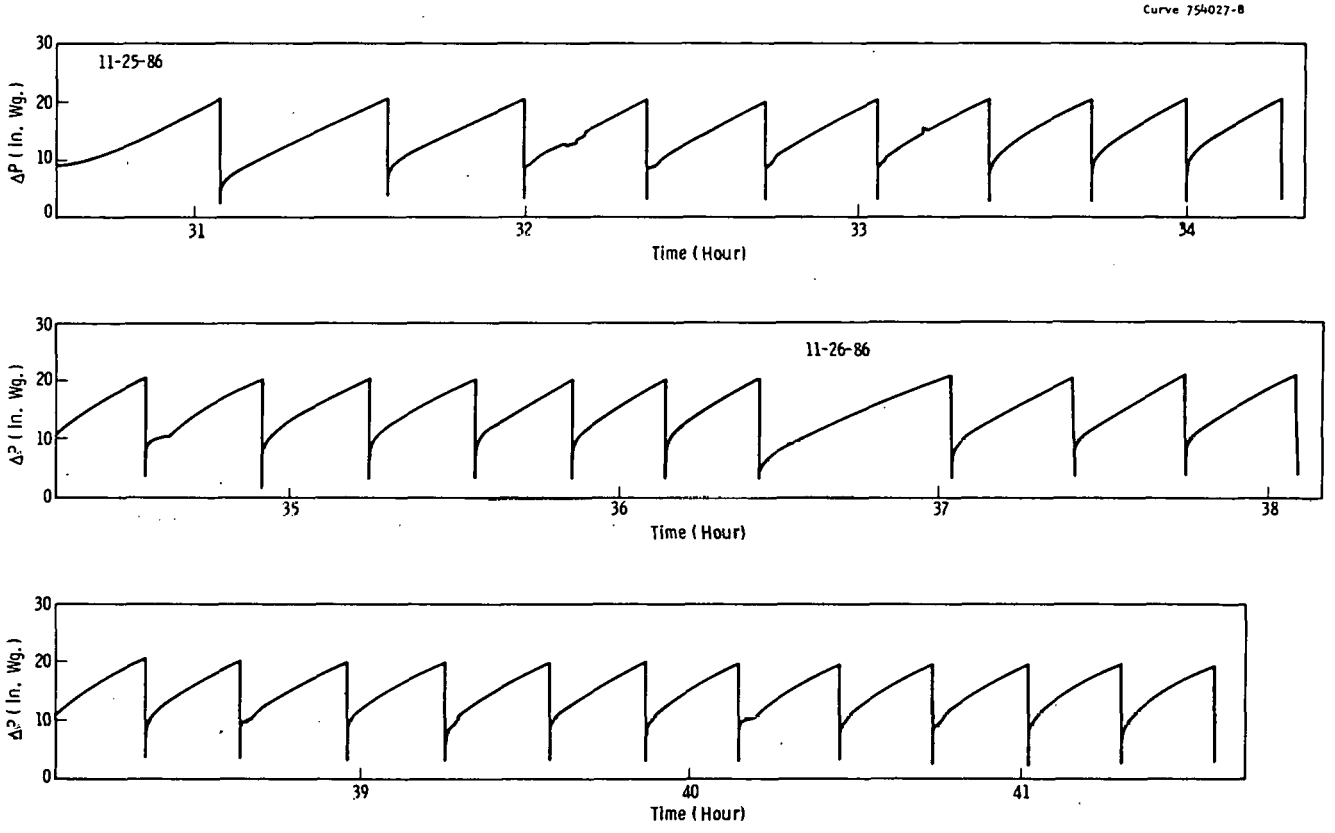



Fig. 2 – Cross flow filter WCXF12-3 ( 11/23 - 24/86) ; T = 1500°F, P = 150 psig, $V_f$ = 3.2 ft/min., $C_{in}$ = 4492 ppm, $\eta$ = 99,95 %

At hour 42 a significant failure was experienced immediately after a pulse cleaning. It was subsequently determined that a delamination had occurred and that a roughly 2 by 6 inch piece had broken from the back corner of the filter. At the time of failure, the element had been exposed to 15 thermal cycles (start up/shut downs) and had 97 cleaning pulses administered to it.

The reason for this failure is not known since the nature of the fracture surfaces indicated good bonding (as good as the parent material), however, it was subsequently determined that the front sealing face had a significant bow in it, and that may have tended to pull or split the element apart when subjected to clamping forces.

## 7. EVALUATION OF FUTURE POTENTIAL WORK:

Recently the contract has been modified to allow relatively large scale test of an array of up to eight full scale filter elements configured such that four modules, each having two elements would be tested. This testing is of great importance for two reasons. First to gain operating information on a relatively large (statistically significant) number of elements all in similar service, and secondly to determine the effects on cleaning of multi-element modules and of several modules operating in parallel.

Recently, as part of the existing program, the filter manufacturers have improved element fabrication techniques yielding small elements with better mechanical properties. It is necessary to examine how well those techniques have translated to full scale elements. Conducting a multi-element test program on the commercial scale elements is a cost effective manner in which to confirm these improvements in a statistically sound way prior to commitment of large scale testing in an actual PFBC system. In a similar fashion, these tests are needed to confirm the pulse jet cleaning process associated with multi-element module operation, as well as parallel operation with several modules.

Westinghouse located suitable test facilities at the KRW Energy Systems, Inc. hot gas cleaning test facility sited at their Waltz Mill pilot plant shown schematically in Figure 3. As a result of several in-depth meetings with KRW technical and contractual personnel, a test program was developed that includes the following features:

- Testing of eight elements, two on each of four modules.
- Test condition nominally set at 1500°F, 150 psig with mass flows of 1.25 lbm/sec and dust loadings from 1 to 5000 ppm.
- A total of 200 hours of testing with plans for a 100 hour continuous run.
- Use of an existing KRW pressure vessel to house the test assembly and to provide ash capacity for up to a 100 hour continuous run.

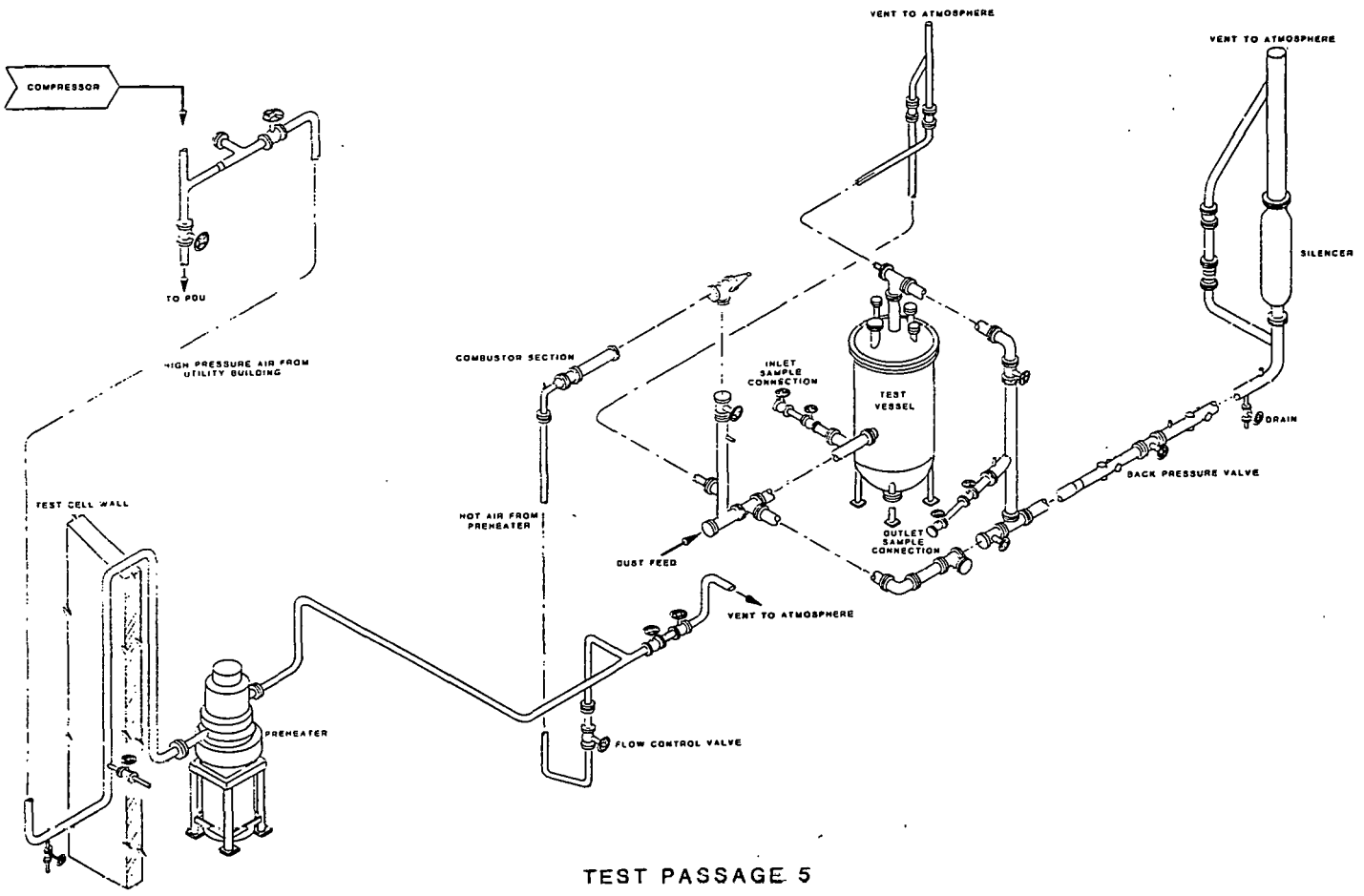


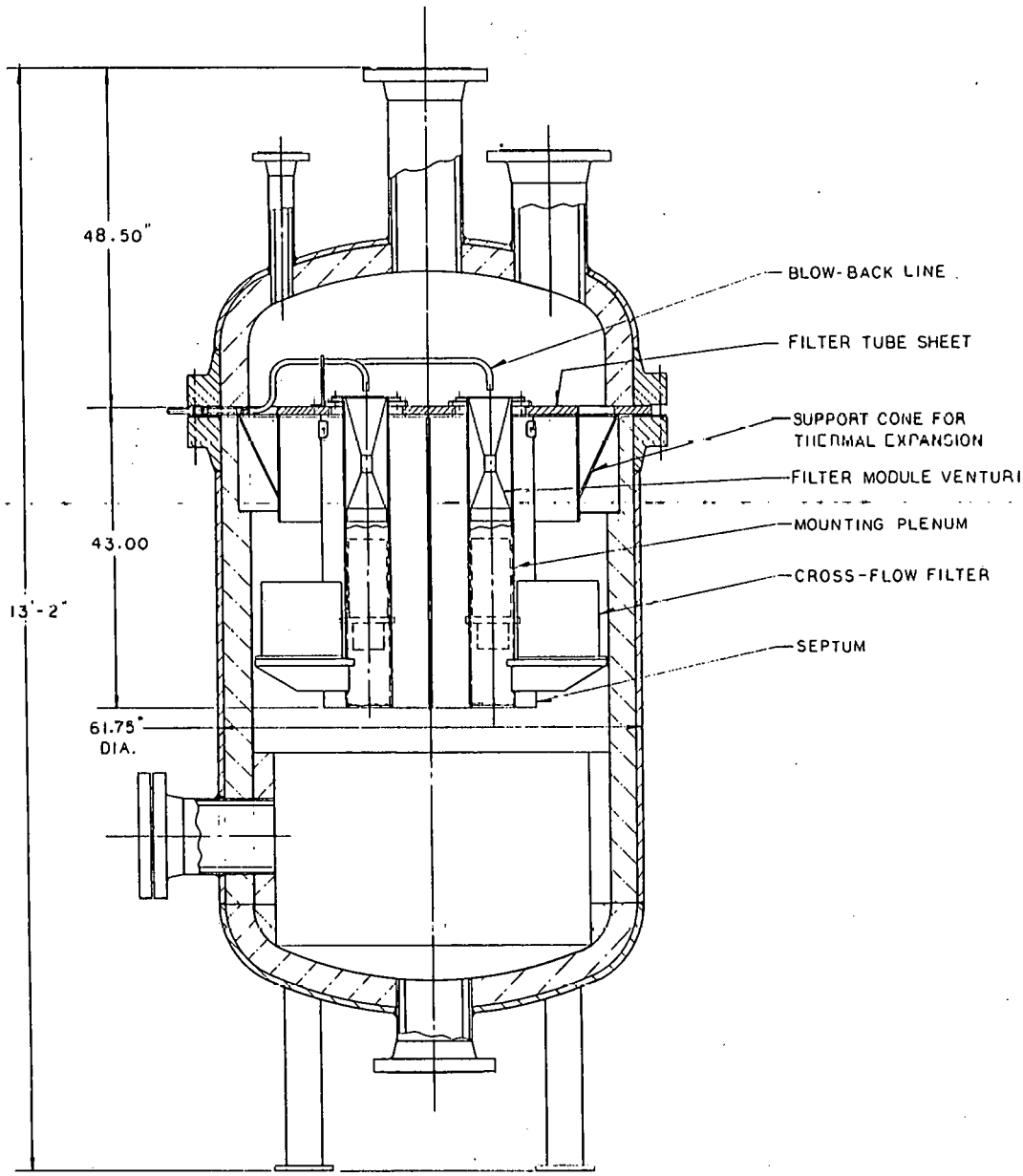

Figure 3 - High Temperature, High Pressure Hot Gas Cleanup Facility

KRW will provide the test services under subcontract to Westinghouse, while Westinghouse will provide equipment consisting of the filter modules and elements and tube sheet (Figure 4), a dust injection system and a system to boost the passage gas temperature from its current 800°F level to the 1500°F level required for test. Additionally, Westinghouse will provide engineering support for test plan development, actual testing, data analysis and program management and control.

8. REFERENCES:

Ciliberti, D. F., et al, Hot Gas Cleanup Using Ceramic Cross Flow Membrane Filters, Final Report under DOE Contract No. DE-AC21-79ET15491, Dec. 1983.

Ciliberti, D. F., et al, Performance Evaluation of a Ceramic Cross Flow Filter on a Bench-Scale Coal Gasifier, Proceedings of the Sixth Annual Contractors Meeting on Contaminant Control In Coal Derived Gas Streams, June 1986, DOE/METC-86/6042 (DE86001088)




CROSS-FLOW FILTER

**Figure 4 - Schematic of 4 Module, 8 Filter Cross Flow Test Unit**

ENVIRONMENTAL ENGINEERING AND ANALYSIS

1. CONTRACT NUMBER: DE-AC21-84MC21046

CONTRACTOR: Radian Corporation
8501 Mo-Pac Blvd.
P. O. Box 201088
Austin, TX 78720-1088
(512) 454-4797

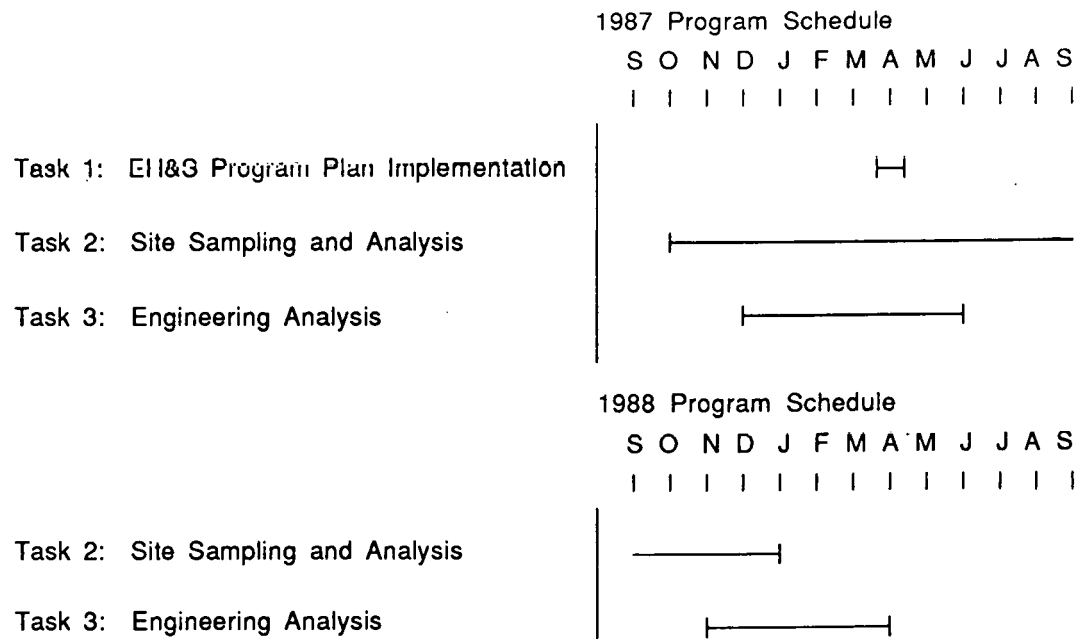
CONTRACTOR PROJECT MANAGER: Dr. Gordon C. Page

PRINCIPAL INVESTIGATORS: Dr. Gordon C. Page
Dr. F. Douglas Skinner
Mr. Dennis P. Raden

METC PROJECT MANAGER: Dr. Wen-Shou Liou

CONTRACT PERIOD OF PERFORMANCE: September 30, 1984 to September 30, 1988

2. SCHEDULE/MILESTONES:




3. OBJECTIVES:

The primary objective of this project is to obtain and evaluate environmental data for advanced synthetic fuel technologies and associated pollution controls (such as gas cleanup and wastewater treatment).

4. BACKGROUND STATEMENT:

The Department of Energy's Morgantown Energy Technology Center (METC) has as one of its primary missions the development of an information and database on the engineering and environmental aspects of advance technologies for the conversion of relatively abundant energy sources (e.g., coal) to clean fuels for a variety of end uses, including substitute natural gas, gas turbine fuel, and the like. A number of synfuels technologies have been or are receiving support from METC, including the Mountain Fuel Resources and KRW gasification technologies, and several raw gas and aqueous waste cleanup technologies. Activities within the present project are designed to obtain and evaluate environmental and process data for these and other synfuels technologies of interest to DOE.

5. PROJECT DESCRIPTION:

Work under the environmental Engineering and Analysis Project has been organized into three separate task areas, each of which is described in the following paragraphs.

TASK 1: ENVIRONMENTAL, HEALTH, AND SAFETY PROGRAM PLAN IMPLEMENTATION

The EH&S Program Plan Implementation Task involves the preparation of a number of Topical Reports on a variety of subjects. Most of the reports document stream characterization work performed at the KRW PDU near Madison, Pennsylvania, or utilize the results of a wastewater treatability study performed earlier under the joint sponsorship of METC, the Gas Research Institute, and the Environmental Protection Agency using wastewater from the same site. The remaining report presents the result of a zero-order trace element distribution model developed as a tool for the estimation of the trace elements present in the discharge streams from the Great Plains Gasification Project.

TASK 2: SITE SAMPLING AND ANALYSIS

The major activities under Task 2 include conducting sampling and analysis programs at several synfuels facilities to obtain environmental, health, and safety data. Testing is being conducted at four test sites. Test Site 1 activities were conducted at the Mountain Fuel Resources PDU in Salt Lake City, Utah. Site 2 involved testing during a test of in-bed sulfur capture using dolomite at the KRW PDU. Work under Test Site 3 will be performed later this summer, again at the KRW PDU, and will emphasize the characterization of streams around a zinc ferrite hot sulfur control module. Test Site 4 has not yet been selected.

Each sampling and analysis program involves the development of a site-specific test plan, the actual on-site testing, sample analyses, and the preparation of a topical report documenting plant operations during the test, presenting all analytical and QA/QC results, and evaluating the

applicability of the data for use in scale-up and process simulation/modeling. The data are used to develop additional Engineering Evaluation Reports as part of Task 3.

TASK 3: ENGINEERING ANALYSIS OF PILOT-, PDU-, AND COMMERCIAL-SCALE DATA

This task requires the development of process flow diagrams, pollutant distributions, engineering models, heat and material balances, data correlations, and scale-up relationships; evaluation of environmental control processes; and the consolidation and evaluation of EH&S data obtained from the sampling and analysis programs conducted under Task 2. A topical report is to be prepared for each of the Task 2 test sites which presents the results of an engineering evaluation of the EH&S data, including heat and material balances; formation,distribution, and fate of pollutant species; analysis of process performance; representative data sets; and quality assurance procedures and results.

Hot Lime Reactor Subtask

An important ongoing activity is the assessment of the technical and economic viability of an alternate approach--Hot Lime Reactor (Hot/CaD)--for removing reduced sulfur species from hot (1500-1800°F) raw fuel gases produced from coal gasification. This approach varies from other hot gas desulfurization technologies in that it uses a "throw-away" sorbent (e.g. dolomite or limestone) rather than a "regenerable" sorbent for capturing reduced sulfur species.

6. RESULTS/ACCOMPLISHMENTS:

TASK 1: ENVIRONMENTAL, HEALTH, AND SAFETY PROGRAM PLAN IMPLEMENTATION

All six of the Topical Reports planned for Task 1 have now been completed (Castaldi 1985, Skinner 1985, Skinner and Hayes 1985, Skinner and Page 1985, Thomas et al. 1987, and Trofe 1985). The results of the wastewater treatability studies show that the wastewater from the KRW PDU is amenable to treatment by steam stripping for the removal of dissolved gases such as ammonia; cyanide precipitation; and biological oxidation for the removal of the low levels of organics and residual ammonia present in the wastewater.

TASK 2: SITE SAMPLING AND ANALYSIS

Reports have been submitted to METC presenting the data obtained during the sampling and analysis programs conducted during the low-sulfur Utah bituminous coal test at the MFR PDU (Site 1) and a high-sulfur Pittsburgh No. 8 coal test (with and without dolomite injection) at the KRW PDU (Site 2). These reports form the basis for the development of the engineering evaluation reports under Task 3.

TASK 3: ENGINEERING ANALYSIS OF PILOT-, PDU-, AND COMMERCIAL-SCALE DATA

An engineering evaluation report has been prepared based on environmental data obtained at the MFR PDU (Skinner et. al. 1987). Sulfur and nitrogen species distributions were developed. As expected, most of the coal sulfur appeared in the raw gas as hydrogen sulfide with lesser concentrations of carbonyl sulfide. About 20% of the coal nitrogen was present in the raw gas as ammonia and hydrogen cyanide. Gas cleanup could be achieved by any of a number of conventional technologies. Process condensate treatment processes would be similar to those that have been proposed for other non-tar producing gasifiers. The gasifier slag/ash and scrubber solids would be classified non-hazardous under RCRA. Another activity under Task 3 was the preparation of a Topical Report which presents a discussion of four process concepts which upgrade and/or use dirty fuels (Raden et al. 1987).

Hot Lime (Hot/CaD) Reactor Subtask

Hot raw fuel gas (1500-1800°F) enters the bottom of the Hot/CaD reactor and flows counter current to the calcium-based sorbent. Sized dolomite or limestone (approximates 1/2 to 3/4 inch particle size) is fed to the top of the reactor, and a spent dolomite/limestone is removed from the bottom of the reactor via lock hoppers. The reduced sulfur species are removed from the raw fuel gas by reacting with the sorbent by the following reactions:

$$CaCO_3 + H_2S \leftrightarrows CaS + H_2O + CO_2 \quad (1)$$

$$CaCO_3 + COS \leftrightarrows CaS + 2\ CO_2 \quad (2)$$

$$CaCO_3 + 1/2\ CS_2 \leftrightarrows CaS + 1\ 1/2\ CO_2 \quad (3)$$

OR

$$CaO + H_2S \leftrightarrows CaS + H_2O \quad (4)$$

$$CaO + H_2S \leftrightarrows CaS + CO_2 \quad (5)$$

$$CaO + H_2S \leftrightarrows CaS + 1/2\ CO_2 \quad (6)$$

The form of the calcium compound which reacts with the reduced sulfur species is dependent on the calcination reaction shown below.

$$CaCO_3 \leftrightarrows CaO + CO_2 \quad (7)$$

This reaction is primarily a function of the Hot/CaD operating temperature and the partial pressure of $CO_2$.

The reactor bottoms (spent sorbent) may be recycled to the gasifier to supplement the limestone used for in-bed desulfurization and to increase

calcium utilization. The reactor bottoms not recycled to the gasifier would be routed to an oxidizer to convert the CaS to $CaSO_4$. Depending on the overall plant configuration, the oxidizer may be a rotary kiln or a circulating fluidized-bed combustor.

Figure 1 is a block flow diagram of an IGCC plant using the KRW gasifier and the Hot/CaD reactor. In-bed desulfurization is performed in the gasifier by introducing dolomite. The raw fuel gas exits the gasification unit at 1675°F and enters the Hot/CaD reactor. The Hot/CaD reactor removes the reduced sulfur species and a portion of the particulates carried over from the gasification unit. Since the removal of particulates and alkali metals from the desulfurized gases may be required to meet gas turbine fuel specifications, the Hot/CaD exit gases are quenched to 1200°F to condense the vapor phase alkali metals. The gas is then filtered to remove the suspended particulate matter to produce a clean gas turbine fuel.

The spent dolomite (CaS*MgO) is crushed to -1/8 inch size and sent to a circulating fluidized-bed oxidizer to convert the CaS*MgO to $CaSO_4$*MgO which can be safely landfilled as a non-hazardous waste. The oxidizer also treats solids from the hot gas filter and requires a small amount of coal. This oxidation step is very beneficial in recovering the energy value of the gasifier ash and spent dolomite. In fact, approximately 7% of the gasifier coal feed energy content is recovered from the gasifier ash and spent dolomite.

The estimated performance of the IGCC plant depicted in Figure 1 is summarized in Table 1.

Figure 2 shows how the coal sulfur content is removed. Greater than 97% of the sulfur contained in the coal feed is captured by the dolomite in the in-bed and Hot/CaD desulfurization steps. A $SO_2$ emission level of 0.156 lbs $SO_2$/MMBtu has been predicted which is well below the federal New Source Performance Standard (NSPS).

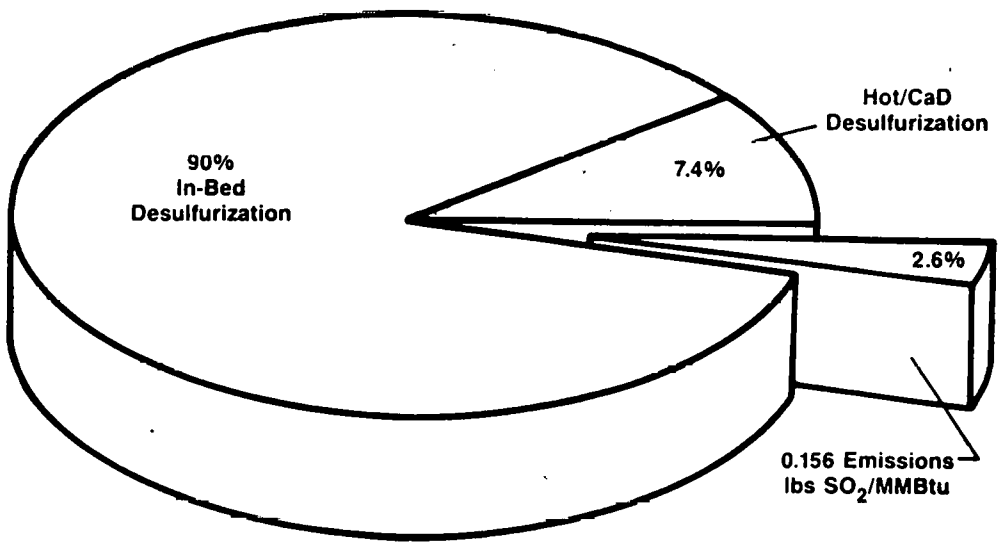



Figure 2. Sulfur Distribution

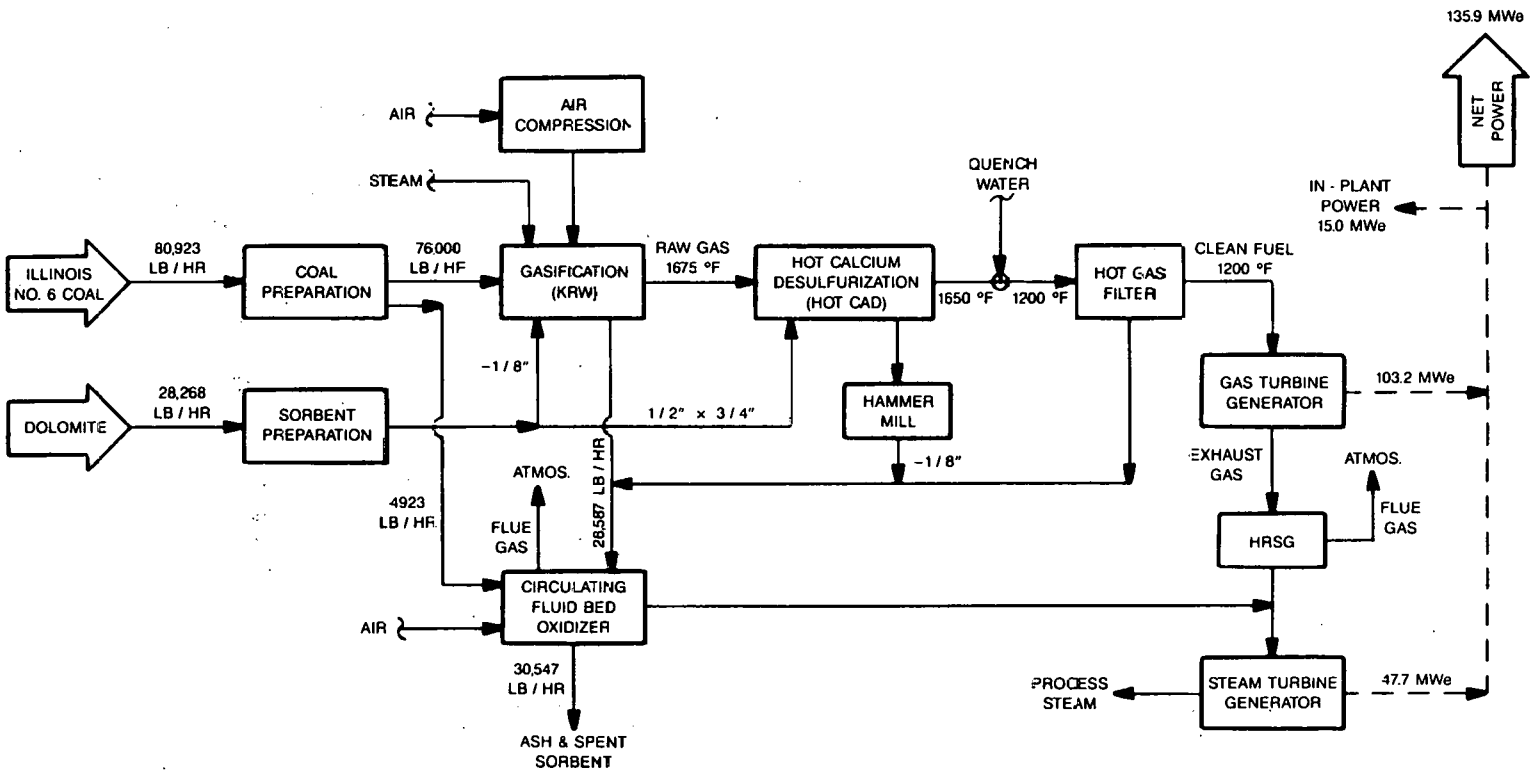



Figure 1. Overall Block Flow Diagram

Table 1. Gasification/Hot Gas Desulfurization System

| | |
|---|---|
| **Gasification/Hot Gas Desulfurization** | |
| Gasifier Coal Feed | 76,000 lb/hr |
| Oxidizer Coal Feed | 4,923 lb/hr |
| Total | 80,923 lb/hr |
| Gasifier Dolomite Feed | 25,508 lb/hr |
| Hot/CaD Dolomite Feed | 2,760 lb/hr |
| Total | 28,268 lb/hr |
| **Power System** | |
| Gas Turbine New Power | 103.2 MWe |
| Steam Turbine Net Power | 47.7 |
| Plant Power Consumed | 15.0 |
| Net Plant Power Output | 135.9 MWe |
| **Overall System** | |
| $SO_2$ Emissions | 0.156 lb/$10^6$ Btu |
| $SO_2$ Captured | 97+% |
| Net Heat Rate | 7285 Btu/KWH |
| Overall System Efficiency (Coal-->Power) | 46.8% of Coal HHV |

The coal-to-power energy efficiency of the KRW-Hot/CaD IGCC configuration is estimated at 46.8%. This is a significant improvement over the first generation IGCC systems, which use commercially-proven cold-cleanup technologies, and conventional coal-fired power plants. Depending on the gasification and cleanup technology used, the first generation IGCC systems generally have a coal to power efficiency of 35% to 40% and conventional coal-fired power plants with flue gas desulfurization have coal to power efficiencies around 36%. The increase in the efficiency for the KRW-Hot/CaD IGCC configuration is primarily due to three factors:

- Elimination of the efficiency losses associated with fuel gas quenching.
- Recovery of ash and spent sorbent energy content.
- Production of a "throwaway" material ($CaSO_4$) rather than a product (sulfur) which has fuel value.

Not only the coal to power efficiency is favorable for a KRW-Hot/CaD power plant, the total construction cost and levelized cost of electricity are also attractive. For example, a nominal 135 MWe KRW-Hot/CaD IGCC facility will have a total construction cost of $1240/KW and a

levelized cost electricity of 56 mills/KWH, compared to $1560/KW and 70 mills/KWH for a conventional coal-fired power plant.

The applicability of the Hot/CaD process to other gasification technologies is limited primarily by the amount of moisture and carbon dioxide in the gas. Excessive amounts of moisture and carbon dioxide will force the equilibria to the $CaCO_3$ form (see Reaction 1). When operating at temperatures high enough to fully calcine the dolomite, a high moisture content will force the equilibria to the CaO form (see Reaction 9).

Table 2 shows the estimated desulfurization performance for several gasification technologies using the Hot/CaD process. With the exception of the oxygen-blown Lurgi Dry Ash gasifier, all of the gasification technologies considered have the potential to use the Hot/CaD process to capture more than 95% of the sulfur.

The following summarizes some of the features of the Hot/CaD process.

- o It uses a technically and economically viable hot gas desulfurization process.
- o It is an abundant and inexpensive sorbent (limestone, dolomite).
- o Sorbent regeneration is not required.
- o It is applicable to most gasification technologies.
- o In-bed desulfurization is not necessary.

In conclusion, hot gas desulfurization and particulate removal greatly enhances the coal to electricity conversion efficiency while meeting the environmental constraints. As with other hot gas desulfurization concepts, the Hot/CaD process shows promise for being commercially viable in the "Gasifier Island" power generation concept.

7. FUTURE WORK:

TASK 1: ENVIRONMENTAL, HEALTH, AND SAFETY PROGRAM PLAN IMPLEMENTATION

All planned activities under Task 1 have been successfully completed. No future work is anticipated at this time.

TASK 2: SITE SAMPLING AND ANALYSIS

The Site 3 Sampling and Analysis program is scheduled for August 1987, and will emphasize characterization of streams around the zinc ferrite hot sulfur capture module which has been installed at the KRW PDU. Testing will be performed during both desulfurization and regeneration modes.

TABLE 2. APPLICATION OF HOT/CAD PROCESS TO OTHER GASIFICATION TECHNOLOGIES

| Gasification Technology | Lurgi Dry-Ash | Texaco | BGC/Lurgi Slagger | Shell | High-Temperature Winkler |
|---|---|---|---|---|---|
| Coal | Illinois No. 6 | Illinois No. 6 | Illinois No. 6 | Illinois No. 6 | No. Dakota Lignite |
| Oxidant | 98% $O_2$ | 98% $O_2$ | 98% $O_2$ | 95% $O_2$ | 98% $O_2$ |
| Hot/CaD Operating Pressure, atm | 20.0 | 20.0 | 20.0 | 20.0 | 10.0 |
| Gas Composition @ Hot/CaD Inlet, vol. %[a] | | | | | |
| $CO_2$ | 15.3 | 10.2 | 3.0 | 1.6 | 8.2 |
| $H_2O$ | 50.5 | 17.1 | 12.2 | 2.0 | 9.1 |
| $H_2S$/COS | 0.65 | 1.1 | 1.2 | 1.3 | 0.4 |
| Others | 33.55 | 71.6 | 83.6 | 95.1 | 82.3 |
| | 100.00 | 100.0 | 100.0 | 100.0 | 100.0 |
| Hot/CaD Operating Temperature °F | 1700[b] | 1700 | 1600[b] | 1525 | 1600 |
| Reactive Calcium Form | $CaCO_3$ | $CaCO_3$ | CaO | CaO | $CaCO_3$ |
| % $H_2S$ Exiting Reactor | 0.178 | 0.04 | 0.016 | 0.002 | .0112 |
| % Sulfur Removal | 72.7 | 96.4 | 98.7 | 99.85 | 97.2 |

NOTES: [a]Does not consider the effects of the water/gas shift reaction through the Hot/CaD reactor

[b]Assumes the gasifier outlet gas can be heated to this temperature

Work to be performed for Site 4 under this same task has yet to be defined and approved by the METC COTR. It is possible that in the event of a favorable engineering and economic evaluation of the Hot Lime Reactor Concept under Task 3 that laboratory-scale testing of sulfur removal by this method could be included as Site 4.

TASK 3: ENGINEERING ANALYSIS OF PILOT-, PDU-, AND COMMERCIAL-SCALE DATA

Work has already begun on the engineering evaluation report covering the Site 2 (KRW with in-bed sulfur capture) characterization work. Similar reports will be forthcoming after the results of the sampling and analysis programs for Sites 3 and 4 are available.

The other work remaining to be performed under this task will be the finalization of the engineering and economic evaluation of the Hot Lime Reactor concept.

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Trofe, T. W. 1985. Basis of Design Report of Suspended Solids Removal and Cyanide Pretreatment for Treating Wastewater from the KRW Energy Systems Gasifier PDU. DOE/MC/21046-1803.

1. CONTRACT NUMBER: DE-FC21-86MC10637

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METC PROJECT MANAGER: Leland E. Paulson

CONTRACT PERIOD OF PERFORMANCE: 4/1/86 to 3/31/90

2. SCHEDULE/MILESTONES: Figure 1 presents a chart of the schedule for the initial year of activities on this project. Bench scale studies were initiated under a previous DOE cooperative agreement, and were extended into this project to provide required design and proof-of-concept data.

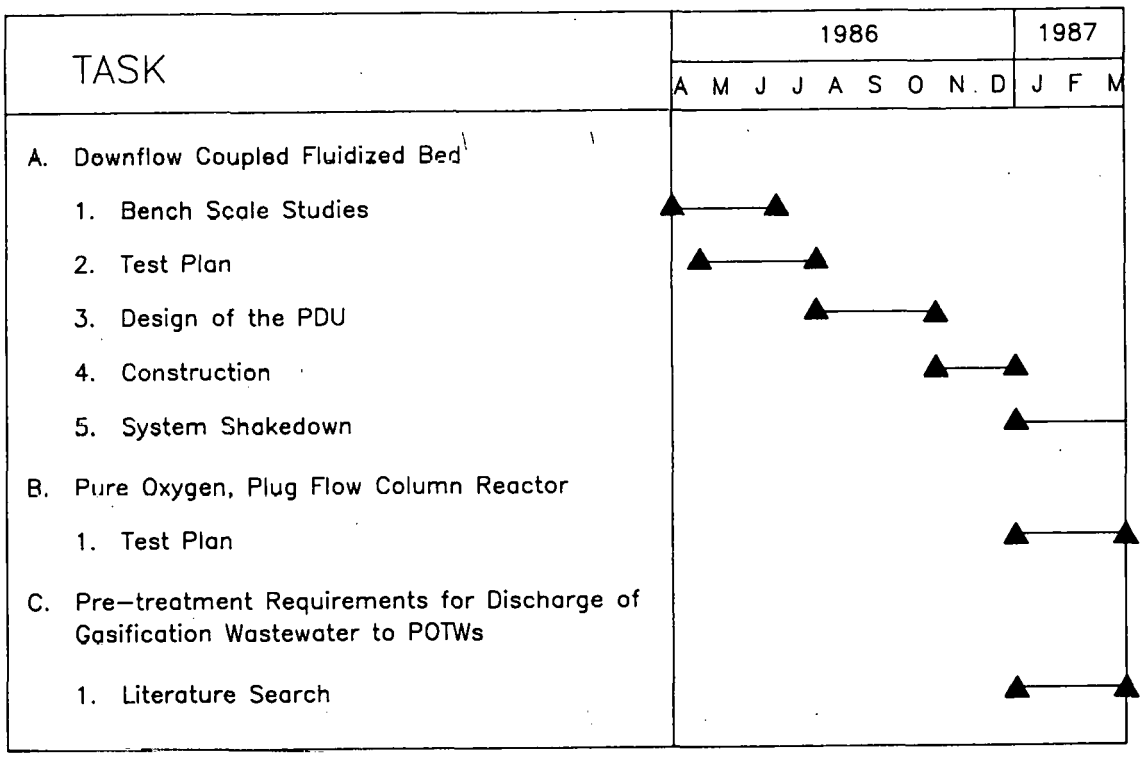



Figure 1. Schedule of activities for project year 1.

3. OBJECTIVES: The principal objective is to expand the scientific and engineering data base on the treatment of gasification wastewater. Efforts are focused on novel methods to achieve the following: 1) combined carbon oxidation/nitrogen removal, and 2) a high-rate biological oxidation reactor. A third effort will examine pretreatment requirements for the discharge of gasification effluents to publicly-owned treatment works (POTWs).

4. BACKGROUND STATEMENT: Synthetic fuels technologies all produce a wastewater that must be treated or reused. Some wastewater streams, particularily certain gasification condensates, are highly contaminated with organic and inorganic compounds. These contaminants include ammonia, thiocyanate, cyanide, phenols, organic acids and numerous other compounds. Treatment scenarios for synfuel technologies with highly contaminated streams often utilize pretreatment by solvent extraction and steam stripping to reduce phenolics and ammonia and acid gases. Following pretreatment, biological treatment is often suggested. Biological treatment is usually less expensive than alternative methods, such as carbon absorption or chemical oxidation. Moreover, biological treatment has the capability to remove organic compounds and ammonia from the wastewater.

Conventional biological treatment processes, such as activated sludge, are subject to poor operation in the presence of toxic compounds, and organic or hydraulic shock loads. Additionally, the low biomass concentrations attainable and the resulting long hydraulic retention times for treatment in the activated sludge process may be economically prohibitive. Improved reactor configurations are needed that can attain high biomass concentrations and are resistant to toxics and other shocks. Fixed-film biological processes typically have much greater stability to toxics and shocks, due to the immobilization of the biomass on support media. Immobilization of the biomass prevents loss (wash out) when growth is inhibited. Additionally, longer solids retention times (SRTs) can be obtained with fixed-film processes, as opposed to suspended growth processes (activated sludge). Long SRTs correspond to slow microbial growth rates. Thus, fixed-film reactors provide a better environment for the establishment of nitrifying (ammonia oxidizing) populations.

Fixed-film reactors of several types have been used, including rotating biological contactors, packed bed columns and fluidized bed columns. Fluidized bed reactors have the following advantages over other biological treatment processes (Andrews 1986, Green 1985):

- o Flow regime approximates plug-flow.
- o Cells are attached and not easily washed out.
- o The beds expand to accommodate gas bubbles or increased biomass (no clogging).
- o High biomass concentrations can be maintained.
- o Good mixing of biomass and substrate.
- o Less susceptible to sudden changes in load or temperature.
- o Low pressure drops across bed (low pumping requirements).
- o Effluent suspended solids concentrations are low.

A specially configured fluidized bed reactor has been tested at the Canadian Wastewater Technology Center (Nutt 1982). This configuration, sometimes called the pre-denitrification process, uses two fluidized beds connected in series. One bed is aerated (oxic), while the other bed is not aerated (anoxic). A conceptual model for the coupled fluidized bed process is shown in Figure 2. This model demonstrates the applicability of this process to wastewaters contaminated with high concentrations of organics and ammonia. This process combines, in a single coupled reactor, three conventionally separated operations, carbon oxidation, nitrification and denitrification. The result is reductions in capital costs, reduced oxygen requirements, and reduced sludge production.

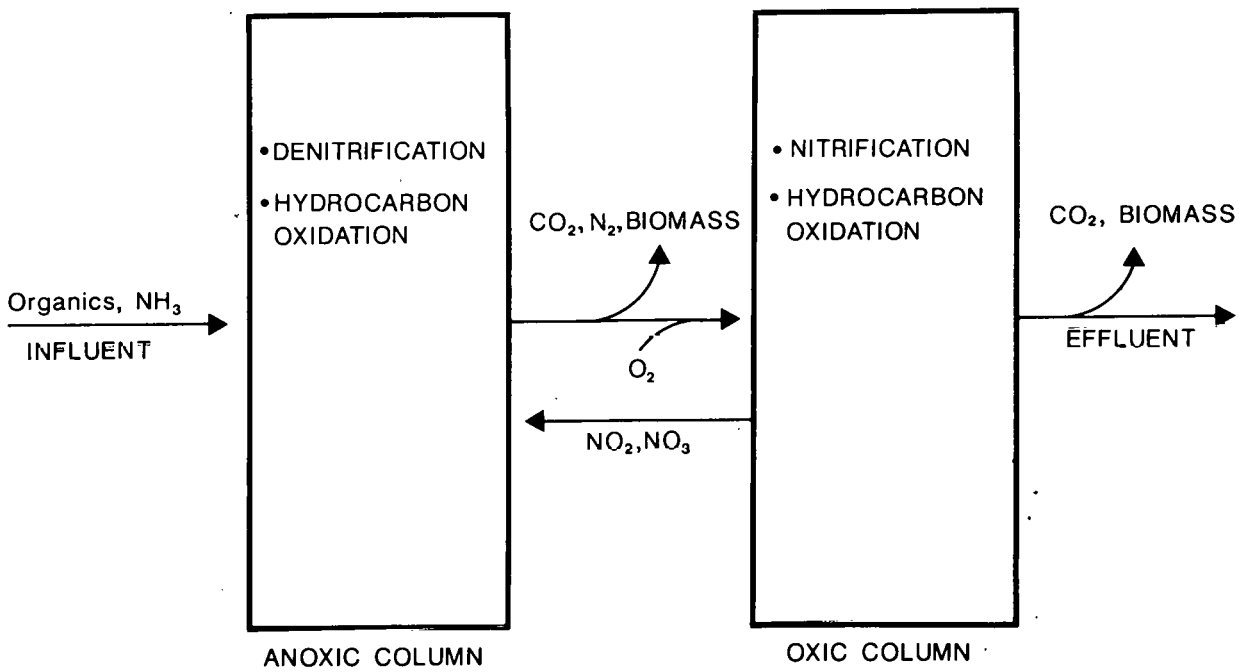



Figure 2. Conceptual model for the biochemical operations in a coupled oxic and anoxic biological reactor.

5. PROJECT DESCRIPTION: To date work has focused on Task A, biological fluidized bed treatment of gasification wastewater. The wastewater used for this research is stripped gas liquor from the Great Plains Gasification Plant near Beulah, North Dakota. Bench scale tests using the conventional upflow fluidization mode, with sand as the media, has demonstrated the applicability of the coupled process for combined carbon and nitrogen removal from SGL. A second bench scale coupled reactor tested a modified fluidization technique. The media used was low specific gravity (less than 1) spheres. Fluidization was achieved by adding the wastewater at the top of the bed, with the media fluidizing downwards. This fluidization method requires less recycle to maintain fluidization than the conventional upflow mode, resulting in energy savings. A process development unit (PDU) has been constructed in the downflow mode for further testing and development of process performance and kinetic data.

6. RESULTS/ACCOMPLISHMENTS: The operating conditions used, and data obtained for each of the bench scale coupled fluidized bed reactors are similar. Therefore, only data from the downflow reactor will be presented. The media used for this reactor was a silicon sphere supplied by 3M Corporation. The specific gravity was 0.4 and the mean size was 0.47 mm in diameter. The columns and clarifiers were constructed of plexiglass. Operations were conducted at room temperature; the pH was controlled between 6.5 and 7.8. The mean hydraulic retention time was 1.06 days with a total reactor volume of 5 liters.

Table 1 shows the mean influent and effluent composition, and removals of various components of the stripped gas liquor. The mean 5 day biochemical oxygen demand ($BOD_5$) for the influent was 1311 mg/l, with an overall removal of 80.5%. Improved performance during the test period, however, resulted in pseudo-steady state $BOD_5$ removals of 90.9%. The mean influent total organic carbon (TOC) content was 690 mg/l, with an overall removal of 73.0%. TOC analyses were not conducted throughout the entire test program.

The mean chemical oxygen demand (COD) influent concentration was 2715 mg/l, with an overall removal of 69.2%. COD removal during steady state was 92.6%. The mean influent ammonia concentration was 1044 mg/l, with an overall reduction of 58.8%. Steady state ammonia reduction was 91.3%. Ammonia removal was complete to nitrogen gases, since nitrite and nitrate were not detected. The concentrations of alkalinity decreased from the influent to the effluent since acid production via nitrification is greater than alkalinity production via denitrification ($2\ H^+/NH_4^+$, $1OH^-/NO_2^-$).

Table 1. Influent and Effluent Stripped Gas Liquor Composition and Removals with the Bench Scale Downflow Coupled Fluidized Bed Reactor

| Constituent[a] | Mean Influent | Mean Effluent | Mean % Removal | Steady-state % Removal |
|---|---|---|---|---|
| Ammonia | 1044 | 430 | 58.8 | 91.3 |
| Nitrate | ND[b] | ND | - | - |
| Nitrite | ND | ND | - | - |
| Alkalinity | 1368 | 567 | 58.5 | - |
| TOC | 690 | 186 | 73.0 | - |
| COD | 2715 | 837 | 69.2 | 92.6 |
| $BOD_5$ | 1311 | 256 | 80.5 | 90.9 |

a. mg/l, except alkalinity (mg/l as $CaCO_3$).
b. ND = not detected.

Figure 3 shows the variations in $BOD_5$ concentrations in the influent and effluent throughout the test period. System acclimation, beginning with diluted feed, is apparent through about day 80. A reactor upset, resulting from a mechanical failure, is evident from day 104 through day 158. Pseudo-steady state is assumed from day 200 through 230.

Figure 4 shows the variations in the influent and effluent chemical oxygen demand (COD) concentrations throughout the test period. The periods of acclimation and upset, noted above, are apparent. Figure 5 shows the variations in ammonia concentrations in the influent and effluent throughout the test period. The effects of acclimation and the mechanical failure, noted above, are also conspicuous for ammonia. Establishment of an active nitrifying population is apparent around day 140. Following the development of an active nitrifying population, improvements in removals of both BOD and COD were noted. These improved removals are due to the presence of nitrate and nitrite. The presence of nitrite and nitrate allowed the anoxic column to become active in carbon oxidation and nitrogen removal.

The results of these bench scale tests have demonstrated the following:

- Removals in excess of 90% for carbon and nitrogen were achieved with stripped gas liquor as the feed.
- From 25 to 70% less flow velocity was required for fluidization with the downflow mode, as opposed to the upflow mode.

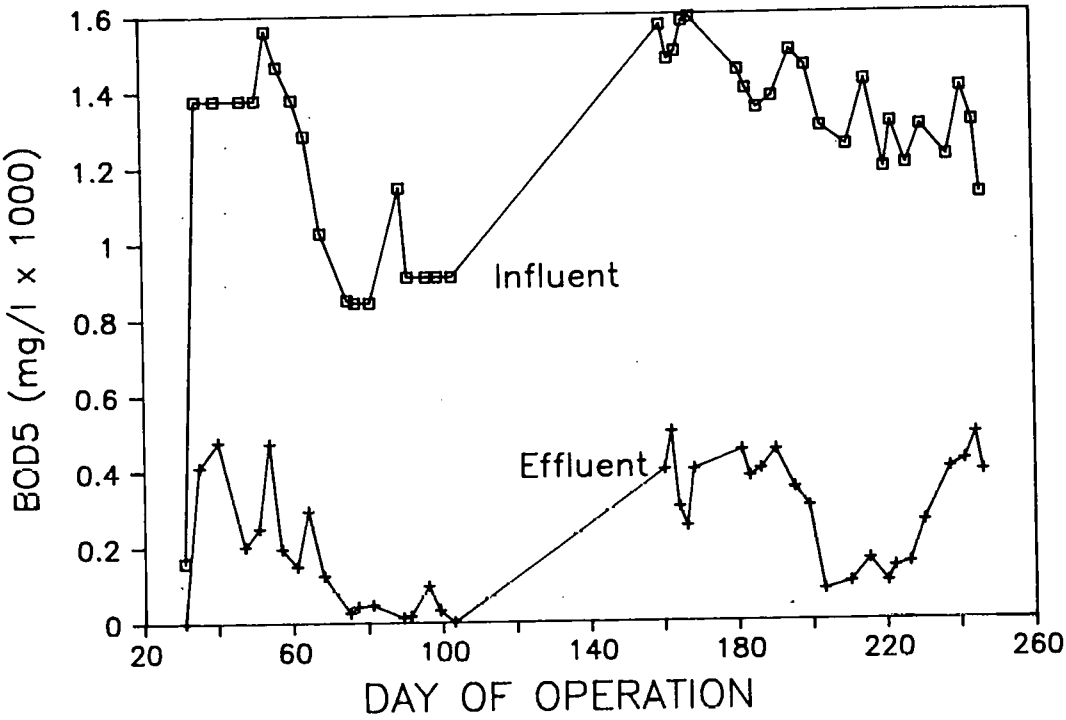



Figure 3. Variations in the $BOD_5$ concentrations in the influent and effluent to the bench scale downflow coupled fluidized bed reactor.

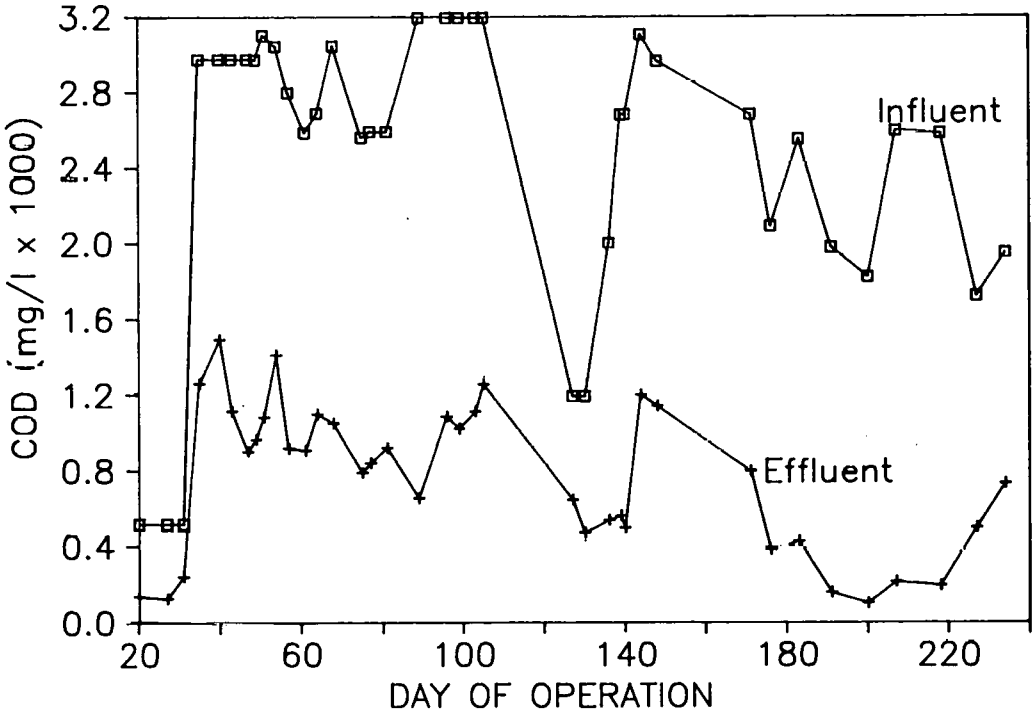



Figure 4. Variations in the COD concentrations in the influent and effluent to the bench scale downflow coupled fluidized bed reactor.

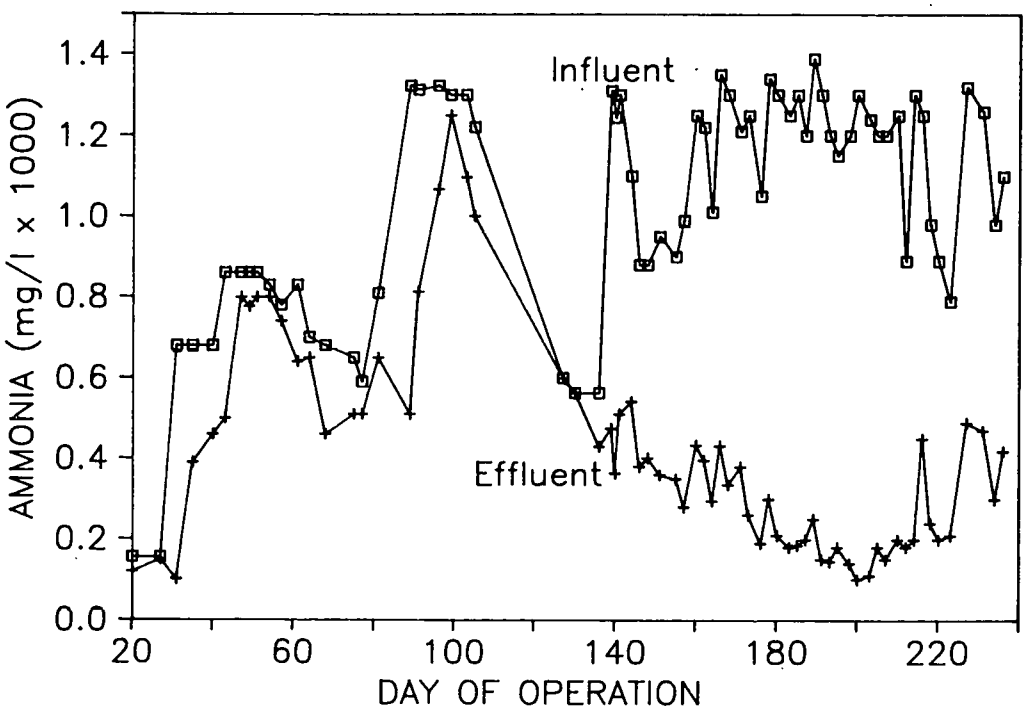



Figure 5. Variations in the ammonia concentrations in the influent and effluent to the bench scale downflow coupled fluidized bed reactor.

The results of these bench scale tests have demonstrated the following:

- Removals in excess of 90% for carbon and nitrogen were achieved with stripped gas liquor as the feed.
- From 25 to 70% less flow velocity was required for fluidization with the downflow mode, as opposed to the upflow mode.
- Stability of the bench scale systems, in terms of sensitivity to changes, was a major problem, which prevented the determination of kinetic parameters. Operations at a larger scale are required.

## 7. EVALUATION OF POTENTIAL FUTURE PLANS:

Based on the promising data obtained in the bench scale research, a process development scale unit (PDU) was designed and constructed. This unit, designed for the downflow mode, is shown schematically in Figure 6. The columns are 2.44 m

(8 ft) in length, constructed of plexiglass, and are equipped with sample ports every 15 cm (6 in). The total volume of the columns is 45 liters. Flow rates to be used will range from about 0.78 liters/hr to 6.3 liters/hr, with resulting hydraulic retention times of 2.4 to 0.3 days.

The unit is equipped with instrumentation for control of pH, temperature, dissolved oxygen concentrations, and fluidization and has back-up systems for air and electrical power. The media to be used for the PDU are ceramic spheres with a specific gravity around 0.7. This media should fluidize at an even lower velocity than the silicon spheres (s.g. 0.4) used in the bench scale research. Recycle will be accomplished with progressing cavity pumps that, since they do not damage biomass, and are capable of constant flows at variable head pressures.

The PDU will be operated at 3 to 4 organic loading rates until steady-state is attained. At steady-state sampling will be performed throughout the bed length resulting in profiles for biomass production and substrate oxidation. Kinetics will then be determined and preliminary economic comparisons will be made between the downflow coupled fluidized bed process and conventional processes.

A second biological treatment reactor will be designed, constructed and operations begin in the next project year. The focus of this bioreactor is high-rate carbon oxidation. The reactor will use a large hydrostatic head to obtain high dissolved oxygen concentrations (Urza 1975). The oxygenated feed and concentrated biomass will be injected into the bottom of a tall column. Treatment of the wastewater will occur as the mass moves up the column in a plug.

## 8. REFERENCES:

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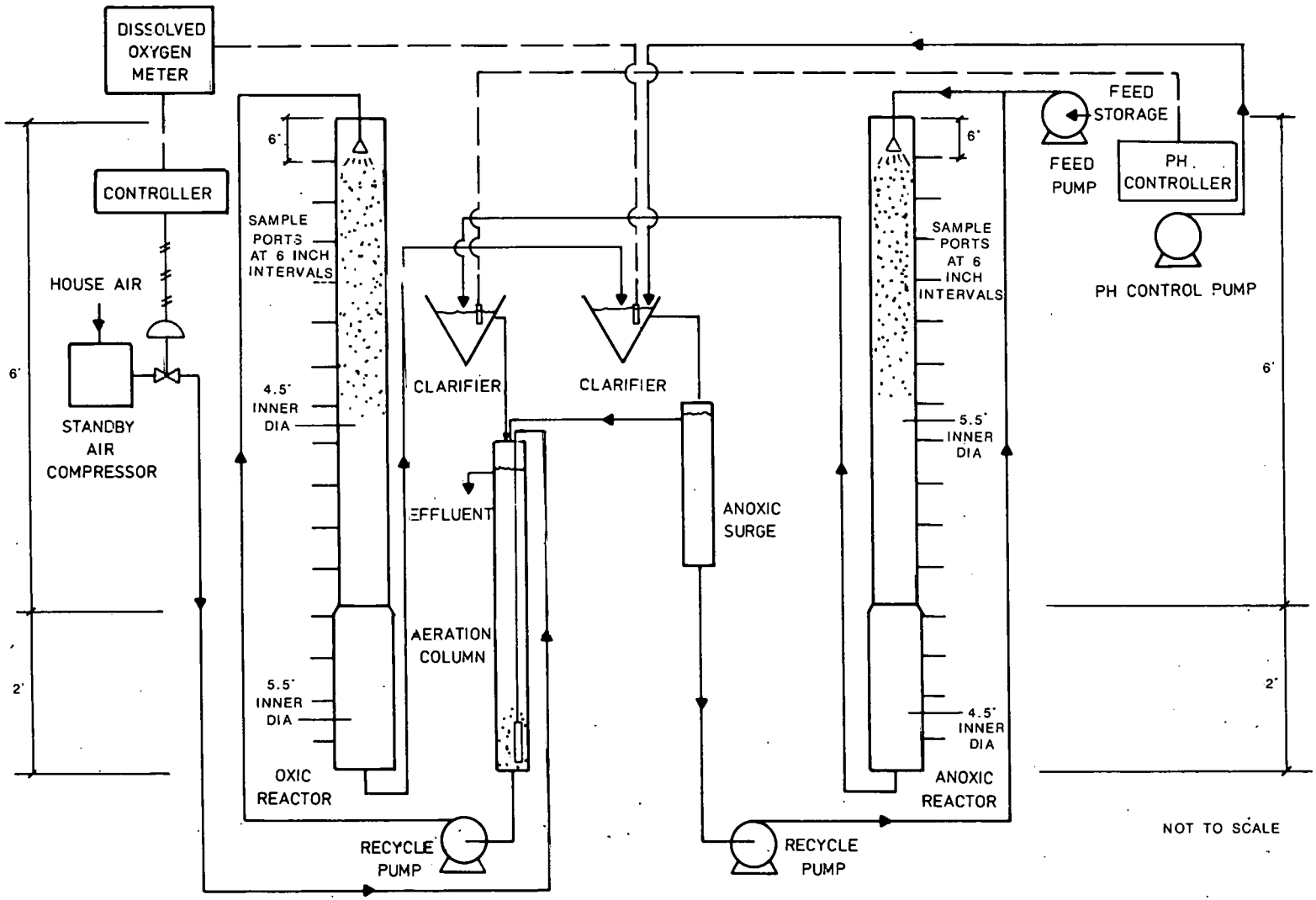



Figure 6. Schematic of the PDU Downflow Coupled Fluidized Bed Reactor.

# A MECHANICAL ANALYSIS OF A CERAMIC CROSS FLOW FILTER

1. CONTRACT NUMBER: DE-AC21-86MC23252

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CONTRACTOR PROJECT MANAGER: David F. Ciliberti

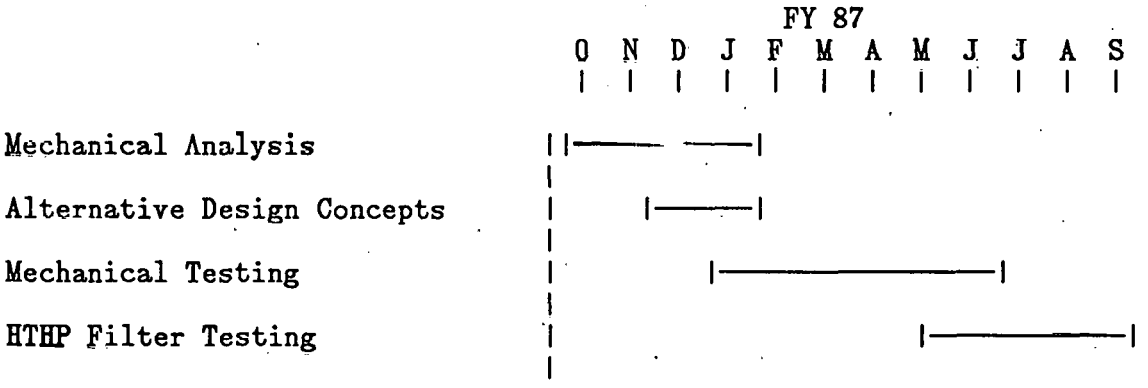
PRINCIPAL INVESTIGATORS: David F. Ciliberti
Thomas E. Lippert
R. N. Kleiner (Coors)

METC PROJECT MANAGER: Randall J. Dellefield

CONTRACT PERIOD OF PERFORMANCE: October, 1987 - April, 1988

2. SCHEDULE/MILESTONES:

Program Schedule




3. OBJECTIVES:

The primary objective of this program is to develop a more fundamental understanding of the mechanical forces exerted on a cross flow filter when in operation so that means can be devised to avoid mechanical failures of the filter and reliability can be improved. The ceramic cross flow filter has been demonstrated to be a superior high temperature and pressure barrier filter suitable for application in both oxidizing and reducing atmospheres, however, a recurrent operating problem has been experienced in virtually all developmental programs to date. This difficulty manifests itself in a tendency of the layered filter to delaminate along the surface formed by two adjacent layers.

4. BACKGROUND STATEMENT:

In the conduct of several developmental programs Westinghouse and Coors have made significant progress in adapting he cross flow heat exchanger to a filtration system. The focus of these programs has been in the development of parameters such as thickness, pore size, porosity and flanging techniques for mounting. In spite of real progress in these areas there has been a persistent history of filter failures in service. We have attempted to explore methods for improved mechanical performance with Coors, however, the structure and focus of previous programs has precluded all but the most preliminary work that is summarized here.

A basis for improvement of the cross flow's resistance to delamination does exist. In the conduct of a recent project Coors personnel undertook a short test program to systematically explore the relative effect of several parameters on the bonding problem. In this effort 12 separate firing runs were made examining the effects of:

- Bonding materials - none, 3 different fluxing clays, a mortar and a slip (dilute suspension of the parent material)
- Weight loading during firing - weighted/unweighted
- Firing temperature - from sinter onset to the melting temperature.

The preliminary conclusions drawn from this work were that higher firing temperatures and the use of a slip infiltrate the back wall of the ceramic body appeared to be the best near term bet for improvements of the bonding and resistance to delamination. It was decided that longer term developmental approaches would include modifications to the mechanical design of the joint between adjacent layers of the body. In subsequent testing of cross flow elements by Westinghouse at the METC gasifier there has been indication of improved delamination resistance for filters that have had a proper application of the slip coating and a high temperature firing schedule.

In another short series of tests conducted at Coors simple test specimens were fabricated and then subjected to different coating and firing regimens in an attempt to correlate these results with observed performance. The results of this work are presented in Table 1 and offer a sound basis for the tenet that mechanical improvements can be made by simple alterations in processing techniques, and that these improvements can be correlated to test results obtained from simple mechanical tests.

The mechanical testing reported in Table 1 was a simple three point bend test on small bars of the filter media. In these tests the bars are supported at either end and than a load is applied at a specific rate to the middle. Since the bar deflects, one surface is placed in tension and is always the site of failure, thereby providing a simple measure of tensile strength. The fact that the most successful filter tests conducted to date have been on a properly coated 2X fired element give a good indication that the test is meaningful.

Table 1. Mechanical Test Results on Cross Flow Materials

| Number of Firings | Coating | Firing Level | Mod of Rupture, (psi) | % Variation |
|---|---|---|---|---|
| 1X | None | High | 1940 | 14 |
| 1X | None | Low | 1800 | 10 |
| 2X | None | High | 2170 | 9 |
| 3X | None | High | 2330 | 10 |
| 2X | 1 Coat | High | 2480 | 17 |

In recent testing on a 2X, high fired, coated test element, more than 1000 pulse cleaning cycles were achieved over a test period that included more than 30 cold start up/shut down cycles, and an accumulation of approximately 250 hours of actual test operation. During this test campaign, internal pulse pressures as high as 10 psi were used for cleaning and no sign of failure was detected. This performance, albeit limited, was clearly superior to previous testing and is considered to be an indication of improved mechanical properties.

5. PROJECT DESCRIPTION:

The major technical difficulty that has been associated with the filter throughout its development is a tendency to delaminate along the alternating layers that result from manner in which the unit is fabricated. This failure is thought to occur during pulse jet cleaning of the filter. It is the major goal of this current program to develop a better understanding of the cause of this type of failure and to develop methods that will reduce or eliminate the problem.

The program consists of the following three technical tasks that are to be carried out in a serial fashion: Task 1 is an attempt to improve the mechanical properties of the cross flow filter, Task 2 is concerned with mechanical testing of candidate joining methods and Task 3 is associated with actual HTHP filtration tests to confirm process improvements.

TASK 1 - The properties improvement task will be initiated with a mechanical analysis of the hydraulic and thermal stresses imposed on the filter during pulse jet cleaning. An existing finite element computer code will be used for the analysis and it will be used to produce stress contours that will locate and quantify regions of high stress. This information will then be utilized to prepare a list of alternative design and fabrication techniques to minimize the problem areas. Having compiled a list of possible improvements, a set of 4 to 6 alternatives will be selected for traditional mechanical testing.

TASK 2 - Mechanical Testing will begin by defining the appropriate test specimen configuration for each of the chosen concepts. Subsequently test specimen for each concept will be fabricated and tested in a statistically meaningful fashion.

TASK 3 - HTHP Filter testing will be conducted on the 2 or 3 most promising concepts. This testing will be carried out on full scale filter elements that have been fabricated incorporating the most promising concepts.

6. RESULTS/ACCOMPLISHMENTS:

Efforts to date have centered on the mechanical analysis of the pressure and thermally induced stresses in the filter during pulse jet cleaning. This analysis is discussed in detail below.

MECHANICAL ANALYSIS (Pressure Stresses):

During the month of November meetings were held with the stress analysis personnel at the Westinghouse R&D Center and an approach for the model to be used was evolved. An initial decision was made to carry out a static analysis of stress distribution due to the pressure forces that occur during blow back cleaning and then to conduct a thermal stress analysis. Based on input from previous cleaning pulse rise monitoring, a maximum internal pressure rise of 10 psi was chosen. Typical values ranged from 3 to 7 psi in practice.

After careful consideration by the stress analysts, a fairly simple "typical unit" was chosen as the basis for calculation and is shown in Figures 1 and 2. This simplified basis is possible because of the symmetry associated with the cross flow filter's construction and because it was deemed to be too costly to consider a full three dimensional analysis. The initial analysis then, is characterized as a two dimensional plane stress, static analysis of the unit cell under pressure loading with the assumption of isotropic material properties. Estimates of the material properties (Youngs Modulus(E) and Poisson's Ratio ($\nu$) were obtained from Coors.

An appropriate finite element grid was constructed and stress contours were computed. In this process it was necessary to estimate the radius of curvature at the unit cell corners. By inspection it was estimated at 0.0015 inches, which is considered to be a very sharp corner and a high stress riser. The grid for this situation is shown in Figure 3 along with the boundary condition chosen for the analysis. These consisted of a zero normal displacement along the rib wall and a zero rotation (from symmetry) at the mid span of the filtering surface. Figure 4 presents the computed displacements (magnified by a factor of 5000), and the resulting stress contours that result from a 10 psi pressure loading. The maximum principle stress occurs at the inner surface of the corner and is estimated to be about 900 psi. This is to be compared with preliminary estimates of a modulus of rupture that is about 2000 psi for the parent

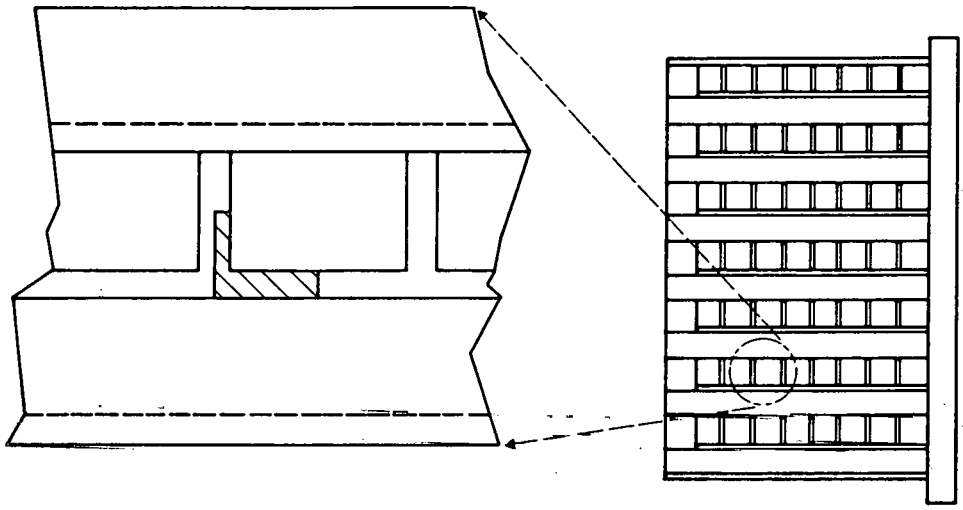


Fig. 1–Schematic of cross flow filter section used in mechanical stress analysis

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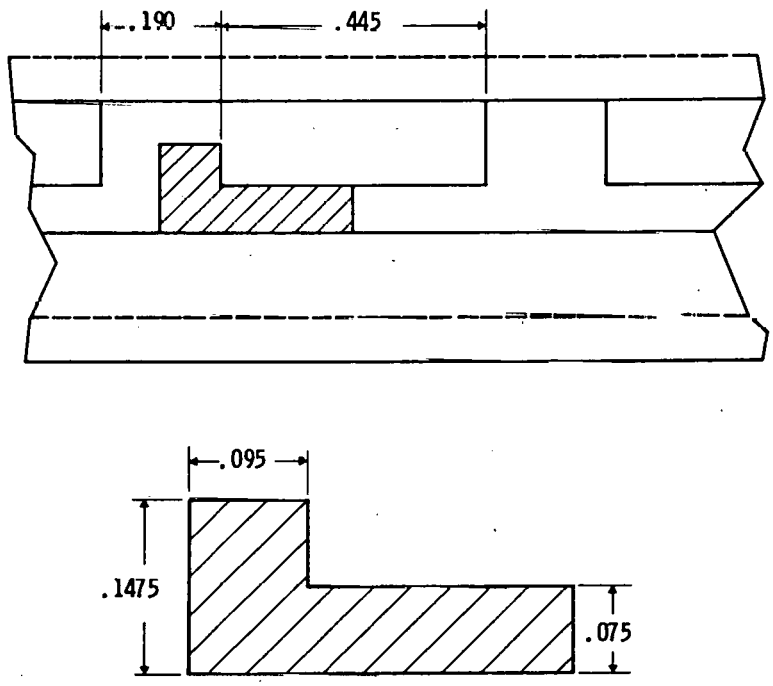



Fig. 2–Detail and dimensions of "Unit Cell" used in finite element stress analysis of cross flow filter

Dwg. 9395A06

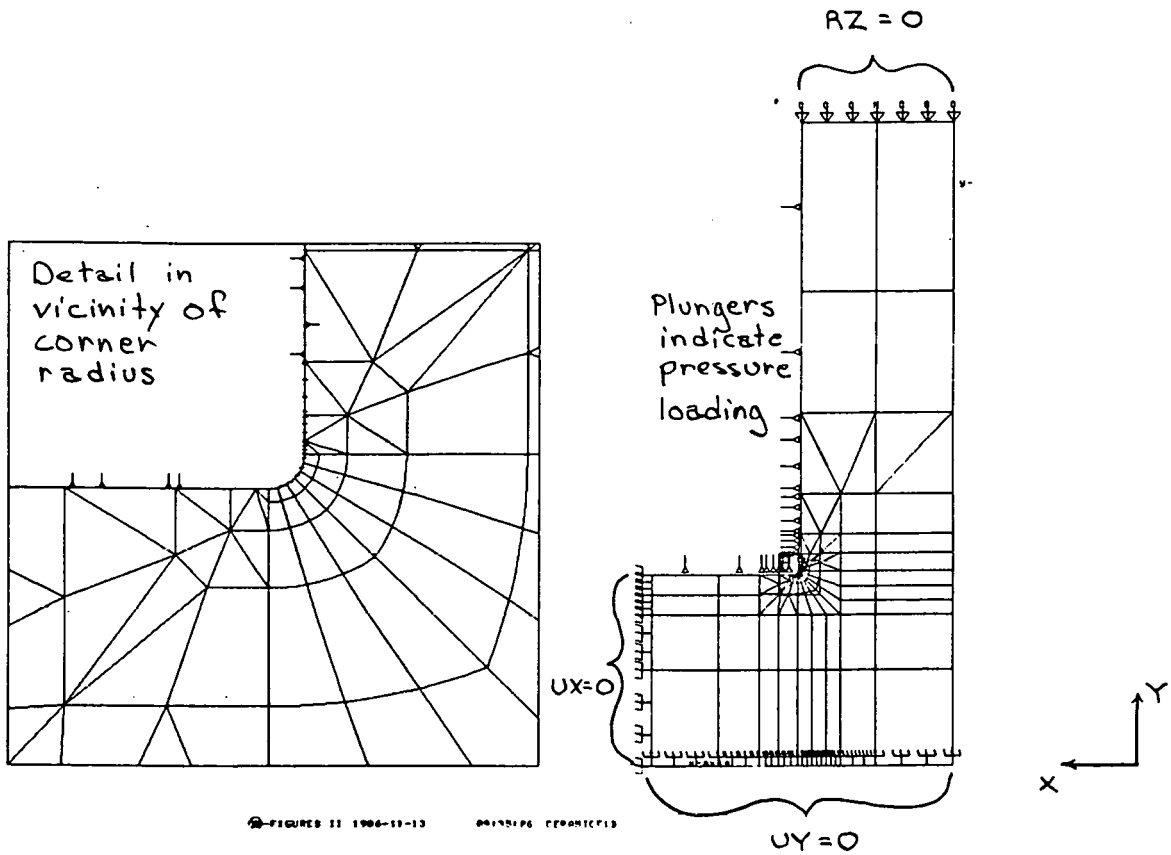



Figure 3 - Finite element mesh of the quarter region model with a 0.0015 inch corner radius

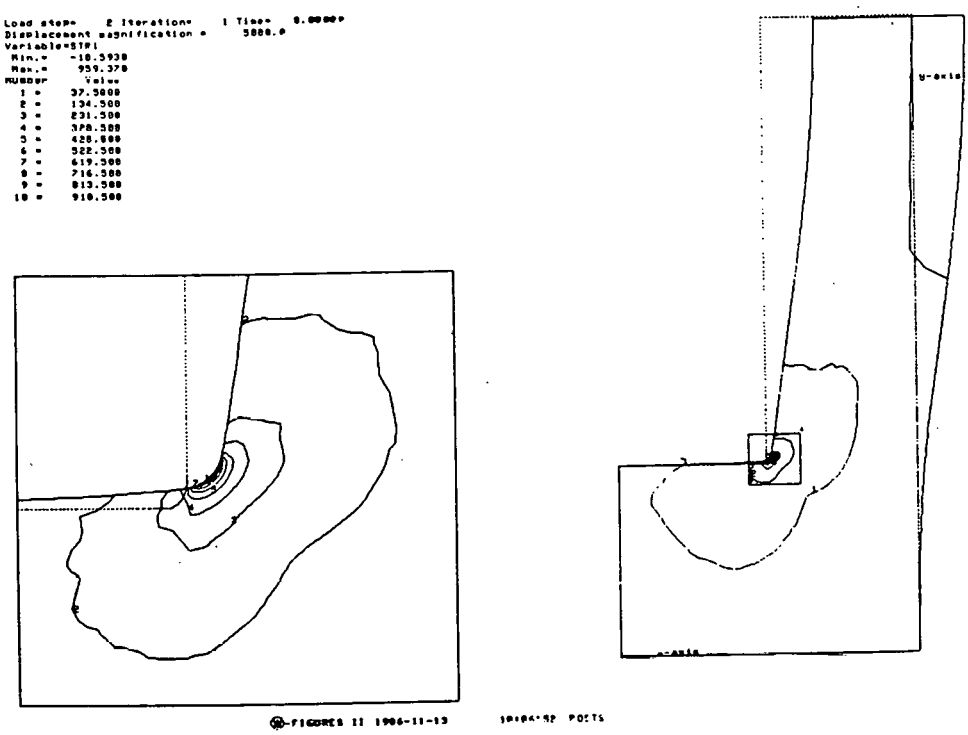



Figure 4 - Principle stress contour plot for the quarter region model with a 0.0015 inch corner radius subjected to 10 psi static pressure loading

material (Table 1). Since this stress is at a maximum right where the rib tips bond or fuses to the next layer, it is quite likely that the actual stress required to cause failure is considerably lower than 2000 psi, and as such this stress level is considered to be undesirable. It should also be noted that this analysis did not as yet include any thermally induced stresses, and these will be shown to add to the actual stress level.

As originally hoped for, the analysis suggested an obvious route to lowering the stress level. In this case it was simply to provide a larger radius in the corners. A new set of calculations was carried out using a more reasonable .020 inch radius. With the larger radius incorporated, the level of stress was reduced dramatically to a maximum value of about 250 psi.

The next step in the mechanical analysis was to conduct a transient thermal analysis for the system under pulsed conditions. This generated temperature profiles within the unit cell which could be input to the finite element stress model in order to produce the thermally induced stresses.

THERMAL ANALYSIS:

To begin the transient thermal analysis, some assumptions had to be made regarding the physical situation. These are explained here with reference to Figure 5 which presents a sketch for the assumed heat transfer model. The analysis has focused on the rectangular quarter section of a support rib as shown in Figure 1. In order to solve the two dimensional unsteady heat transfer equation proper boundary condition for each of the 5 surfaces noted in Figure 5 had to be established. The zero flux condition at Surfaces 3 and 4 can be established by symmetry and while this is not exact for the surface at 5, it is a good approximation. The boundary condition along surface 2 is set by allowing convective heat transfer to occur between the rib wall and the pulse gas flowing parallel to the wall, down the channel. The final surface, is that which comprises the connection of the rib to the porous membrane filtering surface (e.g., surface 1). The major simplifying assumption made here is that the porous membrane through which the pulse gas flows cools in a spatially uniform manner because it is thin and cooled by transpiration (e.g., pulse gas actually flowing through the porous membrane). Because of the enormous internal heat transfer surface provided by the porous media, it is assumed that the gas exits at a temperature in equilibrium with the porous solid. A simple heat balance for this situation is stated as: the rate at which heat is picked up by the pulse gas as it flows through the membrane wall equals the rate at which the filter membrane loses heat.

$$\dot{m}C_{pg}\,(T_f(\theta)-T_p) = \frac{d}{d\theta}\,(m_f C_{pf}(T_f(\theta)-T_{ref}) \qquad (1)$$

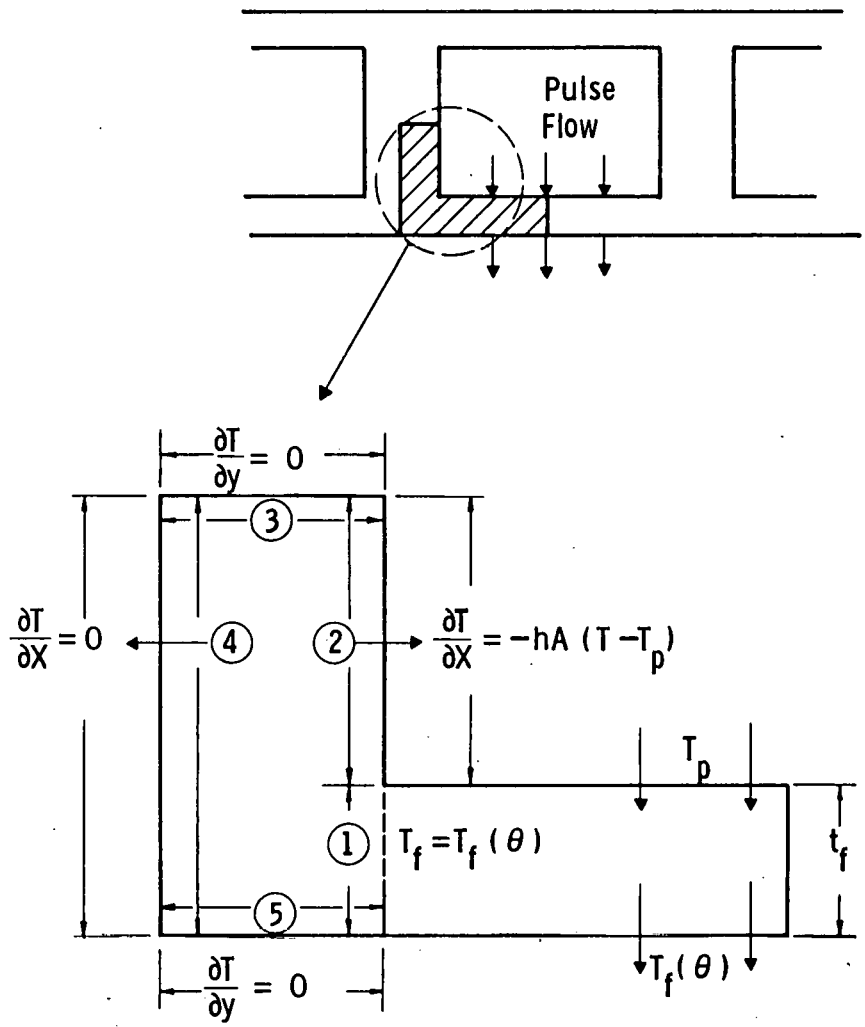



Fig. 5—Model used in transient thermal analysis of cross flow filter during pulse cleaning

Dwg. 9395A09

This equation can be solved quite simply to give the temperature of the filtering membrane as a function of temperature.

$$T_f(\theta) = T_p + (T_f(0)-T_p)e^{-\alpha\theta} \tag{2}$$

$$\text{where } \alpha = \left\{ \frac{\dot{m}_p C_{pg}}{A_f t_f \rho_f C_{pf}} \right\} \tag{3}$$

and

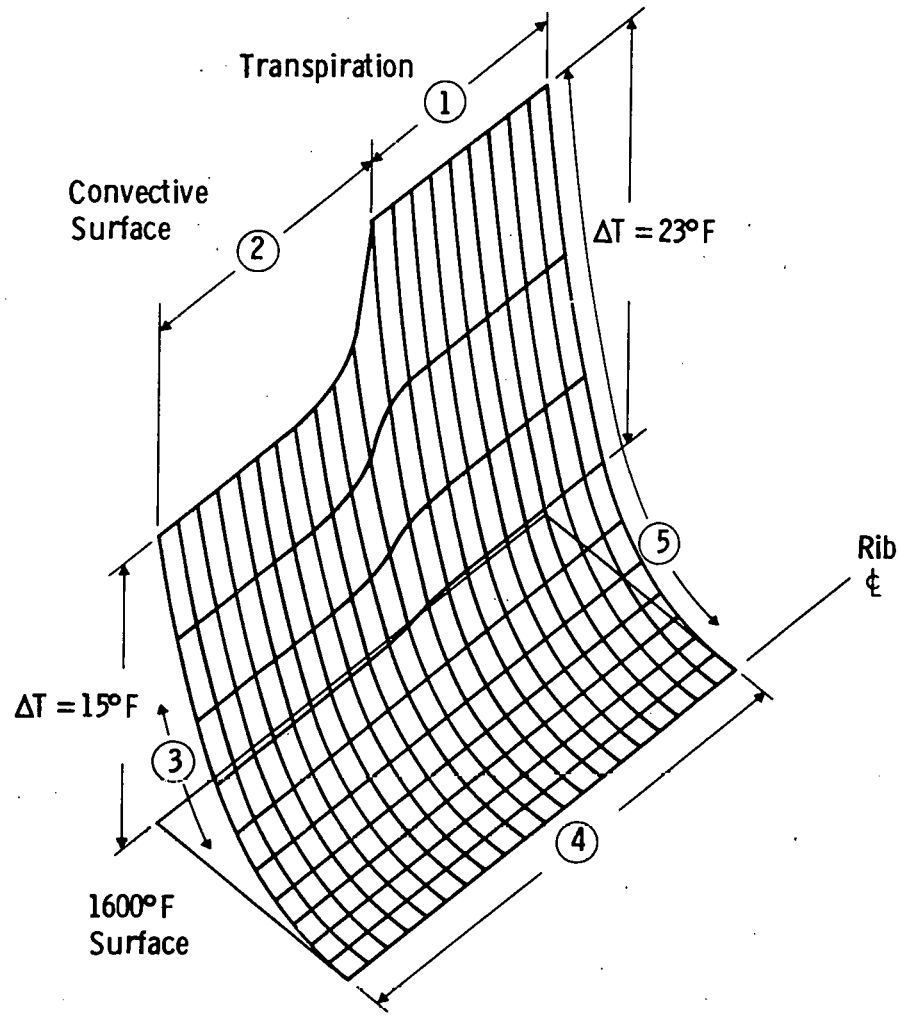
| | | |
|---|---|---|
| $T_f(\theta)$ | = | The filter membrane temperature |
| $T_p$ | = | The inlet pulse gas temperature |
| $\theta$ | = | Time |
| $\dot{m}$ | = | Mass flow of pulse to filter |
| $C_{pg}$ | = | Heat capacity of pulse gas |
| $A_f$ | = | Actual filter membrane area |
| $t_f$ | = | Thickness of membrane |
| $\rho_f$ | = | Bulk density of membrane |
| $C_{pf}$ | = | Heat capacity of filter media |

This equation then can be utilized to establish the temperature along surface 1 of the rib quarter section throughout the pulse duration. These boundary conditions, and an assumed initial condition of uniform temperature in the filter are sufficient to numerically solve the 2-dimensional heat transfer equation in the quarter section of the rib:

$$\frac{\partial T}{\partial \theta} = \left\{ \frac{k_f}{\rho_f C_{pf}} \right\} \left\{ \frac{\partial^2 T}{\partial X^2} + \frac{\partial^2 T}{\partial Y^2} \right\} \tag{4}$$

To carry out the computation a simple explicit finite difference method was employed that gave the temperatures at regular rectangular grid points within the quarter section.

The results of a computation for a typical pulse are presented in Figure 6, which shows a three dimensional plot of the temperature surface at the end of the 100 ms pulse. The distance above the flat, bottom plane surface represents the amount of temperature drop in the rib quarter section due to cooling by the pulse gas. The surfaces (referenced to Figure 5) are labeled to aid in orientation. The analysis shows that




Dwg. 9395A08

Fig. 6—Temperature surface after 0.1 sec pulse for quarter section of cross flow filter rib

surface 1 is driven to the lowest temperature (about a drop of 23°F to 1577 from an assumed initial value of 1600°F). By assumption this transpiration cooled surface is of constant temperature. The convecting surface (2) drops to a value of about 1585°F near the rib midpoint. The plot shows that the region joining surface 1 and 2 is the area of highest temperature gradient and consequently of highest thermal stress. Unfortunately, and not surprisingly, this was previously shown to also be the area of highest stress due to pressure loading. These combined stresses occur at the rib tip-to flat joint which is likely to be the weakest region in the filter assembly.

The remaining task in the Thermal Stress Analysis was to integrate the calculated temperature surface into the finite element stress model so that thermally induced stresses could be quantified. Unfortunately the finite difference solution of the transient heat transfer analysis yields temperature data on a regular rectangular grid and not at the irregular node points of the finite element model. We prepared a two dimensional interpolation subroutine which enabled us to accurately determine the temperatures at the finite element nodes, from the temperature grid produced from the finite difference programs.

After the interpolation process, the finite difference temperature distribution was used to calculate thermally induced stresses in the quarter region model with the .0015 inch corner radius. Principle stress contour plots for this thermal loading appear in Figure 7. The maximum principle stress due to thermal loading were found to be about 1100 psi. Thermally induced stresses were not calculated for the quarter region model with the .020 inch corner radius. Had these stresses been calculated, it is believed that they would have been appreciably lower than those for the quarter region model with the .0015 inch corner radius.

COMBINED PRESSURE/THERMAL LOADS:

The stresses from the 10 psi static pressure loading and the thermal loading were combined with the thermal loading to see the net effect of a pulse jet cleaning cycle. The principle stress contour plots for this combined loading appear in Figure 8. The maximum principle stress for this combined loading was determined to be 2013 psi.

It is interesting to note that for the small radius case, the calculated maximum principle stress for the combined loading is greater than the rupture modulus. (The rupture modulus is roughly equal to the ultimate tensile strength of a material). This should probably not be interrupted as proof that the limits of the ceramic material had been exceeded. Instead, these results indicate more generally that stresses in the corner radii are approaching the limits of the ceramic material, and may explain the observed actual behavior of failures in some cases, and the absence of failures in others.

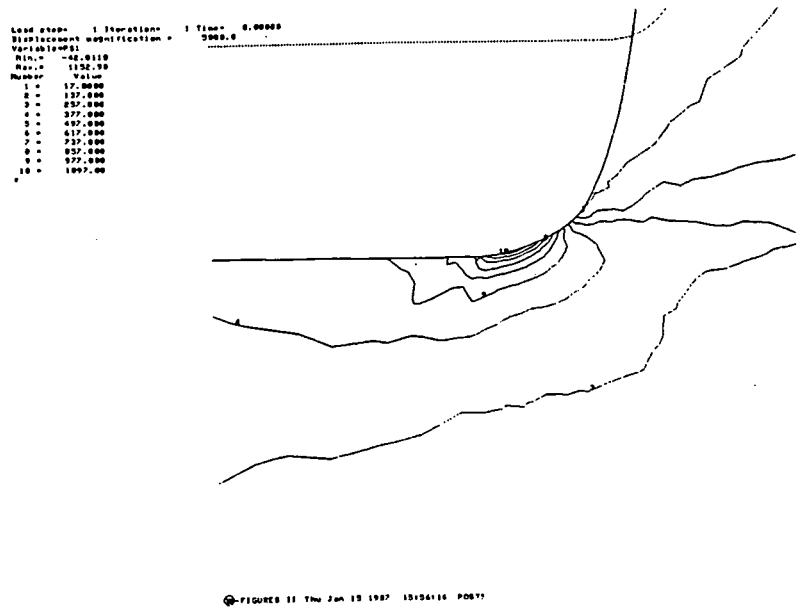


Figure 7 – Detailed view of the principle stress contour plot for the quarter region model with a 0.0015 inch corner radius subjected to thermal loading

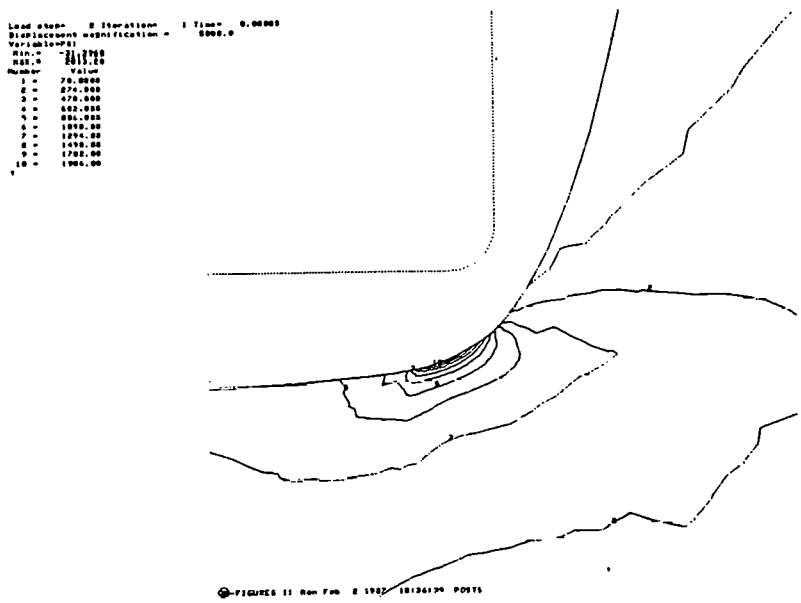


Figure 8 – Detailed view of the principle stress contour plot for the quarter region model with a 0.0015 inch corner radius subjected to both 10 psi static pressure loading and thermal loading

## 7. FUTURE WORK:

Future work in this project will proceed as indicated in the project description. The finite element models will continue to be used to access design options (such as a more generous radius) that will reduce stress concentration. Additionally, Coors and Westinghouse will proceed to the development of alternative design concepts and embody them in simple mechanical test specimens. After statistically significant traditional mechanical testing is completed, a few of the most promising concepts will be incorporated in actual filter media for actual HTHP testing in a PFBC simulator.

# ZIRCONIA CELL OXYGEN SOURCE

1. CONTRACT NUMBER: DE-AI21-84MC21032

CONTRACTOR: Jet Propulsion Laboratory
California Institute of Technology
4800 Oak Grove Drive
Pasadena, California 91109
(818) 354-4917

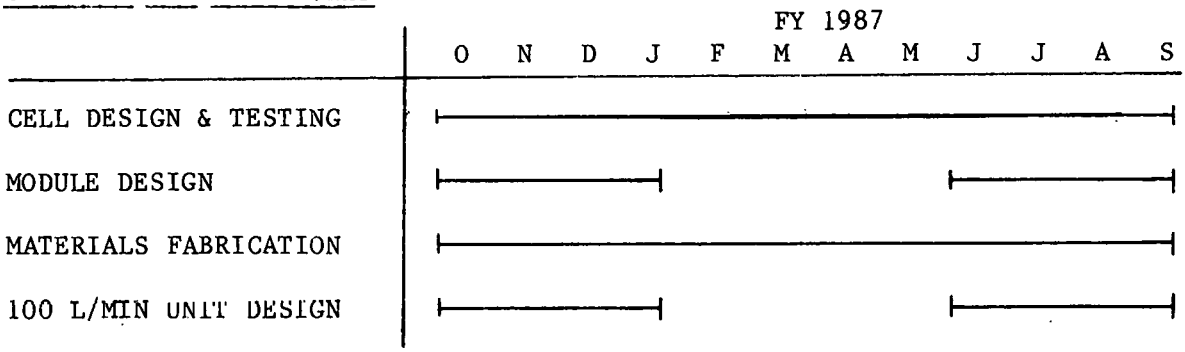
PROGRAM MANAGER (CONTRACTOR): J.W. Suitor

PRINCIPAL INVESTIGATORS: J.W. Suitor
W.J. Marner
J.E. Schroeder

METC PROJECT MANAGER: David Dubis

CONTRACT PERIOD OF PERFORMANCE: June 24, 1984 through March 31, 1988

2. SCHEDULE AND MILESTONES:




3. OBJECTIVES:

The project sponsored by DOE is a five year effort leading to the operation of a 100 liter/min oxygen production unit. During this time an industrial partner will be located to whom the technology will be transferred.

4. BACKGROUND STATEMENT:

The oxygen production unit will consist of a zirconia module for oxygen separation and the ancillary equipment arranged as an oxygen production plant. The zirconia module operates on the principle of electrodialysis.

ZIRCONIA OXYGEN SEPARATION

The oxygen separation ability of zirconia is rooted in the oxygen ion conduction capability of the material. Oxygen vacancies exist in the crystal lattice of the material that provide oxygen conduction sites for transport of oxygen ions through the material. The driving force of this transport is the potential applied across the membrane by a DC power

supply.

A simplified diagram of the oxygen separation process in air is shown in Fig. 1. Air, containing 21 volume percent oxygen, passes over the

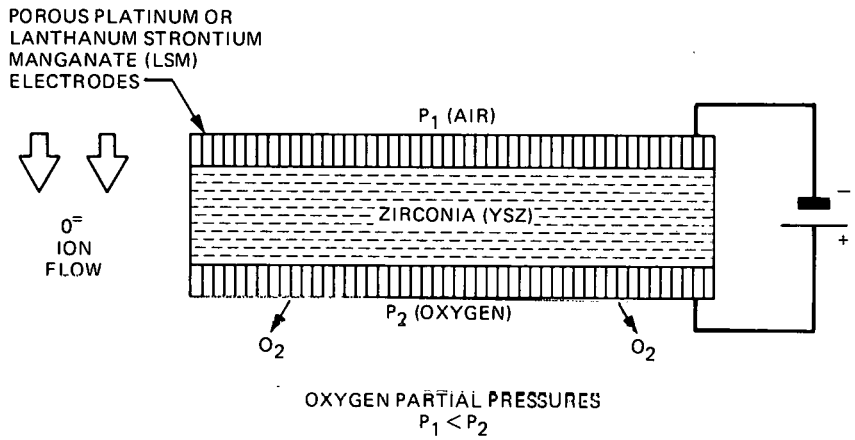



Figure 1 Simplified Cell Schematic.

separation membrane. The membrane consists of the zirconia sandwiched between electronically conductive porous electrodes. Oxygen molecules diffuse through the porous electrode to the zirconia/electrode (cathode) interface. At or near this region, oxygen is decomposed from diatomic molecules to single oxygen ions with a negative valance of two. The electrons are supplied by the DC power supply through the porous electrode. The potential gradient applied by the power supply drives the oxygen ions into the zirconia membrane through the surface oxygen vacancies in the zirconia crystal lattice.

The oxygen ions move through the zirconia from vacancy to vacancy until they appear at the anode zirconia/electrode interface. Here the electrons are given up and are recycled through the power supply thereby completing the circuit. The diatomic oxygen molecule is reformed and diffuses to the free stream surface of the porous electrode.

Energy is consumed in several ways during the separation process. First there is the ohmic energy consumption due to the electron current resistance in the electrodes. Second, there is an equivalent ohmic loss in the zirconia electrolyte due to oxygen ion conduction. Additional ohmic losses can occur at the electrode/electrolyte interfaces. Finally, there is a special energy loss due to "pumping" the oxygen from a low concentration on the air-side (20 volume percent) to a higher concentration (100 volume percent) on the oxygen discharge side. A back EMF is generated by this concentration difference. The back EMF represents the chemical potential difference of oxygen across the zirconia membrane and is called the Nernst voltage.

Requirements for the separation process include the following.

- operation at elevated temperature - the zirconia electrolyte has exponentially higher ion conductivities at higher temperatures. This is due to the increased oxygen vacancy mobility at higher temperatures. Typical temperatures range from 800-1000 C.

- electrodes - oxygen must move freely through the electrodes to arrive at the electrode/zirconia interface requiring a porous electrode. However, a balance between a porous diffusion structure and good electronic conductivity (i.e., less porosity) must be met.

- thin electrolyte - the electrolyte must be thin to reduce the resistance to ion current flow and therefore the power consumption of the cell.

THE OXYGEN PLANT CONCEPT

The plant conceptual design of the Zirconia Oxygen Plant is shown in Fig. 2. Air enters the plant through a low pressure blower and is split into

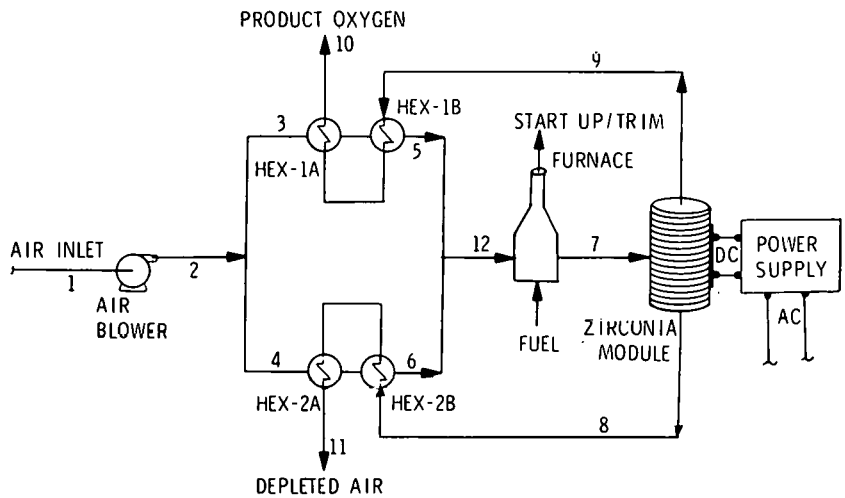



Figure 2. Conce tual Plant Process Configuration.

two streams as it proceeds through heat exchanger trains. The air is preheated in the heat exchangers, extracting energy contained in gases exhausting from the zirconia separation module. The air streams recombine and pass through a start-up/trim furnace. This furnace adds additional heat to permit operation at the desired elevated temperature. The air entering the zirconia module is at or near the proper operating temperature. In the module itself some additional heat recovery will be made to absorb heat generated by ohmic heating in the module. After separation in the zirconia module the oxygen-depleted air and the oxygen return to the preheat exchangers to exchange heat with the incoming air.

The zirconia module will consist of a number of stacks of cells. A possible arrangement using four stacks is shown in Fig. 3. Manifolding

of the gases is done at one end of the module and power is connected to the two ends of the module with the stacks being connected in parallel.

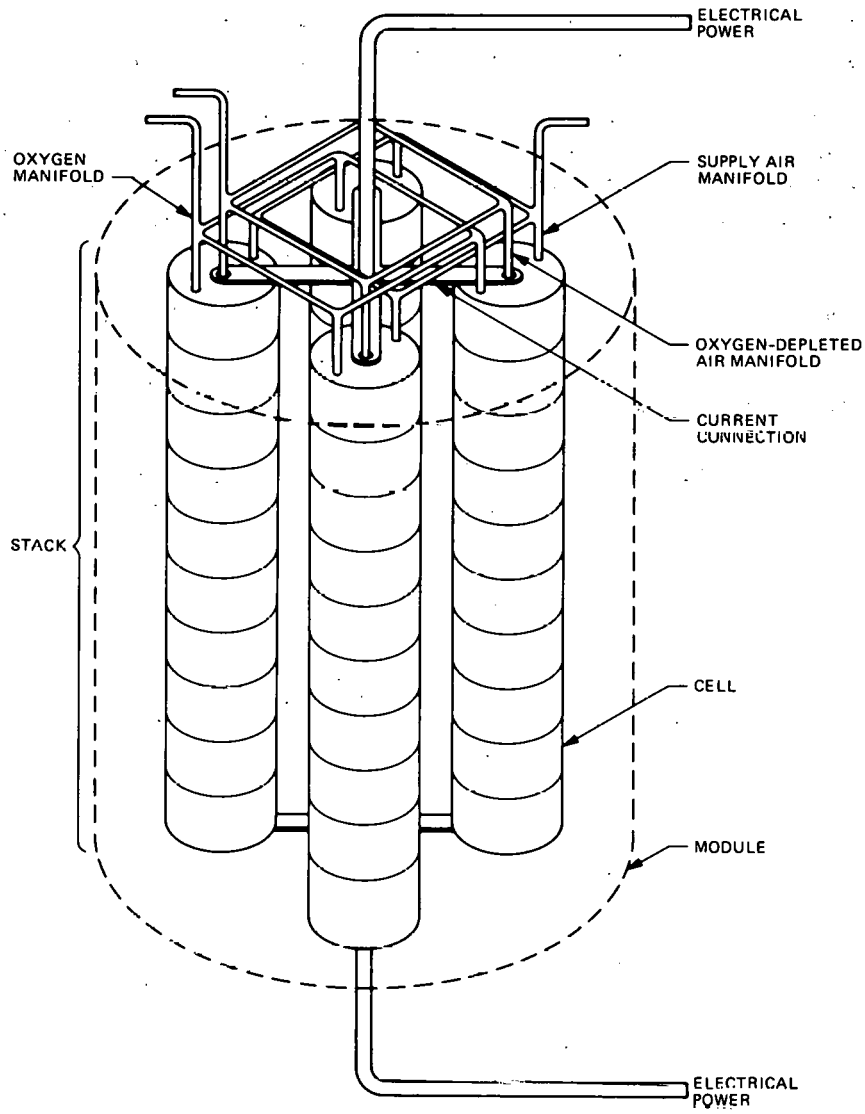



Figure 3. Oxygen Separation Module Containing Four Stacks of Cells

Incoming air will circulate around the stacks prior to entering the stacks removing heat generated by ohmic heating in the stacks.

5. PROJECT DESCRIPTION:

The project has been divided into a stepwise development consisting of the following tasks:

- Task 1 System Development - initial modelling of cell performance, economic studies, and selection of appropriate geometry for system.
- Task 2 Materials Development - initial materials fabrication and identification of major materials issues.

- Task 3 Cell Configuration - refinement of the cell configuration and materials fabrication.
- Task 4 Plant Design - engineering design of the 100 liter/min plant.
- Task 5 Subsystem Components - operation of a 4-stack module producing 3 liter/min.
- Task 6 Plant Testing - operation of the 100 liter/min plant.
- Task 7 Process Scale-up - development of scale-up data and requirements for multi-ton/day plants.

PREVIOUS ACCOMPLISHMENTS

Work prior to the current fiscal year covered Tasks 1,2, and 3 with the following accomplishments:

- Cell Design
  - fabricated and tested several cells of different geometries
  - designed and constructed all ceramic cell
  - operated cells to 275 milliamps/square centimeter
  - designed and fabricated 4-cell stack
- Materials Fabrication
  - identified electrodes and electrolyte materials
  - developed manufacturing capability for ceramic electrodes
  - produced thin (<100 micron) cell membranes by tape casting
  - improved sandwich manufacture technique
  - identified alternate electrolyte material
- Performance Modelling and Economics
  - developed cell performance modelling program for tubular and disk cell
  - conducted preliminary economic analysis and sensitivity study

The current fiscal year has consisted of work on Tasks 4 and 5 with emphasis on 100 liter

- Cell design and testing
- Module design
- Materials fabrication
- Design of the 100 liter/min unit

6. RESULTS/ACCOMPLISHMENTS:

CELL DESIGN AND TESTING

The cell design activity implemented the results of the modelling work reported last year. The results of modelling studies demonstrated the need for a uniform axial conduction of electrons over the entire electrode surface (Fig. 4). Modelling parametric studies showed a substantial improvement in energy consumption using the axial conduction mode as compared to the previous design using axial election conduction (Fig. 5). There were two axial cell configuration developed. The first use a perforated plate of platinum that contacted the electrode surface with the extruded perforations. The second configuration used a rib

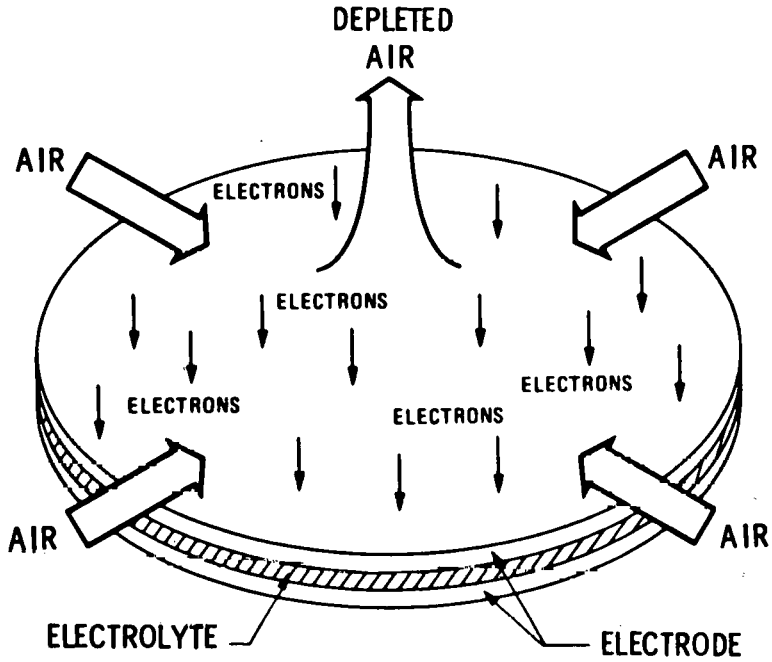



Figure 4. Axial Electron Conduction Schematic

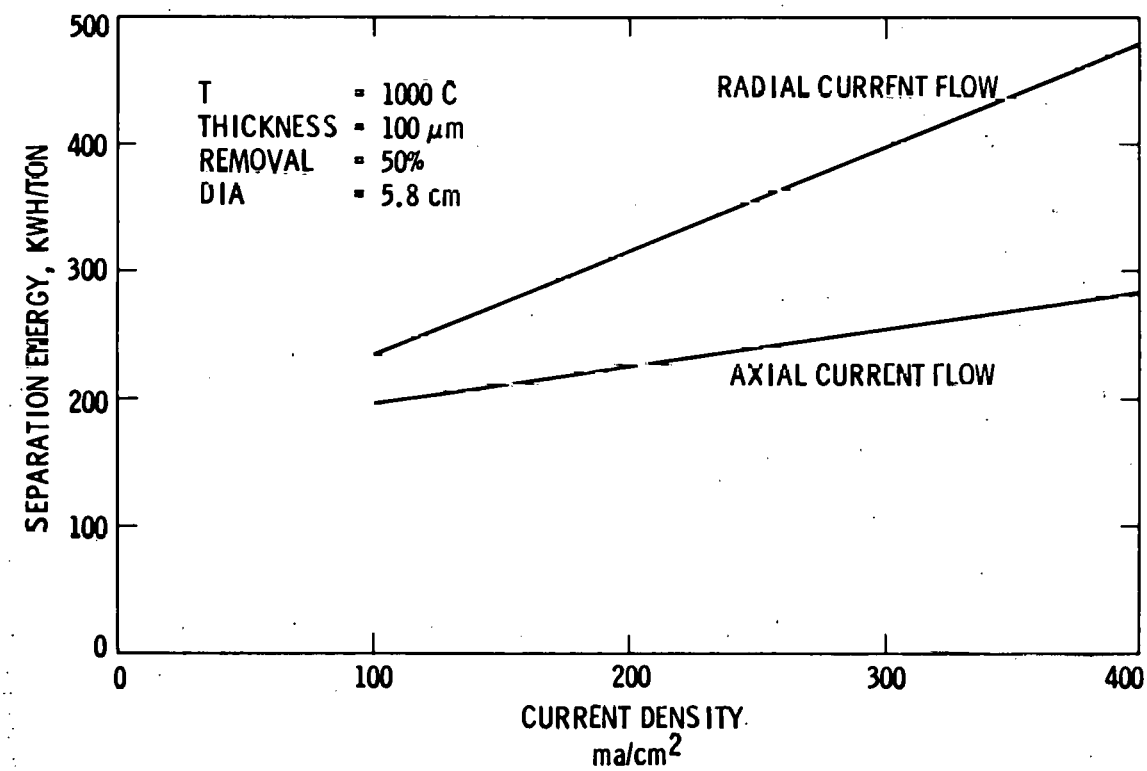



Figure 5. Comparison of Axial and Radial Conduction Models

design that not only contacts the electrode surface but also provides support to the thin zirconia membrane and diverts the flow from the outer circumference to the center of the disk.

A series of tests using various membranes was conducted using the perforated platinum distribution plate. The overall purpose of the tests was to optimize the membrane manufacturing procedure. A summary of all tests conducted is given in Table 1. The membrane improvement tests

Table 1. Summary of Cells Tested During FY 87

| Cell | Purpose |
|---|---|
| D-4 | First JPL disk test |
| D-5 | Sealed disk test |
| D-6 | Axial current test |
| D-7 | LSM only calibration test |
| D-8 | Loose LSM powder on electrode for better contact |
| D-9 | Graded interfacial layer between electrode/electrolyte |
| D-10 | Graded interfacial layer and loose LSM powder |
| D-11 | LSM only calibration test |
| D-12 | Baseline sample test |
| D-13 | Platinum coating on electrode for better contact |
| D-14 | Thin electrode for better oxygen diffusion |
| D-15 | Interfacial layer to reduce cell resistance |

resulted in a fabrication technique that lowered the overall cell resistance by a factor of two (Fig. 6) and identified gas diffusion

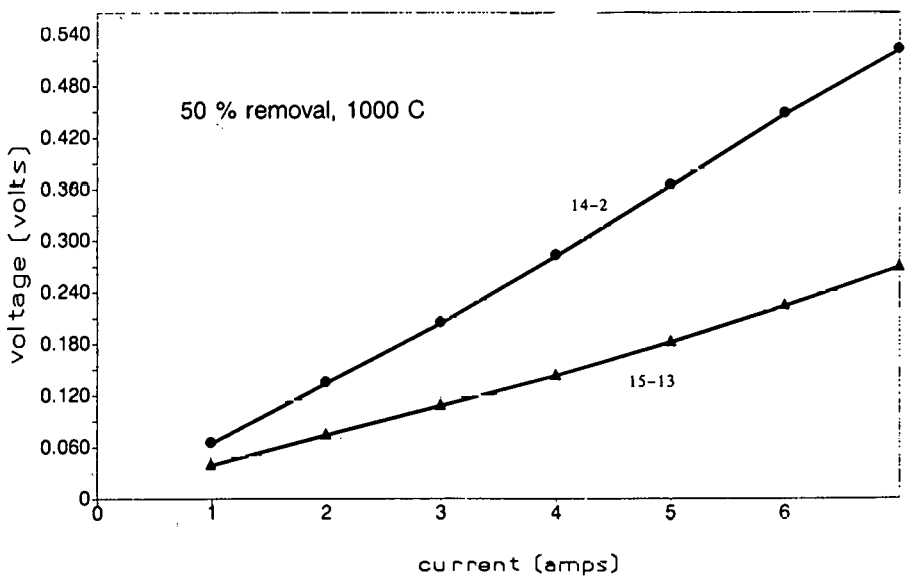



Figure 6. Single Cell Test Results

through the electrodes as a possible source of cell overvoltage.

MODULE DESIGN

The design of a ribbed distribution plate resulted in a preliminary stack design (Fig. 7) that is currently being detailed. There were three

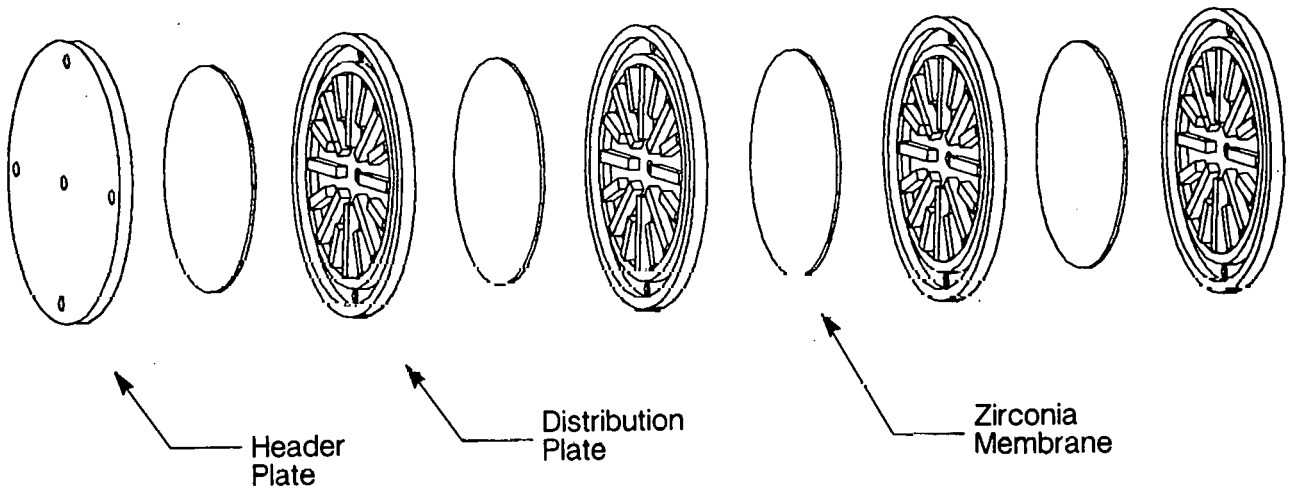



Figure 7. Stack Design with Axial Distribution Plate

candidate materials for the distribution plate identified. These were A-Lava, nickel aluminide, and highly dense LSM electrode material.

The A-Lava is viewed as a short term solution to allow prototype stack operation. The natural is machinable and will be coated with platinum to provide surface conduction of elections. The use of this material allows for simple, easy design improvements.

Nickel aluminide is one of two possible high temperature, oxidation resistant alloy that was developed at Oak Ridge National Laboratory. Electrical resistivity measurements were made of iron aluminide, nickel aluminide, and type 302 stainless steel as a data reference material (Fig. 8). The nickel aluminide was chosen due to the lower electrical resistivity. The corrosion resistance to the LSM electrode material must still be determined.

Finally, the use of LSM as the distribution plate material provides material compatibility with the LSM electrodes but requires development from a fabrication standpoint work is currently proceeding in this area.

MATERIALS FABRICATION

The ability to make zirconia/LSM separation membranes was completed developed during the past fiscal year. The zirconia layer was made a thin as 50 microns and improvements in the electrode/electrolyte interfacial resistance were also made (Fig. 6). The long term effects of

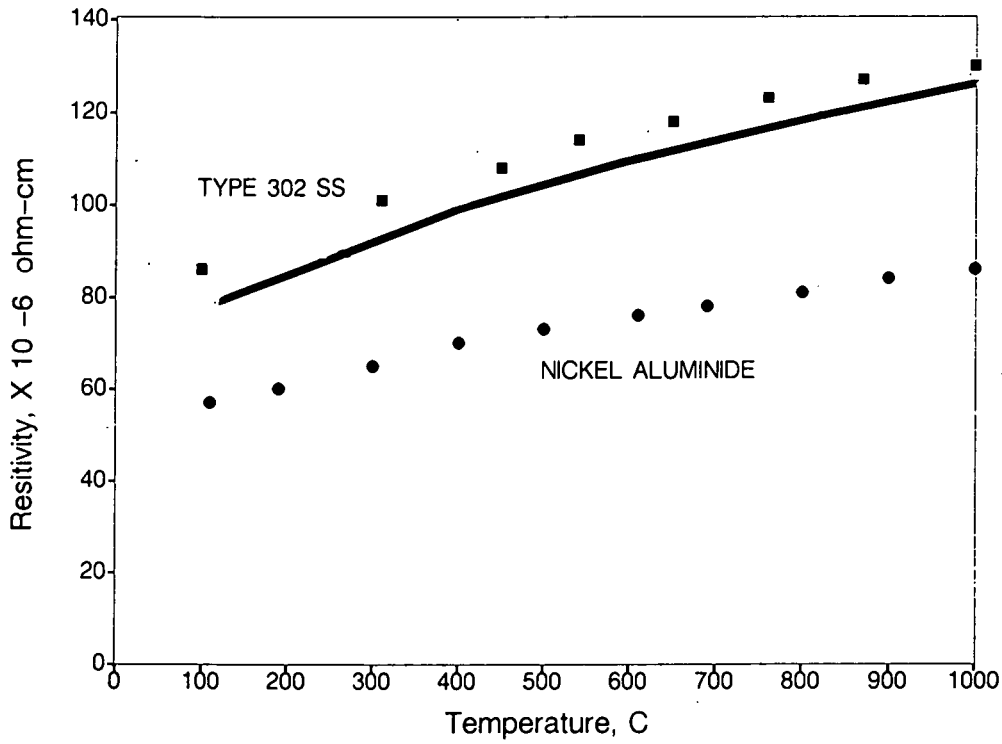



Figure 8. Aluminide Electrical Resistivity Testing

this improvement are yet to be determined.

Bismuth oxide was identified as an alternate electrolyte material during the last reporting period and was successfully tape cast during the current reporting period. Testing of this material is expected soon.

DESIGN OF 100 LITER/MIN UNIT

Individual components for the 100 l/min unit were specified based on a variety of operating conditions to obtain a wide range of plant operating data. Specific components included the heat exchanges, fired heater, blower, and power supply. Instrumentation and unit layout must still be specified.

REPORT

A report entitled, "Development of an Alternate Oxygen Production Source Using a Zirconia Solid Electrolyte Membrane - Technical Progress Report for Fiscal Years 1986 and 1987" was issued in May 1987. The report summarized the results of Tasks 1, 2, and 3. It is available on limited distribution.

7. FUTURE WORK:

The planned work for FY 88 continues to focus on a multistack module. Specifically the planned work for FY 88 includes:

- Final design and fabrication of the distribution plate
- Design, fabrication, and operation of a 1 l/min stack
- Design, fabrication and operation of a 3 l/min module
- Initiation of construction of 100 l/min unit.

# MATERIALS DEVELOPMENT FOR JPL OXYGEN PLANT

1. FTP/A NUMBER: 49677

CONTRACTOR: Argonne National Laboratory
9700 South Cass Avenue
Argonne, Illinois 60439
(312) 972-4250

CONTRACTOR PROGRAM MANAGER: Dr. William A. Ellingson

PRINCIPAL INVESTIGATORS: Dr. Roger B. Poeppel
Dr. Timothy E. Easler

METC PROJECT MANAGER: D. R. Dubis

CONTRACT PERIOD OF PERFORMANCE: October 1, 1980 to September 30, 1988

2. SCHEDULE/MILESTONES:

| | | |
|---|---|---|
| Task 1: | Coordinate program with DOE/ORO/ORNL, METC, JPL, ANL | 10/85-01/87 |
| Task 2: | Cut test samples from tapes, sinter, and examine in preparation for testing | 02/87 |
| Task 3: | Measure the ability of the electrolyte to conform to the shape of the clamping surfaces (Clamping Bend Test) | 04/87 |
| Task 4: | Evaluate the ability of the laminate to support a steady-state thermal gradient (Thermal Gradient Test) | 05/87 |
| Task 5: | Measure the tolerance of the electrolyte to thermal expansion mismatch (Thermal Expansion Mismatch Test) | 07/87 |
| Task 6: | Measure the ability of the electrolyte to deform without breaking under a clamping load (Strain-to-Failure-Test) | 09/87 |
| Task 7: | Prepare a first-year report detailing the possible causes of membrane fracture | 09/87 |
| Task 8: | Determine the reduction in electrolyte-electrode laminate time-to-rupture caused by biaxial stress (Biaxial Stress, Time-to-Rupture Test) | 12/87 |
| Task 9: | Determine the tolerance of the laminate to thermal gradients arising from rapid temperature fluctuations (Thermal Transient Test) | 02/88 |

| | | |
|---|---|---|
| Task 10: | Carry out fractographic analyses of specimens to determine critical flaw types | 04/88 |
| Task 11: | Measure strength of electrolyte at operating temperatures of 600-800°C, in air and in oxygen-enriched air | 06/88 |
| Task 12: | Measure electrolyte strength at 600-800°C with an electric current applied | 07/88 |
| Task 13: | Determine extent of creep behavior under mechanical load at 600-800°C | 09/88 |
| Task 14: | Prepare second-year report detailing results to date | 09/88 |

3. OBJECTIVES:

The purpose of this research program is to establish the durability of thin electrolyte layers so that minimum component thicknesses may be used in a solid oxide oxygen pump, as the means of reducing internal power losses, while still maintaining the required mechanical integrity of the structure. The internal power losses are directly proportional to the product of the thickness and resistivity of the individual component material and inversely proportional to the active area. The reduction of these losses is desirable in order to enhance the solid oxide oxygen pump economics relative to conventional pumping techniques.

Previous and current work in the scientific and industrial communities has proven the feasibility of fabricating thin-section ceramic components by techniques such as tape casting. Proof-of-concept work has also been carried out illustrating that thin ceramic sections can be successfully bonded together as anode/electrolyte/cathode units for fuel cells. Although this technology has been developing rapidly, there is a lack of information on the ability of these structures to survive the stress and/or strains imposed by the assembly configuration and operating conditions.

Several potential failure modes have been identified. These are (1) thermal gradients induced by rapid cooling, (2) thermal gradients induced by nonuniform power dissipation, e.g., high-current hot spots, (3) interfacial stresses resulting from thermal expansion mismatch, (4) tensile and bending stresses introduced by clamping, (5) biaxial bending caused by unbalanced gas pressures across a thin section, (6) local stresses induced by corrosion or chemical reaction between components. The purpose of this program is to assess the importance of each of these failure modes through phenomenological tests, each of which approximates as nearly as practical the conditions leading to one specific failure type.

4. BACKGROUND STATEMENT:

The solid oxide oxygen pump is believed to have the potential for significantly reducing the cost of oxygen generation for the coal

gasification process. The solid oxide oxygen pump concept is based on the oxygen-ion conducting behavior of zirconia ceramics. The particular ceramic electrolyte under development in this project is zirconia doped with 8 mol % $Y_2O_3$. Both the air and oxygen electrodes are made of strontium-doped lanthanum manganite. The approach being taken to fabricate the oxygen pump involves fabrication of thin multilayer structures of ceramic electrode and electrolyte materials by the tape casting process. It is desired to make the laminated structures as thin as possible to minimize internal power losses which are the result of the high resistances of the individual ceramic oxide layers. This study is particularly concerned with determining the types of failure modes that may be associated with the very thin ceramic layers. The fabrication of the layers, and the initial failure mode identification tests, are described in this paper.

## 5. PROJECT DESCRIPTION:

The development and implementation of a solid oxide ceramic oxygen pump in coal gasification systems is believed to have the potential for reducing cost, when compared to other oxygen production systems such as cryogenic pumping. This economic potential can be enhanced through the reduction of internal power losses caused by high internal resistances in the individual ceramic oxide components. For a given component, in particular the electrolyte, the power loss is directly proportional to the electrical resistance, which in turn is proportional to the resistivity of the material multiplied by the thickness of the component.

The electrolyte may be the single most critical material in the solid oxide oxygen pump. In addition to being a conduit for oxygen ions, the electrolyte must prevent the intermixing of the depleted air and enriched oxygen streams. Yttria-stabilized zirconia has been chosen for the electrolyte because it has the best combination of chemical stability, low resistivity, and low parasitic losses of all known oxygen ion conductors. The internal resistance of the electrolyte may be reduced by decreasing its thickness. The minimum practical thickness, however, is determined by the mechanical integrity of the electrolyte.

The results in this paper include a discussion of the development and fabrication of thin tape cast ceramic layers, which involved characterization of the ceramic powders used for the electrode and electrolyte, the development of a tape casting slip formulation, and characterization of the tapes. In addition, the initial results of the first failure mode identification test, which was the clamping bend test, are discussed.

## 6. RESULTS/ACCOMPLISHMENTS:

### Ceramic Layer Fabrication - Tape Casting

Tape casting is a fabrication process which is used extensively in the ceramic industry for manufacturing substrates, capacitors, and microelectronics. It is the technique that has been chosen for forming the thin ceramic layers required for the oxygen pump. Tape casting involves

incorporating a ceramic powder of the desired composition into a slurry or slip which can be poured out onto a suitable substrate, such as glass or a Teflon surface, and spread into a thin layer with a knife-edge or doctor blade. The slip formulation, including the choice of binder, is critical to the process. Many types of binder systems are commercially available. The binders are typically thermoplastic resins or plastics, or cellulosic materials. Each type of binder is compatible with different types of solvents, and the choice of binder system must be made with consideration to its compatibility with the ceramic powder characteristics, and the properties required of the tapes that will be derived from it. In addition to the binder and solvent, other components of the slip include a dispersant to deflocculate the ceramic particles, and a plasticizer to change the glass transition temperature of the binder. In some systems, a lubricant or release agent is incorporated to facilitate release of the tape from the substrate after the solvent has evaporated.

## Ceramic Powder Characterization

Several characteristics of the ceramic electrode and electrolyte powders must be known in order to successfully develop tape casting slips for the fabrication not only of single layers of these components, but also of successively cast layers for single oxygen-pump cells comprising air-electrode/electrolyte/oxygen-electrode. One of the most important characteristics is the particle size distribution of the powder. The range of particle sizes and their number distribution are directly related to the surface area of the powder, which dictates the amounts of binder and other organic slip components required. The particle size distributions for the electrolyte and electrode powders are given in Fig. 1. The zirconia electrolyte material has an average grain size of about 5 μm. Very few grains are larger than about 20 μm in size, and a sizable volume fraction (~30 vol %) is finer than 1 μm. The lanthanum manganite electrode powder is considerably different. An average grain size of approximately 35 μm is observed, with a relatively small volume fraction less than 5 μm. Because of the differences in these distributions, the surface area of the zirconia powder is substantially larger than that of the lanthanum manganite powder. As a result, a greater amount of binder is required for the zirconia tape casting slip.

When necessary, particle size distributions can be altered to some extent by milling the powder to reduce particle sizes, or by calcining the powder to increase the particle sizes as a result of agglomeration. When the sensitivity to changes in organic components is not sufficient to produce the desired tape characteristics, alterations in the ceramic powder particle size distributions are another means of effecting changes.

## Tape-Casting Slip Formulation

The slip formula used for fabrication of the electrolyte tapes is given in Table 1. The binder system is a thermoplastic acrylic ester resin from Rohm and Haas Company, designated Acryloid B-98. This binder is used with a toluene/ethanol solvent system and a plasticizer designated

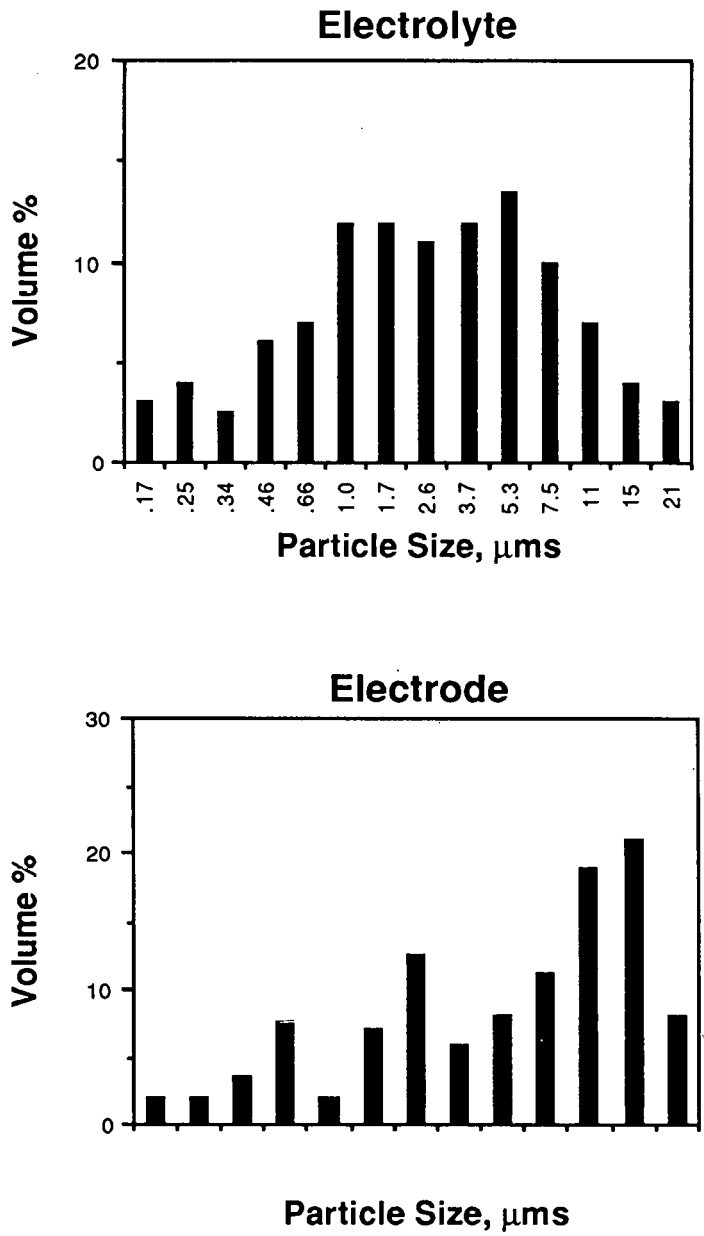



Fig. 1. Particle Size Distributions for (a) the Zirconia Electrolyte Powder and (b) the Lanthanum Manganite Electrode Powder.

Table 1. Electrolyte Tape Casting Slip Formulation.

| Supplier | Component | Amount, g |
|---|---|---|
| Rohm and Haas | B-98 Binder | 3.4 |
| J. T. Baker | Toluene Solvent | 18.4 |
| J. T. Baker | Ethanol Solvent | 12.2 |
| USX Corp. | PX316 Plasticizer | 1.1 |
| Union Carbide | UCON Lubricant | 2.7 |
| ICI Americas | Solsperse 9000 Dispersant | 1.0 |
| Toyo Soda | TZ-8Y Zirconia | 50.0 |

PX316 (manufactured by USX Corporation). The lubricant and release agent is UCON 50-HB-2000 from Union Carbide. Solsperse 9000 dispersant from ICI Americas was used to deflocculate the slip. Yttria-stabilized zirconia (8 mol % $Y_2O_3$) from Toyo Soda Company, designated TZ-8Y, has given the best sintering results to date. This slip is cast on a glass substrate and dries relatively quickly, such that the tapes may be stripped from the glass after about 20 min. The flexibility of the tapes can be altered by changing the amount of plasticizer in the slip. The slip formula for the electrode tapes is given in Table 2.

## Characterization of Tapes

After the tapes are stripped from the substrate, disk-shaped specimens are cut with a punch and sintered to allow the determination of firing shrinkage and density. Specimens cut from electrolyte tapes are approximately 1.5 in. in diameter and 0.004 in. thick before firing. Total firing shrinkages of about 28 to 30% were observed. The densities of the electrolyte specimens were at least 97% of theoretical. In addition to measuring the total shrinkage of the disks, a dilatometer was used to investigate the shrinkage behavior as a function of temperature. Such a shrinkage profile is illustrated in Fig. 2. Two regions of shrinkage behavior are exhibited: that which occurs at low temperatures (200 to 300°C) when the organic components burn out, and that which occurs during high-temperature sintering. Generally, a burnout shrinkage in the range of 2 to 4% is observed when the amount of binder is at its optimal level. Excess binder results in greater shrinkages at low temperature, which may be difficult to tolerate in multilayer systems. The amount of shrinkage during sintering is dictated by the degree of densification of the sample; when densification ceases, shrinkage no longer occurs.

## Failure Mode Identification

Several anticipated failure modes have been identified for study. The disk-shaped specimens described above will be used to test the effects of various internal and external stress fields on the failure behavior of both single-layer and multilayer samples. One of the anticipated failure modes for thin ceramic layers is related to stresses that may arise when

Table 2. Electrode Tape Casting Slip Formulation.

| Supplier | Component | Amount, g |
|---|---|---|
| Rohm and Haas | B-98 Binder | 3.25 |
| J. T. Baker | Toluene Solvent | 17.8 |
| J. T. Baker | Ethanol Solvent | 9.5 |
| USX Corp. | PX316 Plasticizer | 1.0 |
| Union Carbide | UCON Lubricant | 2.0 |
| ICI Americas | Solsperse 9000 Dispersant | 1.6 |
| Anderson Tech. | $(La_{0.8}Sr_{0.2})MnO_3$ | 35.0 |

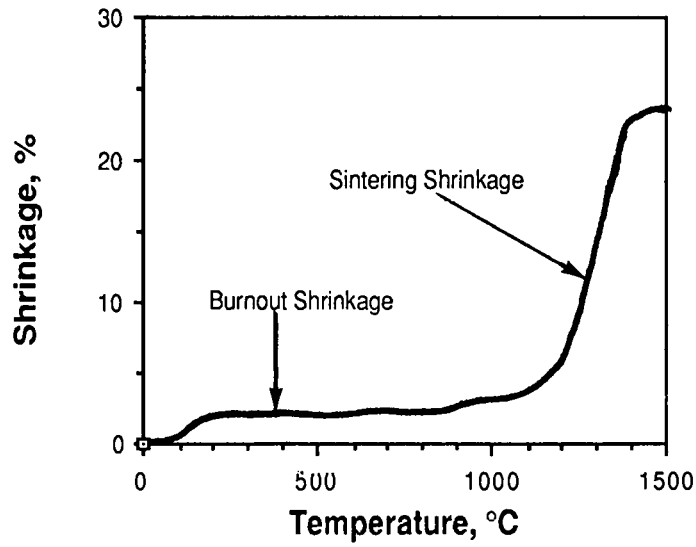



Fig. 2. Firing Shrinkage Profile for a Typical Zirconia Electrolyte Tape.

the membranes are clamped between manifolding surfaces. Although the ceramic layer and the clamping surfaces should be flat, typically some curvature is expected. The first type of failure mode investigation that was carried out was a clamping bend test, which measures the ability of the electrolyte to conform to the shape of a clamping surface. For this test, curved electrolyte disks were compressed between flat clamping surfaces and loaded to failure.

Curved specimens were obtained by placing the disks on zirconia setter plates during firing. Since tape-cast specimens frequently do not fire flat without some type of restraint during firing, the lack of restraint on these samples allowed them to warp slightly, such that varying amounts of curvature resulted.

The test data are presented in Fig. 3, which is a plot of the load at failure as a function of the degree of nonlinearity of the disks. The values on the x-axis were obtained by measuring the gap between the loading surfaces at the point where they first came into contact with the specimen. This value is largest for the specimens with the greatest degree of curvature. A trend of increasing load at failure was observed with increasing flatness of the disks. The equation on the plot corresponds to a logarithmic fit of the data, which yields a coefficient of determination of 82%. These data are being analyzed, with consideration given to existing theories for stress distributions in cylindrical plates and shells. A micrograph of a typical fracture surface is shown in Fig. 4 to illustrate the microstructure of the electrolyte material. Additional tests may also be carried out in the operating temperature range of 600 to 1000°C. Investigation of the fracture behavior of three-layer electrode/electrolyte/electrode tapes will also be of importance. A cross section of a fired three-layer tape is shown in Fig. 5.

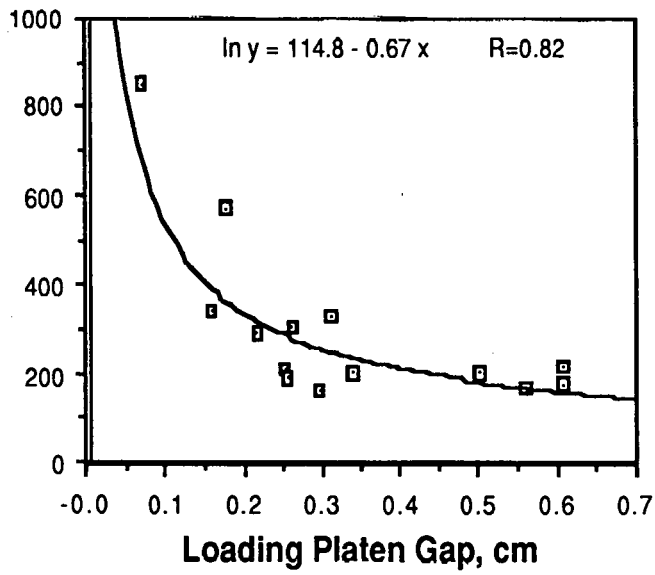



Fig. 3. Load at Failure Determined by Clamping Bend Test, as a Function of the Loading Platen Gap.

Summary

The first months of effort on this project have yielded the following accomplishments:

1. Characterization of the electrolyte and electrode ceramic powders was completed. Powder analyses included particle size distributions, surface areas, and powder morphology.

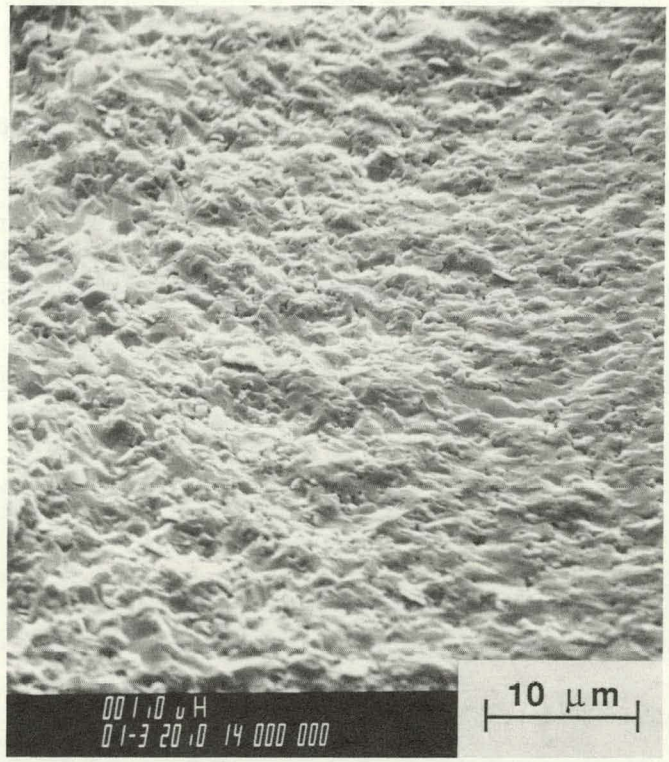



Fig. 4. Micrograph of Typical Fracture Surface of the Zirconia Electrolyte Material. Average grain size about 5 µm.

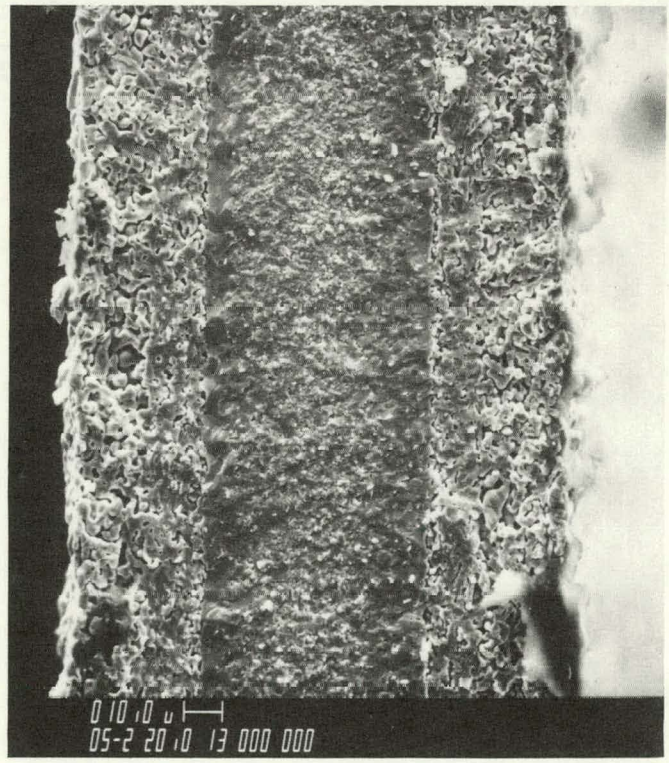


Fig. 5. Micrograph of a Typical Cross Section Through a Three-layer Electrode/Electrolyte/Electrode Tape.

2. Tape casting slips were developed with the aid of the results of the powder characterization analyses. Single layers of electrolyte and electrode tapes were successfully cast.

3. Specimens were cut from the electrolyte and electrode tapes, and fired densities and shrinkages were determined.

4. Firing shrinkage rates were determined by dilatometry to investigate firing shrinkage behavior as a function of temperature. Values for the binder burnout shrinkage and sintering shrinkage components of the total tape shrinkages were obtained.

5. On the basis of the firing shrinkage results described above, slip formulations were adjusted to allow multilayer tape casting of electrode/electrolyte/electrode composites.

6. The first of six failure mode identification tests was carried out. This was the clamping bend test, which involved the investigation of the dependence of load at failure on the degree of curvature of thin layers of the electrolyte material. Higher failure loads were observed for specimens with smaller amounts of curvature.

7. EVALUATION OF POTENTIAL FUTURE PLANS:

Clamping bend tests will be carried out with three-layer composite samples at room temperature and at operating temperatures to investigate failure behavior under the anticipated sealing forces. The test geometry and apparatus for evaluating the effects of a thermal gradient on the multilayer samples will be established. The test details for evaluating the thermal expansion mismatch among the electrolyte, electrode, manifolding, and casing materials will be finalized.

REDUCTION OF EROSION IN ELBOWS DUE TO FLOW FIELD MODIFICATIONS

1. CONTRACT NUMBER: DE-AC21-84MC21349

   CONTRACTOR: West Virginia University
   Morgantown, WV 26506-6101

   CONTRACT PROGRAM MANAGER: E. K. Johnson and K. H. Means

   PRINCIPAL INVESTIGATORS: E. K. Johnson
   K. H. Means
   C. Flemmer
   J. D. Holtzworth

   METC PROJECT MANAGER: D. Dubis

   PERIOD OF PERFORMANCE: Part I, October 1, 1984 - May 16, 1986
   Part II, July 1, 1986 - December 31, 1986

2. SCHEDULE/MILESTONES: See Figure 1

3. OBJECTIVES:

   To investigate the concept of flow field modification as a method of reducing erosion in elbows and bends used in transporting gas-solids mixtures.

4. BACKGROUND STATEMENT

   Coal and other solids are commonly transported through pipes as a gas-solids mixture. Pneumatic transport systems usually contain at least one elbow (bend) in the flow path. The erosion that occurs in these devices presents problems in both the design and operation of these transport systems. State-of-the-art solutions to this problem include: 1) the use of a blind-tee instead of a bend, which accumulates material to protect surfaces, 2) selection of more wear-resistant materials, 3) employing sacrificial material, and 4) altering the design conditions by varying the gas velocity and/or solids loading. To date, each of these options is only a partial solution to the problem. Blind-tees accumulate and release material in an uncontrolled manner, thus upsetting operations, flow measurements, and inventories. Wear-resistant materials have yet to be developed to handle a full range of conditions with a predictable life. The use of sacrificial material in an elbow (bend) has not been an acceptable procedure as the operating characteristics of the transport system will change with time. Altering the operating conditions for elbows (bends) frequently requires a compromise on the efficiency or performance of the process, and the resulting erosion rates have not justified such a practice.

   The purpose of this contract is to investigate the potential for modifying the flow field within an elbow (bend) in order to reduce the erosion

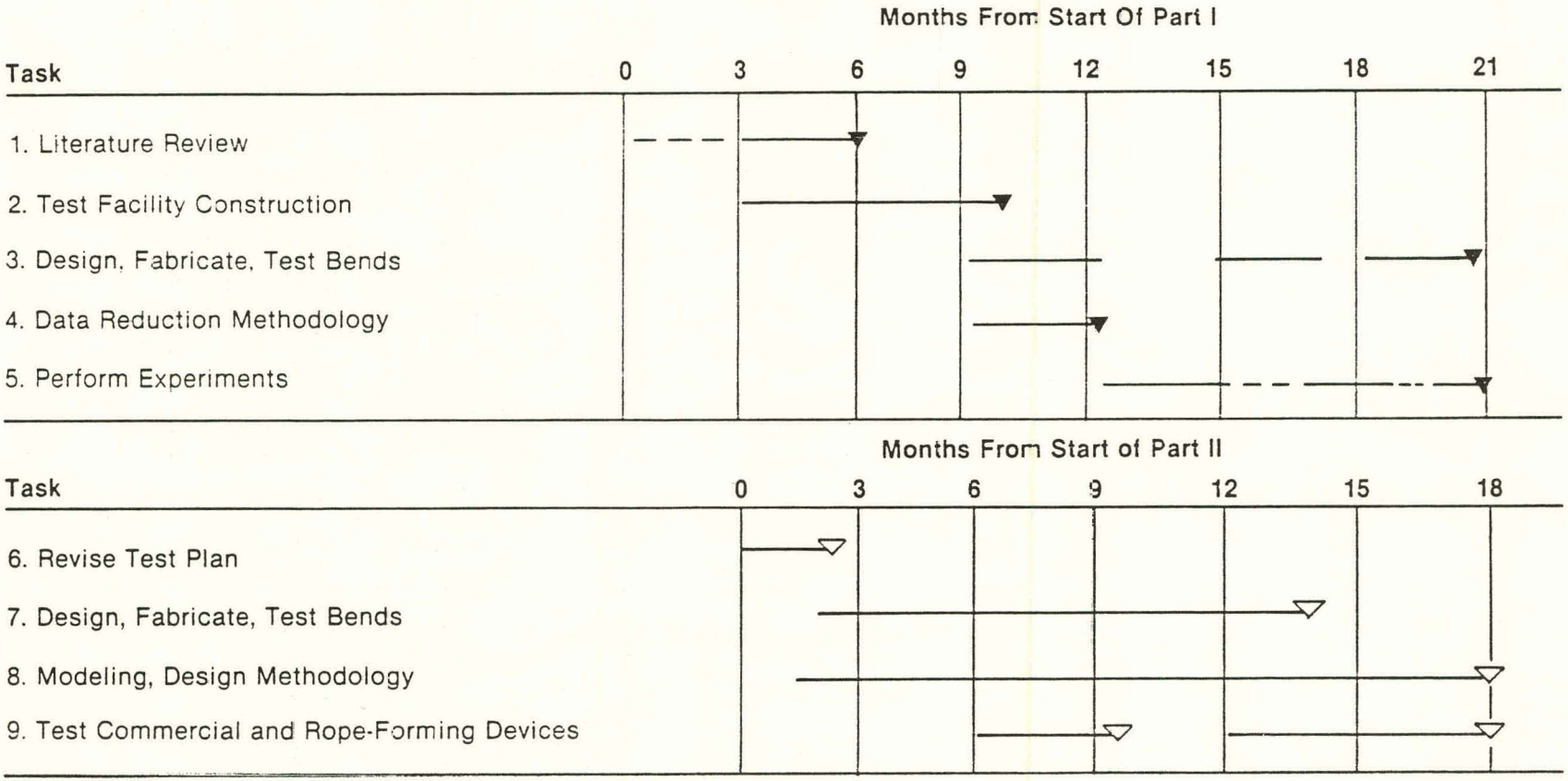



Figure 1: Schedule

rates. Conceptually, jets would move the eroding particles away from the surfaces where the erosion rates are normally the greatest. Also, the particles would be given additional momentum, directed downstream of the bend, thus reducing the pressure drop and acceleration length associated with a standard bend. Because of the lack of knowledge concerning gas-solids mixtures flowing in bends, this contract was formulated in two parts. Part I was an exploratory study to determine if the concept had any merit. Part II is intended to produce more detailed information if the results of Part I warranted further study.

## 5. PROJECT DESCRIPTION

The complete description of gas-solids flow in a bend has not yet been adequately formulated. Consequently, the concept evaluation portion of this project was initiated with several simple bend designs, as typified by the design shown in Figure 2. It may be noted that the flow may be in either direction and one of more jets may be active. The bends were tested in a pneumatic transport loop housed in the Fluidization Research Center at West Virginia University. This loop and the specific results obtained for various bend designs are described in reference [1]. The basic conclusion from Part I was that the concept had merit for further study. This conclusion was based on the fact that the erosion rate had been reduced for relatively high phase-density flow with low jet velocities. The rationale for the reduced erosion rates was that a rope was present in the high phase-density flow and that their rope abraded the bend wall. The air jets are thought to fluidize the rope, thus reducing the abrasive action of the rope on the bend wall. If a rope were not present the erosion rates were usually accelerated by the jets. A simple analytical model has been developed for the reduction of erosion rates due to flow field modification, with ropes, in a horizaontal to vertical bend, reference [2].

In order to establish a goal for the flow field modification concept, a blind-tee was selected as a reference. Erosion rate data was obtained for blind-tee consisting of a standard 1½ inch tee, a cap, and a 4½ inch section of standard 1½ inch pipe welded to the uncapped ends of the tee, Figure 3. Preliminary data indicates that the erosion rate for a blind-tee at high phase-density flow is one-tenth that of a standard $R_B/D = 3.33$ bend at the same operating conditions. Also, the erosion rate for the blind-tee was one-fifth that of the standard bend for low phase-density flow, again based on the same operating conditions. A transparent blind-tee was fabricated for obtaining video tapes of the flow associated with a blind-tee. At low phase-density flows, the particles were dispersed in the flow leaving the blind-tee. Increasing the phase-density led to a rope leaving the blind-tee that was dissipated in a short distance downstream of the tee. A further increase in the phase-density produced a larger rope which oscillated from side-to-side as it moved down the exit pipe. At the highest phase-densities (for the test loop), the solids left the tee in bursts and dune-flow was observed in the exit pipe. The results of this effort are in agreement with the information in the literature [3]. Also, of an exploratory nature, air was

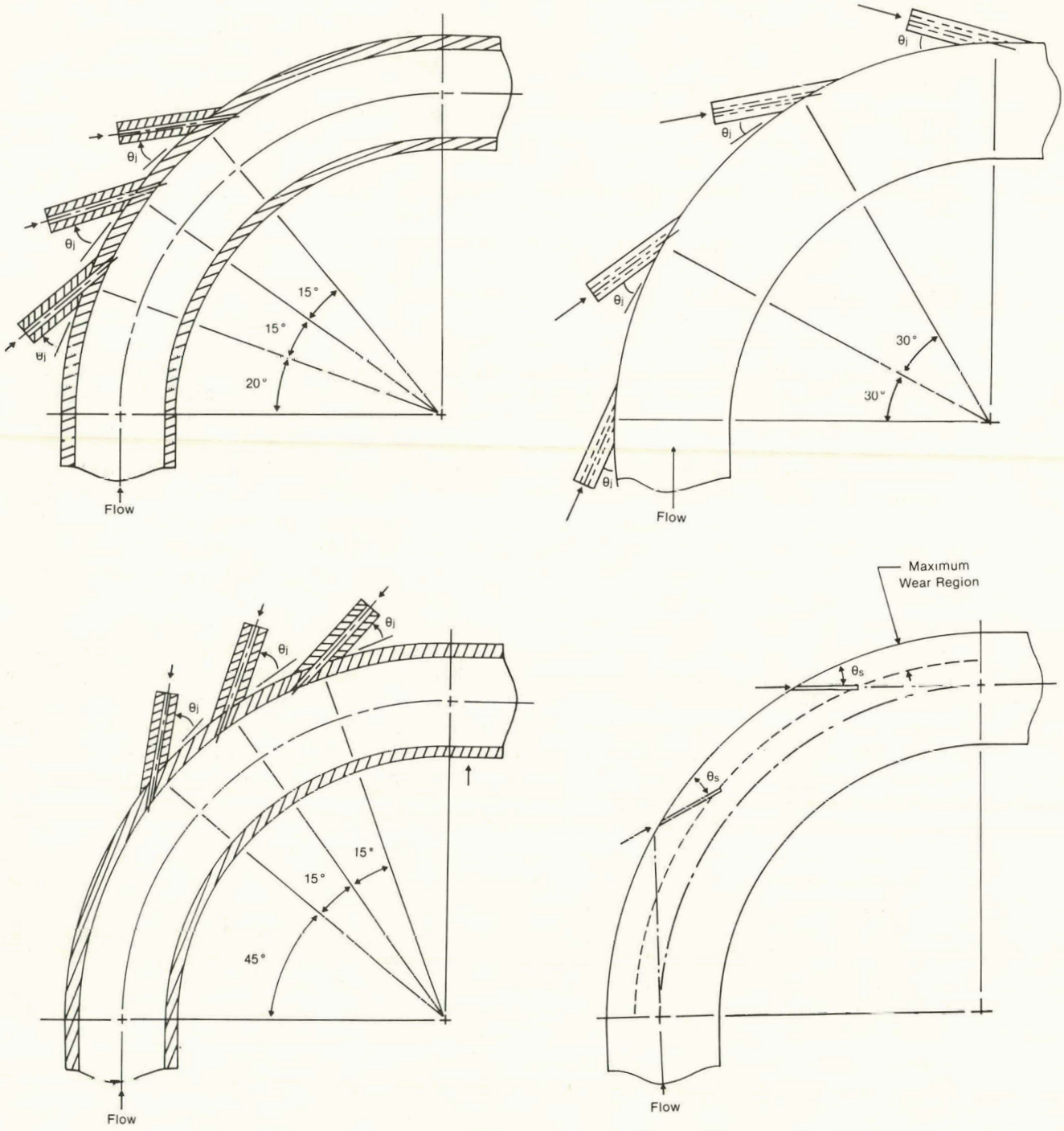



Figure 2. MODIFIED BEND DESIGNS

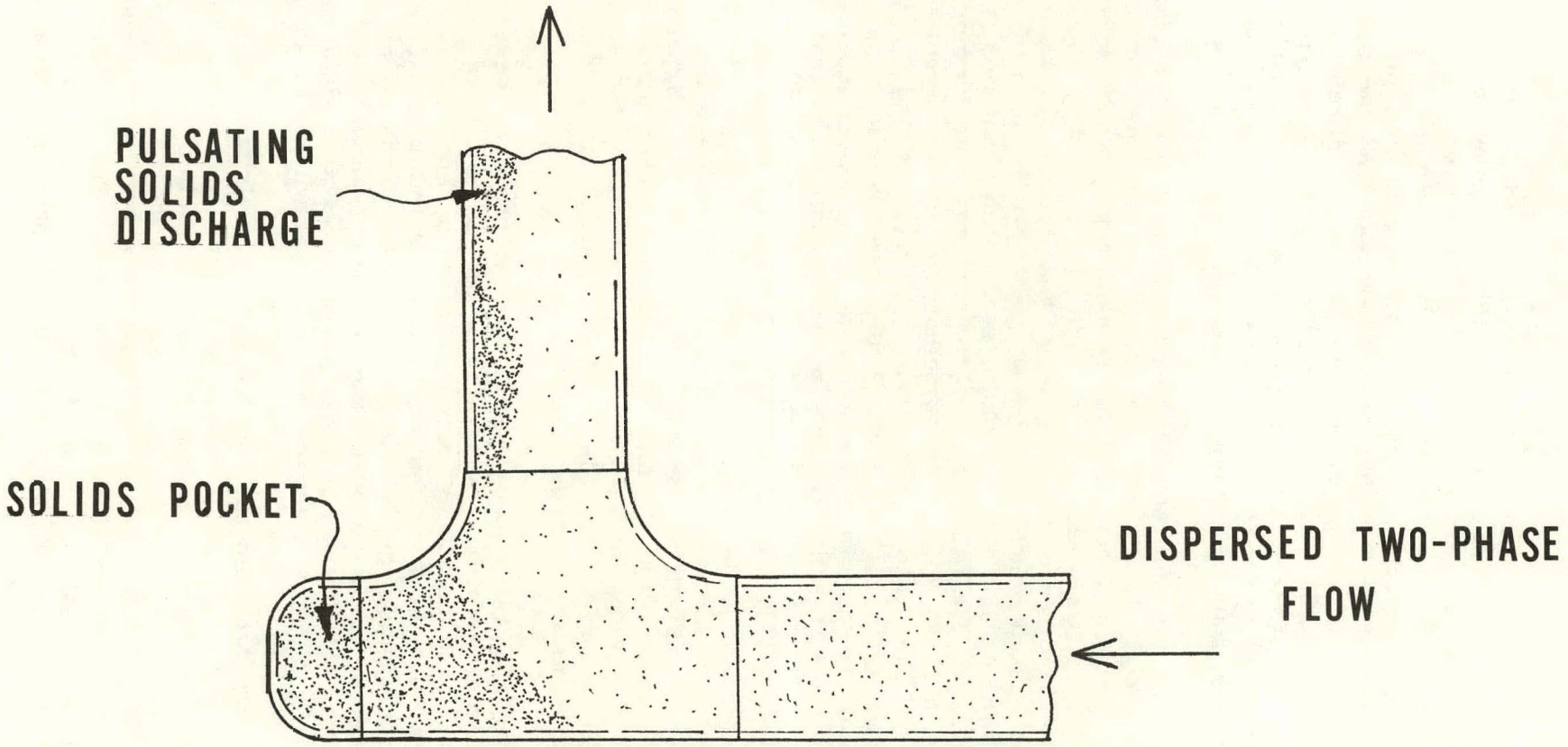



Figure 3.
BLIND TEE

injected through the cap of the transparent blind-tee to fluidize the entrapped particles. The rope leaving this system appeared to persist at high phase densities and for greater distances downstream of the tee. In the non-fluidized tee some of the particles bounce off the entrapped particles while some particles impact and adhere. In high phase density flow a large percentage of the particle impact and adhere to the entrapped particles. These particles then periodically discharge in bulk creating burst and dune flow. The particles move more freely when fluidized. This keeps the particles from adhering and discharging in bulk. This also may decrease the amount of momentum lost to the entrapped particles, thus smoothing out the flow.

The apparent key to the successful development of the flow field modification concept is that a rope be present in the flow approaching a bend. Thus it becomes necessary to develop rope forming devices for low phase-density flows which are outside the rope flow regime. To date, one method for producing a rope has proven to have limited success. An elongated helical spring was placed in the pipe upstream of a bend, as shown in Figure 4. Initially, a rope appeared in the pipe at a phase-density of 3.6 or higher. The spring rope-forming device formed a rope in flows with a phase-density of 2.5 which survived the passage through the bend. However, if a rope existed in the flow upstream of the spring, the spring would destroy the rope. As an interesting note, the combined erosion rate of a copper spring and a standard bend was essentially five-percent less than that for the standard bend alone, for the same conditions.

A simplified analytical model has been developed for high phase-density erosion in a bend in a horizontal-to-vertical flow configuration, [2]. This simple model approach will be extended to other bend configurations and to low phase-density (dilute) flows. A more comprehensive computer model is also being developed. These models will then lead to a design methodology for incorporating the flow field modification concepts into the design of pneumatic transport systems.

As the modeling effort has progressed, several problems have emerged. A search of the literature failed to reveal an abrasive wear rate expression for solid particles moving over a surface. Also, no particle-surface abrasive wear testing device was found in the literature except for those which provide relative data, [4]. Thus an attempt was made to develop an abrasive wear testing device which would produce fundamental data. Initial tests have proven that this data is indeed difficult to obtain. However, several new concepts will be investigated.

In order to support and to evaluate the analytical models being developed, a light attenuation meter is being developed to obtain information on the particle concentration distribution within the flow entering and leaving the bend. This meter, Figure 5, will send a light beam across the diameter of a transparent tube and measure the attenuated light signal arriving at the detector. The combination light source and detector will be rotated around the tube and a plot of attentuation as a function of beam angle will be obtained. This data will

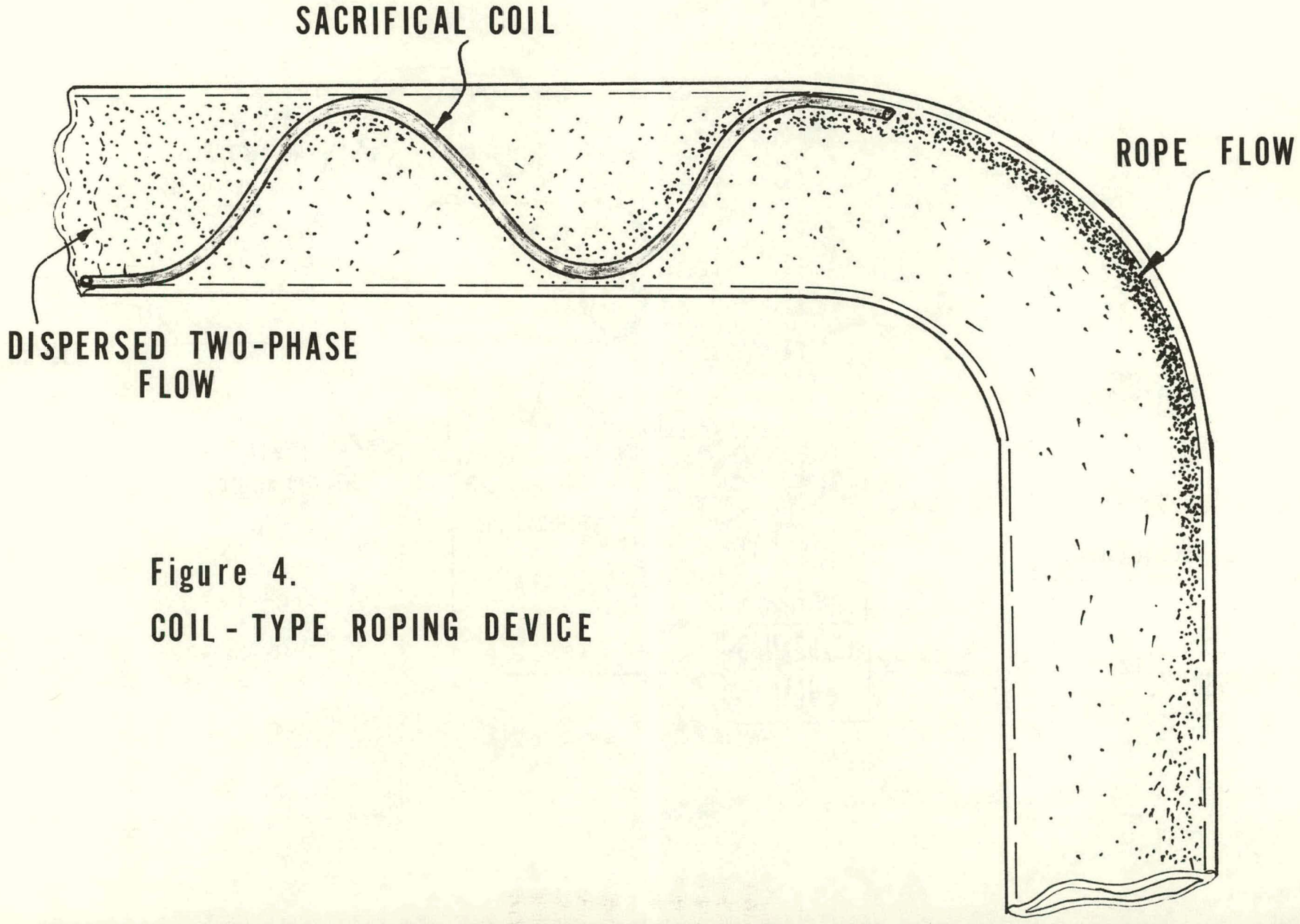



Figure 4.
COIL - TYPE ROPING DEVICE

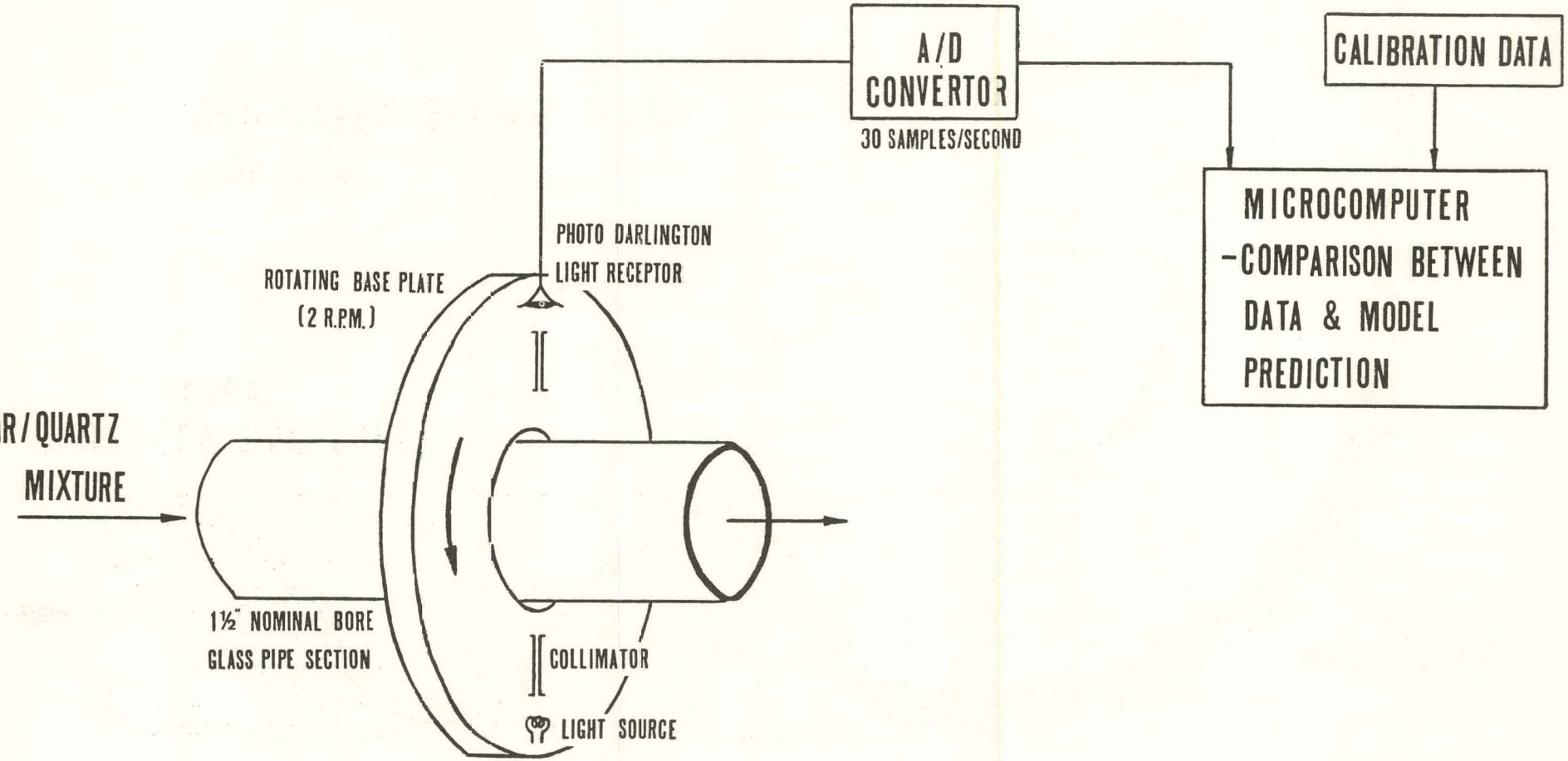



Figure 5.
EXPERIMENTAL VERIFICATION OF THE MODEL

provide information for evaluating assumptions employed in developing the models as well as the results obtained from the models. The experimental pneumatic transport loop has been redesigned and is now being reconstructed. The new loop will allow for longer test runs at high phase-densities and will allow for two pipe sizes for the scaling effort. The initial loop was of 1¼ inch pipe diameter whereas the new loop may have either 1¼ inch or 2 inch diameter pipe. It is also anticipated that the phase-density may be more quickly established for each run in the new loop.

## 6. RESULTS/ACCOMPLISHMENTS

- An initial flow loop with 1¼ inch diameter pipe was designed and built and operated.

- A modified flow loop has been designed for 2 inch diameter pipe, and higher phase density flows and is now being built.

- Demonstrated that air into an elbow (bend) may,
  - decrease the erosion rate
  - change the erosion pattern without changing the erosion rate
  - increase the erosion rate

- Exploratory research has shown that air injection in bends has reduced the erosion for high-phase density flows by at least 10 percent.

- Rope forming devices can create ropes, survive passage through a bend,and reduce erosion.

- A preliminary model has been developed for describing two-phase flow in a pipe.

## 7. FUTURE WORK

To date, the work accomplished on blind-tees and roping devices has been exploratory in nature as the pneumatic transport test loop was being redesigned. Additional exploratory work was accomplished on instrumentation and abrasive wear measurements as the redesigned pneumatic test loop was being constructed. The redesigned loop is now operational and the more comprehensive testing of modified bends and rope forming devices is starting. Also, data will be obtained for any commercially available bends designed to minimize erosion.

In addition to the experimental effort, the development of the mathematical model describing the erosion rate reduction in terms of design and operating conditions for modified bends is continuing. This task will then be the basis for developing a design methodology for implementing the positive results of this project.

## 8. REFERENCES


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2. Johnson, E. K., Means, K. H., Eyler, R. L., and Holtzworth, J. D., "Erosion Processes in Pneumatic Transport Bends With Air Injection," ASME 1987 Pressure Vessel and Piping Conference (to be presented in June 1987).

3. Park, Y. and Zenz, F., "Pressure Loss in Horizontal-to-Vertical Upflow Elbows," Paper D3 in the 5th International Conference on the Pneumatic Transport of Solids in Pipes, April 16-18, 1980, London, England.

4. Means, K. H., "A Survey of Three-Body Abrasive Wear," Final Report submitted to Oakridge Assoc. Universities, August 1986.

# CERAMIC-FIBER CERAMIC-MATRIX HOT-GAS FILTERS

1. FTPA NUMBER: 00218

CONTRACTOR: Oak Ridge National Laboratory
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Oak Ridge, TN 37831-6063
(615) 574-4556

CONTRACTOR PROJECT MANAGER: R. R. Judkins

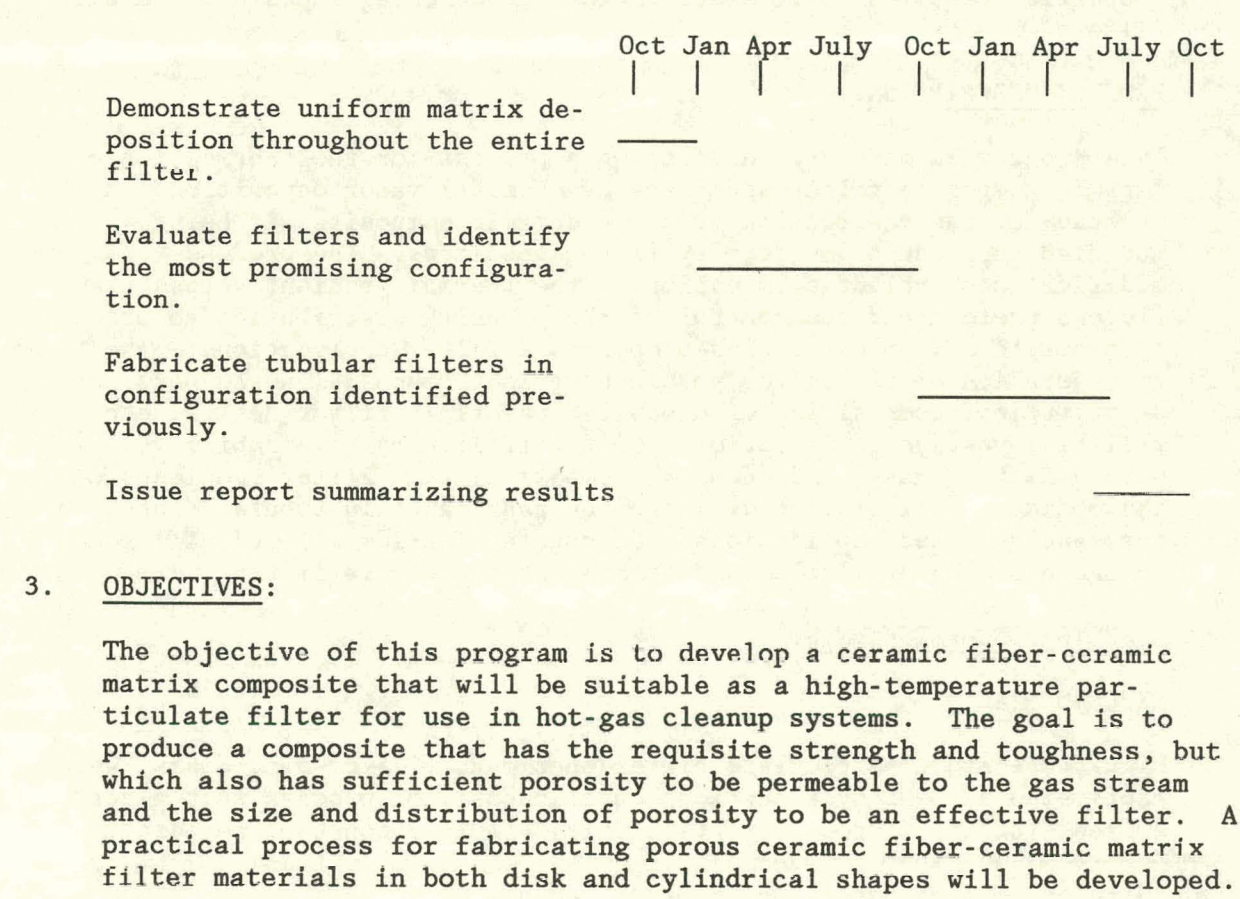
PRINCIPAL INVESTIGATORS: David P. Stinton, ORNL
Ramsay Chang, Acurex Corp.

METC PROJECT MANAGER: D. Dubis

CONTRACT PERIOD OF PERFORMANCE: October 1, 1986 - September 30, 1988

2. SCHEDULE/MILESTONES:

Program Schedule




3. OBJECTIVES:

The objective of this program is to develop a ceramic fiber-ceramic matrix composite that will be suitable as a high-temperature particulate filter for use in hot-gas cleanup systems. The goal is to produce a composite that has the requisite strength and toughness, but which also has sufficient porosity to be permeable to the gas stream and the size and distribution of porosity to be an effective filter. A practical process for fabricating porous ceramic fiber-ceramic matrix filter materials in both disk and cylindrical shapes will be developed.

4. BACKGROUND STATEMENT:

The AR&TD Fossil Energy Materials Program includes development of materials with improved mechanical properties for use in fossil energy systems (Stinton et al. 1986, Caputo et al. 1987). One of the materials is a ceramic fiber-ceramic matrix (SiC) composite made by chemical vapor deposition. In this process a reactive gas which decomposes to SiC at high temperature (1200°C) is forced through a fibrous (Nicalon*) preform. A ceramic matrix material is thus deposited on the fibers, bonding them together, and partially filling the space between fibers. Ceramic fiber-ceramic matrix composites with a fiber volume of up to 60% and densities of up to about 90% of theoretical have been fabricated. Because of the fiber reinforcement, such composites have shown exceptional strain tolerance, thus overcoming the problem of brittle fracture which limits the performance of most ceramics. The work, in support of the Surface Gasification Materials Program has been directed toward developing a modified process to produce ceramic fiber filter materials for use in hot-gas cleanup systems. Fibrous preforms containing fibers of the appropriate diameter, length-to-diameter ratio, and volume loading are partially infiltrated with a ceramic matrix to provide sufficient strength, toughness, and porosity to provide adequate gas flow through the porous fiber medium. Such a composite provides excellent filter efficiency and cleanability and appears to have the mechanical properties required to tolerate the cyclic stresses imposed on ceramic filters.

5. PROJECT DESCRIPTION:

This program is currently developing a process for the fabrication of ceramic composite filter specimens by chemical vapor deposition. A process for the fabrication of dense ceramic composites is being modified to produce low density filter specimens. The process modifications include elimination of the thermal gradient across the fibrous preform and the control of the porosity distribution to produce a composite suitable for high-temperature filter applications. The configuration of the filter specimens (fiber composition and porosity distribution, composition of deposited material, filter design, etc.) will be investigated to optimize filter efficiency, cleanability, strength, toughness, and chemical compatibility. Filter specimens of the optimum configuration will then be fabricated in tubular shapes for candle filter applications. Corrugated fabrics will be utilized to increase the available surface area of the candle filter.

6. RESULTS/ACCOMPLISHMENTS:

EXPERIMENTAL

High-temperature particulate filter specimens (7.5-cm-diam disks) were fabricated at ORNL by a chemical vapor deposition process that placed a free-standing fibrous material (felt) within a constant temperature

*Nicalon, Nippon Carbon Co., Tokyo, Japan.

region (~1200°C) of the resistively heated deposition furnace (Figure 1). The reactants, methyltrichlorosilane ($CH_3SiCl_3$) plus hydrogen, were forced through the felt and deposited a thin layer of SiC on the individual fibers. The process has been developed to the extent that SiC is uniformly deposited across the diameter and thickness of the felt.

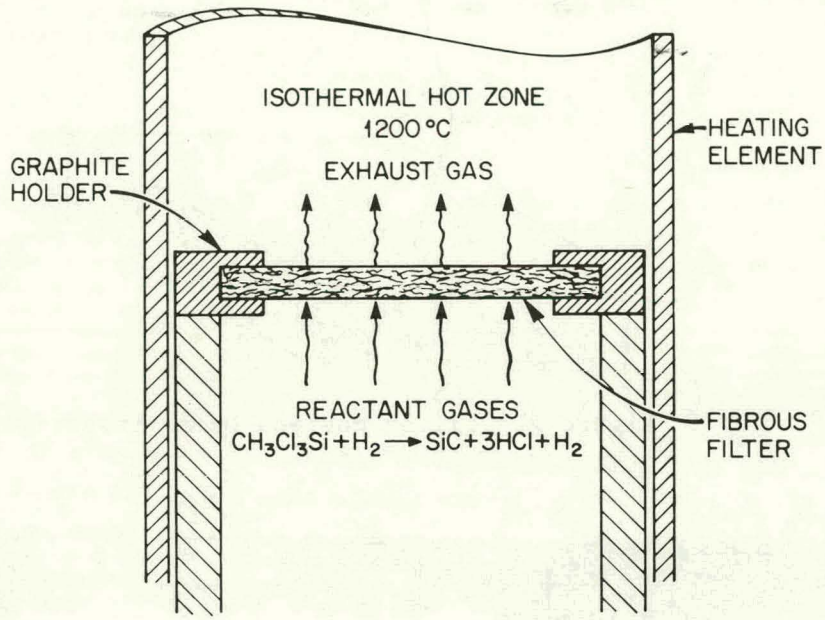



Figure 1. Schematic of chemical vapor deposition process.

Filter medium designs being investigated include free-standing fibrous Nicalon felt, or felt with Nicalon cloth applied to the inner (upstream) surface, the outer surface, or both the inner and outer (downstream) surfaces (Figure 2). The felt functions as the filter medium and the thin layer of silicon carbide bonds the fibers together, thereby providing the necessary mechanical strength to prevent fiber movement or loss during pressure-pulse cleaning. Deposition of SiC on the fibers also firmly bonds the cloth to the felt. Interlocking of fibers as demonstrated in Figure 3 not only provides the mechanical strength but also gives the composite filter very high fracture toughness. In order to minimize the weight of the filter, thin layers of felt were used with a minimum deposition of SiC.

Screening tests of composite filters were undertaken at Acurex Corporation to assess their filter efficiency and cleanability (Chang et al. 1985). Figure 4 shows a sketch of the filter holding arrangement. The only structural support for the filter disk was the clamp around the edge of the disk. The filter specimen was loaded in a horizontal position with the contaminated gas flowing up through the filter. Six specimens (7.5-cm-diam flat disks) were screened using both PFBC flyash and gasifier char at 200°C and 800°C.

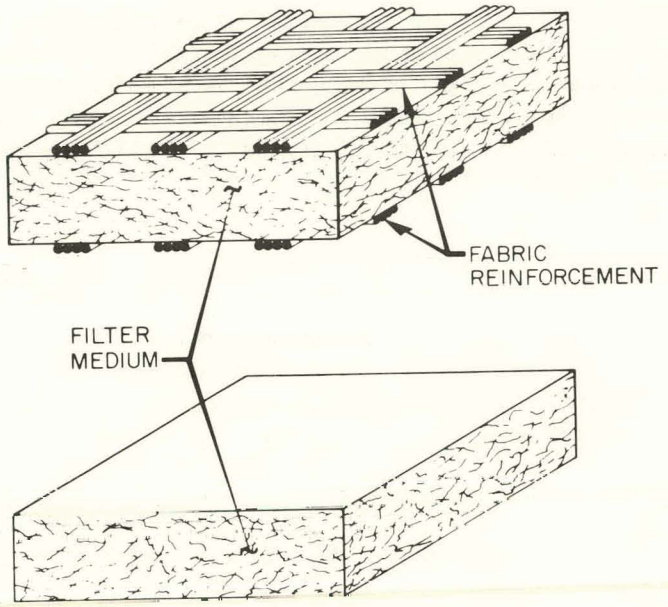



Figure 2. Filter designs being investigated.

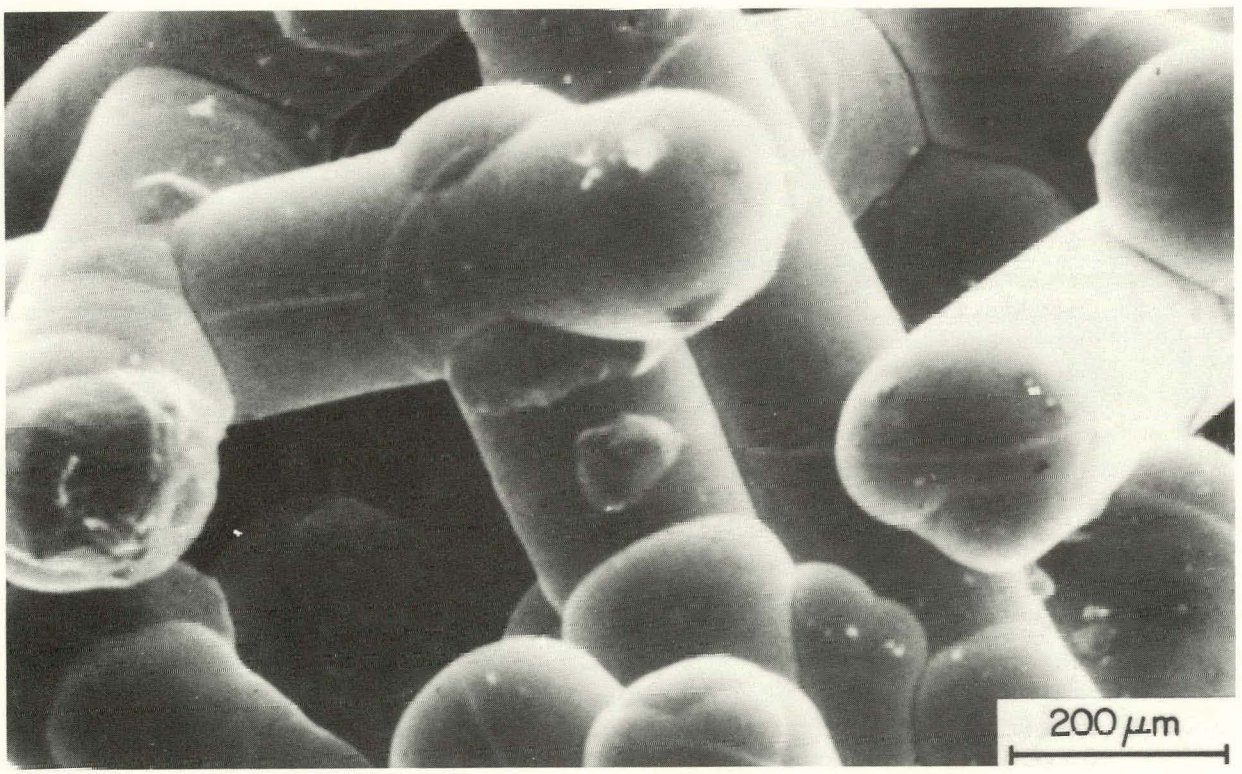



Figure 3. Photograph showing the interlocking of Nicalon fibers with CVD SiC. The deposition of SiC in this photo is much greater than that needed for filter applications but better illustrates the interlocking of fibers.

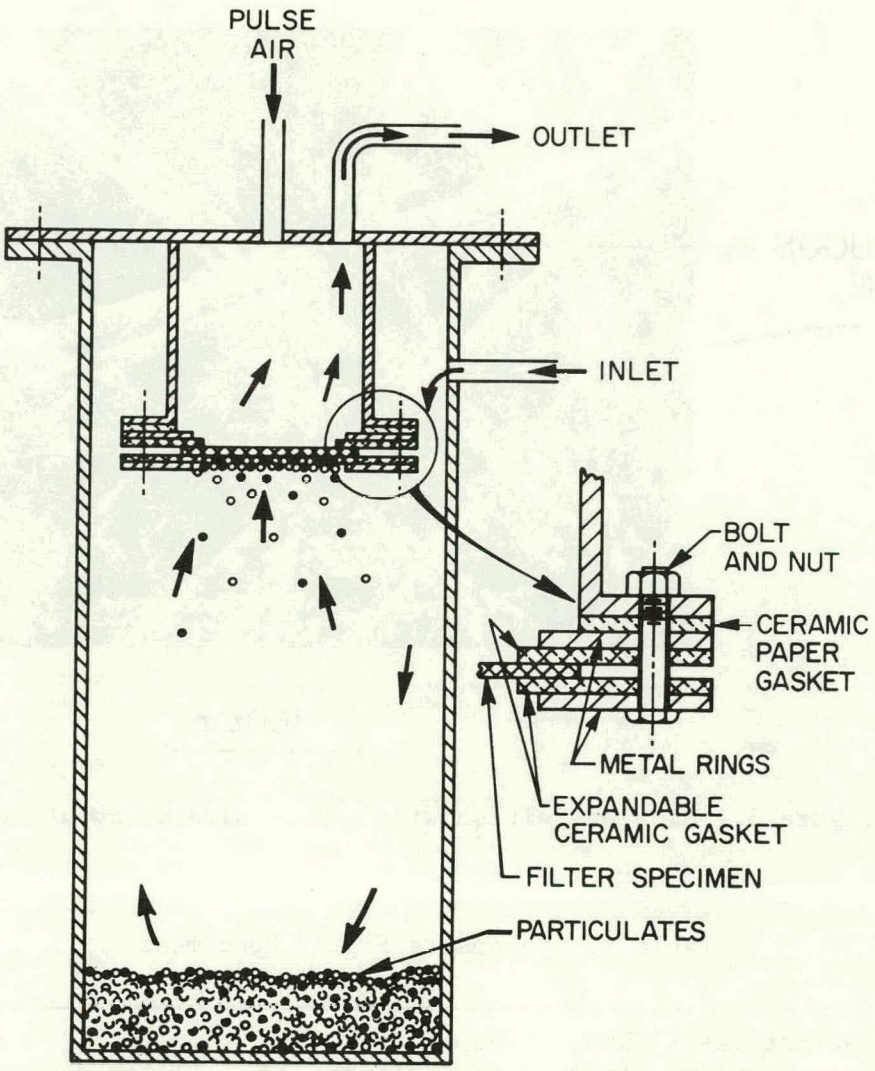



Figure 4. Filter specimen clamping arrangement.

When the first specimens were tested, the edges of the filter were sometimes broken by the restraining fixture. This was corrected by using a ceramic gasket that expanded when heated. With this arrangement, the room-temperature clamping force could be reduced significantly. The gasket also prevented the edge of the fixture from cutting into the filter.

Filter specimens were constructed of a layer of Nicalon felt sandwiched between two layers of Nicalon cloth, with the exception of one sample which had the cloth on one side only. Nicalon felt consists of a three-dimensional array of continuous filaments 15 μm in diameter. The average pore size as shown in Figure 5 is about 100 μm. Because of bridging and agglomeration of the particulates, the Nicalon felt can effectively filter particles significantly smaller than 100 μm. Table 1 describes the conditions under which the various filters were prepared.

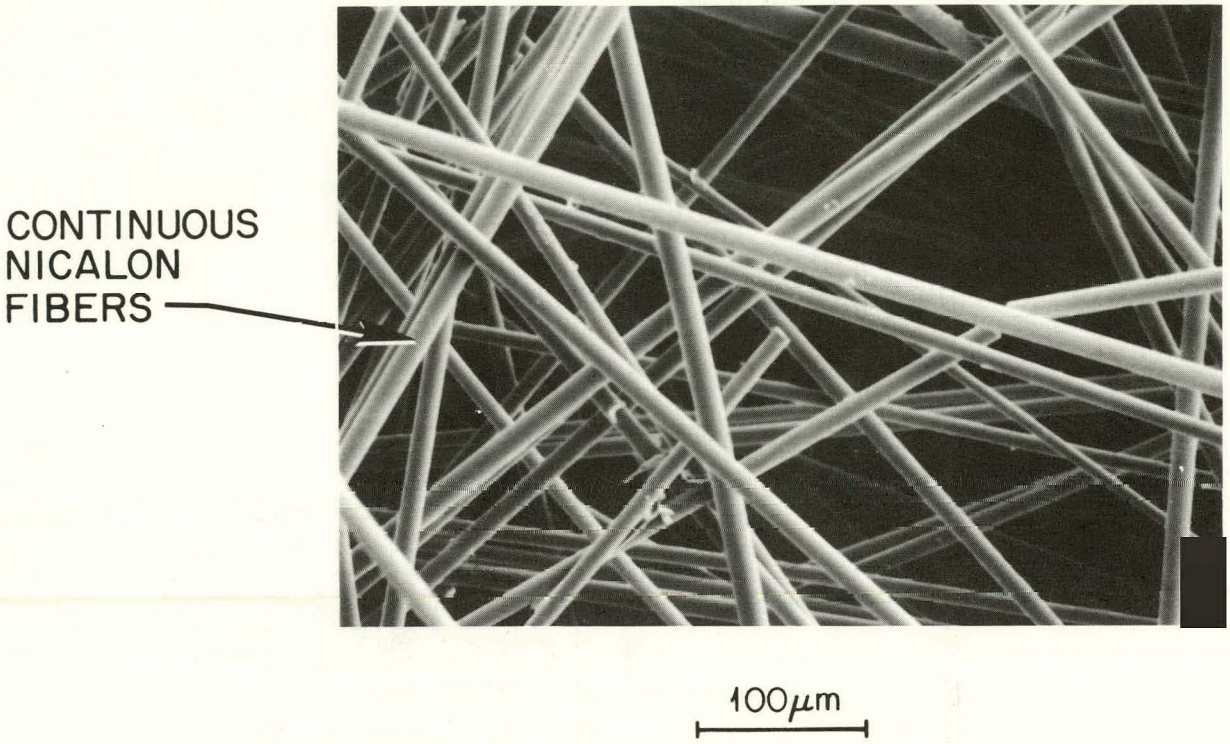



Figure 5. Nicalon felt showing a pore size of about 100 μm.

Table 1. Composite Filter Specimens.

| Number | Reactant gas concentration (g/min) | Run time (h) | Deposition temperature (°C) | Filter design |
|---|---|---|---|---|
| 23 | 0.21 | 2 | 1200 | Plain weave Nicalon upstream and downstream, felt in middle |
| 20 | 0.42 | 4 | 1200 | Plain weave Nicalon upstream and downstream, felt in middle |
| 17 | 0.42 | 4 | 1200 | Open Satin weave upstream only, felt backing |
| 24 | 0.21 | 4 | 1200 | Plain weave Nicalon upstream and dowmstream, felt in middle |
| 16 | 0.24 | 4 | 1200 | Plain weave Nicalon upstream and downstream, felt in middle |
| 21 | 0.42 | 2 | 1300 | Plain weave Nicalon upstream and downstream, felt in middle |

## RESULTS

PFBC flyash and gasifier char as described in Table 2 were used as test dusts. The PFBC flyash has a higher particle density, a smaller particle size, and as revealed by optical microscopy, a rougher surface than the gasifier char. Earlier tests had shown the gasifier char to be less efficiently filtered than the PFBC flyash (Chang et al. 1986, Shackleton et al. 1984). The char did not form a cohesive filter cake, which is probably the reason for less efficient collection.

Table 2. Description of Test Dusts.

| | PFBC flyash | Gasifier char |
|---|---|---|
| Particle Density | 2.87 g/cm$^3$ | 2.18 g/cm$^3$ |
| Particle Diameter | 4.5 μm | 5.5 μm |

The initial tests described in Table 3 were performed at face velocities of 11 to 22 cm/s using PFBC flyash at 200°C. The test specimen with the highest amount of deposited silicon carbide (No. 20) and the specimen with the least amount (No. 23) showed about the same results at these high face velocities. For specimen 20, decreasing the face velocity from 22.2 cm/s to 11.0 cm/s did not appear to have any major effect on dust removal efficiency or cleanability of the fabric. At the end of testing both filter specimens had areas on the clean side which showed evidence of some dust penetration, probably through pinholes in the felt. The edges of the filters had cracked and the layers were starting to delaminate. However, measured collection efficiencies were high considering the high filter face velocities.

Specimen 17 had woven fabric on the upstream side only. The pressure drop across the filter increased rapidly after about 3 h of testing. Use of a higher cleaning pulse pressure (0.36 MPa versus 0.18 MPa) or increasing the cleaning frequency did not slow the increase in the pressure drop.

Specimen 24 was tested at a lower face velocity of about 2.5 cm/s and at 200°C and 800°C. With the exception of the first four hours of testing (test 5), the collection efficiency was higher at the lower face velocities (>99.9% for tests 6 and 7). At the end of testing with PFBC dust, specimen 24 was reused for testing with gasifier char. The collection efficiency kept dropping during the test, apparently because the edge of the filter had broken. There was also a large amount of char between the woven material and the felt on the upstream side. The restraint arrangement was then modified with an expandable gasket material, which extended beyond the edge of the clamp to prevent excessive stress on the filter.

Table 3. Summary of Test Results.*

| Test number | Specimen number/ test dust | Test conditions | Collection efficiency | Test time (hours) |
|---|---|---|---|---|
| 1 | 23/PFBC flyash | 200°C 21.7 cm/s | 99.7% | 4 |
| 2 | 20/PFBC flyash | 200°C 22.2 cm/s | 99.3% | 4 |
| 3 | 20/PFBC flyash | 200°C 11.0 cm/s | 99.4% | 4 |
| 4 | 17/PFBC flyash | 200°C 20.5 cm/s | 99.5% | 4 |
| 5 | 24/PFBC flyash | 200°C 2.5 cm/s | 99.2% | 4 |
| 6 | 24/PFBC flyash | 800°C 2.5 cm/s | >99.9% | 4 |
| 7 | 24/PFBC flyash | 200°C 2.7 cm/s | >99.9% | 4 |
| 8 | 24/Gasifier char | 200°C 2.7 cm/s | 97.0% | 5 |
| 9 | 20/Gasifier char (retest) | 200°C 3.0 cm/s | 99.7% | 5 |
| 10 | 16/Gasifier char | 200°C 3.0 cm/s | 99.4% | 11 |
| 11 | 21/Gasifier char | 800°C 3.5 cm/s | >99.9% | 50 |

*Tests were conducted at 200°C with dust-laden air rather than combustion products. Air or nitrogen (room temperature) was used as the pulse gas for periodically removing dust from the filter surface. A pulse pressure of 0.18 MPa was generally used with a pulse duration of 0.05 s.

Specimen 20 was also retested using gasifier char at 200°C and a face velocity of 3.0 cm/s. The initial collection efficiency of 99.5% gradually improved to 99.7%. When the filter specimen was removed, no char was noticeable on the downstream side.

Specimen 16 was tested with gasifier char at 200°C and a face velocity of 3.0 cm/s. Specimen 16 was a new sample as compared to specimen 20

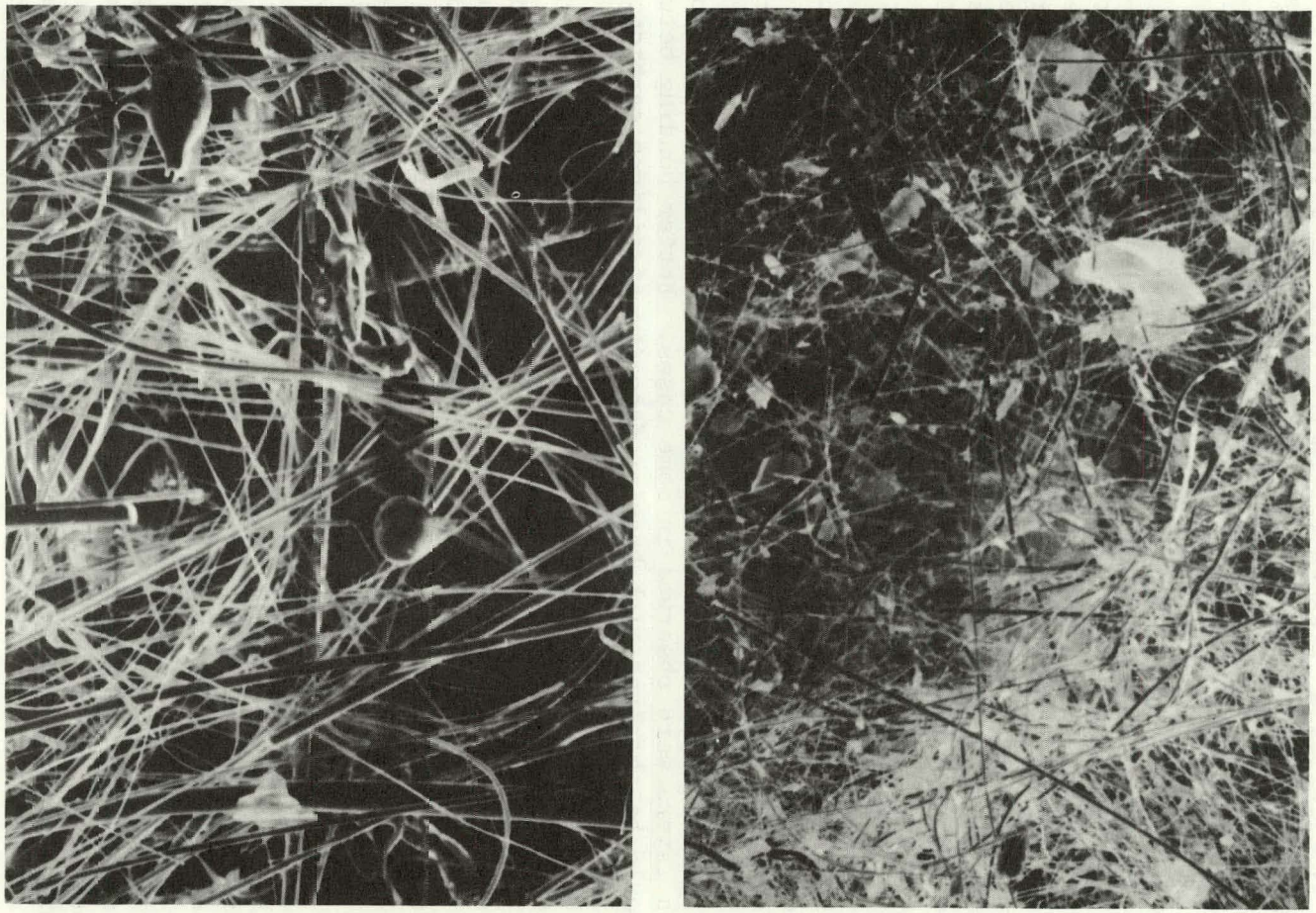



Figure 6. Aluminosilicate papers with reduced pore sizes.

which had been used for testing with PFBC dust prior to testing with char. A slightly lower collection efficiency was measured for specimen 16.

After the short duration tests showing promising results, a specimen was selected for longer duration testing at high temperatures. Specimen 21 was tested at 800°C for 50 h. After an initial collection efficiency of about 99.6%, the filter collection efficiency improved to >99.9%. There was no noticeable damage to the filter and no char was observed on the downstream side of the filter.

## DISCUSSION

The ideal filter should retain 100% of the particulates at the surface since particulates that penetrate the filter medium could not likely be removed during the cleaning cycle. Results from testing the first set of composite filter specimens are very encouraging since collection efficiencies were uniformly high even at very high face velocities. There did not appear to be cleanability problems with the small filter specimens.

Edge fracture occurred in the first few filter specimens tested. A slight change in the fixture and gasketing material appeared to solve the problem. The edge weakness can be partially attributed to reduced deposition of silicon carbide at the edge during fabtrication of the filter. The rest of the filter, although unsupported, had no cracks or other structural failures. Delamination of the felt from the cloth layers were observed in some cases. Better bonding between layers could be obtained with heavier deposits of silicon carbide.

Use of simpler base filter construction will make fabrication of commercial-scale filters easier. Besides the multiple-layered construction used, single-layer construction will also be examined. Use of ceramic paper material or a single layer of texturized ceramic cloth as the base material for chemical vapor deposition of silicon carbide are possible approaches. Filters fabricated from aluminosilicate papers have been prepared but not yet tested. The papers offer the additional advantage of having controlled pore sizes. Figure 6 shows ceramic papers fabricated from continuous filaments 1 to 2 μm in diameter. These papers have pore sizes between 1 and 10 μm. Eventually, tubular preforms consisting of a cylinder of felt, possibly wrapped with continuous filaments, will be infiltrated to produce candle filters.

Candle filters offer a pratical means of removing particulates from a hot gas stream; however, they possess significantly less surface area than cross flow filters. This limitation causes difficulties in actual practice because many very long candles would be required and the overall size of the filter would become very large. Candle filters fabricated from ceramic papers offer a tremendous potential advantage over cloth or felt materials. The surface area of the candle filters fabricated from ceramic paper can be increased tremendously by corrugating the paper prior to deposition of the matrix (Figure 7). The increased surface area would significantly reduce the size and number of candles required for a specific application.

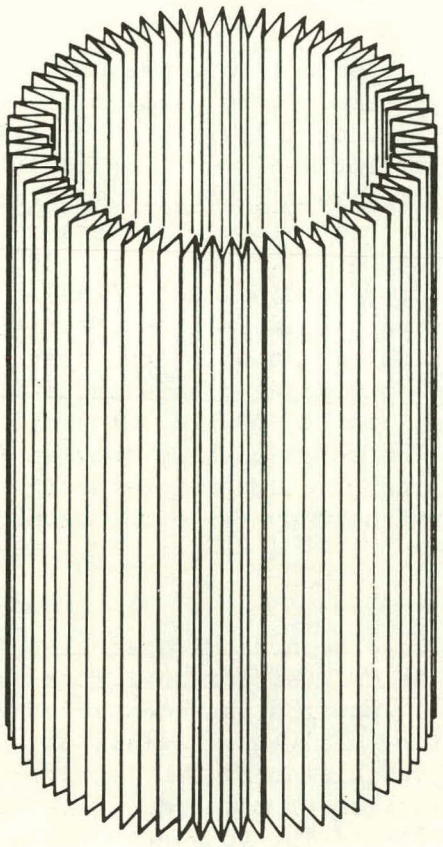


Figure 7. Corrugated papers increase the surface area of candle filters.

The use of different base fiber material and different materials for deposition will also be investigated for composite filter construction. In any case there needs to be a better understanding of how the interaction of the different components of the composite filter affect the performance of the filter.

Chemical compatibility of the filter materials with hot combustion gases must be determined. Composite filters are currently being tested by the National Coal Research Establishment at Stoke Orchard, England, in a coal gasification system. After testing, the filters will be returned for further testing and evaluation. Potential problems could arise because silicon carbide is susceptible to attack by alkali metal compounds at elevated temperatures. For example, sodium could form a low melting (870°C) eutectic with the protective $SiO_2$ film that forms on the surface of the SiC at elevated temperatures. Attack of the protective layer leads to rapid degradation of the SiC. If the reaction causes a significant problem, material other than SiC which is less susceptible to alkali attack will be deposited by CVD.

## CONCLUSIONS

A process utilizing chemical vapor deposition was developed for the fabrication of high-temperature particulate filters. Fibrous materials such as Nicalon felt with a pore size of about 100 μm were evaluated as filter mediums. For additional strength Nicalon felt was sandwiched between layers of Nicalon cloth. Preliminary evaluation of the initial Nicalon filters revealed that cleanable filters with collection efficiencies of >99.9% for either PFBC flyash or gasifier char could be produced. Simpler filter designs need to be investigated since particulates were often trapped between the cloth layer and felt and delamination of the filters was occasionally observed. Filters consisting of aluminosilicate papers with pore sizes ranging from 1 to 10 μm were successfully prepared but have not been tested. The relationships between filter efficiency, cleanability, strength, toughness, preform design, and deposition conditions need to be established to optimize the properties of the filter materials.

## 7. FUTURE WORK:

Composite filters have been fabricated that are very effective in removing PFBC flyash or gasifier char from an effluent stream. However, additional research is necessary to identify an optimum filter configuration. Filter materials of varying composition ($Al_2O_3$, Nicalon, Nextel*) and different CVD materials will be investigated to identify the combination of materials that demonstrate the best chemical compatibility. The toughness or mechanical reliability of the filters must be improved significantly from currently available materials by controlling the quality and quantity of material deposited by CVD. In addition, simple candle filters which maximize the available surface area (corrugated fabrics, etc.) must be designed which are easy to produce commercially.

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*Manufactured by 3M, St. Paul, Minnesota.

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