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Proceedings of the

1980 UCC-ND AND GAT WASTE MANAGEMENT SEMINAR

R 1540

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APRIL 22-23, 1980

Shawnee State Park Lodge
Friendship, Ohio

HOSTED BY GOODYEAR ATOMIC CORPORATION

UNION CARBIDE

GOODYEAR

PREPARED BY
OAK RIDGE NATIONAL LABORATORY
OPERATED BY UNION CARBIDE CORPORATION FOR THE U. S. DEPARTMENT OF ENERGY

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Hosted by
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General Chairman: E. R. Wagner, PGDP
Program Chairman: T. W. Oakes, ORNL

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Session I

SPECIAL PAPERS

Chairperson: H. H. Abee (UCC-ND)

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HEALTH EFFECTS OF LOW-LEVEL RADIATION[*]

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ABSTRACT

Direct effects of low levels of radiation exposure, i.e., at or below the ICRP recommended guidelines, have not been documented. Extensive knowledge of radiation effects at higher levels, e. g., for acute neutron and gamma ray doses, has been obtained from studies of the survivors of the nuclear bombings of Japan, from a few accidents, and from medical related studies. The most important data for early standards setting was based on the radium dial painters of the second and third decades of this century, while the overall most important data are those from the studies in Japan. There are apparent conflicting data for inhaled plutonium from animal studies (dogs) and for the limited human exposures. The implications of the various observed and hypothesized effects will be assessed in view of current concerns about nuclear reactors and waste disposal.

It seems appropriate to begin a new decade with a short review of what we know about the health and environmental effects of low levels of radiation. We can, perhaps, relate what we have learned about radiation effects to those that might be produced by other agents. We can almost certainly approximate the transport of other agents through the environment and food chain on the basis of the knowledge of radioactive materials in the envirosphere.

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[*] Research sponsored by the U. S. Department of Energy under contract W-7405-eng-26 with Union Carbide Corporation.

First, let us recall that we know more, both qualitatively and quantitatively, about the effects of radiation on humans, animals, and the environment than about any other agent, including those known to be hazardous. The widespread controversy over the low-level effects of radiation is not about what we don't know but, paradoxically, about what we do know. The most extensive early studies of radiation effects on a population large enough to provide statistically valid data were those of Robley Evans on radium dial painters and radium chemists. Figure 1 shows one presentation of his data, obtained during the 1930's and 1940's chiefly, and which he still feels to be completely valid. These data served as the basis for radiation standards and guides until the mid-1950's and to some extent, even later. The apparent threshold at 1000 rads to bone corresponds to 1 microcurie (or 1 microgram) of radium in the skeleton. Assuming a threshold at 1 microgram, the ICRP in 1949 agreed on a guideline of 0.1 microgram for occupational workers and 0.01 microgram for nonoccupational exposure. This corresponded to 30 or 3 rem/yr and has, of course, been slightly modified recently by the weighting factor of 0.12 recommended for bone in ICRP Publication 26. The new limit corresponds to 5 rem/year whole body divided by 0.12 for the bone or about 44 rem occupational or 4.4 rem nonoccupational.

Most reputable scientific groups have endorsed the concept that linear extrapolation of effects from doses at which effects have been observed to zero effect at zero dose provides a safe method for predicting health effects. In doing so, they point out that certain effects, when produced by neutrons or other high LET radiations, are closely approximated by such relationship. They also emphasize that all low dose effects from low LET radiations, such as x- and gamma radiations, produce markedly less effects than high LET when the dose is delivered acutely, and generally even less (than low LET given acutely) when fractionated or protracted at low dose rates. Exceptions exist but contribute little to the total cancer picture.

A good example of this is the incidence of leukemia in the Japanese survivors of the nuclear bombings of Hiroshima and Nagasaki. Figure 2 shows the general shape of these curves. Because the number of cases is zero in Nagasaki below 100 rads (or are not observable because of statistical and epidemiologic uncertainties in choosing the comparison populations) the curve is debatable at low doses until additional data are considered. Keep in mind that, due to the differences in bomb designs, the people in Hiroshima were exposed to both neutrons and gamma rays whereas the Nagasaki bomb produced a field of almost pure gamma rays, especially far out in the low dose zone.

However, rather than dwelling on these shapes, let us look at the data in a different manner. For a model, T. D. Jones used Katz's model for cell-killing of red marrow cells as a function of radiation type and dose, Figure 3. The drawing is admittedly simplified, but not so as to be inaccurate for our application. Note that on a logarithmic plot, the straight line defines the percentage of cells that survive a given dose of fast neutrons and that the shouldered curve with the lesser slope gives the same relationship for gamma rays. It is apparent that on a

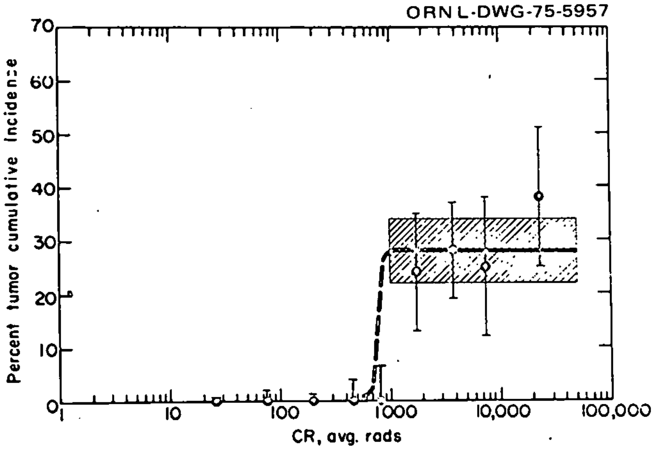

Fig. 1. Effects of occupational radiation exposure.

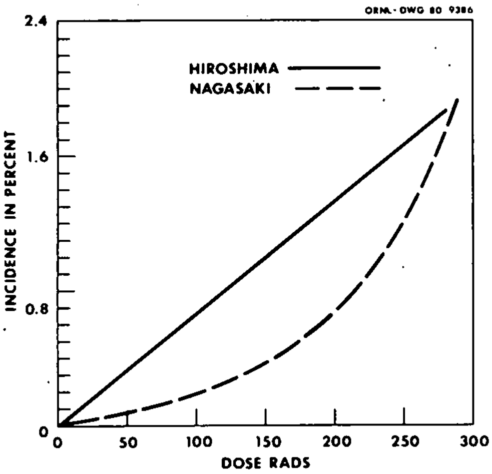

Fig. 2. Radiation-induced leukemia in Hiroshima and Nagasaki.

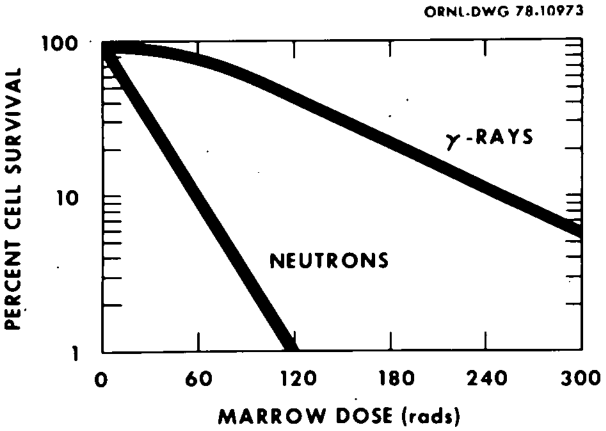

Fig. 3. Effect of radiation on red marrow cells.

linear graph these curves are grossly nonlinear. Now, examine Figure 4 which shows the incidence of acute leukemia in the Japanese, where the extrapolation to zero dose is based on the cell killing model. The incidence increases linearly with the number of marrow cells killed. Figure 5 is a similar plot for chronic leukemia. The linearity still holds but there are two curves indicating a different rate of incidence when neutrons are present as in Hiroshima.

It is clear that the linear model for leukemia induction as a function of the number of cells killed works. What about other forms of cancer? Figure 6 shows that the relationship holds for the composite of all fatal malignancies observed in Hiroshima and Nagasaki. This still does not encompass other forms of radiation or species of animal, so let us examine Figure 7 which shows the incidence of myeloid leukemia in mice. Finally, Figure 8 gives a composite of all data analyzed thus far on humans, although the dosimetry for some of it is not accurate to better than a factor of at least two. Those cases, for which doses are best known, fit well the lines drawn for the Japanese data. Because of uncertainties in collimation of the x-ray beams, the doses to the marrow from the irradiation of the thymus is uncertain, and the doses to the marrow of the pelvis are strongly influrenced by the uncertainties in physical positioning of the sources. Considering the uncertainties in dosimetry, the data appear to support the model for humans.

A short explanation is needed concerning the fraction of marrow (or other) cells killed by non-uniform irradiations. The fraction is obtained by computing the cells killed in each segment of marrow exposed and obtaining the weighted average for the entire marrow involved in hemopoiesis. Of the cases cited, the easiest was the case of the ankylosing spondylitics because the doses were so high, e.g., 2000 rads or more, that essentially all cells within the collimated x-ray beam were killed. Thus, the fraction killed was taken as that fraction of thoracic marrow within the focus of the beam.

Many substances are known to kill cells in the body and to be carcinogenic. Good examples of such are benzene, benzo(a)pyrene, and cigarette smoke. Dose and effect relationships are usually based on one or two points and are generally not known well. It is clear that the quantitative relationships that have been established in radiation protection are far better known than those for any other substance except cigarettes.

Frequently, toxic substances are discovered in unexpected places in the environment. Though we sometimes find unexpected radioactive substances in the environment, nonradioactive chemical species have been less well monitored generally. At ORNL we are taking advantage of our experience with radionuclides and of our available monitoring stations to do an increasingly rigorous documentation of environmental releases and control.

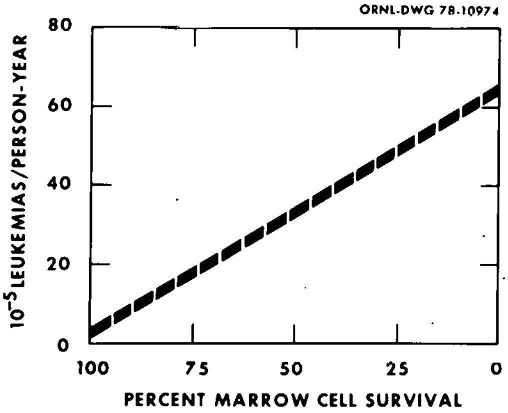

Fig. 4. Incidence of acute leukemia in A-bomb survivors.

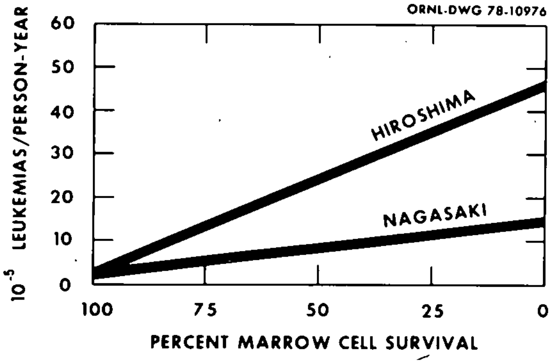

Fig. 5. Incidence of chronic leukemia in A-bomb survivors (Beir).

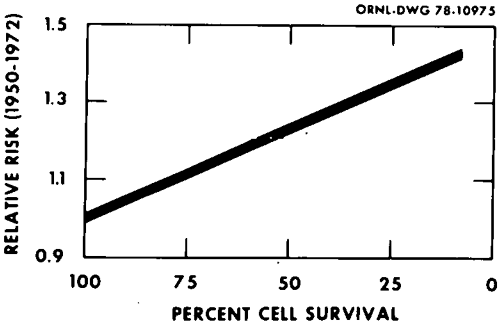

Fig. 6. Fatal malignancies in Hiroshima and Nagasaki A-bomb survivors (leumkemias not included).

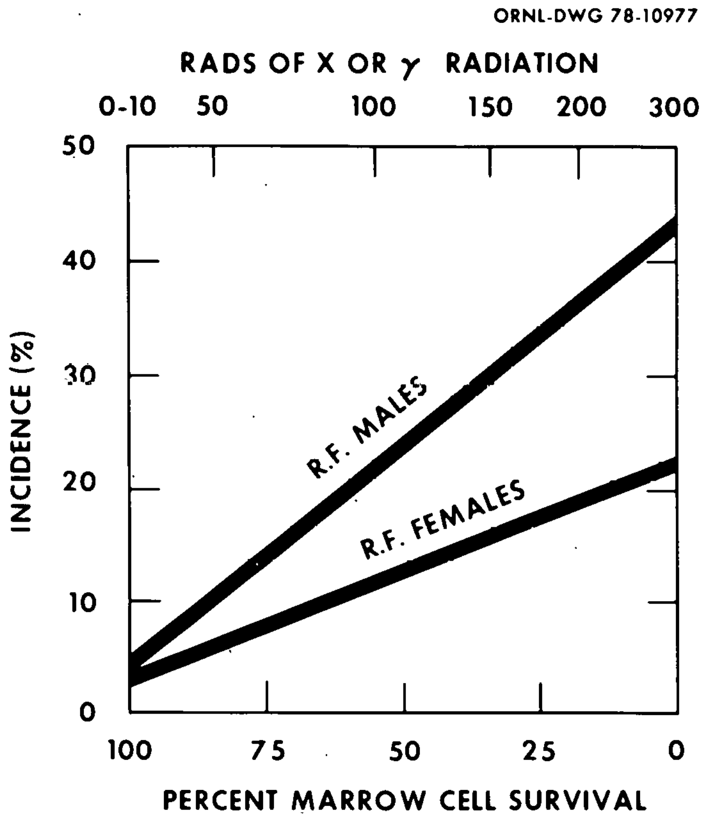

Fig. 7. Myeloid leukemia in mice (Upton).

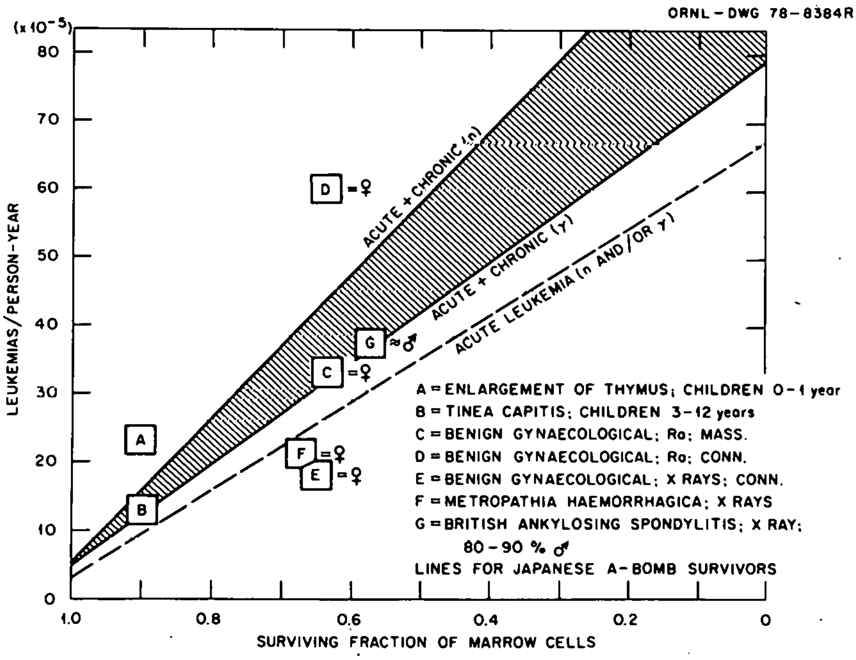

Fig. 8. Cell survival of radiation in humans.

ORO ENVIRONMENTAL MANAGEMENT APPRAISALS

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ABSTRACT

The requirements and purposes for the ORO Environmental Protection appraisals will be presented briefly. A typical appraisal format will be outlined and aspects of the discussions that generally ensue will be characterized. The site-specific factors that tend to make each facility's appraisal unique will be highlighted. Features of the "close-out" will be covered.

Details of the environmental policy questions that now must be dealt with as part of the appraisal will be addressed. The formal "recommendation" will be discussed in terms of the management concept versus actual experience. The appraisal rating criteria developed by ORO's Office of Performance Evaluation, and how these criteria must be applied, will be illustrated. The inherent differences between CPAF and CPFF operation contracts will be outlined.

Finally, some examples of both positive and negative experiences that have resulted from ORO appraisals will be presented, along with some projections for the future.

ORO ENVIRONMENTAL MANAGEMENT APPRAISALS

An ORO Environmental Management Appraisal is an annual event at each of the six major contractor operated facility whereby two or more staff members of the ORO Environmental Protection Branch conduct several days of on-site discussions with appropriate contractor staff to formally assess the status and progress of environmental protection programs. On many occasions, a member of the ORO contract administrator's staff will also participate. A formal report is prepared after the site inspections and discussions, and is provided to the appropriate ORO contract administrator for review and concurrence. The contract administrator generally transmits the report unchanged to the plant manager, along with instructions for implementing any "recommendations" that might be included in the report. In recent years, the Environmental Protection Branch has also had the responsibility for specifying a "contractor performance rating" in the appraisal report. In addition to the plant manager, a copy of the report is provided to ORO's Office of Performance Evaluation (OPE).

Appraisal Requirements

The DOE Manual requires the conduct of various on-site appraisals of all contractor activities and the preparation of the reports. Applicable Manual Chapter references include MC-0504, 0510, 0511, 0513, and 0524.

Formal appraisal efforts, especially in the Health and Safety areas, are considered to be of very high priority by ORO and DOE Headquarters upper level management. In 1978, the Safety and Environmental Control Division was notified that several positions were going to be eliminated and that staffing levels were to be reduced accordingly. This included the loss of one position from the Environmental Protection Branch, reducing the staff level from five to four. Each of the Safety Division branches was asked to detail those normal branch functions that could not be considered of high priority in the limited staffing situation, and that would probably go undone for some length of time. The information prepared by the Environmental Protection Branch indicated the appraisal inspections were considered of low functional priority. Upper management's response stated that all Safety and Environmental Control Division appraisal and report responsibilities were to receive top priority.

The Environmental Appraisal Routine

Before 1969 or so, the fairly modest number of management concerns that could be strictly related to environmental protection were simply covered in other Health and Safety Appraisals. By 1970, the "Waste Management and Pollution Control Branch" had been set up in the Safety Division. This was soon changed to the Environmental Protection Branch, with most of the functional responsibilities that are now associated with this branch.

Environmental appraisal visits were usually arranged informally with key contractor personnel, and a letter from the contract administrator to the plant manager would soon follow to formalize these arrangements. Sometimes the plant visit would occur within three or four weeks from the conclusion of the informal plans. The appraisal discussions generally involved only a few contractor personnel, and ORO allowed a policy whereby a draft of the formal appraisal report could be provided to the contractor staff for review and comment before the final report was prepared. By 1976 or 1977, it had become necessary for the Environmental Branch to submit a proposed agenda or otherwise detail those topics that needed discussion at the appraisal, at the time the plant visit was scheduled. In most cases, the contractor staff now prepares a fairly detailed meeting schedule to facilitate the input from the various plant operation or planning groups that must participate in the ever increasing environmental protection management programs. In some cases, the schedules are broken down into ten-minute increments. A typical appraisal discussion schedule is shown in Fig. 1.

Appraisal Topics

Appraisal discussions are sometimes very unpredictable. Some of the specific topics discussed may relate to very current situations where new information, regulations, or management developments may have necessitated a great deal of detailed contractor/ORO communication just prior to the appraisal visit. In other cases, appraisal topics may not have been discussed by the contractor and ORO since the previous appraisal, or perhaps even an appraisal or event several years in the past. Although the specific topics covered from one plant to the next will broadly vary, most current appraisals can be expected to at least touch on aspects of the following:

- Rad Waste Management
- Effluent and Environmental Monitoring
- NPDES Compliance Status
- Air Emission Compliance Status
- Hazardous Waste Control (Nonrad)
- Oil and Chemical Spill Control (SPCC)
- Conventional Solid Waste Disposal
- Organization and Staffing
- Upper Level Management Support
- Communications with ORO

ANNUAL ENVIRONMENTAL MANAGEMENT APPRAISAL OF ORNL-1979

Wednesday, October 17, 1979

SECTION II

9:00 AM-12:00 Noon	G-236 Classroom	4500 N, Attic
9:00-9:15	QUALITY ASSURANCE ENVIRONMENTAL SURVEILLANCE	K. E. Shank
9:15-9:30	ENVIRONMENTAL MEASUREMENT LABORATORY - Quality Assurance	S. Reynolds
9:30-9:40	STATUS OF LINE ITEM PROJECT	T. W. Oakes
9:40-9:50	METEOROLOGICAL TOWER	T. W. Oakes
9:50-10:00	AIR MONITORING STATIONS	Oakes/Kelly/ Shank
10:00-10:10	MONITORING PROGRAM, including Excess Facilities	K. E. Shank
10:10-10:30	OIL CONTROL PROGRAM	T. W. Oakes
BREAK		
10:50-11:10	ENVIRONMENTAL AWARENESS PROGRAM	T. W. Oakes
11:10-11:25	ENVIRONMENTAL IMPACT STATEMENT	T. W. Oakes
11:25-11:40	NPDES	Kelly/Oakes
11:40-11:50	SPCC PLAN	Kelly/Oakes
12:00-1:00	LUNCH	

Fig. 1. Sample appraisal discussion.

Appraisal Participants

Although there is no formal organizational or management aspect of the ORO appraisal format to account for the various staff functions and personality differences that might be represented by the ORO representatives for any given appraisal effort, the fact remains that the topical coverage and the overall tone of communications for any appraisal is greatly dependent on the interests, abilities and personalities of the principal participants, both for ORO and the contractor. For the plants outside of Oak Ridge, the contractor may expect a relatively rigorous review of those staff functions assigned to the two particular individuals who descend upon him, and perhaps only a token treatment of those subjects normally assigned to the ORO staff who are not participating in the appraisal. If a certain ORO individual is not involved in any of a specific plant's appraisals for several years, serious program deficiencies may develop and go unnoticed. Similarly, too much concentration by one or two individuals at a particular plant can result in an unintended emphasis in a few specific program areas to the detriment of the overall environmental management program. As the scope and depth of the various environmental regulatory programs increase, more and more specialization by both ORO and contractor personnel can be expected to add further to this potential appraisal communications problem.

Plant Specific Factors

For the plants in Oak Ridge, the environmental management staffs can look upon the normal participation of all members of the Environmental Protection Branch (including the Branch Chief, who rarely participates directly in the offsite appraisals) in terms of some obvious advantages, and some perhaps less obvious disadvantages. One fairly severe problem that has impaired the cohesive conduct of the Oak Ridge Site Plant appraisals is the practical availability of the ORO appraisal staff at the right times and places. Since the whole Branch is generally not needed at all times, individuals try to schedule their participation as required, while also trying to keep up with their normal office workload during the three week appraisal period. This is an unrealistic expectation and schedule conflicts invariably come up.

Although the general topics just mentioned are the basic subjects for most of the appraisals, each plant has specific problems or programs that make each appraisal unique.

The Y-12 appraisal just about always centers around a revised status of the burial grounds and other low level rad waste management efforts. Y-12 generally has more interests in mercury contamination, waste oil disposal and steam plant particulate problems than any of the other plants. The Y-12 staff concerned with environmental matters has remained fairly stable over the last few years.

ORNL's situation is typified by a large number of diverse environmental related problems, but fortunately, with most of them being of less magnitude than similar problems at other plants. The Laboratory's rad waste burial grounds are always discussed at the appraisals, along with the continuing deterioration of the Laboratory's extensive environmental monitoring system. ORNL has also had some unique problems with oil and chemical spills and the performance of its sewage plant. The most significant aspect of ORNL's environmental management efforts during the last few years, however, has been the development and implementation of the formal organization of the Environmental Coordinator's Office and staff. Appraisal discussions at ORNL before the designation and centralization of this function were dramatically different.

Appraisal topics for the three Gaseous Diffusion Plants are generally very similar, but with some notable exceptions. Fluoride emissions to air are similar for all three plants, but state standards are radically different. There are diverse waste water effluents from each of the Plants, but receiving stream conditions and the variant standards from one state or U.S. EPA region to another again make each plant's situation unique. Certain differences in management practices and techniques can easily be seen from one plant to another. Although the organization structures and management interfaces with environmental programs are different for each of the six ORO plants; GAT and NLO, at Portsmouth and the FMPC respectively, are noticeably different from any of the UCC-ND operations.

Close-Out

At the end of the appraisal (i.e., ususally Friday morning of the appraisal visit week, for the plants outside of Oak Ridge) or very soon after the conclusion of the plant site visit, an appraisal "close-out" summary or "critique" is presented by the ORO appraisers to the plant manager and other upper level contractor personnel. The close-out will normally include the formal statement of any recommendations that have resulted from the appraisal; or if this is not practical, at least a fairly definite statement that recommendations may be included in the formal report and a brief discussion of the justifications for the recommendations.

Formal Report

The preparation of the formal appraisal report is normally expected "reasonably soon" after the appraisal visit and close-out. The record for the ORO Safety Division getting final reports out after the appraisals has not been very good, and the Environmental Protection Branch certainly contributes to this problem. In mid-1979, a directive came down through ORO upper level management to Mr. W. H. Travis, Director of the Safety and Environmental Control Division, that appraisal reports were henceforth to be prepared within <u>two weeks</u> of the appraisal close-out. Fortunately for the Environmental Protection Branch, both the <u>management close-out</u> and the formal reports remain outstanding for the appraisals conducted for the three Oak Ridge Site Plants during October, 1979 so that technically the Environmental Protection Branch is not in violation of this directive. Except for Goodyear Atomic, all other 1979 ORO facility appraisals have been completed and formal reports finalized.

Appraisal Findings

The Environmental Protection Branch has conducted facility appraisals as follows for the last eight years:

Plant/Year	Dates of Appraisal	Date of Report	Recommendations	Performance Rating
Y-12, 1972	Sept. 18-28, 1972	Jan. 11, 1973	6	—
Y-12, 1973	Sept. 20-24, 1973	Dec. 19, 1973	3	—
Y-12, 1974	Nov. 11-26, 1974	May 15, 1975	3	—
Y-12, 1975	Nov. 5-6, 1975	Mar. 24, 1976	4	—
Y-12, 1976	Aug. 27-31, 1976	Dec. 7, 1976	0	—
Y-12, 1977	Sept. 20-22, 1977	Feb. 3, 1978	2	Excellent
Y-12, 1978	Sept. 4-6, 1978	June 6, 1979	0	Superior
Y-12, 1979	Oct. 16-18, 1979	—	0	Excellent
ORNL, 1972	Sept. 18-28, 1972	Nov. 14, 1972	6	—
ORNL, 1973	Sept. 25-27, 1973	Jan. 4, 1974	6	—
ORNL, 1974	Nov. 11-15, 1974	May 28, 1975	2	—
ORNL, 1975	Oct. 28-30, 1975	Mar. 31, 1976	3	—
ORNL, 1976	Aug. 23-26, 1976	Jan. 12, 1977	0	—
ORNL, 1977	Sept. 27-29, 1977	Feb. 16, 1978	7	Satisfactory
ORNL, 1978	Aug. 29-31, 1978	Mar. 27, 1979	2	Satisfactory
ORNL, 1979	Oct. 16-18, 1979	—	0	Excellent
ORGDP, 1972	Sept. 18-28, 1972	Jan. 11, 1973	4	—
ORGDP, 1973	Sept. 17-19, 1973	Nov. 28, 1973	4	—
ORGDP, 1974	Nov. 20-28, 1974	Apr. 11, 1975	2	—
ORGDP, 1975	Dec. 3-5, 1975	Mar. 24, 1976	1	—
ORGDP, 1976	Sept. 1-3, 1976	Nov. 11, 1976	1	—
ORGDP, 1977	Oct. 4-6, 1977	Feb. 14, 1978	1	Excellent
ORGDP, 1978	Sept. 12-14, 1978	May 29, 1979	1	Superior
ORGDP, 1979	Oct. 29-31, 1979	—	0	Superior
Paducah, 1972	June 27-29, 1972	Aug. 17, 1972	0	—
Paducah, 1973	May 15-17, 1973	June 12, 1973	2	—
Paducah, 1974	Mar. 26-28, 1974	May 28, 1974	3	—
Paducah, 1975	May 13-16, 1975	June 24, 1975	2	—
Paducah, 1976	Apr. 6-9, 1976	June 24, 1976	1	—
Paducah, 1977	Feb. 15-18, 1977	Apr. 19, 1977	0	Excellent
Paducah, 1978	May 23-26, 1978	June 11, 1979	0	Superior
Paducah, 1979	June 12-15, 1979	Sept. 14, 1979	1	Superior
Portsmouth, 1972	May 12-14, 1972	Aug. 25, 1972	1	—
Portsmouth, 1973	June 11-13, 1973	Aug. 27, 1973	3	—
Portsmouth, 1974	Oct. 30-31, 1974	Jan. 31, 1975	0	—
Portsmouth, 1975	July 27-29, 1975	Nov. 4, 1975	1	—
Portsmouth, 1976	June 22-25, 1976	Aug. 13, 1976	2	—
Portsmouth, 1977	Aug. 2-5, 1977	Nov. 8, 1977	0	Excellent
Portsmouth, 1978	May 3-5, 1978	Nov. 1, 1978	1	Excellent
Portsmouth, 1979	---------None conducted due to OCAW Strike-------------------------------			
FMPC, 1972	June 5-7, 1972	Sept. 1, 1972	0	—
FMPC, 1973	Apr. 3-5, 1973	June 7, 1973	0	—
FMPC, 1974	May 22-24, 1974	June 25, 1974	1	—
FMPC, 1975	Aug. 26-28, 1975	Sept. 22, 1975	1	—
FMPC, 1976	June 16-17, 1976	July 1, 1976	0	—
FMPC, 1977	July 6-8, 1977	Oct. 4, 1977	0	Excellent
FMPC, 1978	May 8-10, 1978	Sept. 5, 1978	0	Superior
FMPC, 1979	May 2-4, 1979	Aug. 9, 1979	1	Excellent

Appraisal Performance Criteria

Prior to 1977, all major ORO facilities were operated by contractors on a "Cost Plus-Fixed Fee" basis, or CPFF. Although ORO expected and generally received responsive contractor performance, there was no formal ORO assessment of a contractor's performance in any of the specific non-production areas that would necessarily have any impact on contractor selection or a specific fee received by a contractor. In 1976, the National Lead Company of Ohio, DOE's contractor at the Feed Materials Production Center near Fernald, Ohio, accepted a "Cost Plus Award Fee" or CPAF contract for their operations. Goodyear Atomic soon after also went to a CPAF contract for the Portsmouth Gaseous Diffusion Plant. Environmental Management Appraisals for all the ORO plants were affected by these contractural changes. Prior to this time, the appraisal reports merely discussed the substantive technical issues raised at the appraisals, and formal consideration of contractor performance was limited primarily to their implementation of appraisal recommendations from previous years. The appraisal recommendations themselves, in some instances, were regarded by some individuals as ORO's means of documenting deficient contractor performance; but this was obviously an invalid conclusion relative to the Environmental Management Appraisals, where recommendations only rarely had any relevance at all to the adequacy of the contractor's environmental management program.

Unfortunately, the new ORO appraisal format, generated and largely implemented by the recently formed Office of Performance Evaluation (OPE) did hopelessly entangle the Environmental Protection Branch's previously held concepts of contractor performance evaluation and the purposes of appraisal recommendations.

The idea that personnel in the ORO Environmental Protection Branch can independently evaluate the performance of individual contractor professionals, specify recommendations to remedy program deficiencies, and then apply performance ratings would seem to imply that ORO personnel are intrinsically more knowledgeable of <u>all</u> environmental regulations, engineering practices and management techniques than the contractor environmental program personnel. Given the contractor's vast technical resources and his firsthand understanding of day to day operations at his plant, this notion seems unrealistic to even the most casual ORO observer. However, the less rigorous concept of an environmental appraisal being nothing substantively more than an annual evaluation of environmental program status prepared jointly by ORO and contractor staffs for the upper level management of each cannot be related to the new ORO appraisal policy either. So, like it or not, since 1977 the ORO Environmental Protection staff has been required to include performance criteria evaluations in the appraisal reports and to specify overall performance ratings.

1977 Criteria

For 1977, the first year of CPAF contracts (which dictated the format for CPFF contractors as well) OPE specified three overall performance rating adjectives and required each organizations with an appraisal function to develop specific performance criteria.

The three rating adjectives were as follows:

Excellent-Performance is considered above average.

Satisfactory-Performance is considered average.

Marginal-Performance is considered less than average.

The Performance Criteria developed for the Environmental Management appraisals were as follows:

1. Implement an effective and auditable program for effluent and environmental monitoring which characterizes the discharge, quantifies environmental impact, demonstrates compliance with applicable standards and makes optimum use of available equipment and personnel.

2. Review ongoing and proposed actions in relation to current environmental standards to assure identification and timely completion of corrective actions necessary to achieve and maintain compliance with applicable standards and good engineering practice.

3. Develop a management system including a qualified staff with adequate support to assure compliance with environmental objectives.

Most people considered these criteria to be just vague enough that most individuals could interpret them as suited their interests. Terms like "effective," "auditable," "quantifies," "demonstrates," "make optimum use," "good engineering practices," and "assure compliance with environmental objectives" would have seemed to put the contractor at the mercy of his appraisers, or vice-versa. The "vice-versa" must have been the more prevalent force, as the Environmental Protection Branch specified "excellent" in five out of six appraisals and issued recommendations to only one plant during 1977.

Revised Criteria; 1978 - Present

Fortunately, these criteria could not stand even a short test of time. By 1978, the appraisal rating system had become more complicated and the Environmental Protection performance criteria more straightforward.

There were now five rating adjectives:

Superior-Performance exceeds standard by a substantial margin. Few areas can be cited for improvement, all of which are minor.

Excellent-Performance exceeds standard although improvement may be required in some areas, this is more than offset by better performance in other areas.

Satisfactory - Performance is standard. Areas for improvement are approximately offset by better performance in other areas.

Marginal - Performance is less than standard. Although there are areas of good or better performance, these are more than offset by lower rated performance in other areas.

Poor - Performance is substantially less than standard and many critical areas for improvement can be cited.

The Environmental Management performance criteria had mercifully been reduced to the following:

1. Compliance with applicable environmental protection regulations imposed by Federal, State, regional, and local agencies.

2. Compliance with official DOE-imposed environmental protection requirements.

3. Adequate response to prior-year environmental protection appraisal recommendations.

These criteria were obviously easier for the Environmental Protection Branch to assess, but they also touched on factors that could very easily be outside the normal control of the contractor environmental management staffs, especially numbers one and two. For example, ORGDP has had many, many NPDES violations associated with the total chlorine residual levels measured at their sewage plant discharge points. According to criterion 1, they could have received a fairly severe appraisal rating; while Y-12, which does not have a sewage plant at all, would not have been subjected to such considerations even though sewage generated at Y-12 is received and discharged from a publicly owned treatment facility that is in gross violation of most applicable standards.

To date, the Environmental Protection Branch has made a special effort and achieved some measure of success in applying these performance criteria in a logical and rational manner, relying on an objective evaluation of those factors that are obviously within the control of the contractor's staff.

Appraisal Problems

Soon, the Environmental Protection Branch began running into some of the same appraisal problems being faced by other functional groups at ORO. One of the first directives from OPE on the conduct of appraisals specified that appraisal recommendations had to accompany anything less than a top rating adjective. Therefore, if anything less than a top rating adjective was specified, the appraisal had to include a recommendation, ostensibly related to the deficient area(s). Conversely, if recommendations were developed as a result of the appraisal, was the contractor precluded from receiving a top rating adjective?

These questions more or less faded away unresolved as even more complicated appraisal guidance was received from OPE. In addition to the pseudo-objective task of designating a performance rating adjective, the Environmental Protection Branch was now required, on a quarterly basis, to designate a completely subjective performance rating score for the CPAF contractors; a number on a scale from 1 to 100. A Performance Evaluation Rating Scale Guidelines sheet was provided by OPE to facilitate this task (see Fig. 2). As this scale indicates, an "average CPFF performance was arbitrarily designated as a score of 81, or just a shade over the excellent adjective. Hence, CPAF performance had to be rated on the high side of excellent or superior for the contractor to benefit from the award fee contract arrangement.

As the various ORO staffs began to gain some familiarity with the CPAF rating methods, one important aspect of the CPAF system became perfectly clear: The CPAF contractors obviously did expect to benefit from this contract arrangement and if anything less than a "superior" adjective was designated, or a numerical score less than 100%, the contractor's upper level management usually wanted to know specifically what improvements were needed to attain the maximum possible score. Fortunately, for the Environmental Protection Branch, four out of six of the major plant installations still operate on a CPFF basis, where the performance rating adjective was of some interest to plant staff and management, but not of paramount concern.

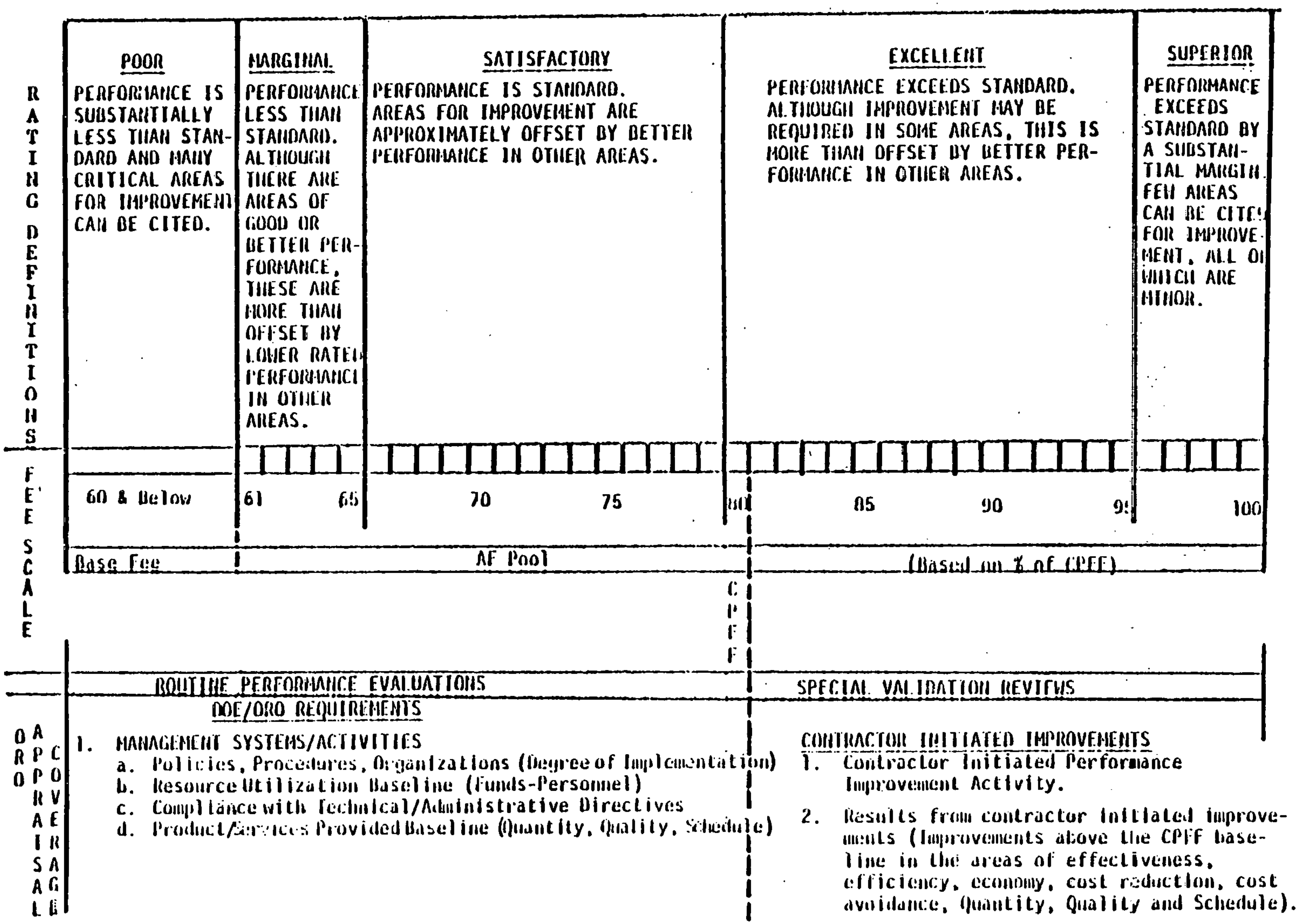
More Criteria Guidance

While the contractor environmental management staffs began comparing performance ratings and appraisal experiences to try to figure out what ORO was doing, OPE began making it more and more difficult for any functional staff to simply specify a superior rating for everybody so as to keep relations on a friendly basis and to keep important communications channels open. In August, 1978, everybody at ORO in the appraisal business received the following instructions:

"1. Adopt the principle that the award fees we (DOE) pay will essentially remain in line with previous payments under CPFF until the contractors demonstrate to ORO's satisfaction, through their own initiative, that improvements have actually been accomplished.

"2. Communicate the above principle to the contractors and request that they assume an innovative and initiating role in providing evidence of improved performance.

"3. Structure the appraisal and evaluation techniques to this principle, with the higher rating levels (i.e., excellent and superior) reserved basically for recognizing contractor initiated self-appraisal activity and actions for improvement submitted to ORO for evaluation.



POOR

PERFORMANCE IS SUBSTANTIALLY LESS THAN STANDARD AND MANY CRITICAL AREAS FOR IMPROVEMENT CAN BE CITED.

MARGINAL

PERFORMANCE LESS THAN STANDARD. ALTHOUGH THERE ARE AREAS OF GOOD OR BETTER PERFORMANCE, THESE ARE MORE THAN OFFSET BY LOWER RATED PERFORMANCE IN OTHER AREAS.

SATISFACTORY

PERFORMANCE IS STANDARD. AREAS FOR IMPROVEMENT ARE APPROXIMATELY OFFSET BY BETTER PERFORMANCE IN OTHER AREAS.

EXCELLENT

PERFORMANCE EXCEEDS STANDARD. ALTHOUGH IMPROVEMENT MAY BE REQUIRED IN SOME AREAS, THIS IS MORE THAN OFFSET BY BETTER PERFORMANCE IN OTHER AREAS.

SUPERIOR

PERFORMANCE EXCEEDS STANDARD BY A SUBSTANTIAL MARGIN. FEW AREAS CAN BE CITE FOR IMPROVEMENT, ALL O WHICH ARE MINOR.

ROUTINE PERFORMANCE EVALUATIONS

DOE/ORO REQUIREMENTS

1. MANAGEMENT SYSTEMS/ACTIVITIES
   a. Policies, Procedures, Organizations (Degree of Implementation)
   b. Resource Utilization Baseline (Funds-Personnel)
   c. Compliance with Technical/Administrative Directives
   d. Product/Services Provided Baseline (Quantity, Quality, Schedule)

SPECIAL VALIDATION REVIEWS

CONTRACTOR INITIATED IMPROVEMENTS

1. Contractor Initiated Performance Improvement Activity.
2. Results from contractor initiated improvements (Improvements above the CPFF baseline in the areas of effectiveness, efficiency, economy, cost reduction, cost avoidance, Quantity, Quality and Schedule).

Fig. 2. Performance evaluation rating scale guidelines.

"4. Align the contractor's objectives and performance criteria with the rating scale and definitions.

"5. Recognize the historical level of the resources provided and the level of activity and performance achieved under CPFF operations as the baseline for measuring performance change."

Additional guidance on rating methods was provided as follows:

"1. The excellent and superior rating levels will be basically reserved for recognizing contractor initiated performance improvement activity and the special actions taken by the contractor to improve performance after the basic requirements of the lower rating levels have also been met.

  "a. It is possible for the contractor to sustain an excellent rating from period to period through effective implementation of the basic DOE/ORO management requirements and sustained CPFF level of performance. However, the amount of award fee associated with this rating of excellent would be basically the same as that received by the contractor under a CPFF contract. The amount of award fee earned by the contractor above the CPFF amount would depend upon the actions initiated by the contractor to improve performance and the results obtained from these actions.

  "b. The superior rating level will be reserved to recognizing specific improvement actions considered by ORO to have special merit after the basic requirements of the lower rating levels have also been met in the rating period.

"2. Deficiencies, if significant, could also offset the recognition of contractor initiated performance improvement actions to the point that the excellent and superior ratings would still not be attained by the contractor."

As 1979 appraisal reports were being prepared, it became necessary for the contract administrator to obtain the informal concurrence of the Office of Performance Evaluation before an appraisal report could be finalized and sent to the contractor. OPE required the contents of the reports to align with their interpretation of the various performance rating adjectives. If any severe problems were cited, or if a number of recommendations appeared, OPE would question "superior" and even "excellent" ratings. If a report did not delineate problems or had no recommendations, OPE usually found the entire report to be deficient. The OPE review process effectively requires reasonably detailed evaluations of contractor initiatives or deficiencies by the Environmental Protection Branch, which invariably could lead to the "we-must-be-smarter-than-them" dilemma mentioned earlier.

Most ORO appraisal groups continued to have problems with the rating criteria, and the potential for serious ORO/contractor communications breakdowns grew. By November, 1979, OPE found it necessary to address the following questions:

> "Several recent inquiries regarding the ORO appraisal system rating policy seem to deal with two basic questions;
>
> 1. Can a contractor sustain a superior rating? And if so...
>
> 2. How?"

OPE's answers were as follows:

> "1. Yes.
>
> 2. By meeting the requirements established for the rating. The criteria were designed to be productive and encourage the contractor to exercise all elements of the management structure in striving for improvements."

OPE went on to give some of the most definitive information provided to date:

> "In some respects, use of the superior rating can be compared to an employee receiving either 'special act' or 'sustained superior performance' awards every six months, which would be an unusual expectation. However, the contractors have a broad base of operations and activities from which greater opportunities exist. To achieve a superior rating for any given rating period, the contractor must demonstrate initiatives within that period that warrant the rating. Initiatives in previous periods should have been recognized and evaluated in that rating period. Under a CPAF arrangement, the contractor also would have received compensation for those initiatives."

Current Status

This brings the status of the ORO appraisal rating system up to date. ORO now faces the 1980 appraisal season, which looks something like this:

Paducah Appraisal	May, 1980
FMPC Appraisal	July, 1980
Portsmouth Appraisal (79 & 80)	August, 1980
Y-12 Appraisal	Oct/Nov., 1980
ORNL Appraisal	Oct/Nov., 1980
ORGDP Appraisal	Oct/Nov., 1980

The Oak Ridge Operations Environmental Protection Branch sincerely hopes that these relatively new appraisal requirements and functions will not significantly diminish the good relations and the free, open communications channels that now exist with all the plant environmental management staffs. The function of the Environmental Protection Branch has never been, nor can it ever be, to second guess or to take ivory tower pot shots at the expense of contractor counterparts. In the real world, the ability of the ORO environmental protection staff to properly perform its function is absolutely dependent on the smooth flow of complete information to and from the contractor organizations. The best interests of the contractor and Oak Ridge Operations must be synonymous when dealing with the current forces that prevail in the state and Federal regulatory agencies. A broad measure of practical conservatism, solidly based on good engineering practices and management methods, is required on the part of any industry that is to continue to operate on a sound financial basis in the current tempest of environmental laws and regulations. It is important to the overall ORO environmental management mission that this be a well established consensus at all levels of contractor and ORO management.

ENVIRONMENTAL REGULATIONS - PAST, PRESENT AND FUTURE (?)

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ABSTRACT

A review of the initiation, development, and implementation of the Clean Air Act, Clean Water Act, National Environmental Policy Act, Resource Conservation and Recovery Act, Toxic Substance Control Act, and the Occupational Safety and Health Act will be given. Projections of possible future changes in these acts will be discussed.

INTRODUCTION

Pollution is an unwanted by-product of the manner in which we produce our goods, transport ourselves and our goods, and generate needed energy. Pollution control is a complex problem involving politics, economics, technology, science, and sociology. In some cases, what may be technically feasible may not be economically acceptable. In the past, industry, agriculture, and individual polluters have found it more economical to discharge waste products into the air, water, and land than to exercise waste control. In recent years, as the public has become increasingly aware of environmental problems, air, water, and land have become regarded as resources within the public domain. Hence, pollution is considered a public problem, a concern not only to those who discharge the pollutants, but also to those who may suffer as a result. Another problem is that only a finite amount of air, land, and water resources exist; because the population is increasing, the portion available for each person is decreasing. The general public is demanding more protection, and Congress has responded by promulgating more environmental legislation in the general areas as given in Table I. This paper will be concerned with the development of laws and regulations in the areas of air, water, and hazardous and toxic materials with emphasis on the development of air pollution regulations.

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Table I. Major federal environmental protection laws

- Air
- Fish and wildlife
- Water
- Hazardous and toxic materials
- Other

CLEAN AIR ACT

The existence of air pollution and the need for legislation to protect the health and welfare of the general public are not modern phenomena. In thirteenth-century England, the burning of soft coal polluted the atmosphere in urban areas to such an extent that in 1723, England passed a law to reduce air pollution from this source.

However, in the United States, it was not until the 1940s that efforts to control the degree of air pollution were initiated. The first measures against air pollution were taken in California (Los Angeles Basin).[1] It soon became apparent that other areas in the country were having air pollution problems. As a result, federal intervention was deemed necessary. The early development of air pollution laws by Congress is interesting; Federal Versus States' Rights[1] being a classic example. The first federally enacted legislation in this area was the Air Pollution Control Act of 1955 (Public Law 84-159), passed on July 14, 1955 (see Table II). This act was narrow in scope and potential, primarily because of the federal government's hesitation to encroach on states' rights. The act considers prevention and control of air pollution at its source to be primarily the responsibility of state and local governments. On June 6, 1960, and October 9, 1962, Congress directed [Air Pollution Control Act Amendments of 1960 (Public Law 86-993) and of 1962 (Public Law 87-761)] the surgeon general to conduct a thorough study of motor vehicle exhausts in terms of their effects on human health. In December 1963, the Clean Air Act of 1963 (Public Law 88-206) was passed. This act provided for the first time federal financial aid for research and technical assistance. Congress recognized the technical and economic feasibility of setting automotive emission standards and passed the Motor Vehicle Air Pollution Control Act of 1965 (Public Law 89-272, October 20, 1965). During 1967, national emission standards for industries were proposed in the Air Quality Act of 1967 (Public Law 90-148, November 21, 1967). On December 31, 1970, the Clean Air Amendments Act of 1970 (Public Law 91-604) was signed into law. This amendment extended the geographical coverage of the federal program for prevention, control, and abatement of air pollution from stationary and mobile sources. Clean air legislative history is given in Table II.

Table II. History of air pollution laws

- The Air Pollution Control Act of 1955.
- Air Pollution Control Act Amendments of 1960.
- Air Pollution Control Act Amendments of 1962.
- The Clean Air Act of 1963.
- Motor Vehicle Air Pollution Control Act of 1965.
- The Air Quality Act of 1967.
- The Clean Air Amendments Act of 1970.

Clean Air Act - Significant Points

1. The EPA shall develop two sets of ambient air quality standards - primary standards for the protection of public health and secondary standards for the protection of public welfare (i.e., aesthetics). These standards shall be periodically reviewed to insure their viability.

2. The EPA shall, in conjunction with the states, divide the country into air quality control regions, based on the regions' compliance with ambient air quality standards. Three classes of regions exist:
    - A. attainment areas, where ambient air quality standards are being met;
    - B. nonattainment areas, where ambient air quality standards are not being met; and
    - C. Class I areas, which are pristine areas (e.g., national parks) requiring special treatment.

3. For attainment and Class I areas, the EPA shall require states to prevent significant deterioration in air quality. State implementation plans shall list maximum allowable increases (increments) in pollutant discharges and maximum allowable concentrations (ceilings) for pollutants in the air.

4. For nonattainment areas, the EPA shall require states to provide a schedule for attaining ambient air quality. EPA shall establish lowest achievable emission rates (based on best available technology) for pollutants in these areas. State implementation plans shall require new sources either to show that their emissions will not adversely affect air quality in the area or to improve the emissions from an existing source (offsets) to eliminate the impact of their facility.

5. The EPA shall establish new source performance standards for new or modified stationary sources that contribute significantly to air pollution. These standards shall be periodically reviewed to ensure that the best available technology is used.

6. The EPA shall establish national emission standards for hazardous air pollutants, where no ambient air quality standard can be set. These standards state the maximum emissions allowable for these pollutants.

7. When violations occur, the EPA shall enforce these regulations if the states do not. This authority includes jurisdiction over all federal facilities.

8. The EPA shall reduce air pollution from the transportation industry by:
    - A. setting emission standards for motor vehicles and aircraft (from both evaporative emissions and exhausts),
    - B. regulating the composition of fuel and fuel additives,
    - C. performing motor vehicle and engine compliance testing (fuel consumption and emissions), and
    - D. planning with the Department of Transportation ways to reduce pollution (e.g., mass transit).

Clean Air Act - Resultant Regulations

1. Ambient air quality standards issued on six compounds.

2. New source performance standards issued for 28 industries.

3. National emission standards for hazardous air pollutants issued for four compounds.

4. Acceptable monitoring practices issued.

Clean Air Act - Foreseeable Amendments

1. Review of ambient air quality standards.

2. Development of new source performance standards for 24 additional industries.

3. Development of national emission standards for hazardous air pollutants for six additional sources.

CLEAN WATER ACT

The legislative history is given in the following table.

Table III. History of water pollution laws

- Rivers and Harbors Act of 1899.
- Watershed Protection and Flood Protection Act of 1954.
- Land and Water Conservation Fund Act of 1965.
- Water Resources Planning Act of 1965.
- Federal Water Pollution Control Act of 1972.
- Coastal Zone Management Act of 1972.
- Marine Protection Act of 1972.
- Safe Drinking Water Act of 1974.
- Coastal Zone Management Act Amendments of 1976.
- Land and Water Conservation Fund Act Amendments of 1977.
- Safe Drinking Water Act Amendments of 1977.
- Clean Water Act of 1977.

Clean Water Act - Significant Points

1. There shall be national goals to:
    A. eliminate the discharge of pollutants by 1985;
    B. attain water quality that protects fish, shellfish, and wildlife and provides for recreation by July 1, 1983; and
    C. prohibit the discharge of toxic pollutants.
2. The EPA shall develop water quality standards necessary to meet the requirements of the act.
3. By July 1, 1977, point sources (other than publicly owned treatment works) shall apply the best practicable control technology currently available. This application shall include consideration of the cost of the technology in relation to effluent reductions, as well as other factors (e.g., process involved, age of equipment, etc.). Point sources discharging to publicly owned treatment works shall meet pretreatment requirements as set by the EPA. By this date, publicly owned treatment works shall meet effluent limitations based on secondary treatment.
4. By July 1, 1983, all publicly owned treatment works shall apply the best practicable technology currently available.

5. By July 1, 1984, point sources (other than publicly-owned treatment works) discharging pollutants considered toxic shall apply the best available technology economically achievable. This application may include elimination of discharges if the EPA finds such elimination to be technologically or economically achievable. This application includes both effluent and pretreatment standards.

6. By July 1, 1984, best conventional control technology shall be applied to pollutants such as biochemical oxygen demand, suspended solids, fecal coliform, and pH (from sources other than publicly-owned treatment works). For other pollutants, compliance with EPA limitations shall be achieved by July 1, 1987.

7. The EPA shall establish new source performance standards based on best available control technology for a minimum of 27 listed industries.

8. The EPA shall regulate discharges due to plant site runoff, spillage or leaks, sludge or waste disposal, and drainage from raw material storage if they are associated with significant contributions of pollutants to navigable waters.

9. There should be no discharge of oil or hazardous substances into or upon the waters of the United States. The EPA shall designate substances to be hazardous based on their potential danger to public health and the environment. A national contingency plant shall be developed for the cleanup of oil or hazardous substances discharged.

10. The EPA shall develop a National Pollutant Discharge Elimination System (NPDES) to issue permits for the discharge of any pollutant(s). Such discharges shall meet the appropriate level of treatment. Requirements for monitoring and reporting shall be included in such permits.

A condensed outline of the Clean Water Act is given in the following table.

Table IV. Clean Water Act (CWA)

- Effluent limitation guidelines.
- Best practicable technology by July 1, 1977 (1983 for publicly-owned treatment works).
- Best available technology by July 1, 1984.
- National Pollutant Discharge Elimination System (NPDES) permits.
- Established requirements for the control of toxic pollutant discharges

Clean Water Act - Resultant Regulations

1. Primary (health-related) drinking water standards have been developed for 21 compounds. Secondary (welfare-related) standards have been developed for 12 compounds.
2. New source performance standards have been developed for 31 industries.
3. Over 300 elements or compounds have been identified as hazardous substances.
4. EPA's list of priority (toxic) pollutants now rests at 129.
5. EPA has developed a comprehensive NPDES program.

Clean Water Act - Foreseeable Amendments

1. Due to concern about contaminated groundwater, EPA is promulgating regulations which
   A. control the injection of fluids underground,
   B. regulate contaminant levels found in groundwater, and
   C. require treatment of groundwater where contamination is suspected before it can be used for drinking water.
2. EPA is amending its primary drinking water regulations.
3. New source performance standards are being generated for 45 new industries.
4. EPA is planning to expand its hazardous substance list to include both carcinogens and additional toxic compounds.

NATIONAL ENVIRONMENTAL POLICY ACT (NEPA)

The National Environmental Policy Act (NEPA) was passed in 1969 and amended in 1975.

NEPA - Significant Points

1. The federal government should use all practical means to assure a safe environment for Americans and act as trustee of the environment for future generations.
2. The federal government should insure that the widest range of beneficial uses of the environment be attained without degrading its quality. The environment in this sense includes cultural and historical as well as natural resources.

3. The federal government should include in every proposal a detailed statement of its environmental impact and alternatives to it.

4. The Council of Environmental Quality was created to:

   A. generate data on the conditions and trends on the quality of the environment,

   B. review federal government activities in light of these conditions and trends, and

   C. prepare an Environmental Quality Report annually for the President and Congress.

NEPA - Resultant Regulations

Requirements for Environmental Assessments and Environmental Impact Statements.

NEPA - Foreseeable Amendments

None.

HAZARDOUS AND TOXIC MATERIALS

One of the first steps in solving the waste management problem is to dispel the belief that waste is so heterogeneous in its composition and so variable in its material properties that individual components cannot be identified. Regulations on waste treatment and disposal in the United States are not recent, since the first known ordinance on refuse was adopted by the Corporation of Georgetown in 1795. Laws and ordinances may prohibit hazardous materials from being placed into solid-waste streams, but these regulations are no guarantee that occasionally such substances will not appear. A list of the laws related to hazardous and toxic materials is given in the following table.

Table V. Laws related to hazardous and toxic materials

- Solid Waste Disposal Act of 1970.
- Resources Recovery Act of 1970.
- Toxic Substances Control Act of 1976.
- Resources Conservation and Recovery Act of 1976.

Alarming levels of highly toxic or diseased cultures have been found in waste areas in the United States.[2]

The Environmental Protection Agency (EPA) has compiled over 400 cases of harmful consequences of inadequate hazardous waste management. Almost every day, the news media carry a story on a dangerous situation resulting from improper disposal of hazardous waste.[3] A recent example is the tragedy at Love Canal in New York State. Other cases include incidents of surface and groundwater contamination, direct contact poisoning, various forms of air and water pollution, and even fires and explosions.[3]

Half of the nation's drinking water is supplied from groundwater sources, and in some areas contamination of groundwater poses a threat to public health. An EPA study in 1975 of a number of generating industries showed that approximately 90% of the potentially hazardous waste generated by these industries was managed improperly for protection of human health and the environment.[3]

The fundamental fact about hazardous wastes is that these materials are a menace to the environment and human health; many materials can injure or kill humans and other living organisms. Some of the waste may accumulate in living organisms and find its way into the food chain.[4] These wastes are in the forms of solids, liquids, sludges, and gases and may be toxic chemicals, acids, caustics, or biological agents.

Creation of the Resource Conservation and Recovery Act (RCRA)

In recent years, EPA and the states have begun to obtain control over the problems of air and water pollution.[4] On the other hand, land protec tion has fallen behind. As the laws control air and water pollution, the burden on the land will increase. The ultimate fate of the pollutants removed from the air and water have become a great concern.[3] As Congress stated in Section 1002(b)(3) of the RCRA of 1976:

> "As a result of the Clean Air Act, the Water Pollution Control Act, and other Federal and State laws respecting public health and the environment, greater amounts of solid waste (sludge and other pollution treatment residues) have been created. Similarly, inadequate and environmentally unsound practices for the disposal or use of solid waste have created greater amounts of air and water pollution and other problems for the environment and for health."

RCRA was enacted by Congress on October 21, 1976, in order to address the problems associated with waste disposal. EPA estimates that approximately 270,000 waste-generating facilities and 10,000 transporters will be regulated. Approximately 30,000 of the waste-generating facilities will require treatment, storage, or disposal permits. Also under this Act, approximately 35 million metric tons per year of hazardous waste mainly from industrial sources will be controlled. Another several hundred million tons per year of high-volume, relatively low-risk waste, such as certain mining waste, will be brought under limited control pending further formulation of rules.[3]

RCRA was built on the foundation of the Solid Waste Disposal Act of 1965 and the Resource Recovery Act of 1970, and was developed "to provide technical and financial assistance for the development of management plans and facilities for the recovery of energy and other resources from discarded materials, for the safe disposal of discarded materials, and to regulate the management of hazardous waste."[3]

Intention of RCRA

Congress intended RCRA to address the following problems.[2]

1. The increasing amount of waste material being generated as a result of the national economic and population growth.

2. The financial, intergovernmental, management, and technical problems associated with solid waste collection, treatment, and disposal.

3. Open dumping of solid waste, which needlessly pollutes valuable land resources and pollutes the nation's air and water resources.

4. The wasteful burial of recoverable resources.

5. Environmental and human health dangers resulting from improper disposal of hazardous waste.

6. Increasing amounts of pollution control residues destined for land disposal resulting from other environmental regulation (Clean Air Act, etc.).

7. The need to continue to develop solid waste as an energy source.

On December 18, 1978, in the Federal Register, the EPA stated that final judgments have not been made on this program. A number of issues must be resolved and alternatives reviewed. EPA also anticipates that additional issues and alternatives may be identified during the comment period. One of the remaining major issues is balancing the need to protect the environment and human health from the adverse impact of mismanagement of small quantities of hazardous waste with the need to hold the administrative economic burden under RCRA within reasonable and practical limits.[2]

The statute that established RCRA set a deadline of April 1978 for the promulgation of these regulations, and EPA has been sued for not meeting that deadline. Therefore, the agency will be acting as quickly as possible to create a system to manage hazardous waste by promulgating sections of RCRA one at a time through the Federal Register process.

Sections of the RCRA

RCRA is a complex Act. The subtitles and Sections of the Act are given in the paper entitled, "A Brief Review of the Resources Conservation and Recovery Act (RCRA),1976."[5] Its significant points are:

1. The EPA shall develop criteria for identifying the characteristics of hazardous waste and listing of particular wastes to be regulated. Generators of such waste shall be required to keep records of the amount of waste generated, to label and package the waste properly, to inform transporters and disposers of the waste of its nature, and to participate in a manifest system which will keep track of the waste.

Transporters of the waste shall be required to keep records of the waste transported, to participate in the manifest system, and to deliver the waste only to the facility listed on the manifest.

2. The EPA shall develop performance standards regarding treatment, storage, or disposal of hazardous waste. Owners of treatment storage or disposal facilities will be required to locate, design and operate their facilities according to EPA's standards, to obtain a permit for these activities, to participate in the manifest system, and to develop contingency plans for unanticipated damage due to their operation. Owners shall provide assurances of financial responsibility consistent with the degree of risk associated with their operation.

3. The EPA, in conjunction with the states, shall develop state solid waste management plans to ensure cooperative efforts among regions that share common problems. These plans shall consider

    A. the type of disposal practices required to protect the surrounding water (ground and surface) and air;

    B. characteristics of the waste, including the potential for resource recovery; and

    C. political, economic, financial, and other problems associated with a common disposal strategy.

4. The EPA shall develop criteria for sanitary landfills and shall prohibit the operation of open dumps.

5. The EPA, in conjunction with other branches of the federal government (e.g., Department of Commerce), shall encourage

    A. greater commercialization of resource recovery technology,

    B. greater development of markets for recovered materials, and

    C. research and development to reduce the amount of solid waste and to improve the disposal of unsalvageable wastes.

RCRA - Resultant Regulations

1. EPA has promulgated regulations which define hazardous waste and how waste must be tested to determine its hazard.

2. The EPA has required all generators, transporters and disposers to file for permits.

3. The EPA has issued the first set of criteria for storage, treatment, and disposal facilities.

RCRA - Foreseeable Amendments

1. The EPA will continue to issue criteria for storage, treatment, and disposal facilities.

2. Legislation is currently in Congress to create a $1.6 billion superfund to pay for the cleanup of abandoned or closed hazardous waste disposal facilities. This fund, which would be accumulated largely by charges to industry, will permit prompt action to clean up facilities presenting an imminent and substantial danger to health or the environment.

TOXIC SUBSTANCES CONTROL ACT

Toxic Substances Control Act - Significant Points

1. Adequate data should be developed regarding the effects of chemicals or mixtures of chemicals on health and the environment; those responsible for the manufacture or processing of such chemicals or mixtures should also be responsible for developing these data. Adequate authority should exist to regulate chemicals posing an unreasonable risk to health and/or the environment; this authority, however, could create undue barriers to innovation.

2. The EPA shall determine if a chemical or mixture poses an undue risk to health or the environment or if there is insufficient data to determine a chemical's risk.

3. The EPA shall, where necessary, require that testing be performed on a chemical to determine its risk and prescribe the testing that must be performed.

4. Upon determining that a chemical or mixture poses an undue risk to the public or the environment, the EPA shall take one or more of the following actions:

    A. prohibit the manufacture, processsing, or distribution in commerce of the substance or mixture for a particular use or above a certain concentration;

    B. limit the amount manufactured, processed, or distributed;

    C. require labeling to document the substance's risk;

    D. require specific disposal strategies; and/or

    E. require records documenting the amounts of the substance handled.

5. The EPA shall develop specific regulations for labeling and disposal of polychlorinated biphenyls (PCBs).

6. The manufacture, processing, distribution in commerce, and use of PCBs in a manner other than a totally enclosed system is prohibited.

7. The EPA may commence a civil action to seize a chemical substance or mixture it considers an imminent hazard or to seek relief against the person who manufactures, processes, distributes in commerce, or disposes of such a substance or mixture. Relief may include notification of purchasers, public notice, recall or replacement of the substance, or any combination of the above actions.

Toxic Substances Control Act - Resultant Regulations

The EPA has issued regulations on the labeling and disposal of PCBs.

Toxic Substances Control Act - Foreseeable Amendments

1. The EPA is preparing standards for testing and data development for new substances.

2. The EPA is preparing premanufacture notification requirements, review procedures, and hazard labeling requirements.

3. The EPA is developing regulations for the identification and disposal of asbestos in schools, commercial buildings and vessels, and other industrial uses.

4. Regulations have been proposed to prohibit the use of PCBs in transformers located in food processing plants.

OCCUPATIONAL SAFETY AND HEALTH ACT (OSHAct)

The legislative history of OSHA is given below:

1966 - Federal Metal and Nonmetallic Mine Safety Act.
1969 - Federal Coal Mine Health and Safety Act.
1970 - Occupational Safety and Health Act (OSHAct) signed into law. Its stated purpose was "to ensure so far as possible every working man and woman in the nation safe and healthful working conditions and to preserve our human resources."[6] The OSHAct covers approximately 55 million employees throughout the nation.

OSHAct - Significant Points

1. Occupational Safety and Health Administration (OSHA), under the Secretary of Labor, has the responsibility for promulgating and enforcing occupational safety and health standards.

2. The Secretary of Labor performs the investigation and prosecution aspects of the enforcement process.

3. Occupational Safety and Health Review Commission adjudicates cases resulting from an enforcement action initiated against an employer by OSHA when any such action is contested by the employer or by his employees or their representatives.

4. National Institute for Occupational Safety and Health (NIOSH) has the following primary functions:
   - A. develop and establish recommended occupational safety and health standards,
   - B. conduct research experiments and demonstrations related to occupational safety and health, and
   - C. conduct education programs to provide an adequate supply of qualified personnel to carry out the purposes of the OSHAct.

OSHAct - Resultant Regulations and Requirements

1. Occupational safety and health standards that specify the permissible concentrations of airborne contaminants or permissible levels at physical exposures (includes regulations on heat stress, noise, dust concentrations, and fire protection).

2. Recordkeeping and reporting requirements:
   - A. A log of occupational injuries and illnesses.
   - B. An annual summary of occupational injuries and illnesses.
   - C. Records of employee exposure to toxic substances or harmful physical agents.
   - D. Other records such as logs of inspections and tests.

3. Establishment of threshold limit values (TLVs) for exposures to toxic materials and harmful agents. Specific procedures are outlined for making these TLV determinations (e.g., solvents, asphyxiants, toxic gases).

Future of OSHA

The development of new occupational safety and health standards is a continuing process by NIOSH. Several criteria-standards documents on worker exposures to toxic substances or harmful physical agents are published each year. Threshold limit values are also periodically changed as a result of NIOSH research and evaluation.

Other major environmental protection laws are listed in Table VI. The number of laws versus years is given in Fig. 1.[7] New directions for environmental laws will most likely be in the area of hazardous and toxic materials. Also, water pollution control will no doubt receive a great deal of attention over the next five years.

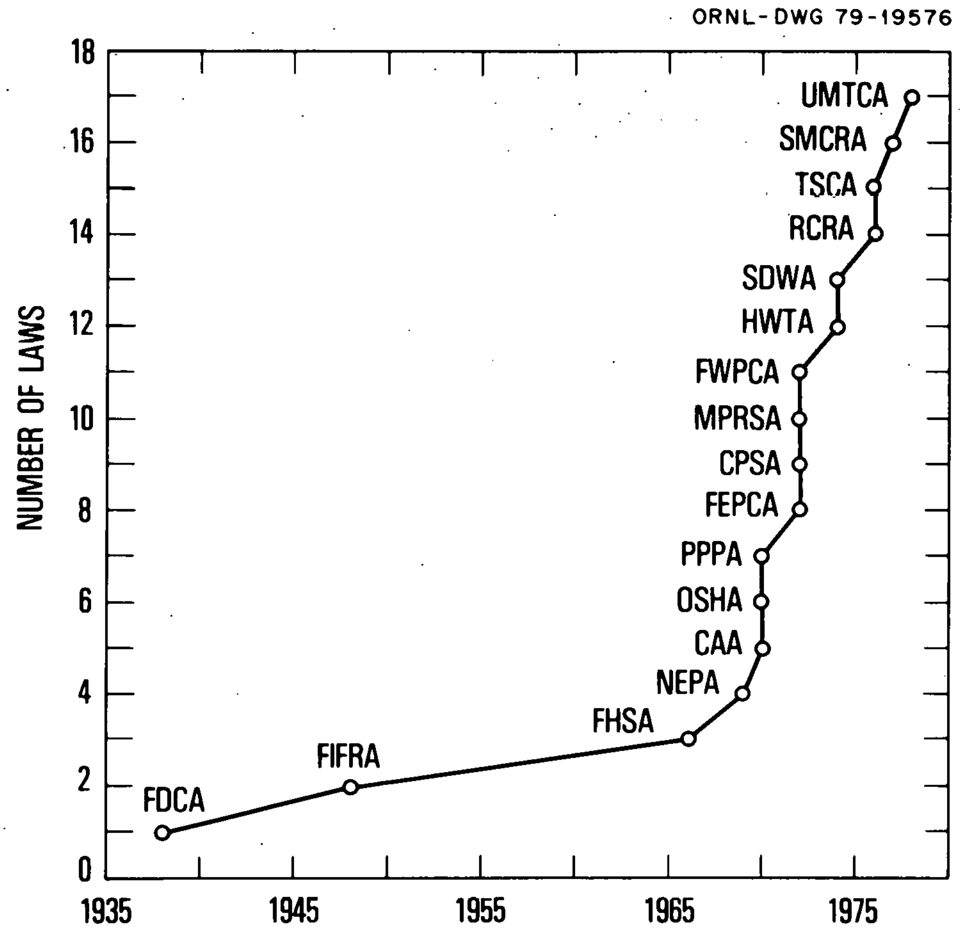

Fig. 1. Number of environmental protection laws versus years.

Table VI. Other major environmental protection laws

- National Historic Preservation Act of 1966.
- National Environmental Policy Act of 1969.
- Noise Control Act of 1972.
- Pesticide Control Acts.
- Surface Mining Control and Reclamation Act of 1977.

REFERENCES

1. K. Wark and C. F. Warner, Air Pollution: Its Origin and Control, A Dun-Donnelley Publisher, New York, 1976.

2. Office of the Federal Register, Hazardous Waste Guidelines and Regulations, U.S. Government Printing Office, Washington, D.C., Dec. 18, 1978.

3. Congress of the United States, Resource Conservation and Recovery Act of 1976, Public Law 94-580, Oct. 21, 1976).

4. Office of the Federal Register, Environmental Protection Agency, Hazardous Wastes, U.S. Government Printing Office, Washington, D.C., 1975.

5. T. W. Oakes and K. E. Shank, "A Brief Review of the Resources Conservation and Recovery Act (RCRA), 1976," in Proceedings of the 1979 UCC-ND Waste Management Seminar, Oak Ridge, Tennessee, March 6-7, 1979.

6. U.S. Department of Health, Education, and Welfare, The Industrial Environment -- its Evaluation and Control, U.S. Government Printing Office, Washington, D.C., 1973.

7. S. A. Carnes, E. D. Copenhaver, et al., Impacts of the Resource Conservation and Recovery Act on Energy Supply, ORNL/OIA PA-15, 1980.

SECOND ROUND NPDES PERMIT:
REQUIREMENTS AND COMPLIANCE

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ABSTRACT

The process of the issuance of the "Second Round" NPDES Permit for the Portsmouth Gaseous Diffusion Plant is nearing completion. Several aspects of the permit process and the ensuing results are of interest. In general, no attempt was made by the Ohio EPA to participate in the permit process. U.S. EPA, Region V, did not attempt to establish or apply GAT standards to the PGDP (GAT) effluents. Instead, the Water Quality standards of Ohio were applied at the drainage ditch discharges to the receiving stream. The monitoring requirements for the sewage plant are directed toward identifying any "industrial discharges" present in the sewage plant effluent by April, 1981, with a view toward modifying the permit at that time.

The permit was divided into two time periods (Present till October, 1982) and (October, 1982, to February, 1985). Much more stringent requirements characterize the latter permit period; in essence, the permit allows only 2.5 years to achieve compliance. In addition to limits on heavy metals, new parameters governed by permit requirements include residual chlorine, pentachlorophenol, phosphorus, and ammonia. Compliance with this permit will require several interim measures and the rearrangement of the 1980 LIP, "Control of Water Pollution."

(Paper not available for publication)

PERFORMANCE OF POLLUTION ABATEMENT FACILITIES

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ABSTRACT

In response to new environmental regulations, a number of treatment facilities have been constructed to meet standards. This paper provides a review of these facilities, applicable regulations, and an assessment of the effectiveness of the treatment process.

(Paper not available for publication)

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ORNL DECONTAMINATION AND DECOMMISSIONING PROGRAM*

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ABSTRACT

A program has been initiated at ORNL to decontaminate and decommission surplus or abandoned nuclear facilities. Program planning and technical studies have been performed by UCC-ND Engineering. A feasibility study for decommissioning the Metal Recovery Facility, a fuel reprocessing pilot plant, has been completed.

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ORNL DECONTAMINATION AND DECOMMISSIONING PROGRAM

J. P. Bell

UCC-ND Engineering

Introduction

In response to the Department of Energy's Surplus Facilities Management Program, Oak Ridge National Laboratory (ORNL) has implemented a decontamination and decommissioning (D&D) program. This program is expected to span several decades and cost over $100,000,000. The program is currently in the early planning stage but will eventually involve significant levels of planning, management, engineering, and decommissioning operations. In addition, the program may include construction of special facilities and equipment such as a central system for processing decommissioning wastes, mobile laboratories, and other specialized mobile equipment.

A number of ORNL facilities built for use in specific programs will no longer be needed due to changing objectives or completion of work. Those facilities which are contaminated by residual radioactive materials and cannot currently be adapted for use by other programs must be decontaminated and decommissioned to minimize or eliminate the potential for release of radioactivity to the environment. Currently, 29 ORNL facilities have been designated for decommissioning. This list is now undergoing further refinement to meet the requirements of the national program. Included in the current list are four nuclear reactors, various reactor experimental loops, numerous waste tanks, four process facilities, and various miscellaneous contaminated facilities and sites.

The goals of the ORNL program are derived from the national program goal. ORNL D&D Program goals are:

- To protect public health and safety by decontaminating and decommissioning selected surplus facilities.

- To maximize options for the future use of land and facilities.

A systems management approach will be used to accomplish the D&D program at ORNL. In this approach the D&D program will be treated as a major system made up of numerous subsystems (the individual D&D projects). Since the projects have interrelated requirements, assets, and liabilities, the systems management approach is expected to save redundant expenditures of manpower and money. Initially this concept will include establishment of a central program office, an early program definition and planning effort, conceptual engineering studies on high priority projects, development of a technical information base, research and development activities, and analysis of interfaces with other ORNL programs such as waste management.

Engineering Activities

In May 1979, UCC-ND Engineering was asked to conduct engineering studies in support of the ORNL D&D Program. The initial engineering effort has resulted in completion of the following documents:

- ° Technical Manual for Decontamination and Decommissioning
- ° Preliminary Planning Guide for Radiological Characterization and Monitoring for the ORNL D&D Program
- ° Engineering Management Plan
- ° Feasibility Study Report for Decommissioning the Metal Recovery Facility

D&D Technical Manual

A technical manual covering the technical subjects of concern to the D&D Program has been prepared. This manual summarizes the technical information compiled to date in support of the D&D Program. Reference material, which has been derived from Time and Material subcontractors' reports and other sources, is documented in the manual. The purpose of the manual is to provide a technical reference handbook for D&D design engineers; the manual will also serve as a vehicle for passing information gained in early D&D operations to the engineers working on later D&D projects. The manual will be periodically updated as new information is developed through R&D and engineering studies and actual D&D projects.

The manual is divided into the following sections:

- ° Regulations: Summarizes the regulations applicable to D&D.
- ° Site characterization: Covers the requirements for radiological and nonradiological data needed to characterize D&D sites.
- ° D&D methods: Describes equipment and procedures for accomplishing D&D operations.

- Hazard and Waste control: Discusses methods for reducing safety hazards and preventing discharges of pollutants during D&D operations.
- Waste categories and packaging: Covers classification and packaging of contaminated wastes generated during D&D operations.
- Waste storage and disposal: Describes storage and disposal methods for D&D wastes.
- Special facilities and equipment: Discusses special facilities and equipment that could be used in support of D&D operations.
- Transportation: Covers waste transportation requirements for D&D operations.

Prelininary Planning Guide For Radiological Characterization Of Facilities

A major element of successful D&D operations is the ability to make accurate radiological characterizations of a facility before, during, and after D&D operations. This characterization must include a map of radiation readings and an inventory of contaminating nuclides by kind, quantity, and location. Because of the extensive and unique nature of radiometry requirements for D&D, early planning must be accomplished. The purpose of the planning guide is to establish current state-of-the-art for radiometry as related to D&D work, describe the application of radiometry techniques, and identify areas where further development is needed. As yet the extent of the required radiological measurements has not been established, nor has the UCC-ND organization responsible for planning and performance of radiological characterizations been designated. Because of these uncertainties, the document has been issued in preliminary form and will be refined later.

Engineering Management Plan

The objectives of the engineering management plan are to:

- Provide an initial planning basis
- Set goals and objectives
- Define the program
- Establish design criteria

- Devise the general method for accomplishing objectives
- Establish a program management structure
- Determine an initial schedule and budget
- Identify areas needing further study and planning

Highlights of some topics covered in the D&D engineering management plan are discussed below.

Decommissioning Options

In the ORNL D&D Program feasibility studies will be conducted to determine the most cost-effective approaches to decommissioning candidate facilities. There are generally three categories of decommissioning. They are:

- Dismantlement.
- Safe storage: entombment, passive protective storage (mothball), custodial storage (layaway).
- Conversion and reuse.

Dismantlement

Dismantlement may be described as including those actions required to remove all radioactive or contaminated material from the facility such that any residual radioactive contamination would be at levels that would permit unrestricted release of the property. This is the most extensive mode of decommissioning and requires immediate commitments of a large amount of money, personnel, and radioactive waste storage space. Dismantling will consist of:

- demolishing and/or removing, packaging, and transport and storage of bulk radioactive material and activated components contained within the facility being decommissioned;
- decontamination, disassembly, and removal of any structures, systems, or components that may be identified for reuse or salvage;
- decontamination of all remaining radioactively contaminated structures, systems, and components to a contamination level consistent with unrestricted release; and the collection, processing, packaging, transport, and storage of all radioactive waste generated in the decontamination tasks.

Advantages of the dismantlement mode include the unrestricted release of the facility property at the conclusion of decommissioning. This permits restoration of the property to its original condition or the unhindered construction of a new facility for any purpose whatsoever. Attendant to the unrestricted release of the facility are the benefits that no security, maintenance, surveillance, or additional action is required at the facility location after decommissioning by dismantling. Further, there is a maximum reduction in the hazard potential for future public health and safety.

The prime disadvantage of dismantlement is generally the immediate, high-level commitment of money and manpower required for such an extensive program. Additionally, due to the very large extent of decontamination and demolition required to remove almost all traces of radioactive material, large quantities of radioactive waste will be generated which will require packaging, transport, and storage and which will subsequently result in a relatively great potential for occupational exposure.

Safe Storage

Safe storage is defined as those actions required to place and maintain a nuclear facility in such a condition that future risk to the public safety from the radioactive material contained within the facility is within acceptable bounds, and that the facility with its radioactive inventory can be safely stored for as long a time as desired. Unlike dismantlement, the safe storage mode of decommissioning does not result in the near-term unrestricted release of the facility. Facility preparation for safe storage generally includes the removal, packaging, transport, and storage of almost all bulk quantities of radioactive material (solids, liquids, and gases) and possibly the decontamination, dismantling, and removal of selected systems or components tagged for interim storage, reuse, or salvage. However, future actions, after the passage of time sufficient for natural decay, will include subsequent removal of all radioactive materials within the facility to a level consistent with unrestricted release. Whereas the dismantlement mode reduces the potential health and safety impact on the public by removal from the facility of almost all sources of radioactivity, the safe storage options utilize a combination of both removal of sources of radioactivity and making inaccessible all remaining radioactive sources.

The subsets of safe storage (entombment, passive protective storage, and custodial storage) are discussed below.

Entombment

Entombment is the encasement of radioactive materials in concrete or other structural material sufficiently strong and structurally long-lived to assure retention of the radioactivity until it has decayed to levels which permit unconditional release of the facility.

Comprehensive cleanup and decontamination are coupled with the construction of physical barriers around areas containing significant quantities of radioactivity. These barriers should be sufficiently strong to make accidental intrusion impossible and deliberate intrusion extremely difficult.

Typical activities in the entombment process include the removal of bulk radioactive material and equipment scheduled for reuse or salvage, and the major decontamination of the facility with attendant collection, processing, packaging, transport, and storage of the decontamination wastes. It is essential to minimize the volume of the hardened entombment and to release as much of the facility as practicable. Surveillance, less frequent than with other safe storage modes, will be required to assure radiologically leak-tight integrity of the entombment and to detect and correct any major structural degradation. It should be noted that in many instances the natural decay time and inventory of the radionuclides may be such that the time required to reach unrestricted release levels may exceed the demonstrated structural integrity life of most materials. Therefore, the costs for repair and maintenance should be anticipated. Electronic surveillance may be utilized to detect accidental or deliberate intrusion.

The major advantage of the entombment mode of facility decommissioning is the major reduction in potential hazard to public health and safety. This is partially due to the removal of some quantities of radioactive materials, but is primarily accomplished by the relatively permanent, on-site entombment of large quantities of the facilities' radioactive inventory. Local entombment reduces both public and occupational exposure risks by reducing radioactive material transport activities. Additionally, due to the relatively permanent nature of the entombment structure, only infrequent surveillance will be required.

Disadvantages of entombment include a major commitment of both money and manpower, with the attendant large potential for occupational exposures due to both decontamination and entombing activities. While these disadvantages are large compared with other modes of safe storage, they are less extensive than with the dismantling mode. Another disadvantage, which is inherent with all safe storage modes, is the necessity for immediate restrictions on the facility and its property due to the presence of significant quantities of radioactive materials. In the case of entombment, this restriction will be very long lasting.

Passive protective storage (mothball)

Mothballing will generally leave the facility intact except for the removal of both bulk quantities of radioactive material and salvagable, or reusable items. The option for reactivation of the facility at a future date most likely will be precluded by such actions as sealing and equipment removal. Passive protective storage can be characterized as an improved-stability holding action, whereby natural decay and improved confinement will decrease the potential public health and safety hazards from radiation exposure. During this holding period, new management options and decommissioning methods may be developed and analyzed. Passive protective storage will generally include a combination of partial decontamination and sealing, or fixing of residual contamination, both of which will reduce the potential impact on public health and safety. The facilities' perimeter penetrations will then be sealed to prevent personnel entry and radionuclide escape. Facility sealing methods may consist in welding metal caps, shutters, and doors over portals and passageways, as well as covering with concrete. A moderate surveillance program will be required to assure seal integrity and to detect attempts at intrusion.

Advantages of the passive protective storage mode include a moderate, immediate reduction of the potential public health and safety hazard at a moderate expenditure of money and manpower. The inherent time span generated by this holding action will permit research and development of advanced decontamination, disposal, and demolition techniques, where needed. Further, in-depth management option assessment can be conducted prior to some subsequent firm commitment of increased amounts of money and manpower in order to complete decommissioning.

Disadvantages, in addition to the immediate restriction on the facility and its property use, include the moderate surveillance required and moderate quantities of radioactive waste generated during the partial decontamination.

Custodial storage (layaway)

In this decommissioning alternative, the facility will, in general, be left intact, with the exception of the removal of all bulk quantities of radioactive material. If necessary, the facility could be reactivated. A minimum cleanup and decontamination effort will be conducted. This decontamination, combined with the bulk radioactive inventory removal, will reduce the long term potential public health and safety impact. The choice of decontamination methods will be limited to those which will not result in equipment or structural damage prohibiting subsequent facility operation. All openings in the facility perimeter will be sealed, and all entrances will be secured by at least locked doors or the equivalent. An extensive surveillance program will be required to prevent accidental or deliberate intrusion into the facility and subsequent exposure to radiation or the dispersal of radioactivity beyond the confines of the facility. The major decommissioning activity utilized in this case to prevent radionuclide exposure is to render the radionuclides inaccessible within the facility, thus preventing their introduction into exposure pathways.

The prime advantage of the custodial storage decommissioning mode is that relatively unlimited future options remain open. These options range from the future reactivation of the facility for its original use, to any of the previously described decommissioning modes. Also included is the future option for conversion and reuse for a new activity. Inherent in this mode is a time period in which master plan facility utilization needs may be modified or redirected, and wherein new and more efficient decontamination methods or techniques may be developed. Additional advantages stem from the minimal decontamination effort undertaken in this decommissioning mode. These include: the lowest initial commitment of money and manpower, the least amount of radioactive waste generated, and the lowest potential for immediate occupational exposure.

The disadvantages inherent in the custodial storage decommissioning mode include: a minimum reduction in the potential health and safety hazard due to the low level of decontamination effort expended, a continuing need for extensive surveillance to assure that an increase in the potential health and safety hazards does not materialize, and the immediate unavailability of the facility and its property for other uses.

Conversion and Reuse

Conversion and reuse, while not strictly encompassed within the definition of decommissioning, should be considered as a mode of facility decommissioning. It is a management option that should be evaluated in the planning phase, since it directly competes with the previously described decommissioning modes and may involve many of the decommissioning activities inherent in the other modes. Conversion and reuse may be generally defined as modifications to an existing nuclear facility in order to perform a new function or to enable it to continue performing activities similar to its original function. It is difficult to make general comparisons between conversion and reuse and the other modes of decommissioning because the extent of the decommissioning activities common to all modes is highly dependent on the new use or functions. For instance, although decontamination, partial demolishment, and structural modifications may be required, the degree or extent of these activities will be governed by the needs or requirements set by the new use activities.

The principal advantages of conversion and reuse are encompassed in the potential for cost effective reuse of existing major structures and equipment already emplaced in the facility subject to decommissioning. A possible disadvantage may be encountered in that a specific new use must be identified so that economic drawbacks and potential health hazards can be evaluated in the decommissioning mode selection process. The goal is to convert to other beneficial uses with a minimum of restrictions.

Program Decision Strategy

A wide variety of alternatives are available to the D&D Program, some of which may be best addressed at the program level, while others most effectively at the project level. Decisions concerning decommissioning mode, D&D methods and procedures, and detailed project scheduling and resource allocation can best be made at the project level. At the program level, decisions that affect all the D&D projects should be made as early as possible. Program-level decisions include D&D criteria, site priorities, requirements for common facilities and equipment, generic technical development, master planning, scheduling, and resource allocation.

An interdependent relationship exists between the D&D Program and its individual projects. The entire program and each project will be more effectively and efficiently completed if the decision making process recognizes and addresses these interdependencies.

Figure 1 shows the relationship of program and project decisions for the D&D Program. Note that the decision-making process is iterative, which is necessary because the consequences of each decision may not be fully understood until subsequent decisions are made and evaluated. If the consequences of an earlier decision are unacceptable or not optimal, that decision can be changed, which may require changes in subsequent decisions.

The first decision that must be made is to translate program objectives into specific measurable criteria that can be used by the engineering designers and program managers. In some cases, regulations will contain measurable criteria. In other cases where regulations are nonexistent or only provide general guidelines, criteria must be developed from management policies. In some cases, management policies may dictate more stringent criteria than needed to comply with regulations.

Once criteria are established, priorities for decommissioning the various sites can be established. In addition, D&D projects can begin, since criteria for determining decommissioning mode (final site conditions after D&D) will be available.

Requirements for special equipment and facilities should be established at the program level. The decision must be made at this point to either construct central processing facilities and special equipment or to handle the requirements for each project separately. This decision has a significant impact on the schedule. If, for example, central waste processing facilities are to be built, project waste generation must be scheduled to properly interface with completion of these facilities.

After the above issues are considered, a master schedule can be prepared for the program, and resources can be allocated. During the early phases of the program, the schedule and resource allocations will be very rough estimates and subject to extensive changes. As the program

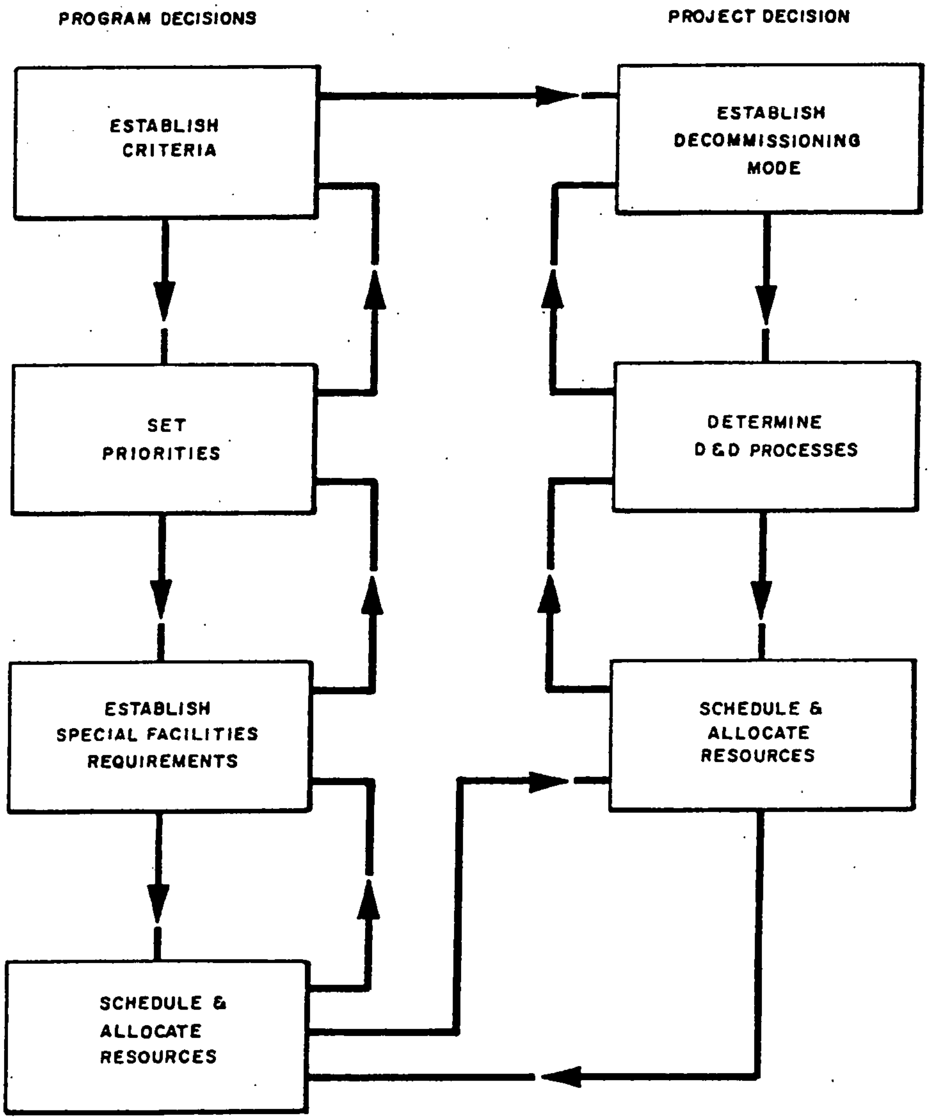

Fig. 1. D&D decision process.

matures, scheduling and resource estimates should become increasingly representative of actual time, money, and manpower requirements. Scheduling and resource allocation will be a highly iterative process, with budget or resource availability imposing constraints on scheduling.

At the project level, the initial decision is to determine the decommissioning mode. Options may involve dismantlement, entombment, decontamination and reuse, mothballing, layaway, or various combinations of these. Once the decommissioning mode has been determined, the methods for accomplishing the decontamination and decommissioning will be established. Scheduling and resource allocation can then be done subject to constraints imposed by program management.

Decisions at the program level focus on interactions between the various D&D projects. These interactions must be investigated if meaningful program decisions are to be made. Program decisions can be made by treating the D&D Program as a large system made up of numerous subsystems. The purpose of the large system is to accomplish the overall program objectives. The functional requirements (criteria) for each subsystem (project) are defined at the program level so that the overall objectives are met. If each project were then completed independently, the overall program objectives could be met. Treating each project independently, however, would not necessarily result in minimization of cost, radiation exposure, or safety hazards. The strategy for making program-level decisions should be one that establishes project relationships that optimize cost, radiation exposure, and safety hazards. Project relationships are defined by common D&D criteria, project priorities, scheduling, and resource allocations.

The goal of the program level decision-making process is to minimize program cost, radiation exposure, and safety hazards. Often, reduction of radiation exposure and safety hazards results in increased cost. In fact, if no cost limitations were considered, radiation exposure and safety hazards could be reduced to unmeasurable levels. In practice, some reasonable cost limitations must be considered. The cost-effectiveness of equipment and facilities that reduce exposure or risks must be evaluated. Only cost-effective options will be implemented. There is no generally agreed upon method for determining whether an alternative is cost-effective in reducing radiation exposure or safety hazards. Another problem involves the difficulty of numerically quantifying safety hazards. If numerical values can be defined and weighting factors are assigned to the different elements to be optimized, optimization algorithms can be developed for manual or computerized processing.

Criteria

Criteria must be established to provide standards to guide the decontamination and decommissioning of each site. Specific quantitative criteria should be established at the program level which can be used as design criteria at the project level. It is recognized that these criteria may be revised during the life of the program in response to changes in regulations or management policies.

Criteria must, as a minimum, assure compliance with applicable regulations. Existing regulations do not, in all cases, provide adequate quantitative standards to function as design criteria. It is necessary, therefore, to establish more definitive criteria or to delegate the criteria determination to project-level engineering. If criteria are established by each project design group, the results may satisfy the requirements for those projects without satisfying the objectives of the D&D Program. It is therefore recommended that common criteria be adopted at the program level to provide functional requirements for each project. This will facilitate project approvals by having preapproved design criteria. It will increase engineering efficiency by eliminating the need to study and develop criteria for each project and will assure uniform standards for each project. If necessary, modifications to the criteria can still be made at the project level.

Once the decision to establish criteria at the program level has been made, the decision making process involves selection of specific criteria. The purpose of the criteria is to translate general regulations and program objectives into functional requirements that can be used by the D&D designers. Since the regulations and objectives are not explicit, some latitude can be allowed in the possible criteria. The major impacts of the criteria will be on the cost and scheduling of D&D projects. In general, the more stringent the criteria, the higher the cost, and the longer the schedule. It is clear that the criteria must optimize reduction of radiation hazards, cost, and scheduling. Optimization of criteria can best be accomplished by testing the criteria against actual D&D projects. The initial criteria should be applied to early D&D projects at the feasibility study stage. The cost of the project to meet the criteria can be estimated, and the effect of reducing the stringency of the criteria can be evaluated. If significant cost reductions can be gained by small deviations from the criteria, modifications to the criteria should be considered. No formal optimization process for criteria development is foreseen. Program and higher-level managers must make management judgments concerning the cost benefit of the criteria based on input from technical advisors.

Priorities

Since budget and other constraints will not allow the D&D of all sites to proceed simultaneously, the setting of priorities becomes an important consideration. That the D&D of some facilities may not be completed for 20 years or more makes it imperative that priorities be set in a manner that considers all of the relevant factors.

A preliminary attempt at a computer aided optimization of D&D site priorities at the Hanford Reservation has been done by Battelle-Pacific Northwest Laboratories.[1] Since approximately 600 facilities are involved, a formal optimization process was necessary. With approximately 30 facilities at ORNL, a formal, computerized process is probably not necessary. The general approach used by Battelle is, however, of value in developing a prioritization method for ORNL. Battelle's method uses four criteria for determining priority:

- potential off-site radiological hazard;
- potential on-site radiological, physical, and chemical hazard;
- cost of continued maintenance and surveillance;
- compatibility with projected future uses of the site.

Systems for weighting the four criteria and estimating performance of each facility on each criterion were developed. Subjective weighting factors were determined by a panel of knowledgeable individuals. Information in a computerized facilities data base was used to estimate performance against criteria. A priority index was then established for each facility. The intent of the prioritization effort at Hanford is to guide future D&D planning but not to make decisions, since the ultimate decision making responsibility lies with DOE.

It is recommended that a prioritization study be conducted as part of the program definition study of all 29 surplus facilities. Methodology for optimizing priorities can be developed during the study. In addition to the criteria used by Battelle, the following factors should be considered.

- availability of necessary technology,
- time to complete,
- availability of resources.

Special Facilities and Equipment

The D&D operations at all of the sites require a number of common functions. These requirements might be met by utilizing common facilities and equipment designed and constructed at the program level for use on all D&D projects. The following are possible facilities and equipment that should be considered:

- decontamination and waste processing facility,
- portable containment unit,
- robots and remotely controlled tools,
- portable shields,

- special waste containers,
- liquid waste handling systems,
- ventilation equipment,
- special tools,
- special monitoring instruments,
- special transportation equipment,
- mobile laboratories,
- mobile change houses and lunch rooms.

The decision to acquire special equipment and facilities at the program level or to allow each project to stand alone will have significant effects on the program schedule. If common facilities and equipment are to be used, the D&D operations phases of the projects will be constrained by availability of the common equipment and facilities. On the other hand, if special equipment and methods must be developed for each project, the duration of the projects will likely be extended.

Conversion of facilities on the D&D list to D&D processing facilities should be considered. This may result in cost savings over the construction of new facilities. The facility could be partially decontaminated and converted for use during the D&D Program, with final decontamination and decommissioning at the completion of the program. Facilities should be identified and scheduled for early conversion.

Facilities and equipment for common use on all D&D projects should be constructed only if savings in overall program cost or reduction in worker radiation exposure results. If a higher program cost results from procurement of special facilities and equipment, but exposure is reduced, a cost-benefit analysis will have to be done to determine whether the expenditure is justified. To be effective, this decision must be made early in the program. Unfortunately, cost estimates and personnel exposure projections will be inexact early in the program.

This decision should be made after the program definition study is complete, so that size and functional requirements for special facilities and equipment can be established. Consideration can also be given to conversion of facilities on the D&D list for use in subsequent D&D work. A study and estimate should be made after the overall site study to define the major facilities and equipment requirements and to estimate their cost. Potential cost savings and exposure reductions should be estimated. Based on an economic analysis and a cost-benefit analysis of exposure reduction, the optimum approach can be recommended. Since estimates at this stage will not be very accurate, sound engineering judgment will be needed in making this decision.

Schedule and Resource Planning

The overall program schedule reflects the previous decisions in addition to budget and manpower limitations. Constraints due to unavailability of waste disposal or other facilities will affect the schedule. Postponement of certain projects to allow time for development of new equipment and methods may be in order.

Engineering Decision Strategy

Initially, in selecting the decommissioning mode for a facility, each possible mode is to be evaluated in terms of the criteria. Those alternatives which do not satisfy the criteria can be eliminated. If more than one decommissioning mode meets the criteria, the optimum mode must be chosen. The choice will depend on cost and planned future use of the site. In the project feasibility study, viable alternatives should be covered, and costs should be estimated for each D&D mode together with worker exposure estimates for each. In the simplest case, the least costly mode that meets the criteria will be selected. In most cases, the least costly mode will be the most restrictive for future site uses.

Depending upon future plans for the site, a management decision may be made to accept a higher-cost D&D mode to allow for a less restricted use of the site. Even though the criteria may be satisfied, D&D modes other than complete dismantling entail some risk of radiation exposure to ORNL personnel or the public. Depending on the cost differential, it may be advisable to select a more expensive mode that presents a lesser risk over a lower-cost, higher-risk mode. This will be a management decision based on a cost-benefit analysis, which should also consider the differences in worker exposure to achieve the different modes. The ultimate decision will rest with DOE. Engineering will recommend an approach to D&D Program management in the feasibility study. Prior to or early in the conceptual design phase, the decommissioning mode must be selected.

A D&D process will be outlined for each feasible decommissioning mode during the feasibility study. Once the decommissioning mode is selected, the process will be developed in more detail in the conceptual design and further refined in the detailed design. Numerous choices will have to be made on each project concerning equipment, procedures, and sequences of activity. Generally, these decisions will result from an optimization of cost, worker radiation exposure, and safety. A key issue will be the use of machines in place of men in order to reduce exposure. In some cases this may be less costly; in others the cost of remote machine operations may be greater. If so, the decision must be made on the basis of a cost-benefit evaluation. Since no specific criteria for acceptable cost-benefit ratios are available, these decisions will rely on engineering judgment, with ultimate management approval.

The project schedule will be established after the decommissioning mode and D&D method have been decided. For larger D&D projects, computer aided scheduling may be desirable, since these projects will span several years and consist of many operations. As soon as the project schedule is completed, the program master schedule should be updated to reflect any schedule changes. Any schedule conflict discerned at the program level can then be resolved by project or program schedule adjustments. Resources to complete the project will be allocated subject to constraints imposed by program management. An iterative process of scheduling and resource allocations will be carried out to adjust the project schedule to available resources.

Project scheduling will primarily be controlled by the time required to accomplish the sequence of tasks needed to achieve the end result. For an individual project, it is not expected that manpower limitations will be a constraint. It will be necessary to eliminate budget uncertainties before the D&D operations phase of a project to ensure that once the D&D work is begun, it can be completed without leaving the site in a hazardous condition. An option to be considered in scheduling is the performance of D&D operations on other than a normal work week, day shift basis. It may be possible to compress the schedule in this manner, but the attendant increased costs and hazards must be assessed.

A major factor will be the availability of money and manpower. Optimization of the schedule will be done by budget and manpower leveling. Assumptions must be made for money and manpower availability, since these factors will probably be uncertain throughout the program. As D&D engineering and operations are performed, the new information wil be used to improve cost and manpower estimates for future projects.

Program Organizational Structure

A formal program organization has been recommended to facilitate accomplishment of the D&D program at ORNL. The matrix organizational concept will be employed to allow utilization of personnel from other UCC-ND Organizations. The program office will be headed by the Program Manager who will be supported by the following major functional elements:

- Project Management
- Engineering
- Operations
- Configuration Management
- Logistics
- Program Control
- Health and Safety
- Procurement
- Quality Assurance
- Administrative Services

Figure 2 is the proposed functional organization chart for the program.

It is not expected that the full organization will be in effect until the program is well established. Initially, a small cadre organization is proposed. The cadre will perform the initial program activities and form the nucleus for building the full program organization. The initial cadre will be headed by the Program Manager supported by project management, engineering, planning, and administration functions. Additional support can be obtained from other UCC-ND organizations as required. Figure 3 shows the cadre functional organization.

Program definition study

An understanding of the scope and magnitude of the entire D&D effort is paramount to developing an optimum D&D Program. The purpose of the proposed study is to develop an understanding of the problem and to determine viable alternative solutions to meet program objectives. Program costs and schedules are to be determined on a rough order of magnitude (ROM) basis. The information derived from the study will be used to formulate program decisions with a high degree of confidence.

The study will include, but will not be limited to, the following major tasks as related to the candidate 29 facilities:

- collect available facility data,
- develop preliminary facility characterization data,
- determine viable decommissioning modes,

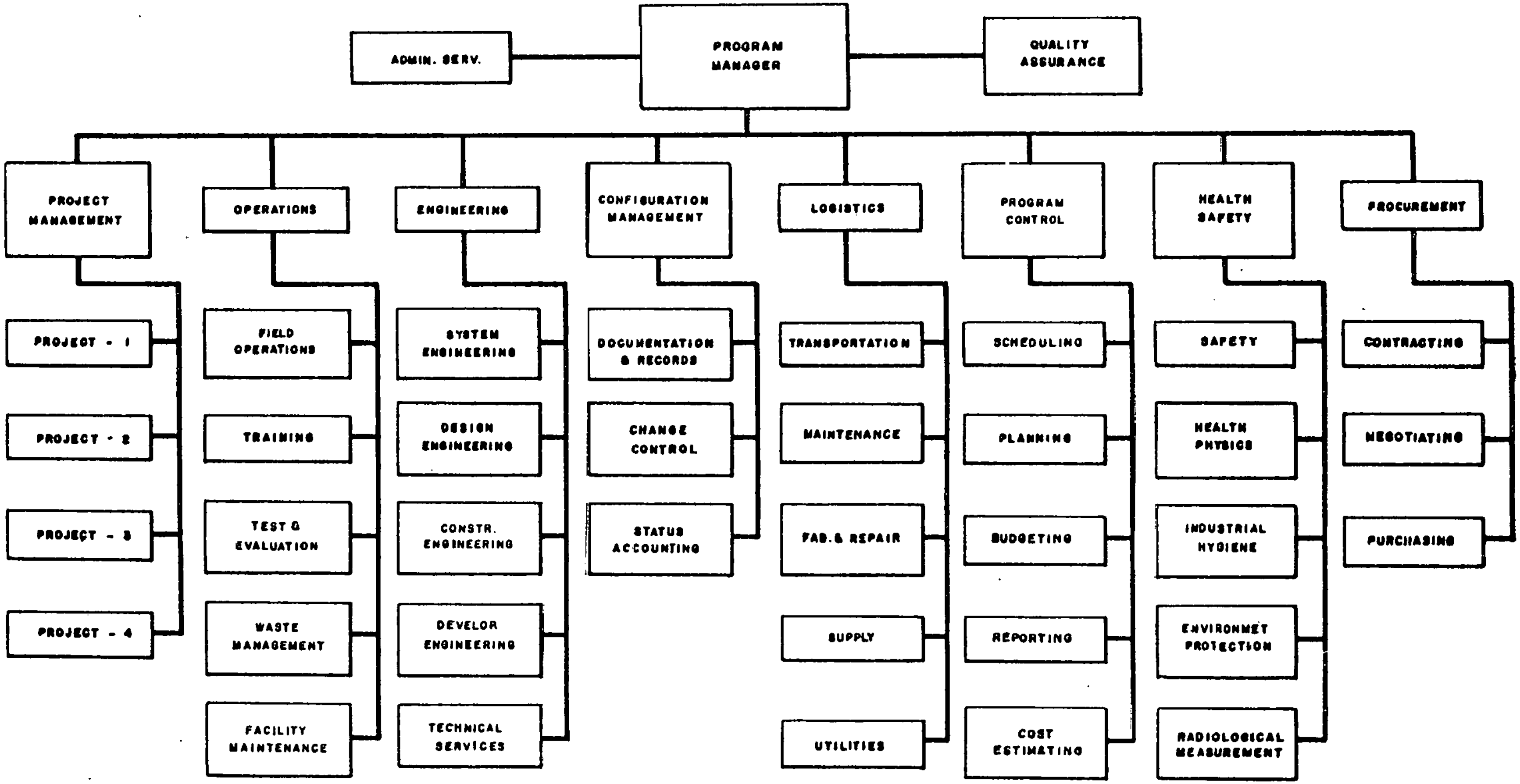

Fig. 2. Functional organization of ORNL D&D program office.

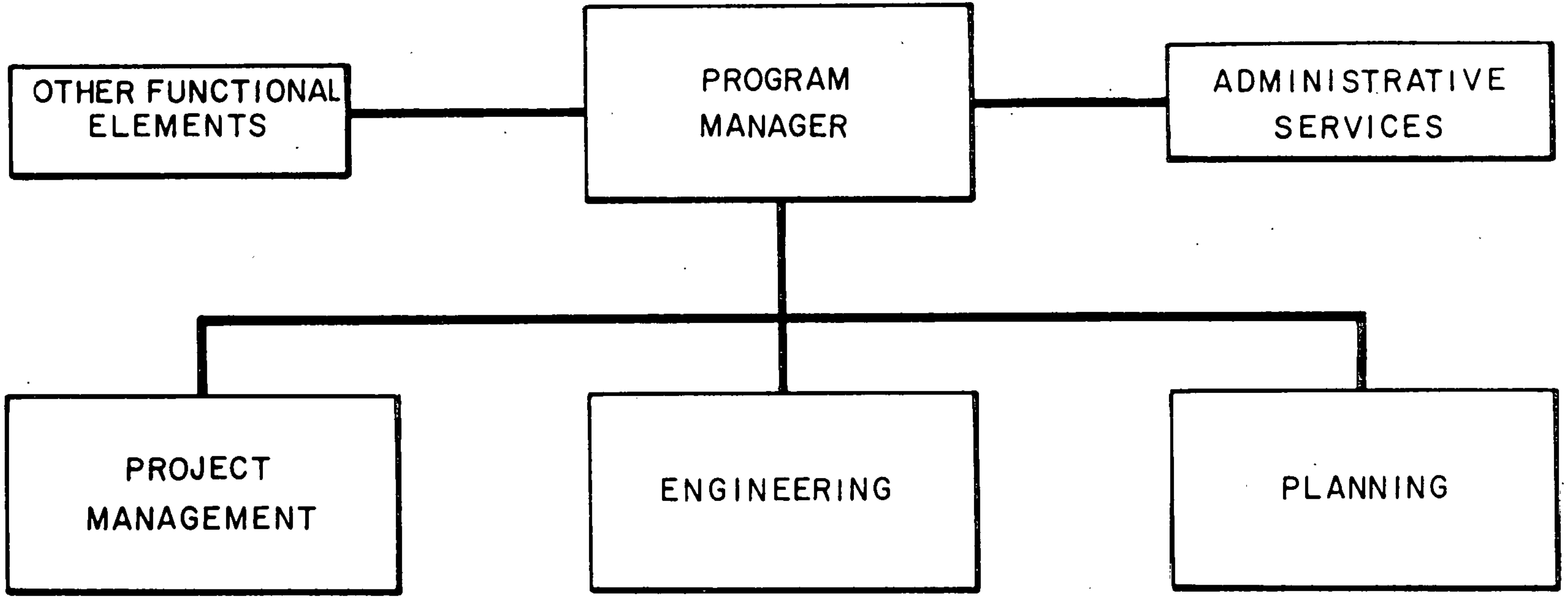

Fig. 3. Functional organization of ORNL D&D program office cadre.

- estimate types and quantities of waste resulting from D&D operations,
- identify special or unique problems,
- determine current and projected maintenance and surveillance costs,
- determine and analyze potential modes of release of radioactivity,
- determine and analyze potential radiation exposure to D&D operational personnel,
- determine D&D project priorities,
- determine special D&D support facilities and equipment requirements,
- evaluate utility of converting a specific facility to a support facility,
- determine overall D&D Program schedule,
- determine program cost estimates (ROM),
- determine acquisition strategy for the proposed program schedule.

Research and development planning

Special mechanical equipment. High- and intermediate-level solid waste. Batelle Columbus Laboratories,[2] in their preliminary study, has suggested some specialized equipment for use during the D&D Program. Included in their lists were several shielded devices that will enable an operator to be located in a high radiation field while performing various mechanical operations. This proposal reinforces the aforementioned suggestion to examine all facilities on a preliminary basis. One would have to ascertain that sufficient room was available in a shielded cell to introduce and maneuver the shielded devices.

The devices suggested for use in high- and intermediate-level activity areas are as follows:

Slave-survey module: This unit is essentially a biologically shielded operator's cab associated with remote manipulators for performing instrument or smear operations (light duty). It would be equipped with a self-contained life support system with a backup respirator for emergency egress, an on-board systems power source, instrument and supply storage on-board and accessible to the remote manipulators for radiological surveys, and audio and video output to the control van (to be discussed later). The module is not self-propelled, but must be transported by the master module (also to be described later). This slave-survey module and its associated master module would be specially developed one-of-a-kind units that would require appreciable amounts of R&D and engineering.

Slave D&D module: This module is similar to the slave-survey module, except that it is fitted with heavy-duty remote manipulators for performing D&D operations. It also contains a tool storage bin containing necessary cutting tools for volume reduction.

Master module: This module is envisioned as a self-contained motorized unit built on a forklift type of chassis to support the shielded control cab. The master module would be used to transport slave-survey and slave-D&D modules to the work site.

It would also be used to tow for short distances a shielded waste transport trailer.

Shielded waste transport trailer: This unit essentially is a flatbed semitrailer equipped with a self-contained shielded cab mounted over the fifth wheel, a biologically shielded operator cab, a crane mounted on the trailer for handling waste drums, a shielded transport container for 55-gal drums, radiation monitoring equipment within the cab monitored in the control van, and audio and video output to the control van.

Control van: A converted motor home would be outfitted to direct all remote operations. Audio-video and computer equipment would provide a complete monitoring and control facility.

Hot cell (portable): A few cells would be constructed on low-boy trailers and equipped with manipulators, shielding, and auxiliary equipment to permit cleaning, disassembly, and volume reduction of contaminated solids.

Hot cell (permanent): Several large cells equipped with manipulators, heavy-item handling equipment, and adequate shielding will be necessary for the treatment of remote-handled solid waste brought in from various ORNL facilities. These cells would be permanently located and might consist of existing facilities modidified to meet D&D requirements.

All of the above facilities would require significant design and R&D effort that would have to be started several years in advance of their projected use in D&D operations. Other items suggested by Battelle Columbus that might require some R&D were a portable electropolishing and/or acid leach unit, a metal melting unit, and a high-capacity high-pressure compactor.

Low-level solid waste. Items suggested by Battelle for handling low-level solid waste were: a volume-reduction facility, a transport vehicle, and an incineration unit. Hopefully, the first two items could be similar to those described for high-level waste. The incineration unit would require more study, particularly at the engineering level.

Supporting facilities. Central radiation monitoring and chemistry laboratory. Very little R&D should be required for this facility, but engineering would be required to be certain that all D&D requirements were met. Existing facilities might meet part of the requirements.

Health physics van. A D&D Program would be facilitated by the use of a field facility equipped with instrumentation for personnel dosimetry, radioanalysis, and other radiological measurements. This facility preferably could consist of a converted motorized home, and probably could be patterned after those used by the off-site monitoring group at ORNL.

Technology. High-level radiological measurements. The ability to perform a detailed radiological characterization inside of a high-radiation cell is in doubt. Particularly troublesome would be attempting to determine the extent to which contaminants have penetrated concrete or leaked behind stainless steel cell liners. An assessment of the present capabilities for making such measurements, the amount of R&D required if the capabilities are lacking, and the feasibility of attempting such measurements need to be studied. Indications are that detailed characterization in high-radiation fields has not been attempted in other D&D operations. This topic is discussed in more detail in Sect. 2, "Site Characterization," ORNL D&D Program technical manual. Problems of radiological assessments in general are discussed in document X-OE-110, Feasibility Study for Building 3505 Decontamination.

Decontamination methods. Many chemicals and techniques have been used for decontaminating the surfaces to be encountered in the various ORNL facilities. A literature survey (if not already available) will help establish the possibilities. Some additional experimental work on a small scale may be required to verify the choice of method(s). In fact, separate facilities may require small-scale tests.

Realistic simulations may be difficult, but some effort will probably be needed to avoid generating large volumes of waste solutions that are not effective. The organization to conduct laboratory or bench-scale tests needs to be determined.

Mechanical methods. Several mechanical methods have been proposed for decontaminating surfaces, especially concrete. Some of these are Vacu-Blasters, floor grinders, and "scabblers." Decisions need to be made as to whether these devices will be tested using simulated conditions or tested on a small scale D&D effort. If they ever are to be operated remotely, some engineering and testing will be required to provide the remote operation capabilities. See Doc. X-OE-110 for a more detailed discussion of this topic.

Disassembly methods. The need for R&D on remote cutting methods, especially for concrete, is also discussed in more detail in Doc. X-OE-110.

Feasibility Study for Decommissioning the Metal Recovery Facility

The Metal Recovery Facility was a pilot and small-scale production nuclear fuel reprocessing plant operated at ORNL during the 1950's. Now abandoned for 20 years it contains widespread residual contamination, including transuranics. No further use of the facility is anticipated; therefore, decontamination and decommissioning are planned to eliminate potential hazards and to return the land area to usable condition. Figure 4 is a floor plan of the facility.

The following decommissioning options were considered in the feasibility study:

- ° No action
- ° Decontaminate and reuse
- ° Protective storage
- ° Entombment
- ° Complete removal
- ° Combinations of above

Criteria were established to provide a basis upon which to select the decommissioning option. Criteria for decommissioning have not been well established by regulatory agencies; therefore, D&D criteria were borrowed from general radiation protection and waste disposal regulations. Different regulations apply depending on whether the facility is restricted from public access or unrestricted. More stringent criteria are required for unrestricted sites. The Environmental Protection Agency calls for a time limit of 100 years as the maximum for which a site can be planned to be restricted. After that period, it must be considered to be unrestricted to the general public. This criterion was used for this study.

Based on the criteria, the only decommissioning options found to be acceptable are complete removal of the building and removal or entombment of the adjacent canal. Because of the long decay time for the plutonium contamination in the building (up to 250,000 years), the no action protective storage or entombment options are considered unacceptable. Decontamination and reuse of the building was ruled out because the required decontamination would damage the building's structural integrity. Because the canal contains shorter lived contaminants (cesium and strontium) entombment is considered to be a viable option since the below ground entombment structure can be expected to remain structurally sound for an adequate decay period (up to 1000 years).

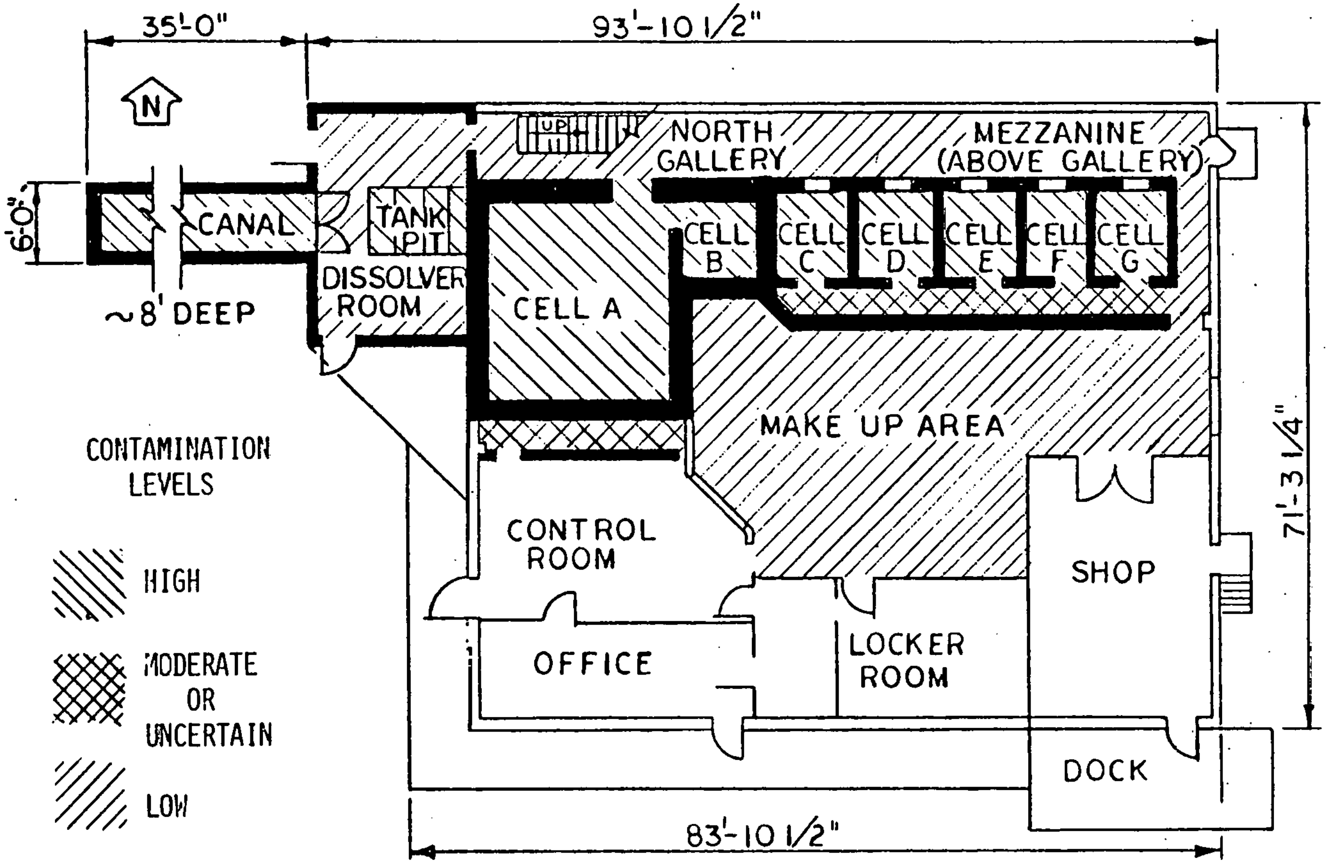

Fig. 4. Floor plan of metal recovery facility, Building 3505.

Table 1 is a summary cost estimate for D&D of the Metal Recovery facility. As can be noted from the estimate, the project is highly labor intensive. Much of the work will require air-suited workers and health physics support, reducing the labor efficiency drastically. A large amount of labor is required to remove the contaminated surface layer from the concrete cell walls to reduce the volume of transuranic waste which must be placed in retrievable storage. If automated, remote equipment can be developed to perform this and other tasks, significant cost savings may be achieved.

The cost estimates in table 1 do not include the cost of waste disposal off the building site. Table 2 gives the estimated waste quantities which will be generated by the D&D of the facility. Contaminated soil on the site is included in the estimated waste volume.

TABLE 1

3505 DECOMMISSIONING

SUMMARY COST ESTIMATE

(FIRST QUARTER FY-80 DOLLARS)

ESTIMATE A - INCLUDES REMOVAL OF CANAL AND WASTE TANKS

	MATERIAL	LABOR	TOTAL
BUILDING REMOVAL COST	1,210,000	14,800,000	16,010,000
CANAL REMOVAL COST	250,000	1,170,000	1,420,000
WASTE TANKS REMOVAL COST	10,000	60,000	70,000
TOTAL	1,470,000	16,030,000	17,500,000

ESTIMATE B - INCLUDES ENTOMBMENT OF CANAL AND WASTE TANKS

	MATERIAL	LABOR	TOTAL
BUILDING REMOVAL COST	1,210,000	14,800,000	16,010,000
CANAL ENTOMBMENT COST	30,000	310,000	340,000
WASTE TANKS ENTOMBMENT COST	10,000	40,000	50,000
TOTAL	1,250,000	15,150,000	16,400,000

TABLE 2

3505 DECOMMISSIONING ESTIMATED WASTE QUANTITIES

TRANSURANIC	900 FT^3
HIGH-LEVEL BETA-GAMMA	1,300 FT^3
LOW-LEVEL BETA-GAMMA	200,000 FT^3
LOW HAZARD	25,000 FT^3

REFERENCES

1. Litchfield, J. W. and J. C. King, Decommissioning and Decontamination Planning for Hanford Nuclear Facilities Using Multiattributed Decision Analysis, BNWL-SA-6007, Battelle Pacific Northwest Laboratories (May 1977).

2. Goldthwaite, W. H., et al., Identification of General and Special Facilities' Decommissioning and Decontamination Activities, Battelle Columbus Laboratories (September 28, 1979).

3. Technical Manual for Decontamination and Decommissioning Program, X-OE-115, Oak Ridge National Laboratory (April 1980).

4. Milford, R. P., Planning for Radiological Characterization and Monitoring for the ORNL Decontamination and Decommissioning Program, X-OE-124, Oak Ridge National Laboratory (April 1980).

5. Engineering Management Plan for Decontamination and Decommissioning Program, X-OE-114, Oak Ridge National Laboratory (April 1980).

6. Feasibility Study Report for Building 3505 Decommissioning, X-OE-110, Oak Ridge National Laboratory (April 1980).

Session II

WASTE OIL AND SPILL CONTROL

Chairperson: J. M. Napier (Y-12/UCC-ND)

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WASTE OIL DISPOSAL AT THE DEPARTMENT OF ENERGY FACILITIES AT OAK RIDGE, TENNESSEE*

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D. D. Stroud and M. Sanders (Y-12)
J. R. Jones and T. W. Oakes (ORNL)

ABSTRACT

The disposal of waste oil generated at the USDOE facilities in Oak Ridge has become a significant problem in recent years. The presence of radioactivity and other contaminants in some oils prohibits the use of commercial disposal and oil reclamation firms, and, thus, often necessitates on-site disposal. Recent and proposed federal regualtions have and will continue to control all waste oil disposal operations, including those of the Department of Energy.

In order to ensure adequate and acceptable disposal of waste oils, a special committee of UCC-ND personnel located in Oak Ridge was established in December 1978 and asked to make appropriate recommendations for both near-term and long-range operations. Included in this paper is a brief description of the efforts of the committee, the associated efforts of development and engineering personnel, and conclusions and recommendations pertaining to UCC-ND waste oil disposal.

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*Based on work performed at the Oak Ridge Gaseous Diffusion Plant operated by the Union Carbide Corporation, Nuclear Division, for the Department of Energy.

WASTE OIL DISPOSAL AT THE DEPARTMENT OF ENERGY FACILITIES AT OAK RIDGE, TENNESSEE*

The disposal of waste oils and coolants is currently and will continue to comprise a significant portion of the overall waste disposal effort at the USDOE facilities in Oak Ridge. While a small quantity of the oils can be and are sold to commerical reclaimation firms, the majority cannot, primarily due to the presence of different contaminats, including radioactivity and PCB's. It is thus mandatory that acceptable means of disposal be provided by UCC-ND within the DOE reservation.

Current Generation, Storage, and Disposal Practices/Problems

The three Oak Ridge plants generate several different types of waste oils and coolants, but the majority can be classified as either water-soluble machine coolants, water-insoluble hydrocarbon oils, water-insoluble mineral oils, or water-insoluble synthetic oils. In general, the majority of the water-soluble coolants are generated by the large machine shops located at the Y-12 and K-25 sites. The primary generator of the hydrocarbon oils is the K-25 cascade lube oil system with smaller quantities being generated by routine vehicle maintenance at all the plants. The waste mineral oils and synthetic oils are generated at all the sites, primarly as a result of maintenance on electrical equipment, diffusion pumps, vacuum pumps, and hydraulic systems.

The water-soluble machine coolants generally do not contain detectable PCB's or enriched uranium and consist of about 95 percent water and only 5 percent oil. They are very ameneable to the biological degredation process currently employed at the Y-12 plant. Since this process produces an environmentally-acceptable effluent which should continue to comply with all proposed regulations, it is anticipated to be the primary means of disposal for the coolants for the next several years.

The method(s) of disposing of hydrocarbon, mineral and synthetic oils is dependent upon the concentration of contaminants. In general, the oils containing less than predetermined safe levels of all such contaminants are sold to commercial reclaimation firms.

The disposal of oils containing greater than the predetermined level of any one or a combination of contaminants is a much more complex process. For example, waste oils containing greater than 50 ppm of normal or depleted assay uranium, any level of enriched uranium (greater than 0.71% U-235), any detectable PCB's and/or greater than 1 ppm of beryllium are not sold and thus must be disposed of in some other manner. In the past, all such oils having criticality safety approval (i.e. nonfissile oils) were landfarmed at the Y-12 site. Due to the complications associated with landfarming oils containing even trace levels of PCB's the decision was made to discontinue all landfarming of oils containing any detectable PCB's as of July 2, 1979. As a result of this decision a significant quantity of oil has been and will continue to be accumulated in storage. The oils containing less than 50 ppm of PCB's and less than the predetermined levels of other contaminats may be disposed of in any manner that does not result in direct entry into the environment. Oils containing greater than 50 ppm but less than 500 ppm of PCB's may be shipped to a commercial PCB disposal facility or burned in EPA approved high-efficiency incinerators/steam boilers. The oils containing greater than 500 ppm of PCB's are required to be incinerated in EPA approved PCB incinerators. Since none of these oil/PCB disposal methods are currently acceptable for wastes containing enriched uranium, all PCB-containing oils are being stored until appropriate uranium data can be obtained. Depending on the content of the uranium and/or other contaminants, the appropriate method(s) of disposal/storage can be and are determined. The various options for disposing of the wastes are discussed in subsequent sections of this report.

Waste oils that do not contain detectable levels of PCB's but do contain greater than the prescribed level of any other contaminant are landfarmed at the Y-12 site. While this means of disposal is currently environmentally-acceptable and legal, it will probably be prohibited by the Tennessee RCRA regulations, when they become effective. It is thus anticipated that landfarming will provide a viable means of waste oil disposal only through 1980. After this time increased storage in anticipation of acceptable long-term disposal will be required.

Development and Engineering Studies

In order to provide a sound technical basis on which to make decisions regarding long-range disposal of waste oils, several development and engineering studies were initiated in early 1979. At the Y-12 plant a major effort was expended on the study of removal of PCB's from waste oil through evaporation/distillation, solvent extraction, and absorption techniques.

The distillation system consisted of a two-inch diameter glass column that contained eighteen inches of 1/4 inch raschig ring packing above and below the feed point, a two liter glass reboiler, a feed preheater, and a distillate collection-reflux system. The column was operated at 5 mm Hg absolute pressure in the condenser and 10 - 15 mm Hg absolute pressure in the reboiler. The oil used for the study had a boiling range of approximately 200°C - 550°C at 760 mm Hg pressure. The feed oil contained approximately 3000 ppm of PCB's and during distillation the PCB's concentrated in the distillate.

During operation of the column, the reflux ratio and the temperature of the reboiler were varied to determine PCB removal and the feed split (feed to distillate/feed to bottoms), with the most important result being the amount of PCB's remaining in the bottoms. A summary of the test results follows:

[1]Reboiler Temp. (°C)	Reflux Ratio	Distillate Temp. (°C)	Feed Split	PCB in Bottoms (ppm)
290	9.0	185	25/75	950
290	2.5	195	30/70	250
300	2.0	210	40/60	55*
310	2.5	215	45/55	35*
320	2.5	220	50/50	10*

Calculations are being made to define through-put rates for various column sizes and column lengths.

[1] Temperature at 10 - 15 mm Hg Absolute Pressure

Solvent extraction is also being investigated as a means of removing PCB's from contaminated oil. The criteria for a favorable solvent include an affinity for PCB's, immiscibility with the oil, and inability to form emulsions. Approximately thirty solvents have been tested to date with only furfural showing favorable characteristics. The study was conducted using oil contaminated with approximately 80 ppm PCB. The PCB's distributed equally between the furfural and the oil, and the oil was approximately 5% soluble in the furfural.

A third approach to removing PCB from oils is being investigated through the use of commercially available PCB absorbers. One such absorber consists of a filer unit containing a rubber compound for removal of PCB from transformer oils. Two units have been ordered for evaluation in the laboratory and in field tests.

A development study is being conducted at ORGDP to investigate removal of enriched uranium from waste oil to facilitate safe and environmentally-acceptable disposal. Laboratory analyses reveal that uranium concentrations in waste oil at ORGDP generally range from 400 ppm to 58,000 ppm.

Scoping studies have indicated that three filtration methods can reduce uranium concentrations. Absolute filter paper reduced uranium from 9,000 ppm to 150 ppm, but the effective flow rate was small. Cross-flow filtration through porous tubes reduced the uranium concentration from 31,000 ppm to 840 ppm while concentrating the residue to 81,000 ppm; however, tube pluggage occurred during operation. Pressure filtration was also investigated extensively and uranium removal to concentrations of less than 50 ppm were achieved on some samples. Laboratory tests were also conducted on several types of filter precoats to determine filtration rates. In one test run with precoat pressure filtration and a coarse cellulose filter aid, the concentration of uranium in the filtrate was found to decrease from 1400 ppm to 50 ppm. However, effective filtration did not occur until a layer of tar-like material had formed on the filter cake. These filtration studies are continuing.

In conjunction with the various development efforts, UCC-ND Engineering conducted a study of the feasibility of cleaning waste oils for recycle and/or reuse as fuel in oil-fired steam generating boilers. In general the study consisted of four options - two involving treatment and two involving ultimate disposition/reuse. The treatment (cleaning) processes evaluated were simple evaporation and distillation, and the dispositon alternatives included burning in a new package oil-fired boiler and burning in modified existing oil-fired boilers. Included as auxiliaries to both clean-up alternatives were a storage building, oil-water separators, filters, storage tanks, preheaters, and the required pumps and piping.

Based on preliminary results of the aforementianed development work, the engineering study concluded that the treatment processes would produce from 80,000 to 90,000 gallons of clean oil each year and a waste sludge that would amount to about 30% of the original volume of waste oil. This particular study did not include provisions for disposing of the waste material. The capital costs of the various treatment/reuse alternatives were estimated to be from \$1.9 million to \$2.2 million, as escalated to FY-1984-2. The annual operating cost of any one of the options was estimated to be about \$160,000.

Long-term Disposal Alternatives

Given the results of the development and engineering studies, several alternatives means of waste oil disposal will be evaluated, primarly on the basis of technical feasibility, economics, and regulatory compliance. As mentioned previously, the existing method for disposing of non-PCB, water-soluble machine coolants by biological degradation in an old cooling tower basin is currently in compliance with all applicable regulations and is expected to remain in compliance with proposed RCRA regulations. It has thus been concluded that it should be continued to be utilized as the primary means of coolant disposal.

The disposal of water-insoluable oils presents a more complex problem, primarly due to the presence of various contaminants, that cannot be adequately solved with existing resources. While the current practice of storage of these oils certainly precludes any immediate unacceptable disposal, it is apparent that some means of disposal must ultimately be provided. As described in previous sections, it has been determined that after proper treatment, such as filtration and/or distillation, the majority of the waste oils could be reused or burned as fuel. Unfortunately, the cost of such a system would be high, (about \$2 million) and the identified processes would produce sludges containing concentrated PCB's, uranium and other contaminants. The disposal of the sludges would then present a similar disposal problem, on a smaller scale, as did the PCB/oil materials.

Another long-term alternative that should provide for complete disposal of waste oil and produce only an inorganic residue with concentrated uranium would consist of a high-temperature incineration system. This system could be designed and constructed to handle both solids and liquids of varying viscosities, including PCB's, waste oils, and organic solvents such as kerosene. Such a system is currently included in the "Gaseous Diffusion Long-Range Plans" for FY-1983 at a budgeted cost of $25 million.

The feasibility of each of these options is being studied by UCC-ND engineering personnel and a decision regarding the optimum means of long-term disposal will be made in the near future.

Since any new disposal system will not be funtional for several years, each plant will be required to provide adequate interim storage. Such storage must be in compliance with all applicable regulations and, especially in the case of the PCB's, will require significant capital expenditures.

WASTE OIL MANAGEMENT AT THE OAK RIDGE NATIONAL LABORATORY

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ABSTRACT

It is the policy of the Oak Ridge National Laboratory (ORNL) to require that oily substances be handled and disposed of in a manner that protects the environment and personnel from harm. Federal regulations prohibit the discharge of oil into navigable waters, with stiff penalties possible to violators.

A strict waste oil management program has been developed and implemented because of the potential for oil problems resulting from the large and varied uses of oil at the Laboratory. Also, past records of improper discharges of oil have mandated immediate corrective actions.

In order to resolve the problems of waste oil at the Laboratory, the ORNL Waste Oil Investigation Committee was formed on March 14, 1979. The work of the committee included a survey of every building and area of the Laboratory to locate the presence of oil and the pathways of oil discharges to the environment. The committee also provided a basis for the development of oil spill procedures and waste oil disposal.

The Department of Environmental Management (DEM) of the Industrial Safety and Applied Health Physics

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*Operated by Union Carbide Corporation under contract W-7405-eng-26 with the U.S. Department of Energy.

Division at ORNL has the responsibility of developing environmental protection procedures for the handling and disposal of oil. It approves storage and collection facilities, disposal methods, and disposal sites for oil-containing wastes. The DEM has developed and implemented an ORNL Environmental Protection Procedure for oils and an oil spill prevention and countermeasure plan. In order to familiarize ORNL personnel with the problems and procedures of waste oil, the DEM has held seminars on the subject.

This report reviews the findings of the Waste Oil Investigation Committee and the actions of the Laboratory management and the DEM in dealing with the waste oil problem at ORNL.

INTRODUCTION

The widespread uses of oils at ORNL create two environmental management considerations: oil spills and the generation of waste oils. Repeated occurrences of oil spills, with the underlying environmental and regulatory implications, brought about the formation of the Waste Oil Investigation Committee (WOIC). The purpose of the WOIC was to assess the waste oil problems and make recommendations for corrective actions. Inventories of oil use and oil storage and a survey of potential pathways to surface waters were completed. Special problem areas were identified, and changes were made to prevent future spills. This paper reviews the remedial actions taken at ORNL to deal with oil problems.

The Department of Environmental Management (DEM) has primary responsibility in dealing with the problems of waste oils. Some of these duties include responding to oil spills, coordinating cleanup activities, certifying that waste oils are not contaminated with radioactivity or PCB's, developing and implementing a Spill Prevention Control and Countermeasure (SPCC) Plan, and inspecting oil storage facilities. The work of the WOIC has been used by the DEM as a basis for developing policies and procedures to be used in waste oil management.

The Analytical Chemistry Division has been developing simple methods for identifying oil and lubricants at ORNL to facilitate rapid identification of spills and their sources. Special considerations are needed in dealing with the problems of radioactive or PCB-contaminated oils, because these oils can not be handled or disposed of in the same manner as uncontaminated oils. A stringent screening procedure has been required to assure the identification of either radioactive or PCB contamination in oils. Both types of contamination have been discovered in oils that were not expected to be contaminated. The Department of Energy (DOE) has recently requested a survey of all oils on hand at ORNL. This survey includes the sampling of all oil-containing equipment and subsequent analysis for PCB contamination.

REGULATIONS RELATED TO OIL

Federal and state laws regulate the discharge of oils into navigable waters. The following is a summary of pertinent regulations applicable to ORNL oil discharges:

1. The Clean Water Act (Federal Water Pollution Control Act [FWPCA], as amended by the Clean Water Act of 1977) provides for (1) immediate notification of the appropriate agency of the U.S. Government of any discharge of oil or hazardous substance into or upon navigable waters of the U.S., (2) assessment of civil and criminal penalties for discharge of oil or hazardous material in violation of the FWPCA, and (3) recovery of the cost of cleaning up spills of oil or hazardous materials. Penalties are established in the FWPCA on the basis surrounding the circumstances. In addition, Section 311(b) authorizes criminal penalties of not more than $10,000 or one year imprisonment, or both, for failure to make the required reports in a reportable incident. To be in compliance with the permits for discharge under the National Pollutant Discharge Elimination System (NPDES), oil and grease concentrations at the NPDES sampling points on White Oak Creek and Melton Branch can not exceed a daily average of 10 mg/ℓ. Compliance with NPDES is a requirement of the FWPCA, Section 402.

2. EPA Regulations on Discharge of Oil (40 CFR 110) say that no person shall discharge or cause or permit to be discharged harmful quantities of oils into or upon waters of the United States, violate applicable water quantity standards, or cause a film or sheen upon or discoloration of the surface of the water.

3. EPA Regulations on Oil Pollution Prevention (40 CFR 112) establish procedures, methods, and equipment requirements to prevent the discharge of oil from nontransportation-related facilities into navigable waters, including requirements for preparation and implementation of Spill Prevention Control and Countermeasure Plans.

4. EPA Regulations on Liability Limits for Small Onshore Storage Facilities (40 CFR 113) establish liability limits for small onshore storage facilities and apply to oil discharges which are not proven to be the result of negligence or willful misconduct.

5. EPA Interim Regulations on Civil Penalties for Violations of Oil Pollution Regulations (40 CFR 114) establish civil penalties for violation of requirements in 40 CFR 112.

6. EPA Regulations on Criteria for State, Local, and Regional Oil Removal Contingency Plans (40 CFR 190) establish criteria for

development and implementation of state, local, and regional contingency plans by state and local governments in consultation with private interests to ensure timely, efficient, coordinated, and effective action to minimize damage resulting from oil discharges.

7. Coast Guard Regulations on Oil Spills (33 CFR 153) prescribe Coast Guard notification of the discharge of oil or hazardous substance, the procedures for the removal of a discharge of oil, and the costs that may be imposed or reimbursed for the removal of a discharge of oil or hazardous substances.

8. Tennessee Water Quality Criteria (Chapter 1200-4-3) establish criteria for water conditions, including the following section:

   "Solids, Floating Materials, and Deposits — There shall be no distinctly visible solids, scum, foam, oily slick, or the formation of slimes, bottom deposits or sludge banks of such size and character; as may impair the usefulness of the water as sources of domestic and industrial water supplies; that may be detrimental to fish and aquatic life or to recreation; that may interfere with livestock watering, wildlife, and navigation."

9. Tennessee Effluent Limitations and Standards (Chapter 1200-4-5) describe the maximum daily concentration of oil and grease allowed in effluents as (1) 30 mg/ℓ and (2) no visible or floating oil or grease.

ENVIRONMENTAL EFFECTS

Oils differ from most substances which pollute aquatic environments in that they are largely insoluble, forming coherent masses which float on the surface or become stranded on the shore and can thus cause damage at a considerable distance from their point of release.

The most immediate effects of an oil spill are those on wildlife and aquatic life. Waterfowl are especially vulnerable. Their waterproofing and heat insulation depends on the fine structures of feathers which, unfortunately, have a great affinity for oil. It penetrates or clogs the plumage. In attempting to preen itself clean, an affected bird further disarranges its feathers and also swallows a considerable amount of oil. Thus, a bird exposed to an oil spill may die due to exposure, drowning, or toxicity from the ingested oil.[1]

The deleterious effect of oils on fish is due to the film formed over the gill filaments, preventing the exchange of gases, and resulting in anoxia and suffocation.[2] Also, the dissolved oxygen content of the content of the water is reduced by surface blockage. The potential for biological accumulation of carcinogenic compounds in the flesh of fish exposed to oil is significant. Also, the taste of fish exposed to oil is tainted, causing harmful effects on commercial and sport fishing.

Besides toxicity, negative effects on plant life result when an oil film interferes with light penetration and, thus, photosynthesis. Further, harmful chemical and physical effects on benthic organisms may occur when residual or degradation products of an oil spill settle to the bottom.

A serious potential hazard from an oil spill is the effect on drinking water. Conventional water treatment systems, such as the surface water intakes for the Oak Ridge Gaseous Diffusion Plant and the Kingston municipal water supplies, can be disturbed by the presence of oil. Besides fouling the treatment process, the presence of oils in drinking water presents a health concern.[3]

Sewage treatment is adversely affected by excess amounts of oils. Fouling of sewer lines, pumps, and treatment processes may occur.[4]

Shore contamination by beached oil represents biological as well as property damage. The tendency of oil to cling to shore surfaces, such as beach sand and sea walls, and the resultant property damage are well established. This is perhaps the most apparent and widely publicized damaging aspect as attested to by lawsuits on the part of tourist interests and property owners.

WASTE OIL INVESTIGATION COMMITTEE WORK

Repeated occurrences of improper discharges of oil, many of which were reportable to DOE, resulted in the formation of the Waste Oil Investigation Committee (WOIC) at ORNL to inventory the existence of oil and the pathways of oil spills to waterways. In addition, the committee's study provided information on which to base oil handling and oil spill procedures.

As a result of the committee's study and recommendations, the following actions were taken:

1. Identified and reviewed all sumps at ORNL that might be a source of oil discharge and subsequently inspected on a quarterly basis.
2. Inspected all elevator shafts for oil leakage on a quarterly basis.
3. Discontinued the use of bladder bags for oil storage at the steam plant.
4. Reviewed all diking for integrity, especially diking around PCB-containing transformers.

5. Identified and documented all equipment containing one or more gallons of oil (results computerized and updated periodically).

6. Inventoried the quantity of oil on the ORNL site and looked at purchases versus use and disposal on an annual basis.

7. Identified all effluent discharge points to creeks and determined the drainage area serving each discharge point.

8. Identified and documented all building drains.

9. "Fingerprinted" (by analysis) types of oil most used at ORNL.

The committee held a total of 16 meetings during the period from March 14, 1979 to May 29, 1979.

A major portion of the WOIC's work involved oil-related surveys and inventories at ORNL. These were necessary to evaluate the potential for oil problems and to correct existing ones.

An ORNL inventory of oil storage containers and oil-containing equipment was made in terms of building location, quantity and type of oil, and type of containment.

Transformers are an additional source of oil waste at ORNL. An inventory was made of transformer location and oil quantity and type for all transformers in service at ORNL.

Due to the diversity of oil use and continuous variation in oil stocks at ORNL, it was difficult to obtain a precise projection of the waste oil generation rate. Based on stock withdrawals for the 12-month period ending March 31, 1979, the minimum quantity of waste oil generated was estimated to be 12,000 gals/yr, not including quantities of used oils currently on hand, solid lubricants, greases, some nonreclaimable lubricants, or materials received on special purchase orders (∿ 88,000 gals/yr).

A survey was made of outfalls from ORNL buildings to waterways that are potential pathways for reportable spills. First and Fifth creeks flow into White Oak Creek. White Oak Creek and Melton Branch constitute the two major waterways on the Oak Ridge Reservation. An updated inventory of ORNL plant effluents was completed.

Some of the oil spill occurrences were traced to building sumps that overflowed during periods of heavy rainfall, causing release of oil to the environment. A survey of active sumps at ORNL was made.

Construction sites at ORNL present special problems related to oil waste. A survey of oil use at construction sites was made, and arrangements were made to brief construction site personnel on the ORNL oil policy.

DEPARTMENT OF ENVIRONMENTAL MANAGEMENT

The Department of Environmental Management's (DEM) primary functions and responsibilities in regard to waste oil disposal and oil spill occurrences are as follows:

1. Review engineering design of new handling and disposal facilities for compliance with environmental regulations.
2. Approve storage and collection facilities, disposal methods, and disposal sites to be used for oil-containing waste.
3. Monitor waste oil disposal facilities to ensure compliance with regulations and to minimize the risk of negative environmental effects.
4. Specify approved disposal methods and sites for each oil-bearing liquid or solid waste.
5. Provide written certification of cleanness for each lot of waste oil to be offered for public sale.
6. Complete part three of Form UCN-13553 in Oil Disposal Procedure.

In case of an oil spill, the person discovering the spill has the responsibility of reporting it to his immediate supervisor and the DEM, which, in turn, is responsible for coordinating spill cleanup operations and for reporting the spill to ORNL management and DOE.

The DEM is also responsible for keeping Laboratory personnel informed of current environmental protection procedures. This information is transmitted by means of Environmental Awareness Seminars. In the case of the oil problem, special "oil procedure" workshops open to all ORNL personnel were held by the DEM. Over 400 employees attended these sessions. The ORNL Environmental Protection Manual prepared by the DEM contains procedural guidelines for the handling and disposal of specific substances, including foils. The ORNL Environmental Protection Manual contains procedures for handling oils (PCB and non-PCB). In addition to these procedures, Environmental Protection Information Bulletins, which address specific and immediate problems when the need arises, are distributed at the Laboratory. Through the ORNL Environmental Protection Manual, the Environmental Protection Information Bulletins, and the Envionmental Awareness Seminars, the DEM is able to keep the Laboratory informed on current environmental protection regulations and procedures.

The ORNL Waste Oil Management Program requires up-to-date, accurate records of oil spill occurrences at the Laboratory. The DEM maintains files that include individual reports on each spill. These reports describe the origin of the spill, personnel involved, cleanup procedures, corrective actions, and photographs.

OIL SAMPLING AND IDENTIFICATION

The Analytical Chemistry Division has been developing simple methods for identifying oils and lubricants which are kept in inventory at ORNL. The purpose of this activity is to provide an inexpensive and rapid capability for identifying spills in the plant area and for quickly finding possible sources of spills.

Oil spill identification has been an important problem for analytical chemists in recent years. The U.S. Coast Guard maintains a program in forensic oil spill identification[5] to assess liability for cleanup costs of coastal waters where oil spills have occurred. Although the petroleum industry has long been involved in the characterization of oils, there are problems in analyzing oils spilled on water which are unique and which make conventional analyses (e.g., pour point and viscosity) useless. Oil spilled in the environment is subject to physical conditions that can rapidly change its composition. Four principal changes that can occur are (1) loss of volatile components, (2) dissolution of polar species, (3) photochemical degradation, and (4) biological degradation. Depending upon weather and aging time, an oil discovered in the environment may be difficult or impossible to relate to the original oil before weathering. Some effort is being made to partially circumvent this problem by various artificial weathering schemes. The problem at ORNL is somewhat simpler than that faced by the U.S. Coast Guard. The approximately thirty different oils and lubricants used throughout the plant are finished products rather than crude oils which undergo greater weathering effects.

Several analytical methods have been developed and successfully applied to oil spill identification. A short review of these techniques is in order here to provide a background for understanding the development of methods being used at ORNL. First, no single method of analysis can provide unequivocal identification unless the possible number of candidates is substantially limited. Because the ORNL inventory of lubricants and oils is limited to about thirty types (some of which are highly distinctive) a single type of analysis seems feasible for at least screening a sample.

The U.S. Coast Guard has concentrated on the use of four analytical procedures: (1) infrared spectroscopy, (2) fluorescence spectroscopy, (3) gas chromatography, and (4) thin layer chromatography. Each of these techniques offers special capabilities and advantages:

1. Infrared Spectroscopy (IR) is an especially simple technique that can easily be applied routinely. The

use of Fourier transform instruments makes both high resolution and the analysis of small samples possible through signal averaging. Reproducibility of data is poor unless sample preparation techniques are standardized. Comparison and possible matching of IR data can be done by examining an overlay of the spectra on a light box. Observed differences by IR spectroscopy are usually small for similar oil types. A peak-by-peak comparison can often distinguish samples; lists of peaks useful for crude petroleum identification have been published.[6]

2. Fluorescence Spectroscopy offers one of the most sensitive analytical tools for the identification of aromatic mixtures. The techniques range widely from simple methods that measure a single fluorescense spectrum at a set ultraviolet excitation frequency to methods that employ instruments and computers to produce "contour plots" of excitation frequency versus emission frequency, giving a detailed fingerprint.

3. Gas Chromatography (GC) offers the simplest approach to identification of oils. While GC data are seldom sufficient to positively identify oil, these data do serve well for screening. If two or more different detectors are used when a sample is analyzed, the flame photometric detector (FPD), which is especially sensitive to sulfur compounds, is used in conjunction with a flame ionization detector (FID) which is sensitive to all hydrocarbons. If the effluent stream in a GC analysis is split for simultaneous FPD and FID analysis, a dual-response chromatogram gives a dual fingerprint, which is a very powerful identification tool.

4. Other analytical measurements are invoked for additional data helpful for identifications. Mass spectrometry (MS) can be used alone or in combination with GC (GC/MS) for fingerprinting an oil, but this method is more involved and usually uses specialized modes of operation, such as field ionization desorption or low-voltage ionization. Liquid and thin layer chromatography sometimes offer fast identification if the list of possibilities is small.

ORNL maintains an inventory of 33 types of oils and greases. Beginning in May, 1979, a modest study was begun to see if these oils could easily be distinguished by a simple analysis. Infrared absorption spectrometry and GC analysis were used to test oils from the inventory stock.

Infrared absorption (IR) spectra are simple to obtain, and certain key peaks can be measured in the 600-1800 cm^{-1} range which are known to be useful in distinguishing oils. However, other peaks often used for crude oil identification are not sufficiently intense in these refined oils to make analysis possible. Thus, IR is considered helpful but not sufficient for screening among the ORNL oil and grease types.

Gas chromatographic profiling was deemed a more promising method, and a study was undertaken. Twenty-five oils, fuels, and lubricants were analyzed on a 3-meter (10-ft) Dexsil 400 packed column. The conditions chosen were used for all the analyses: temperature programmed from 100°C to 300°C at 2°/min after an initial hold of 8 min, 48 x 10^4 Pa (70 psig) He carrier gas. The dilution factor in methylene chloride and the amount injected varied, depending upon the material.

Examination of the GC profiles showed qualitative and quantitative differences sufficient to distinguish all the oils and greases in their neat state. However, weathering or mixing of oils and greases as might occur in spill situations would make identification difficult in some closely related oil types.

A soil sample taken near the High Flux Isotope Reactor (HFIR) cooling tower pumps contained an extractable grease that was most closely matched with an EA-type (gear lubricant) grease. Other spills have been examined with positive identifications being made in each case.

Some weathering studies are in progress to ascertain the efficacy of using simple GC profiling for real samples of environmental spills. Other analyses are likely to be required for positive identifications of different brands meeting the same specifications or different lots of the same brand.

The U.S. Environmental Protection Agency (EPA) currently requires that oil spills that produce a visible sheen on navigable waterways be reported to the agency. The major problem associated with measuring these spills is determining the thickness of the sheen. The method currently used at ORNL is time-consuming. The results yield a conservative quantity.

Considerable time was spent on a literature search investigating "state-of-the-art" methods. This search yielded one method developed by EPA and a recommendation from M. J. Hickey on how to quantify the spill. The latter is inexpensive, fast, and can be implemented by present personnel with no new training. This method utilizes an empty coffee can (or a can of similar configuration), a metal ring with snap clamp, and some kind of sorbent material such as cheesecloth. This apparatus is lowered into and penetrates the sheen. The apparatus is then removed, and a plastic cover is placed on the bottom opening. In the laboratory, several variables can then be established, and the thickness of the sheen determined. The other method was developed by EPA. The procedure would require a camera (capable of taking color pictures), a comparison chart (available from the American Petroleum Institute (API), and some formal orientation of existing personnel. To establish a sheen thickness, this method uses a natural phenomenon, the reflectivity of the oil-air and oil-water interfaces. Experimental evidence exists to substantiate this phenomenon. To quantify an oil spill, a color picture is taken and later compared with the color chart. The disadvantages to this scheme are outlined in the EPA report. One worth mentioning is that the reliability of the picture will decline as the picture angle deviates from vertical.

CONCLUSION

ORNL Waste Oil Generation

Approximately 50,000 gals/yr of waste oils are generated at ORNL. The annual quantity generated can be expected to increase, based on past trends and projected activities at the Laboratory.

ORNL Waste Oil Disposal

Waste oils must first be separated into types before disposal. If there is any likelihood that the oil may be contaminated with either radioactivity or PCB's, the substance must be analyzed by the Analytical Chemistry Division.

If oil contains radioactivity, it is shipped after approval by the DEM to the ORNL burial ground for storage. In the future, plans are to dispose of this type of oil by hydrofracture, if regulations will permit.

If oil contains PCB's, depending upon the contaminant level, the oil is disposed of as follows:

1. Oil containing PCB concentrations between 5 and 500 ppm are disposed of by an outside contractor in an EPA-approved hazardous waste landfill.

2. Oil containing greater than 500 ppm of PCB's is stored onsite. This type of oil will be treated or disposed of when an acceptable system is operable.

Waste oils that are proven to contain less than 5 ppm of PCB's and no radioactivity are separated into types: oils (e.g., machine oils, crankcase oils, etc.), gasoline, kerosene, animal and vegetable oils, coolants, and special mop solutions. After approval by the DEM, segregated oils are transported to the Salvage and Reclamation Facility. Approved disposal procedures for uncontaminated oily material are as follows:

1. Oily cloth and paper will be incinerated at the K-25 site.

2. Oily absorbent booms will be burned at the ORNL steam plant.

3. Other oily solids will be land-farmed at the K-25 site.

4. Animal and vegetable fats, coolants, and special mop solutions will be disposed of at the Y-12 site.

5. Nonradioactive liquid oils with less than 5 ppm of PCB's will be recycled by an onsite public sale. The successful bidder will be responsible for pumping the waste oil from ORNL's tank.

Implications of EPA's Hazardous Waste Regulations on ORNL's Waste Oil Practices

Regulations being implemented under the Resource Conservation and Recovery Act may call for changes in ORNL oil procedures. As proposed, waste oil becomes controlled under RCRA, then current means of disposal may no longer be acceptable. Of special concern would be the problem of radioactive contaminated oil, unless the hydrofracture system is permitted under EPA regulations for underground injection.

Waste oil management at ORNL has improved significantly, largely due to the coordinated efforts of the WOIC, the DEM, the Analytical Chemistry Division, and the Salvage and Reclamation Department.

REFERENCES

1. A. Nelson-Smith, "Effects of Oil on Marine Plants and Animals" in Water Pollution by Oil, Proceedings of Seminar, May 4-8, 1970, Aviermore, Scotland, pp. 273-279 (1971).

2. J. R. Pfafflin and E. N. Ziegler, Editors, Encyclopedia of Environmental Science and Engineering, Vol. 11, pp. 688-693, Gordon and Breach Science Publishers, New York (1976).

3. A. E. Martin, "Water Pollution by Oil - Some Health Considerations" in Water Pollution by Oil, Proceedings of Seminar, May 4-8, 1970, Aviermore, Scotland, pp. 153-159 (1971).

4. J. R. Simpson, "The Effects of Oil on Sewers and Treatment Plants" in Water Pollution by Oil, Proceedings of Seminar, May 4-8, 1970, Aviermore, Scotland, pp. 97-101 (1971).

5. A. P. Bentz, "Oil Spill Identification", Analytical Chemistry, Vol. 48, p. 454A (1976).

6. Ibid, p. 468 (1976).

SPILL CONTROL INITIATIVES AT PADUCAH*

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INTRODUCTION

EPA regulations require that spills of oil and certain hazardous chemicals be reported immediately to the National Spill Response Center. Failure to report spills can result in criminal penalties of up to a $10,000 fine and imprisonment up to one year. Civil penalties and clean-up costs can be assessed against the person or firm responsible for the spill.

During the 1978-1979 period, three reportable oil spills occurred at the Paducah Gaseous Diffusion Plant and were reported in accordance with established reporting procedures. All three spills were investigated by the U. S. Coast Guard which has a marine safety office located in nearby Paducah, Kentucky.

Although two of these spills were relatively small (less than 50 gallons), one spill exceeded 17,000 gallons and was considered to be a major spill. The large spill resulted from misvalving of No. 2 fuel oil at the C-600 steam plant in March, 1979. As a result of this spill, accident investigations were conducted by Paducah Plant management and by DOE. Table 1 shows the major recommendations resulting from these accident investigations.

Also as a result of these spills and recommendations from the investigations, plant management increased actions to prevent future spills. Recommendations from the oil spill investigations were given priority, and action plans were monitored by use of the Quality Assurance Follow-Up Log System. QA coordinators from each division followed the progress of the action plan to insure timely completion of each step.

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Table 1

MAJOR RECOMMENDATIONS RESULTING FROM C-600 FUEL OIL SPILL

1. Plug sewer connections under road and in pipe trench at C-600. Include an alarm audible in the C-600 Control Room at C-300.
2. Dike around the C-600 fuel oil tank truck unloading point.
3. Tag out, or otherwise make inoperable, all lines that could result in the release of oil and hazardous material. Label all valves clearly as to operation and direction of flow.
4. Assure proper training for operators involved with operations which could result in the release of oil or chemicals.
5. Install oil containment booms in Big Bayou and Little Bayou Creeks.
6. Install inclined pipe dams on all plant storm drain ditches near the plant perimeter.
7. Place protective curbing posts around potential spill points.
8. Install high and low level alarms on the C-600 fuel oil storage tanks. Establish a conservative low level alarm set point for the oil level in the storage tanks.

SPILL AWARENESS CAMPAIGN

Plant management also appointed a committee to implement a public relations campaign concerning spill prevention. This committee consisted of the Plant Emergency Director, W. E. Thompson; Plant QA Coordinator, E. A. Waggoner; and Environmental Control Department representative, M. C. Conrad. This group developed a comprehensive program to insure that (1) each individual in the plant is aware of his responsibilities concerning spill prevention, reporting, and control, and (2) overall responsibilities for spill prevention are accepted by the line organizations responsible for oil and hazardous material usage and storage.

The major elements of PGDP's spill awareness campaign are shown in Table 2. The first three items are fairly routine and will not be discussed further in this paper. The last two items are unique and may be useful in other spill prevention programs.

Table 2

MAJOR ELEMENTS OF SPILL AWARENESS CAMPAIGN

1. Plant Bulletins
2. Poster Campaign
3. Videotape Presentations on Spills
4. Enlist Support of Key Plant Organizations
5. Integrate Spill Prevention into Existing Quality Assurance Programs

PROGRAM SUPPORT

Because of the wide diversity of activities at the Paducah Gaseous Diffusion Plant, it is virtually impossible for a small staff organization such as the Environmental Control Department to keep abreast of all equipment and activities for which spill potential exists, making it necessary to depend on other plant organizations for considerable input. The increased efforts of other plant organizations were developed to provide a more comprehensive approach to spill prevention. The Plant Protection Department routinely patrols all areas of the plant including the plant perimeter and security gratings on effluent ditches. The Quality Evaluation Department routinely inspects equipment throughout the plant. The assistance of these plant organizations should prove invaluable in spotting potential spill hazards at an early stage.

QUALITY ASSURANCE

In order to re-examine the spill problem at Paducah, the Kepner-Tregoe approach to problem solving and decision-making was used. First, a situation analysis was performed to formulate and address concerns regarding the overall spill prevention program. In conducting the situation analysis, key people were contacted and records of previous actions were reviewed. Questions were asked concerning efforts made to make plant personnel aware of their individual responsibilities associated with spills.

Considerable prior effort was recognized that resulted in a plant survey conducted as a result of a previous spill investigation. This survey identified potential spill sources, the possible release points and a brief description of present surveillance and control activities. Current engineering projects were identified and reviewed which were directly related to environmental protection and which involved varying actions related to spills.

The major job elements used in the QA assessment were identified in this situation analysis and situation statements were prepared. After reviewing the information following the situation analysis the concerns were identified.

These concerns are addressed in the Quality Assurance assessment as to significance, impact, and the probability of an adverse significant consequence occurring. The potential significant quality failures identified in the assessment are addressed in the QA plan in accordance with the probability that the failure will occur. The QA plan defines the consequences of each potential failure and establishes responsibility and actions required to adequately address each potential failure. The QA plan is shown in the Appendix.

The chief benefit of the QA plan is that responsibility for spill prevention and control rests on operating groups in the line organization. A mechanism is set up whereby existing facilities are reassessed for spill potential on a periodic basis. Audits of each division's spill prevention facilities and procedures will be performed annually by the Environmental Control Department. Any deficiencies noted in the audit will be corrected using the QA follow-up log system.

OIL CONTAINMENT

One significant improvement in PGDP's spill control efforts was the installation of pipe dams on every plant effluent ditch where the discharge of oil was deemed possible. These oil containment dams are relatively quick and easy to install and require a minimum of engineering effort. The dams are also quite inexpensive, costing an average of approximately $2,000 each to construct.

The idea for the pipe dams was picked up by K. A. Ross, shift superintendent, while attending a spill control conference. This containment method was initially used at PGDP in emergency containment of oil spills in which one of the dams was constructed in approximately three hours. The success of the emergency dams led to the permanent installations of inclined pipe dams on the plant effluent ditches.

The pipe dam consists of an earthen dam with pipe sections installed at an angle, upstream end submerged. Key design criteria include: (1) sizing the pipe cross sectional area to meet flow requirements, (2) setting elevations such that water will not back up into building floor drains, and (3) installing the pipe such that the top of the submerged end of the pipe is at least two feet below the water surface to prevent carry through oil due to vortex action during high flow periods.

Other than the obvious advantage of trapping oil before it reaches Big Bayou or Little Bayou Creeks, the pipe dams have several other side benefits:

1. A few hours' hold-up capacity is created in the plant drainage system.
2. Inflatable rubber pipe stoppers could be used at these locations to completely block effluent flow for a few hours.
3. The dam effluent provides aeration.
4. Spot flow checks can be made using bucket and stopwatch method.

In summary, installation of pipe dams in plant drainage systems at PGDP has provided protection against accidental oil spills in a reasonable time frame and at a relatively low cost. Other installations may wish to consider this technique as either a means of emergency spill control or as a permanent installation.

Table 3

ADVANTAGES OF PIPE DAMS

1. Inexpensive
2. Quick to install
3. Effective for both large and small spills
4. Effective during rainy weather
5. Requires minimum of engineering effort

APPENDIX: Quality Assurance Plan, "Protecting the Environment from Spills"

1. SCOPE

This QA plan addresses the potential significant quality problems that were identified in the QA assessment and that were judged to have a high or unknown probability of occurring. This plan is very general in nature and is intended to be the vehicle for placing the burden on the line organizations to deal with all phases of spill prevention, control, cleanup, reporting, etc.

This plan identifies the general actions required by the line organizations. As each division assesses systems in which a potential for a significant spill exists, specific actions to address spills will emerge in subsequent QA plans and/or procedures.

As noted in the assessment, the potential problems addressed in this plan are not those which would ordinarily be covered in a QA program since hardware is only vaguely involved. However, the use of the QA approach may be beneficial if it causes spills to be addressed in subsequent QA assessments of operating systems or components in which the proper functioning of hardware <u>is</u> related to spill control and prevention. Those who use this plan should fully understand this deviation from normal QA application.

2. REFERENCES

2.1 QA Assessment - Protecting the Environment from Spills
2.2 SPP-72 - Reporting, Controlling and Cleanup of Oil and Hazardous Material Spills
2.3 Spill Prevention, Control and Countermeasure Plan (Environmental Control Department)
2.4 Section 311 (B)(2)(A) - Federal Water Pollution Control Act
2.5 SPP-D-515 - Waste Management and Environmental Pollution Control (Includes the Paducah Supplement)
2.6 SPP-D-516 - Unusual Occurrences - Notification, Investigation and Reporting

3. POTENTIAL SIGNIFICANT QUALITY PROBLEMS - CONSEQUENCES

Failures involving the prevention, detection, containment, cleanup, and reporting of spills may cause a environmental insult of a magnitude that will cause the plant to be out of compliance with state and federal regulations. If an out-of-compliance situation develops, legal action may be taken against the plant including the levying of fines, closing down a system or, in a very severe violation, even the plant could be shut down. The imposing of a jail sentence, in the case of gross negligence by an individual or individuals, is a possibility.

Following are the potential significant quality problems identified in the QA assessment that have a high probability of occurring. Consequences associated with the potential problems, should they develop, are shown. QA activities to prevent the problems from developing are listed in Section 4.

3.1 Plans and Procedures Either Unavailable or Inadequate. The lack of, or the inadequacy of, plans and/or procedures for spill prevention and control can be the basis for no actions or inadequate actions being taken to prevent and control spills. Without good procedures and their implementation, spills can be expected to occur; and when they do occur, containment, cleanup, and reporting can be expected to be inadequate.

3.2 Failure to Detect or Report a Significant Spill. Any detection failure can result in an insult to the environment, a safety hazard and, in some instances, damage to a process or surrounding equipment and facilities. Failure to report a spill, in addition to the above consequences, may result in a penalty or fine, system shutdown, or facility shutdown. In severe cases of gross negligence, as previously noted, a jail sentence might be imposed.

3.3 Personnel Are Not Alert to Spills or Aware of Their Responsibilities.
Any deficiency in this area can lead to consequences defined in sections 3.1 and 3.2.

3.4 Systems Are Inadequate for Containment and Subsequent Cleanup. Any inadequacy of a containment system will directly result in a strong possibility that a serious spill may, after occurring, be further released to the environment. The existence of a containment system indicates that a system has been previously assessed as having a potential for a significant spill; therefore, any weakness would have the potential for severe consequences.

3.5 Investigations and Reports Fail to Identify the Real Cause of the Spill and, Therefore, Corrective Actions Aren't Adequate. Corrective actions are usually only as good as the information upon which those actions are based. Failure to determine the real cause of the problem can only set the stage for a repeat occurrence since adequate corrective actions will not have been taken.

3.6 Spills Are Not Prevented or, When They Occur, Are Not Contained or Cleaned Up in Accordance With Prescribed Methods. This potential problem was listed during the assessment as one that would be significant if personnel training was inadequate. Spills occurring for any reason are serious and may result in any or all of the consequences listed in section 3.2. Lack of personnel training, associated with other possible causes of spills, only tends to compound the possibility that they will occur and that serious consequences will result.

4. QA ACTIVITIES

The quality assurance activities that are required to address the probable significant failures listed in section 3 are outlined in this section. As stated before, the actions listed in this plan are mostly administrative in nature and are intended to place the burden directly on line organizations to follow through with specific actions. These further specific actions will be detailed when divisional assessments are made and QA plans and/or procedures are written for systems or components in which oil or hazardous materials are involved.

Some preliminary actions have already been taken in the plant to address recommendations growing out of investigations of spills. These actions should be reviewed and revised as necessary when the activities listed in this section are implemented. Other existing procedures addressing spills will also need to be reviewed in light of this QA plan.

The activities required for preventing and controlling spills are much more meaningful and effective when they are defined in a plan or procedure for a particular facility, system, or component in which the material is used. If the potential for a spill of a particular material is not directly associated with a facility, system, or component, then prevention and control will have to be addressed in a "stand alone" procedure or in a procedure jointly covering other similar materials. This would be true for materials in stores or being transported under varying conditions and modes.

Some of the specific QA actions that should be taken to prevent those potential significant problems listed in section 3 are as follows:

4.1 Plans and Procedures Either Unavailable or Inadequate. Line organizations are all required to conduct formal QA assessments on all major systems, facilities, and components in the plant. If oil or other hazardous materials are involved, the control of associated potential spills will be one of the major job elements in the assessment. (See QA-P-4, Guidelines for Conducting QA Assessments.) The assessment will further examine the significant failure, or failures, that might occur and the probability of the failure occurring. This activity will apply to the job element for spills along with other job elements in the system, facility, or component being assessed.

As specified in the assessment guidelines, a QA plan is required if the probability of a significant failure is high or uncertain. If the probability is low, existing procedures are assumed to provide adequate protection.

If a QA plan is required, along with procedures for spill prevention, control, cleanup, etc., line organizations are required to prepare the necessary documents and to see that they are fully implemented. Sufficient periodic audits should be conducted to assure that the plans and/or procedures are being followed.

If oil or other hazardous materials are in systems or locations that will not be covered by an assessment, other procedures must be prepared and implemented to provide confidence that potential spills are properly protected against. The procedures should further assure that, should a spill occur, it will be promptly detected, reported and cleaned up in accordance with specified guidelines.

4.2 Failure to Detect or Report a Significant Spill. For each hazardous material and oil source that provides the potential for a spill, the appropriate division or divisions must have an up-to-date procedure addressing that potential. (See section 4.1.) The procedure must specifically define any detection system needed, the associated alarm system, and the means of continually monitoring the reliability of the system.

The detection system may simply be a systematic surveillance of a system or area with routine recorded checks to be made, the people responsible, frequency, and sign-off that the checks were made. The procedure should also address whether the potential spill is a continuing threat or if it is only associated with a specific plant activity, such as a transfer operation, change-out of system hardware, etc.

The procedure must also address the reporting of a spill -- reportable quantities, who is responsible for reporting, to whom the report is to be made, paperwork to be completed, etc. Penalties associated with failure to report a spill should be specified. Visual reminders should be evident at all potential spill locations regarding detection and reporting and should be defined in the procedure.

4.3 Personnel Are Not Alert To Spills or Aware of Their Responsibilities. Each division must be able to show that their personnel training program includes all activities associated with potential spills. Training records must indicate training in this area. Front line supervisors are responsible for alerting personnel to the potential for spills associated with assigned activities, including reviewing appropriate procedures associated with specific job assignments. (See section 4.2.)

4.4 Systems Are Inadequate for Containment and Subsequent Cleanup. For engineered projects involving oil or hazardous materials, a principal job element in the assessment of a system will be protecting against spills and providing for their detection, containment, etc. For existing systems, line organizations will be responsible for assessing the systems to determine the adequacy for containment and/or cleanup capability. Where inadequacies are found, criteria must be developed and an ESO or work order prepared to cause an appropriate modification to be made to the system or component.

It should again be noted that addressing spill potential may be just one among several job elements in a regular QA assessment. A separate assessment just for spill prevention and control would be a duplication of effort unless that were the only job element involved.

4.5 Investigations and Reports Fail to Identify the Real Cause of the Spill and, Therefore, Corrective Actions Aren't Adequate. Spill investigations, like quality investigations, are not considered adequate unless the real cause is determined and reported. Just identifying a hardware failure, a human error, etc., is not enough if the hardware failure can be traced to a poor design, improper usage, wrong type procured, improper maintenance, etc. Or, in the case of human error, the report is not complete until it addresses the adequacy of a procedure (or lack of a procedure), training, contributing conditions, etc.

Line department heads are responsible to see that the investigations are initiated and reviewed for meeting the above criteria. They are responsible to interface the investigation with any investigation required by the Environmental Control Department or, in the case of a major spill, with an associated DOE investigation.

The investigating reporting format and general guidelines will be established by the Environmental Control Department in concert with the Shift Superintendent Coordinator.

4.6 Spills Are Not Prevented or, When They Occur, Are Not Contained or Cleaned Up in Accordance with Prescribed Methods. Actions recommended to address this potential problem are generally covered in sections 4.1 through 4.5. Procedures that are prepared by the line organizations should carefully follow cleanup guidelines established by the Environmental Control Department.

Cleanup activities should be carefully defined and should address safety, equipment used, cost, quantities reclaimed, disposal, etc.

5. SUPPLEMENTAL ACTIVITIES

5.1 Audits and Follow-Up. Line organizations are required to schedule periodic audits of plans and/or procedures to assure that they are being followed. This general QA plan will be audited annually by the Environmental Control Department for compliance.

Recommendations from all audits, as well as investigations, will be entered into a follow-up log in which a person is named for being responsible for the follow-up actions. The log indicates a target completion date and the date final action is taken. Division managers will be responsible for naming someone to monitor the follow-up system to see that priorities are established and that any delinquent actions are immediately flagged.

The follow-up log system presently in use in the QA program will be suitable for this application.

5.2 Records. Records will be maintained in each division and in the Environmental Control Department in a manner that makes them accessible and auditable.

THE MANAGEMENT OF POLYCHLORINATED BIPHENYLS AT THE ORGDP*

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ABSTRACT

The program for controlling the use, handling, storage, and disposal of polychlorinated biphenyls (PCBs) and PCB wastes at the ORGDP is described. Special emphasis is placed on the various administrative programs that have been incorporated to help ensure that plant personnel and the environment are adequately protected and that all applicable regulations are met.

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*Based on work performed at the Oak Ridge Gaseous Diffusion Plant operated by the Union Carbide Corporation, Nuclear Division, for the Department of Energy.

THE MANAGEMENT OF POLYCHLORINATED BIPHENYLS AT THE ORGDP

Polychlorinated biphenyl (PCB) fluids, which are generically known as askarels, have been used commercially since 1929 for cooling and insulating electrical equipment in applications requiring fire resistant fluids. PCBs also have several other characteristics which are desirable for the electrical industry. They provide for good heat transfer, and have good dielectric properties and chemical stability. However, it is the chemical stability that has necessitated stringent control to prevent entry into the environment. Once PCB has been introduced into the environment, it is essentially impossible to remove.

PCBs were first recognized as a widespread environmental pollutant in 1966. The Toxic Substances Control Act[1] (January 1, 1977) was the first regulation to govern PCBs. PCBs were the only chemicals mentioned specifically by name in these regulations. On February 17, 1978, the Environmental Protection Agency (EPA) published regulations[2] which outlined in detail the disposal and marking regulations for PCBs and on May 31, 1979, the EPA published what was termed the final regulations[3] for PCBs. These regulations placed even more stringent requirements on the use of PCBs.

The final EPA rule defines PCB as any substance, mixture, or item containing 50 ppm PCB or greater. These regulations also define a new category of transformer which was labeled as PCB-Contaminated. This category includes transformers that were originally designed to use PCB-free dielectric fluids but in reality contain between 50 ppm and 500 ppm of PCB as a result of contamination that occurred in manufacturing or servicing operations. According to the final regulations, as many as 38 percent of all mineral oil transformers contain between 50 ppm and 500 ppm PCB but PCB concentrations above 500 ppm are rare. A mineral oil transformer need not be tested to determine if it is PCB-Contaminated. It may be assumed to be PCB-Contaminated and then treated according to the rules as such. If the decision is made to test mineral oil transformers, then the results govern the final disposition of the transformer.

Since the promulgation of the final PCB regulations, no ORGDP mineral oil transformers have been removed from service for disposal. However, 30 drums of waste mineral oil have been generated through routine maintenance of transformers. Testing of these 30 drums revealed that nine contained greater than 50 ppm of PCBs, with two containing greater than 500 ppm of PCBs. Fourteen were found to contain from 5 ppm to 50 ppm of PCBs. Additional testing of mineral oil transformers will be conducted and appropriate actions regarding replacement/containment/disposal will be initiated.

As stated earlier, the final regulations established a PCB material as any substance, mixture, or item with 50 ppm or greater PCB. However, there is one major exception to the 50 ppm limit. The use of waste oil containing any detectable concentration of PCBs as a sealant coating or dust control agent is prohibited.[3] Prohibited uses include, but are not limited to, road oiling, general dust control, pesticide or herbicide carrier, or rust preventative. The dumping of waste oil (e.g., in a field) is considered use as a dust control agent and is prohibited by this rule. These types of activities could result in the rapid and direct entry of PCB into the environment. Persons who process, distribute in commerce, or use waste oil must assume it contains PCBs unless it has been tested and found to contain none. If the oil is found to contain less than 50 ppm, it can be used as a fuel or in any other way that does not result in direct entry into the environment. The EPA estimates that the largest economic impact of the PCB regulations will be to the prohibitions placed on waste oil.[3]

During 1979, over 700 drums of ORGDP waste oil were tested for PCB. Of these 700 drums, 78 drums (11%) were found to contain some level of PCB. Of the 78 drums containing PCB, 34 drums contained 50 ppm to 500 ppm, 31 drums contained less than 50 ppm, and 13 drums contained greater than 500 ppm PCB. It is difficult to determine the current extent of PCB contamination since waste oil has been allowed to accumulate in the past with very little attention to its origin. Mineral oil, which is a known contributor to the problem, has not normally been segregated. Currently, all waste oil is being sampled for PCBs and uranium prior to a determination on ultimate disposal. In addition, new administrative measures have been initiated to better determine the origin of waste oils. The measures, which generally include provisions for documentation for each container of oil received, should help in determining new sources, if existant, of PCB contamination.

Storage facilities for PCBs must meet the criteria established by the EPA.[3] The facility must have an adequate roof and walls to prevent rain water from reaching stored PCBs. It must have an adequate floor and continuous curbing with a minimum 6" high curb and it must be able to contain a volume of PCB equal to twice the largest single container or 25 percent of the total PCB stored therein. Also it should not be located at a site below the 100 year flood elevation.

Currently, at the ORGDP, there are two PCB storage areas meeting all the EPA criteria. The first facility contains approximately 3,000 square feet of storage space and according to regulations will accommodate approximately 6,000 cubic feet of PCB waste. As of April 1, 1980, approximately 1/4 of the available space in this facility had been used for storage. There are approximately 2,200 square feet of storage space in the second facility which will accommodate 4,400 cubic feet of PCB waste. Approximately 1/4 of this space had been used for storage as of April 1, 1980. With the scheduled maintenance activities and the continual generation of waste oil, it is estimated that over half of the available space for PCB waste will have been used by the end of 1980. Since the ORGDP has very limited experience with PCB contamination in oil, it is difficult to ascertain how long these facilities will provide adequate storage. A new storage facility has been budgeted for 1981 to provide storage for waste oil.

During the past two years, over 70,000 Kg of PCB waste have been shipped off site to EPA approved landfills for disposal. This includes 27 transformer casings and over 100 drums of solid waste including capacitors, sorbent materials, dirt, etc. Much of this material resulted from a program at the ORGDP to eliminate all outside PCB transformers. At this time, only four outside PCB transformers remain and these transformers have been scheduled to be replaced during the next two years. During the past two years, it is estimated that over 1/4 of a million dollars have been expended to comply with PCB regulations (See Table 1). This includes administrative, maintenance, laboratory, storage, and disposal cost. It is estimated that routine cost to comply with these regulations will exceed $100,000 annually. In order to assure compliance with the PCB regulations at a minimum economic cost, very close administration must be exercised.

Table 1

PCB Cost Over Past Two Years

Item	Cost in $1,000s
Containment of PCB equipment	85
Disposal	50
Administration	50
Maintenance	40
Laboratory	30
Equipment	10
Miscellaneous	?
Sum	>265

References

1. Toxic Substances Control Act, Public Law 94-469, January 1, 1977.

2. Federal Register Vol. 43, No. 34, February 17, 1978.

3. Federal Register Vol. 44, No. 106, May 31, 1979.

EXTENDING THE LIFE OF MACHINING COOLANTS THROUGH THE USE OF A BIOCIDE

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ABSTRACT

The Oak Ridge Y-12 Plant(1) currently uses about 10^6 liters per year of water-based machining coolants. These coolants, on the average, last about one month in the machines before they are discarded. The most common reason for discarding the coolants is because of deterioration caused by bacterial action.

Two biocides are being tested in an experimental program to extend the usable life of these machining coolants. Since the used coolants are eventually disposed of in a biological reactor, any biocide used must have a relatively short life-span. Preliminary data from field tests, using two production machines, have shown that the life of the coolants can be extended by at least a factor of five.

INTRODUCTION

The Oak Ridge Y-12 Plant currently uses six major different types of water-based machining coolants. These coolants are purchased as an organic concentrate which is diluted with water to a 2-5% organic solution before use. The exact composition of the organic portion is normally proprietary, but most coolants contain chlorinated or sulfonated

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(1) Oak Ridge Y-12 Plant operated for the Department of Energy under U. S. Government Contract W-7405-eng-26.

paraffins, amines, polyglycols, and similar molecules. Many of the coolants also contain significant amounts of sodium nitrite.

Most of the time these coolants will start deteriorating after 2-3 weeks due to bacterial action and are thrown away about every four weeks on the average. The discarded coolants are disposed of in an aerobic, activated sludge reactor. An experimental program is in progress to extend the usable life of these coolants by using a biocide to stop bacterial deterioration. The biocides being tested slowly degrade in the presence of oxygen, so they should not interfere with the operation of the coolant degradation reactor.

MATERIALS AND METHODS

Two different biocides are being tested in this work. The first, called Oil-Perge from Dearborn Chemical, contains methylene bisthiocyanate as the active ingredient. The second is from IMC Corporation called Tris-Nitro and contains 2-nitro-2-methoxy 1,3-propanediol. Both of these biocides have been tested on a laboratory scale in five of the coolants that are used in the Plant.

A beaker of coolant is stirred during the day and left motionless at night to simulate the oxygenation cycle in the machines. The bacteria concentration in the coolant is measured using Easicult TTC biological testers from Orion Diagnostica. Bacteria seed is added to the coolants periodically to simulate machine shop conditions.

The length of time that the biocide remained effective was measured for different biocide concentrations in each of the coolants. Field tests are being conducted using Oil-Perge biocide and Trim-Sol coolant in two production machines.

RESULTS AND DISCUSSION

The first combination of coolant and biocide tested in the laboratory was Trim-Sol and Oil-Perge. It was found that 100 ppm of Oil Perge (10 ppm of active ingredient) would stop all bacterial growth for three weeks on the average. Tris-Nitro biocide was also tested on Trim-Sol coolant. Addition of 500 ppm of the active ingredient stopped all bacterial growth for 12 weeks.

Oil-Perge was next tested in Dascool-4407 coolant. Use of 10 ppm of the active ingredient stopped all bacteria growth for seven weeks. Tris-Nitro biocide was not effective in Dascool-4407 coolant. The reason for this is not known at the present time, but it is being investigated by the manufacturer of the biocide.

Rustlick-BX and Rustlick-288C coolants were tested with both biocides. None of these combinations produced effective results. Both of the Rustlick coolants contain fairly high concentrations of nitrite; this may interfere with the biocides, but it has not been proven yet.

Trim-EP was the last coolant tested in the laboratory. Addition of 10 ppm of the Oil-Perge active ingredient was effective for two weeks and addition of 500 ppm of the Tris-Nitro active ingredient was effective for three weeks.

Two field tests are in progress using Oil-Perge and Trim-Sol coolant in production machines. A lathe with a 120-liter coolant capacity and a grinder with a 4000-liter capacity were used in these tests. A weekly addition of 10 ppm of the Oil-Perge active ingredient was needed to keep the coolant bacteria free. The coolant in these machines has lasted for five months compared to the normal life of one month. The color of the coolant has faded over this time period, but no other signs of deterioration have been detected.

The cost of the biocide for each weekly dose is about 100 times less than the cost of the coolant, so use of the biocide should result in a significant cost savings in outside purchases as well as in internal disposal costs for the used coolants.

Session III

WASTE DISPOSAL AND HAZARDOUS MATERIALS

Chairperson: L H. Stinton (ENGR/UCC-ND)

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SURVEY OF UCC-ND WASTES

H. A. Abee (Y-12), M. C. Conrad (PGPD),
M. E. Mitchell (ORGDP), J. M. Napier (Y-12),
T. W. Oakes (ORNL), and M. Sanders (Y-12)

ABSTRACT

A detailed survey of all wastes generated by the four UCC-ND installations has been conducted. The primary objective of the survey was to provide sufficient information to develop an overall plan for disposing of UCC-ND wastes, with special emphasis being placed on categorizing the wastes according to type of disposal required, the ultimate goal being to provide centralized treatment and/or disposal facilities where feasible.

In general, the survey identified approximately 150 waste streams which constitute existing or potential treatment/disposal problems requiring correction and for which funding for new facilities has not been approved. It is anticipated that about 55 of these wastes could be adequately disposed of in a centralized incinerator or incinerators, and approximately 50 could be disposed of in appropriate centralized burial grounds. The wide variety of materials that could be incinerated will present costly design and operational concerns. Likewise, the many inorganic solid wastes considered suitable for burial will create design and operational concerns which must be resolved in accordance with proposed regulations.

(Paper not available for publication)

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MANAGEMENT OF SOLID WASTE*

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ABSTRACT

Compliance with the latest regulatory requirements addressing disposal of radioactive, hazardous, and sanitary solid waste requires the application of numerous qualitative and quantitative criteria in the selection, design, and operation of solid waste management facilities. Due to the state of flux of these regulatory requirements from EPA and NRC several waste management options were identified as being applicable to the management of the various types of solid waste.

This paper highlights the current regulatory constraints and the design and operational requirements for construction of both storage and disposal facilities for use in management of DOE-ORO solid waste. Capital and operational costs are included for both disposal and storage options.

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Prepared for the U. S. Department of Energy under U. S. Government Contract W-7405-eng-26

*ORNL/ENG/INF-80/1

MANAGEMENT OF SOLID WASTE

1. INTRODUCTION

Management of sanitary, hazardous and radioactive solid waste produced at the Department of Energy-Oak Ridge Operations (DOE-ORO) facilities requires careful waste management planning to provide compliance with applicable regulatory criteria. The criteria are the product of a myriad of proposed or promulgated regulations, including requirements mandated by the Resource Conservation and Recovery Act (RCRA) for sanitary and hazardous waste disposal, and criteria proposed in 10CFR61 by the Nuclear Regulatory Commission (NRC) addressing management of low-level radioactive waste (LLW). Waste management planning covers waste characterization and quantification, transportation and handling, treatment, storage, and disposal. The subject of this paper will be limited to alternatives for waste storage and disposal. Regulations proposed by EPA and NRC addressing management of solid waste will be briefly reviewed. Preliminary designs for two disposal and three storage alternatives will be presented with associated Rough Order of Magnitude (ROM) costs.

2. REGULATORY REQUIREMENTS (CRITERIA)

Solid waste management regulations affecting DOE plants are being promulgated by three agencies - EPA, NRC, and DOE.

EPA has issued guidelines under the RCRA applicable to management of nonhazardous waste in the Federal Register, Vol. 43, No. 25, February 6, 1978, and Vol. 44, No. 59, March 26, 1979. These guidelines provide the detail required to locate, design, and operate sanitary landfills in a manner acceptable for licensing by EPA. Also under the RCRA , criteria to ensure proper management of hazardous wastes from "cradle to grave" were proposed in the December 18, 1978 Federal register, Vol. 43, No. 243, some of which were promulgated in February, 1980. The remainder is expected to be promulgated in April and October of 1980. In addition, EPA proposed general guidelines for management of radioactive waste in the November 15, 1978 Federal Register, Vol. 43, No. 215.

Currently there are bills under consideration that propose to allow NRC to regulate new DOE low-level radioactive waste facilities. NRC has issued proposed criteria for shallow land burial of low-level radioactive waste in 10CFR61. NRC's criteria tend to parallel EPA's criteria for burial of hazardous waste. Both EPA and NRC require that a pathways analysis be completed at the proposed site to verify that radioactivity will not migrate from the disposal area at levels exceeding environmental protection standards.

3. DESIGN OF ALTERNATIVES

The complex and dynamic state of regulatory requirements addressing the disposal of hazardous and radioactive waste may require that temporary storage of waste pending the promulgation of final criteria be included as a process step in comprehensive solid waste management plans.* Additionally if radioactive contamination precludes the release of scrap metal to the public, facilities may be needed for storage of metal scrap until either a resource recovery process is made available or contamination limits acceptable for public release are established.

Summaries of the design and costs of five alternatives, two for waste disposal and three for waste storage are included in this paper.

The two disposal alternatives include the design of a sanitary landfill and the design of a burial trench to comply with the EPA criteria proposed in the December 18, 1978 Federal Register for disposal of hazardous waste**. The three storage options include: the design of a metal building to serve as a warehouse for waste; the design of below grade concrete trenches; and the use of concrete cubes as storage containers.

Criteria common to all storage and disposal options include siting requirements, service extension, design capacity, and security requirements. Suitable sites were assumed available on Federally owned land. Surface preparation, utilities, fencing, lighting, and phased construction for disposal trenches and storage facilities are provided. Disposal volume was assumed to be approximately 3 x 10^6 ft^3 and storage volume 2 x 10^6 ft^3. Phased construction of the facilities was designed to provide capacities for storage or disposal of 1/6 of the waste storage or disposal requirements.

Disposal Alternatives

Two disposal systems which utilize shallow land burial (SLB) for disposal of contaminated waste are designed and costed. The major difference between the designs is a leachate control system which is provided for one option. Following are descriptions of the designs for each option.

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*In the paper, hazardous refers to the RCRA classification system, radioactive is defined as in the Atomic Energy Act of 1954 and is excluded from the RCRA hazard definition, and sanitary refers to nonradioactive and nonhazardous.

**The NRC criteria for design of a LLW, shallow land burial (SLB) facility listed in 10CFR61 approximately parallel EPA's criteria for hazardous waste disposal.

Unlined Shallow Land Burial

The unlined shallow land burial disposal option will be similar in design and operation to a sanitary landfill. Trenches will be excavated as needed, filled, and covered for waste disposal. The design for disposal of 3×10^6 ft^3 will require 28 acres of land and can be layed out as shown in Figure 1.

Surface runoff originating outside the site boundary will be diverted from the site, and a surface runoff collection system will collect precipitation falling within the 28 acres. The surface runoff from the site will flow through a settling pond before being discharged from the site boundary. No provisions for removal of organics and metals from the runoff are included. Leachate from the working section of the disposal trench will be collected for transport to a waste treatment facility (not provided as part of this study). No provisions are included for collection of leachate from a completed trench.

The first trench, when trench and fill operations are completed, will occupy an area 160' x 487' and will contain 1/6 of the total design volume of waste for disposal.

A building to provide for temporary storage of waste during inclement weather or low volume waste generation periods, and a tank for temporary storage of contaminated leachate are provided in the design. Table 1 lists the assumptions made in order to complete engineering studies for unlined shallow land burial.

Table 1. Assumptions Specific to the Design of
Unlined and Lined SLB Facility

1. The potentiometric surface will be 25' below grade required for hazardous and radioactive waste facilities only.
2. Mounding of the waste on a 3:1 slope will satisfy regulatory requirements.
3. Groundwater monitoring wells will be provided.
4. A surface runoff diversion structure will be provided around the perimeter of the site.
5. A drainage system will be provided for the collection and discharge of precipitation falling in the site boundary.
6. The access roads will be designed solely for DOE use.
7. The runoff settling pond will be lined with clay obtained off-site.
8. An auxiliary fuel tank, a waste storage facility, and a maintenance pad will be provided.

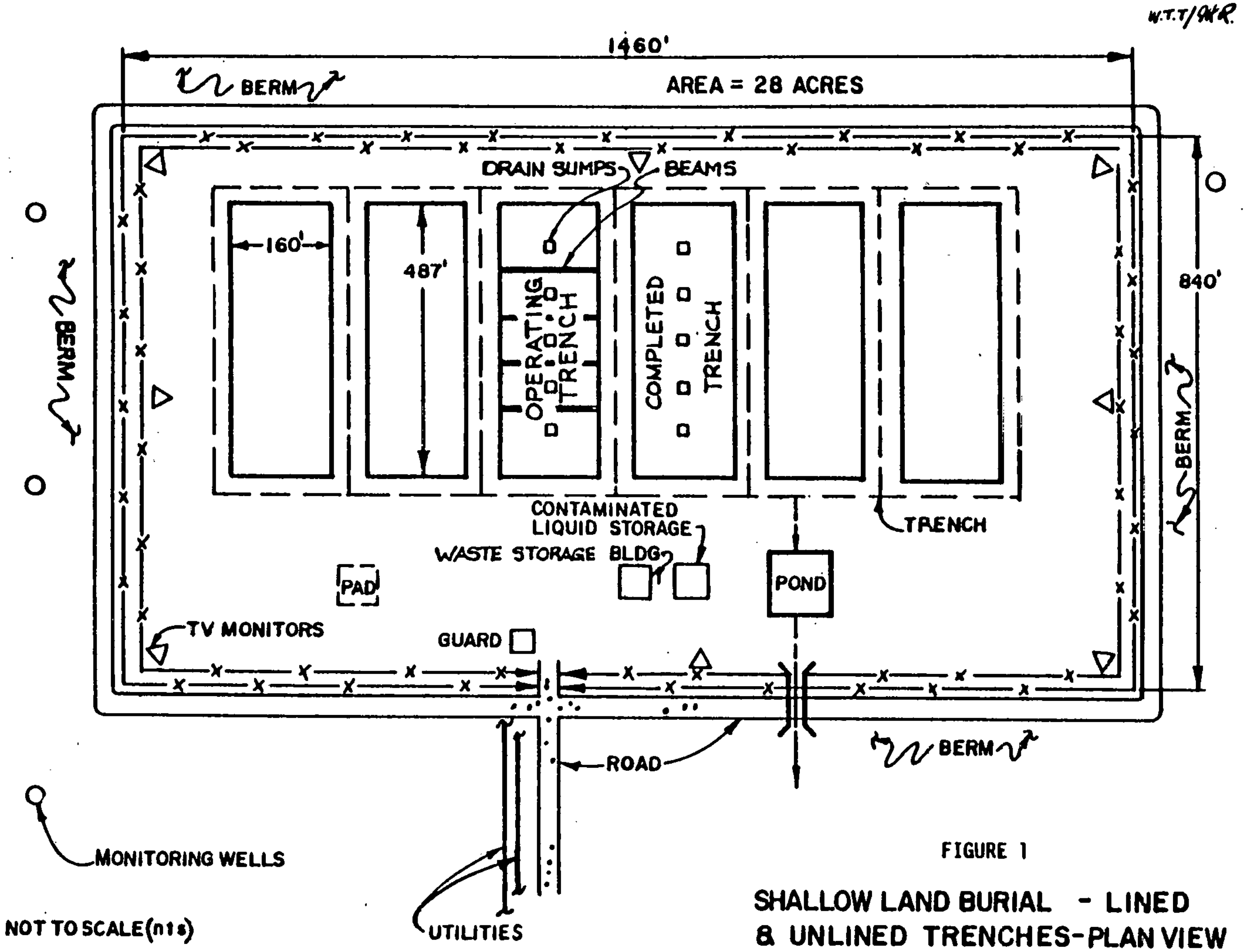


FIGURE 1

SHALLOW LAND BURIAL - LINED
& UNLINED TRENCHES-PLAN VIEW

Lined Shallow Land Burial

The lined shallow land burial disposal option is designed to comply with the proposed RCRA guidelines for hazardous waste disposal. Lined shallow land burial will entail all the requirements previously addressed for unlined shallow land burial and will also include trench lining and leachate containment, collection, and transfer systems. The first trench will be constructed about 487' x 160' x 16' to accommodate approximately 1/6 of the total design volume of waste.

Figure 1 shows a plan view of the site and Figure 2 presents an elevation view of the trench with the leachate containment and collection systems identified. Leachate containment is accomplished through the use of a five foot thick clay liner in the trench. One foot of gravel placed on top of the clay liner and sloped at a grade of 1% towards the drainage sumps serves as a leachate collection system. French drains are designed in the gravel layer and extend radially from five sumps equally spaced along the centerline of the trench base.

The 1000 gallon sumps contain pumps which will transfer the leachate to the leachate storage tank. The collected leachate will be transported by tank truck to an offsite treatment facility (not costed in this study).

The sides of the trench will slope 3:1 and be lined with the clay and gravel. Ten feet of the usable trench depth will be below grade with the remaining six feet above grade. The waste will be mounded on a 3:1 slope. A clay cap, earthen fill, and a top soil cover will be placed over completed sections of the trench.

The 160' x 487' trench is compartmentalized into five subtrenches by one foot high dikes to allow runoff from working sections to be collected by their individual sump. Runoff from nonworking sections will be discharged through the surface drainage system.

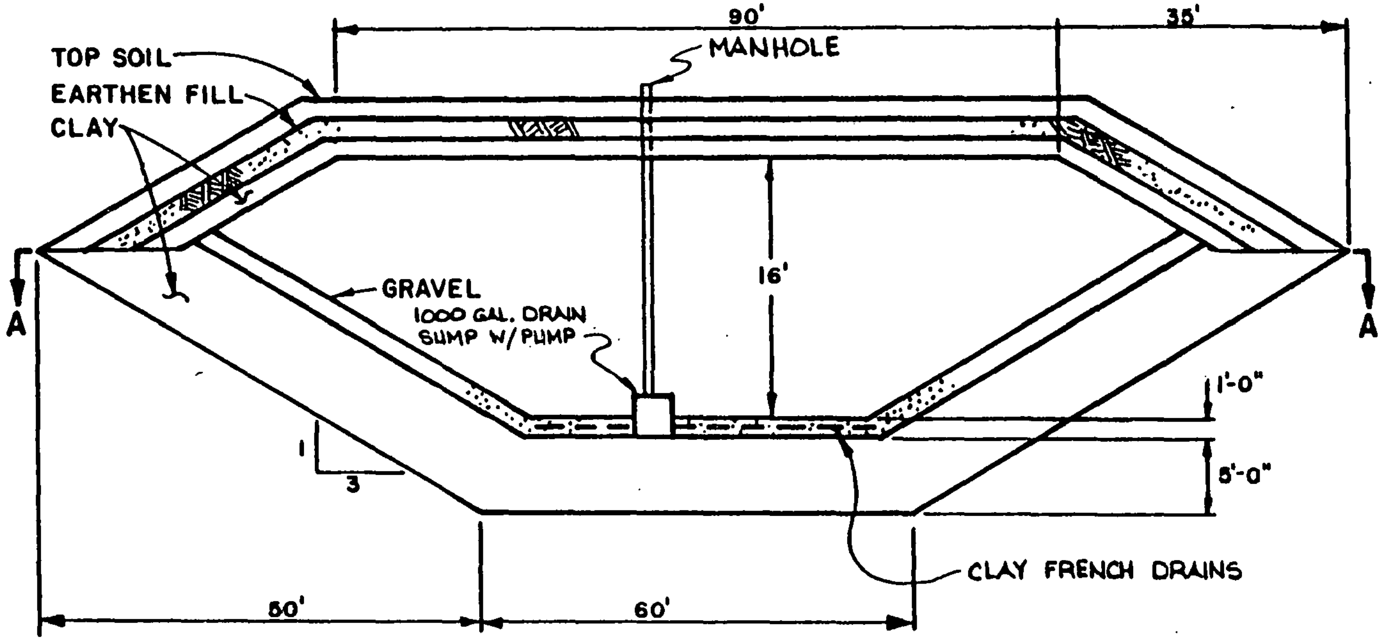
Assumptions that were made for design of the lined shallow land burial facility include those listed in Tables 1 and 2.

FIGURE 2

SHALLOW LAND BURIAL

LINED TRENCHES

ELEVATION VIEW



W.T.T./P.M.R.

Table 2. Assumptions specific to the design of the lined SLB disposal facility.

1. The trench will be designed in accordance with the proposed guidelines for a hazardous waste disposal facility required by EPA and discussed in F. R. Vol. 43, No. 243, pp 58946 - 59028, 12/18/78.

2. Thirty percent of the trench volume will be allowed for daily cover and void space.

3. The clay will be obtained off-site.

4. The bottom of the clay liner will be a minimum of five feet above the maximum groundwater level.

5. Mounding of the waste above ground will comply with all regulatory requirements.

Waste Storage Alternatives

Three storage options are identified as being amenable to the storage of hazardous/radioactive waste or contaminated metals. Some of the general design features are the same for each of the options, most noteably utilities and road access, and the application of phased construction. The design of pretreatment and packaging facilities is not included in the analysis of storage alternatives.

Storage in a Metal Building

A large prefabricated metal building constructed on eight acres of land is one option costed for storage of 2 x 10^6 ft^3 of waste. The building shown in Figures 3 and 4 is designed so that waste could be stacked to a maximum height of 30 feet on a slope of 2:1 by the use of a skip hoist and front end loader. The building dimensions of 140' x 180' provide for the utilization of a large width, to minimize volume wastage due to stacking. Another benefit of this design is the relative ease of expanding the facility to accommodate additional waste. Three large roll-up metal doors are included in the building design to facilitate unloading and stacking operations. The walls of the facility are not designed to handle a bearing load brought on by the placement of waste against the sides. Ventilation will be supplied by roof ventilators with lighting provided to meet the minimum safety requirements for a warehouse storage structure.

FIGURE 3

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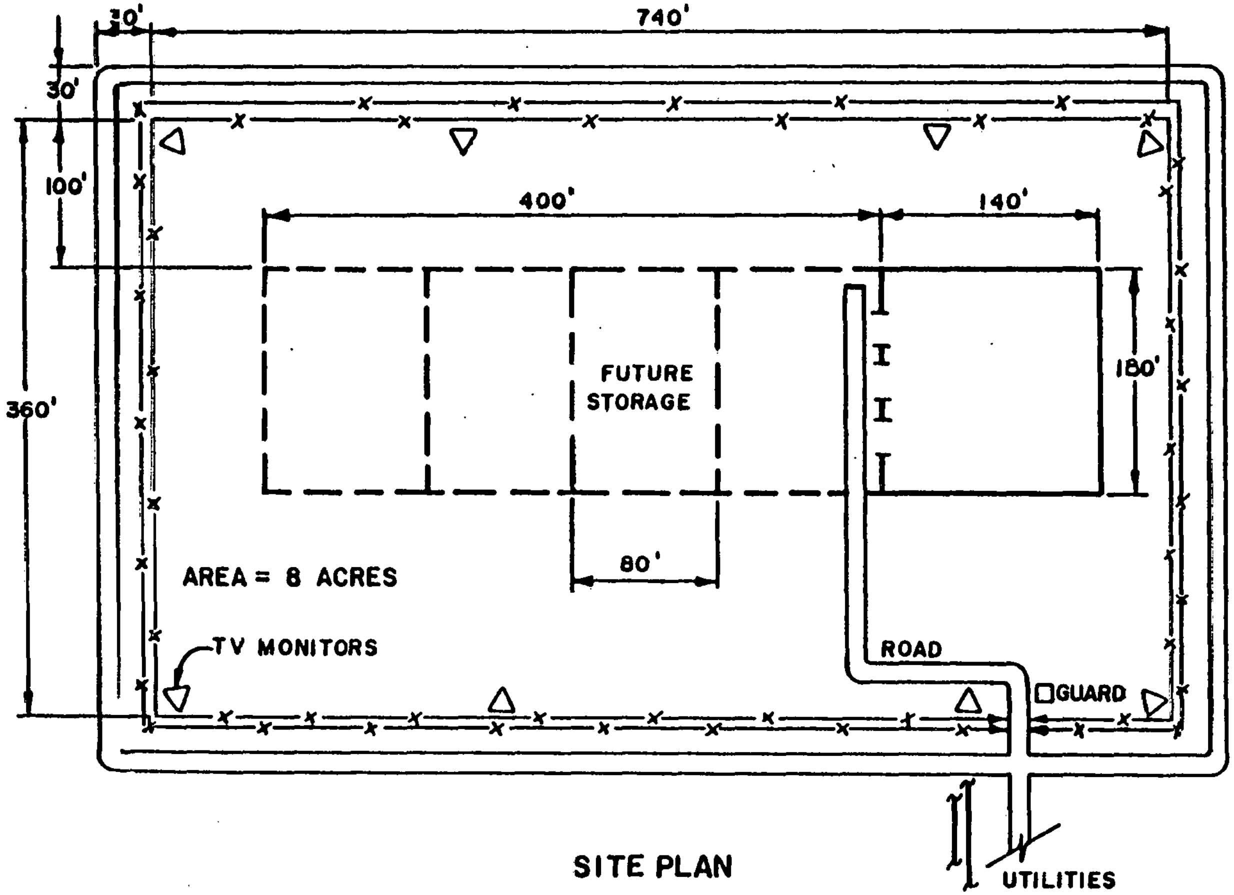
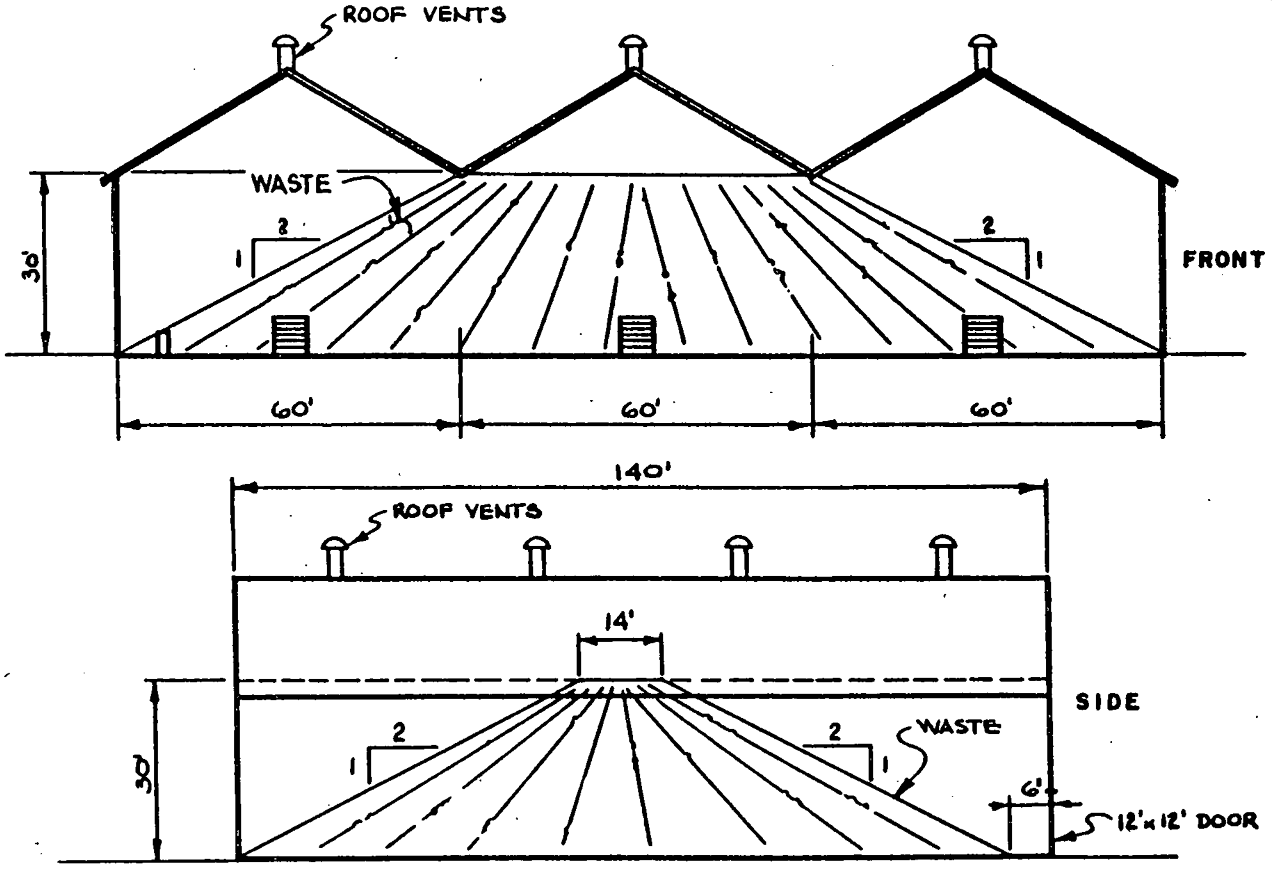
METAL BUILDING FOR METAL SCRAP STORAGE



SITE PLAN

FIGURE 4

METAL BUILDING FOR METAL SCRAP STORAGE



ELEVATION

W.T.T/HS

There are no provisions in the design for diversion or collection of any surface drainage.

Storage in Concrete Trenches

Storage in concrete trenches was identified as a second option. The design of these facilities provides the most secure containment afforded by any of the three storage alternatives. Figure 5 shows the site plan and Figures 6 and 7 show sectional views of the storage trench.

To minimize hydrostatic head on the exterior surfaces of the trench a french drain system will be provided. Both interior and exterior drains will flow by gravity to two separate 1000-gallon sumps. Contaminated liquid will have to be collected and treated.

Noncontaminated water will be pumped to a settling pond and discharged from the site.

Table 3 lists assumptions applicable to the design of the concrete trench storage facility.

Table 3. Assumptions Pertaining to the Design of Concrete Trench Storage Facilities

1. The potentiometric surface will be 15' below grade.
2. The area required will be 15 acres.
3. A temporary waste storage building will be provided.
4. Additional trenches may be constructed with a common wall.
5. Monitoring wells for ground water sampling will be provided.
6. A surface water diversion system will be provided.
7. The design will include a conveyor to dump the waste across the 30' span of the trench.

Storage in Concrete Cubes

The third option consists of storage in concrete cubes. The cubes are to be constructed of six inch reinforced concrete and have a five foot cubical interior dimension. Site layout is shown in Figure 8. It is estimated that 11 acres will be required for storage of 2 x 10^6 ft^3 of waste assuming that the cubes will be stacked two high and allowing the void area between cubes to equal 30% of the area of the cubes. The design requires that the cubes be purchased offsite and received on-site ready for filling. Full cubes will have prefabricated caps grouted in place. Assumptions pertaining to the design for storage of scrap in cubes are listed in Table 4.

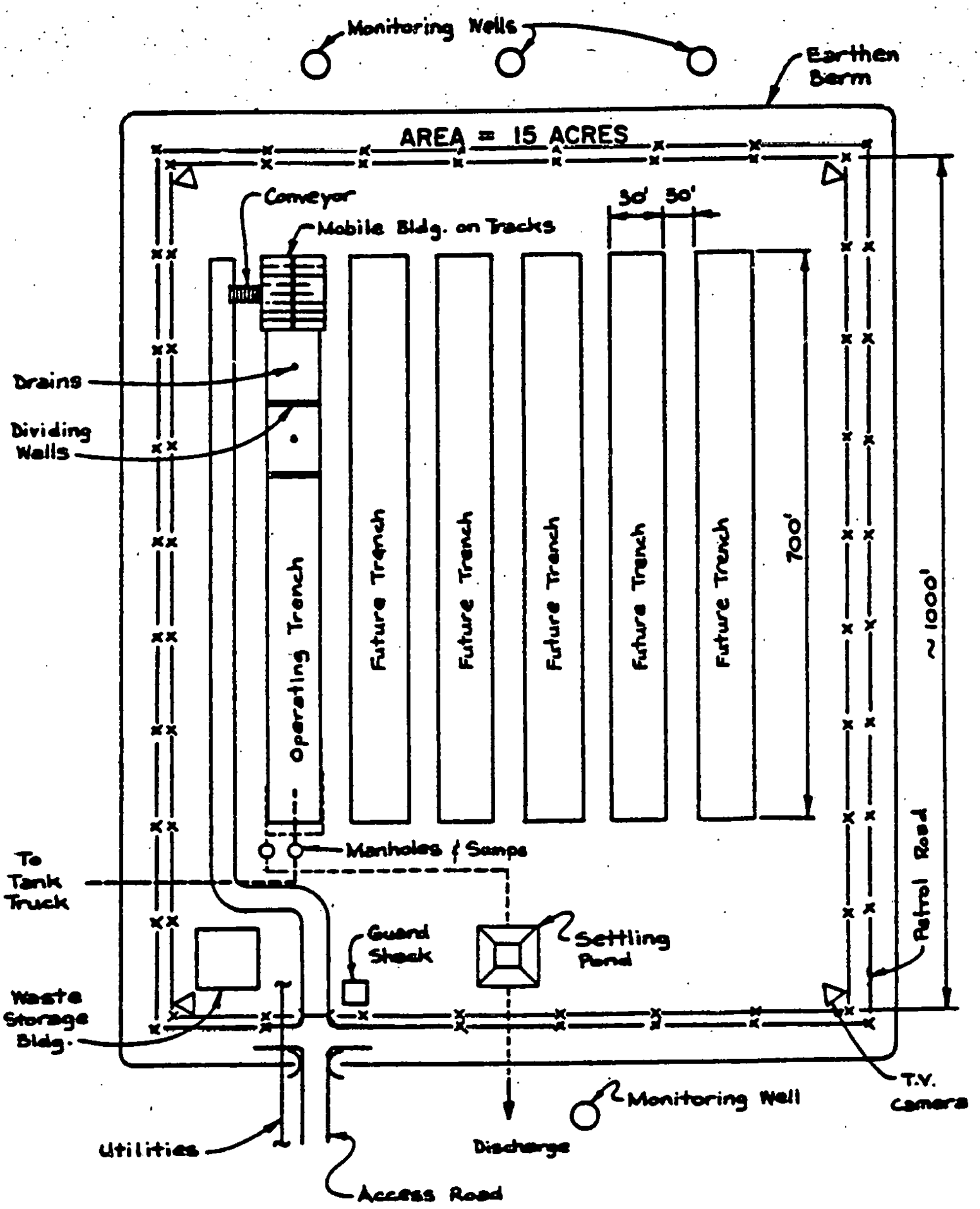


FIGURE 5

CONCRETE TRENCHES FOR METAL SCRAP STORAGE - SITE PLAN

W.T.T. / R.M.S.

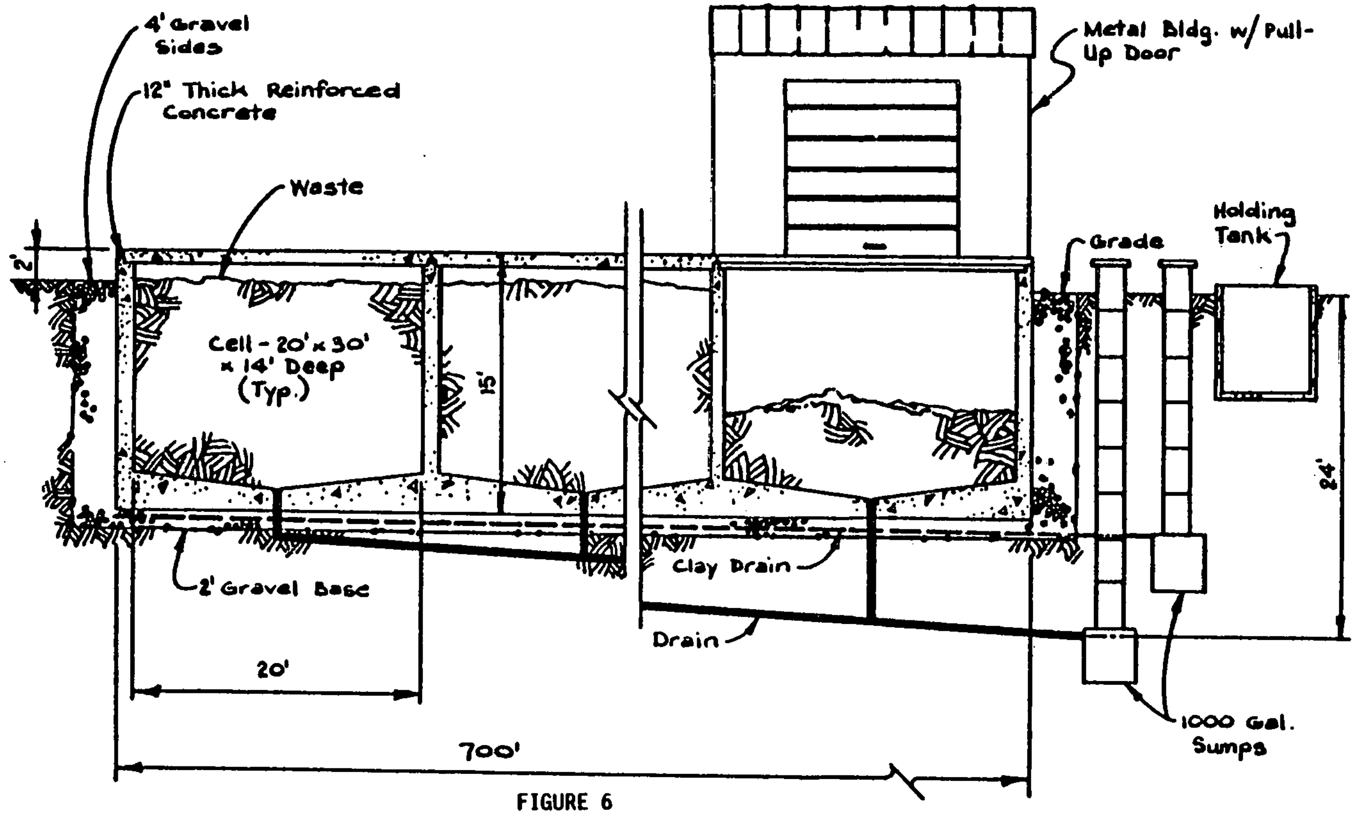


FIGURE 6

CONCRETE TRENCHES FOR METAL SCRAP STORAGE

LONGITUDINAL SECTION

W.T.T./R.M.S.

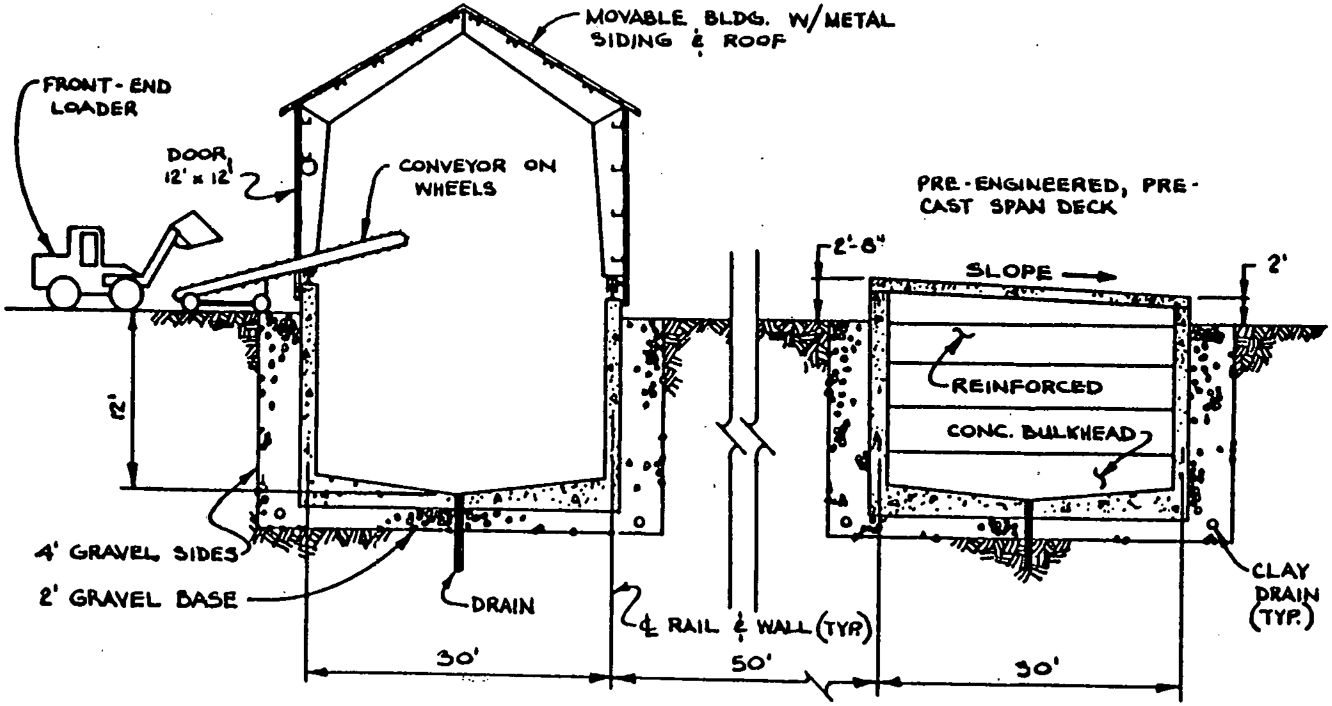


FIGURE 7

CONCRETE TRENCHES FOR METAL SCRAP STORAGE

CROSS SECTION

W.T.T./R.M.S.

FIGURE 8

CONCRETE CONTAINERS FOR METAL SCRAP STORAGE

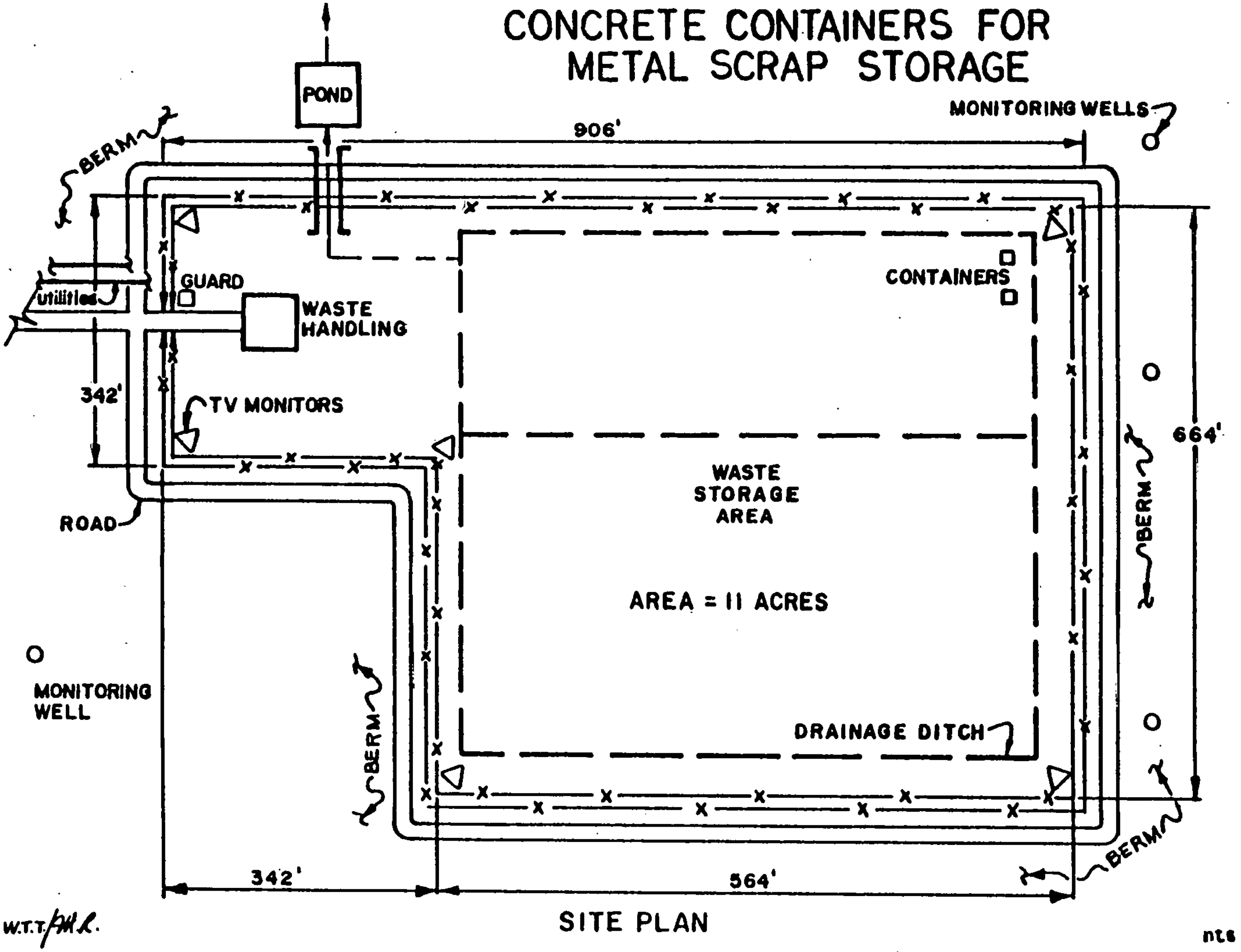


Table 4. Design Consideration for Storage of Contaminated/Waste in Cubes

1. A waste handling building will be included.
2. A surface water diversion structure will be provided.
3. Monitoring wells will be included.
4. A large forklift to handle empty and full cubes will be provided.

4. OPERATIONAL REQUIREMENTS

Operational requirements for each option are summarized in this section. The operational plans for each option share the following assumed criteria: the facility will operate 250 days/yr for eight hours/day; and waste packaging or pretreatment operations are not considered in this evaluation. It is realized that any pretreatment and/or packaging processes could impact real estate and building volume allowances.

Operation of the Unlined Shallow Land Burial Facility

Operation of the unlined shallow land burial facility will be similar to operation of a sanitary landfill. The waste will be transported to the disposal site and placed into the trench or into the temporary waste storage building. Excavation of the trench will preceed the placement of waste by only a few days to minimize the collection of surface water in the trench. Typically, a D-7 caterpillar tractor will perform most of the excavation while end loaders will handle the waste at the storage facility and serve as backups to the D-7.

Site and equipment maintenance are included in the operation plan. Assumptions concerning the operation of the unlined shallow land burial facilty are presented in Table 5.

Table 5. Assumptions for the Operation of the Unlined Shallow Land Burial Facility

1. Waste will be transported to the disposal site in two dump truck loads per day. (The exact transportation mode will be dependent on security requirements).
2. A dump truck will be required on-site to haul waste from the storage facility to the disposal trench.
3. The storage facility will provide a 5 day storage capacity.
4. The waste will have a daily soil cover placed over it.
5. Equipment will be available on loan from a DOE plant for removal of solids out of the runoff retention pond.
6. Water diverted around the facility will not be collected and treated since it is not a point source.
7. Any precipitation falling into an open trench will be pumped out and into a tank truck for transport to an off-site liquid treatment facility (not costed in this study).

Operation of the Lined Shallow Land Burial Facility

The trench will be divided into five sections each separated by clay berms. Rainfall collected in the working section of the trench can be contained separately between the section berms. As filling operations progress runoff from the working section will be pumped to a holding tank. When a section is filled to capacity a cap composed of clay, fill earth, and topsoil layers will be constructed. Leachate collected in filled and capped sections will be pumped to a holding tank. Runoff collected in nonworking sections will be pumped to the surface water collection system.

Operation of the Building Storage Option

Waste will be picked up in a form suitable for hauling to the waste storage facility. The waste will be stored on the building's concrete floor and later transported to a waste pile or placed onto a skip hoist with a front end loader. The skip hoist will place the waste to a predetermined maximum height of 30 ft. The front end loader will also be required to position the skip hoist for properly mounding the waste.

Equipment maintenance and building repair were included in operating costs. Expansion of the facility will be accomplished by lengthening the building at intervals to lengths suitable for handling a predetermined quantity of waste.

The operation of this facility is the least weather dependent of all storage operations.

Operation of the Concrete Trench Storage Facility

Waste will be transported to the trench site and unloaded adjacent to the operating section of the trench. No provisions are made for storage of waste due to adverse weather. A front end loader will pick up the waste and place it onto a conveyor that will spread the material evenly over the area of the working section. After approximately 30 days of operation the trench section will be full at which time a crane will position the building, which was located over the working section of the trench, over the next empty section. The crane will then place span deck caps over the full section.

It is assumed that a crane will be available for 1 day out of every 35 days to handle the span deck and building, and that a tank truck will be available to transport leachate and runoff.

A new trench will be constructed adjacent to the old trench as more storage space is needed.

Storage in Concrete Cubes

The last storage option was estimated to be the most labor intensive. The waste will be received on-site and stored in the waste management building. In the building the waste will be placed into prefabricated concrete cubes with the use of a front end loader. The cubes will be capped with a prefabricated concrete cap and sealed with grout. A forklift, designed to handle the cubes, will load two full cubes onto a trailer and then pull the trailer out to the storage area. After positioning the trailer, the forklift will disconnect and unload the cubes stacking them two high. About two cubes per day will be required to store the waste generated.

5. COST ESTIMATES

Bills of Materials (B/M's), which were prepared and estimated for each option by Engineering, contain not only all construction requirements needed for the development of capital costs but also lists equipment needed for daily operation of the facility.

Operational schedules were developed concurrently with the B/M's so that complete operational costs could be included in the estimates. Table 6 presents ROM cost estimates for each option. This table represents preliminary ROM estimates for comparison purposes, and should be recognized as figures corresponding to the preliminary design studies. Several assumptions required to estimate costs are listed in Table 7.

Table 6 shows the breakdown of the total cost figures. Capital costs represent all costs that would occur in the initial phase of facility construction. Operating costs include all charges associated with the daily operation of each facility, e.g. truck operation, security guards. Future capital or expense cost includes costs for expansion of the initial facility to accommodate future waste and the purchase of any equipment which would need replacement.

Table 6. ROM Costs for Solid Waste Management

Options	Total Initial Capital[1]	Future Capital Expense[1,2]	Total[1]	Costs/ft^3
SLB (3 x 10^6 ft^3) Unlined Trench	2.0	0.7	8.6	$2.86
SLB (3 x 10^6 ft^3) Lined Trench	3.0	5.2	13.5	$4.50
Storage (1.7 x 10^6 ft^3) Metal Building	1.0	1.1	5.8	$3.87
Storage (1.7 x 10^6 ft^3) Concrete Trench	1.5	3.1	8.1	$4.80
Storage (1.7 x 10^6 ft^3)	2.7	6.8	13.5	$7.90

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[1] Numbers represent millions in 1979 dollars.

[2] Capital/Expense figures are for total expansion costs associated with each option.

Table 7. Assumptions for Cost Development

1. All facility costs include estimates for security requirements.
2. All costs include 20% for engineering and 30% for contingency and are in 1979 dollars.
3. The costs are ball park estimates to be used for comparison.
4. The estimates are based on steady state waste generation.
5. The cost figures cannot be extrapolated on a straight line basis to obtain dollars per cubic foot for various production rates. The estimates for the two disposal options represent two extremes. A combination of the two disposal methods would not result in a cost exceeding the estimate for hazardous waste disposal.

Cost Summary

As expected the disposal option utilizing shallow land burial of low-level nonhazardous waste in an unlined disposal trench is the less costly of the two disposal options. The principal difference in capital cost is due to the clay liner and leachate collection system as required under RCRA for hazardous waste management facilities. Although unlined shallow land burial trenches are lower in capital cost, they are higher in operating cost. The higher operation cost resulted from a greater amount of earth work required for day to day trench excavation and fill. These costs were incurred as capital costs in the lined trench option.

The cost differential for the three storage options was primarily the capital cost incurred initially and during the phased expansion.

It is of interest to note that the fee charged at commercial radioactive waste disposal operations is in the range estimated in this paper.

No estimates have been made for any potential "perpetual care" requirements.

SOLID WASTE DISPOSAL STUDY *

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ABSTRACT

Solidification studies conducted on sludge from the K-1407C Retention Basin confirm that cement fixation is a viable method for disposal of waste solids. A model is presented relating cement requirements and sludge moisture level to the final storage volume required for cement fixation. The sludge volume and ultimate disposal cost are strongly related to the moisture of the processed sludge. Dewatering efforts with the sludge using polymer dewatering aides and centrifugation are discussed.

SUMMARY

The 1981 Line Item Project 81-R-506, Environmental Protection and Safety Modifications - Phase I, requires the development of solidification methods to permanently dispose of sludge. Among the sludge disposal methods presently available are fixation with polymer, asphalt, glass, calcium-silicate, or cement. A review of these methods and characterization of the sludges has been reported by McGinnis.[1] Because cement fixation is a straight forward and well recognized waste disposal technique, this method was chosen as the preliminary design basis for the conceptual design of this project.

The solid waste at ORGDP should be converted into a form that will be easy to store, will be of a permanent nature, and could be recoverable at a later date if necessary. To withstand the abuse of handling equipment and to meet toxic waste criteria, the waste in the fixed form should have an ultimate compression strength greater than 300 psi. The strength is determined by a structural integrity testing procedure included in the EPA guidelines.[2]

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*K/ET-5017

This paper describes the solidification studies performed on sludges from the K-1407C retention basin. These studies were made to determine the optimum operating range of the Central Sludge Treatment Facility and to evaluate cement fixation as a method of sludge disposal. The critical parameters studied were ultimate compression strength and toxicity leachate levels.

Because costs were felt to be related to final storage volume, the effect of the sludge moisture content on the volume of the waste after cement fixation was also determined. It was found that dewatering the sludge from the nominal sludge moisture content of 60% or greater to a moisture content of 40% reduced the final concrete volume by 44%. Further dewatering was found to be unnecessary since additional water would then be required for cement hydration.

A mathematical model was developed to quantify the major parameters and to serve as a design basis for the Central Sludge Treatment Facility. A model allowing the calculation of the cement requirements to obtain a given strength is presented. This model shows the strong correlation that exists between the water/cement ratio and the strength of the cured concrete. A relationship showing the sludge density as a function of the sludge moisture level was developed. These functions are combined in a comprehensive model which permits determination of a final waste volume as a function of cement addition, sludge moisture, and strength requirements.

The following conclusions are drawn from this study:

1. The cement-fixed waste passes the EPA standard leach test for toxic substances;
2. The addition of cement improves the handling characteristics and produces a permanent monolithic waste which could be reclaimed if necessary;
3. A structural strength of 300 psi, which provides adequate permanency, can be obtained with little increase in volume by adding cement; and
4. Dewatering sludge significantly reduces the cement requirement and landfill space requirement for sludge disposal.

EXPERIMENTAL AND RESULTS

Final strength of the fixed material is determined by laboratory testing according to ASTM C513-69. For this test the grout is cast in 2-in. cubes and is cured for 28 days in a constant humidity environment. Strength is calculated by measuring the yield strength per unit area of the specimen. Compressive strength is the governing parameter for industrial concretes and has proved useful in conducting this solidfication study.

Sludge at the test moisture level is blended in a laboratory mixer, Figure 1, to achieve a homogeneous mix. The resulting concrete is placed in thin layers into a mold attached to a vibrating table. This allows any voids caused by trapped air to be filled. The loaded molds are smoothed by trowel after vibrating for 10 min. The molds and vibrating table are shown in the photograph of Figure 2. The molds are then placed in a sealed container at 100% humidity for 24 hr. The samples after initial curing are wrapped with a water-impermeable wax paper, Parafilm M, and allowed to set during the 28 day curing period.

STRENGTH MODEL DEVELOPMENT

Compressive strength for several runs at various sludge moisture levels are plotted against the water-to-cement ratio (w/c) as shown in Figure 3. The w/c is a common strength determinant in concrete formulation. The points are adequately modelled by the hyperbolic equation

$$\text{Strength} = 2088/(w/c) - 377 \; . \qquad (1)$$

Transformation of the equation by substitution of the term c/w for 1/(w/c) results in the following linear equation:

$$\text{Strength} = 2088(c/w) - 377 \; . \qquad (2)$$

A plot of Equation 2 is shown in Figure 4. The correlation coefficient for the model is $R^2 = 0.995$. Dewatered and cured sludge with no cement addition gave strengths of 17 to 284 psi. This material rewet easily when exposed to moisture and is not suitable for disposal.

TOXICITY TEST RESULTS

Under the Environmental Protection Agency's proposed guidelines for the identification of hazardous wastes,[2] a waste is considered hazardous if it is listed as a part of the guidelines or if it is ignitable, corrosive, reactive, or toxic. Although the wastes studied in this project are generally not ignitable, reactive, or corrosive, toxic substances are present in the sludge. The Environmental Protection Agency requires that a specific laboratory leach test be performed and that the leachate have concentrations of specified metals less than 10 times the drinking water standards to be considered nontoxic. Testing of the solids in this study for the leaching of toxic substances indicated that wastes solidified with various levels of cement meet the EPA quidelines.

In this extraction procedure, the sample cube is added to 16 times its weight of water and held at a pH of 5 for 24 hr. Then, the amount of water is increased to 20 times the sample's weight. After the cube is removed, the water is analyzed for the presence of the eight specified toxic elements. Test results are compared with the EPA guidelines in Table I. Although the results of only three samples are shown in Table I, the tests showed that the leachates from all of the cement-fixed samples were within the EPA limits.

Figure 1

LABORATORY PREPARATION OF CONCRETE MIXTURE

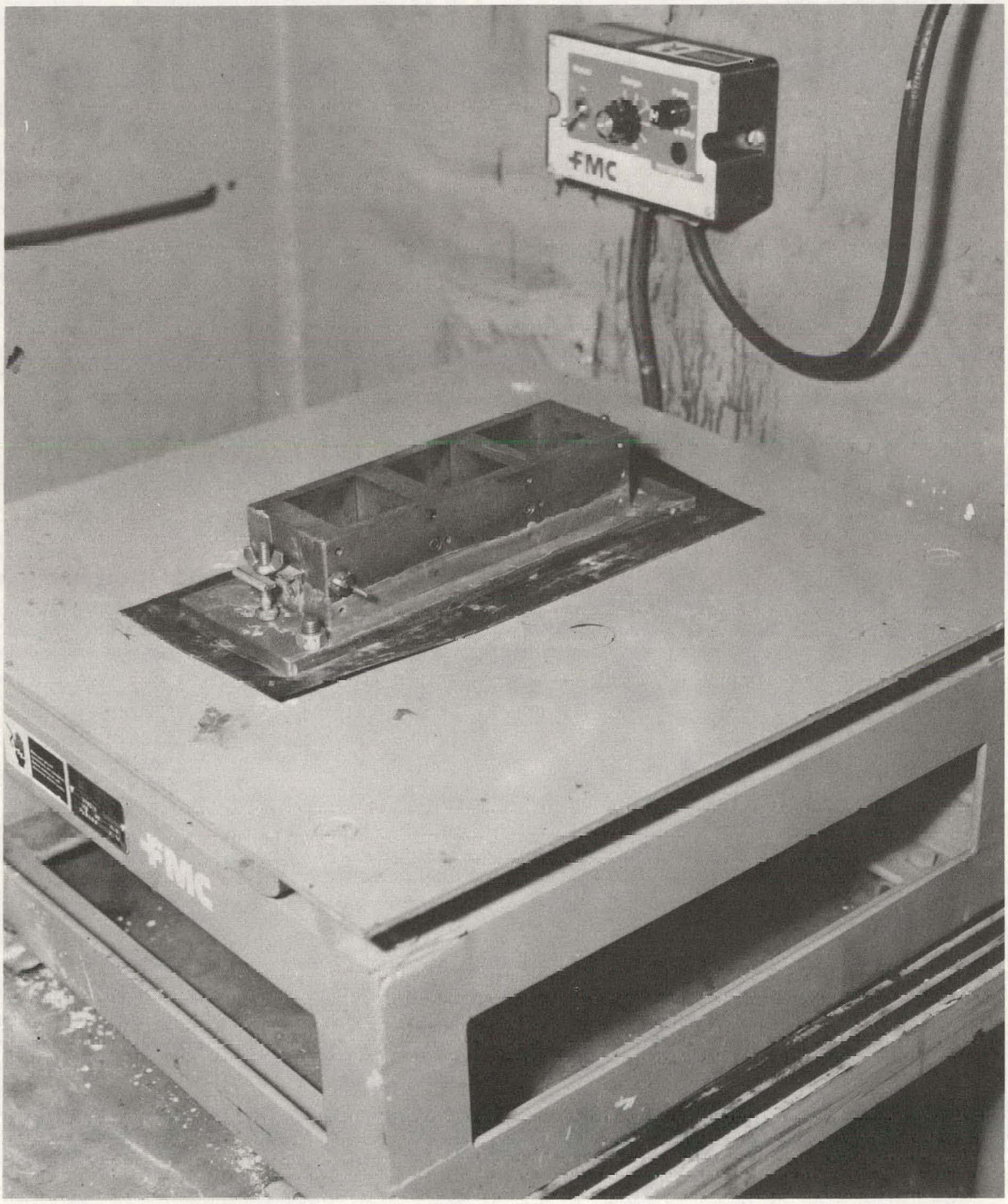

Figure 2

ASTM CONCRETE MOLD MOUNTED ON VIBRATING TABLE

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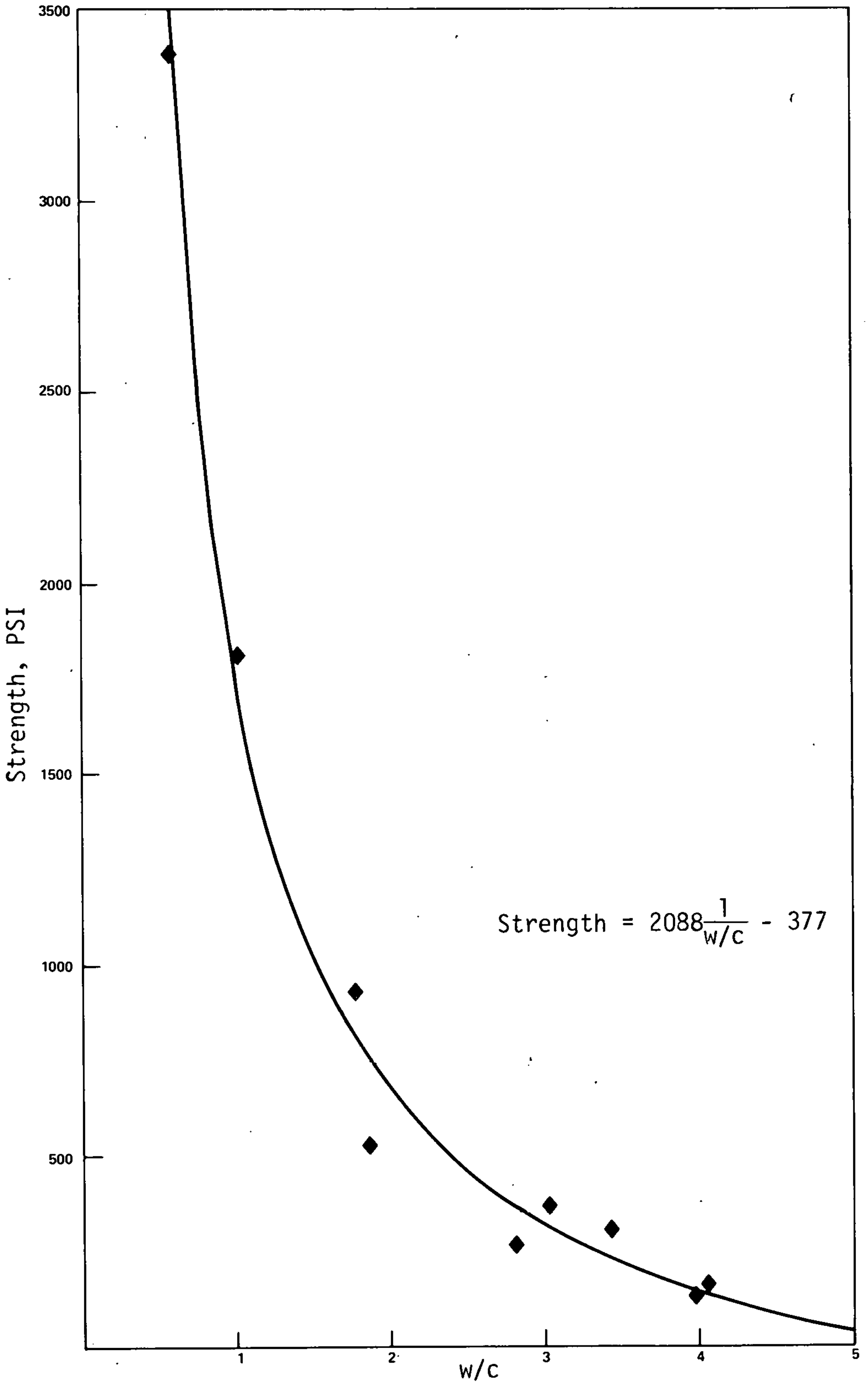

Figure 3
HYPERBOLA FOR w/c VS. STRENGTH

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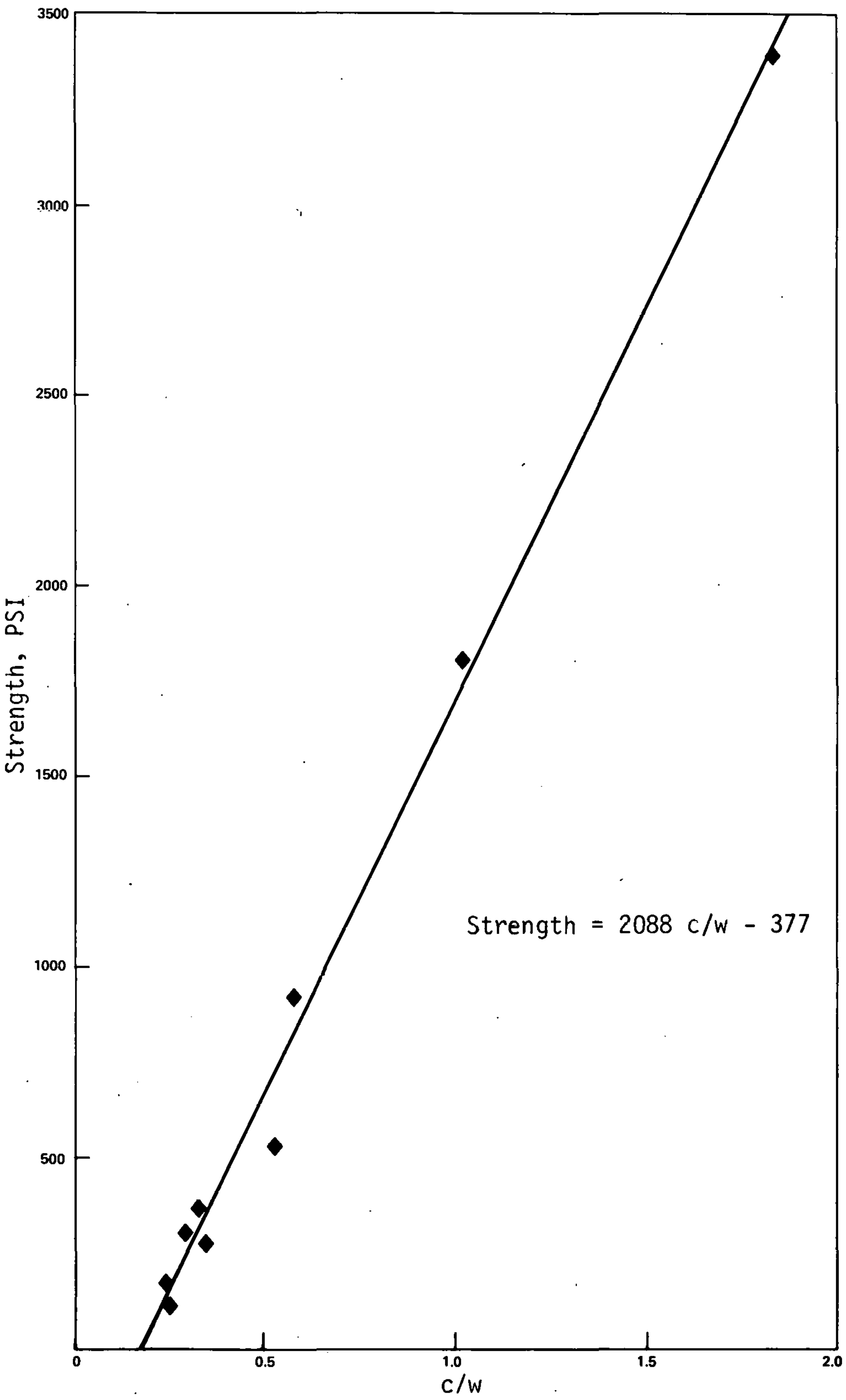

Figure 4
STRAIGHT LINE FOR c/w VS. STRENGTH

Table I

LEACH TEST RESULTS

(μg/ml except as noted)

Toxic Elements	EPA Guidelines†	Concrete w/c = 4.1	Concrete w/c = 3.2 With Polymer	Dried Sludge
Arsenic	0.50	< 0.005	< 0.005	< 0.05
Barium	10.0	< 0.30	< 0.30	0.75
Cadmium	0.10	< 0.05	< 0.05	< 0.05
Chromium	0.50	< 0.05	< 0.05	0.06
Lead	0.50	*	*	*
Mercury	0.02	0.0005	0.0001	0.022
Selenium	0.10	< 0.005	< 0.005	0.007
Silver	0.50	< 0.05	0.05	< 0.05
Uranium	$45^{\dagger\dagger}$	0.008	0.014	1.260
Technetium, μCi/mℓ	$1 \times 10^{-2\dagger\dagger}$	$< 4.5 \times 10^{-6}$	$< 4.5 \times 10^{-6}$	$< 6.7 \times 10^{-6}$

†EPA Guidelines, see Reference 2.
*Previous lab sample results report no detectable lead.
††DOE Guidelines, see Reference 3.

Toxicity leaching tests were also performed on a sample of dried sludge with no cement added. The leachate from this sample also passed the toxicity test except for mercury, but it disintegrated during the structural integrity test and formed sludge when rewetted. Thus, although the addition of cement is not necessary to prevent the leaching of most of the toxic elements, it is needed to give the sludge sufficient strength to survive handling during disposal and to allow retrieval if desired in the future.

Tests were performed to learn if the polymer used to dewater sludge would have an adverse effect on the toxic extraction test results. As shown in Table I, the leachate levels for all of the elements tested were very similar to those for the samples with no polymer.

SLUDGE SOLIDS DENSITY

The strength model developed in Figure 4 is independent of sludge moisture content. Sludge as received from the K-1407C Retention Basin can be fixed over the moisture range of 35% to 100%. The volume of the final cement-encapsulated sludge is a function of the sludge moisture content. The final volume should be minimized to conserve landfill space and cement requirements.

Densities of sludge at several moisture levels were measured. The calculated dry density of the sludge is 2.24 g/cm^3. These density measurements are plotted in Figure 5. A hyperbola of the form

$$y = \frac{2.24}{1 + 1.24x} \qquad (3)$$

where y = Density of the wet sludge in g/cm^3, and
x = Sludge moisture level in % ,

forces the model to meet the boundary conditions of dry density of 2.24 g/cm^3 and 100% moisture density of 1.0 g/cm^3. Good fit is noted in Figure 5. The model correlation coefficient is $R^2 = 0.89$.

ANALYSIS OF DENSITY AFTER CEMENT ADDITION

By combining the density model with the strength vs w/c model, a composite model to define fixed sludge density at constant strength can be developed. Figure 6 presents the final model. Specification of final strength and sludge moisture level allows determination of the sludge density. The utility of the model can be illustrated by considering two examples.

Example 1: The sludge has a 60% moisture content (point A on the graph). To fix this sludge in concrete having a w/c of 2.5 (strength of 450 psi), cement must be added to make it approximately a 19.5% constituent. This cement addition gives a dry concrete density of 0.47 g/cm^3 as shown by point B.

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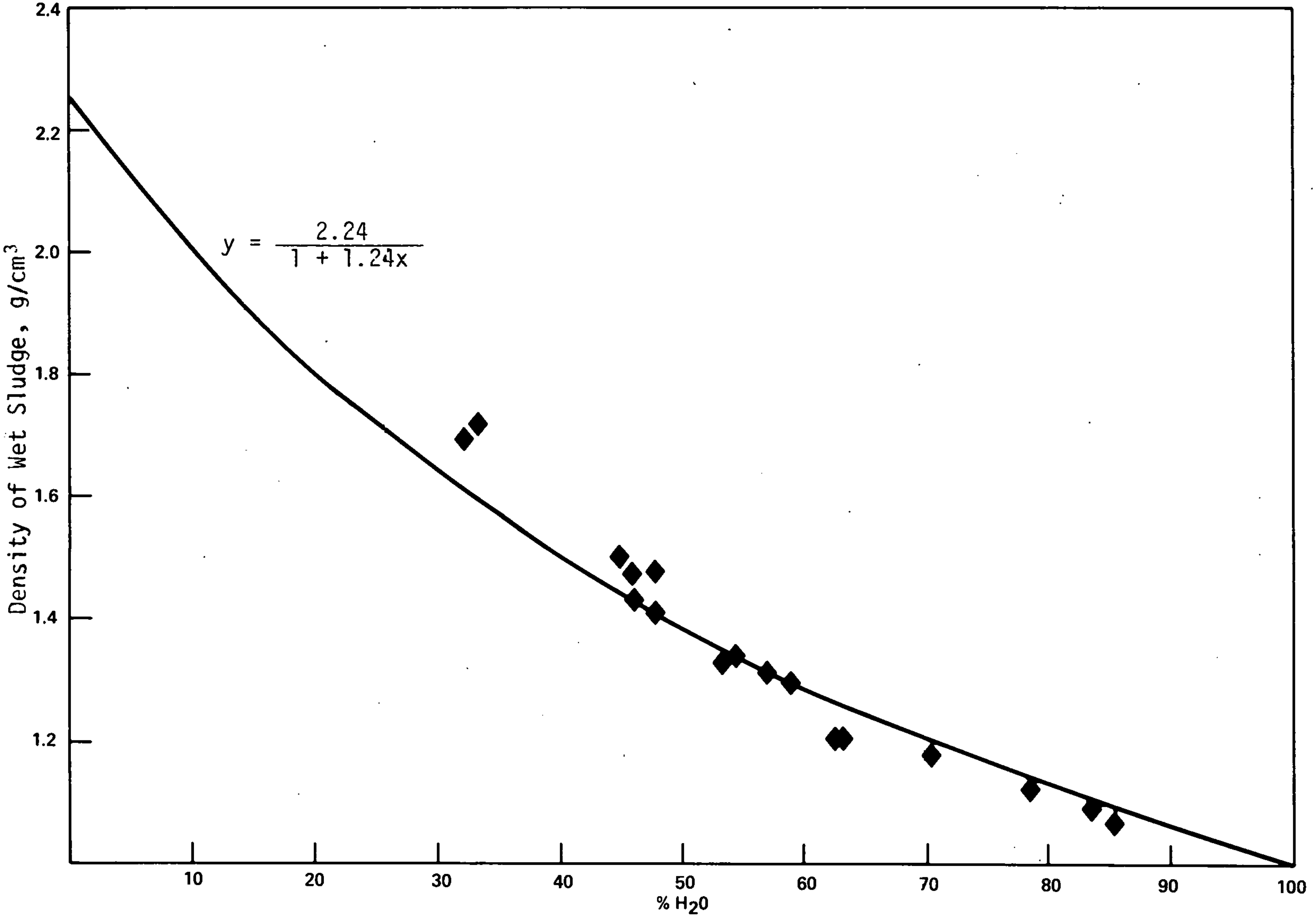

Figure 5

THEORETICAL CURVE FOR DENSITY OF WET SLUDGE VS. % MOISTURE
Experimental points from Table VI are shown on curve as ◆'s.

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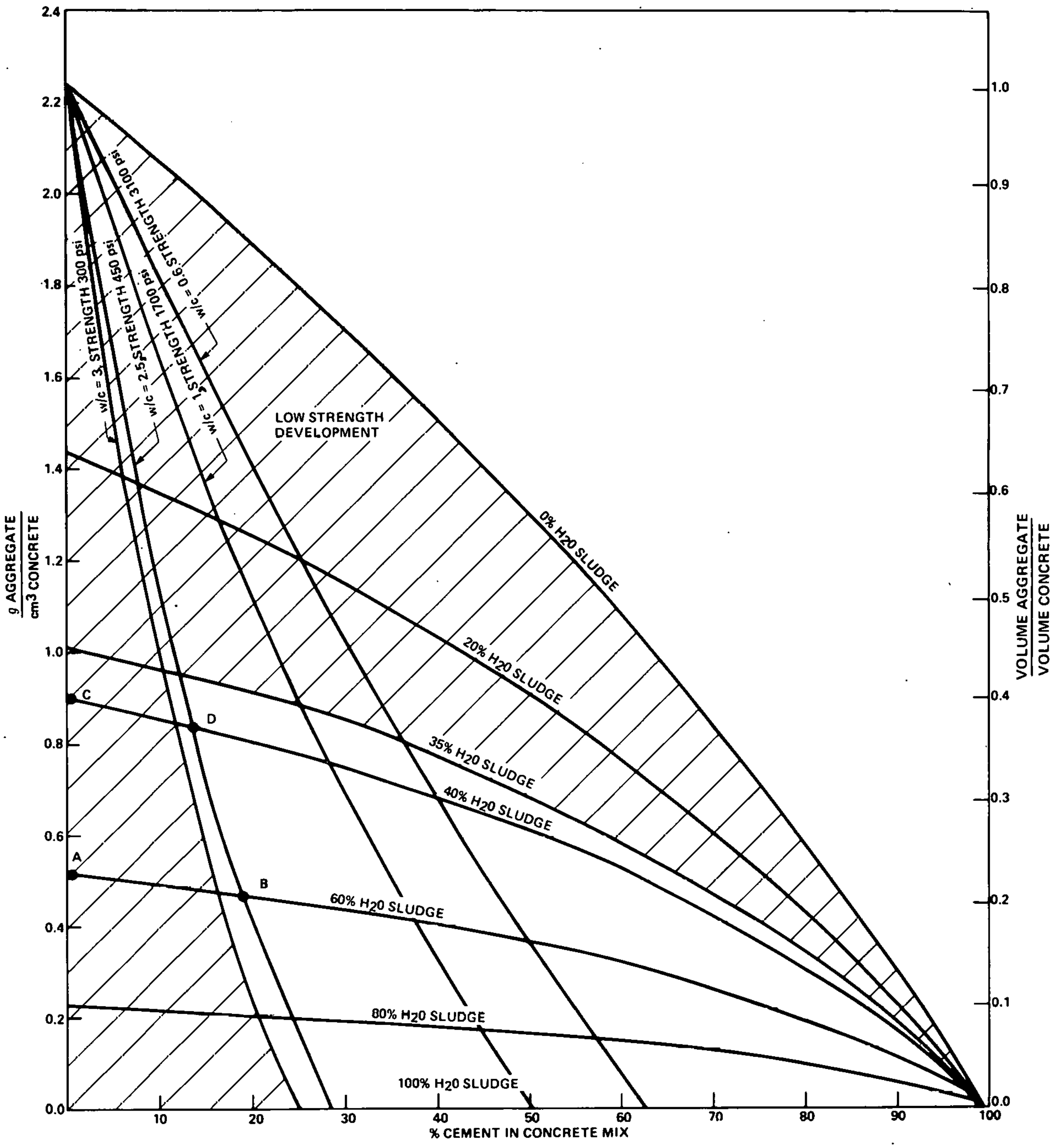

Figure 6

DENSITY ANALYSIS CURVES

Example 2: If the sludge in Example 1 is first dewatered to a 40% moisture content, point C, then mixed with cement, as shown by point D, to give the same w/c (strength) as in the example above, the resulting dry concrete density is 0.83 g/cm^3. Dewatering the sludge from 60 to 40% then adding cement increases the density of the concrete by

$$\frac{0.83 - 0.47}{0.47} \times 100 = 76.6\%,$$

and decreases the volume to be disposed of by

$$(1 - \frac{1}{1.766}) \times 100 = 43.4\%.$$

Dewatering the sludge with no addition of cement from 60 to 40% moisture increases the density of the wet sludge by

$$\frac{0.89 - 0.51}{0.51} \times 100 = 74.5\%,$$

and so decreases the amount of wet sludge to be handled by

$$1 - \frac{1}{1.745} \times 100 = 43\%.$$

It is interesting to note that dewatering before addition of cement significantly decreases the volume of waste to be disposed of while increasing the strength. For the case described in Example 2, the fixation method increased the density from 0.51 g/cm^3 (wet sludge density) to 0.84 g/cm^3 (concrete density) while decreasing the volume of the waste by 39.2%. By using the fixation method developed in this project, the resulting volume is only 16% of the volume produced using the tentative recipe given in the conceptual design report.

CONCLUSIONS

The following conclusions are drawn from this study:

1. The cement-fixed waste passes the EPA standard leach test for toxic substances;
2. The addition of cement improves the handling characteristics and produces a permanent monolithic waste which could be reclaimed if necessary;
3. A structural strength of 300 psi, which provides adequate permanency, can be obtained with little increase in volume by adding cement; and
4. Dewatering sludge significantly reduces the cement requirement and landfill space requirement for sludge disposal.

REFERENCES

1. C. P. McGinnis, "Solid Waste Disposal Study," *Compilation of papers Presented at the 1979 UCC-ND Waste Management Seminar, March 6-7, 1979 (U);* Union Carbide Corporation, Nuclear Division, Oak Ridge Gaseous Diffusion Plant, Oak Ridge, Tennessee; March 1979 (K/C-1347).

2. "Environmental Protection Agency, Hazardous Waste: Proposed Guidelines and Proposal on Identification and Listing," Section 250.13, *Federal Register,* Volume 43, No. 243, December 18, 1978.

3. "DOE Maximum Permissible Concentration Guidelines For A Mixture of Uranium Isotopes in an Uncontrolled Area," *DOE Manual, Appendix 0524, Annex A, Table II,* March 30, 1977.

THE IMPACT OF THE KENTUCKY HAZARDOUS WASTE REGULATIONS ON THE PADUCAH GASEOUS DIFFUSION PLANT

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ABSTRACT

Kentucky recently passed emergency Hazardous Waste Regulations by which the PGDP was required to register as a generator of hazardous waste. The plant's experience thus far in dealing with the hazardous waste regulations is presented, and plans for compliance are discussed.

(Paper not available for publication)

Prepared for the Department of Energy under
U.S. Government Contract W-7405-eng-26

DEVELOPMENT OF A HAZARDOUS WASTE MATERIALS LANDFILL AT THE PADUCAH GASEOUS DIFFUSION PLANT*

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ABSTRACT

Anticipated promulgation of stringent regulations governing the disposal of hazardous chemical wastes has prompted the development of engineering design work on a new Hazardous Waste Materials Landfill for the Paducah Gaseous Diffusion Plant. A planned element of the FY 1981 Line Item "Control of Water Pollution and Solid Waste, Phase I," the two-module landfill incorporates a leachate monitoring system, a ground-water monitoring system, leachate barrier and surface water collection system for disposal of hazardous waste materials above ground level. Conceptual design criteria and cost information for development of the landfill are provided.

Prepared for the Department of Energy under
U.S. Government Contract W-7405-eng-26

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*KY/G-370

Certain existing and proposed operations at the Paducah Gaseous Diffusion Plant may generate waste materials that could qualify as hazardous and/or toxic substances according to guidelines in 40 CFR 250 (Federal Register, Volume 43, No. 243, December 18, 1978). Recognizing this potential at PGDP, specific facilities have been proposed in the FY-1981 Line Item Environmental Protection and Safety Modifications, Phase 1, 81-R-506 (formerly Control of Water Pollution and Solid Waste, Phase 1, 81-OR-16) to treat and dispose of all such waste materials in an environmentally acceptable manner. These facilities include a dewatering and chemical fixation operation, a temporary storage pad and a landfill.

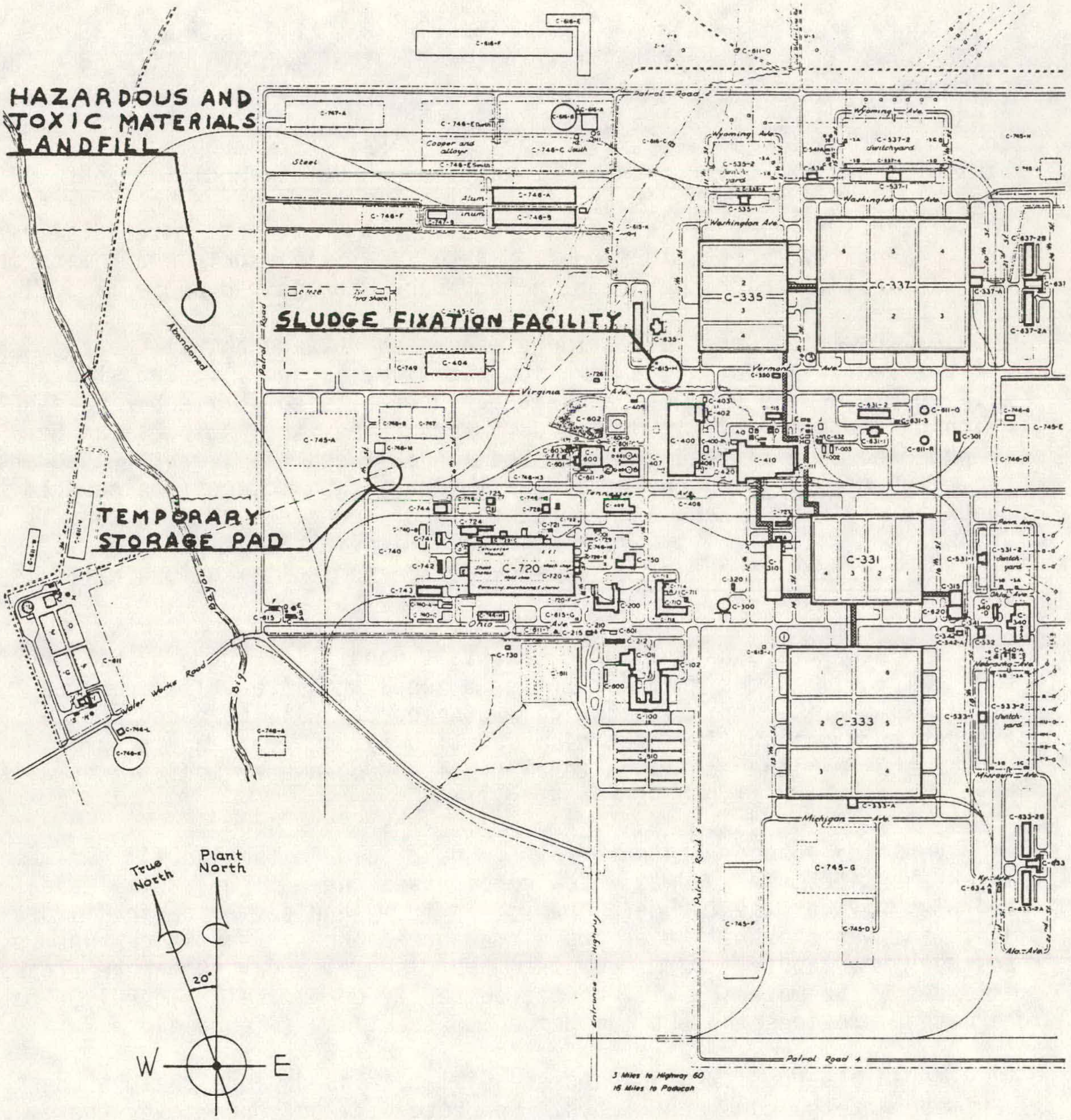
All hazardous and toxic sludge generated at Paducah will be chemically fixed in a new Sludge Fixation Facility (Figure 1). The sludges will be mixed with concrete and placed into molds to form concrete blocks weighing approximately 1,000 pounds. When cured, these blocks can be transported on a flatbed truck to the landfill or to a Temporary Storage Pad (Figure 2). This storage pad will be an 1,800 square foot covered concrete pad with diking around the pad and a concrete sump to contain any leak or spill from the storage area. Materials destined for disposal in the landfill, which are not amendable to chemical fixation, will also be stored on this pad.

The new Hazardous and Toxic Materials Landfill (Figure 3) will be a two cell facility designed for proper disposal of materials generated over a 15-year period. The two cell concept, as will be noted shortly, assures the availability of a disposal site in the event any problem develops with either cell. A total of nine groundwater monitoring wells have already been placed at the site.

Vehicles loaded with materials to be placed in the landfill will enter the site on a roadway which encompasses the entire landfill area and also divides the two developed cells from land set aside for future use. The vehicles will then travel on a cell access road which runs up and over the landfill berm down into the disposal area. Concrete blocks or other waste material will be placed neatly on the cell floor in a pattern that provides the optimum degree of stability (Figure 4).

Materials not fixed in concrete will be placed along the outside perimeter of the concrete blocks. Concrete will be poured over these materials to fix them in place and to provide a stable subsurface for the next layer of concrete blocks. Specific features of the new landfill were carefully designed to insure compliance with laws and regulations, efficient operations, low maintenance, optimum monitoring capability and minimum environmental insult.

Construction of the landfill will be achieved by excavating each cell to a depth of seven feet and sloping the inside walls at a three to one ratio. The initial bottom layer will be a one foot thick layer of sand in which the Leachate Detection System will be located. This will

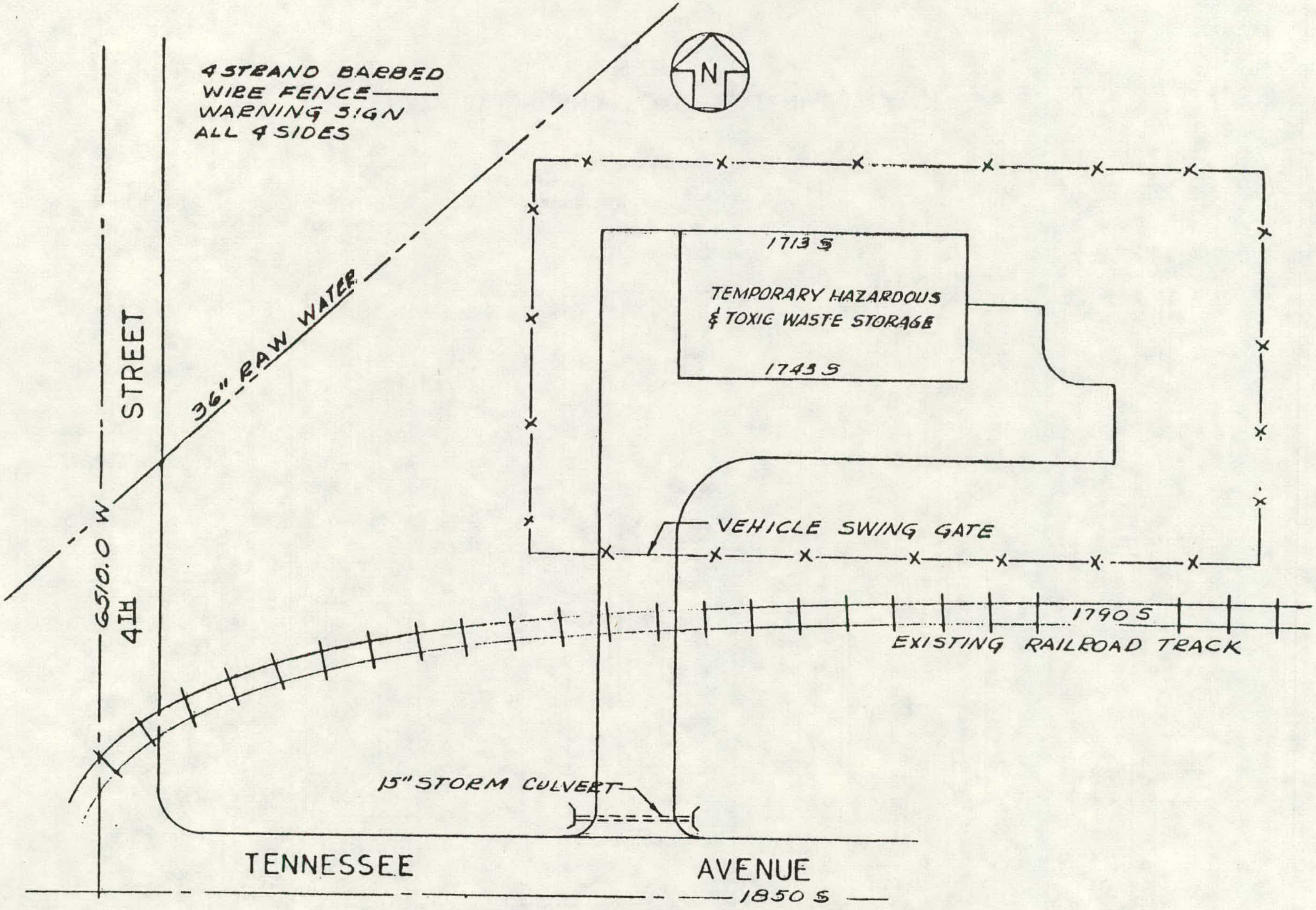


PADUCAH GASEOUS DIFFUSION PLANT

HAZARDOUS AND TOXIC MATERIALS TEMPORARY STORAGE AND LANDFILL

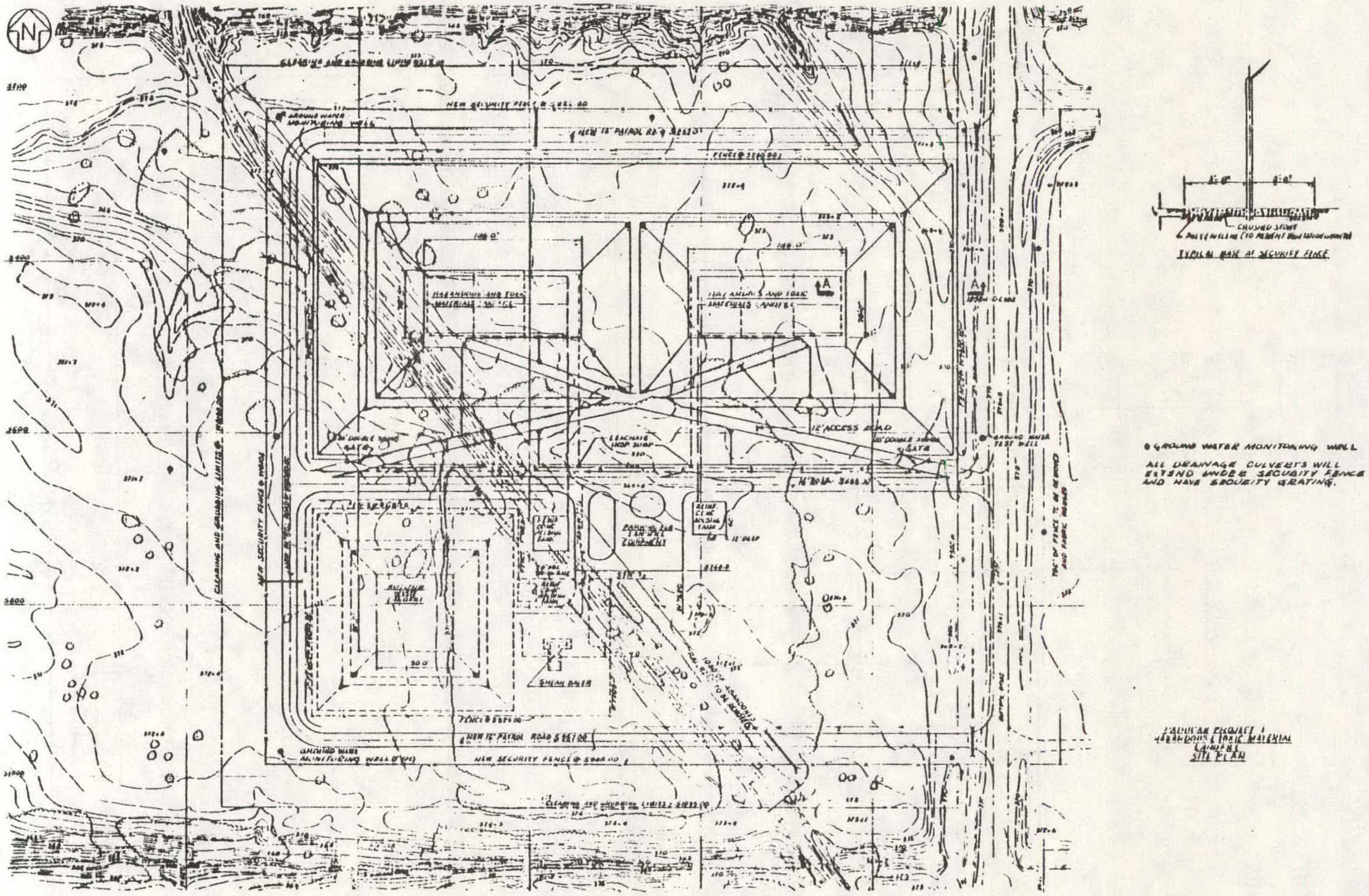
LOCATION PLAN

FIGURE 1



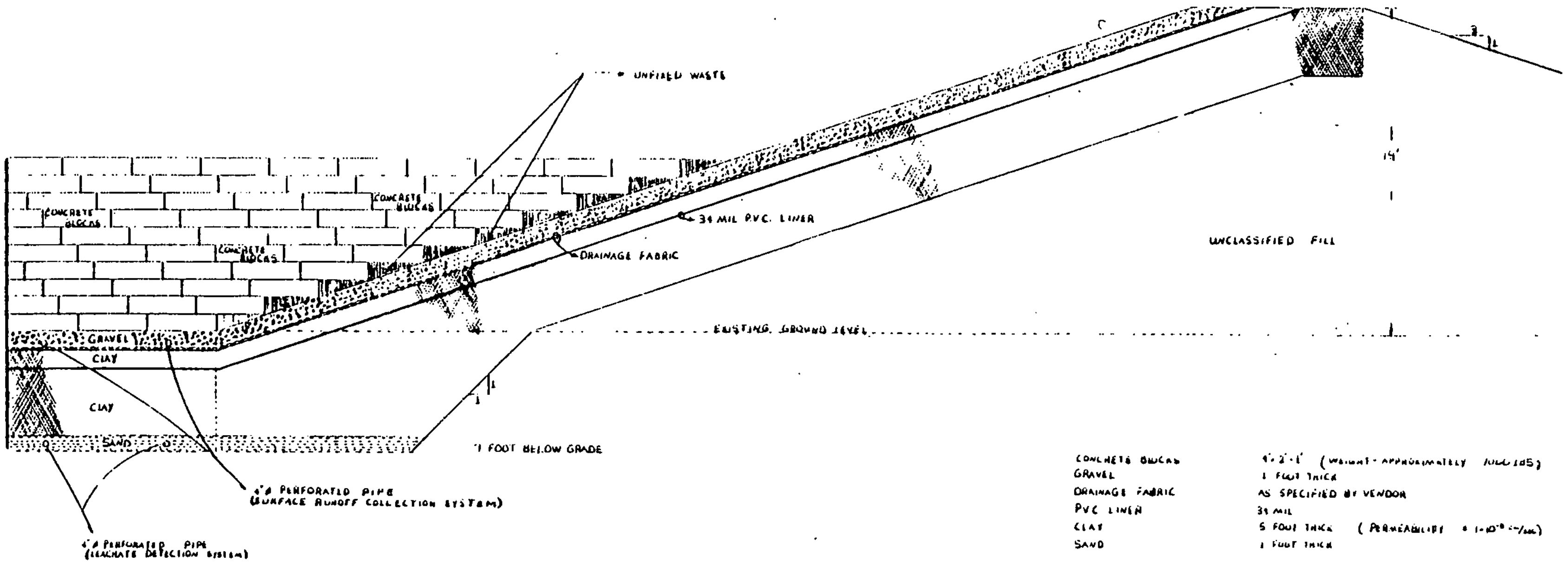
TEMPORARY HAZARDOUS AND TOXIC WASTE STORAGE
SITE PLAN

FIGURE 2



HAZARDOUS AND TOXIC MATERIALS LANDFILL
SITE PLAN

FIGURE 3



CONCRETE BLOCKS	4'×2'×1' (WEIGHT - APPROXIMATELY 1000 LBS)
GRAVEL	1 FOOT THICK
DRAINAGE FABRIC	AS SPECIFIED BY VENDOR
PVC LINER	30 MIL
CLAY	5 FOOT THICK (PERMEABILITY ≤ 1×10^{-7} cm/sec)
SAND	1 FOOT THICK

HAZARDOUS AND TOXIC MATERIALS LANDFILL
TYPICAL SECTION

FIGURE 4

be covered by a four foot thick layer of clay (permeability = 1×10^{-7} cm/sec), 34 mil PVC liner and an additional one foot of clay. A layer of drainage fabric will cover the clay. The final layer will be one foot of graded gravel in which the Surface Runoff Collection System will be located. These layers and sections will cover both the bottom and inside walls of the landfill.

The Leachate Detection System in the bottom layer of sand is a network of four inch perforated pipe and selectively located sampling wells. Periodic sampling of liquid in the wells should detect any breach of the landfill's protective liner system. In addition, the system layout will serve to minimize the difficulty of finding the approximate breach location.

Precipitation falling on the landfill cell will flow by gravity to the Surface Runoff Collection System. Surface runoff water will enter the perforated pipe network and gravity flow to a 4,000 gallon capacity reinforced concrete holding tank. Each cell has its own holding tank. Analysis of the collected water will determine the proper manner of disposal.

A subsurface investigation of the proposed landfill site at PGDP revealed that depth to groundwater ranges from 22 feet to 51 feet. Such knowledge affords PGDP the opportunity of excavating to a depth of seven feet and installing the protective liner system. This method of construction should reduce any adverse consequences of seismic activity (PGDP is located in an area of Zone 3 seismic activity) thereby enhancing long-term protection of groundwater. It also permits disposal operations to commence at very near the same surface elevation of surrounding terrain which will minimize any adverse consequences from tornadic events.

While PGDP plans to construct its landfill in the manner described, it should be noted that the design could be modified to satisfy site specific requirements. With land being a prime commodity at most facilities in need of a hazardous material landfill, the PGDP design could be modified to make use of an area which had been previously considered but rejected. Land with a high groundwater table is one example of an area where the PGDP design could be feasible.

Land used for the PGDP Hazardous and Toxic Materials Landfill will be restricted for future use after closure and capping of the site. Any future use of the land will have to be conducted in a manner that will prevent disturbance of the integrity of the final cover, barrier and monitoring systems.

CONSOLIDATION OF WASTE DISPOSAL ACTIVITIES AT THE PGDP*

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Fabrication and Maintenance Division
PGDP/UCC-ND
Paducah, Kentucky

ABSTRACT

Various waste disposal activities at the PGDP were consolidated in May 1979 into a line department function. This action was precipitated by the need to provide a more timely and efficient response to the implementation of state and federal guidelines and to provide a coordinated interface with waste related project planning and site utilization. Significant activities are discussed.

All open-type disposal sites previously receiving low-level radioactive waste have been closed, and low-level wastes are now disposed of in a single site. One additional burial ground is being held in standby, but future use of the site is currently not anticipated. Biodegradation of organic waste (primarily oils) has been discontinued due to the ineffectiveness of the operation. Significant operational changes have also been implemented for the sanitary and industrial landfills. In all of these areas, documentation has been improved to meet the "cardle to grave" concept of waste disposal.

Major problem areas remaining include contaminated scrap metal disposal, UF_4 drum disposal, and development/implementation of a management system for hazarous wastes and waste oils.

An additional activity has been the assessment of land areas needed to accommodate present and future waste disposal operations, as well as other site needs. This study culminated in a systematically structured plan for site land use.

Prepared by the Department of Energy under
U.S. Government Contract W-7405-eng-26

*KY/F-129

CONSOLIDATION OF WASTE DISPOSAL ACTIVITIES AT THE PGDP

P. A. Getz and H. Pulley
PGDP/UCC-ND, Fabrication and Maintenance Division

INTRODUCTION

In May of 1979, various waste disposal activities/responsibilities at the PGDP were consolidated with the formation of the Material Terminal Management Department in the Fabrication and Maintenance Division. The basic responsibility assigned to the department was the administration of waste disposal functions, including transportation, temporary storage, and terminal disposal of all scrap and waste materials generated at the PGDP. This paper highlights some of the activities related to this responsibility, and addresses anticipated future problems in the area of waste disposal.

ORGANIZATION

As both the magnitude and complexity of environmental regulations increased, advantages were identified associated with a more consolidated waste disposal program at the PGDP. Some of these advantages are outlined in Figure 1. Prior to consolidation several divisions, and various sections within these divisions, were directly involved in waste disposal operations. This, at times, proved somewhat inefficient with respect to the timely implementation of guideline changes, facility planning, and overall management of waste disposal operations. Consequently, these various operations were consolidated into a Line Function. Organizational makeup is outlined in Figure 2.

OPERATIONAL ACTIVITIES

The disposal of low-level radioactive waste (LLW) at the PGDP is under the control of DOE; however, pending legislation could extend NRC's authority to include any new and/or existing DOE site, with some involvement of states and EPA. DOE disposal criteria for solid LLW, draft NRC regulations (Draft 10CFR61), and proposed EPA regulations all emphasize volume reduction, future generation risk assessments, incorporation of natural and engineering barriers to nuclide migration, and leachate control. Disposal practices were reviewed relative to these areas, as well as the total operating aspects of LLW disposal. This review revealed that two "open-trench type" disposal sites receiving metal shavings from the C-720 shops could be closed and the shavings stored in drums for future smelting and that only 1-2% of the waste going to a third site was contaminated. This contaminated portion of the waste could be easily segregated, drummed, and stored in the remaining active disposal site, C-404. These actions have been implemented.

The remaining active site, C-404, is a converted holding pond which was constructed with an on-grade tamped clay bottom and tamped clay-lined, Waste Disposal Activities at the PGDP were Consolidated to:

1. Assure that waste disposal is an integral consideration of future project planning.
2. Provide a more effective and better regulated disposal program.
3. Provide a timely response to changes in regulatory requirements.
4. Provide a more effective interface between
    (a) requirements interpretation,
    (b) short- and long-term planning,
    (c) implementation of criteria,
    (d) day-to-day activities.

Figure 1

The Material Terminal Management Department Encompasses the Total Waste Disposal Program.

1. Hourly personnel provide disposal services.
2. Adequate equipment is assigned to the department.
3. Progessional personnal provide guidance on
    (a) analytical requirements,
    (b) waste processing and/or storage,
    (c) site and/or equipment needs.

Figure 2

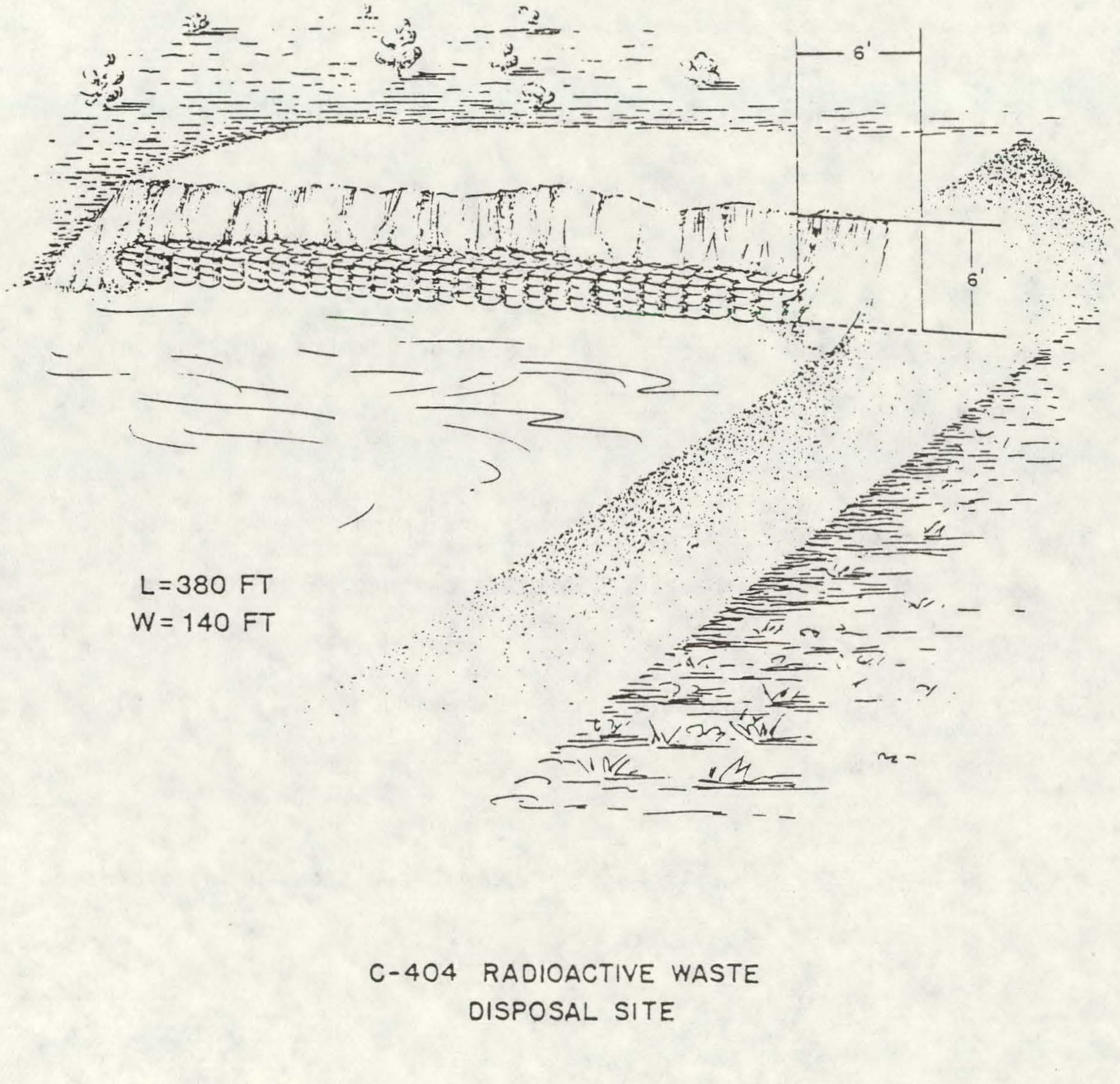
six-foot high dikes enclosing an area 380 feet long by 140 feet wide. Several years ago the area was covered with dirt and clay to a level approximately six feet above ground level and slightly mounded to facilitate runoff. This upper layer now serves as the base for the disposal of drummed uranium containing wastes. Once a sufficient number of drums has accumulated, a dirt and clay cover is applied. A schematic of the site is shown in Figure 3. This site has a remaining area sufficient to accommodate low-level plant waste for another eight years. A new site or expansion of the existing site will be required at that time.

Closure of the three sites necessitated that greater control be placed on material entering C-404. These controls consist of volume reduction, more aggressive segregation, and maximum space utilization. Radioactive waste burial criteria were provided by the PGDP Environmental Control Department and are summarized in Figure 4.

Another area in which changes were made involved the disposal of waste oils by landfarming. Several plants have indicated very successful landfarming operations; however, the process at the PGDP proved ineffective and was discontinued. This was attributed primarily to undesirable geological and climatological features. Soils in the area are largely alluvial in nature, covered with a blanket of loess (fine clay). Recent drilling for monitoring wells in an area close to the oil disposal plots indicated the depth of the loess at roughly eight feet and having a determined permeability of 10^{-3} to 10^{-6} cm/sec. While the climate in the area is moderate, approximately 45 inches of precipitation occurs annually. The rainfall tends to occur in short periods of intense precipitation. The fine nature of the upper clay results in a tendency to saturate the top of the soil quickly, with rainwater then accumulating in any depressed area. Thus, without extensive excavation and addition of soil with more suitable characteristics, landfarming of waste oils is not considered to be an effective option for the PGDP.

Currently, waste oils are being stored awaiting the completion of a receiving-distribution facility. A schematic of the facility is shown in Figure 5. It simply consists of a diked concrete base, three 8,000-gallon tanks, transfer capabilities, a sampling station, and space for storing sludge and/or other organics. Drums of oil will be brought to the facility, sampled, and characterized. Noncontaminated oil will be placed in a tank for reclamation off-site. Contaminated oils will be placed in a spearate tank for later disposal, either in the existing PGDP steam plant, or by incineration if an incinerator is made available in the Nuclear Division. By this segregation-characterization mode of operation, it is felt that a significantly larger percentage of the oil generated can be reclaimed off-site.

UF_4 drum disposal has been an increasing problem at the PGDP. UF_4, currently being supplied to the Department of Defense, is pulverized, screened, and repackaged in 55-gallon drums which meet DOT requirements. This repackaging results in the generation of "waste" drums which contain a slight amount of UF_4; consequently, they are classified as LLW. A drum compactor and portable vacuum cleaner has been purchased to clean and



C-404 RADIOACTIVE WASTE
DISPOSAL SITE

Figure 3

PGDP Low-Level Radioactive Waste Burial Criteria

1. Transuranic content is not to exceed 10 microcuries/kilogram.

2. Technetium-99 content is not to exceed 0.1 curies/kilogram.

3. Uranium-235 assay is not to exceed 0.7% or uranium recovery be deemed infeasible.

4. All precipitation sludge, reject UF_4, trapping materials, floor sweep, etc., must be packaged in plastic-lined 55-gallon drums.

5. Scrap metal (non-pyrophoric) must be drummed or cut to size to minimize volume.

6. Small radioactive sources must be drummed and encased in concrete.

Figure 4

THE FUTURE OIL HANDLING SYSTEM IS BASED ON SAMPLING AND SEGREGATION

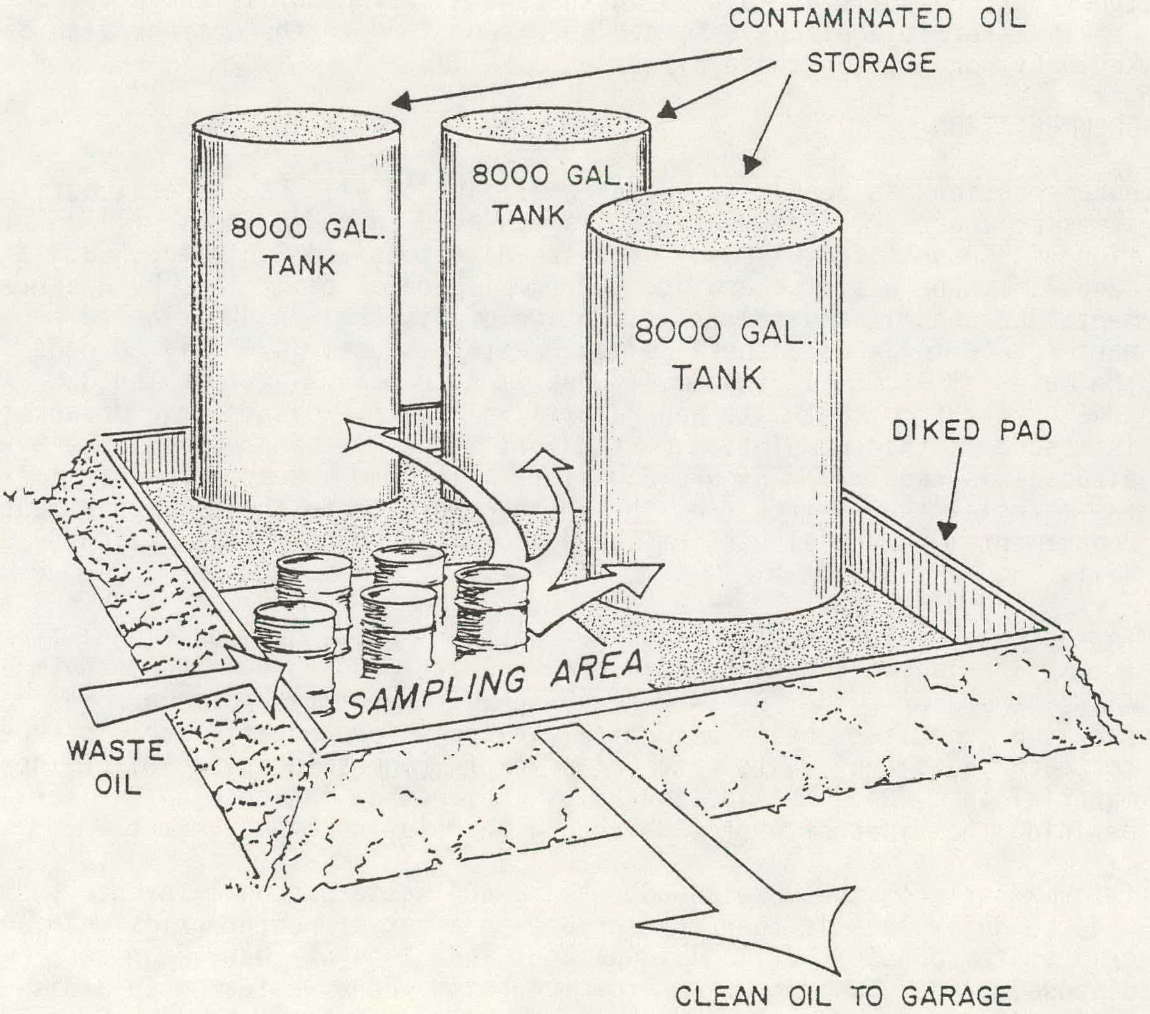


Figure 5

compact the current inventory of drums. This operation will provide a volume reduction of approximately 10. The compacted drums will be returned to the contaminated scrap yard and terminal disposal will be accomplished by the method(s) selected to dispose of the contaminated scrap metal. A drum washing and compacting system is currently being installed as part of the pulverizer-screening system and in the future drums will be washed and compacted as they are generated.

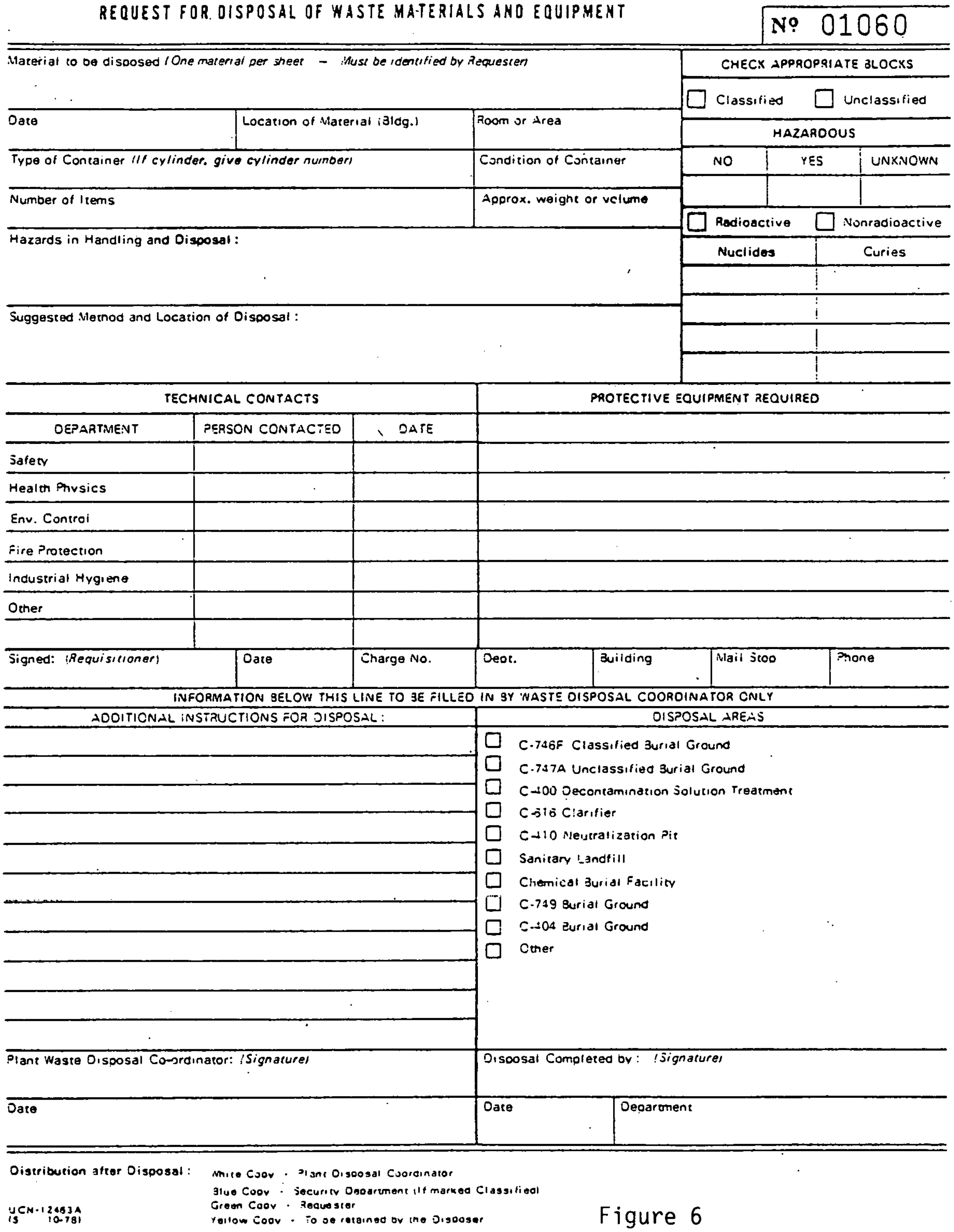
Other changes have been enacted in the operation of the Sanitary and Industrial Landfills. These changes have primarily been made to provide better leachate control. At the Sanitary Landfill rubbish is deposited in a slightly inclined trench and compacted and covered daily (when possible). The sides of the site are sloped to an approximate 3:1 ratio. Construction spoils are placed in the Industrial Landfill and covered weekly. Permit applications have been submitted to the Commonwealth of Kentucky for both of these sites.

DOCUMENTATION

Documentation has been made an integral part of all the disposal activities at the PGDP. Documentation is achieved in three steps: (1) completion of "Request for Disposal of Waste Materials and Equipment," UCN-12463A, by the waste generator, (2) completion of daily logs by departmental personnel, and (3) transcription of disposal information to a master grid for each disposal site. Waste disposal is initiated once the Material Terminal Management Department receives a completed UCN-12463A form from the waste generator. For routine disposals a "blanket" is issued so that completion of the form is not necessary each time a disposal is required. Figure 6 depicts this form. Responsibility for the material then shifts from the waste generator to the MTM Department. Departmental personnel perform the disposal and record this action on a daily log.

In the case of low-level radioactive waste disposal, an additional form (shown in Figure 7) must be completed and attached to UCN-12463A by the waste generator. The "C-404 Waste Disposal Inventory" form requires that the generator obtain a chemical analysis for specific radioisotopes for each package of waste material prior to requesting disposal of the material in C-404. This action helps ensure that the internal criteria defining the types of wastes which can be held in C-404 are met.

Information from the UCN-12463A, the "C-404 Waste Disposal Inventory," and the daily logs is then transcribed to a set of master grids. This grid system consists of individual logs and a set of charts for each disposal area. Two mechanisms for recording where wastes go in a disposal site are used depending on the disposal facility chosen. Disposal of wastes in C-404 Radioactive Waste Burial Facility and the C-746-F Classified Burial Facility is documented by use of a two-dimensional array system. Disposal at other sites such as the C-746-K Sanitary Landfill is documented in a one-dimension fashion such as the portion of the trench used each quarter.



REQUEST FOR DISPOSAL OF WASTE MATERIALS AND EQUIPMENT

Nº 01060

Material to be disposed *(One material per sheet — Must be identified by Requester)*			**CHECK APPROPRIATE BLOCKS** ☐ Classified ☐ Unclassified
Date	Location of Material (Bldg.)	Room or Area	**HAZARDOUS**
Type of Container *(If cylinder, give cylinder number)*		Condition of Container	NO | YES | UNKNOWN
Number of Items		Approx. weight or volume	☐ Radioactive ☐ Nonradioactive
Hazards in Handling and Disposal :			**Nuclides** | **Curies**
Suggested Method and Location of Disposal :			

TECHNICAL CONTACTS			PROTECTIVE EQUIPMENT REQUIRED
DEPARTMENT	PERSON CONTACTED	DATE	
Safety			
Health Physics			
Env. Control			
Fire Protection			
Industrial Hygiene			
Other			

Signed: *(Requisitioner)*	Date	Charge No.	Dept.	Building	Mail Stop	Phone

INFORMATION BELOW THIS LINE TO BE FILLED IN BY WASTE DISPOSAL COORDINATOR ONLY

ADDITIONAL INSTRUCTIONS FOR DISPOSAL :	DISPOSAL AREAS
	☐ C-746F Classified Burial Ground ☐ C-747A Unclassified Burial Ground ☐ C-400 Decontamination Solution Treatment ☐ C-616 Clarifier ☐ C-410 Neutralization Pit ☐ Sanitary Landfill ☐ Chemical Burial Facility ☐ C-749 Burial Ground ☐ C-404 Burial Ground ☐ Other
Plant Waste Disposal Co-ordinator: *(Signature)*	Disposal Completed by : *(Signature)*
Date	Date | Department

Distribution after Disposal :
White Copy - Plant Disposal Coordinator
Blue Copy - Security Department (If marked Classified)
Green Copy - Requester
Yellow Copy - To be retained by the Disposer

UCN-12463A
(S 10-78)

Figure 6

C-404 DISPOSAL INVENTORY

Description of Contents:

Source (Building, Process, etc.):

Date Delivered to C-404:

Batch # (if applicable):

Date Disposed: *

# of Drums:

Person Responsible:

Location:

Phone:

Drum #	Net Weight (Pounds)	Grid * Location	Sample # (if applicable)	ANALYSES **					
				U (gr/gr)	^{235}U(%)	^{237}Np(ppb)	^{239}Pu(ppb)	^{230}Th(ppb)	^{99}Tc(ppm)

Comments:

---

* To be completed by Material Terminal Management Department.

** For drums containing similar material, a composite sample is sufficient.

PT–2277

Figure 7

Much of this information attained from these efforts is inventory-type information and is not required by the regulatory agencies; however, benefits from this information have resulted. The need for an expansion to the classified burial yard was identified and has been scheduled, while a FY-83 Line Item Project for a LLW site has been deferred.

Improvements to the documentation will continuously be made. The development and implementation of a computer program to handle this data is being planned. Transfer of this data to a computer file will help achieve easier and more effective data storage, retrieval, and manipulation.

SITE UTILIZATION

In order to determine whether the Paducah plant-site is adequate to support all existing, planned, and projected operations, a site utilization study was conducted to systematically review and define "reserved" land areas necessary for continued plant operations. Land areas immediately surrounding the plant-site have been conditionally leased to the Kentucky Fish and Wildlife Department for use as a game reserve; recall of this land is possible should this study reveal the need. This evaluation also provides a mechanism for realizing effective land utilization and is considered to be a "working and planning" tool which will be revised and updated as conditions warrant.

FUTURE PROBLEMS

Existing and/or anticipated guidelines indicate several areas where future problems seem imminent relative to disposal operations. Some of the more significant problems that will linger for the next few years are (1) PCB disposal, (2) contaminated metal scrap disposal, (3) hazardous waste disposal, and (4) oil disposal. Planned or anticipated systems to deal with these areas are (1) a new sanitary landfill, (2) expansion of classified landfill, (3) storage pad and fixation facility of hazardous landfill, and (4) a PCB incinerator. Some systems, such as a PCB incinerator and a scrap metal smelter, would probably constructed at one of the Oak Ridge sites since such a facility could serve all UCC-ND plants.

THE ORGDP
HAZARDOUS MATERIALS MANAGEMENT PROGRAM*

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Environmental Management Group
Oak Ridge Gaseous Diffusion Plant

ABSTRACT

A description of the development and subsequent implementation of the ORGDP Hazardous Materials Management Program is presented. In addition to a general discussion of the major aspects of the program, specific examples of problems and solutions are presented.

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*Based on work performed at the Oak Ridge Gaseous Diffusion Plant operated by the Union Carbide Corporation, Nuclear Division, for the Department of Energy.

THE ORGDP HAZARDOUS MATERIALS MANAGEMENT PROGRAM

The uranium enrichment industry was born out of a massive effort to produce a product while simultaneously developing the technology to do so. A great variety of chemicals were, and continue to be, used in the enrichment process, development efforts, and support operations. New laws written in the 70's focused fresh attention on chemical hazards and established new priorities for their handling and disposal. The Occupational Safety and Health Act, the Clean Air Act, the Clean Water Act, the Toxic Substance Control Act, and finally the Resource Conservation and Recovery Act delivered the impetus to radically change chemical handling and disposal practices throughout industry in America.

The challenge of these laws is being met through a number of procedures and programs at ORGDP, including the Hazardous Materials Management Program.

Properly used and handled hazardous materials present minimal risk. Knowing the hazards of a material and working with it in accordance with current instruction and procedures virtually eliminates any hazard.

The problem with hazardous materials stems from their inappropriate or improper procurement, storage, transportation, use and disposal; which may arise from ignorance, convenience, or intent. Excessive exposure to hazardous materials, for whatever the reason, is a problem that can result in occupational disease and death. Introducing new chemical products to the plant without considering their hazards, precautions for use, or developing disposal strategies invites compounded problems in the future. "Pack-ratting" chemicals for future use or stashing them away instead of disposing of them properly may create hazardous conditions and complicated disposal problems when a disposal must eventually be made. Incompatible storage of chemicals, unidentified materials, deteriorated containers, and improper disposals of hazardous materials endanger life, property, and the environment.

An effort has been made at ORGDP to address the numerous problems associated with chemical products. The Hazardous Materials Management Program, which is augmented by a Standard Practice Procedure, provides the necessary cradle to grave control over chemicals at ORGDP by centrally controlling and monitoring hazardous materials operations. A general description of the program, including the major aspects of the procedure, is presented in the following paragraphs.

It is the policy of the ORGDP to effectively manage hazardous materials by providing plant personnel with guidelines to safely and correctly procure, transport, store, and use hazardous materials. Specific disposal guidelines are found in a separate procedure.

The Hazardous Materials Coordinator's position was established to direct and coordinate the program as well as provide training, guidance, assistance and information regarding the procedure and hazardous materials in general. Although the Hazardous Materials Coordinator oversees the program, it is each division superintendents' responsibility to have a program implemented and properly functioning in their respective divisions.

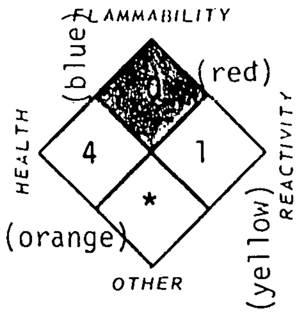
The definition of a hazardous material is based upon a rating scheme for chemicals (borrowed from the National Fire Protection Association, and modified) which has been adopted by ORGDP and the other Nuclear Division plants. Under this system, all materials are rated on a "zero" to "four" scale for health, fire, reactivity, and criticality safety with other "special hazards" noted separately. A rating of "zero" indicates no hazard while a rating of "four" indicates an extreme hazard. Any material rated a "three" or "four" in any one or more of the four hazard categories is a controlled hazardous material subject to the Hazardous Materials Procedure. A colorful hazard diamond divided into four colored segments is used as a label for hazardous materials. Each segment of the diamond represents one of the hazard categories and each is rated "zero" to "four". This diamond, with the name of the material above it, provides quick information about the chemical. Figure 1 is an example of the hazard diamond.

Each of the various aspects of the program is addressed separately in its own section. Procurements rely on review by the requisitioner, a divisional representative, and a Stores or Purchasing individual. A more detailed discussion of this aspect of the procedure is presented later. Transportation of hazardous materials is guided by Department of Transportation regulations found in Title 49, Code of Federal Regulations, for off-site shipments; while in plant movements merely require labeling and protection from shifting materials on or in the vehicle. The section of the procedure addressing use of hazardous materials sets forth guidelines for labeling, training employees, posting Control Hazardous Materials cards, and responding to chemical releases. The storage section of the procedure stipulates requirements for labeling, marking, and segregation of materials, as well as physical storage area requirements.

The key to successful hazardous material control is the control of procurement. Under the ORGDP program, procurements of hazardous materials must be carefully reviewed and recorded. The presence of a hazardous material in the plant is subsequently controlled with accountability for materials serving as the means to that end. Direct procurements must be reviewed for hazards and provided with a hazard rating by the Hazardous Materials Coordinator or the Industrial Hygiene Group.

A person, from the users division, on the authorized signature list for hazardous materials must review the needs for the material and sign the requisition before it can be processed. The receiving report for the material is forwarded to the Computer Science Department for keypunching and subsequent listing on the ORGDP Hazardous Materials Accountability Report. This report lists all hazardous materials procured since February 1979 as well as the persons accountable for each of the

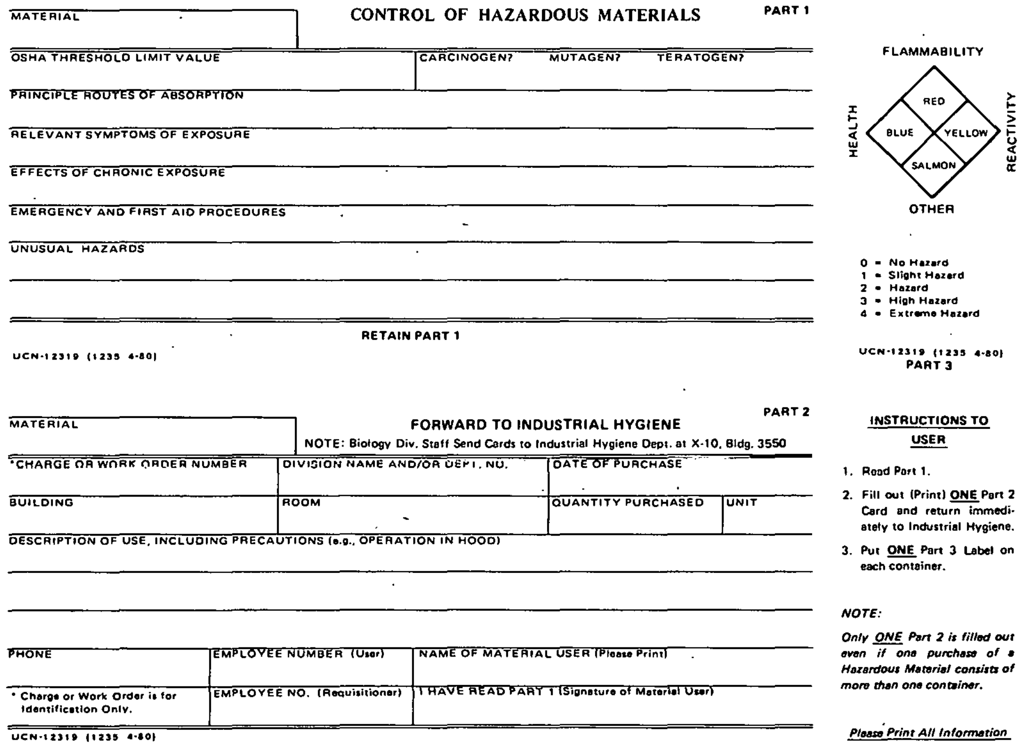
Nitric Acid



* oxidizer

0 = *No Hazard*
1 = *Slight Hazard*
2 = *Hazard*
3 = *High Hazard*
4 = *Extreme Hazard*

Figure 1 Hazard Diamond'



MATERIAL

CONTROL OF HAZARDOUS MATERIALS **PART 1**

OSHA THRESHOLD LIMIT VALUE
CARCINOGEN? MUTAGEN? TERATOGEN?
PRINCIPLE ROUTES OF ABSORPTION
RELEVANT SYMPTOMS OF EXPOSURE
EFFECTS OF CHRONIC EXPOSURE
EMERGENCY AND FIRST AID PROCEDURES
UNUSUAL HAZARDS

RETAIN PART 1

UCN-12319 (1235 4-80)

MATERIAL

PART 2

FORWARD TO INDUSTRIAL HYGIENE

NOTE: Biology Div. Staff Send Cards to Industrial Hygiene Dept. at X-10, Bldg. 3550

*CHARGE OR WORK ORDER NUMBER
DIVISION NAME AND/OR DEPT. NO.
DATE OF PURCHASE
BUILDING
ROOM
QUANTITY PURCHASED
UNIT
DESCRIPTION OF USE, INCLUDING PRECAUTIONS (e.g., OPERATION IN HOOD)
PHONE
EMPLOYEE NUMBER (User)
NAME OF MATERIAL USER (Please Print)
* Charge or Work Order is for Identification Only.
EMPLOYEE NO. (Requisitioner)
I HAVE READ PART 1 (Signature of Material User)

UCN-12319 (1235 4-80)

0 = No Hazard
1 = Slight Hazard
2 = Hazard
3 = High Hazard
4 = Extreme Hazard

UCN-12319 (1235 4-80)
PART 3

<u>INSTRUCTIONS TO USER</u>

1. Read Part 1.
2. Fill out (Print) ONE Part 2 Card and return immediately to Industrial Hygiene.
3. Put ONE Part 3 Label on each container.

NOTE:

Only ONE Part 2 is filled out even if one purchase of a Hazardous Material consists of more than one container.

Please Print All Information

Figure 2 Control of Hazardous Materials Card materials and their respective locations. Quarterly inventory cards, sent to the chemical holders, provide a mechanism to update the monthly accountability report and ensure that a physical check for the hazardous materials takes place.

If the hazards of a material cannot be determined from available literature, the manufacturer is requested to provide hazard information, generally in the format of a Material Safety Data Sheet, before the material can be obtained.

Store's stocked hazardous materials are similarly controlled with an authorized signature required for their issuance. These items are identified in the store's catalog by the numerical hazard rating following the name of the material.

The control of hazardous materials, through accountability and quarterly review, provides various interested parties with the opportunity of continually screening the use of hazardous materials through the monthly accountability report. The report is especially useful to the Industrial Hygiene Group for alerting them to chemical related health problems.

The control of hazardous materials, derived from the procedure, serves as a management tool but falls short of fully protecting individuals and the environment. Today's efforts are directed at hazardous materials awareness through education and audits.

An emphasis has been placed on educating plant personnel as to the nature of the hazardous materials they are working with and proper handling and emergency procedures to be followed. Knowledge of the hazards of a material, as well as correct precautions and handling procedures, promotes respect and virtually insures the employees self-protection. Hazardous material training programs are being established for new employees. Control of Hazardous Materials Cards (see figure 2 for an example), issued with each hazardous material, provide a minimum amount of information about the material and are posted or filed in the work area for review by employees at their own convenience.

All containers of materials are required to be identified as to their contents while hazardous materials are required to bear the colorful hazard diamond described earlier.

One week each Spring is dedicated to hazardous materials education. The 1980 hazardous materials week focused on "awareness" as the theme, with a videotape serving as the focal point of the week, and being shown to all employeesa as part of the formal April safety meeting. The hazardous materials week demonstrates management's concern for the hazardous materials program and serves as a mechanism for delivering a specific hazardous materials message. During this week, an attempt is made to put the subject "up front" in the employee's mind through the use of posters, a Nuclear News article, a Plant Managers Bulletin, and, of course, the videotape. The idea is to sell the hazardous materials program to the plant population with hype, and then let the program coast through the rest of the year on momentum and demonstrated concern.

"Demonstrated concern" can best be translated as auditing the hazardous materials program throughout the plant. These audits serve to educate employees and give them personal attention. They learn that hazardous materials awareness is not a once-a-year phenomena but a day-to-day concern. These audits point out unacceptable practices such as incompatible storage of chemicals, and aid in locating potential problems before they become accidents. Audits have turned up unidentified materials, very old chemicals, and chemicals that individuals were unaware of.

Audit reports are prepared and sent to the department supervisor for review and, when needed, remedial action. Copies of these reports are sent to the respective division superintendents, the Industrial Hygiene Group, the Safety Department, the Shift Superintendent, and any other organization affected by an audit. The distribution of the reports has proven to be effective means of insuring correction of problems. Follow-up inspections are generally scheduled three months following the initial audits.

We feel that many benefits have been derived during the first 14 months of hazardous materials management at ORGDP. The quantity of chemicals in the plant has been reduced, and old and unidentified chemicals have been removed for disposal. Plans for utilizing a commercial disposal company on a routine basis have been set in motion. Industrial Hygiene and others have been aided by the information provided in accountability and audit reports. Awareness among employees has been raised to a new level. Hazardous materials problems have been prevented by the new controls and the ongoing audits.

Although hazardous materials management continues to evolve at ORGDP, it has met the challenge of hazardous materials control head-on.

Dup

PROGRESS REPORT ON THE DESIGN OF A LOW-LEVEL WASTE PILOT FACILITY AT ORNL

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A. S. Pruitt

UCC/ND Engineering
Oak Ridge National Laboratory
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ABSTRACT

All low-level radioactive solid wastes, excluding TRU wastes, are disposed of by shallow land burial at the Oak Ridge National Laboratory. Contaminated liquids and sludges are hydrofractured. The TRU wastes are stored in a retrievable fashion in concrete storage facilities. Currently, the capacity for low-level radioactive waste burial at the Oak Ridge National Laboratory is adequate for another six years of service at the current solids disposal rate which ranges between 80,000 and 100,000 cu ft per year. Decontamination and decommissioning of a number of ORNL facilities will be a significant activity in the next few years. Quantities of radioactive materials to be stored or disposed of as a result of these activities will be large; therefore, the technology to dispose of large quantities of low-level radioactive wastes must be demonstrated. The UCC-ND Engineering Division, in concert with divisions of the Oak Ridge National Laboratory, has been requested to prepare a conceptual design for a facility to both dispose of the currently produced low-level radioactive wastes and also to provide a test bed for demonstration of other processes which may be used in future low-level radioactive waste disposal facilities. This facility is designated as the Low-Level Waste Pilot Facility (LLWPF).

This paper describes the status of the conceptual design of a facility for disposal of the subject radioactive waste. The effort will require cooperation between the divisions of the Oak Ridge National Laboratory, the UCC-ND Engineering Division, the Department of Energy, and an Architect-Engineer to accomplish the design of the LLWPF and its construction.

*Operated by Union Carbide Corporation for the U.S. Department of Energy under contract W-7405-eng-26.

The proposed lcoation of the LLWPF is the Thorium Uranium Recycle Facility (TURF), Building 7930. Located at the Oak Ridge National Laboratory, TURF was constructed in the mid-1960s as a part of the Atomic Energy Commission's Thorium Utilization Program. Due to changes in the HTGR recycle program this facility is now available for other uses. The TURF facility has roughly 2200 sq ft of heavily shielded cell area and approximately 5000 sq ft of available unshielded area under roof. Currently it is felt that with minor modifications this facility can be used to house the special facilities and services required for the low-level waste pilot facility.

Progress Report on Design of the Low-Level Waste Pilot Facility

INTRODUCTION

Currently, all low-level radioactive solid wastes, excluding TRU wastes, are disposed of by shallow land burial at the Oak Ridge National Laboratory (ORNL). Presently, the capacity for low-level radioactive waste burial at ORNL is adequate for another six years of service at the current solids disposal rates. However, ORNL facilities will be conducting significant activity on decontamination and decommissioning of certain areas in the next few years. Therefore, the total low-level waste requiring disposal per year will increase significantly.

The Engineering Division, in concert with divisions of ORNL, was requested by DOE to prepare a feasibility study for a facility to dispose of the currently produced low-level radioactive waste and provide a test bed for demonstration of other processes which may be used in future low-level radioactive wastes disposal facilities. This facility has been designated the Low-Level Waste Pilot Facility (LLWPF).

In conjunction with this feasibility study, a low-level waste verification report was conducted to determine, from available data, the volume and composition range of low-level waste produced at ORNL. Due to the nature of work conducted at ORNL, and the limited records which exist on waste volume and composition, the waste verification report represents only a "best-guess" for the low-level waste streams. The following table is the compositional breakdown assumed and the approximate volumes expected for processing through the LLWPF.

Combustible Material	Noncombustible Material
75% Cellulose	45% Metal
20% Plastics	25% Concrete
3% Rubber	25% Soils
1% Metal	5% Ceramics
1% Glass	

Quantity (Annual)	30,000 ft^3 Combustible 50,000 ft^3 Noncombustible
Density Range (lbm/ft^3)	4.5-8 Combustible 50-75 Noncombustible

The proposed location of the LLWPF is the Thorium Uranium Recycle Facility (TURF), Building 7930. The TURF was constructed in the mid-1960s as part of the Atomic Energy Commission's Thorium Utilization Program. Due to changes in the HTGR recycle program, the TURF facility is available for other uses. The TURF facility has roughly 2200 sq ft of heavily shielded cell area and approximately 5000 sq ft of available unshielded area under roof. The third building from the bottom of the photograph in Figure 1 is the TURF building.

The LLWPF will consist of five major systems. These systems are summarized below.

Receiving and Material Handling

Low-level waste from the operations of ORNL stored in containers will be received at the TURF facility as either combustible or noncombustible materials. The noncombustible waste will be in the form of metal framework, instrument racks, ceramics and metal process equipment. The combustible waste will be received in burnable, standardized cardboard boxes approximately 18" x 18" x 24" in size.

An addition to the TURF building will be required to enhance capabilities for receiving and handling of low-level waste material. This addition will be a metal frame prefabricated type building on the south side of the existing TURF building. This addition will house equipment for monitoring waste acceptability along with equipment for size reduction of noncombustible items. Storage prior to transfer to the processing areas will be provided in this area.

Pelletizing

Currently, the method for volume reduction of waste material receiving major attention at ORNL is pelletization. The material will be pelletized and then fed to the existing ORNL hydrofracture operations for final disposal. The pelletizing area will be located on the third floor and will require a large portion of the area above the hot cells in the TURF facility. Figure 2 shows the third floor area where pelletization will be located.

Briefly, the process in this area will include equipment to shred, adjust the moisture content, meter and mix the appropriate ingredients including the coal tar emulsion binder and sodium silicate additives. This material will be fed into a pellet mill which will be an extrusion type pelletizer producing pellets approximately 1/8-in-diam and 1/4-in-long. The pellets will be stored prior to transfer to the hydrofracture site in the material handling area.

ORNL-Photo 9375-1

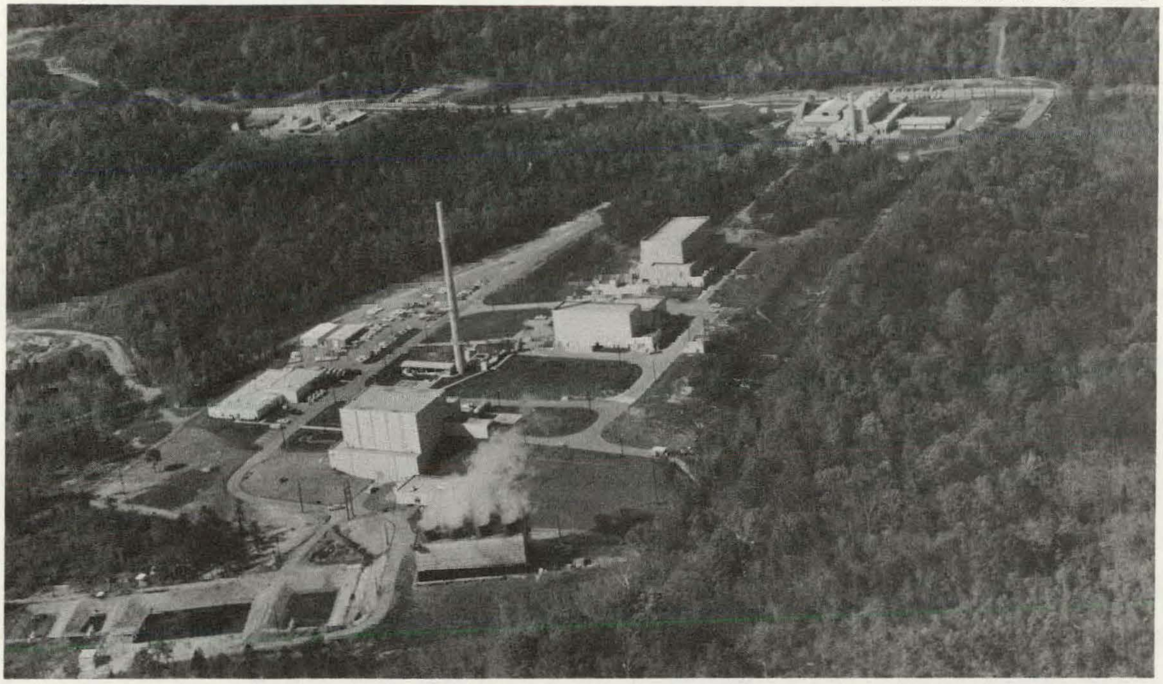

FIGURE 1. Proposed location of the Low-Level Waste Pilot Facility.

ORNL-Photo 0771-78

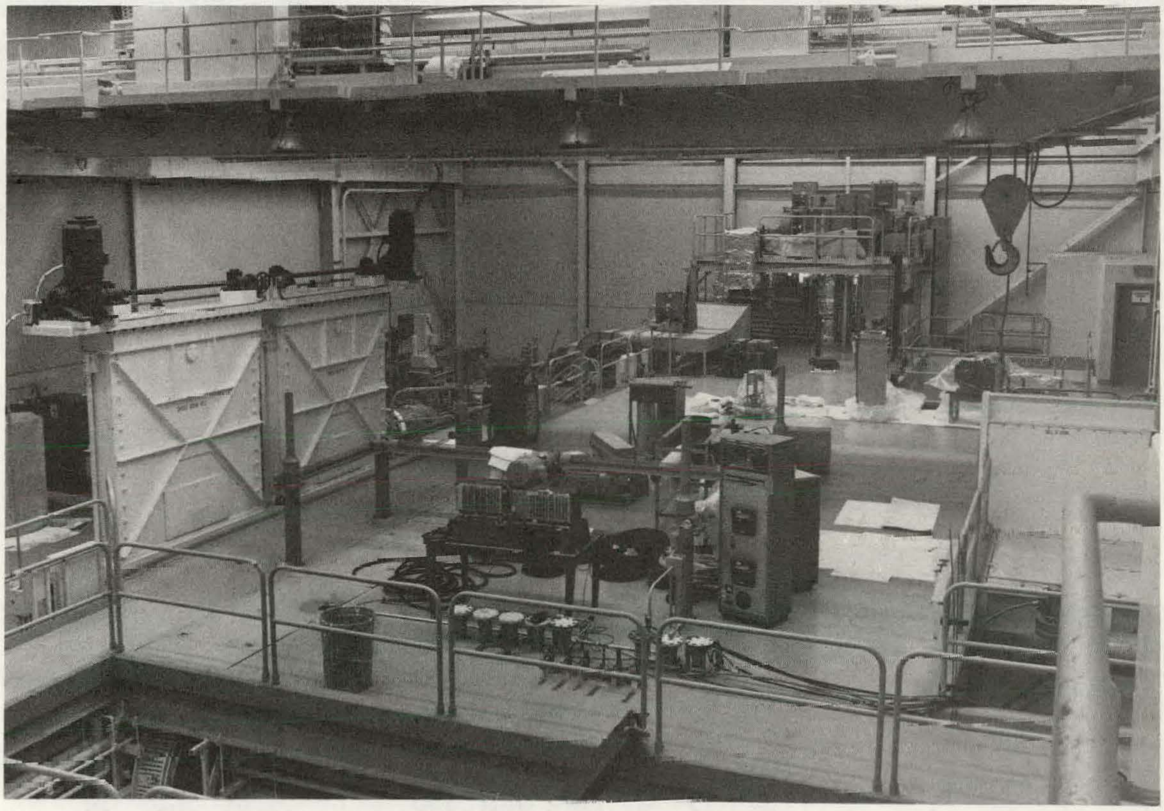

FIGURE 2. Third floor area of the TURF facility.

Incineration

An optional method for volume reduction of combustible waste material is incineration. Presently, the LLWPF will include a system for incineration of treated or untreated waste. The incinerator system will be located in Cell "D" of the TURF facility. Cell "D" is approximately 20 ft by 40 ft long with roughly 25 ft of available head room. Access to the equipment will be achieved by removing the cell roof plug to provide direct access to the equipment from the third floor.

In conjunction with the LLWPF feasibility study a study was conducted by UCC-ND Engineering on present incinerator methods and their ability to meet LLWPF design criteria. The conclusions and recommendations of this study indicate the incinerator system should consist of a batch fed dual chamber controlled air incinerator. The incinerator will be equipped with an automatic ash removal system and an exhaust cleanup system.

Metal, Cutting and Melting

For use in volume reduction of noncombustibles low-level waste material a metal cutting and melting facility is planned for LLWPF. This will be a development system and the equpment to be included will depend on both space availability in the TURF building and funding limitations. Currently, the conceptual design will include an approximately 1000 lb capacity induction furnace for melting ferrous-size-reduced metals and an approximately 300 lb capacity resistance furnace for melting non-ferrous-size-reduced metals. The metal cutting area will be located in the building addition area in conjunction with material handling. The metal melting facility will be located in Cell "C" as shown in Figure 3.

Glass Crushing

To enable the LLWPF faciilty to size reduce noncombustible material such as thin ceramics and glass, an engineering-scale glass crushing system is projected to be installed. This system will consist of an enclosed hammer mill capable of producing size-reduced material for use in ORNL's hydrofracture facility.

CURRENT PROJECT STATUS

The overall project schedule shown in Figure 4 was developed assuming: 1) funding will be made available by DOE so that conceptual design can start by October 1980, and 2) line item funding will be approved for a FY-82 (October 1981) detailed design start.

An Architect-Engineer (A-E)was required for the completion of the feasibility study and will most likely be retained for conceptual design and detailed design for the sake of continuity of effort and also for schedule savings as the A-E selection process need not be repeated. The A-E which has been selected is Bechtel.

ORNL-Photo 0769-78

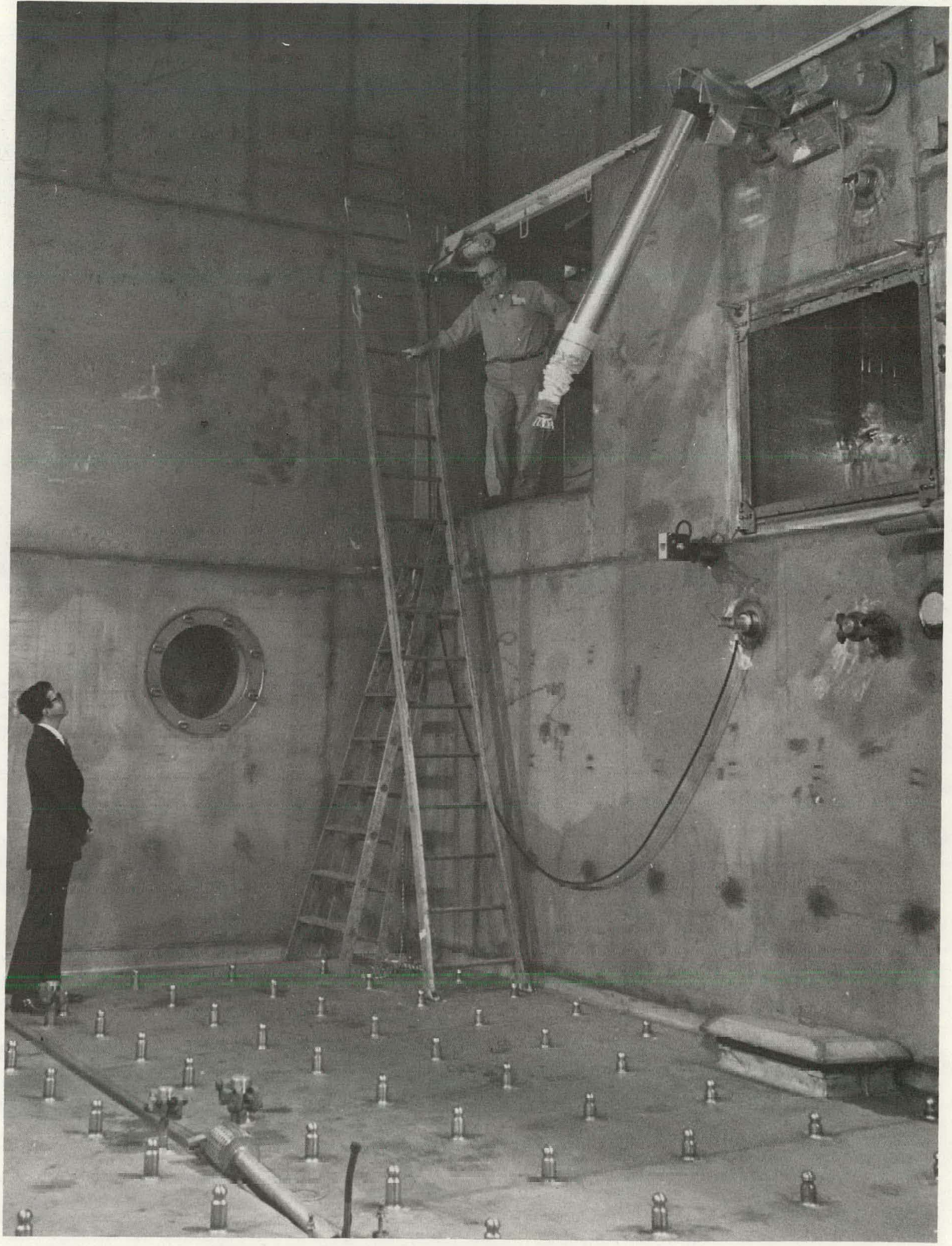

FIGURE 3. Cell "C" of the TURF facility.

NUMBER	MILESTONE DESCRIPTION	DATE
1	Preliminary Energy and Material Balances	4/01/80
2	Preliminary Layouts with Specific Major Equipment Identified	4/01/80
3	Preliminary Schedule 44	4/01/80
4	Feasibility Study Drawing List and Schedule	4/01/80
5	Finalize Estimate Outline per DOE Cost Code	4/15/80
6	QA Assessment	6/01/80
7	Review and Approval of Final Estimate	7/01/80
8	Final Schedule 44 to ORO	7/15/80
9	Issue Schedule Logic Diagrams - design, procurement, and construction, including obligation	8/01/80
10	Safety Document Recommendation with Hazards List to ORO	8/01/80
11	Final Feasibility Study Document and Design Criteria Submittal	8/01/80

FIGURE 4

The A-E firm will prepare the final criteria for the feasibility study; the feasibility study; cost estimates, including the engineering man-hour estimate for conceptual design detailed design (Title I and Title II); and other documents as required by DOE and the UCC-ND procedures. The A-E is presently completing preliminary energy and material balances and feasibility study drawing list.

The projected schedule for Title I and Title II design requires approximately one year for completion. The completion of the design effort and submittal of the construction bid package is thus expected by October 1982. It is assumed that UCC-ND advance procurement and associated Title III services will start during Title II design. A sufficiently lengthy period has been allowed for advance procurement, as there are some specialty items, namely the pelletizer, incinerator, furnaces and chemical process equipment that may require some modification to commercially available items. A total of approximately three years has been allowed for FPPC construction which includes an allowance of over one year for the FPPC procurement of non-specialty items.

PROJECT PROBLEM AREAS

The feasibility study, to date, has raised a number of problems for consideration. These problems are currently being studied and possible options investigated. These areas of concern can be divided into two categories: 1) Building limitations, and 2) Process changes.

Building limitations - Due to the thermal nature of the incinerator process and the metal melting process, ventilation requirements are critical. Each hot cell area is currently limited to 3000 cfm ventilation. A review of the internal cell heat loads has indicated that the temperature of the hot cells in TURF will probably exceed 120°F during operation. This is due in large part to the in-cell lighting fixtures. The existing lighting fixtures are simple reflectors with 1500 watt tungsten halogen lamps. Currently, options being considered include additional cooling capacity by utilizing water coils and/or replacing lighting fixtures with more efficient high pressure sodium lamps.

The building will limit process equipment sizes due to the limited access openings of the hot cells. Accessibility to equipment will be a maintenance concern. Due to these problems, all process equipment will be designed in modular form for ease of disassembly and removal.

Process changes - Due to the test bed design of the facility, certain process changes will become effective during the study. Currently no pellets have been hydrofractured. When a test hydrofracture shot has been made certain pelletization process criteria may be refined. This same problem exists with the incineration of pelletized material. Currently no data exists on burning characteristics of pelletized waste material. When development data becomes available certain refinement to the incinerator process may be required.

CONCLUSIONS

Due to the large volume of radioactive waste generated at ORNL, disposal of waste material has become a major concern. A large share of the generated waste at ORNL is low level. Therefore, the ability to greatly reduce the volume of waste material becomes of major importance. Further the ability to process the volume of low-level radioactive waste into a form acceptable to storage methods which completely remove the waste from the biosphere is of tremendous importance. Therefore, the functions of the LLWPF in processing the low-level waste generated at ORNL for the purpose of final disposal at the hydrofracture facility is of major importance.

Session IV

AIR POLLUTION CONTROL

Chairperson: M. E. Mitchell (ORGDP/UCC-ND)

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REMOVAL OF GASEOUS FLUORIDES*

M. G. Otey

Technical Services Division
Paducah Gaseous Diffusion Plant

ABSTRACT

Gaseous fluorides are present in the effluents of several diffusion processes and represent a potential source of environmental insult. Fluorides may exist in these streams as Refrigerant-114, UF_6, ClF_3, HF, F_2, or other subspecies. The concentration of fluorides in these streams is usually low and removal is consequently difficult; however, many effluent streams do require cleanup prior to discharge to the environment. In a series of factorially designed experiments, the effects of total gas flow, temperature, and fluoride gas flow were statistically defined for the removal of ClF_3, HF, and F_2 from air streams with solid sorbents. The solid sorbent studies represent new, promising technology which could have significant impact on the gaseous diffusion plants both from an environmental control and operational standpoint. Loading factors and material utilization were determined to allow an economic comparison to be made between four different material types. Further studies showed $CaCO_3$, which was found effective for removing these three fluorides in the factorial design, to be ineffective in trapping UF_6. Subsequent mixed-gas studies indicate this material is a very effective selective sorber of reactive fluorides, such as ClF_3, in the presence of UF_6.

INTRODUCTION

To comply with future air quality standards for gaseous fluoride emissions at the PGDP, studies are being made to evaluate the most feasible and efficient method of trapping fluorides from the effluents of the different processes. Although this work is in direct support of environmental projects, its results are applicable in other areas. Throughout the diffusion plants there are several areas where fluorides, either single or multiple species, are controlled and/or processed. The solid sorbent studies represent new, promising technology which could have significant impact on the gaseous diffusion plants.

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Prepared by the U. S. Department of Energy under
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Scoping studies of solid sorbents and reaction conditions have been conducted. In a series of statistically designed experiments, the effects of total gas flow, temperature, and fluoride gas flow were studied for eight dry chemicals in a 1-in. diameter fixed bed designed to remove three separate fluoride gas species [hydrogen fluoride (HF), fluorine (F_2), and chlorine trifluoride (ClF_3)] from an air stream. The trapping materials selected for the test include two brands of four different material types: soda lime, oolitic calcium carbonate ($CaCO_3$), calcium oxide (CaO), and activated alumina (Al_2O_3). Further studies have identified the oolitic $CaCO_3$ to be an effective selective sorber of active fluorides in the presence of UF_6.

CONCLUSIONS

Statistical evaluation of the data has identified total gas flow as the most significant variable while bed temperature was the second most significant variable. Fluoride gas flow was not a significant variable in the experiment. The oolitic $CaCO_3$ was identified as the best material selection based on cost and performance. Further studies have identified oolitic $CaCO_3$ as an effective selective sorber of active fluoride in the presence of UF_6 with minimal retention of the uranium.

Plans are being completed at PGDP to utilize $CaCO_3$ in a fixed bed removal system to control HF emissions from the C-746 Scrap Pretreatment Facility. In addition, the use of the limestone as a selective sorber of active fluoride in the presence of UF_6 is also being considered for facilities at PGDP.

EXPERIMENTAL DESIGN[1]

The 48 run experiment developed for the study is a replicate 2^3 factorial design, one for each gas type, in terms of the three process variables: total flow, fluoride gas flow and initial bed temperature. Each of the three factorial designs were designed to answer the following questions about each of the three fluoride gas species.

1. What are the main effects of each of the eight dry chemicals on the experimental responses?

2. What are the main effects of the three process variables on the experimental responses?

The eight dry chemicals and the two levels of each of the three process variables are listed in Table 1. A complete factorial design that

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[1] Developed by Dr. C. K. Bayne, Y-12 Plant, Oak Ridge, TN

Table 1

THE LEVELS OF THE CONTROLLED EXPERIMENTAL VARIABLES

Controlled Variables	Level
A. Gas Type	1. F_2 2. ClF_3 3. HF
B. Gas Flow Rate	1. 100 sccm 2. 200 sccm
C. Total Flow Velocity	1. 800 sccm 2. 8000 sccm
D. Reactor Temperature	1. 200°F 2. 600°F
E. Dry Chemical	1. Al_2O_3, (activated) sample 1 2. Al_2O_3, (activated) sample 2 3. Soda Lime, sample 1 4. Soda Lime, sample 2 5. $CaCO_3$, (oolitic) sample 1 6. $CaCO_3$, (oolitic) sample 2 7. CaO, sample 1 8. CaO, sample 2

used all combinations of the dry chemicals and process levels would require 58 experimental runs for each fluoride gas and would require an excessive amount of time to complete. Therefore, an experiment was designed to examine the main effects of the dry chemicals and the main or linear effects of the process variables while sacrificing information on the two-, three-, and four-factor interactions among the dry chemicals and process variables.

EXPERIMENTAL APPARATUS AND PROCEDURE

A drawing of the system used in the experimental runs is shown in Figure 1. The 1-in. OD, 14.5-in. long reactor was filled to a depth of 12 in. for each run. Prior to each run, the prepared bed was dried at 600°F with an air purge for a minimum of 15 hours. A differential pressure transducer was used to monitor the differential pressure across the bed, and a constant temperature oven was used to heat the packed bed and gas preheater. Temperatures were monitored at the bottom or inlet of the bed, 4-in. level, 8-in. level, and 12-in. level or outlet using thermocouples and thermowelds located at the cross-sectional center of the bed.

For these experiments, the fluoride gases (F_2, ClF_3, and HF) were not mixed, but each individual gas was examined separately. The dry air introduced into the system was used to control the total flow velocity into the packed bed reactor. A gas sampling manifold was used to collect bulb samples of the inlet and outlet gas for analyses. Sample points were available at the 4-in. and 8-in. levels of the bed but were not routinely used.

The eight dry chemicals used in the experiment were selected on the basis of previous experience, information in the literature, and commercial availability. Sodium carbonate was not included, since it is not readily available on the market in granular or pellet form which is needed in fixed-bed trapping.

Bulb samples of the inlet gases were taken prior to and following each run while the gas mixture was bypassing the reactor. Samples of the outlet gases were taken at systematic intervals during the run. From these analyses, fluoride trapping efficiencies[2] and in the case of the ClF_3 runs, chloride trapping efficiencies were calculated for each run. Temperature profile and efficiency plots with respect to time were made for each run from the generated data. From the efficiency plot, the time

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[2] $$\frac{\text{Inlet gas concentration} - \text{Outlet gas concentration}}{\text{Inlet gas concentration}} \times 100$$

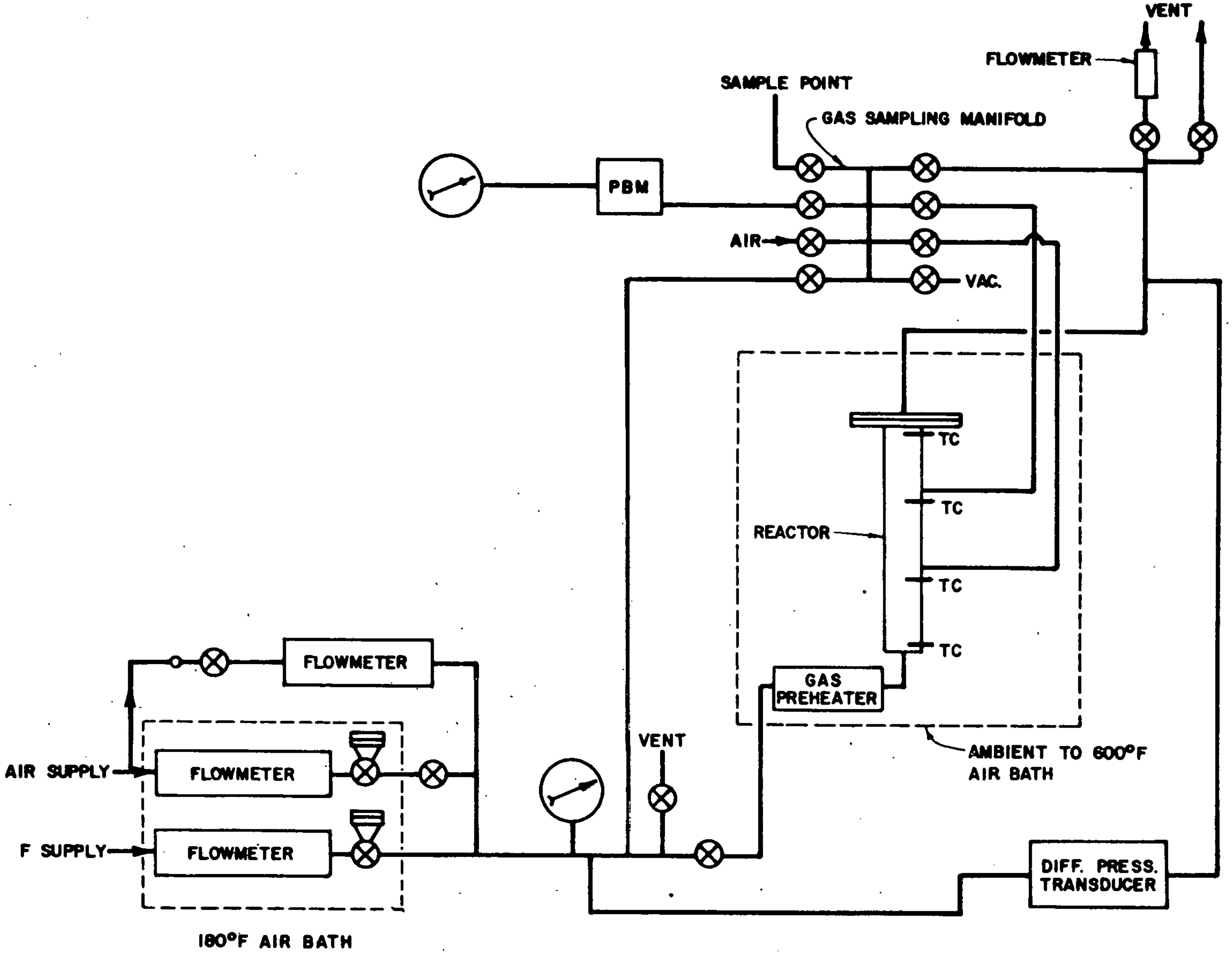

Fig. 1. Flouride trapping study system

to reach breakthrough was determined which allowed the loading factor[3] at breakthrough to be calculated. Breakthrough is defined as the point where the outlet concentration first begins to increase and is determined from the efficiency plot. Loading factor at breakthrough is calculated using the average inlet gas concentration, total gas flow, time to reach breakthrough, and the initial weight of bed material. One bulb sample of the outlet gases was taken near the beginning of each run for infrared and/or chromatographic analysis to determine the species of any gaseous reaction products.

Following each run, the weight change of the trapping material was determined. The bed material was then ground, blended, and sent for fluoride and x-ray diffraction analyses. Material from the ClF_3 runs were also analyzed for chloride, chlorates, and perchlorates.

EXPERIMENTAL DATA

Table 2 is a summary of trapping material types, conditions of the runs, and the fluoride loading factors obtained at breakthrough. Very similar loading factors were obtained with the three fluoride gases at similar conditions and trapping materials. Fluoride loading factors for all the runs ranged from essentially no loading to 55%. The high temperature, low velocity runs with activated Al_2O_3 gave the highest fluoride loading factors. All the material types, ignoring brands and selecting optimum conditions, gave loading factors ranging from 24% to 55% and suggest that all are effective trapping agents for these fluorides under appropriate conditions.

Maximum fluoride removal efficiencies ranged from approximately 91% to greater than 99% with exception of those runs which showed almost instant breakthroughs. Maximum temperature inflections due to heats of reaction ranged from 2°F to 560°F for F_2, <1°F to 679°F for ClF_3, and 10°F to 152°F for HF. Examples of removal efficiencies and temperature plots with respect to time are shown in Figures 2 through 5. The temperature rises experienced in the 1-in. OD reactor are less than thermodynamic predictions or what would be experienced in larger diameter traps at equivalent gas velocities and is attributed to heat dissipation in the small reactor. Therefore, these temperature increases should not be taken at face value but only as relative indicators. The temperature inflections at the various levels in the bed proved to be a good indicator of the location of the reaction and served as a means of predicting trap depletion. Only the HF runs at 200°F with soda lime and CaO showed

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[3] $\frac{\text{Fluoride trapped, grams}}{\text{Initial bed material, grams}} \times 100$

Table 2

SUMMARY OF RUN CONDITIONS AND LOADING FACTORS

Trapping Material	Superficial Velocity, ft/sec	Initial Bed Temp., °F	Loading Factor at Breakthrough, %[1]		
			HF	F_2	ClF_3
Soda Lime, sample 1	1.4 (8000 sccm)	200	32	7	16
Soda Lime, sample 1	0.2 (800 sccm)	600	37	31	36
Soda Lime, sample 2	0.1 (800 sccm)	200	-[2]	19	22
Soda Lime, sample 2	2.3 (8000 sccm)	600	9	18	22
$CaCO_3$, (oolitic) sample 1	0.1 (800 sccm)	200	26	-[3]	-[3]
$CaCO_3$, (oolitic) sample 1	2.3 (8000 sccm)	600	7	13	3
$CaCO_3$, (oolitic) sample 2	1.4 (8000 sccm)	200	5	-[3]	-[3]
$CaCO_3$, (oolitic) sample 2	0.2 (800 sccm)	600	32	31	24
CaO, sample 1	1.4 (8000 sccm)	200	4	8	2
CaO, sample 1	0.2 (800 sccm)	600	30	41	24[4]
CaO, sample 2	0.1 (800 sccm)	200	7[5]	12	22[4]
CaO, sample 2	2.3 (8000 sccm)	600	3	3	3
Al_2O_3, (activated) sample 1	1.4 (8000 sccm)	200	6	3	7
Al_2O_3, (activated) sample 1	0.2 (800 sccm)	600	55	54	51
Al_2O_3, (activated) sample 2	0.1 (800 sccm)	200	22	40	34
Al_2O_3, (activated) sample 2	2.3 (8000 sccm)	600	18	39	28

[1] $\frac{\text{grams } F^{-} \text{ x } 100}{\text{grams initial bed material}}$

[2] Bed material partially powdered and plugged trap causing termination of run

[3] Instant breakthrough [4] Some fusing of bed material noted

[5] Bed material partially powdered

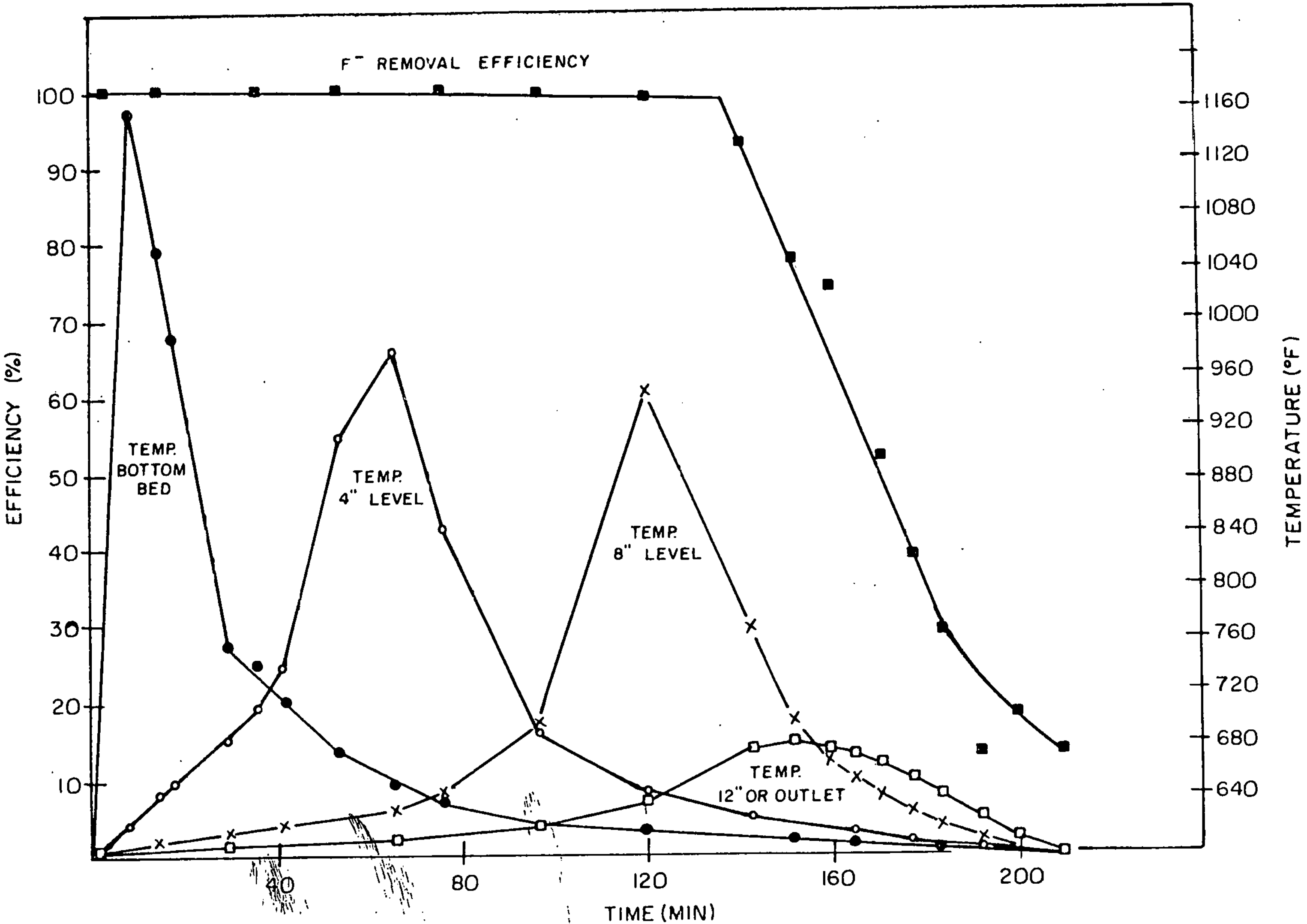

Fig. 2. Efficiency and temperature profile curves for F_2 and CaO, run No. 10

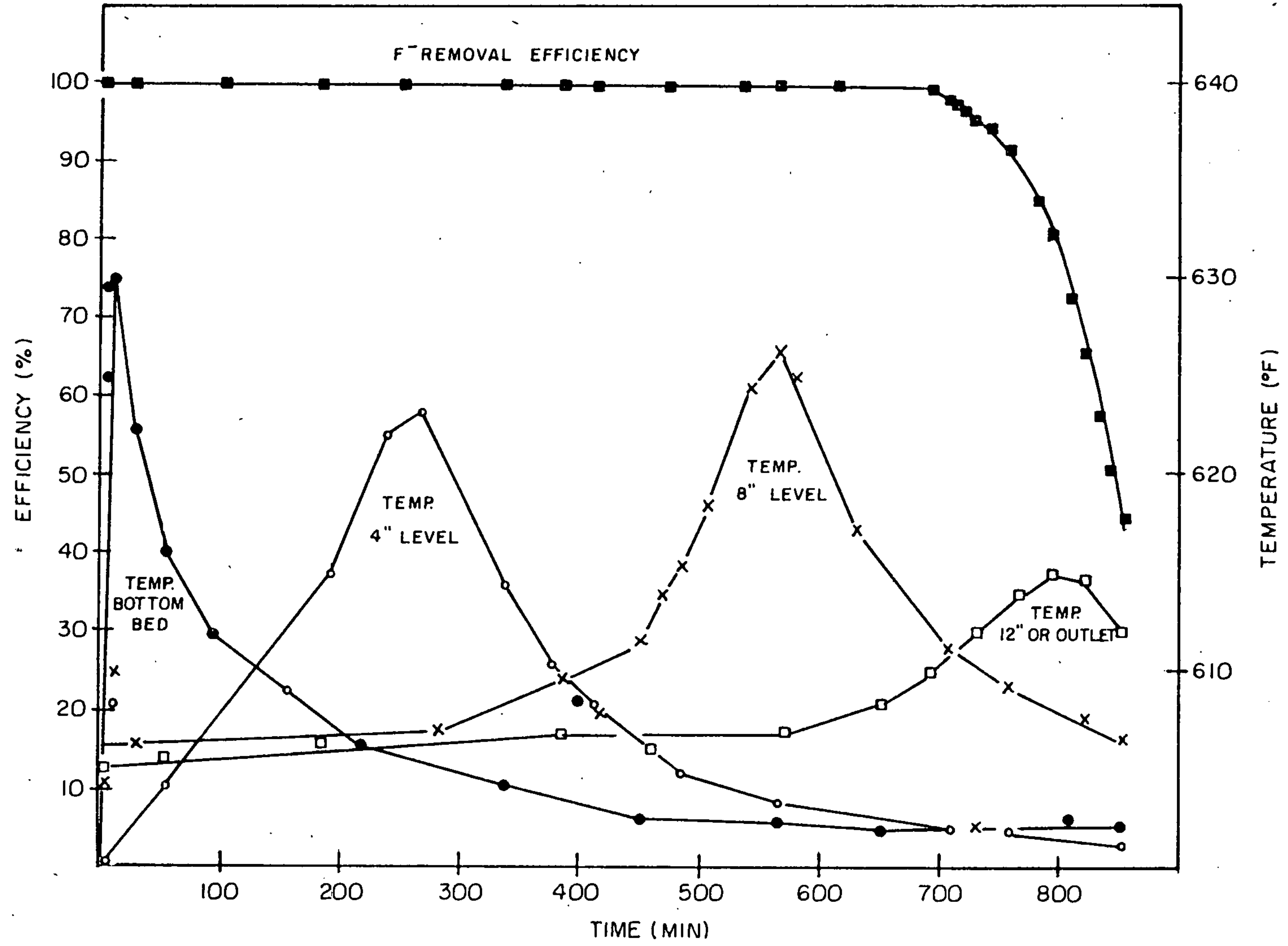

Fig. 3. Efficiency and temperature profile curves for HF and Al_2O_3, run No. 14

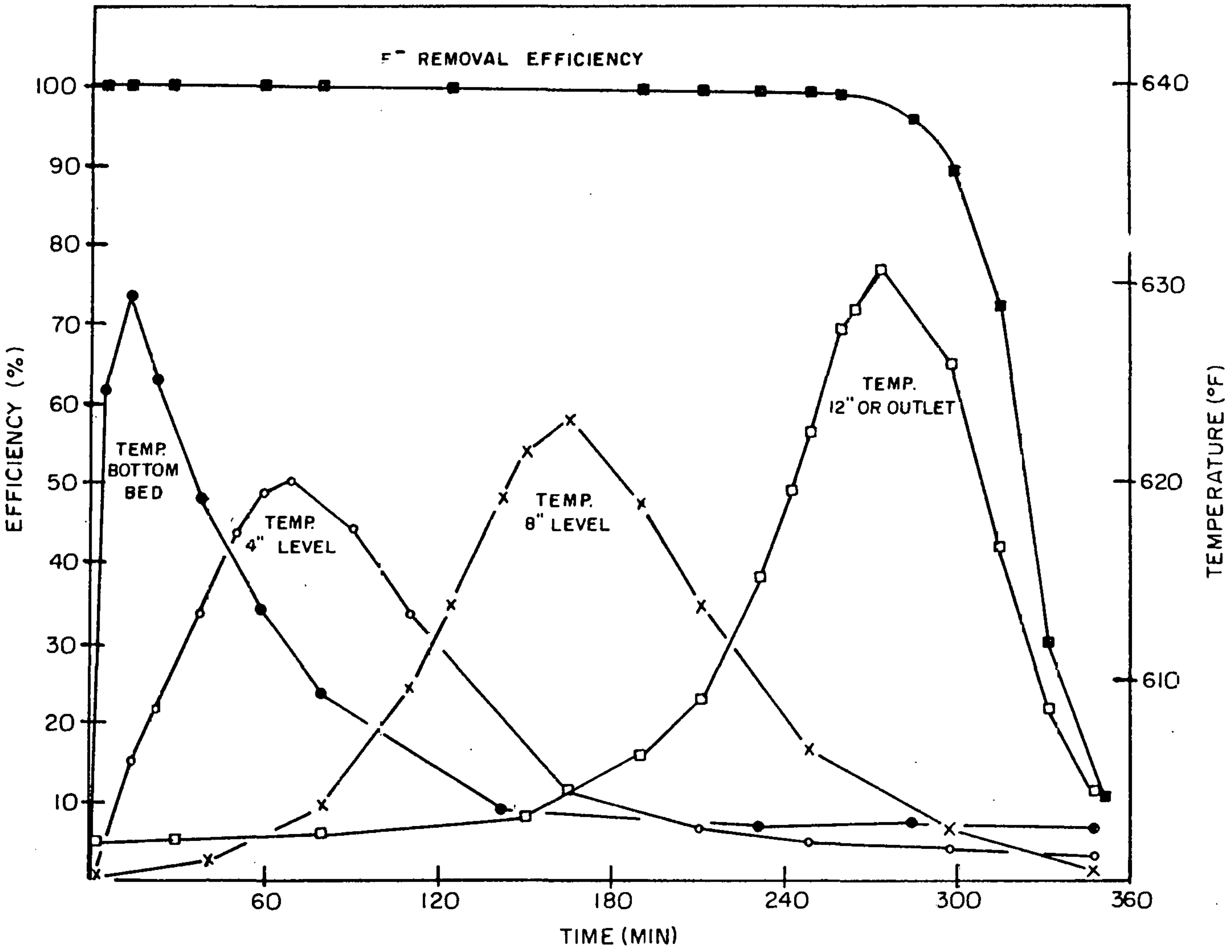

Fig. 4. Efficiency and temperature profile curves for HF and $CaCO_3$, run No. 18

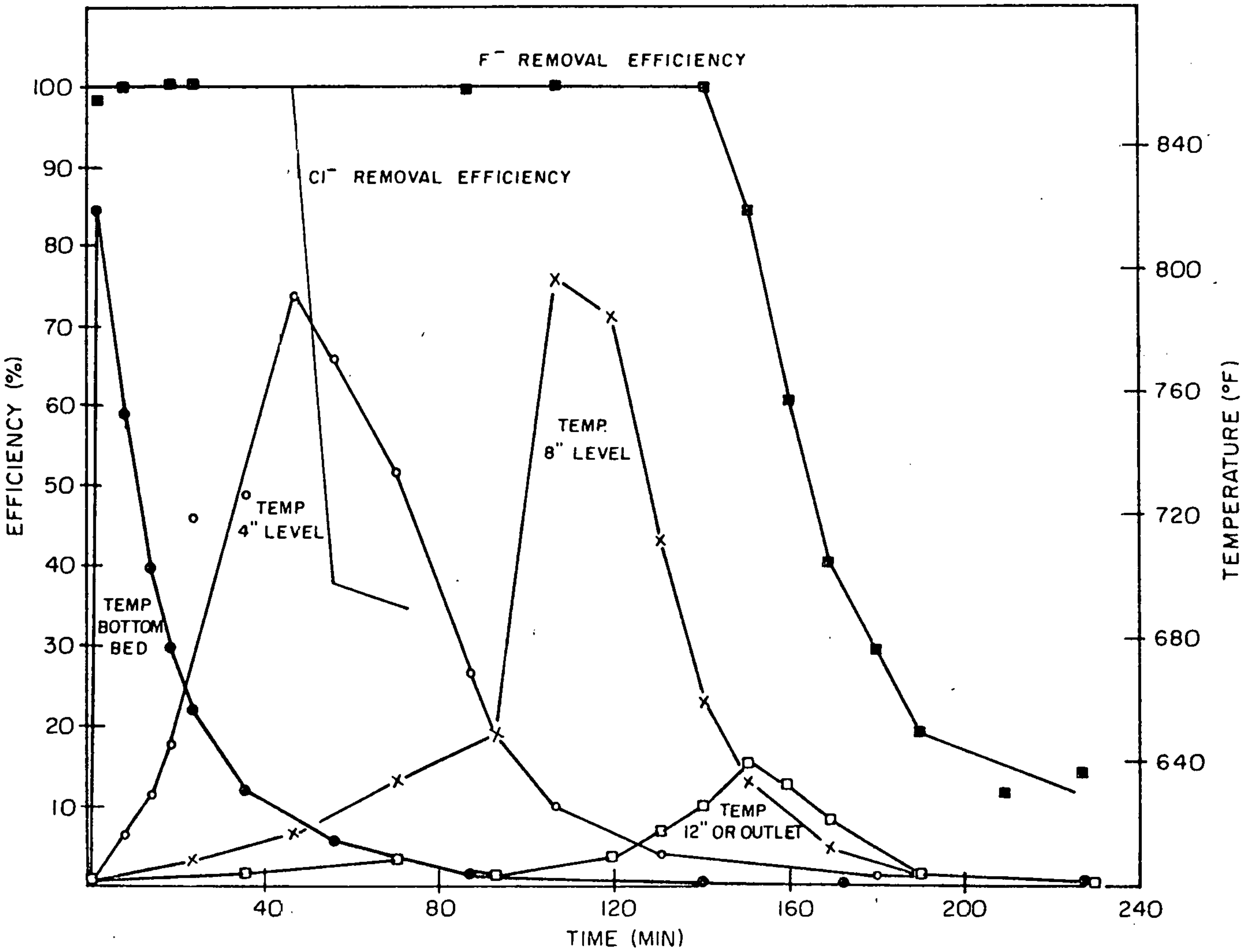

Fig. 5. F⁻ and Cl⁻ efficiencies and temperature profile curves for ClF_3 and soda lime, run No. 34

a very significant increase in pressure drop across the bed during the runs. Materials from these runs experienced powdering in the bed, and this explains the increasing pressure drop. Some fusing of the bed material occurred during two ClF_3 runs with CaO but did not result in a detectable pressure drop across the bed.

None of the bed materials in the ClF_3 runs proved very satisfactory for chlorine removal. Efficiencies were fairly high for the high temperature, low velocity CaO runs and the high temperature, low velocity soda lime runs. However, the trapped chlorine was displaced in most cases as the fluoride migrated through the bed. Analyses of the depleted beds showed <0.1% to 0.8% chlorate and <0.1% to 1.7% perchlorate being formed.

X-ray diffraction analyses did not show any major unexpected compounds being formed in the bed materials. Also, infrared and chromatographic analyses of gas samples taken at the beginning of the runs did not show any unexpected gaseous products being formed. These gas samples were specifically examined for oxygen difluoride (OF_2) and none was detected at a detection limit of 0.2%.

STATISTICAL EVALUATION[4]

In the statistical evaluation several responses were considered; however, the percent fluoride loading factor at breakthrough was chosen as the best representation of performance. From this evaluation the optimum operating conditions are found to be the low level of total flow (800 sccm) and the high level of temperature (600°F) with flow being the most significant variable. Fluoride flow was found not to be a significant variable in the experiment. The fluoride load factor responses for each gas were fitted to a linear equation where:

LOAD = MEAN + DRY CHEMICAL EFFECT + TOTAL FLOW + TEMPERATURE + RANDOM ERROR.

The magnitude of calculated intercepts was used to rank the dry chemicals as shown in Table 3. Based on this evaluation activated Al_2O_3 appears best for F_2 and ClF_3 removal and soda lime is best for HF removal.

From an operational standpoint, however, the increased plugging which occurred in the soda lime and CaO runs with HF at 200°F would

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[4] Dr. C. K. Bayne, Y-12 Plant, Oak Ridge, Tenn.

Table 3

ESTIMATES OF THE INTERCEPTS AND SLOPES FOR THE PERCENT LOADING FACTORS (PREDICTION EQUATION WITH STANDARD ERRORS IN PARENTHESES)

Fluorine

$$\text{LOAD} = \underset{(9.98)}{\text{INTERCEPT}} - \underset{(0.51 \times 10^{-3})}{2.38 \times 10^{-3}} \text{ TOTAL FLOW} + \underset{(0.92 \times 10^{-2})}{4.41 \times 10^{-2}} \text{ TEMPERATURE}$$

Dry Chemical	Intercept
1 Al_2O_3, (activated) sample 2	32.34
2 Al_2O_3, (activated) sample 1	21.34
3 CaO, sample 1	17.34
4 Soda Lime, sample 1	11.84
5 Soda Lime, sample 2	11.34
6 $CaCO_3$, (oolitic) sample 2	8.34
7 CaO, sample 2	0.34
8 $CaCO_3$, (oolitic) sample 1	-0.66

Chlorine Trifluoride

$$\text{LOAD} = \underset{(10.04)}{\text{INTERCEPT}} - \underset{(0.51 \times 10^{-3})}{2.29 \times 10^{-3}} \text{ TOTAL FLOW} + \underset{(0.92 \times 10^{-2})}{2.75 \times 10^{-2}} \text{ TEMPERATURE}$$

Dry Chemical	Intercept
1 Al_2O_3, (activated) sample 2	30.08
2 Al_2O_3, (activated) sample 1	28.08
3 Soda Lime, sample 1	25.08
4 Soda Lime, sample 2	21.08
5 CaO, sample 1	12.08
6 CaO, sample 2	11.58
7 $CaCO_3$, (oolitic) sample 2	11.08
8 $CaCO_3$, (oolitic) sample 1	0.58

Hydrogen Fluoride

$$\text{LOAD} = \underset{(14.46)}{\text{INTERCEPT}} - \underset{(0.74 \times 10^{-3})}{2.17 \times 10^{-3}} \text{ TOTAL FLOW} + \underset{(1.33 \times 10^{-2})}{2.78 \times 10^{-2}} \text{ TEMPERATURE}$$

Dry Chemical	Intercept
1 Soda Lime, sample 1	32.92
2 Al_2O_3, (activated) sample 1	28.92
3 Al_2O_3, (activated) sample 2	18.42
4 $CaCO_3$, (oolitic) sample 2	16.92
5 CaO, sample 1	15.42
6 $CaCO_3$, (oolitic) sample 1	14.92
7 CaO, sample 2	3.42
8 Soda Lime, sample 2	2.92

discredit these materials as the best selection without further development to circumvent these problems. In addition, the HF runs did not show a statistical difference in the bed materials at the 10% significance level. Because of time and resource constraints, the two brands of each material were not exposed to identical conditions of temperature and gas flows which make it difficult to select one brand over the other. It is apparent from the data that activated Al_2O_3 operated at 600°F and a superficial gas velocity of 0.2 ft/sec gave the highest loading factors of all materials and for all three fluoride gases. However, other considerations, such as material cost, should be taken into account when selecting the optimum trapping material and the statistical evaluation should not be used exclusively for optimum material selection. Table 4 compares trapping costs of the four material types using the maximum loading factor obtained and cost information available at the time of this report. It is apparent that $CaCO_3$ has the best cost benefit even with a somewhat lower loading factor.

Table 4

COST COMPARISON OF FLUORIDE TRAPPING MATERIALS

Material	Material Cost, \$/lb Material	Maximum Fluoride Loading Factor, %	Material Trapping Cost, \$/lb F^-
Activated Alumina	0.23	55	0.42
CaO	0.014	41	0.03
Soda Lime	0.497	37	1.34
$CaCO_3$	0.005	32	0.02

SELECTIVE SORPTION STUDIES

Following the completion of the factorially designed experiments, additional scoping tests were initiated to determine the efficiency of these materials in trapping uranium hexafluoride (UF_6). These studies were instrumental in identifying oolitic $CaCO_3$ as a selective sorber of active fluorides in the presence of UF_6 and have led to mixed gas trapping studies involving ClF_3 and UF_6. Table 5 summarizes one of many laboratory runs which have been made with a 1" OD x 12" long bed and two pilot plant tests made with a 3" OD x 12" long bed. Total fluoride loading factors, obtained from bed analyses following 100% ClF_3 breakthroughs, ranged from 22% to 32% with only 1.8% to 3.0% uranium retention.

Table 5

SELECTIVE SORPTION OF ClF_3 FROM UF_6 STREAMS WITH $CaCO_3$

Exposure Conditions	Laboratory Test	Pilot Plant Test #1	Pilot Plant Test #2
Reactor size	1" OD x 12" long	3" OD x 12" long	3" OD x 12" long
Initial bed temperature, °F	600	550 - 650	550 - 650
Superficial mass velocity, $lbs/min/ft^2$	2.8	2.7 - 3.5	2.7
ClF_3 concentration, mol. %	9.0	2 - 3.7	6 - 8
UF_6 concentration, mol. %	6.5	60 - 90	70 - 90
Results			
Total F^- loading factor, %[1]	32	22	31
Total Uranium retention, %	1.8	3.0	2.6
Uranium +4, %	<0.2	0.6	0.5
Temperature increase, °F	173	170	230

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[1] $\frac{\text{gram } F^-}{\text{gram initial bed material}}$

Further laboratory tests were made to determine if higher temperatures, which might be encountered due to heats of reaction, would initiate a $CaCO_3$ - UF_6 reaction. Exposures were made at 800°F, 1000°F, and 1200°F as shown in Table 6. These tests indicate that to 1000°F the uranium retention remained in the 2% to 3% range, however, above 1000°F a substantial increase in retention was observed.

Even though the 2% to 3% residual uranium on the spent material is of minor sigificance, studies with additional ClF_3-N_2 treatments have been made to determine if clean-up steps are possible. These studies show that either very long exposure periods at 600°F or very high temperatures (~1000°F) are required to remove a significant amount of the uranium residue from the spent material.

Table 6

HIGH TEMPERATURE EXPOSURE OF UF_6 TO $CaCO_3$

	% U	% U^{+4}	% F^-
800°F Exposure-bed analysis:	2.3	<0.2	5.2
1000°F Exposure-bed analysis:	2.7	<0.2	2.9
1200°F Exposure-bed analysis:	25.9	1.8	12.9

AN ALTERNATE APPROACH FOR MEETING AMBIENT GASEOUS FLUORIDE STANDARDS

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ABSTRACT

Alternate methods for achieving compliance with Kentucky ambient fluoride regulations were examined for emissions resulting from PGDP cascade activities. Among the methods considered were: (1) installation of scrubbers, (2) planning emissions to coincide with meteorological conditions favorable for dispersion, and (3) increasing the stack height within good engineering practice. Based on evaluation of present and anticipated future operating conditions, a recommendation was made to increase the stack height to 200 feet. This approach was found to be the most practical and cost-effective means of maintaining compliance and has received concurrence from both the DOE Safety and Environmental Control Division and the Kentucky Division of Air Pollution Control.

With the shutdown of UF_6 production and UF_6 reduction facilities at Paducah in 1977, no compliance difficulties with ambient fluoride standards had been anticipated. This expectation was based on weekly air samples at ten monitoring stations scattered along the perimeter fence, Department of Energy property boundary, and at points one mile from the plant (see Figure 1). However, the Kentucky Division of Air Pollution Control (DAPC) ultimately determines compliance by mathematical modeling with concentrations predicted at locations and for time periods not necessarily covered by actual sampling and analysis. During the early work on FY-1980 Line Item Project Gaseous Effluent Control, dispersion modeling calculations indicated that the Paducah Gaseous Diffusion Plant could exceed what were at that time primary ambient standards as a result of intermittent (~1% of the time) gaseous fluoride discharges from the C-310 purge cascade vent. The current applicable limits not to be exceeded more than once annually at any single point location are given in Table 1. For short-term releases the most difficult standard with which to comply would be the 4.5 ppb (measured as hydrogen fluoride) in a 12-hour period.

*REPORT NUMBER: KY/L-1068

Prepared for the U. S. Department of Energy
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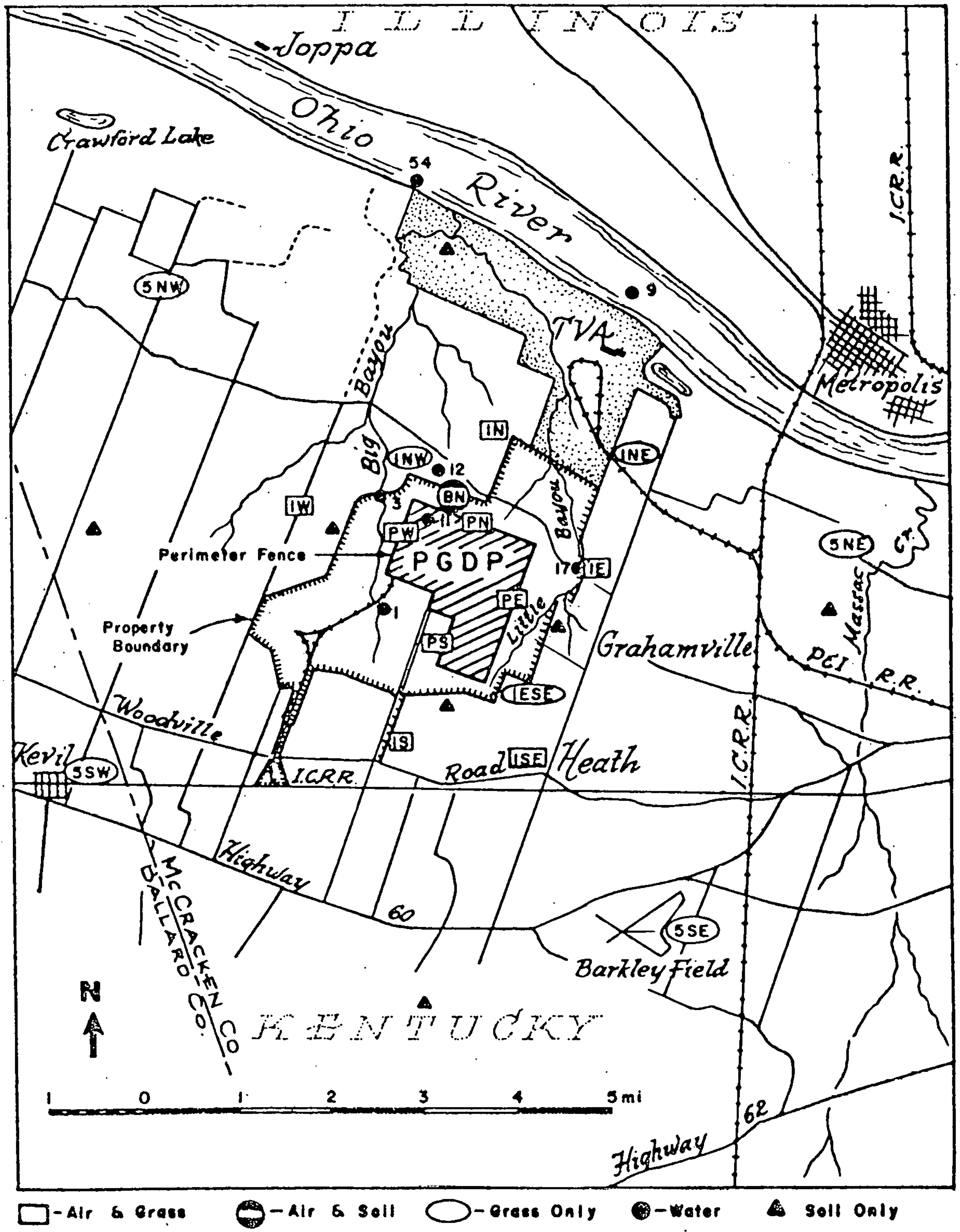

Figure 1

LOCATIONS OF SAMPLING POINTS

Table 1

KENTUCKY AMBIENT FLUORIDE LIMITS

Gaseous HF	Primary Standard	Secondary Standard
12-hour Average	-	4.5 ppb*
24-hour Average	1000 ppb	3.5 ppb*
1-week Average	-	0.97 ppb**
1-month Average	-	0.6 ppb***
Annual Average	500 ppb	-

* Former primary standard identical.
** Former primary standard of 2 ppb.
*** Former primary standard of 1 ppb.

A copy of the model in use by the Kentucky DAPC and referred to as the "Multipoint" model was obtained for use in evaluating projected cascade activities. Upon examining the computer code of the "Multipoint" model, it was found to be based on the conventional gaussian plume model as described in Turner[1] with no allowance for plume reaction with the ground (which is questionable for hydrogen fluoride):

$$\chi = \frac{Q}{\pi \sigma_y \sigma_z u} \exp\left[-\left(\frac{h^2}{2\sigma_z{}^2} + \frac{y^2}{2\sigma_y{}^2}\right)\right]$$

where: χ = ground-level concentration (g/m^3)

Q = pollutant release rate (g/sec)

σ_y, σ_z = dispersion parameters which depend on atmospheric stability and downwind distance from the release (m)

u = wind speed (m/sec)

h = effective release height (m)

y = distance from sampling point to plume centerline

The model was found to predict 1-hour concentrations from continuous releases and, since no meteorological input was initially supplied for use with the model, the exact procedure by which the Kentucky DAPC would estimate 12-hour violations from intermittent emissions was unclear.

Nevertheless, the problem was approached by assuming the probability of an emission exceeding the standard as the product of two independent probabilities. The first was the probability that unfavorable meteorological conditions exist, and the second was the probability that the source is actually emitting. Data from a 10-year summary[2] of Paducah area weather was used in determining meteorological probabilities. In this summary, each hourly observation is characterized by stability class, wind speed, and wind direction. For each possible combination, the maximum 1-hour ground-level concentration for each modeled emission was calculated from both the perimeter fence outward and the DOE boundary outward. The resulting concentration was divided into 54 (the product of

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[1] D. B. Turner, Workbook of Atmospheric Dispersion Estimates, U. S. Department of Health, Education, and Welfare, Cincinnati, OH, 1969.

[2] Wind Distribution by Pasquill Stability Classes, Station 03816, Paducah, Kentucky, 1955-1964, National Climatic Center, Asheville, NC.

the 4.5 ppb standard and the applicable 12-hour period) and rounded to the next higher integer to yield the number of hours that condition would have to persist to cause the standard to be exceeded. Finally, the probability of observing that condition for the required number of hours during the release was obtained assuming that the hourly observations were random and followed a Poisson probability distribution (which can provide probabilities of specified numbers of telephone calls per unit interval of time, given numbers of defects per unit length of wire or thread, etc.[3]).

The conclusions with regard to compliance based on this initial evaluation using an adaptation of the "Multipoint" model for Paducah's IBM 1130 are summarized in Table 2. It can be seen that Activity 3 will cause the 12-hour limit to be exceeded at the DOE boundary two thirds of the time and nearly always at the perimeter fence.

Uncertainly arising from this unique treatment of meteorological data remained as the procedure outlined could not handle a situation in which the standard could be exceeded as a result of differently classified adverse conditions during the release. Additionally, meteorological conditions do not necessarily vary randomly from hour to hour. Nevertheless, the procedure used was felt to be the best available approach with the information available at that time.

After completion of the above study, the Kentucky Division of Air Pollution Control furnished a copy of the "CRSTER" uneven terrain model along with hourly meteorological observations from the entire year of 1964. The DAPC also agreed to drop the assumption of complete plume reflection for reactive gases such as hydrogen fluoride (effectively halving the concentrations predicted by the equation given earlier). Meteorological data from 1964 were selected primarily because of availability in a convenient computerized form. Additionally, beginning in 1964, 36 compass points were selected for reporting wind direction in contrast to the prior practice of using 16. The "CRSTER" model still uses essentially the same dispersion equation, dispersion parameters, and plume analysis as the "Multipoint" model. Receptors are selected in each possible wind direction at several distances from the source. During the computer calculations, each observation of wind direction is perturbed ± 5 degrees to allow for potential fluctuations. The only apparent adjustment for uneven terrain is a correction to release height based on difference in elevation between the source and receptor.

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[3] I. Guttman, et al., Introductory Engineering Statistics, 2nd Edition, John Wiley & Sons, Inc., New York, NY, 1971, p. 38.

Table 2

ESTIMATED INSTANCES OF EXCEEDING 12-HOUR AMBIENT FLUORIDE LIMITS FOR MODELED ACTIVITIES

Cascade Activity	Number of Annual Emissions	Cases of Exceeding Limit	
		Fence	Boundary
1	61	42	25
2	52	0	0
3	26	25	18
4	313	0	0
5	104	91	58

When use of the "CRSTER" model was first discussed with the DAPC, that agency produced sample print-outs including: (1) maximum hourly and maximum 24-hour concentrations for each day, (2) annual mean concentrations at each receptor, (3) highest and second highest 24-hour concentrations at each receptor, (4) highest and second highest three-hour concentrations at each receptor, and (5) highest and second highest 1-hour concentrations at each receptor. It was mentioned that the model is used much more frequently for other pollutants; thus, the time periods do not address fluoride standards. Recalling that the regulations establish limits "not to be exceeded more than once annually at any single point location," the DAPC did not exactly use a strict interpretation of the wording. If only one year of meteorological data was used by the control agency in making predictions, only the highest single prediction on the page listing highest concentrations at each receptor was discarded. Emission limits were then based on the next highest prediction even though it occurred at a different receptor. However, if more than one year of meteorological data was available, the highest predictions at all receptors were discarded.

After obtaining clarification that the standards would only be applied at the DOE boundary and that 12-hour periods would run from either midnight to noon or noon to midnight, the "CRSTER" model was rewritten and simplified for use on Paducah's IBM 1130. None of the simplifications were expected to increase emission limits above those calculated by the DAPC and, in fact, represented more stringent assumptions which that agency could later employ. Table 3 summarizes predictions at the DOE boundary for days selected on which difficulty in meeting the 12-hour standard could be expected on the basis of fairly constant wind directions. It was determined that the maximum fluoride emission from the cascade in any 12-hour period could be held at or below 50 lb (expressed as fluoride ion), and, for modeling purposes, a continuous, uniform release of this maximum quantity from the present stack height of 68 feet was assumed for the entire period. The maximum predicted concentration at any receptor was found to be 26.29 ppb as HF, indicating that reduction of the 12-hour emission to 8.6 lb F^- would be necessary to bring about a condition in which the 12-hour ambient limit would not be exceeded.

DISCUSSION

Among the more practical suggestions made for ensuring no compliance difficulty with Kentucky ambient fluoride standards that could be exceeded as a result of cascade fluoride emissions were: (1) simply taking no action, (2) administrative controls (planning cascade activities at times such that emissions would coincide with meteorological conditions favorable for pollutant dispersal), (3) installing a scrubber system, and (4) increasing the stack height within good engineering practice limits. Table 4 summarizes each of these alternatives along with the associated risks.

Table 3

PREDICTED CONCENTRATIONS AT DOE BOUNDARY FOR MAXIMUM RELEASE FROM PRESENT 68 FT STACK

Day	Period*	Maximum 12-hour HF Concentration (ppb)
1-8	1	2.19
	2	2.14
2-16	1	1.45
	2	11.83
2-18	1	6.36
	2	4.57
3-3	1	8.45
	2	2.07
3-12	1	0.80
	2	4.84
4-25	1	2.80
	2	4.36
5-10	1	9.33
	2	4.27
5-15	1	16.05
	2	4.27
5-17	1	3.73
	2	2.48
5-21	1	12.65
	2	3.22
5-31	1	10.27
	2	14.26
6-1	1	17.25
	2	8.18

*Period 1 is 12-hour period ending at noon while period 2 begins at noon.

Table 3 (Continued)

PREDICTED CONCENTRATIONS AT DOE BOUNDARY
FOR MAXIMUM RELEASE FROM PRESENT 68 FT STACK

Day	Period*	Maximum 12-hour HF Concentration (ppb)
6-28	1	11.73
	2	8.35
6-30	1	2.37
	2	4.80
7-1	1	6.02
	2	10.65
7-10	1	13.05
	2	5.74
7-20	1	13.66
	2	10.63
7-21	1	15.01
	2	9.18
7-23	1	17.20
	2	15.52
7-24	1	20.01
	2	15.30
7-26	1	9.03
	2	11.72
8-16	1	1.25
	2	2.15
8-17	1	7.63
	2	2.56
8-25	1	1.62
	2	5.68
9-19	1	4.69
	2	21.37

Table 3 (Continued)

PREDICTED CONCENTRATIONS AT DOE BOUNDARY
FOR MAXIMUM RELEASE FROM PRESENT 68 FT STACK

Day	Period*	Maximum 12-hour HF Concentration (ppb)
9-26	1	5.68
	2	2.61
9-29	1	1.31
	2	10.29
10-24	1	26.29
	2	20.77
11-4	1	10.85
	2	3.79
11-7	1	15.93
	2	2.45
12-7	1	9.44
	2	3.80
12-9	1	2.67
	2	7.32
12-20	1	2.09
	2	4.26
12-28	1	5.60
	2	4.10

Table 4

ALTERNATIVES FOR ACHIEVING COMPLIANCE WITH AMBIENT FLUORIDE STANDARDS FOR C-310

Alternate Technology	Frequency of Exceeding Ambient Standards Per Year	Capital Cost (Millions)	Operating Cost (Millions)
1. No Action	10-20	-	-
2. Administrative Controls	1-5	-	-
3. Scrubber Systems	Variable*	4	≥0.2
4. Increased Stack Height	0.50**	0.25	Minimal

* Depends on down time
** Passive system incurs no down time

In light of later clarifications by the Kentucky Division of Air Pollution Control and best available information on current or projected operating conditions, data from the initial study were reexamined, and 10 to 20 cases per year of exceeding the 12-hour standard were projected, assuming normal meteorological variations. If the emissions were to all coincide with worst-case meteorological conditions, the annual projection could increase to 25 to 40 cases. The alternative of taking no action was, therefore, rejected because of its associated unacceptable high frequency of exceeding the standard.

Administrative controls without capital expenditures were projected to reduce the number of cases of exceeding the standard to one to five. This alternative would likely have met the legal requirements but would be somewhat undesirable from an operating standpoint. Additionally, not all incidents are administratively controllable (e.g., equipment failures), and administrative controls may not always be available due to safety concerns. Furthermore, extensive monitoring and on-stream analysis of stack emissions (along with the associated record keeping and access by state personnel to these records) would probably be required.

A scrubber system (when on stream) would have virtually eliminated the probability of exceeding the standard but at a capital cost of approximately $4,000,000 and an annual operating cost of $200,000. Additionally, a sludge possibly requiring fixation and burial in an approved landfill would have been generated, and administrative controls could still have been necessary during maintenance on the system.

The alternative of increasing the stack height to 200 ft (2 1/2 times local building height and within "good engineering practice") was evaluated using the modified "CRSTER" model. From Table 5, it may be seen that the maximum predicted 12-hour concentration, assuming a uniform release of 50 lb F^- over 12 hours, is 2.66 ppb (corresponding to an allowable release of 85 lb F^-). This emission limit compares to the limit of 64 lb F^- computed by another, more conservative approach in the attached Appendix.

CONCLUSIONS AND RECOMMENDATIONS

The alternative of increasing the stack height within good engineering practice limits was selected as the most practical and cost-effective means of providing passive protection against planned and accidental emissions. For the maximum anticipated fluoride emission rate of fifty pounds in any 12-hour period, no cases of exceeding the standards would be expected with wind speeds over 2 m/sec (observed at nearby TVA's Shawnee Steam Plant at 200 feet 93% of the time). Combined with the already low frequency of emission (~1% of the time), one case of exceeding the standard would be expected every two years (0.07 x 0.01 x 730 = 0.5). This would not be in violation of the standards. Capital cost for this alternative will be approximately $250,000, which could be

Table 5

PREDICTED CONCENTRATIONS AT DOE BOUNDARY FOR MAXIMUM RELEASE FROM PROPOSED 200 FT STACK

Day	Period*	Maximum 12-hour HF Concentration (ppb)
1-8	1	1.00
	2	1.02
1-23	1	0.74
	2	0.43
2-16	1	0.68
	2	2.48
2-17	1	0.22
	2	0.70
2-18	1	0.61
	2	2.62
2-20	1	0.54
	2	0.32
5-15	1	0.91
	2	0.28
5-21	1	0.63
	2	0.36
5-22	1	0.95
	2	0.60
5-30	1	1.18
	2	1.67
5-31	1	1.72
	2	1.82
6-1	1	1.65
	2	0.21

*Period 1 is 12-hour period ending at noon while period 2 begins at noon.

Table 5 (Continued)

PREDICTED CONCENTRATIONS AT DOE BOUNDARY
FOR MAXIMUM RELEASE FROM PROPOSED 200 FT STACK

Day	Period*	Maximum 12-hour HF Concentration (ppb)
6-3	1	0.50
	2	0.77
6-28	1	1.46
	2	1.47
7-1	1	1.11
	2	1.85
7-6	1	0.39
	2	0.86
7-10	1	0.32
	2	1.12
7-20	1	2.53
	2	1.83
7-21	1	1.58
	2	1.46
7-23	1	1.31
	2	0.35
7-24	1	2.06
	2	0.26
7-26	1	1.43
	2	0.75
8-14	1	0.71
	2	2.55
8-18	1	0.88
	2	0.69
8-25	1	0.41
	2	2.44

Table 5 (Continued)

PREDICTED CONCENTRATIONS AT DOE BOUNDARY
FOR MAXIMUM RELEASE FROM PROPOSED 200 FT STACK

Day	Period*	Maximum 12-hour HF Concentration (ppb)
9-10	1	0.46
	2	1.11
9-14	1	1.46
	2	0.74
9-19	1	0.78
	2	0.41
9-22	1	1.16
	2	0.42
9-26	1	1.35
	2	0.68
9-29	1	0.91
	2	1.48
10-17	1	1.47
	2	0.34
10-24	1	0.60
	2	1.91
11-4	1	2.63
	2	1.82
11-6	1	0.44
	2	1.83
11-7	1	0.93
	2	1.59
11-13	1	0.50
	2	0.75
11-16	1	0.37
	2	1.72

Table 5 (Continued)

PREDICTED CONCENTRATIONS AT DOE BOUNDARY
FOR MAXIMUM RELEASE FROM PROPOSED 200 FT STACK

Day	Period*	Maximum 12-hour HF Concentration (ppb)
11-18	1	0.46
	2	0.56
12-5	1	0.55
	2	0.81
12-20	1	0.96
	2	0.33
12-28	1	2.66
	2	0.51

less than the annual operating cost of a scrubber system and less than the annual interest on a scrubber system's capital cost. Furthermore, since fluoride is not a national or regional problem such as sulfur dioxide where taller stacks are not considered acceptable and since the approach is within good engineering practice, the Kentucky Division of Air Pollution Control has agreed with the validity of extending the C-310 stack.

APPENDIX

Calculations Supporting Selection of Stack Height Increase

The calculations performed to demonstrate that compliance with the state of Kentucky's ambient gaseous fluoride regulations could be achieved by an increase in the stack height (within good engineering practice) of the C-310 purge cascade vent have been summarized. The diffusion equation and dispersion parameters used in these calculations are identical to those employed by the state of Kentucky. Using this model, which is based on the methods of Turner[1], the maximum allowable emission rate was calculated as a function of release height to ensure that the maximum concentration at the DOE property boundary would not exceed the 12-hour standard of 4.5 ppb. It was assumed that the maximum concentration occurs where $\sqrt{2}\sigma_z = H$ and that the σ's are related to the maximum concentration by:

$$\sigma_y \sigma_z = \frac{Q}{\pi u e \chi_{max}}$$

where: σ_y = horizontal dispersion parameter

σ_z = vertical dispersion parameter

H = effective height of release

Q = release rate

π = 3.1416

u = wind speed

e = 2.7183, the base of natural logarithms

χ_{max} = concentration not to be exceeded

Knowing the release rate, wind speed, concentration not to be exceeded, and downwind distance beyond which this concentration must not be exceeded, one can determine the product $\sigma_y \sigma_z$ at that distance. That value of $\sigma_y \sigma_z$ and the selected downwind distance determine a point on Figure A-1[2] yielding a stability class (or a point between stabilities). The σ_z for this stability (or point between stabilities) can be

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[1] D. B. Turner, Workbook of Atmospheric Dispersion Estimates, U. S. Department of Health, Education, and Welfare, Cincinnati, OH, 1969.

[2] Ibid., p. 33.

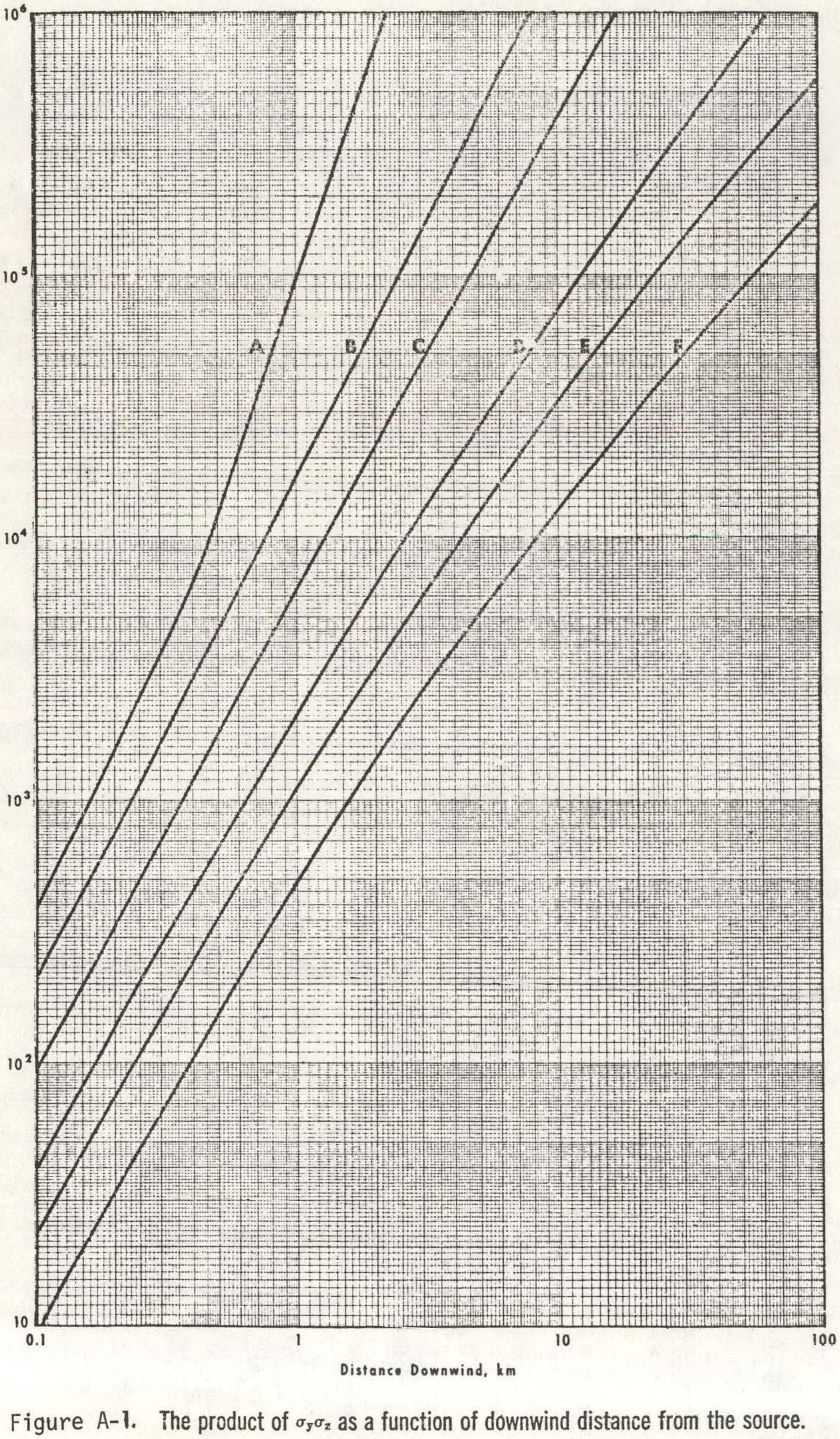

Figure A-1. The product of $\sigma_y\sigma_z$ as a function of downwind distance from the source.

Effective Height

determined from Figure A-2.[3] The required effective stack height may then be calculated from $H = \sqrt{2}\sigma_z$. As a safety factor, the effective stack height can be taken as the physical stack height, assuming no additional plume rise from buoyancy and vertical momentum of the exiting gases.

Attachment 1 demonstrates the effect of release height on the maximum allowable fluoride emission rate. Wind speeds greater than the assumed 2 m/sec can be expected at an elevation of 200 ft approximately 93% of the time, based on observations at TVA's Shawnee Meteorological Facility (see Attachment 2). The design distance of 1.4 km was selected as the shortest distance between the source and the DOE property boundary measured in a reportable wind direction (see Attachment 3). The correction for a 1-hour sampling time takes into account that the σ_y and σ_z parameters correspond to a sampling time of about 10 minutes and was calculated from:

$$\chi_s = \chi_k \left(\frac{t_k}{t_s} \right)^p$$

where: χ_s = desired concentration estimate for the sampling time, t_s

χ_k = concentration estimate for the shorter sampling time, t_k

p = approximately 0.17

A final remark about the maximum allowable emission rate may be necessary to prevent misinterpretation. This quantity is expressed as an amount of fluoride which may be emitted over a 12-hour period. The emission may occur at any time within the period as long as the maximum allowable total is not exceeded. The worst case would be in the event the emission occurs over a 1-hour period (or less). Since wind data are normally hourly observations, one must assume a constant direction for each 1-hour period. If the emission were allowed to occur over a longer time period, there is some probability that the wind direction could change, and the effect on a receptor would be diminished. The calculation provides protection for the worst case.

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[3] D. B. Turner, Workbook of Atmospheric Dispersion Estimates, U. S. Department of Health, Education, and Welfare, Cincinnati, OH, 1969.

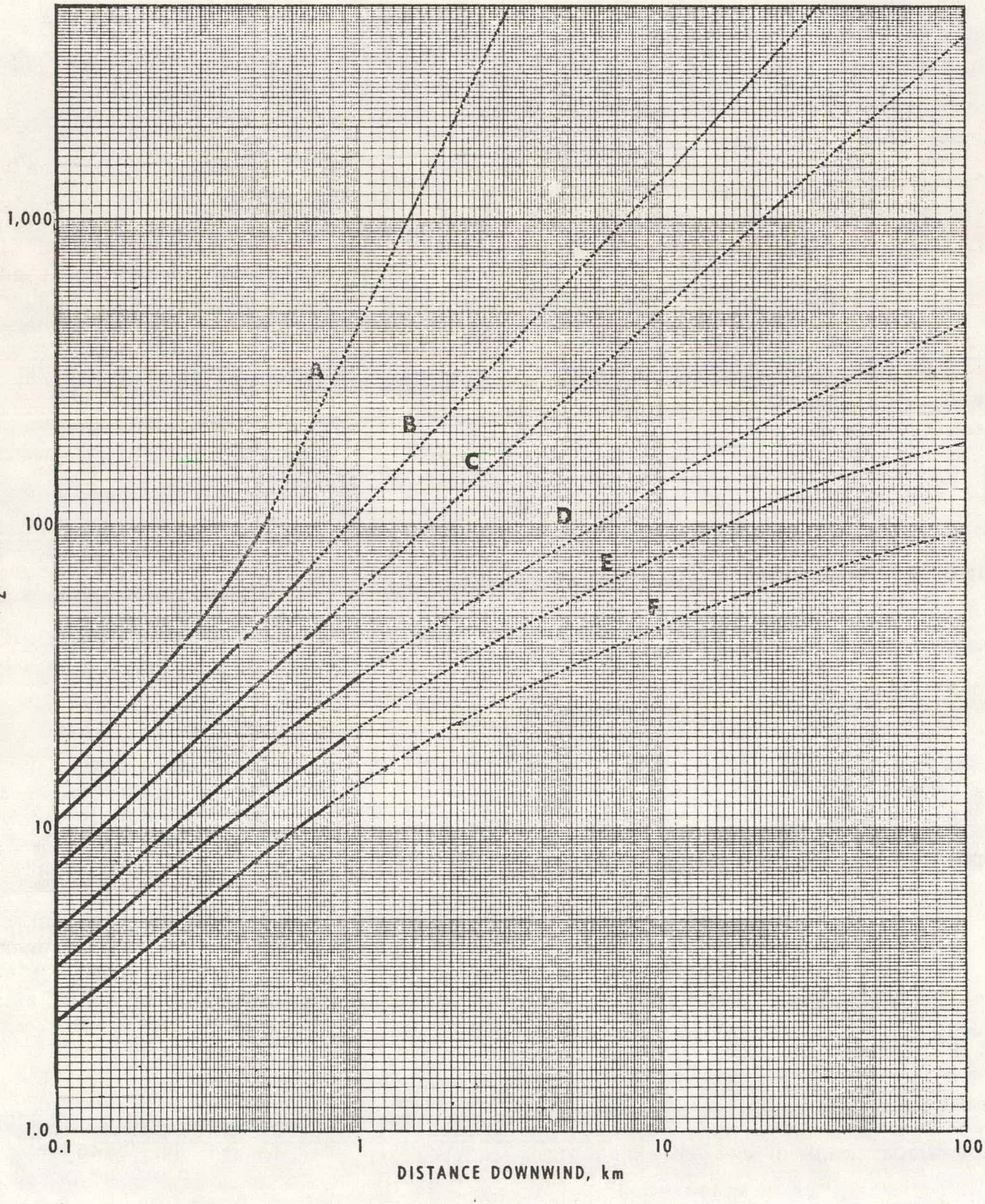
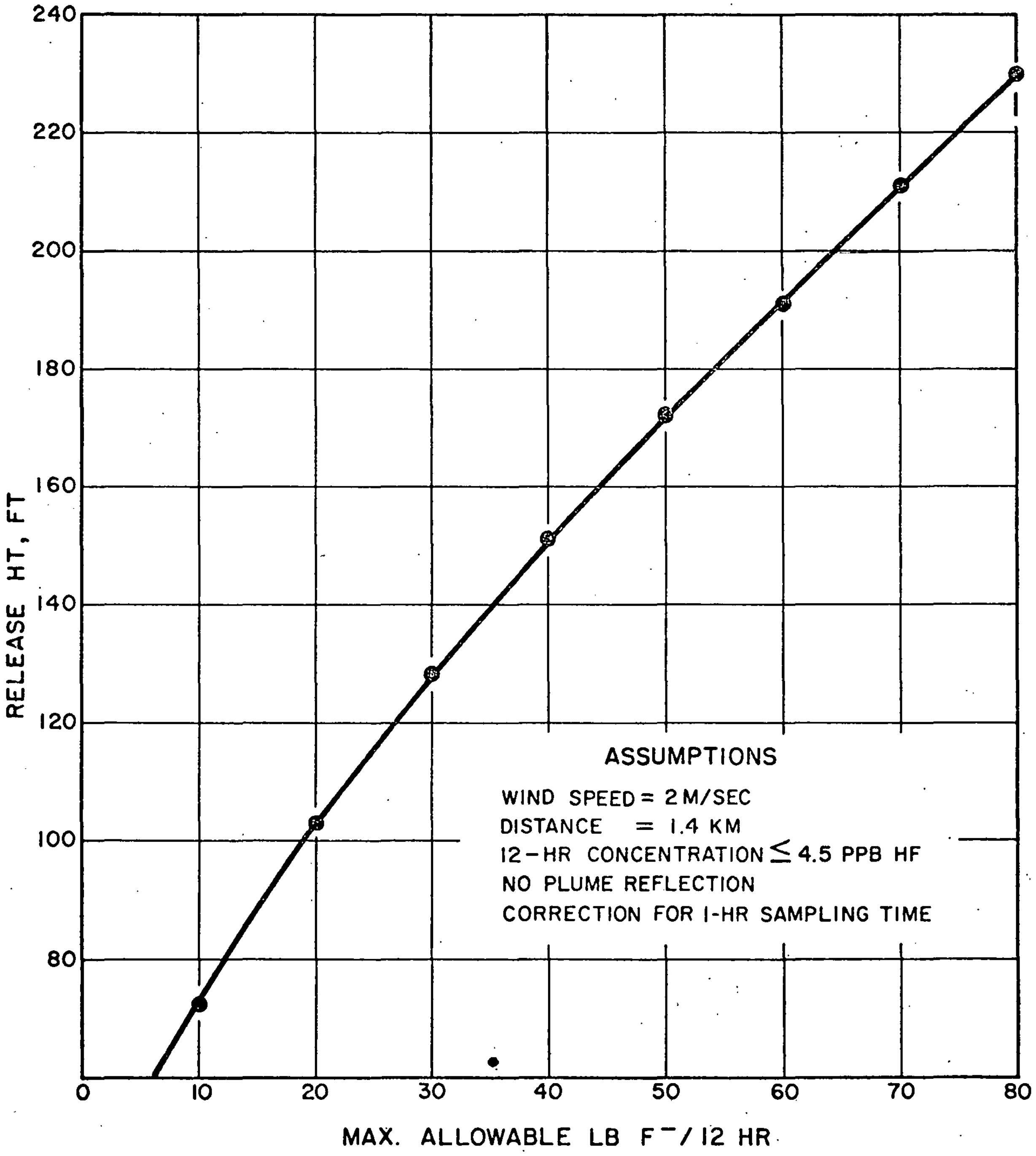


Figure A-2. Vertical dispersion coefficient as a function of downwind distance from the source.

Estimates

Attachment 1



EFFECT OF RELEASE HEIGHT ON ALLOWABLE FLUORIDE EMISSIONS

JOINT PERCENTAGE FREQUENCIES OF WIND SPEED BY DIRECTION.

DISREGARDING STABILITY CLASS

SHAWNEE MET FACILITY

OCT 23, 75 - SEP 30, 78

WIND DIRECTION	WIND SPEED(MPH) 0.6=1.4	1.5=3.4	3.5=5.4	5.5=7.4	7.5=12.4	12.5=18.4	18.5=24.4	>=24.5	TOTAL
N	0.01	0.17	0.51	0.94	3.55	2.32	0.27	0.01	7.78
NNE	0.01	0.26	0.69	1.20	3.05	0.78	0.05	0.0	6.04
NE	0.02	0.27	0.64	1.20	3.12	0.53	0.0	0.0	5.78
ENE	0.01	0.26	0.92	1.16	2.65	0.33	0.02	0.0	5.35
E	0.01	0.20	0.72	1.12	2.84	0.42	0.04	0.0	5.35
ESE	0.01	0.15	0.60	0.83	2.20	0.65	0.01	0.0	4.45
SE	0.0	0.21	0.72	0.74	2.29	0.80	0.08	0.04	4.88
SSE	0.0	0.10	0.54	0.88	2.45	1.55	0.21	0.06	5.87
S	0.01	0.25	0.56	1.08	4.49	3.11	0.78	0.13	10.41
SSW	0.0	0.20	0.50	0.79	4.17	4.83	1.56	0.29	12.34
SW	0.01	0.17	0.35	0.65	2.44	2.03	0.77	0.29	6.71
WSW	0.01	0.14	0.36	0.71	2.64	1.69	0.50	0.17	6.22
W	0.02	0.17	0.47	0.63	2.07	1.25	0.27	0.07	4.95
WNW	0.01	0.16	0.37	0.49	1.40	1.15	0.33	0.08	3.99
NW	0.01	0.16	0.31	0.62	1.96	2.16	0.80	0.19	6.21
NNW	0.0	0.09	0.24	0.26	1.13	1.37	0.43	0.06	3.58
SUBTOTAL	0.14	3.04	8.50	13.30	42.45	24.97	6.12	1.39	99.91

TOTAL HOURS OF VALID WIND OBSERVATIONS	25205
TOTAL HOURS OF OBSERVATIONS	25776
RECOVERABILITY PERCENTAGE	97.8
TOTAL HOURS CALM	6

ALL COLUMNS AND CALM TOTAL 100 PERCENT OF JOINT VALID OBSERVATIONS

METEOROLOGICAL FACILITY: LOCATED AT SHAWNEE STEAM PLANT
WIND SPEED AND DIRECTION MEASURED AT THE 61.00 METER LEVEL

DATE PRINTED: 01/27/79

MEAN WIND SPEED = 10.9 MPH

Attachment 2

Attachment 3

SHORTEST DISTANCE BETWEEN SOURCE AND DOE PROPERTY BOUNDARY FOR EACH WIND DIRECTION

Wind direction	Distance to DOE boundary, km
N	1.4
NNE	1.6
NE	1.9
ENE	2.2
E	2.3
ESE	2.0
SE	2.0
SSE	2.2
S	1.8
SSW	3.1
SW	3.2
WSW	2.5
W	1.8
WNW	1.7
NW	1.4
NNW	1.8

For longer time periods for which ambient fluoride standards exist (e.g., 24 hours), a maximum allowable emission can be calculated as:

$$Q_s = Q_k \frac{X_s t_s}{X_k t_k}$$

where: Q_s = desired maximum allowable emission for time t_s having an ambient standard X_s

Q_k = maximum allowable emission for the shorter time period t_k having an ambient standard X_k

As an example, Attachment 1 shows that for a release height of 200 ft, the maximum allowable 12-hour emission is approximately 64 lb F^-. To calculate the maximum allowable 24-hour emission, substitution into the above equation yields:

$$Q_s = Q_k \frac{X_s t_s}{X_k t_k} = (64) \frac{(3.5)}{(4.5)} \frac{(24)}{(12)} = 100 \text{ lb } F^-$$

TECHNETIUM REMOVAL FROM PLANT VENT STREAMS

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GOODYEAR ATOMIC CORPORATION

Technetium
Purge Cascade
Environmental Effects-Technetium
Emissions-GDP

ABSTRACT

Environmental regulations further restricting certain airborne effluent radionuclide concentrations, including technetium-99, are likely in the future. Feasibility studies of various polishing/trapping processes for reduction of technetium-99 emissions from vent streams have been initiated at GAT. Existing plant aluminum oxide (Al_2O_3) trap systems, primarily intended to ensure removal of all but trace amounts of uranium, have been monitored for technetium removal efficiency, especially from the top and side purge cascade vent streams. Results indicate that present Al_2O_3 vent stream cleanup systems offer a significant potential for technetium reduction under actual operating conditions with inlet trap concentrations in the vicinity of 1 ppm Tc. Below concentrations of 0.1 ppm, more sensitive sampling techniques are needed to better characterize trap performance. Developmental studies into alternative control processes, utilizing potentially more effective trapping agents, are currently in progress with a mobile test apparatus connected directly to the plant vent source.

INTRODUCTION

With major responsibility for radioactive discharges now under jurisdiction of the Environmental Protection Agency and the Nuclear Regulatory Commission, airborne radionuclides are likely to be restricted further than the current DOE guidelines dictate. Recently, the radionuclide of greatest concern at the gaseous diffusion plants has been technetium-99, a low energy beta emitter which is produced in nuclear power reactors during U-235 fissioning[1] and fed to the enrichment plant as a trace contaminant in UF_6 reactor return. The control of uranium is incorporated into the design of the diffusion plants. Gaseous forms of technetium, however, tend to be rejected to the atmosphere via the vent streams. As a result of its higher specific activity, annual airborne discharges of technetium-99 (curies per year), although well within DOE guideline limits, have been considerably higher than those of the principal uranium isotopes. Studies conducted by ORNL regarding selective concentration of technetium in the food chain and subsequent radiological exposure assessments[2] suggest, but do not prove, that airborne releases of 1 curie per year may be excessive. Although certainly far from conclusive, such information is of the type that influences EPA decisions regarding low levels of radiation as potential hazards to the public. The tendency toward minimum exposure risk might well mandate safety factors involving atmospheric technetium releases, resulting in limits that are considerably below 1 curie per year. This is particularly significant at GAT since emissions of 5.9 curies per year have been experienced as recently as 1976, although the most recent discharges are below 1 curie per year due to improved control systems.

The input of technetium to the Portsmouth cascade has decreased substantially since about 1975, and the amount of technetium in the cascade gases has dropped considerably since that time. The potential for a gradual decrease in the concentration of airborne emissions exists. However, there is evidence that it would take a long time to reach an acceptably low level of emissions by this route. Consequently, studies have been in progress at GAT to evaluate polishing/trapping processes which selectively reduce concentrations of technetium from plant vent streams to levels equivalent at least to those of uranium in curies per year, or to the lowest, practically achievable levels.

Existing Plant Vent Systems

Gaseous streams containing technetium primarily involve three plant vents at Portsmouth: the top purge cascade, the side purge cascade and the cold recovery vents. Airborne emissions from the X-705 Decontamination Facility are also possible during cascade removal of equipment; however, special purging operations that precede disassembly operations essentially eliminate this area as a significant airborne source.

The vent streams from the top and side purge cascade pass through banks of activated alumina (Al_2O_3) traps prior to atmospheric discharge. The cold recovery area utilizes banks of NaF traps during most operations, although Al_2O_3 traps are available and employed when inert gases are processed.

The Al_2O_3 traps at the top and side purge vents were designed to act as a back-up system to remove remaining traces of UF_6 gas before discharge to the atmosphere. The gaseous diffusion process is the key plant control mechanism limiting the amount of UF_6 introduced into the vent streams. In contrast, air and other lighter-than-UF_6 impurities, including technetium, were not intended to be retained as efficiently as UF_6, and their release via the vent streams is a normal part of the operation. For the cold recovery area, cold trapping and sodium fluoride (NaF) traps are the major systems limiting the final UF_6 emissions. The NaF traps is the last means for limiting air discharges of uranium to as low a concentration as is reasonably achievable.

The principal questions that must be answered regarding gaseous technetium are as follows.

1. Is technetium effectively removed as the vent gases pass through the existing trap systems primarily intended for UF_6?

2. Are these systems adequate or are much better methods required? What newer or improved processes are available?

Table 1 outlines the general approach for answering some of the questions. The adequacy of any trapping process cannot be ascertained unless limits or restrictions have been clearly defined. Given the environmental questions raised by the ORNL study, it is not possible to state at this time what emission limits will ltimately be mandated by the EPA.

Table 1 Reduction of Tc Emissions from Plant vent Streams

1. Determine performance of existing systems
   a. Al_2O_3 traps at top purge.
   b. Al_2O_3 traps at side purge.
   c. NaF traps at cold recovery.
2. Scope other potential control/reduction/polishing processes.

Performance Tests on Existing Plant Trap System

In order to assess the efficiency of activated Al_2O_3 traps (F-1 Grade Al_2O_3 from Alcoa), a series of special technetium removal tests were conducted in late 1978 to early 1979 and late 1979 to early 1980 on the top and side purge vent gases before and after passage through the Al_2O_3 trap systems at X-326. The traps consist of 5-inch OD x 6 feet deep, corrosion resistant reactors in parallel banks of three, serving as multiple fixed bed systems. The first series of tests showed encouraging results as shown by Figures 1 and 2. In Figure 1 decontamination factors (DF = Tc Inlet Conc. ÷ Tc Outlet Conc.) of 25-100 are readily apparent at inlet technetium concentrations in the approximate range of 0.5-3 ppm. For the side purge vent gases where concentrations were about 1/50th those of the top purge at that time, decontamination factors in the neighborhood of 1 to 6 are noted (Figure 2). These 21 data sets for both the top and side purge cascades have been restructured in histogram from Figure 3 to illustrate the wide distribution in inlet concentrations.

The testing was repeated about one year later when the power was at reduced levels. Some Al_2O_3 traps had been recharged in the interim. More than 30 data sets have been obtained in the latest series of top purge performance tests conducted between November 11, 1978, and January 30, 1980, in preparation for laboratory screening tests with small scale mobile trapping equipment. Results are depicted in Figure 4. In contrast to average inlet concentrations of 1.5 ppm for the first test series (obtained in 1978-79), concentrations averaged 0.3 ppm technetium about one year later. However this may have been temporary, since data collected beginning early in February 1980 indicated techneitum levels above 1 ppm were again recurring, possibly as a result of feeding old cylinder heels of Paducah product several months earlier. Average decontamination factors for the last series of tests was 36 at inlet concentrations of 0.3 ppm. Corresponding data were collected for the side purge vent but the information has not been completely interpreted due to large variation of concentration results which are at or near the limit of precise detection. Below approximately .05 ppm more sensitive sampling techniques are needed to better characterize trap performance.

The relationship between average decontamination factor (DF) and inlet technetium concentration obtained from all data is summarized by Figure 5. Clearly DF values become lower as Tc inlet concentration decreases. The implication is that the more dilute the vent stream becomes the lower the technetium removal efficiency. It is expected that more data will be collected, and technetium loading on Al_2O_3 will be determined, when trap recharging is required. From the loading characteristics for the top and side purge vent traps, capacity estimates for various installations and required time between future changeouts can be projected for effective technetium removal opera-

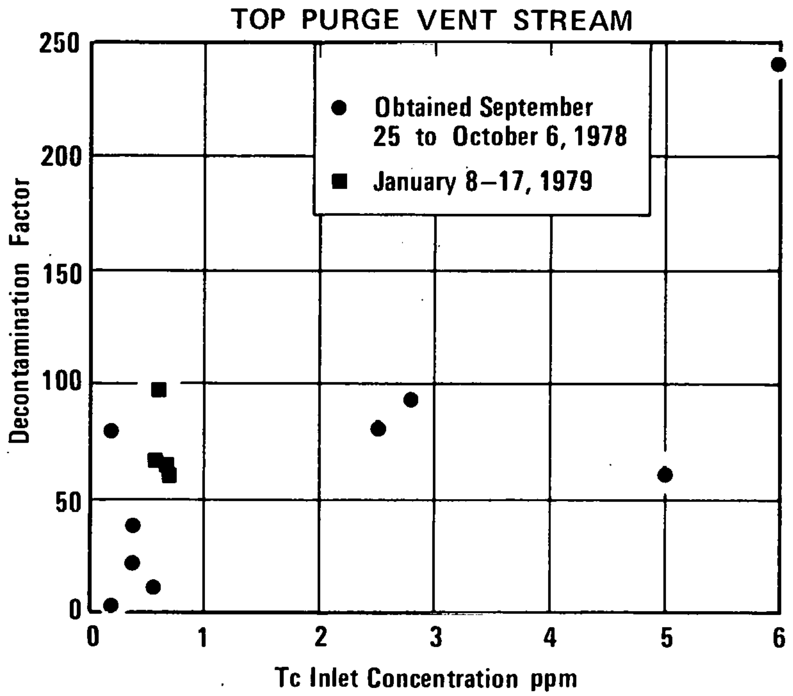


FIGURE 1 TOP PURGE VENT STREAM Tc DECONTAMINATION VIA Al_2O_3 TRAPS VS. INLET CONCENTRATION

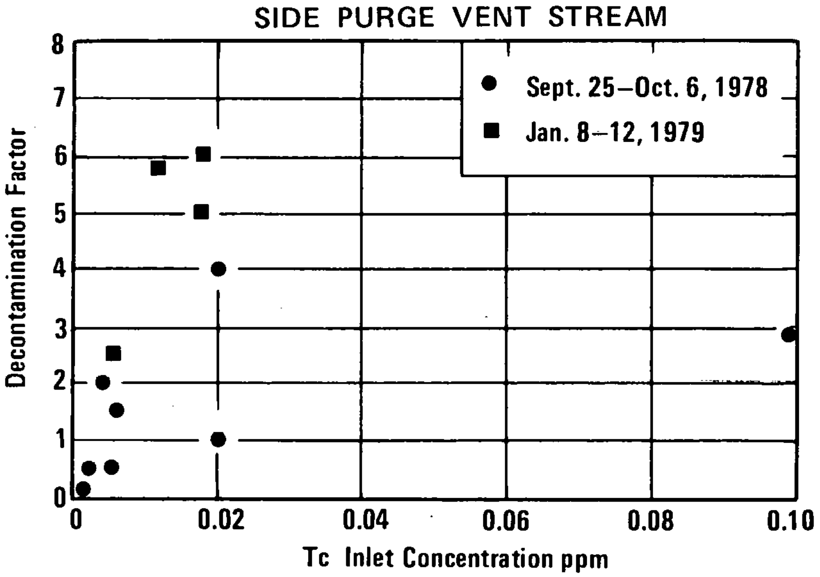
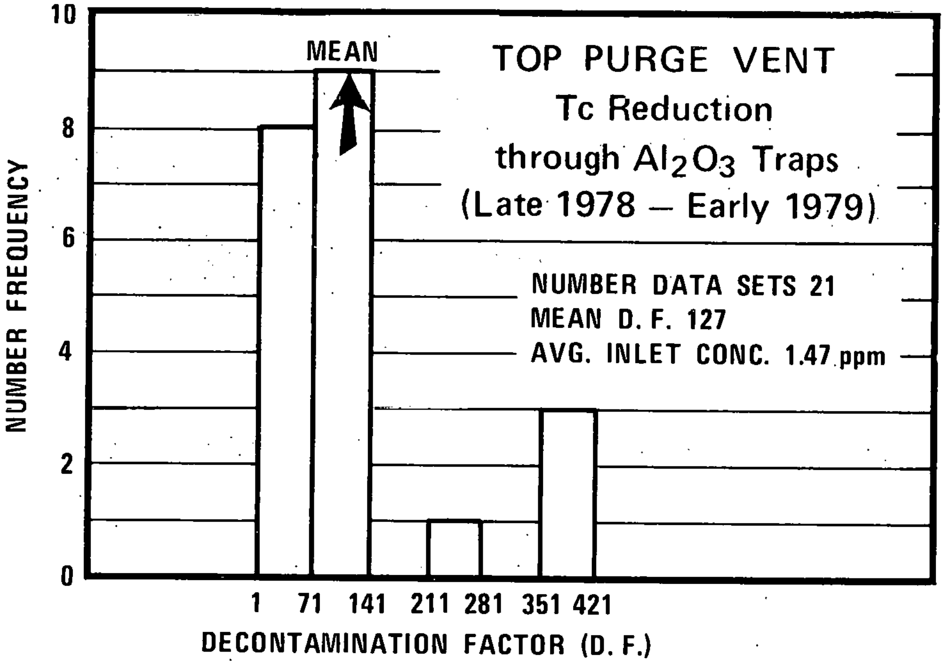


FIGURE 2 SIDE PURGE VENT STREAM Tc DECONTAMINATION VIA Al_2O_3 TRAPS VS. INLET CONCENTRATION



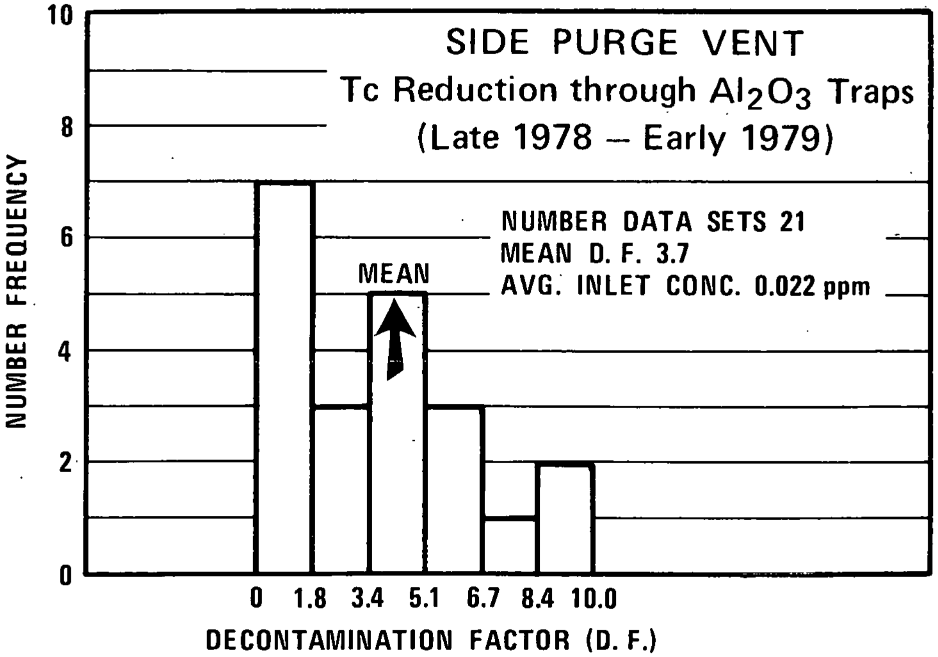
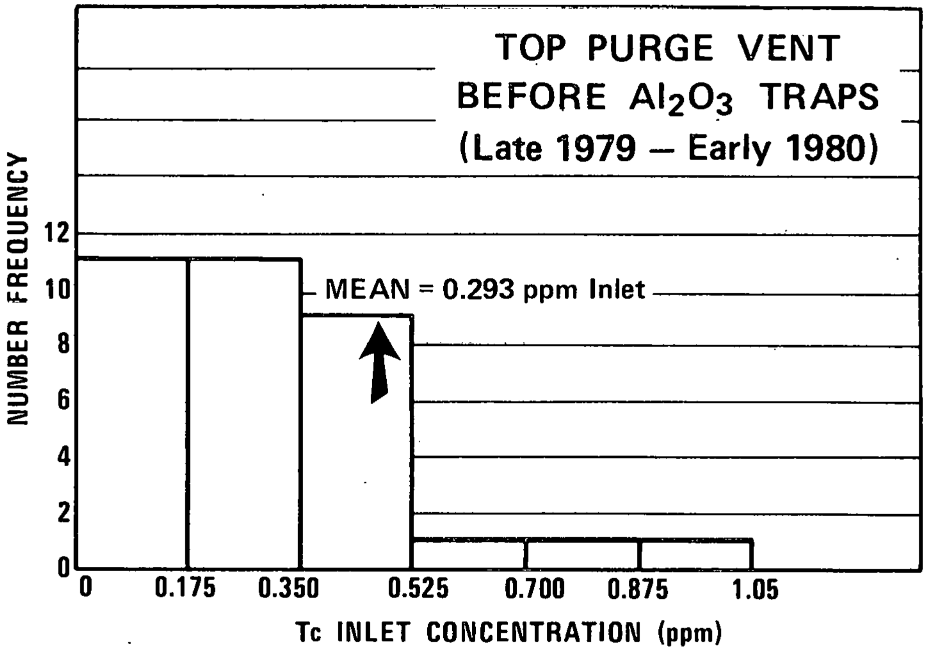


FIGURE 3 Tc REDUCTION AT TOP AND SIDE PURGE VENTS



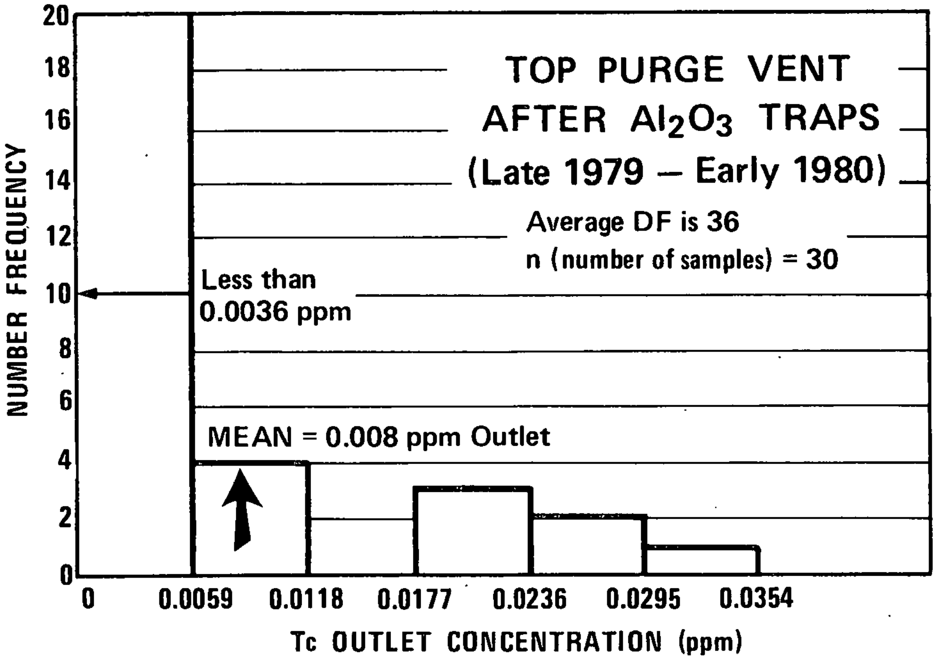


FIGURE 4 TOP PURGE VENT BEFORE AND AFTER Al_2O_3 TRAPS

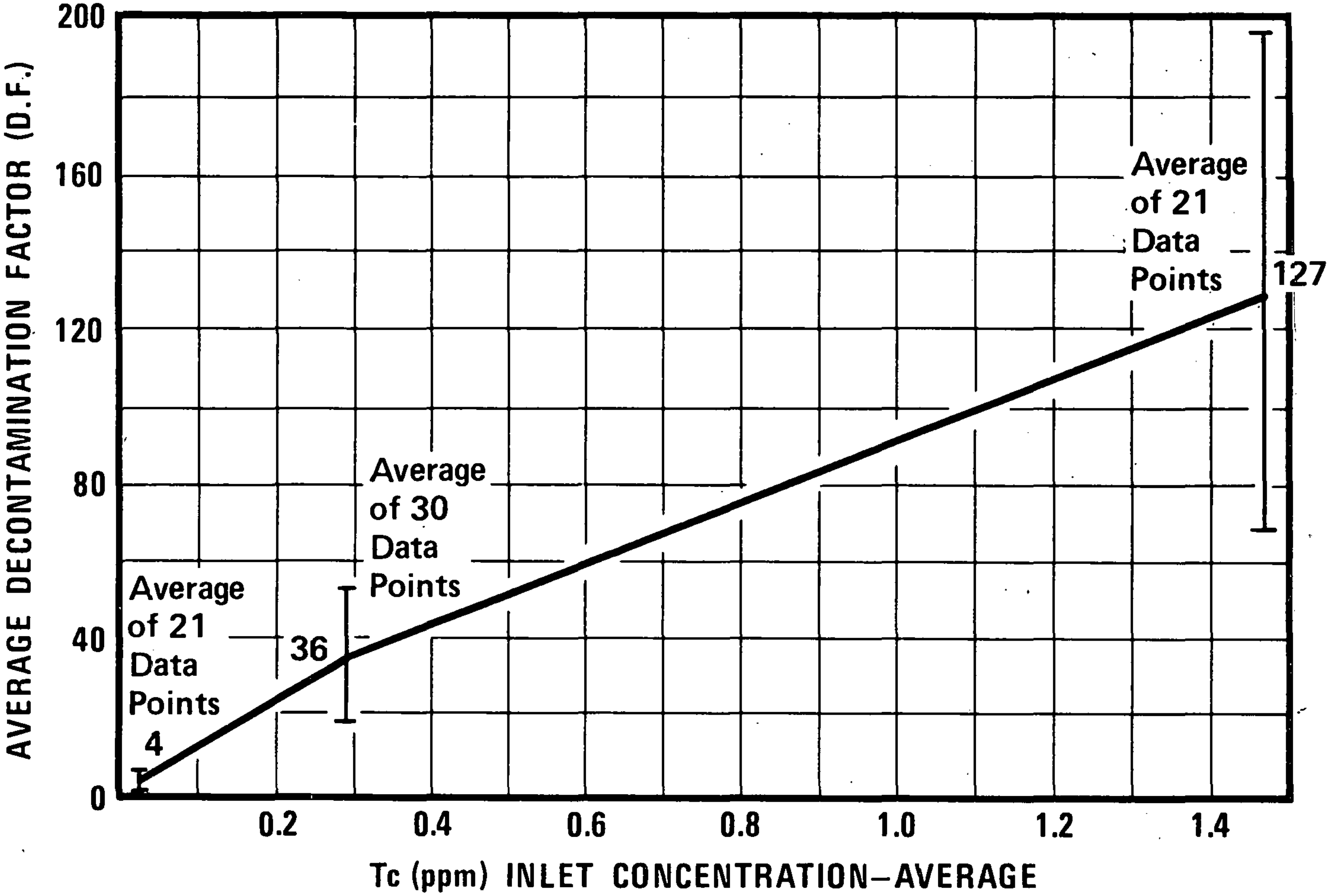


FIGURE 5 SUMMARY DATA FOR Al_2O_3 PLANT TRAP SYSTEM

tions. The operating performance of activated Al_2O_3 to greatly curtail Tc emissions in the concentration range of 0.3-1.5 ppm represent the first demonstrations that the same trapping agent employed for UF_6 control, can serve extremely well for Tc emissions as well.

Experimental Trapping Studies

Screening of trapping/polishing processes are in progress using a small scale mobile apparatus tied in parallel across the plant Al_2O_3 trap system of the top purge cascade. A schematic representation of the apparatus is shown in Figure 6 and a photograph of the equipment in actual operation is shown in Figure 7. Magnesium fluoride (MgF_2) performance evaluation for low velocity runs is currently in progress for a 3-inch OD x 30-inch deep bed as shown in Figure 8. The first twenty days of operation resulted in DF values of up to 250 and outlet concentrations of below 0.01 ppm technetium. Thereafter, low level technetium leakage occurred with average outlet concentrations of 0.03 ppm being observed. After more than 70 days of operation, the trap still retains more than 90% of the technetium but it is apparent that performance is inferior to an activated Al_2O_3 trap in terms of low level leakage at longer operating times. In special corrosive vent gas applications, where short term surges of technetium might be encountered, MgF_2 could be preferable to Al_2O_3. There is also the possible advantage of in-situ regeneration with MgF_2 pellets which Al_2O_3 may not offer. MgF_2 trapping technology[3] is used to remove technetium-99 at the 10-200 ppm level in cascade gases containing high concentrations of UF_6 by parallel side stream operation. The use of MgF_2 at the vent stream location is the first demonstrated usefulness at the sub-ppm concentration range. A list of potential trapping agents planned for screening is shown in Table 2. The evaluation plan involves selecting the trapping material that will best eliminate low level leakage and that will be independent of effects caused by the presence of corrosive gases. All comparisons at this point are with reference to activated Al_2O_3 traps. Note that the laboratory trapping system is capable of controlled heating. This will permit evaluation of chemical reaction disposal (via gas-solid reaction) as well as adsorptive processes.

If sufficiently accurate data are obtainable, attempts at modeling the fixed bed technetium trapping processes will be undertaken. This should enhance understanding of the process and contribute toward more confident predictions of scale-up parameters for larger installations and extrapolation of performance to lower concentrations (< 0.01 ppm) where analytical data are only marginally reliable by current sampling methods.

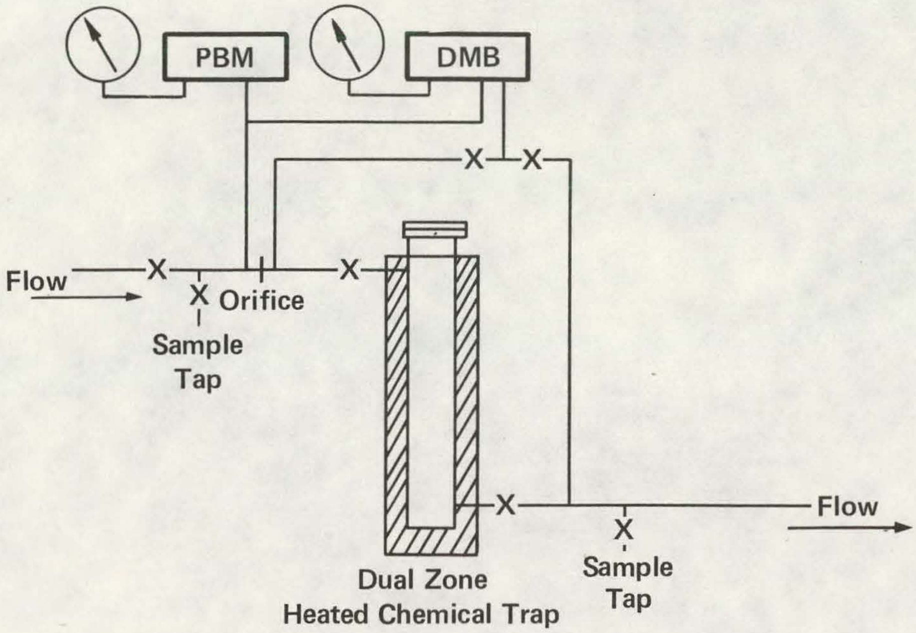


FIGURE 6 BASIC APPARATUS FOR
EXPERIMENTAL TRAPPING STUDIES

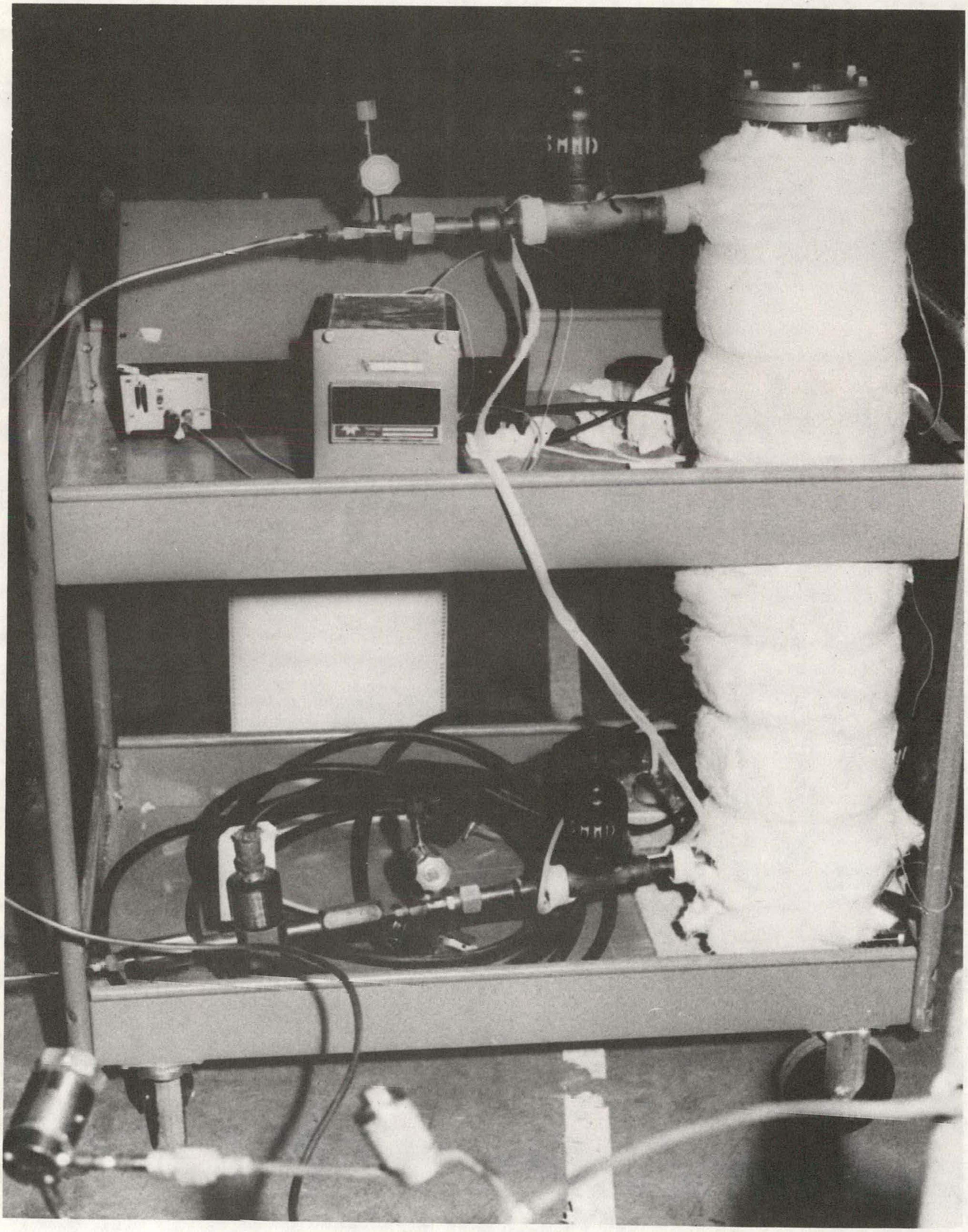


FIGURE 7 MOBILE TEST APPARATUS
CONNECTED TO VENT GAS SIDESTREAM

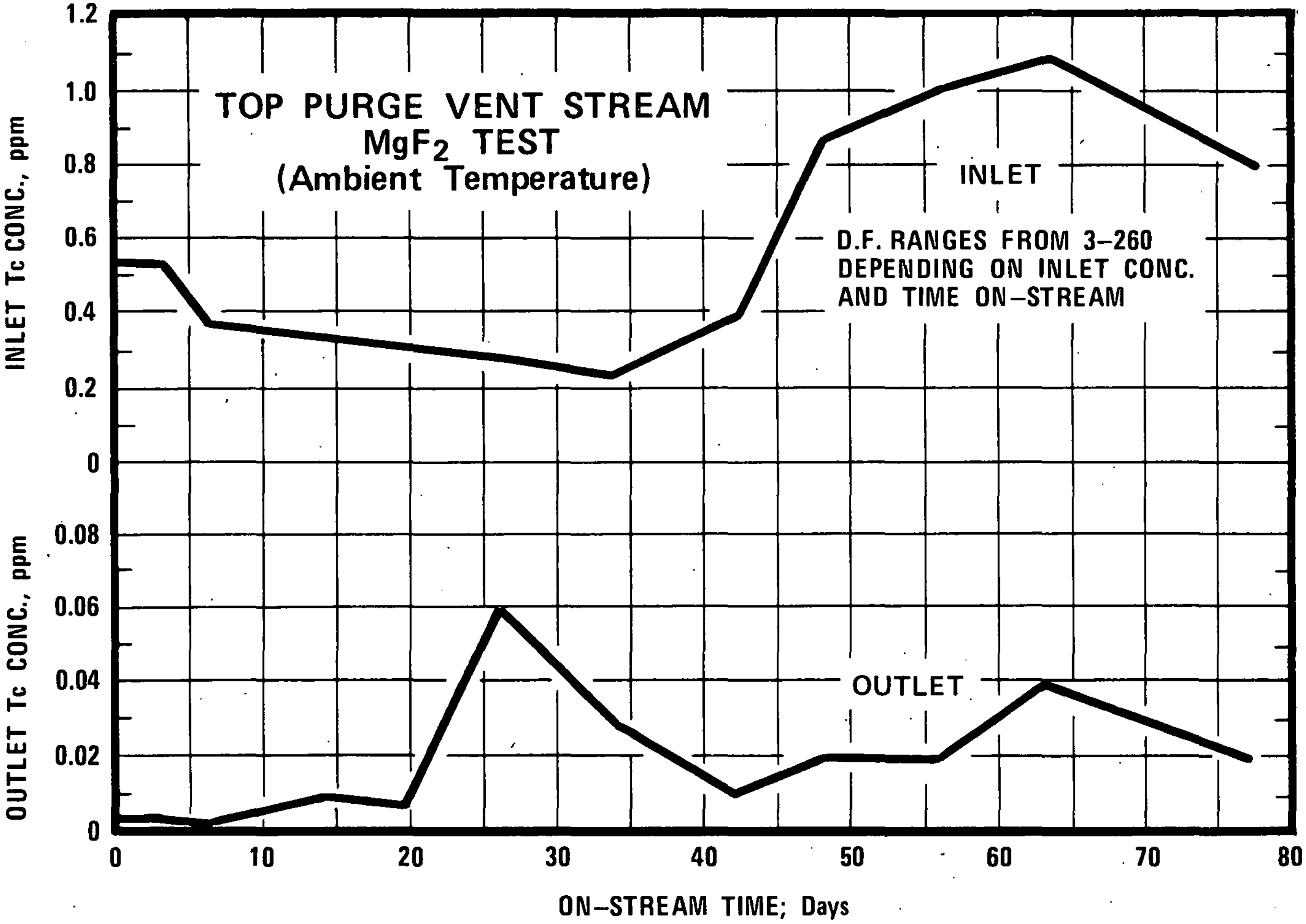


FIGURE 8 TOP PURGE MgF_2 TEST

TABLE 2 TRAPPING AGENTS SCHEDULED FOR SCREENING TEST RUNS

Trapping Agent	Expected Partial Reversibility of Tc Adsorption
MgF_2	Yes
Activated Al_2O_3	No
Soda Ash (Na_2CO_3)	No
NaF	Yes
Oolitic Lime ($CaCO_3$)	No
"Fluorinated" Al_2O_3	?
$CaSO_4$	Yes

CONCLUSIONS

1. Activated Al_2O_3 traps play an important role in reducing Tc from some plant vent streams under existing operating conditions.
2. Trapping efficiency for Al_2O_3 drops off sharply with decreasing Tc inlet concentration.
3. Initial screening tests with MgF_2 pellets show it is effective, but inferior to activated Al_2O_3, for Tc removal from vent streams. However, MgF_2 is corrosive-gas resistant, while Al_2O_3 may not be resistant in terms of Tc removal performance in the presence of F_2.
4. More accurate analytical techniques for monitoring gaseous Tc below 0.05 ppm must be developed.

REFERENCES

1. K. V. Kotegev, O. N. Pavlov, V. P. Shvedov, "Technetium," in Advances in Inorganic Chemistry and Radiochemistry, Volume II, H. J. Emeleus and A. G. Sharpe, Editors, Academic Press, New York, 1968, p. 1.

Dup

NO_x SCRUBBING AT ORNL*

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Consolidated Fuel Reprocessing Program
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ABSTRACT

Concern over the level of emission of nitrogen oxides (NO_x) from nuclear fuel reprocessing facilities has focused the efforts of research, development and engineering on ways of reducing their concentration in off-gas streams. Research began back in January of 1976. A scrubber design which incorporated the research work began in mid September of 1978. The scrubber is presently being fabricated and will become a part of the Integrated Process Demonstration (IPD) facility.

This paper will present an introduction to the chemistry of NO_x and will discuss the problems associated with its removal from off-gas streams. The IPD NO_x off-gas system components will be presented and the system interfaces with the other IPD systems will be shown. The computer model used to design the scrubber will be discussed and the results from the program will be presented. The paper will conclude with a brief description of other scrubber applications and will mention areas of continuing research.

INTRODUCTION

This work was performed for the Integrated Equipment Test (IET) Facility. This facility is a part of the Oak Ridge National Laboratory

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*Research sponsored by the Nuclear Power Development Division, U.S. Department of Energy under Contract W-7405-eng-26 with Union Carbide Corporation.

(ORNL) Consolidated Fuel Reprocessing Program (CFRP). When construction is complete, the IET facility will be an experimental engineering laboratory for testing and evaluating process equipment trains used for reprocessing nuclear fuel from liquid metal fast breeder reactors.

One part of the IET project is the Integrated Process Demonstration (IPD) area. Process equipment which has evolved from development efforts will be combined with supporting process equipment to form process systems. The IPD systems will form a completely integrated process which will demonstrate nuclear fuel reprocessing technology from equipment, system, and process standpoints.[1]

The NO_x off-gas system is one of many process systems within the IPD area. Figure 1 illustrates all of the IPD systems and their interfaces with one another. As shown, the NO_x off-gas system is only one part of the overall off-gas treatment block.

This paper reviews the development work completed for the NO_x off-gas system and discusses the purpose of each process component within the system. A mathematical model for predicting the absorption of NO_x into water or dilute nitric acid was developed. An engineering scale sieve-plate column was used to gather a data base for developing and testing the model.[2] The model was modified to predict the absorption of NO_x in bubble-cap columns and was used to size and specify the NO_x absorption column (NO_x Scrubber) in the NO_x off-gas system.[3] The NO_x off-gas system is designed to support the NO_x Scrubber by providing cooling and motive force to the process streams within the system.

DEVELOPMENT[3]

The overall chemical reactions involved in the steady-state absorption of NO_x compounds into water or dilute nitric acid are adequately represented as follows:

$$2\,NO_2(g) = N_2O_4(g), \qquad (1)$$

$$N_2O_4(g) = N_2O_4(\ell), \qquad (2)$$

$$N_2O_4(\ell) + H_2O(\ell) \rightarrow HNO_3(\ell) + HNO_2(\ell), \qquad (3)$$

$$3HNO_2(\ell) = H_2O(\ell) + HNO_3(\ell) + 2NO_2(g), \qquad (4)$$

$$2NO(g) + O_2(g) \rightarrow 2NO_2(g), \qquad (5)$$

where (g) and (ℓ) indicate gas and liquid species respectively. The important mechanisms involved in the absorption of NO_x compounds with greater than 1 vol % NO_2^* ($NO_2 + 2N_2O_4$) are: (1) the absorption of NO_2^* resulting in the production of liquid HNO_2 and HNO_3; (2) the dissociation of liquid HNO_2 into liquid HNO_3 and gaseous NO; and (3) the gas phase oxidation of NO to NO_2.

ABNØX is the computer program which models the absorption of NO_x in bubble-cap columns using water or dilute nitric acid as the scrubbing liquor. The program is designed to calculate the extent of reactions 1-5 for each stage within the column. Beginning with the bottom stage,

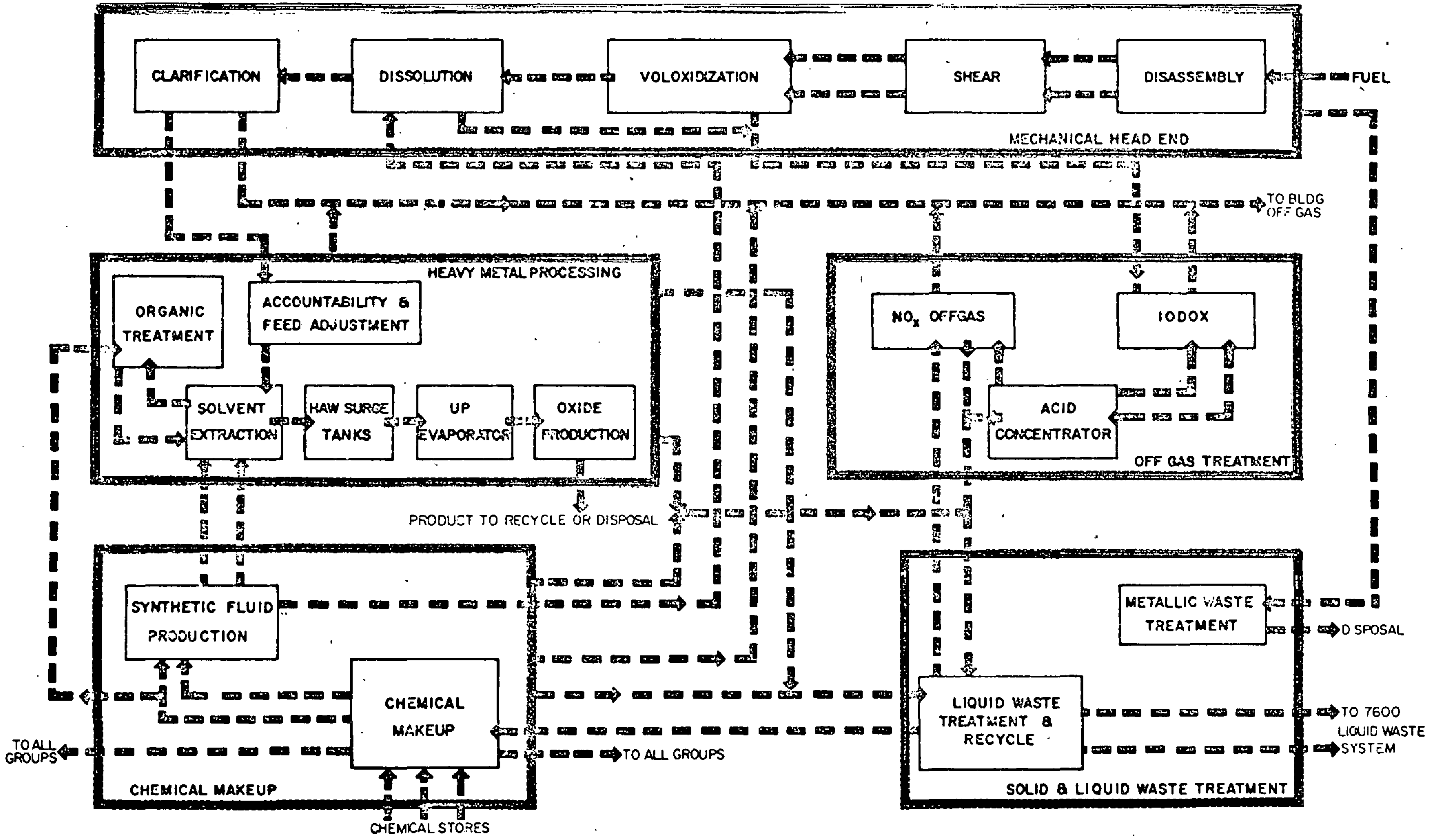


Figure 1. IPD Process Systems with Interfaces

ABN0X performs a stage-by-stage computation for $X_{NO_2^*}$, X_{HNO_2}, and X_{NO} where:

$X_{NO_2^*}$ = conversion of NO_2^*, the ratio of the change in the partial pressure of NO_2^* to the partial pressure entering the stage,

X_{HNO_2} = conversion of HNO_2, the concentration decomposing per plate divided by the concentration of HNO_2 entering the plate,

X_{NO} = conversion of NO in the free space between the plates, the ratio of the partial pressure of NO oxidized to the partial pressure of NO entering the gas space.

Values for $X_{NO_2^*}$, X_{HNO_2} and X_{NO} are sequentially determined and applied to the plate's inlet conditions to obtain the inlet conditions for the next stage. This procedure is continued until the conditions at each stage are determined. The moles of acid produced are then compared to the moles of NO_x absorbed. If the difference is not within the program's error limit the stage to stage procedure is repeated until the error limit is obtained.

ABN0X is written in Fortran and consists of a main program and seven subroutines. A macroflowsheet of ABN0X is presented in Figure 2. Basically, ABN0X consists of a main program for data input and output and for calling the process model PR0C. Subroutine PR0C calculates component partial pressure and concentration profiles of the gas and liquid phases through the use of the other six subroutines. Subroutines FR0TH and EVAL calculate $X_{NO_2^*}$, NITRUS and EVALN calculate X_{HNO_2}, and GAS and EVALG calculate X_{NO}.

The use of ABN0X requires a tower description, operating temperature and pressure, and composition of the feed streams. The feed gas flow rate and component partial pressures are on a dry gas basis. ABN0X computes the water vapor partial pressure for the column operating temperature and makes appropriate adjustments to the gas flow rate and component partial pressures. The input variables (in order of program input) are:

1. Number of column trays (plates)
2. Inside diameter of column, m
3. Submergence of the bubble-cap slot, measured from the center of the slot to the top of the downcomer plus one half of the tray's liquid gradient (see Fig. 3), m
4. Height of the center of the slot from the plate (see Fig. 3), m
5. Height of the free space between trays (see Fig. 3), m
6. Total pressure (ABN0X assumes constant pressure), atm
7. Operating temperatures (ABN0X assumes constant liquid phase temperature), K
8. Feed gas flow rate (dry gas basis), m^3/s
9. Scrub solution flow rate at operating temperature, m^3/s
10. Concentration of HNO_3 in the scrub solution feed stream, kg·mole/m^3
11. Concentration of HNO_2 in the scrub solution feed stream, kg·mole/m^3

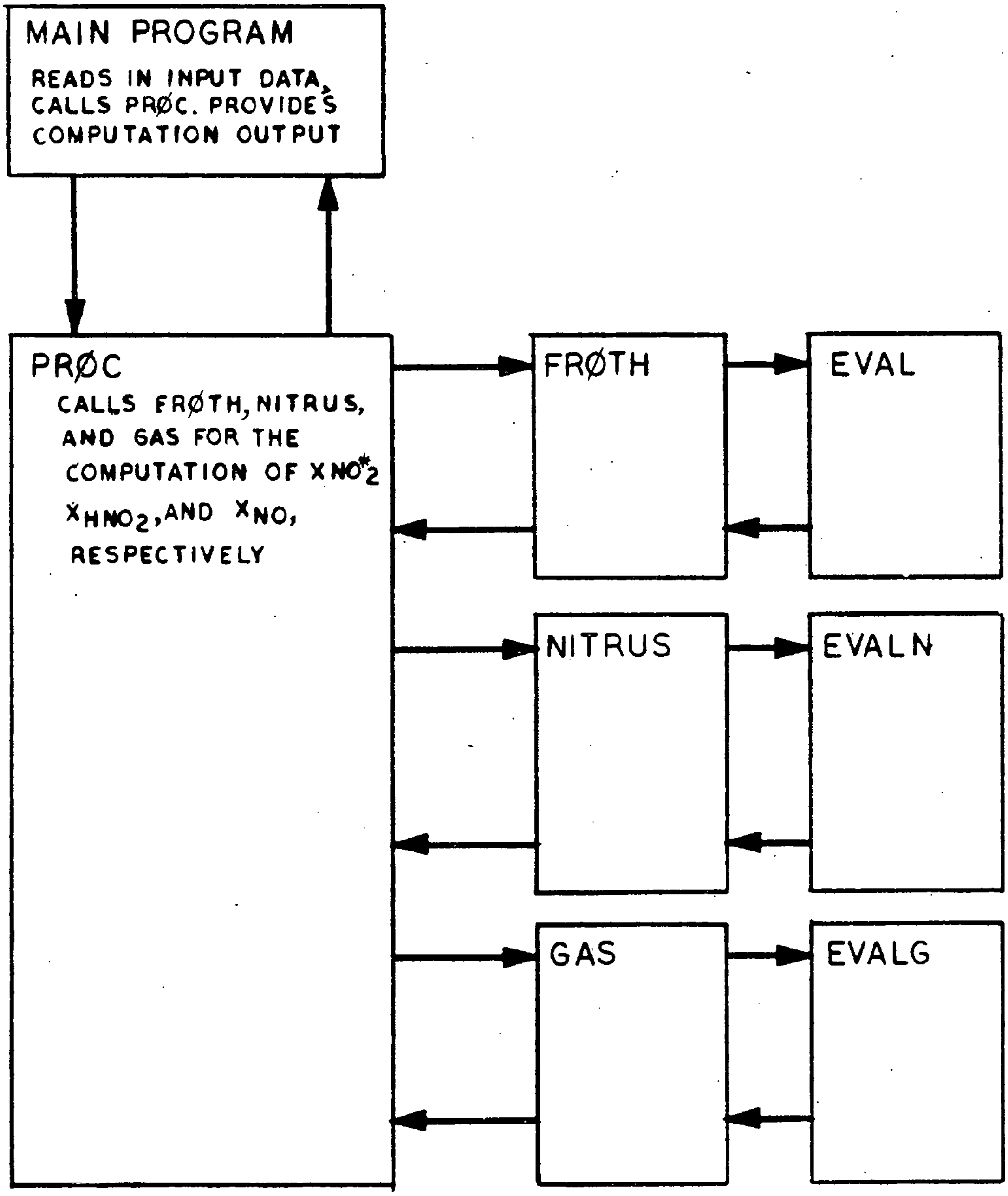
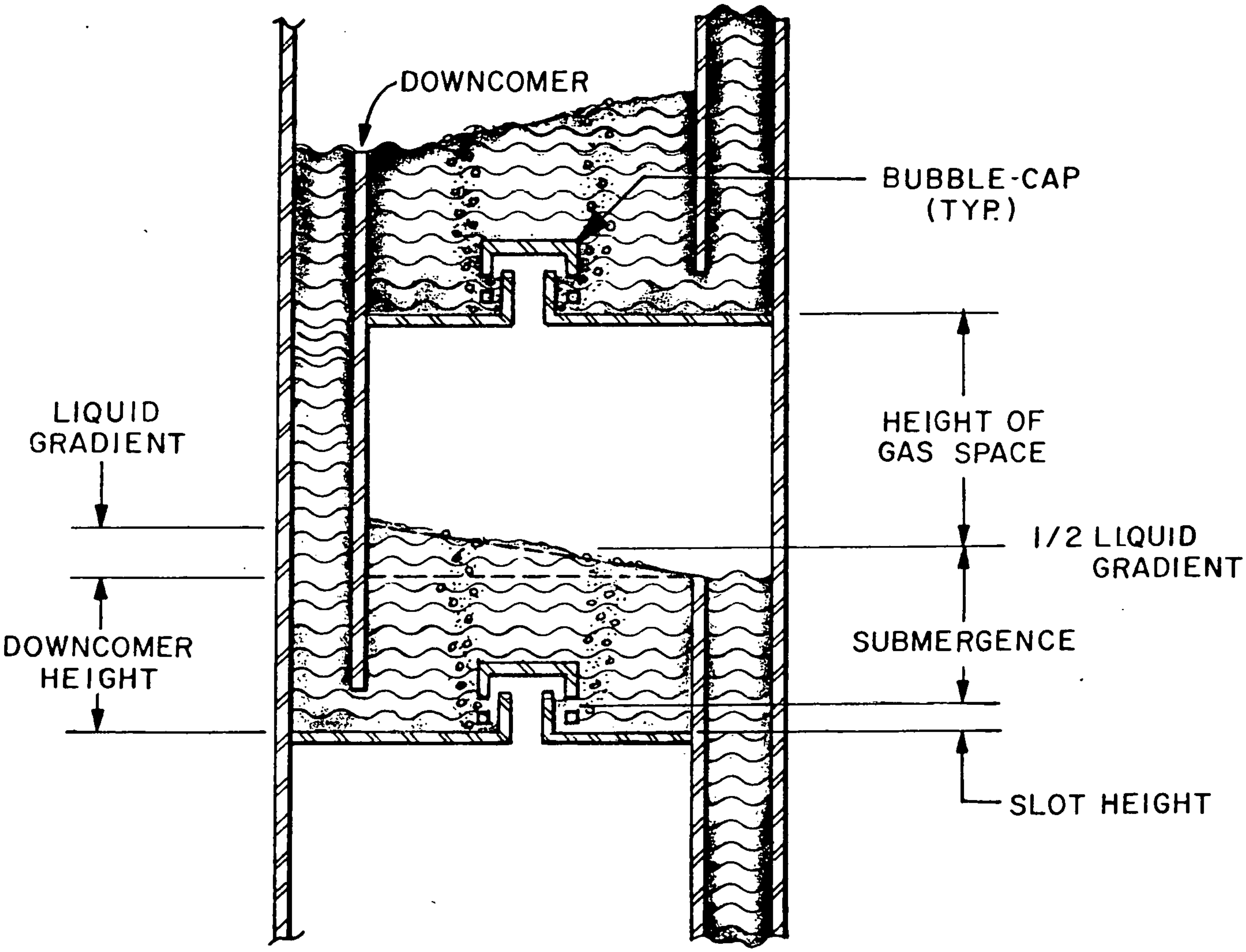


FIG. 2. MACROFLOWSHEET OF ABNØX



CROSS SECTIONAL VIEW OF A BUBBLE CAP-TOWER

FIGURE 3.

12. Feed partial pressure of NO_2^* (dry gas basis), atm
13. Feed partial pressure of NO (dry gas basis), atm
14. Feed partial pressure (dry gas basis) of inert gases (ie., N_2O, N_2, CO_2, etc.), atm
15. Feed partial pressure of O_2 (dry gas basis), atm

Based on the column description and operating conditions, the column's NO_x removal performance is calculated. The program's output contains:

1. NO_x removal efficiency, dimensionless
2. Effluent gas flow rate, m^3/s
3. NO_x effluent partial pressure (wet gas basis), atm
4. Concentration of HNO_3 in the scrub solution effluent stream, $kg \cdot mole/m^3$
5. Concentration of HNO_2 in the scrub solution effluent stream, $kg \cdot mole/m^3$
6. Column profiles of liquid and gas concentrations and conversions of NO_2^*, HNO_2, and NO.

Although ABN0X was developed to simulate NO_x absorption in a multistage bubble-cap column, it can be applied to simulate NO_x absorption in sieve tray[4] or valve tray columns. All that is required is an estimation or prediction of the gas-liquid interfacial area for each column.

DESIGN

The NO_x off-gas system was designed with the aid of ABN0X to reduce off-gas concentrations of NO_x and nitric acid. As shown in Figure 1, the off-gas feed for the NO_x off-gas system is generated by the liquid waste and acid concentration systems. Off-gases from the other IPD systems and the NO_x off-gas system are vented to the building off-gas system.

Off-gases from the liquid waste system are cooled in the Feed Gas Condenser, and the condensate is returned to that system. The cooled gas is then mixed with off-gas from the acid concentration system. The gas mixture is compressed in the Feed Gas Compressor, scrubbed in the NO_x Scrubber and released to the building off-gas system. The Scrub Solution Recirculation Pump and Cooler are support equipment for the NO_x Scrubber. The Seal Pot provides a vacuum break for the liquid waste system and the Entrainment Separator removes condensate from the feed gas.

Off-gas flow rates with a maximum NO_x concentration of 15 vol % and in a range of 2.83×10^{-3} to 8.46×10^{-3} m^3/s (6 to 18 cfm) at .986

atm pressure and 35°C are expected for the NO_x Scrubber. The scrubber is designed according to ABN0X to meet a maximum discharge limit of 1 vol % NO_x during a maximum feed condition of NO_x.

The NO_x off-gas system's Feed Gas Compressor cools the off-gases from the liquid waste system. This cooling is required to maintain the NO_x Scrubber at or below the design temperature of 35°C. The condenser was conceptualized as being a vertical tube side condenser with a gas-liquid separator in the process outlet. Through the use of a heat exchanger design program it was determined that a shell side condenser could perform as well as the tube side condenser with a significantly lower capital cost. The Feed Gas Compressor is rated for 42,000 J/s (143,350 Btu/h) and reduces the off-gas from 95 to 35°C. It requires 4542 ℓ/h (20 gpm) of cooling water at 30°C and returns the water at 38°C.

The Entrainment Separator is a wire mesh pad which is firmly fit within a 2 in. pipe spool that is 12 in. long.

The Feed Gas Compressor for the NO_x off-gas system is a liquid ring type compressor capable of handling the low off-gas flowrates along with performing several additional functions. The compressor creates the required vacuum for the liquid waste and acid concentration systems. The liquid seal within the compressor is completely mixed with the feed gas and therefore acts as an additional absorption stage for NO_x and as a second heat exchanger for cooling the feed gas. The use of a compressor in the system enables the scrubber off-gas to be recycled for feed gas makeup during periods of low flow.

The NO_x Scrubber is the heart of the NO_x off-gas system. It consists of twelve (12) bubble-cap trays with seven (7) bubble caps per tray. The column was specified as having a .61 m (2 ft) OD, however, the fabricator (Koch Eng. Co. Inc.) has elected to build the vessel with a .61 m (2 ft) ID. This change reduces the column's superficial gas velocity which in turn creates more gas residence time and higher NO_x absorption efficiencies. The column tray spacing is .61 m (2 ft) and the design scrub solution flowrate is 340 ℓ/h (1.5 gpm). The absorption process of NO_2^* is highly exothermic and a heat balance on the column indicated that approximately two thirds of the total heat to be generated would be created on the bottom three trays. Cooling coils on the bottom trays are not used because of severe space limitations and the desire to use a cartridge tray assembly. A cool recirculation stream to one of the bottom trays will be used to remove the heat of absorption. The column is designed to operate with a maximum recirculation rate of 4520 ℓ/h (20 gpm). Heat removal in the column enhances the rate of oxidation of NO to NO_2. Temperature and sampling measurements will be made on the column during operation to evaluate ANB0X. The bubble caps will have risers which are higher than the tray's overflow weir height. This design allows for an infinite turndown ratio and therefore fluctuations in the off-gas feed will not affect the hydraulics of the column. This reasoning is the basis for using a bubble-cap column in the NO_x off-gas system.

The support equipment for the NO_x off-gas system includes the Scrub Solution Recirculation Pump, Scrub Solution Cooler, and a Seal Pot. The Pump produces a total differential head of .06 Pa (20 psi) to overcome the pressure drops associated with the cooler, compressor, scrubber and mixer. The pump's capacity is 5223 ℓ/h (23 gpm). The cooler removes both the heat of absorption and heat of compression. The unit is rated for 6945 J/s (23,700 Btu/h) and is a helical coil model. The Seal Pot is designed to lose a water seal and break the NO_x off-gas system vacuum if an upset occurs. This protection is required for the vessels in the liquid waste system.

OTHER SCRUBBER APPLICATIONS AND CONTINUING RESEARCH

Another application of NO_x scrubbing at ORNL is the treatment of off-gas from the dissolution process. This process is part of the mechanical head-end equipment train in the IPD area (see Fig. 1). This application uses a packed scrubbing tower. The column is .30 m (12 in.) in diameter and has a packing depth of 7.62 m (25 ft). The packing material is 13 mm (1/2 in.) ceramic Intalox Saddles. This effort is being supported with engineering research studies designed to produce a mathematical model for NO_x absorption in packed towers.

The building off-gas system is another scrubbing application at ORNL. The system's scrubber is 1.83 m (6 ft) in diameter and 6.63 m (21 ft, 9 in.) high. The scrubber has a 2.13 m (7 ft) packed bed. The scrubber, support equipment and instrumentation are being purchased as a complete package from Croll-Reynolds. The scrubber's packing material will be Croll-Reynolds' polypropylene Spiral-Pac, size #2. The package includes a 20 HP recirculation pump, flow, level and temperature indicators along with the recirculation piping and valves.

SUMMARY

The NO_x off-gas system is the product of the combined efforts of development personnel and engineering designers. The development effort produced a model which was used to size and specify an NO_x absorption column. The engineering effort integrated support equipment with the development concept to form a process system. This process system will become part of the IET-IPD facility at ORNL.

REFERENCES

1. UCC-ND Engineering and Advanced Fuel Recycle Program, Title I Design Report for Integrated Prototype Equipment Test Facility I, X-OE-58 (February, 1978).

2. R. M. Counce and J. J. Perona, "Gaseous Nitrogen Oxide Absorption in a Sieve-Plate Column," Ind. Eng. Chem. Fundam. 18, 400-406 (1979).

3. R. M. Counce, A User's Guide to ABNØX, a Computer Program Designed to Simulate the Nitrogen Oxide Removal Efficiency of a Multistage Bubble-Cap Tower, ORNL/TM 6938 (September, 1979).

4. R. M. Counce and J. J. Perona, "A Mathematical Model For Nitrogen Oxide Absorption in a Sieve-Plate Tower," Ind. Engr. Chem. Proc. Des. Devel. 19, In Press (1980).

CONTROL OF R-114 LOSSES AT THE GASEOUS DIFFUSION PLANTS

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ABSTRACT

Substantial quantities of R-114 are lost to the environment each year by the gaseous diffusion complex. Successful studies have been conducted at PGDP to allow identification and correction of some of the major sources of releases, both directly to the atmosphere and via the RCW system. Details of the procedures including description of instrumentation requirements are discussed.

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SMELTER PRETREATMENT AND POLLUTION CONTROLS

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ABSTRACT

The existing Industion Furnace Facility at the Paducah Gaseous Diffusion Plant is presently being modified to allow melting of contaminated nickel scrap generated from the three-plant upgrading programs. The modification involves the installation of a pretreatment system to remove nickel fluoride from the contaminated scrap. Previous plant tests have demonstrated that the nickel fluoride on the scrap agressively attacks the high alumina refractory lining used in the induction furnace. The system now under construction will pretreat the nickel scrap by removing the fluorides. As a result of the fluoride removal, gaseous HF emissions are generated which must be captured and removed prior to atmospheric release.

From laboratory development and pilot plant test data generated by the Paducah Gaseous Diffusion Plant, a fixed-bed $CaCO_3$ trapping system utilizing oolitic limestone was designed to remove HF from the gaseous effluent. The design features of the abatement system including reactor scale-up, instrumentation/monitoring equipment, materials of construction, and operation are discussed. Construction costs are presented to demonstrate the magnitude of capital investment involved when development data is translated into a viable processing system.

Prepared for the Department of Energy under
U.S. Government Contract W-7405-eng-26

INTRODUCTION

As a result of the three-plant upgrading programs at the gaseous diffusion plants, large quantities of clean and contaminated nickel scrap will be available for recovery. In the early 1970's plans were initiated and conceptual design was started for a smelter facility to recover the scrap at the Paducah Gaseous Diffusion Plant. In 1976, construction of the facility was completed and recovery of clean nickel began.

After the initial inventory of clean nickel scrap was melted, a production test melt was conducted on contaminated nickel scrap. The test proved that contaminated nickel scrap aggressively attacked the smelter's furnace lining refractory and gaseous fluorides were emitted to the extent that the scrap could not be safely recovered. Therefore a system had to be developed and designed to treat the contaminated nickel scrap prior to melting.

The project entitled Smelter Pretreatment and Pollution Controls, the subject of this report, is the system designed for that sole purpose. The main point of discussion, however, focuses on the pollution control system for abatement of hydrogen fluoride emissions. Laboratory development, engineering design, and construction costs are presented.

PROCESS DESCRIPTION

The conceptual process for pretreatment of the contaminated scrap involved several questionable parameters that had to be developed. Thermodynamic data was needed to determine the most efficient method for removal of the nickel fluoride and to specify the consequences of removal. Thus, there was a "hand-in-hand" design and development effort between Technical Services and Engineering to determine the most viable alternatives.

The most promising alternative found was the reaction of the nickel scrap with a mixture of 20% steam and 80% nitrogen at a temperature of 1100°F and 30 minutes retention time. To accomplish these parameters on a production scale, a rotary calciner was chosen as the most practical processing equipment. Due to the nature of the reaction and production requirements of 2500 lb/hr, considerable quantities of hydrogen fluoride were calculated to be produced as a by-product. Therefore, a HF abatement system was necessary to treat the off-gas prior to atmospheric release.

HF EFFLUENT CONTROL SYSTEM

Previous investigation[1] and literature searches had revealed that one of the most promising systems for HF abatement was a fixed-bed system utilizing $CaCO_3$ as trapping media. Experimental tests were therefore undertaken simultaneously with preliminary engineering design to transform theory into an operable $CaCO_3$ trapping system.

The greatest concern with regard to design was the efficiency or capability of a fixed-bed $CaCO_3$ system to remove hydrogen fluorides. Other important parameters needed were: 1) expected trap life, 2) optimum particulate size of the $CaCO_3$, 3) loading factors, and 4) temperature excursions since the reaction is exothermic in nature.

As shown in Table 1, development began with a 12" x 1" OD reactor in the laboratory and was later translated into a pilot plant testing system closely approximating the conceptual design for the pretreatment system's $CaCO_3$ reactors. The data generated from both testing systems paralleled each other in data generation and thus gave the information required for scale-up. This information was then translated into the process flow diagram as seen in Figure 1.

HF CONTROL SYSTEM SCALE-UP

With the parameters known and the operational modes understood, the HF control system design could now be finalized. There were several important operational considerations, however, that had to be provided to insure a viable processing system.

One important factor involved reactor heat up since operation demanded that a reactor be in hot standby at all times. To provide for this capability a forced air heating system coupled with the two reactors was incorporated. The system was designed to provide minimum heat-up times and to allow switching of reactors without upsetting production.

Gas velocity through the reactors (one of the most important factors in design) had to be assured as experienced from laboratory data. Therefore, based upon the off-gas quantities, the reactors were designed for a maximum velocity of approximately 0.4 ft/sec. To maintain the reactor control pressure or flow a steam ejector was incorporated at the outlet of the system.

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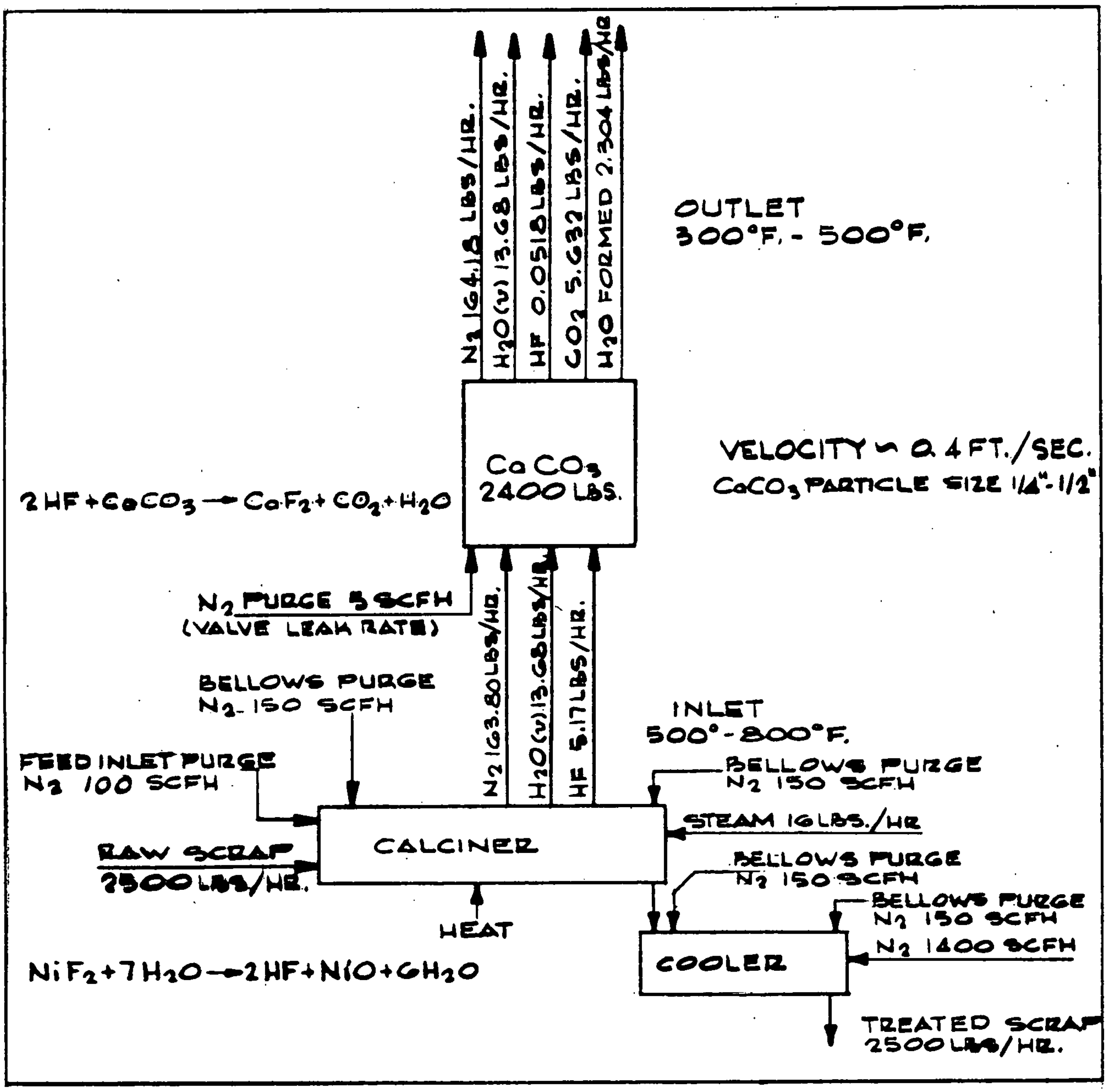
[1] R. C. Limatainen and M. Levenson, Absorption Of Some Halogen Gases From Air By A Limestone Bed And A Spray Tower; Argonne National Laboratory, April 1, 1953.

TABLE 1

HF EFFLUENT CONTROL SYSTEM

Laboratory Development Studies	Pilot Plant Test	Pretreatment System Reactors (Scale-Up Parameters)
CaO_3 Trapping Media (oolitic)	$CaCO_3$ Trapping Media (oolitic)	$CaCO_3$ Trapping Media (oolitic)
1" OD x 12" Reactor	18" OD x 48" Reactor	2' OD x 10'-0" Reactor
Bed Temperature - 200°F	Bed Temperature - 300°F	Bed Temperature - 275°F - 300°F
Inlet HF Concentration (Vol)- 29.4% (average)	Inlet HF Concentration (Vol)- 23% (average)	Inlet HF Concentration (Vol) 5% - 20%
Gas Velocity - 0.1 ft/sec	Gas Velocity - 0.3 ft/sec	Gas Velocity - 0.4 ft/sec
Loading Factor - 26%	Loading Factor - 25%	Loading Factor - 20%
ΔP = 0.1 inches H_2O	ΔP = 12-15 inches H_2O	ΔP = 12-15 inches H_2O
Breakthrough - 3 hr 34 min	Breakthrough - 11 hr 23 min	Breakthrough - ~ 3 1/2 days
Efficiency - 99%	Efficiency - 99.9%	Efficiency - 99%
Maximum Temperature Rise - 43°F	Maximum Temperature Rise - 760°F	Maximum Temperature Rise - 800°F



PROCESS FLOW DIAGRAM - ROTARY CALCINER/$CaCO_3$ TRAPS

FIGURE 1

Due to the corrosive nature of hydrogen fluoride at low concentrations and to the range of reaction temperature (500°F - 800°F) involved, the reactors' materials of construction were a concern. Thus, to insure structural integrity and to allow for corrosion, INCONEL materials (600 series) were chosen for fabrication. As a result of these considerations, Figure 2 depicts the HF off-gas process flow scheme and Figure 3 shows the actual design and specifications for reactor fabrication.

INSTRUMENTATION/MONITORING CONTROLS

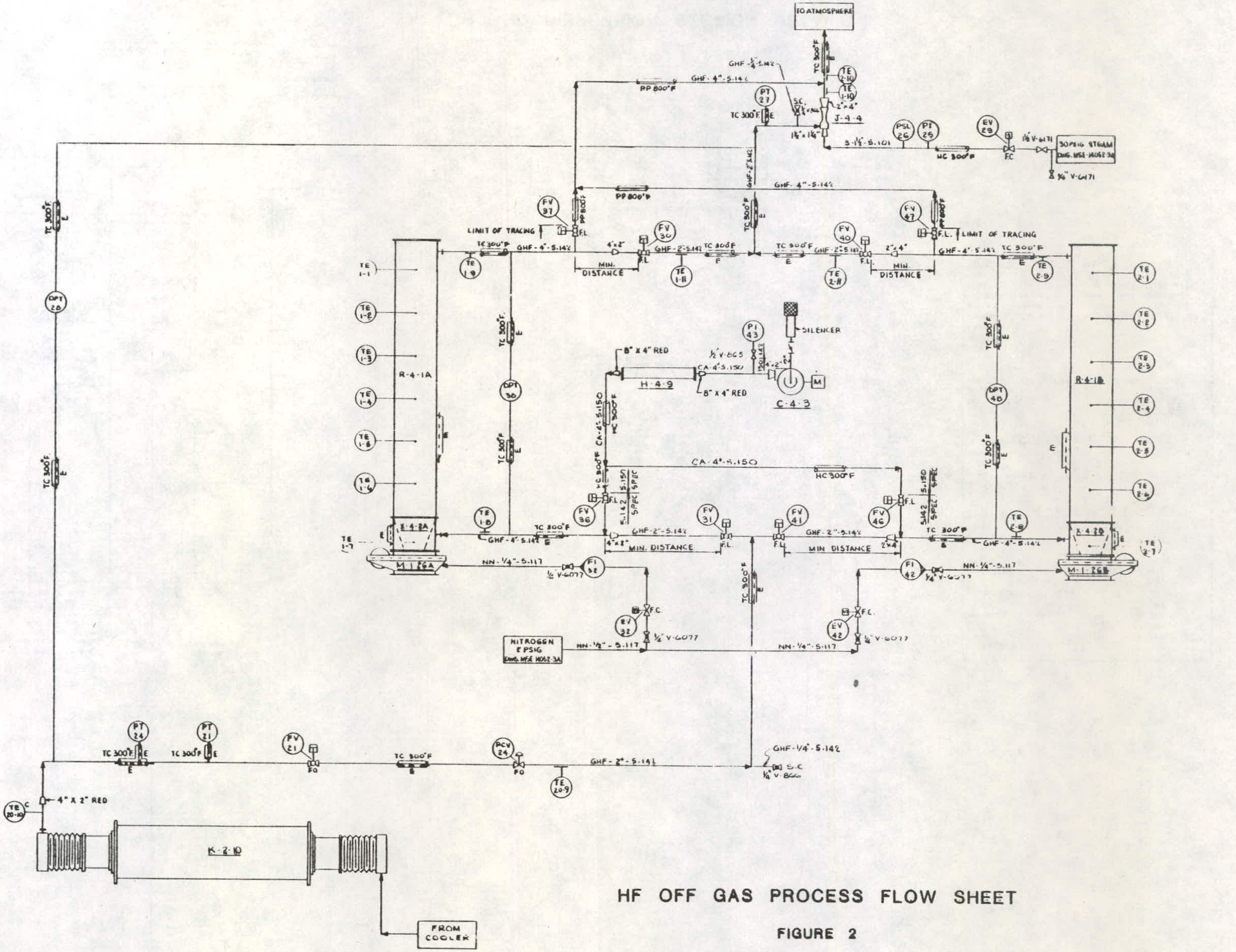
The most imperative operational consideration was the ability to monitor the HF control system. Therefore, to insure complete control, the necessary instrumentation was provided.

Instrumentation included an interlock system between the off-gas pressure (flow) and steam ejector in order to control the velocity through the $CaCO_3$ reactors. In addition, all the control valves for the off-gas piping system were electrically interlocked to assure proper flow by valve sequencing and temperature controlled to prevent HF condensation. Another consideration was the monitoring of reaction rate temperatures to determine reactor breakthrough. As a result, thermocouples were incorporated throughout the length of each reactor for temperature measurements.

Figure 4 shows the HF reactor/calciner instrumentation system. Zone reaction temperature and differential pressure across each reactor will be monitored. From laboratory and pilot plant test data reaction temperature curves were developed and will be used as a standard at operation start-up to determine when the $CaCO_3$ trapping media is spent. After sufficient operating experience is gained new breakthrough curves will be established for the system. Furthermore, samples ports will be provided to monitor inlet and outlet HF off-gas concentrations as a secondary precaution/back-up method to the instrumentation to assure HF emissions are within design parameters.

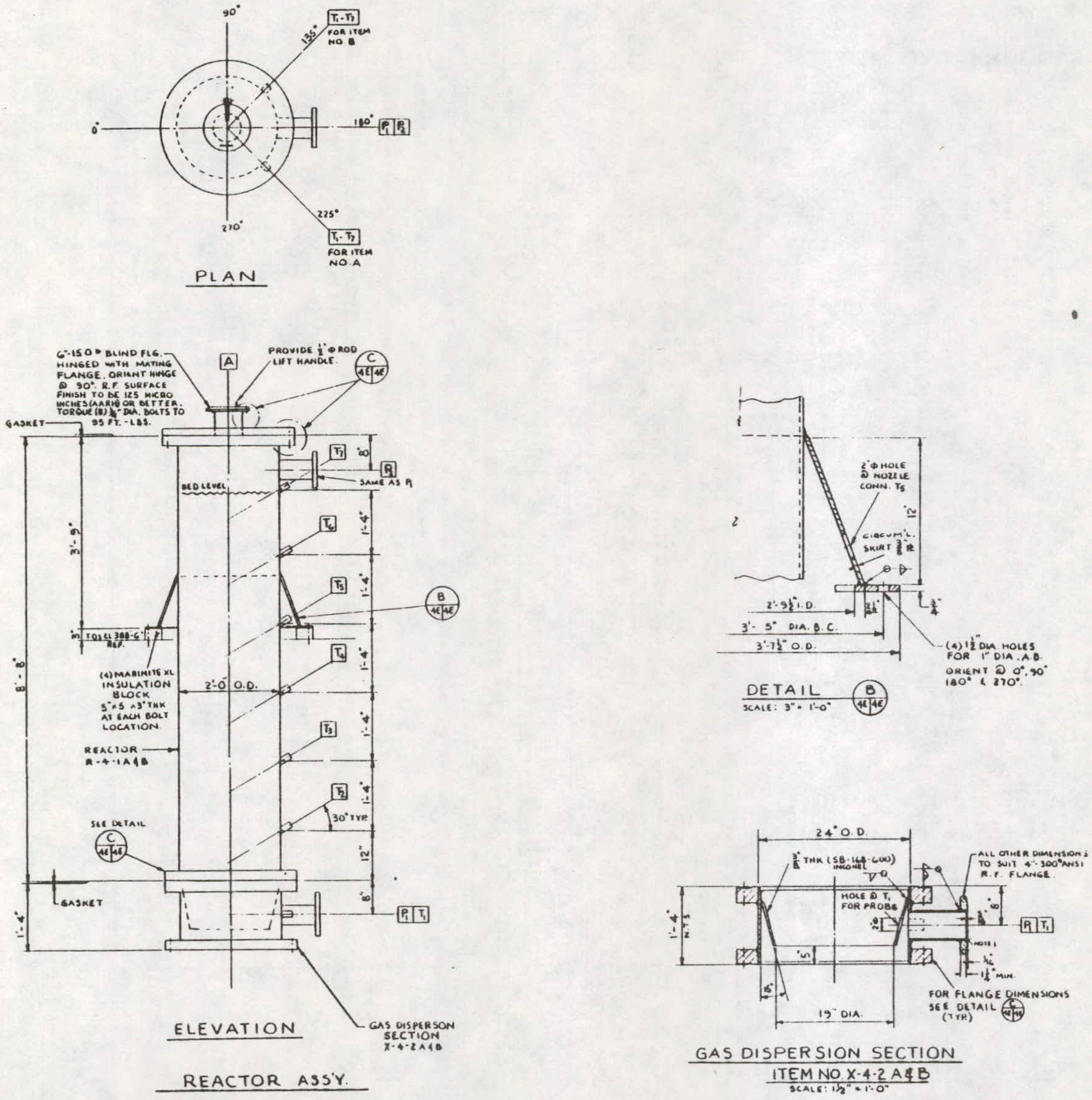
CONSTRUCTION COSTS

The materials of construction for reactor fabrication, as previously stated, will be INCONEL (600 series). Todays market prices for such materials are highly unstable. Therefore, it is difficult to predict or estimate a cost for such equipment that will be fabricated by an outside vendor. However, the reactors of discussion have been purchased at a cost of $143,100.



HF OFF GAS PROCESS FLOW SHEET

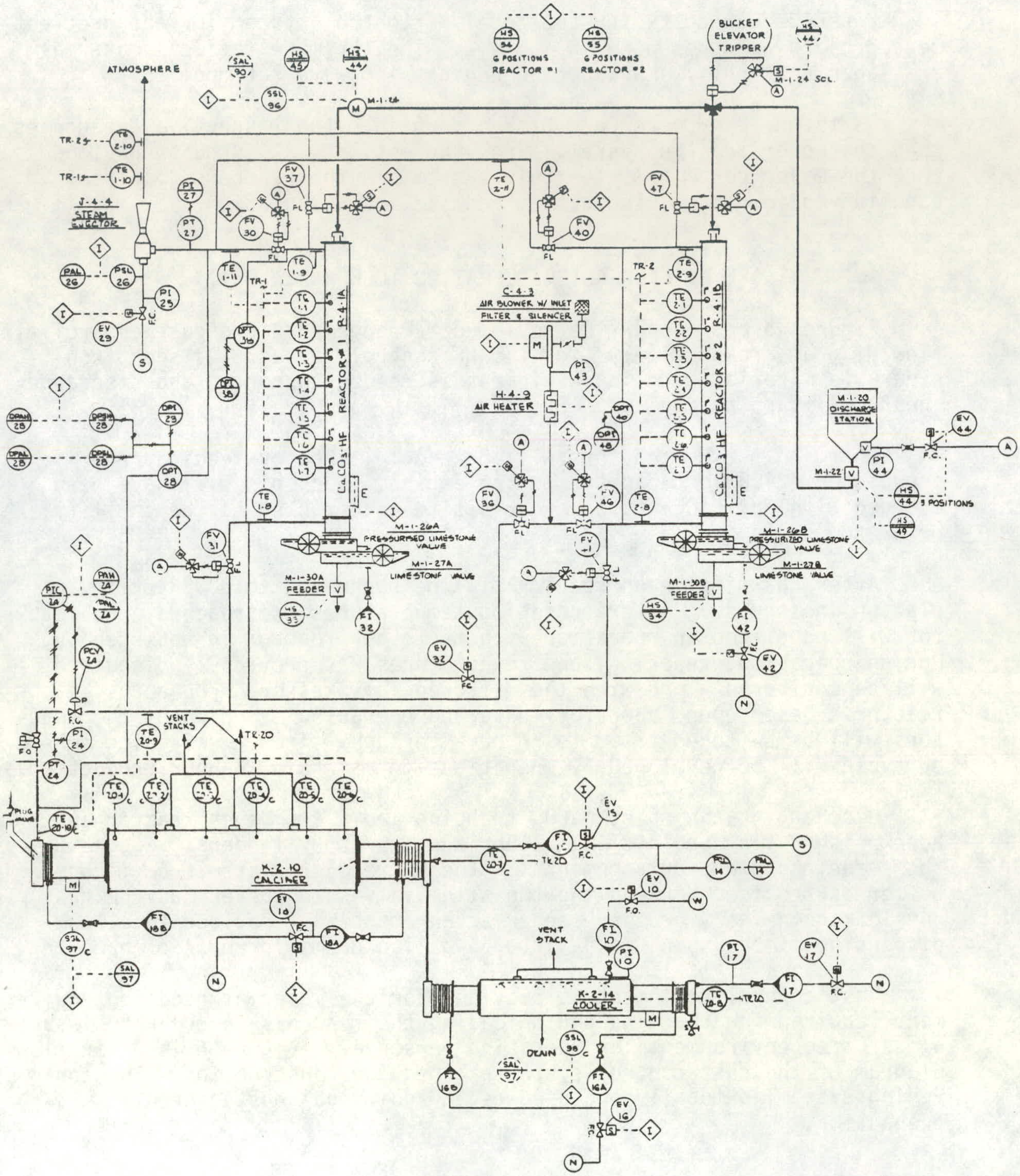
FIGURE 2



HF REACTOR AND DISPERSION SECTION DETAILS

FIGURE 3

DESIGN CONDITIONS
FULL VAC & 15 psig 1000 °F
psig °F
OPERATING CONDITIONS psig 800 °F
psig °F
SPECIFIED CORROSION ALLOW 3/32"
WIND LOAD —
SEISMIC ZONE 3
CODE 1977 ASME SEC. VIII DIV. 1 CODE STAMP NO
P.W.H.T. — RADIOGRAPHY SPOT
MAWP — LIMITED BY —
SHELL SPEC SB-168-600 INCONEL 1/4" THK
JOINT EFF 85 %
HEAD SPEC SB-443-625 INCONEL BLD. FLG. (SEE DWG)
JOINT EFF 100 %
CLADDING OR LINING SPEC —
(EXCEPT AS NOTED)
GASKET SPEC FLEXITALLIC INCONEL 600 w/ FLEXICARB FILLER
SUPPORT SPEC SB-168-600 INCONEL, HOT ROLLED
EXTERNAL PIPE SPEC SB-167-600 INCONEL, SMLS
INTERNAL PIPE SPEC —
FLANGE SPEC SB-443-625 INCONEL
RATING SEE DWG
FACING R.F.
PAINT —
INSULATION —
FIREPROOFING —
SHIPPING WT 3250# OPERATING WT 4600# TEST WT 5100#
ELEVATION MEASURED FROM BASELINE —
ORIENTATION MEASURED CLOCKWISE FROM 0°. NORTH IS 0°
PROJECTION MEASURED FROM ℄ OF VESSEL TO EXTREME FACE OF FLANGE
CAPACITY 30 CU. FT [redacted] DENSITY 83 LB/FT³ (CaCO₃)



HF REACTOR AND INSTRUMENTATION APPLICATION

FIGURE 4

Construction costs for the total HF control system for the pretreatment project are presented in Table 2. The estimate reflects material and labor cost only. Markups and engineering were not applied.

As shown, the costs were broken down into the respective categories that characterized the system. From the estimate it is quite obvious that the major cost items for this system are the reactors, material handling equipment, piping system and the instrumentation.

HF REACTOR OPERATION (GENERAL)

Figures 5 and 6 show the equipment arrangements and dust control air flow diagram, respectively, for the HF control system. As seen, considerable material handling equipment is needed to convey and discharge the $CaCO_3$ trapping media.

Charging the HF reactors will be accomplished by feeding from preweighed (2400 lb capacity) portable bins. Each bin will have been charged with dry $CaCO_3$ at a vendor's site and trucked to the facility prior to use.

After charging, each reactor will be preheated to 300°F prior to placing in service. After operating temperatures are reached, one reactor will be placed in operation with the other reactor in hot standby. During operation, reaction zone temperatures, as previously discussed, will be monitored along with the differential pressure drop across each reactor. Based upon laboratory data and operating experience, the reactors will be switched prior to HF breakthrough. Thus a switching scheme or cycle will be developed by Operations to maintain 24-hour production.

Discharging the spent $CaCO_3$ trapping media from each reactor is accomplished via double slide valves and vibratory feeders. Figure 5 shows the equipment arrangement for the HF reactor system. A nitrogen buffer is provided between the two slide valves to prevent any HF gas out-leakage. The vibratory feeder arrangement was provided to allow dispensing of the spent $CaCO_3$ into 55-gallon drums for ease of handling.

Dust control equipment is provided for the material handling equipment required for charging and unloading the reactors in order to insure a dust free environment for operating personnel. Figure 6 is a air flow diagram of the dust control system planned for construction. The conveying system is totally enclosed as an additional dust control precaution.

TABLE 2

ESTIMATED CONSTRUCTION COSTS FOR HF REACTORS*

Item	Material ($)	Labor ($)
Reactors	$ 143,100	$ 1,500
Material Handling Equipment	58,500	4,600
Electrical	9,500	4,400
Structural	10,000	4,700
Instrumentation	25,500	9,900
Dust Control Equipment	7,500	5,000
Heating System	7,500	600
Piping System	33,300	13,600
Insulation	600	700
Steam Ejector	900	600
SUBTOTAL	$ 296,400	$ 45,600
TOTAL COSTS	$ 342,000	

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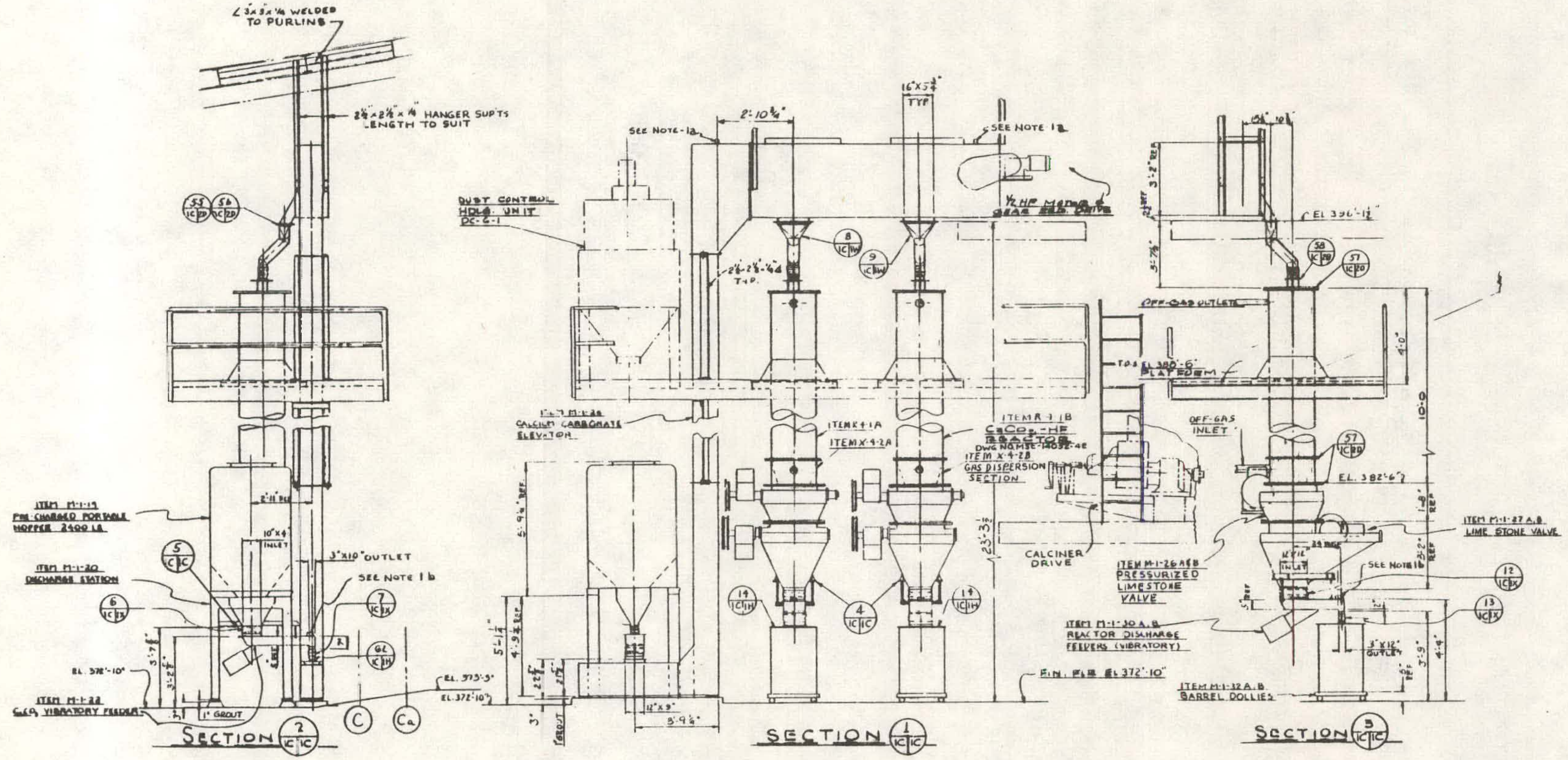
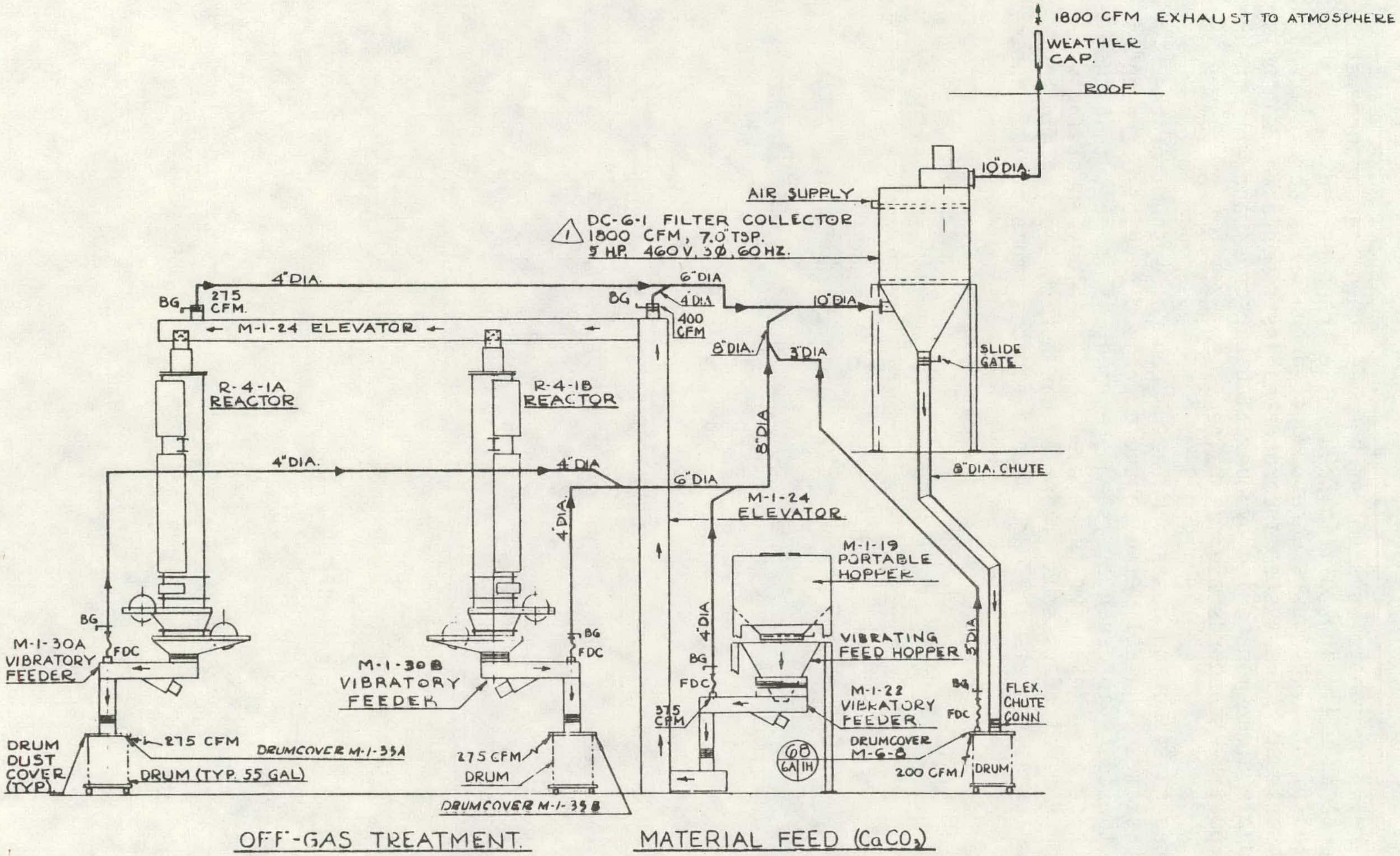
*FY-1980-2 Dollars



HF REACTOR EQUIPMENT ARRANGEMENT

FIGURE 5



HF REACTOR DUST CONTROL AIR FLOW DIAGRAM

FIGURE 6

SUMMARY

In general a HF control system has been designed that incorporates fixed-bed reactors utilizing oolitic $CaCO_3$ as a trapping media. Laboratory and pilot plant tests were conducted on the system followed by engineering scale-up. The system incorporates instrumentation controls that will enable close monitoring by operating personnel and will insure ambient air quality standards are maintained.

Estimated construction costs for the HF control system for the Smelter Pretreatment and Pollution Controls project have been presented. Even though the costs for such a system are high, it is felt that the best system has been chosen for the project. Technology involving wet scrubbing for removal of gaseous fluorides was not considered due to the secondary treatment systems that are needed for the process by-products.

DESIGN OF THE SULFUR DIOXIDE AND PARTICULATE AIR MONITORING NETWORK FOR THE OAK RIDGE NATIONAL LABORATORY FOSSIL STEAM PLANT*

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Key Words

Optimization, Monitor Network, Air Quality, Particulate Matter, Sulfur Dioxide, Coal Conversion Fossil Plant.

ABSTRACT

A mathematical computer model was used for the development of an ambient air monitoring system at Oak Ridge National Laboratory (ORNL). This system was designed for optimal placement of sulfur dioxide and particulate air monitors around the ORNL fossil steam plant. The development of the model and the design of the network will be discussed. Possible expansion of this system for inclusion of additional sources at ORNL and other plants in the area are reviewed.

INTRODUCTION

As part of the nation's energy management program, the steam plant at the Oak Ridge National Laboratory is being converted from oil and gas to coal fired operation. An important part of the overall conversion process

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*Operated by the Union Carbide Corporation under contract W-7405-eng-26 with the U.S. Department of Energy.

is the determination of the environmental impact of the coal burning on environmental pollution levels in the vicinity of the Laboratory. A model for the optimal design of an air quality monitoring system was used for the development of a network of samplers to monitor the air quality impacts of the fuel conversion. This paper provides a description of the model used, presents the current results of the design effort, and suggests further refinements in the data and models used in the study.

MONITOR NETWORK DESIGN MODEL

The optimal air quality monitor network design model used in the study was developed by Hougland et al., [Ho-76(a), Ho-76(b), Ho-77, Ho-79]. It is based on the concept of siting service facilities to satisfy a set of demands. It considers each pollutant source-meteorological condition pair as a demand to be served, if possible, by a monitor site chosen from a large set of potential monitor sites. The optimal network design is that limited subset of the potential monitor sites which maximizes a measure of overall network monitoring capability.

The measure of the capability for a potential monitor site to "serve" a source-meteorology pair's "demand" is called a coverage factor. These factors are defined as the product of the frequency of occurrence of the meteorological condition, the strength of the source, and the fraction of the maximum concentration from the source-meteorology pair that can be measured at the potential monitor site. This is expressed as

$$A_{ijk} = \mathrm{FREQ}(k) \times \mathrm{STR}(i) \times \frac{\mathrm{CONC}_{ijk}}{\mathrm{CMAX}_{ik}} ,$$

where

A_{ijk} = coverage factor for source i, potential monitor j and meteorology condition k,

FREQ_k = frequency of meteorology condition k,

STR_i = strength of source i,

CONC_{ijk} = resultant concentration at potential monitor j, and

CMAX_{ik} = maximum concentration from source-meteorology pair ik.

To calculate the objective function for a set of tentatively assigned monitors, the program assigns monitoring responsibility for a source-meteorology pair to the assigned monitor site with the largest coverage factor for that pair. The sum of all such assigned coverage factors is the objective function value.

The optimal network design is that subset of the total number of potential monitors which has the largest objective function sum. An upper limit to the value of the sum can be calculated by assuming all potential sites to be assigned a monitor and then calculating the objective function value. The ratio of the objective function value for a particular monitor network to the maximum objective function value is called the Monitor Network Rating. It provides an objective comparison between networks.

To construct the network, an initial site is chosen, specifically the site with the largest sum of coverage factors to all source-meteorology pairs. Additional sites are then added to the network using the criteria of maximum increase in the value of the objective function. The process terminates when a predetermined maximum number of sites to be assigned is reached.

Source and meteorological data are taken from the available data for the study. Concentrations, both maximums and those at potential monitor sites, are calculated using the PTMAX, DBTRCX, DBTSIG, and BEH072 computer codes from the Environmental Protection Agency's UNAMAP air quality modeling package (Tu79).

DESIGN PROBLEM

The Oak Ridge National Laboratory steam plant is located in Bethel Valley, approximately 12 kilometers southwest of Oak Ridge, Tennessee. The predominant terrain features are a series of ridges running from southwest to northeast and the Clinch River. At the steam plant, the valley is about 1 kilometer wide.

Best available source and meteorological data were used. Figure 1 indicates the distribution of meteorological data by wind speed and direction <u>in which it is blowing</u>. The meteorological data was further broken down into Pasquill-Gifford stability classes C and E with 70 percent of the data in the E class and 30 percent in the C class. It was assumed that wind speed measurements were taken at a height of 10 meters. It should also be noted that the predominant wind directions are along the axis of Bethel Valley as shown in Figure 2, a map of the Oak Ridge National Laboratory area showing the predominant terrain features.

Source data are shown in the following table:

Table 1. Source Data for Oak Ridge National Laboratory Steam Plant

Particulate emissions	88	tons/year
Sulfur dioxide emissions	1280	tons/year
Stack height	53	meters
Stack exit velocity	13.7	meters/second
Stack diameter	2.7	meters
Stack gas temperature	450	degrees Kelvin

Table 2 lists the various meteorological conditions (which are duplicated in each of 16 wind directions), the distance to the maximum concentration for that meteorological condition and the relative concentration or "Chi/Q" value.

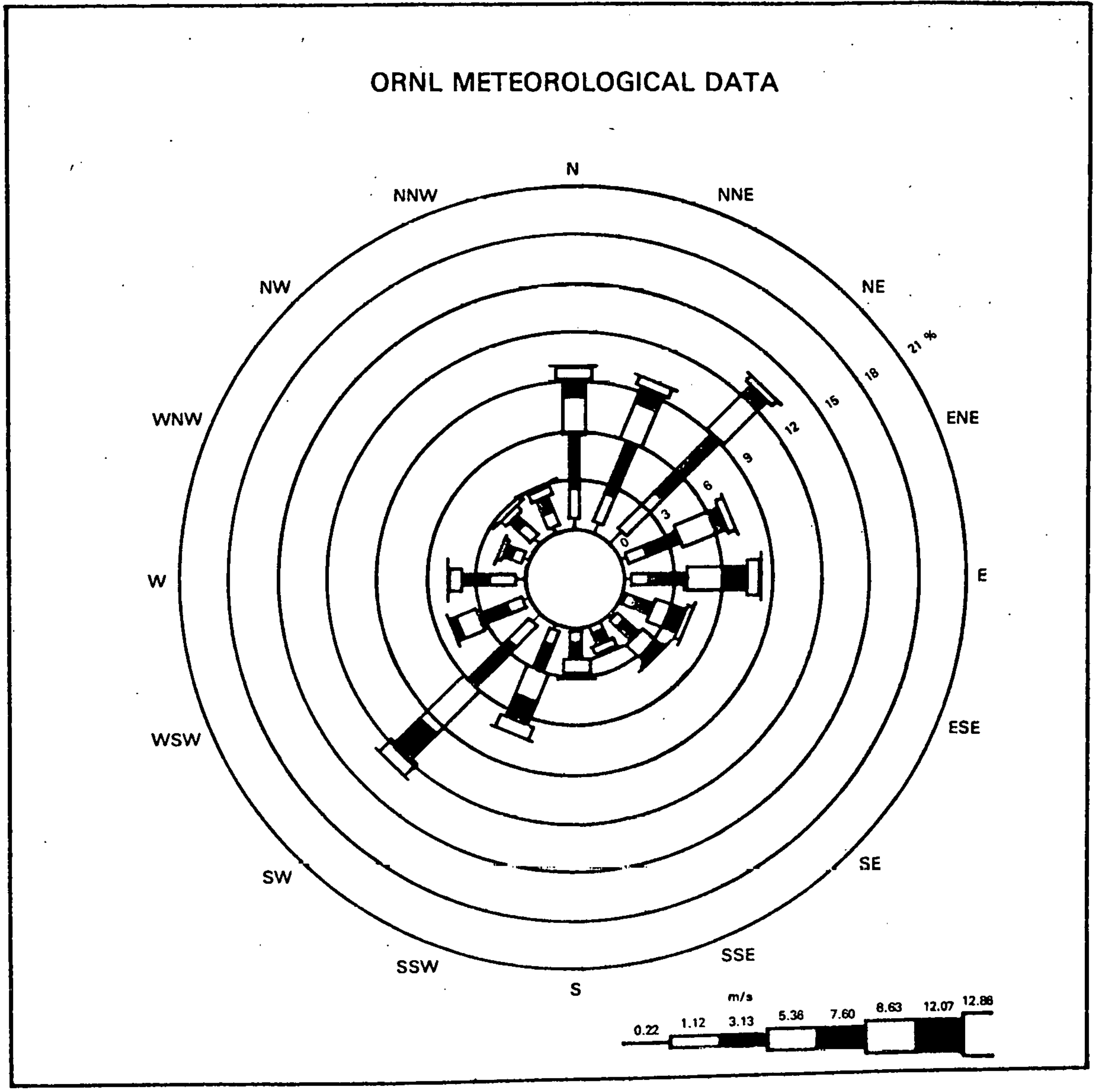

Figure 1
METEOROLOGICAL DATA FOR THE OAK RIDGE RESERVATION

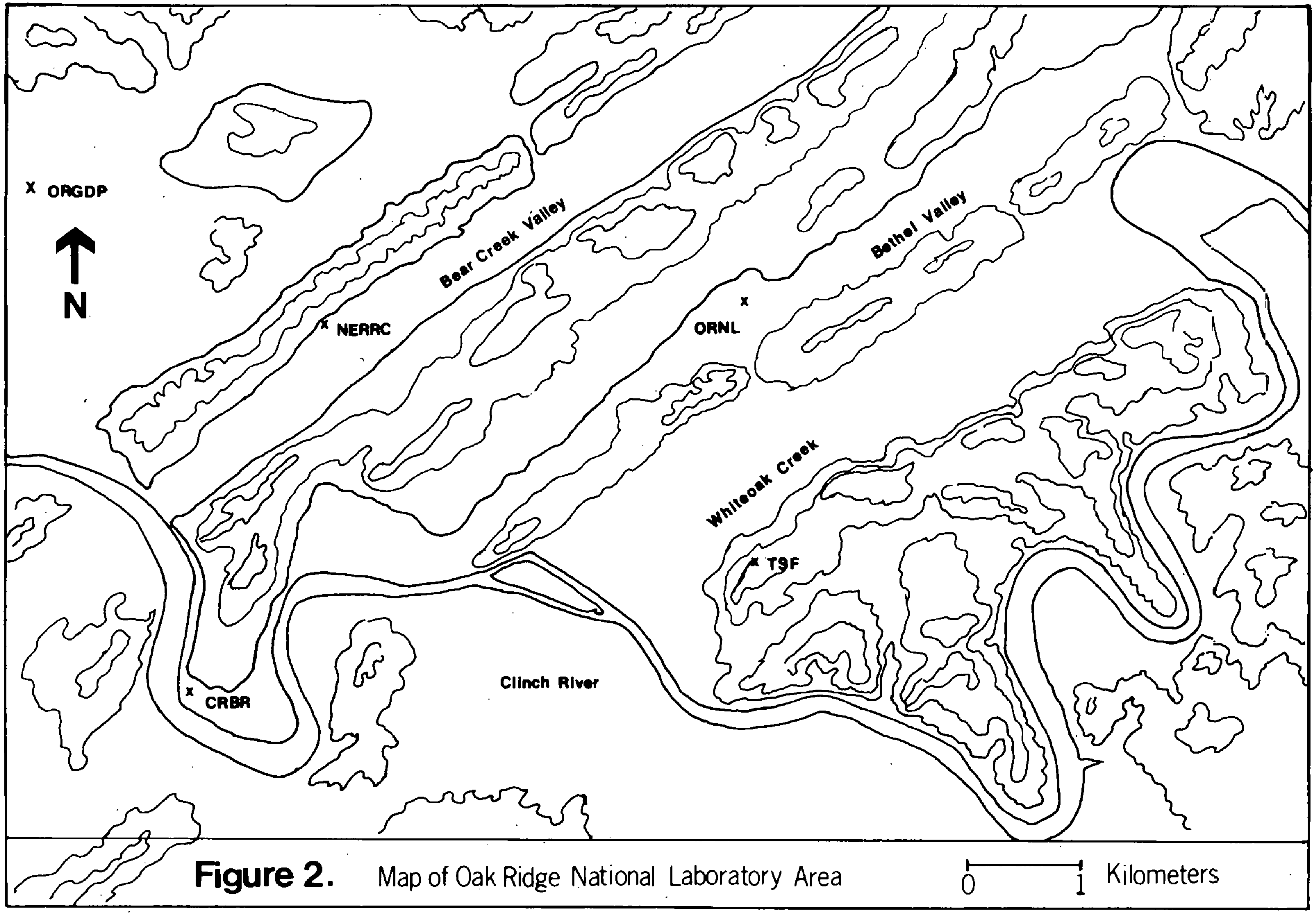

Figure 2. Map of Oak Ridge National Laboratory Area

Table 2. Maximum Concentration Data for ORNL Steam Plant

Stability	Wind Speed (m/s)	CMAX	
		Distance (Km)	"X/Q" $(\times 10^6)$
C (3) (Total frequency = 0.305)	∿0.9	4.46	0.97
	3.13	2.28	0.95
	5.36	1.55	1.12
	7.60	1.26	1.15
	9.83	1.11	1.13
	12.07	1.01	1.01
	12.96	0.98	1.07
E (5) (Total frequency = 0.695)	0.22*	12.02	4.54
	1.12*	12.02	0.89
	3.13	8.52	0.55
	5.36	7.15	0.43
	7.60	6.42	0.36
	9.83	5.96	0.31
	12.07	5.64	0.28
	12.96	5.54	0.27

* To prevent unreasonably large plume rise values using the Briggs plume rise formulation, wind speeds under 2 m/s were set to 2 m/s for plume rise determination.

The much greater frequency of E stability, (2.3 times more frequent than C stability), and the much greater distances to E stability maximum concentrations lead to the preliminary conclusion that the optimal network design model will prescribe a network with high priority sites assigned to E stability meteorological conditions rather than C stability conditions. This in fact happened.

The optimal air quality monitor network design for the Oak Ridge National Laboratory steam plant is shown in Figure 3. The numbers next to each site indicate the priority of installation. The highest five priority sites do, in fact, match the high-frequency wind directions along the axis of Bethel Valley. In addition their distance from the steam plant indicates that they are probably assigned to measure stability E conditions and the low-wind speed C condition. Examination of the computer code output of monitoring responsibilities confirms that this is the case. The four "inner," low priority sites are also shown to be assigned monitoring responsibility for stability C conditions with wind speeds above 3.13 m/s.

Figure 4 is a plot of the value of the monitor network rating as each site in the optimal network is added in priority order. It is notable that 50 percent of the maximum network rating is achieved when only five monitors have been assigned to the network. Two-thirds of the maximum rating has been achieved when only nine sites have been assigned. The four

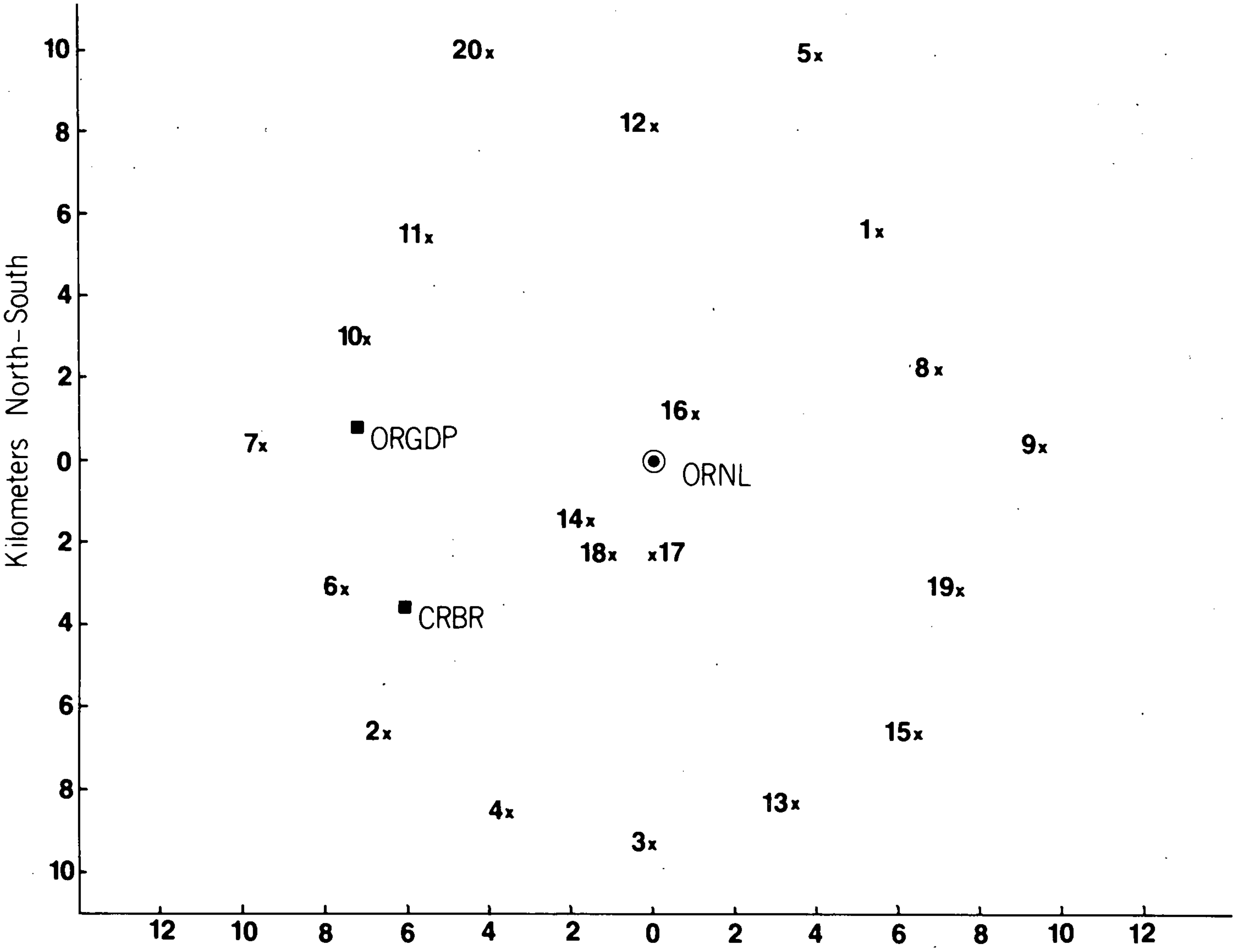

Figure 3. Optimal Air Quality Monitor Network Design
(Numbers give the priority of each site.)

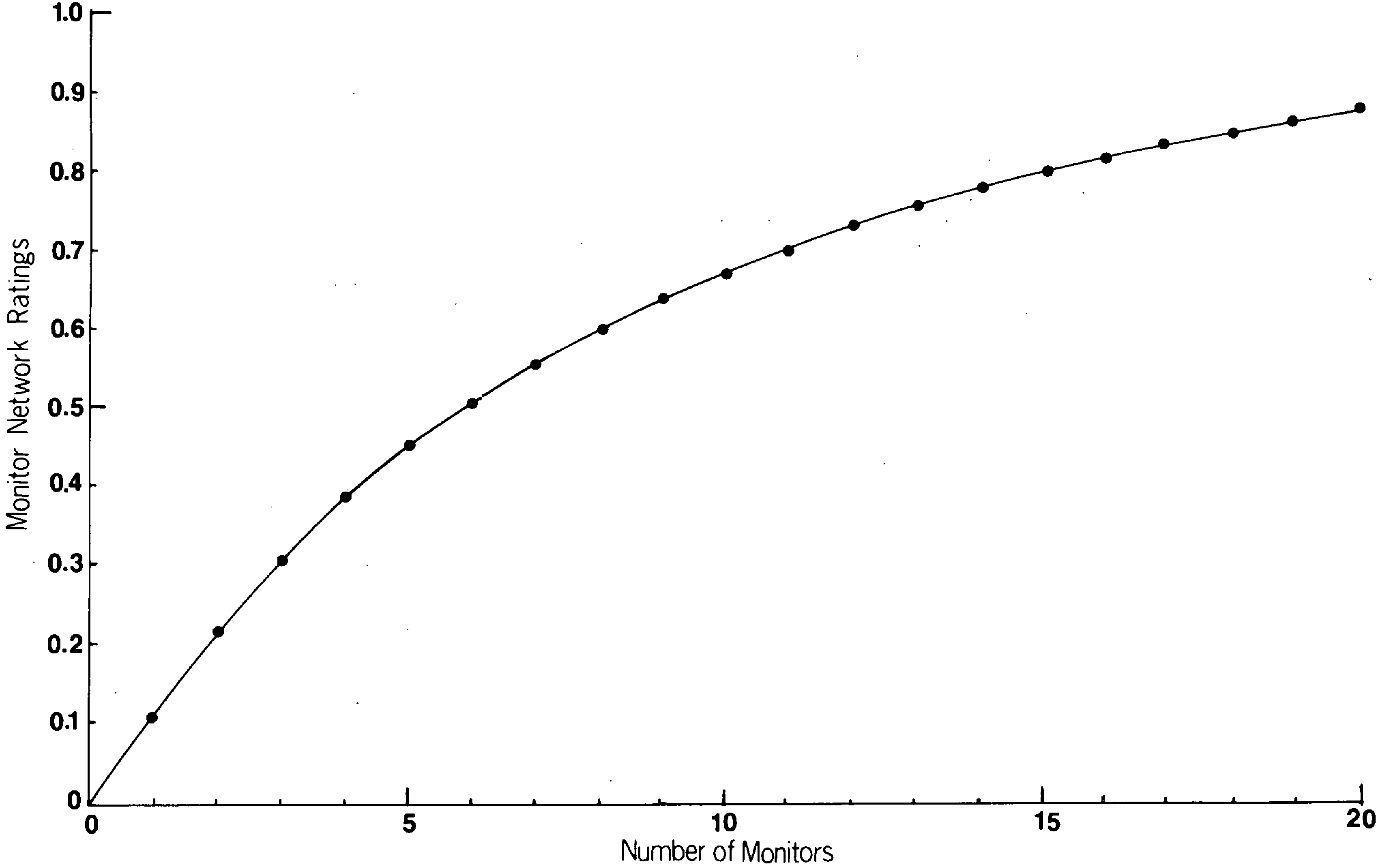

Figure 4. Monitor Network Ratings for Oak Ridge National Laboratory Network Design

"inner" sites which are assigned responsibility for stability C conditions make neglible contributions to the network rating in comparison to the sites assigned responsibility for E stability conditions in those wind directions.

CONCLUSIONS AND DISCUSSION

The optimal air quality monitor network design model of Hougland et al., provided an air quality monitor design for the Oak Ridge National Laboratory steam plant fuel conversion that is responsive to the meteorological data provided and the assumption that the "Gaussian Plume" dispersion model of the EPA computer codes is applicable to the Oak Ridge area.

The fact that the locations of some of the high priority sites are several kilometers from the steam plant and across one or more ridge lines makes it doubtful that they would truly monitor the steam plant under the given meteorological conditions. This conclusion is reinforced by examination of other compilations of Oak Ridge meteorological data (Sl-68) which show valley-bottom wind directions predominately aligned with the valley axis while ridge-top wind directions frequencies show no such strong influences.

Several courses of action must be considered because of the rough terrain in the study area and its impact on the meteorological conditions used. The first is to disregard stable conditions and other conditions resulting in maximum concentrations over 4 to 6 Km away on the grounds that they never would occur anyway. This is not advisable as the maximum impacts will occur, somewhere, and it is the Laboratory's responsibility to measure them. Another action is to go back to the basic meteorological data and calculate a complete range of stabilities for the Oak Ridge National Laboratory area. This would remove the 70 percent preponderance of classically nighttime E stabilities from the data base and thereby allow a more realistic monitor network design.

Another alternative is to use a rough terrain dispersion model. This could be an EPA model such as the VALLEY (Tu-79) code, or it could be a "research" code for the estimation of a complete wind field for the laboratory area followed by the solution of the partial differential equations for the resultant pollutant concentration field. The codes of Sklarew (Sk-77) and Baker (Ba-80) are two possible candidates for this purpose. Pursuit of this alternative would create the need for a more complete meteorological data base than is presently in use. Possible sources for more data included other Union Carbide facilities in the Oak Ridge area, the Tennessee Valley Authority's Kingston and Bull Run steam plants, the Clinch River Breeder Reactor, and the National Oceanic and Atmospheric Administrations Laboratory in Oak Ridge.

The monitor network technique used for this study could be extended to the design of monitor networks for other Oak Ridge area coal conversion projects and to include the effects of other large sources of pollution, notably the two TVA plants previously mentioned, in the design of the coal conversion monitor networks. Some work has been done on model verification of stack releases using ^{131}I as a tracer [0a-76(a), 0a-77(a)] and also for automobile exhaust releases [0a-76(b), 0a-77(b)].

REFERENCES

Ho-76(a) Hougland, E. S. and Stephens, N. T., "Air Pollutant Monitor Siting by Analytical Techniques," *Journal of the Air Pollution Control Association*, 26(1) (January 1976).

Ho-76 Hougland, E. S., Stephens, N. T., and Hughes, J. M., "Air Pollutant Monitor Siting by Analytical Techniques II; Multiple Pollutants," paper presented at Air Pollution Control Association Annual Meeting, Portland, Oregon, June 1976.

Ho-77 Hougland, E. S., *Air Pollution Monitor Network Design Using Mathematical Programming*, Ph.D. Dissertation, Virginia Polytechnic Institute and State University (May 1977).

Ho-79 Hougland, E. S., "Air Pollutant Monitor Siting by Analytical Technique III: A Case Study," in *Proceedings of the Specialty Conference on Quality Assurance in Air Pollution Measurements*, Air Pollution Control Association, March 1979.

Tu-79 Turner, D. B., "Atmospheric Dispersion Modeling : A Critical Review," *Journal of the Air Pollution Control Association*, Air Pollution Control Association, March 1979.

Sl-68 Slade, D. H., (ed.), *Meteorology and Atomic Energy*, TID-24190, U.S. Atomic Energy Commission, 1968.

Sk-77 Sklarew, R., Fabrick, A., and Wilson, J., *Point Source Model Evaluation and Development Study*, Science Applications, Inc., (March 1977).

Ba-80 Baker, A. J., Soliman, M. O., and Pepper, D. W., "Environmental Release Prediction with a Nonclassical Split Finite Element Algorithm," paper presented at the AMS-APCA Second Joint Conference on Application of Air Pollution Meteorology, New Orleans, Louisiana, March 25, 1980.

Oa-76(a) Oakes, T. W., Shank, K. E., and Easterly, C. E., "Iodine-131 Air Concentrations: A Comparison of Calculated Versus Measured Values," *Trans. Am. Nucl. Soc.* 24, 109-110 (1976).

Oa-76(b) Oakes, T. W., Furr, A. K., Adair, D. J., and Parkinson, T. F., "Neutron Activation Analysis of Automobile Exhaust Pollutants," in *Proceedings of the International Conference on Modern Trends in Activation Analysis*, Munich, Germany, September 1976.

Oa-77(a) Oakes, T. W., Shank, K. E., and Easterly, C. E., "Verification of an Air-Transport Code Using Iodine-131 Tracer," *Health Physics* 33, 681 (December 1977).

Oa-77(b) Oakes, T. W., Furr, A. k., Adair D. J., and Parkinson, T. F., "Neutron Activation Analysis of Automobile Exhaust Pollutants," *J. Radioanal. Chem.* 37(2), 881 (1977).

Session V

WATER POLLUTION CONTROL

Chairperson: E. R. Wagner (PGPD/UCC-ND)

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EVALUATION OF ALTERNATIVES FOR DISPOSAL OF HEAVY METAL SOLUTIONS CONTAINING NITRATE*

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ABSTRACT

A cost comparison of using biological denitrification for disposal of heavy metal and nitrate containing filtrates versus sale of the untreated solution to a metals recovery firm has been conducted. The data on cost of denitrification came from cost estimates prepared in 1979-1980 and escalated to the completion date of 1986. The estimated cost for biological denitrification as compared to the current best disposal indicates that the biological system is five times more expensive. In addition, biological decomposition of nitrate waste containing residual heavy metals was investigated using laboratory scale reactors to define operating rates with metal contaminates present. The complex operating conditions of biodenitrification combined with the present generation rate would result in a disposal cost of $431/barrel of gold dissolver filtrate.

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INTRODUCTION

The gold recovery operation involves dissolving gold-plated scrap in a 64% nitric acid solution. The gold is filtered out and the remaining solution contains large quantities of heavy metals and nitrates. The levels of metals present in solution can be seen in Table 1. The waste solution is treated by lime precipitation at pH 9 and a rotary vacuum filter is used to dewater the resulting sludge. The sludge is hazardous according to EPA leachability test and will be stored in a hazardous waste landfill. A diagram of the lime precipitation system is given in Figure 1. The filtrate is high in nitrate concentration and Table 2 shows batches of solution and the level of nitrate. The generation rate of the dissolver filtrate solution averaged 628 gallons/month with a maximum expected future generation rate of 1,000 gallons/month.

DENITRIFICATION PROCESS

Laboratory studies of the dissolver filtrate as the feed solution for a biological denitrification process have been performed. The solution has many disadvantages as a feed for biological decomposition. Sodium present in the feed solution (600-3,000ppm), combined with a residual silver level varying from 1-50ppm, has been toxic to the bacteria at high feed rates. The calcium present from the lime precipitation process reduces to 5ppm or less the amount of soluble phosphate in solution to serve as a micronutrient. Operator control would be extensive due to possible upset in the reactor from the batch feed process and scaling on the pumps from the saturated calcium feed solutions. The dependence on bacteria to provide optimum decomposition of nitrate can be significantly changed by an imbalance in the carbon-to-nitrogen feed ratio, high or low pH, reactor temperature, and withdrawal of active bacteria in sludge removal.

COST OF THE DENITRIFICATION SUBPROJECT

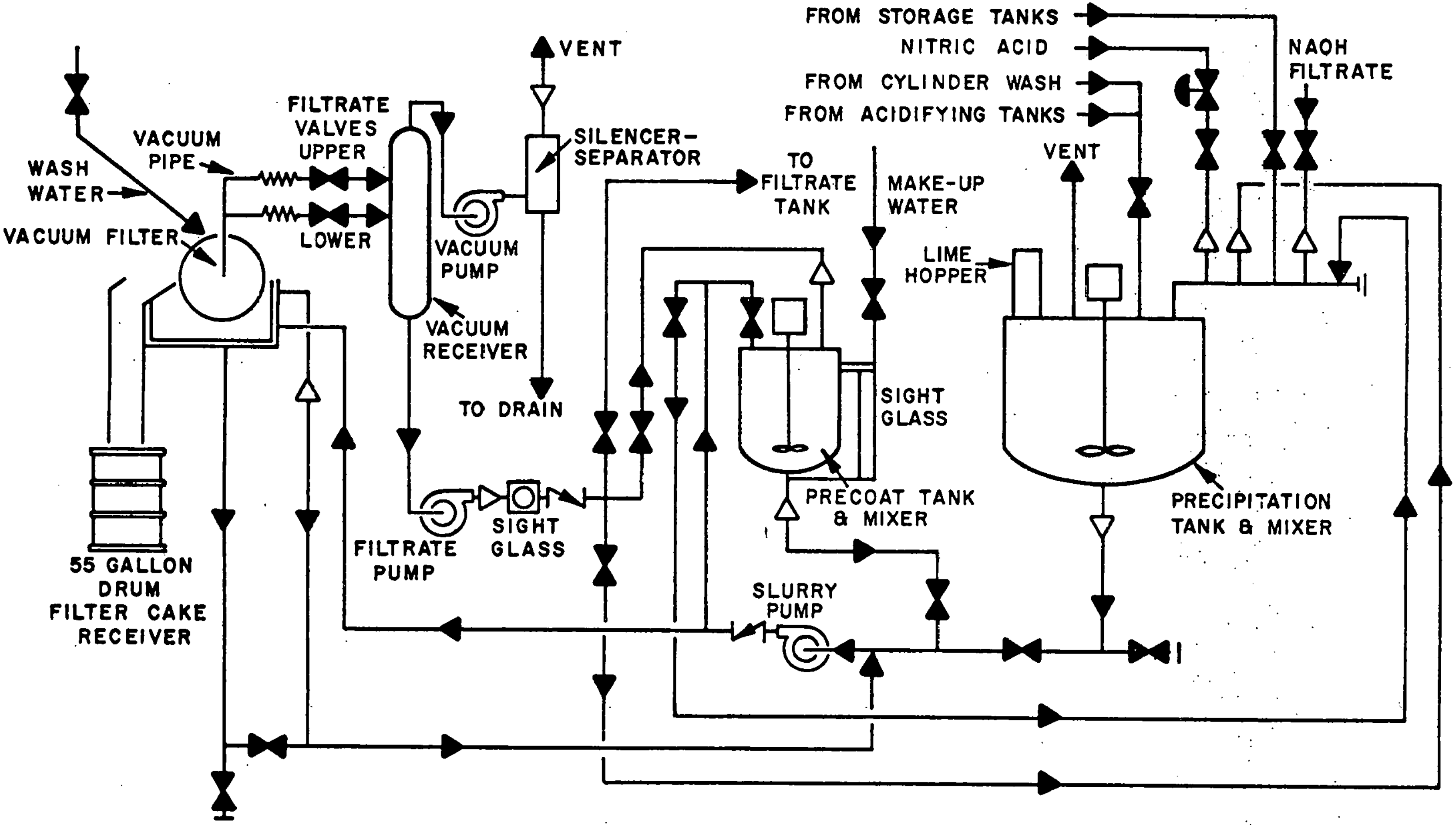
The conceptual design cost estimate in the FY-1981 and FY-1982 line item projects in water pollution control contained denitrification as a subproject. Both were reviewed to obtain data on the cost shown in Table 3. A total of $176,135 is given; however, markup on materials, labor, and general contractor costs produces a total subcontract cost estimate of $264,864. Engineering cost and contingency increase the cost to $397,296. The date of completion for this project is 1986 and after escalation yields a cost of $607,477. However, this figure does not include laboratory

TABLE 1
IMPURITY LEVELS IN GOLD DISSOLVER SOLUTIONS

Batch Number	Metal Ion Concentration			
	Pb, ppm	Cu, ppm	Zn, ppm	Ag, ppm
3	24	20,000	100	3,400
9	9,000	170,000	83,000	2,200
11	9,200	147,500	70,000	2,460
18	4,800	86,500	45,000	1,250
20	1,000	17,600	10,800	72
26	1,900	34,000	18,000	23
30	6,113	116,235	52,520	1,349
31	1,007	90,100	49,025	5
Average	4,130	85,241	41,055	1,345

TABLE 2
NITRATE LEVEL IN WASTE DISSOLVER FILTRATES

Batch Number	NO_3, g/l
40	129
51	105
58	92
61	103
65	60
69	55
70	55
78	43



LIME PRECIPITATION SYSTEM

FIGURE 1

TABLE 3
CONCEPTUAL DESIGN COST ESTIMATE FOR DENITRIFICATION

Equipment (tanks, reactors, mixers)		$55,700
Pumps		$16,500
Instrument		$29,600
Piping		$22,160
Electric		$ 7,360
Concrete		$ 1,870
	SUBTOTAL	$133,190
LABOR	2,863 Hours	$42,945
	TOTAL	$176,135

equipment, operating cost (chemicals, operators, and maintenance) and sludge disposal. These items will require a minimum of $200,000 additional expense. At an effective 10% interest rate over the expected 20 year plant life, the cost per year is $94,845. The maximum generation rate would produce 220 drums (55 gallon)/year, which would cost $431 per drum for treatment.

SALE OF SOLUTION ALTERNATIVE

The sale of the untreated dissolver solution for the value of the metals in solution, or paying a chemical disposal firm for the treatment of the waste would be less expensive if the total cost of the line item denitrification subproject is considered. The outright sale of the solution would yield approximately $800,000 savings plus the sale price of the solution. Even if the solution was given to a recovery firm or a small price was paid for the chemicals recovery a savings of approximately $800,000 is expected. In addition to the savings already mentioned no proposed hazardous waste generator fees would be incurred because the solution would be considered a byproduct for another company's use. The vendor requires chemical analyses before accepting the solution. Further requirements imposed upon the chemical recovery firm by PGDP are shown in the listing below.

> Personnel and materials to remove approximately 2,000 gallons of nitrate solution for approved recovery of heavy metals contained therein. Pertinent information is contained in the Material Description Section (the Materials Description Section shows a listing of the analyses). Removal and recovery must be subject to the following specifications:
>
> 1. Transportation of solution will be restricted to tank truck and transport vehicle must be placarded in accordance with DOT regulations found in 49CFR100-199.
>
> 2. Shipping papers must be prepared according to requirements found in 49CFR100-199.
>
> 3. Waste solutions, sludges, containers, etc., resulting from the recovery operation must be treated, stored, or disposed of in conformance with applicable federal and/or state regulations.
>
> 4. A manifest shall be used and the transporter and facility owner/operator shall sign the manifest upon receipt of the material. The owner/operator shall return the original of the manifest to the generator (PGDP) within 30 days after takeout of material.

5. All EPA and DOT regulations must be fully complied with.

NOTE: Bids will also be entertained for the disposal of this material; however, priority will be given to reclamation. In the event disposal services are bid, all specifications will apply. Additionally, disposal must be accomplished in an EPA disposal facility licensed to dispose of material shown under the Material Description Section. Facility must also be approved by PGDP Material Terminal Management Department, and Environmental Control Department before disposal is effected.

Title to material will pass to contractor upon acceptance of material by their driver and contractor shall assume full responsibility for such material thereafter.

A major factor affecting disposal versus recovery option is the value of metals and the quantity in solution. If disposal is the only method of handling the waste a range of 1980 prices per drum is $65-150. At this price denitrification is approximately five times more expensive than outright sale of the solution to a disposal firm handling hazardous waste.

The storage area where the dissolver solutions will be kept is being cleaned to ensure no detectable amount of uranium will be present in the stored solutions. The solution will undergo periodic sampling to detect any uranium contamination. These steps are being taken to help the effort for sale of the solution.

CONCLUSIONS

Denitrification has worked in laboratory scale reactors at a reduced nitrate decomposition rate due to the interferences in the feed solution. The dissolver solution is a low volume of waste (maximum 12,000 gallons/year) and its generation rate is erratic. The resulting concentration of nitrate will vary depending on the amount of nitric acid needed to destroy the gold-plated scrap. The sale of solution is the recommended method of treatment. The cost saving for sale or even with drummed chemical disposal outweighs the price for the denitrification subproject.

CHROMIUM RECOVERY FROM SLUDGE PRODUCED AT THE X-616 LIQUID EFFLUENT CONTROL FACILITY

L. E. DEACON
GOODYEAR ATOMIC CORPORATION

Chromium Recovery
Liquid Wastes-GDP
Environmental Control-GDP
Waste Management-GDP

ABSTRACT

Current EPA regulations require the removal of hexavalent chromium from liquid effluents to a concentration not exceeding 0.05 ppm prior to discharge. At GAT the chromate corrosion inhibitor present in the recirculating cooling water (RCW) blowdown is removed, prior to discharge to the Scioto River, at the X-616 Liquid Effluent Treatment Facility. The resulting chromium hydroxide-containing sludge is stored in unlined earthen lagoons. Resource Conservation and Recovery Act (RCRA) regulations are directed toward recovery and recycling of materials, e.g., chromium recovery for reuse in the RCW system. Several techniques have been investigated at GAT for chromium recovery from RCW blowdown. The most effective recovery scheme was found to be one in which insoluble chromium hydroxide was oxidized to water soluble sodium chromate by mixing the X-616 sludge with soda ash and calcining the mixture. The chromium was then removed from the insoluble residue by a water leach. Pilot plant studies have been completed which indicate average recovery efficiencies of approximately 96 weight percent of available chromium in the sludge. However, the final leachate residue still contains sufficient leachable chromium (> 0.5 ppm) so that it must be considered a hazardous waste.

Economic studies have shown that sludge dewatering and burial (with or without fixation) is currently the most economical disposal alternative, while chromium recovery by sludge calcination/leaching

is most attractive from an environmental standpoint. Should chromium recovery again become a viable option at some future date, further development will be needed to allow ultimate residue disposal in sanitary landfill areas.

SUMMARY

Hexavalent chromium in the form of sodium chromate (Na_2CrO_4) is present in the GAT RCW (recirculating cooling water) system to provide corrosion protection for metallic components of the system. Current EPA regulations require the removal of hexavalent chromium to a concentration not exceeding 0.05 ppm before discharge of the blowdown from the RCW system to the Scioto River. At Portsmouth, chromium removal to the specified limit is accomplished by the X-616 Chromate Removal Facility. The chromium is reduced to the trivalent form using sulfur dioxide. The reduced chromium and other metals such as zinc are removed by adding lime to induce metal hydroxide precipitation. The insoluble resultant sludge is stored in earthen lagoons.

Sludge disposal in additional lagoons is restricted by the availability of suitable sites. Lagoon disposal will also be restricted by the new Resource Conservation and Recovery Act (RCRA) regulations requiring lagoon liners and extensive monitoring schedules. The optimum long-term solution to the sludge disposal problem is one in which the chromium would be recovered for reuse. The remainder of the insoluble sludge should ideally be environmentally safe and easily disposed of in nonhazardous landfill areas.

Several methods were investigated to recover the chromium from this sludge for reuse and at the same time minimize sludge storage problems. These were wet oxidation techniques using peroxide, persulfate, and permanganate salts; and gaseous oxidation techniques using ozone, chlorine, and fluorine. None of these proved as effective or technically feasible as a method consisting of high temperature calcination of a sludge and soda ash (sodium carbonate) mixture, followed by water leaching of the calcined product to recover hexavalent chromium as sodium chromate. Laboratory studies of this process defined optimum conditions of temperature (900-950°F) and reactant concentration (10:1, Na_2CO_3:Cr, wt. ratio) for calcination. Further work has been done to demonstrate technical feasibility of the recovery scheme on a pilot plant scale. Commercially available sludge dewatering, mixing, and calcination equipment has been successfully employed in tests on sludge from the X-616 facility. Average recovery efficiencies for hexavalent chromium were found to be approximately 96 weight percent of the available chromium in the X-616 sludge. In the process, the fluffy, gelatinous, X-616 waste sludge is converted to a

dense, gravelly residue with a reduction in volume by a factor of 10 or more. The single-stage leaching residue, however, retains sufficient soluble hexavalent chromium to make it unsuitable for unrestricted landfill disposal. Additional work will be necessary to optimize the leaching process.

On the basis of a recent comparison of economic and environmental factors, DOE has approved plans for near-term chromium sludge disposal via temporary surface impoundment in storage lagoons, in compliance with RCRA regulations. This means of disposal is now being implemented at Portsmouth. For long-term disposal however, chromium sludges may constitute an economically recoverable resource deserving of further development effort.

INTRODUCTION

Due to concentration of dissolved solids in the Recirculating Cooling Water System caused by evaporation in the cooling towers, periodic blowdowns are used to remove the excess solids and prevent precipitation of solids in the Freon condenser piping. Once the carcinogenic effects of hexavalent chromium were identified, it was no longer allowable to discharge these blowdown wastes directly to the environment. This resulted in much stricter effluent discharge limits, and the hexavalent chromium limit was set at 0.05 mg/l for the state of Ohio. Methods for meeting this limit were subsequently investigated. Ion exchange removal of chromium was first considered but laboratory studies indicated that this process could not consistently remove hexavalent chromium to the target level. As discharge limit problems arose with other methods, the sulfur dioxide (SO_2) reduction/lime-precipitation process seemed most feasible for scale-up. The sulfur dioxide reduction/lime-pecipitation process for removal of chromium, the process used in the X-616 Chromate Removal Facility, was finally chosen over ion exchange because: (a) installed equipment costs for the former were roughly one-half and (b) ion exchange removal could not meet the effluent discharge limits for hexavalent chromium (0.05/mg/l). Ferrous sulfate ($FeSO_4$) reduction was also considered as an alternative to sulfur dioxide, but was rejected because of the voluminous amounts of sludge it produced.

The flowchart of the X-616 process is shown in Figure 1. RCW blowdown enters X-616 via the pH reduction tank, where sulfuric acid was originally added to reduce the pH to 3.0. The water flows into a second tank where SO_2 is added to reduce the hexavalent chromium (Cr^{6+}) to trivalent chromium (Cr^{3+}). The water goes to the reaction well of the clarifier where lime (CaO) in slurry form is added to raise the pH to 8.5. Insoluble metal hydroxides are formed which precipitate to the bottom of the clarifier. The water is removed at the

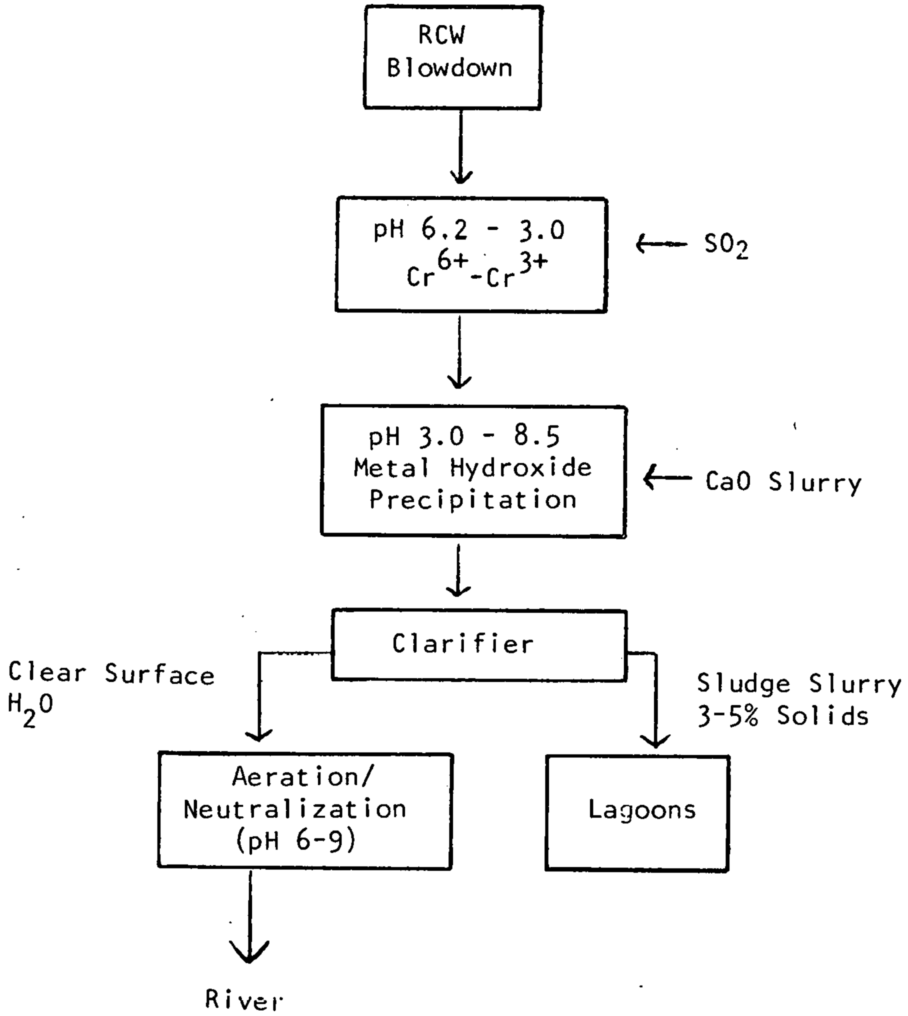


FIGURE 1 FLOWCHART OF THE X-616 PROCESS

surface and drains to a neutralization tank. Here it is aerated and neutralized to pH 6-9, prior to being pumped to the river. The sludge is periodically pumped to nearby lagoons. The chemical reactions for the reduction and precipitation of chromium in the X-616 are:

$$2H_2CrO_4 + 3H_2SO_3 \rightarrow Cr_2(SO_4)_3 + 5H_2O$$

$$Cr_2(SO_4)_3 + 3Ca(OH)_2 \rightarrow 2Cr(OH)_3\downarrow + 3CaSO_4$$

During the development phase of the X-616 project, it was recognized that if the reduction-precipitation process for the removal of chromium from the RCW blowdown was used, waste sludge in open lagoons would be a problem. An economic study showed that the most expensive item for the plant would be the disposal lagoon, with replacement of the sodium chromate corrosion inhibitor being approximately 30 percent of total plant costs (1970).[1]

Pursuant to the expected sludge lagooning problem, alternate sludge disposal/ chromium recovery schemes were surveyed for possible use.[2,3] Most of the investigations were in the areas of wet oxidation techniques, using peroxide, persulfate, and permanganate salts; and gaseous treatments using ozone, chlorine, and flourine. Solid-state oxidation via high temperature open-air calcination, however, gave the most promising results. The earlier recommendation favored ion exchange in conjunction with the reduction-precipitation method. While it seems reasonable, this proposal does not reduce the sludge volume being stored in the lagoon. In addition, chromium recovery alone will not economically justify any deviation from the present process.

Chromium recovery would aid in the recovery of costs incurred by any sludge disposal method, if the two operations could be accomplished together. A feasible method using high temperature calcination to form sodium chromate was developed in the laboratory, through modification of processes used by the industry.[4,5] The successful method would attempt to recover most of the chromium from the X-616 sludge while producing a residue which is suitable for nonhazardous landfill. The proposed limit for chromium in the residue leachate would be 0.5 ppm. This limit is in accordance with proposed laws for identifying hazardous waste as documented in the Federal Register, Vol. 43, No. 243 of Monday, December 18, 1978. This process depended upon the following chemical reactions for the formation of sodium chromate:

$$\underset{\text{(sludge)}}{4Cr(OH)_3} \xrightarrow{\text{Heat}} 2Cr_2O_3 + 6H_2O\uparrow \qquad (1)$$

$$2Cr_2O_3 + 4Na_2CO_3 + 3O_2 \xrightarrow{\text{Heat}} 4Na_2CrO_4 + 4CO_2\uparrow \qquad (2)$$

Theoretically, 2.04 parts by weight of soda ash are needed to react with one part chromium to form sodium chromate. The sodium chromate producing industry uses a ratio of about 3.13 to one, soda ash to chromium, and an excess of lime to eliminate certain metallic interferences. The proposed process uses more soda ash, due to a lower initial chromium concentration, and no excess lime, due to laboratory experience with reduced chromium recovery because of lime additions.

The chromium recovery process was first applied in the laboratory in 1977 to actual X-616 produced sludge.[6] Characterization of the sludge indicated modifications in the process would be required. Chromium values were several times higher than those originally expected and, due to the better chemical efficiency in the X-616 operation, less lime could be recovered from the sludge. Additionally, high silica concentrations in the sludge posed a definite problem in the calcine at the required temperatures. Silica produces "glassing" of surfaces and, in rotary kilns, causes plugging.

Typical characteristics of the X-616 sludge are shown in Tables 1 and 2. Table 1 indicates that the major portion of the sludge has a fine particle size of 1.3 - 4.5 microns, while Table 2 shows the elemental composition.

TABLE 1 PARTICLE SIZE ANALYSIS OF X-616 SLUDGE

Particle Size (microns)	Percentage Distribution
1.2	8.6
1.3 - 4.5	64.0
4.6 - 7.8	19.6
7.9 - 11.1	4.6
11.2 - 14.4	2.3
14.5 - 17.7	0.7
17.8	0.2

The revised sludge treatment procedure evolving from this laboratory work called for mixing the X-616 sludge (as dry as possible) with soda ash in a ratio of 10 parts soda ash to one part chromium on a dry weight basis. This mixture was to be fed into an appropriate calciner operating at a temperature of 950°C and retained for one hour. The calcined product would then immediately be dumped to an agitated water leach tank, where the sodium chromate, having a solubility of 87.3 grams per 100 milliliters of cold water, would be leached into the water. The sodium chromate solution would be removed and stored. Periodically, the solution would be transported to the point where the chromate inhibitor is added. Here the remaining portion (22 percent) of the corrosion inhibitor package ($ZnSSO_4 \cdot H_2O$ $Na_6(PO_3)_6$, $NaHSO_4$) would be added to the solution. After dilution and pH adjustment, the inhibitor solution would be injected into the RCW system. The insoluble residue would be removed from the leach tank, washed and dewatered. The rinse solution would be used as partial make-up to the leach tank. The solids would be transported to a landfill site for disposal. Figure 2 shows a flowchart schematic for a chromium recovery plant based upon these laboratory studies.

TABLE 2 X-616 SLUDGE CHEMICAL CHARACTERIZATION

Element	Dry Weight Percentage
Al	0.68
Ca	2.48
Cr	9.70
Cu	0.02
Fe	0.62
Mg	23.34
Mn	0.03
Ni	0.01
Pb	0.003
Si (as SiO_2)	25.80
Ti	0.06
Zn	2.03
Cl	Trace
P	Trace
S	Trace

Arrangements were made to provide equipment on plantsite to examine this proposed chromium recovery scheme on a pilot plant basis. The pilot plant work would determine the technical feasibility of applying the chemical process to an operational plant facility. The essential equipment selected was: (a) Polyfilters filter-leaf press for dewatering the X-616 sludge slurry, (b) Baker Perkins mixer for mixing the soda ash and sludge, and (c) Harrop Precision Furnace Company calciner for producing sodium chromate from the chromium hydroxide sludge and soda ash mixture.

EXPERIMENTAL

I. SLUDGE DEWATERING

Sludge is presently discharged from the X-616 clarifier to the sludge lagoons, in a liquid slurry containing 3-5 weight percent suspended solids. The sludge cannot be processed in this form and must be dewatered to a cake that is as dry as possible.

Three types of equipment were considered for dewatering: a centrifuge, a rotary vacuum filter, and a filter leaf type press. During cooperative laboratory/vendor test programs, the filter leaf press produced the driest cake.

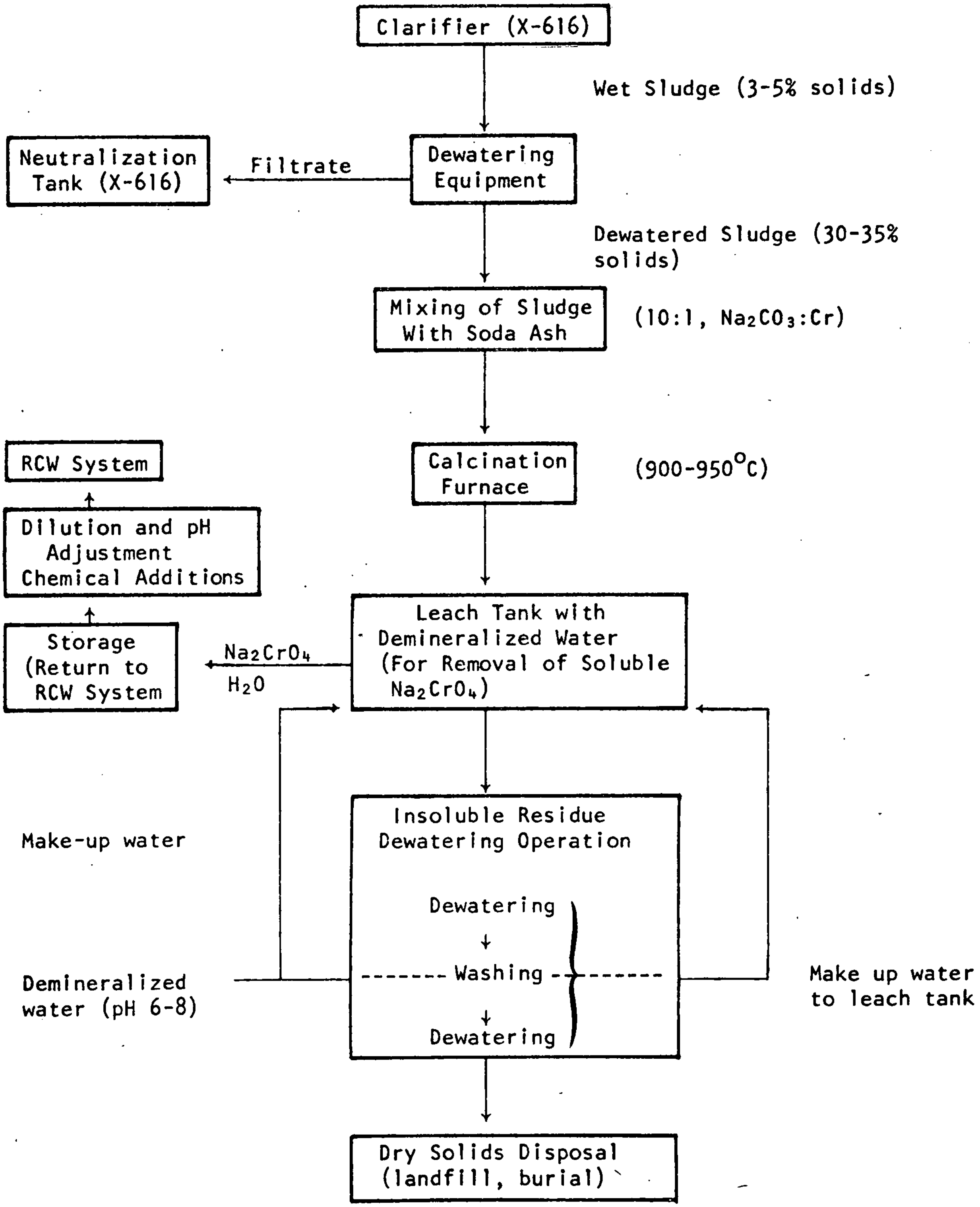


FIGURE 2 CHROMIUM RECOVERY PLANT FLOWCHART

A filter leaf press was subsequently rented from Polyfilters, Inc., Bethlehem, Pennsylvania, for pilot plant testing on plantsite. Sludge was pumped to the press by a Sandpiper air-activated diaphragm pump capable of pressurization to 100 psig. A cake volume of approximately 0.5 cubic foot was collected on filter cloths held securely between polypropylene plates. Water containing a minimal amount of suspended solids passes out of the press and is discharged.

Plantsite tests run with this press met with marginal success. While a sludge cake containing 35-40 weight percent solids was desired, the average cake produced contained only 30 weight percent solids when dewatered from a slurry containing 5 weight percent solids. The 30 percent solids filter cake is very deceiving as it appears to have the dry and crumbly characteristics of sludge cakes which are much drier. The driest cake of the test contained 33 weight percent solids, and was dewatered from a diluted slurry containing 1-2 weight percent solids. This batch dewatering operation required 4-1/2 hours while only 2-1/2 hours were needed for 30 weight percent solids cakes. Operations were conducted in a sequence of initial loading for 20-30 minutes at 20 psi, followed by loading at 100 psi for the indicated time periods. Temperature of the slurry was approximately 24°C. All filtrates were very clear.

Similar testing by Ingersoll-Rand at their Liquids/Solids Separation Equipment Laboratory in Nashua, New Hampshire, produced results much the same as those obtained on plantsite with the filter-leaf press. Ingersoll-Rand equipment consisted of a 360 x 1 Lasta Filter Press in which provision is made to compress the sludge cake after it is loaded on the filter cloths to expel any residual water. Experience has shown the compression step to be especially effective under conditions where a shorter cycle time is critical. Ingersoll-Rand reported their tests to yield a cake dryness of 30.4 weight percent solids with an operating sequence of: feed 13-15 minutes, compress 9-10 minutes, and core blow 10 seconds.[7] Shorter and longer feed cycles were evaluated with the longer cycles exhibiting no increase in solids loading rates. The major drawback of the Lasta equipment is its capital cost. The cost of the unit with auxiliary support systems is nearly 2-1/2 times the cost of a similar Polyfilters package. Dewatering by use of a centrifuge was eliminated from consideration after receiving the results of testing at Western States Machine Company, Hamilton, Ohio.[8] Centrifuge dewatering test results indicated a cake solids concentration of 15.7 weight percent without polymer and 13.4 weight percent with polymer added. Such slurries are not dry enough for economical use in any type calciner, since increased calciner capacity would be required.

II. Mixing of Sludge and Soda Ash

Once the sludge has been dewatered as much as possible, sodium carbonate (Na_2CO_3) soda ash, must be added in the proper ratio. It is very important that the soda ash be thoroughly mixed for the most efficient oxidation of chromium in the sludge.

The sludge/soda ash mixing study was initiated at a vendor demonstration and test center since no such equipment was available on plantsite. The vendor having the most modern and easily accessible test facility is Baker Perkins of Saginaw, Michigan.

Testing was performed using their MP-50 Twin-Screw Continuous Mixer. The test material was X-616 sludge and soda ash previously shipped to the Saginaw testing center. No dewatered sludge was then available so a thickened sludge, which contained 11.5 weight percent solids, was used. Results were very poor and no amount of operating expertise could improve them. The resulting product was a wet slurry, which was more fluid than that being added. It appeared that the shear force of the meshing twin screws had further fluidized the sludge. The fine dry soda ash became lumpy in the mixer output, and the batch was not homogenous.

Since it was apparent that the available sludge was too wet, it was spread thinly over a mat and allowed to dry. Mixtures of 30 and 40 weight percent solids were thus prepared. These sludge mixtures were then fed to the mixer. The 30 percent solids mixture showed much handling improvement; the 40 percent solids mixture produced a firm extrusion, with soda ash evenly dispersed throughout the batch. Final test results indicated that the twin-screw mixer could possibly be used, and should be further evaluated using dewatered sludge containing at least 30 weight percent solids.[9]

The Baker Perkins MP-50 Twin Screw Mixer was available on a rental basis, as a portable laboratory machine for pilot plant testing or for low volume applications. It was believed that such a unit could be used with dewatered sludge from a filter press to produce the feed for a calcination device. Therefore, arrangements were made to obtain a rental unit on plantsite for the purpose of further testing and to provide feed for a calciner.

As onsite pilot plant dewatered sludge became available, sludge and soda ash in the selected dry weight ratio were fed into the mixer. Initial dewatered sludge material contained less than 30 weight percent solids due to inexperience in using the filter press. Problems developed in feeding, as the mixer feed portal is only two inches in diameter and the wet sludge mixture plugged the opening. The feed opening is designed for dry powders which are gravity-fed to the twin-screw mixing unit. With more experience the solids content increased, producing a drier sludge cake (above 30 weight percent), and the plugging problem lessened. When informed of this problem, Baker Perkins' representatives indicated that larger production-scale models could be adapted with an additional screw-feeder to eliminate mixer input plugging.

Another type of mixing was considered although no actual equipment testing was performed. A ribbon blender, or similar equipment, could be used if only coarse mixing should be required. Testing with the calciner later eliminated this possibility since data showed that very homogenous mixing would be required. Further test results to verify this conclusion are shown in the calciner operations section of this report.

III. SLUDGE CALCINATION AND LEACHING TESTS

A. Calciner Materials Corrosion Studies

After the sludge and soda ash mixture has been prepared, it is chemically processed to form sodium chromate. This process is endothermic, therefore a suitable calciner must be provided. From previous laboratory work, the optimum temperature range was found to be 900-1000°C. This temperature exceeds the 851°C melting point of soda ash, thus establishing a corrosive environment which is very detrimental to most metals.

Since some metal surfaces would be exposed to the environment within the calciner, a search for the most corrosion resistant metals was made. Harrop Laboratories, Columbus, Ohio, subjected nine samples of alloy metals to the corrosive environment which the metals would have to withstand in GAT sludge-calcining operations. A sample of each alloy was half immersed in a mixture of equal parts of sludge and soda ash in a crucible. These samples, along with identical coupons not subjected to the corrosive environment were placed in a 900°C furnace for seven full days. Table 3 lists the nine alloys and describes their resistance to corrosive attack. Inconels 671 and 690 were the least susceptible to attack. Comparison photographs are shown in Figure 3.

Similar corrosion testing was conducted on plantsite using coupons submitted by Atek Metals Center, Incorporated, Cincinnati, Ohio, and Huntington Alloys Products Division, Huntington, West Virginia. Atek submitted coupons of Hastelloy 5S1, C-276, and C-47 while Huntington provided coupons of Inconel 671 and 690. Coupons were half immersed in a mixture of equal parts of dried sludge and soda ash, and

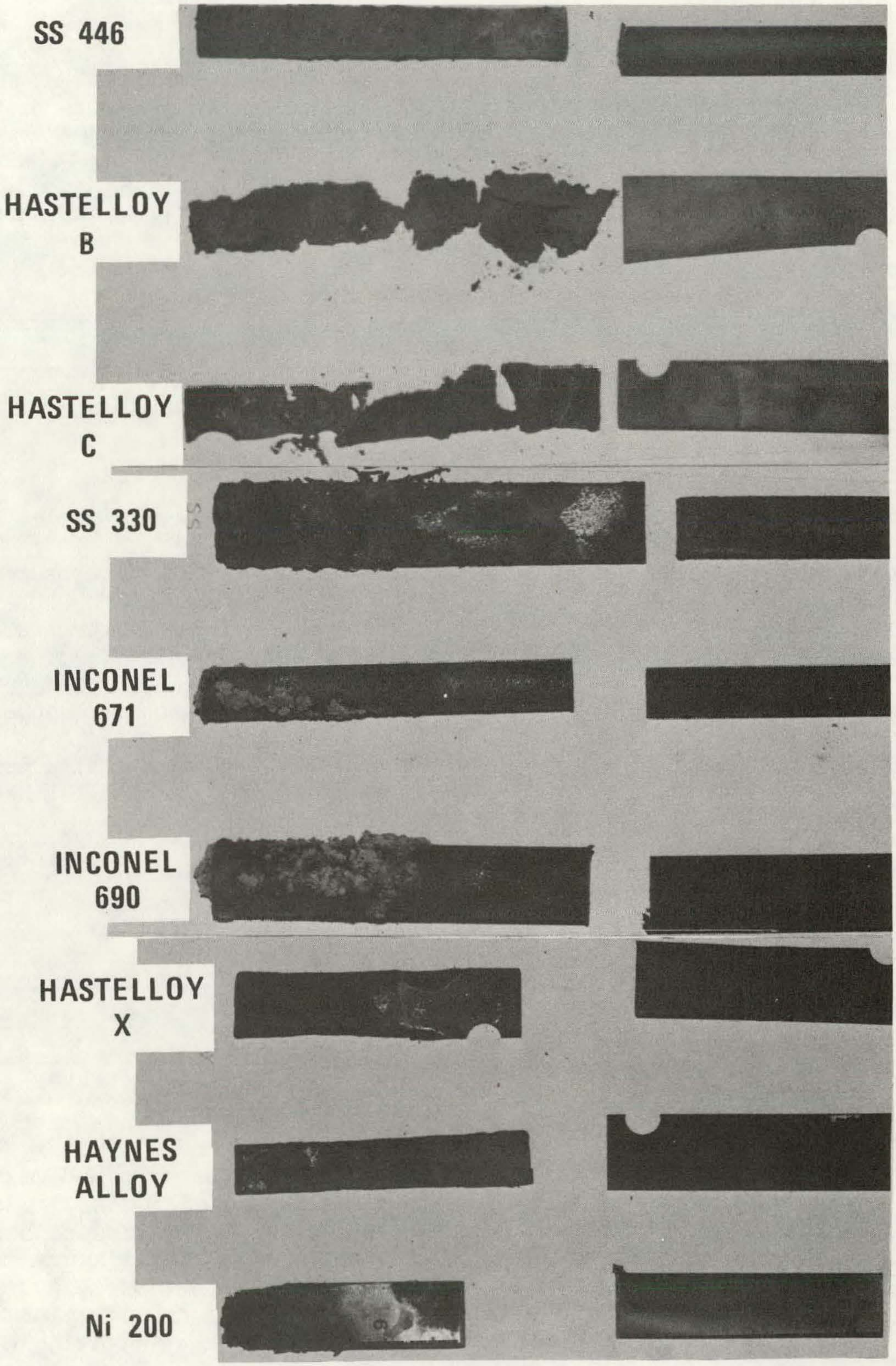


FIGURE 3 CORROSION TEST RESULTS FROM HARROP LABORATORY

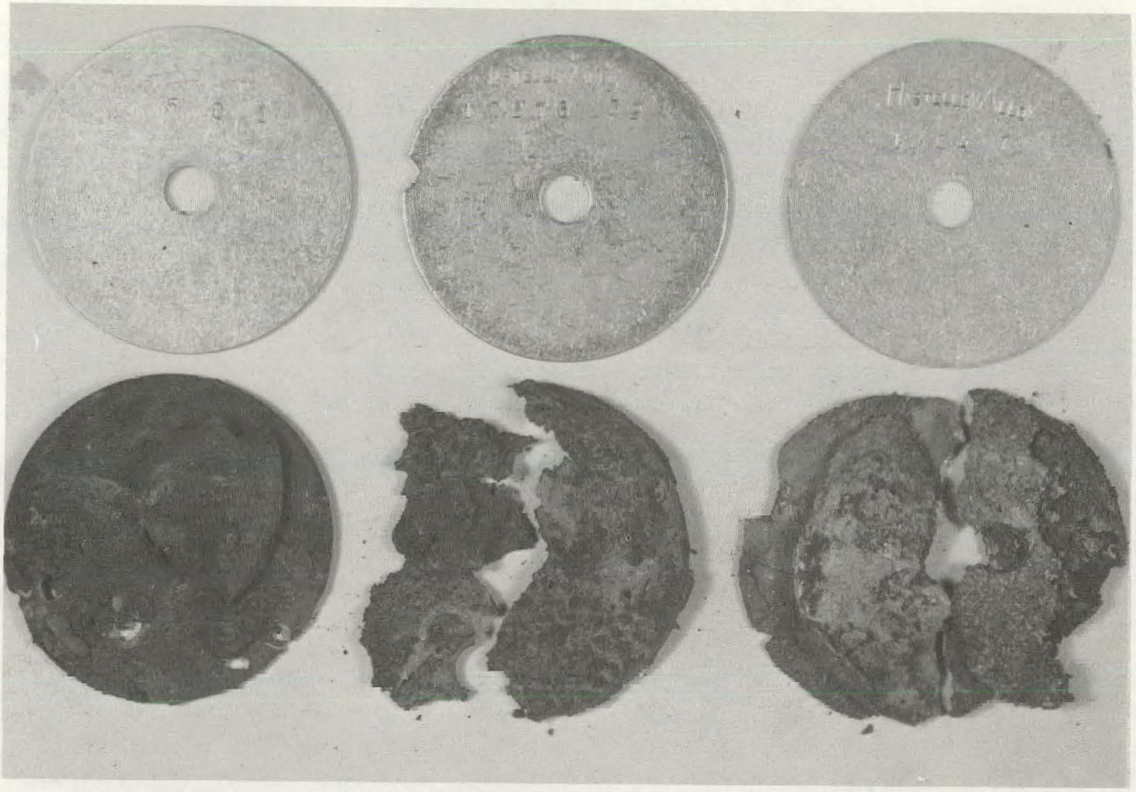
calcined at 950°C for 44 hours. Hastelloy alloy 5S1 was very corroded while alloys C-276 and C-47 were nearly consumed. Inconel alloys 671 and 690 were intact and only slightly corroded. Comparison photographs are shown in Figure 4. The Inconel alloys were returned to the furnace and tested for 30 days total. Inconel alloy 671 was slightly corroded as was alloy 690, but alloy 690 was less corroded than alloy 671. Inconel alloys 671 and 690 should therefore be selected for use in this particular environment.

TABLE 3 METAL TESTING AT HARROP LABORATORIES

Sample	Description
Stainless Steel 446	Moderate attack with scale formation.
Hastelloy B	Extreme attack, worst sample.
Hastelloy C	Extreme attack, 2nd worst sample.
Hastelloy X	Exposed portion 60 percent consumed.
Haynes Alloy #25	Entire sample evenly 50 percent consumed.
Nickel 200	Exposed portion 50 percent consumed.
Stainless Steel 330	Light attack, it appears that a protective scale forms to stop further corrosion.
Inconel 671	Very light attack, tied with Inconel 690 for least corrosion.
Inconel 690	Very light attack, similar to Inconel 671

B. Calciner Design, Procurement, and Installation

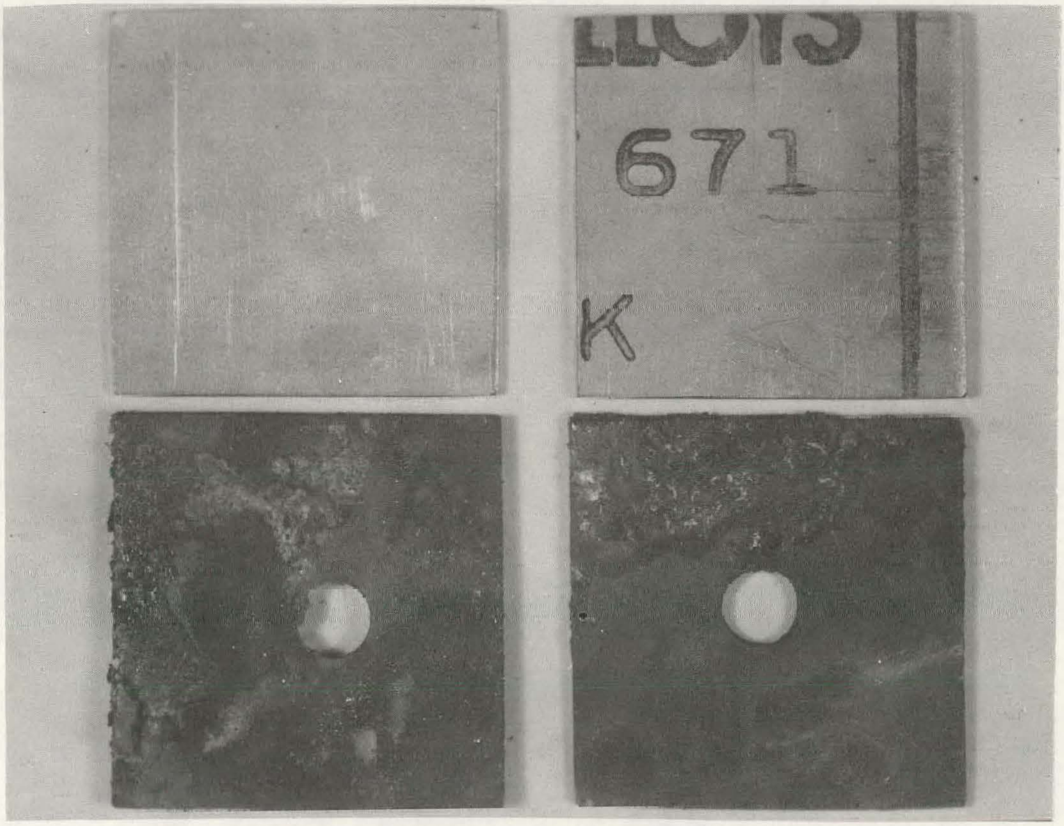
The design of the calciner will have an indirect effect on efficiency of the chemical reaction, and ultimately the percentage of chromium recovered. Some agitation and mixing must occur both to prevent the adhesion of the sludge and soda ash mixture to the calciner walls, and to provide aeration of the mixture for complete chromium oxidation. The agitation must not be too forceful or excessive hexavalent chromium dust will be released to the surrounding areas, even though scrubbers should be provided to control the nor-



HASTELLOY
5S1

HASTELLOY
C–276

HASTELLOY
C–47



INCONEL 690

INCONEL 671

FIGURE 4 PLANTSITE CORROSION TEST RESULTS mal dusting. A deleterious effect occurring in rotary type kilns, regardless of agitation, would cause "glassing" that is produced from large amounts of silica, similar to the amount contained in the X-616 sludge. This "glassing" would plug the rotary kiln if not periodically removed.

After successful attempts to obtain a rental calciner for pilot plant evaluation, a used "osciplate" unit was purchased from the Ball Corporation, Muncie, Indiana. "Osciplate" is the term used to describe a calciner design that uses "pusher" plates for moving calcined materials downward over a stairstep arrangement of heating trays or "hearths." This arrangement provides aeration of the sludge while producing little dust, and eliminates the need for elaborate scrubbers to collect process dust. The manufacturer, Harrop Precision Furnace Company of Columbus, Ohio, agreed to convert one gas-fired calciner module to indirect electrical heating. On delivery to plantsite, the "osciplate" calciner was erected, with associated auxiliary systems, in the X-760 Chemical Engineering Building.

Figures 5, 6, 7, and 8 are photographs of the calciner after installation. Figure 5 shows front and side views of the module. Figure 6 shows the calciner module with the leach tank in place. The picture of the leach tank illustrates the plenum whereby the calcined product exits the calciner and enters the leach tank without exposure to the environment. The plenum is sealed by submersion below the water level of the leach tank. Also pictured is the mixer which agitates the water in the leach tank. Figure 7 shows the location of the hydraulic system which operates the pusher plate mechanism. The pusher plates move the sludge through the calciner and also provide mixing to prevent adhesion of sludge to the hearths. Figure 8 shows, in View A, the electrical cabinet containing the transformers which supply variable amounts of electricity to the Globar heaters in the calciner. Figure 8 (View B) shows the control system for automatic operation of the pusher plate mechanism. The left switch and meter controls the frequency of cycles of the pusher plates to regulate the speed of sludge moving through the calciner. The right switch and meter control the amount of sludge moved by each cycle of the pusher plates. A preset electrical interlock will override a short stroke of the pusher plates and extend the plates to their maximum travel for moving all sludge to the next hearth.

C. Calciner Operation and Test Runs

Short strokes are used to provide mixing and aeration of the sludge with small amounts moving to the next hearth. It was determined experimentally that a sequence of two

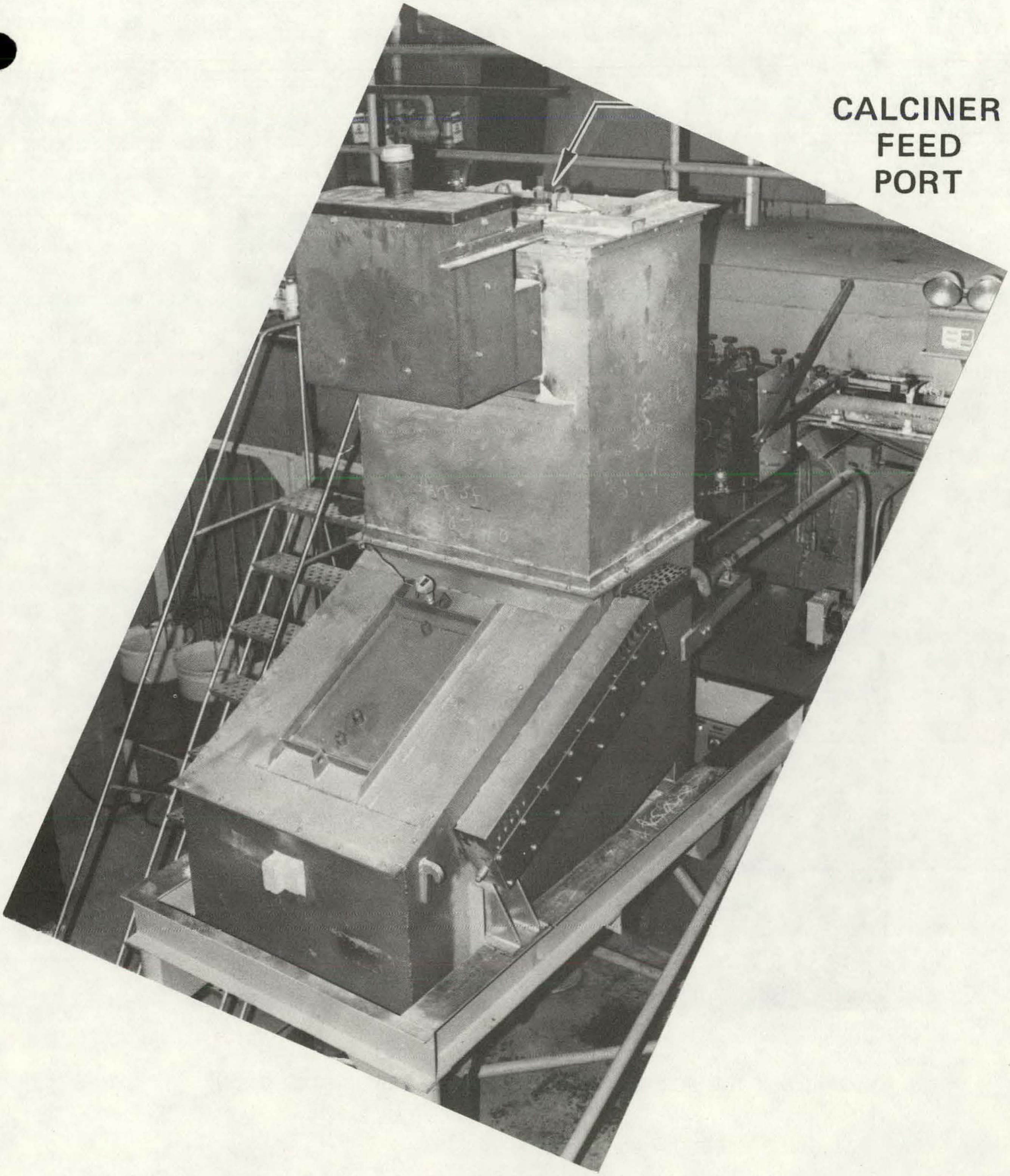


FIGURE 5A ONE MODULE OF THE OSCIPLATE CALCINER (OVERHEAD VIEW)

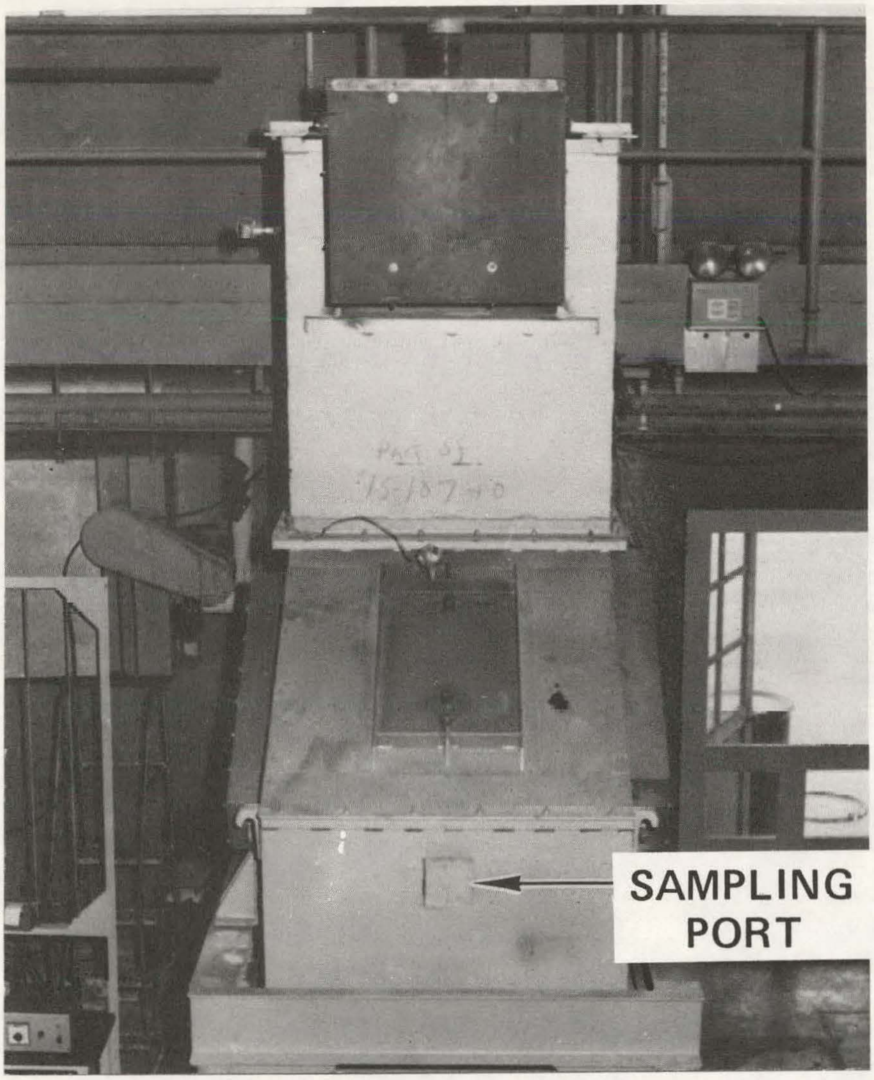


FIGURE 5B ONE MODULE OF OSCIPLATE CALCINER (SIDE VIEW)

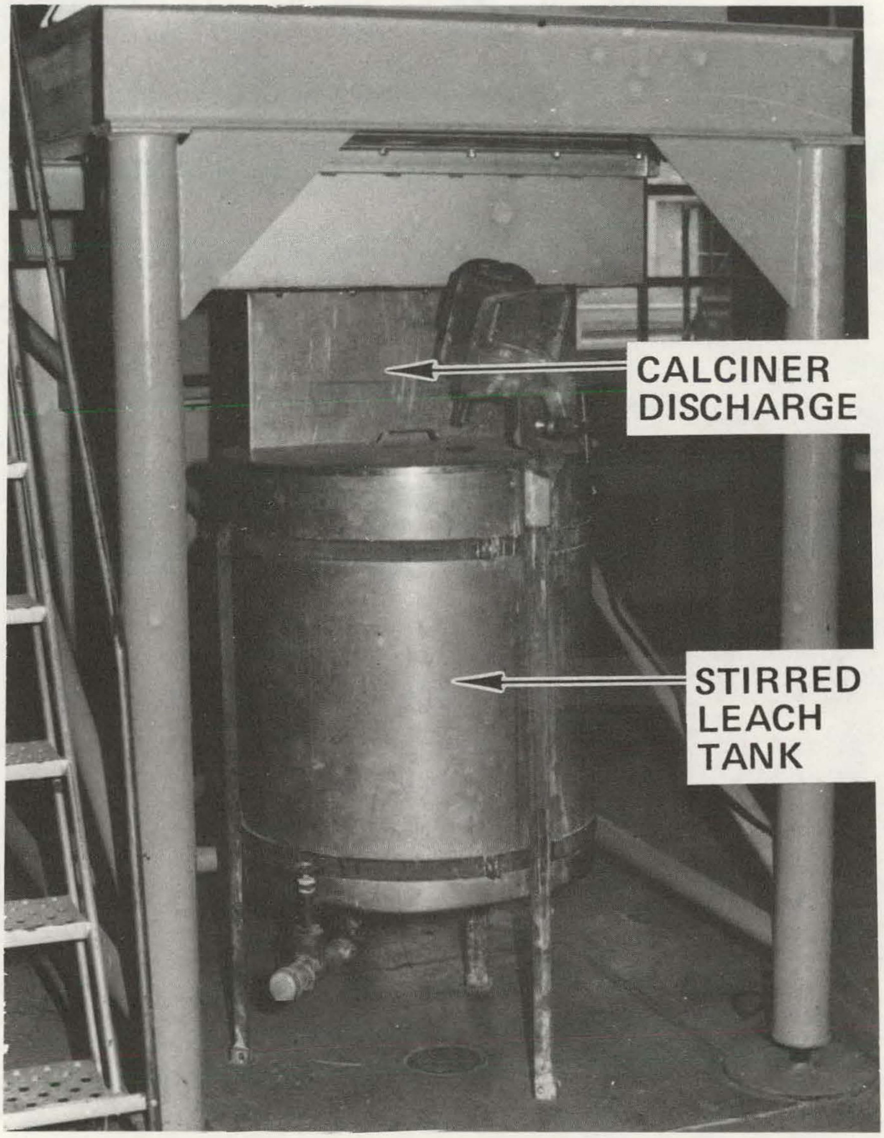


FIGURE 6 CALCINER WITH LEACH TANK

PUSHER-PLATE DRIVE MECHANISM FOR SLUDGE MOVEMENT

PUSHER PLATES DRIVE

PUSHER PLATES (INSIDE)

FIGURE 7 CALCINER WITH HYDRAULIC CONTROL FOR MOVEMENT OF PUSHER PLATES

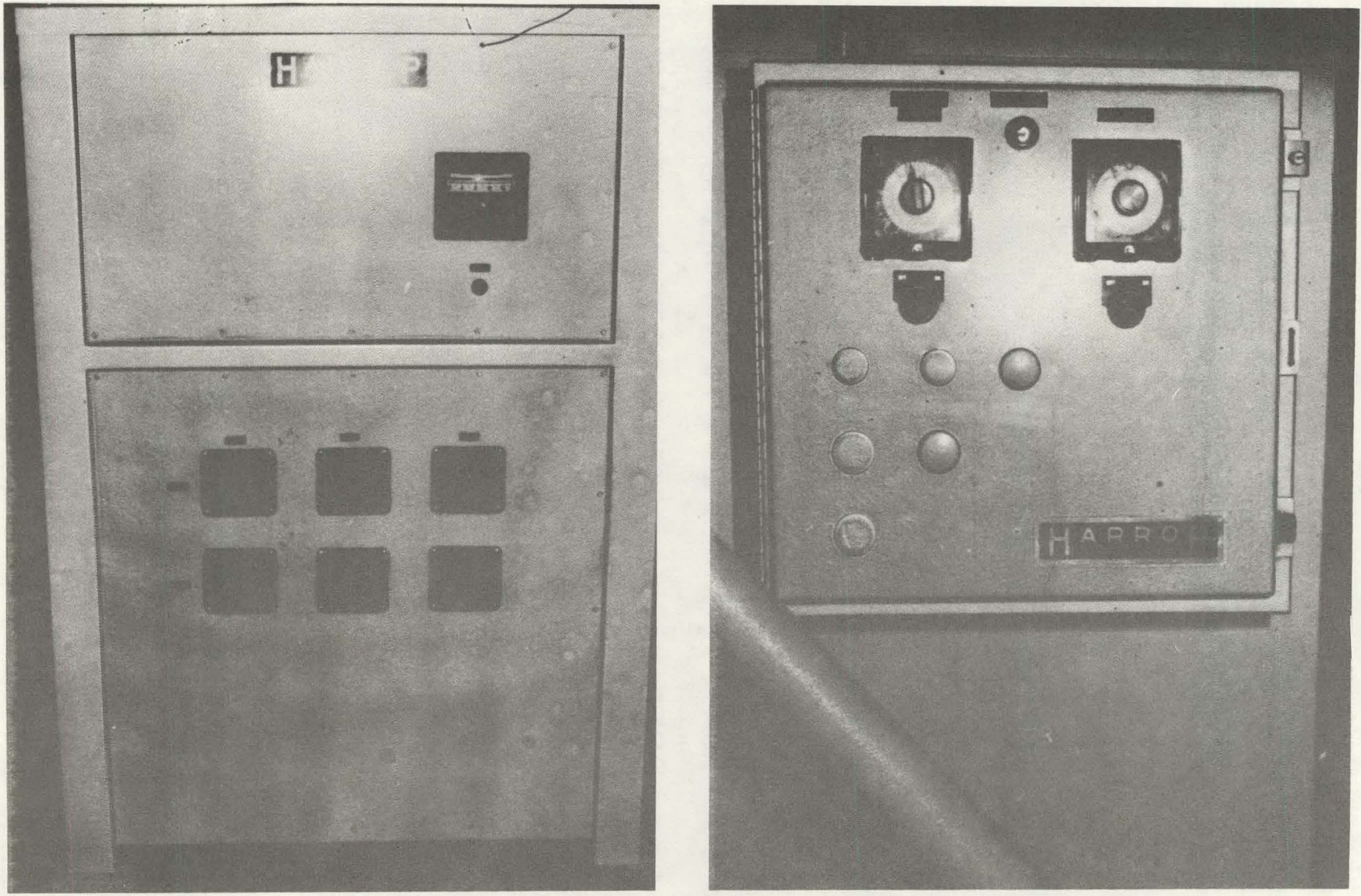


FIGURE 8 ELECTRICAL CABINET AND CONTROL PANEL

short strokes followed by one long stroke with five-minute intervals between strokes allows a one-hour retention time of the sludge in the calciner. With a depth of two inches of sludge on the 22-inches wide by 40-inches long hearth, this sequence will produce a throughput of one cubic foot of sludge per hour.

Initial tests with the calciner were aimed at determining the degree of mixing needed to attain good hexavalent chromium recovery, i.e., greater than 90 percent of the average available chromium content.

Tests were begun by using a mixture that was manually mixed in a dry weight ratio of equal amounts of sludge and soda ash. This ratio assumes that the chromium content is 10 weight percent of the sludge, since the soda ash should optimally be added in the proportion of 10 parts of soda ash to each part of chromium. The moisture content of the sludge must be measured as it is critical to the weight ratio.

The first tests were performed using dry sludge with lumps of one-inch diameter, decreasing in size to a powder. The result was a recovery of 44 weight percent, at best, of the available chromium. The calciner temperature was 950^{o}C, and the sludge and soda ash were mixed in equal proportions. A repeat of this test with similar but less coarse sludge, produced results of chromium recovery up to 59 weight percent. This indicatd the need for a more homogenous mixture.

The next tests used sludge containing 30 weight percent moisture. Due to the wetness, the dry soda ash tended to cling to the lumps. The results were better but not enough to be usable. A follow-up test in which hourly additions were made increased the chromium recovery from 62 to 66 weight percent.

Tests were continued using the sludge and soda ash mixture produced in the twin-screw mixer test. The mixture had been stored several weeks and had dried to flakes. Analyses of the mixture showed the chromium content to be 6.5 weight percent. The tests were performed in the same manner as before. The temperature of the calciner was 950^{o}C. The pusher plates were operated in a sequence of two short strokes followed by one long stroke with five-minute intervals between strokes.

Samples were taken to be leached and analyzed to determine the amount of conversion from trivalent chromium to hexavalent chromium, which is recovered and recycled. Recoveries were much higher than in the previous tests. This success is the direct result of more homogenous mixing of the sludge and soda ash. Typical results of 950°C calcination are shown in Table 4. Lower results occurred at the beginning of the tests during startup. Lower recoveries were also seen when interrupted feeding occurred during normal operation. Large, coarse pieces of unreacted sludge, having insufficient amounts of soda ash or inefficient mixing of sludge and soda ash, also produce the lower recovery shown after 3.0 hours calcination time.

TABLE 4 TYPICAL TEST RESULTS AT 950°C
(Sludge: Soda Ash = 1:10; Cr 10%)

Calcination Time (hrs.)	Chromium Recovery as Weight Percent
0.5	45.2
1.0	86.5
1.5	96
2.0	96
3.0	92.3
4.0	96
5.0	96

A vendor test was performed by Nichols Engineering and Research Corporation using a Herreshoff rotary-hearth furnace.[10] Test results with this unit appear to be very good. Recalculation of results using analyses performed on plantsite indicates that the 77 weight percent recovery as reported should be much better. The average recovery of samples taken after 30, 45, 60 and 75 minutes of elapsed time is 91.3 weight percent. The report states that slightly more excess oxygen could be added to increase the chromium recovery value. One test also examined the effect of increasing the concentration of soda ash in the mixture. This test failed as the material formed large chunks and adhered to the hearth. Overall, the test showed that a rotary-hearth furnace could possibly be adapted for use in the sludge calcination process.

D. Leaching of Insoluble Calciner Residues

A sample of insoluble residue was taken from the leach tank to be washed and dewatered. The sample was tested to ensure that less than 0.5 ppm chromium would leach into the ground water from stored residues. The test indicated that at least 5 ppm chromium could be released to the water. Therefore, single stage leaching of calcined products may not effectively remove enough chromium to produce an environmentally safe residue for unrestricted disposal. Additional work would be required to determine what further calcination/leaching optimizations can be made.

CONCLUSIONS

A process for recovery of chromium from X-616 produced sludge has been shown to be feasible for scale-up, although further work is required to optimize the final leach process. Tests have shown that 96 weight percent of the chromium in the X-616 sludge can be recovered as soluble sodium chromate. The post-leach problem, i.e., delayed action solution of additional hexavalent chromium from leached residue, was not anticipated and did not appear until the process had reached the pilot plant phase. Possible approaches which may solve the problem vary from multi-stage countercurrent hexavalent chromium extractors, to washing the final leach residue with a reducing solution such as sulfurous acid.

The sludge from the X-616 clarifier must be dewatered to a cake that is as dry as possible. Using the Polyfilters filter leaf press, a cake was produced which contained 30 weight percent solids. Other associated tests indicated this dryness to be the minimum. Additional dryness is beneficial in minimizing handling problems while reducing the fuel demand capacity for the calciner by eliminating the need for moisture removal heat.

The dewatered sludge must be very finely mixed with soda ash in the dry weight ratio of 10 parts soda ash to one part chromium. Incomplete reaction, reducing the amount of chromium recovered, occurred in the calcination process when the sludge and soda ash mixture became coarse and poorly mixed. The Baker Perkins mixer accomplished the necessary fine mixing.

The calciner will be operated in the temperature range of 900-950°C. The interior exposed metal parts of the calciner should be fabricated from Inconel 690 or 671, which are capable of withstanding the reaction zone corrosive environment. Selection of the type of calciner is also important as agitation and aeration of the sludge mixture must occur with minimal dusting of hexavalent chromium to avoid operator exposure. The "Osciplate" calciner proved to be very effective, while a rotary kiln was not recommended due to extreme dusting and glassing which plugs the kiln. High temperature calcination will recover the valuable chromium while also reducing by a factor of 10 the volume of sludge which must be finally stored. If the delayed leaching problem cannot be resolved, the leach residue (or residual sludge) would have to be stored in a hazardous waste landfill. Although the volume of original sludge is substantially reduced by calcination, requirements for restricted residue storage will not favor overall economics of the chromium recovery process.

The simplest and most economical short-term alternative is continued sludge storage in lagoons.[11] In light of the recent DOE decision to continue interim lagoon sludge storage, GAT is implementing lagoon expansion. These lagoons will be constructed to allow recovery of the chromium in accordance with RCRA regulations.

ACKNOWLEDGEMENT

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REFERENCES

1. Cooper, M. H., and Netzer, W. D., Economics of Restricting Plant Chromate Emission, GAT-532-70-125, Goodyear Atomic Corporation, Piketon, Ohio, June 8, 1970.

2. Holland, M. E., Removal and Recovery of Hexavalent Chromium from Industrial Effluents - A Literature Survey, GAT-786, Goodyear Atomic Corporation, Piketon, Ohio, February 21, 1975.

3. Holland, M. E., Possible Methods for Recovery of Chromium from RCW - Pro-duced Sludge, GAT-T-2216, Goodyear Atomic Corporaiton, Piketon, Ohio, July 5, 1974.

4. Deacon, L. E., Chromium Recovery from RCW - Produced Sludges by Open-Air Calcination, GAT-T-2326, Goodyear Atomic Corporation, Piketon, Ohio, March 31, 1975.

5. Deacon, L. E., Holland, M. E., and Kaplan, R. I., Chromium Recovery from Sludges Produced from Chromate - Inhibited Cooling Water, GAT-T-2374, Goodyear Atomic Corporation, Piketon, Ohio, September 12, 1975.

6. Deacon, L. E., Chromium Recovery from X-616 - Produced Sludge: Rotating Cylinder Studies, GAT-521-77-269, Goodyear Atomic Corporation, Piketon, Ohio, August 19, 1977.

7. Knapp, L., and Welcome, W., Laboratory Test Report for Goodyear Atomic Corporation, P-49, Ingersoll-Rand Company, Nashua, New Hampshire, March 30, 1978.

8. Hater, G. R., Process Feasibility Estimate for Goodyear Atomic Corporation, 8L-26, The Wester States Machine Company, Hamilton, Ohio, February 13, 1978.

9. Colby, C. E., Customer Demonstration Center, CST No. 4410, Baker Perkins Incorporation, Saginaw, Michigan, February 15, 1978.

10. Pilato, Dr. Joseph M., Calcination of Chromium Sludge with Sodium Carbonate in the 18-inch Furnace, FX-1715, Nichols Engineering and Research Corporation, Belle Mead, New Jersey, May 1, 1978.

11. Miller, R. R., Alternatives for Future Management of X-616 Sludge: A Com-parison of Economic and Environmental Factors, GAT-A-211, Goodyear Atomic Corporation, Piketon, Ohio, August 27, 1979.

Technical Data Recorded in GAT-NB-4918 by L. E. Deacon

IDENTIFICATION OF MICROORGANISMS IN BIOLOGICAL REACTORS AT THE Y-12 PLANT

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Identification, Bacteria, Microorganisms, Biological Reactor, Denitrification, Machining Coolants, Waste Disposal

ABSTRACT

The Oak Ridge Y-12 Plant[a] operates two biological denitrification reactors for disposing of concentrated nitrate waste solution and one aerobic biological reactor for disposing of used machining coolants. The predominant microorganisms in these biological reactors have been identified to assure the safety of the reactors. No strict pathogens were found in any of the samples analyzed. Bacteria belonging to groups that contain opportunistic pathogens were found in all of the reactors. Opportunistic pathogens can invade hosts with compromised defense mechanisms, such as burn patients, but they are not dangerous to healthy humans and are commonly present in the environment.

INTRODUCTION

During the past year, the Y-12 Plant has generated 190,000 kg of waste nitrate ions from its uranium recycle operations. Of this amount, 125,000 kg have been recycled back into the Plant as nitric acid or aluminum nitrate, and the remaining 65,000 kg were converted into nitrogen

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[a] Operated by the Union Carbide Corporation, Nuclear Division for the Department of Energy.

gas in the biological denitrification reactors. This recycle and disposal system has been in operation since October 1976. The system consists of a distillation system for recovering nitric acid, a crystallization system for recovering aluminum nitrate, and two 100,000-liter biological denitrification reactors. During the past year, the distillation system has recovered 61,000 kg of nitrate ions as nitric acid which was used in the Plant. The crystallization system has recovered 64,000 kg of nitrate ions in the form of aluminum nitrate, which is used as a salting agent in the uranium recycle system. The biological denitrification reactors have converted 126,000 kg of waste nitrate ions into nitrogen gas. Of this total, 65,000 kg were generated in the Y-12 Plant and 61,000 kg came from other DOE plants.

Three samples from these reactors have been analyzed for predominant bacteria types to verify the safety of the biological reactors. The reactors are labeled D-713 and D-712. The D-713 reactor was started in October 1976, and the D-712 reactor was started one year later.

The Y-12 Plant generates approximately 10^6 liters per year of waste machining coolants which are disposed of in an aerobic biological reactor. These coolants are about 98% water and 2% organics. The exact composition of the organic portion is normally proprietary, but generally contains chlorinated or sulfonated paraffins, tertiary amines, polyglycols, and similar molecules. Many of the coolants also contain significant amounts of sodium nitrite.

Since May 1977, these waste coolants have been disposed of in a 110,000-liter, activated sludge reactor. An old concrete cooling tower basin was adapted for this use. Four floating aerators provide the mixing and aeration required. An adjacent 8,000-liter basin serves as a settling chamber. The bacterial sludge sinks to the bottom of the settling chamber and is returned to the reactor. The effluent is discharged into a septic drain field.

The organic concentration of the waste coolants entering the reactor has averaged 40,000 mg/L chemical oxygen demand (COD). The COD of the effluent from the settling chamber is normally less than 1000 mg/L ($>$ 97% removal). The reactor has processed an average of 3000 liters per day of waste coolants.

MATERIAL AND METHODS

The concentration of viable bacteria in the samples was determined by standard dilution and plating techniques. The samples were shaken vigorously before dilutions to suspend all solids. Dilutions were made in nutrient broth and plated on nutrient agar in triplicate. The viable bacterial concentrations reported here are an average of the three plates.

The samples were streaked on nutrient agar, and the colonies appearing at the end of the streak (predominant bacteria) were selected. These colonies were restreaked until they all yielded a single colony type, three consecutive times. Colony and cell morphology and gram reactions were determined on actively growing cultures. The isolates were identified based on morphology, pigment, denitrification, and growth on various substrates. Many of the growth characteristics were determined using API-20E kits from Analytab Products. The Eighth Edition of Bergey's Manual[1] was the primary source of information for identifying the isolates. Several other publications were used for the characteristics of specific bacteria types.[2-6]

RESULTS

A total of three samples from the denitrification reactors and one sample from the waste coolant reactor have been analyzed to date. The sample from the waste coolant reactor was taken on March 29, 1979. One sample was taken from the older denitrification reactor (D-713) on April 3, 1978, and samples from both denitrification reactors were taken on January 23, 1979. The results of the viable bacteria concentration analysis for all of these samples are shown in Table 1.

Waste Coolant Reactor

Thirty different bacteria types and three protozoa types were isolated from the waste coolant reactor solution. Twenty of the bacteria isolates were identified to the genus level. The remaining 10 isolates did not fit the characteristics of any of the established genera. The three protozoa species were identified by Dr. William Young, a protozoalogist from VPI, based on microscopic examination. *Lembus pusillus* and *Bodo cruzi* occurred with the greatest frequency, and a *Cercobodo* species was present in lower numbers. Protozoa are commonly found in bacterial waste treatment systems. They feed on the bacteria which helps remove excess bacterial cells. The identification of the bacteria isolates is summarized in Table 2.

The genus *Pseudomonas* contains bacteria that are gram-negative rods with polar flagella and strictly respiratory metabolism. Eight of the bacteria isolates fit these characteristics. One other isolate had these characteristics, but it also had a striking colony morphology that resembles the genera *Biejerinckia* and *Derxia*. The tests performed were not sufficient to distinguish between these three genera.

Members of the genus *Microcyclus* are described as gram-negative, curved bacteria that are nonmotile with strictly respiratory metabolism. Four of the isolates from the waste coolant reactor possessed these characteristics. One other isolate was similar to the above isolates except that spiral structures were formed by chains of the dividing cells. These spiral structures are characteristic of the genus *Spirosoma*.

The genus *Nocardia* contains branched cells with strictly respiratory metabolism. They are commonly found in soil and are known for their ability to degrade hydrocarbons. Two of the isolates fit into this genus. The *Nocardia* are considered to be opportunistic pathogens, which means that they can infect humans whose resistance has been lowered by some other means.

Table 1

Viable Bacteria Concentration in Biological Reactors

Reactor	Sampling Date	Viable Bacteria Concentration (colony forming units/mL)
Waste Coolant	March 23, 1979	1.8×10^9
D-713	April 3, 1978	1.2×10^9
D-713	January 23, 1979	2.5×10^9
D-712	January 23, 1979	1.1×10^9

Table 2

Identification of Bacteria Isolates

Genus	Number of Isolates
Pseudomonas	8
Pseudomonas, Biejerinckia, or Derxia	1
Microcyclus	4
Spirosoma	1
Nocardia	2
Nonpathogenic Coryneform Group	2
Acinetobacter	1
Alcaligenes	1
Unknown	10
Total Number of Isolates	30

Two of the isolates fit into the cornyeform group which are described as gram-positive rods of irregular outline. This group contains some pathogenic bacteria. However, neither of these isolates have the characteristics of the known pathogens which are the best described organisms of the coryneform group.

The description of the genus Acinetobacter is somewhat vague but appears to require: (1) gram negative; (2) nonmotile; (3) oxidase negative; (4) strictly respiratory metabolism; and (5) morphology tending toward cocci or coccobacilli. One of the isolates possessed all of these characteristics. There is only one species described in this genus, and it is considered to be an opportunistic pathogen.

The genus Alcaligenes is similar to the genus Pseudomonas except for peritrichous flagella. One of the isolates fits this description.

One of the isolates from the waste coolant reactor was a flexible rod with peritrichous flagella. No genus described in Bergey's Eighth Edition is both flexible and motile by means of flagella. The remaining nine isolates are all nonmotile, gram-negative rods with respiratory metabolism. These characteristics are not consistent with any of the presently recognized genera.

Denitrification Reactors

The April 1978 sample from the D-713 reactor contained 16 predominant bacteria types. All of these isolates were capable of at least partial denitrification. The January 1979 sample from this reactor contained 15 predominant bacteria types, seven of which were nondenitrifiers. The January 1979 sample from the D-712 reactor contained only five predominant bacteria types, all of which were capable of at least partial denitrification. The results of the bacterial identification analysis are summarized in Table 3.

The different strains of Pseudomonas flourescens found in the bioreactors were almost identical except for colony morphology. They are all gram-negative rods with polar flagella that produce fluorescent pigment. All of these isolates were capable of denitrification ($NO_3 \rightarrow N_2$ [gas]). Pseudomonas aeruginosa, an opportunistic pathogen, is quite similar to Pseudomonas fluorescens, so part of these isolates could belong to this species even though none of them exactly matches the listed characteristics.

The original denitrification experiments at the Y-12 Plant were inoculated with a culture of Pseudomonas stutzeri. Eight different strains of this species were found in the first sample from the D-713 reactor. They had completely disappeared nine months later when the second sample was taken.

Six different types of gram-negative, nonmotile rods with strictly respiratory metabolism were found in the three samples. All of these isolates were capable of denitrification. These bacteria do not fit into any currently recognized genera.

Table 3

Summary of Isolate Analyses from Biological Denitrification Reactors

Identification	Number of Isolates D-713 (April 1978)	 D-713 (January 1979)	 D-712 (January 1979)
Pseudomonas fluorescens	5	4	1
Pseudomonas stutzeri	8	0	0
Denitrifying *Pseudomonas* species	1	0	2
Nondenitrifying *Pseudomonas* species	0	2	0
Unknown denitrifying species	1	3	2
Moraxella osloensis	1	0	0
Flavobacterium	0	1	0
Unknown nondenitrifying species	0	3	0
Nonpathogenic coryneform group	0	2	0
Known pathogens	0	0	0

Three varieties of denitrifying Pseudomonas species were found in the reactors. Two of these isolates did not produce nitrite or nitrogen gas when utilizing nitrate ions. Some ammonia was detected in the culture medium, and it is likely that N_2O gas, which is soluble, was also produced. The conversion of NO_3^- ions to NH_3 has been noted in the literature.[7] The amount of ammonia produced depends on pH, carbon source, and other factors. A small, but variable, amount of ammonia is present in the nitrate waste stream entering the reactor. If ammonia is being produced by the bacteria in the reactors, the amount produced is completely masked by the ammonia in the feed.

No known pathogens were found in any of the samples. There may be some strains of Pseudomonas aeruginosa, which is an opportunistic pathogen, in the reactors. This species is commonly found in the environment and is not considered to be dangerous to healthy humans.

CONCLUSIONS

Thirty predominant bacteria types have been isolated from the Y-12 Plant waste coolant reactor. Twenty of these isolates have been identified as belonging to one of seven known genera. Ten of the isolates did not fit into any currently established genera.

Three of the isolates belong to genera that contain opportunistic pathogens. One of these is an Acinetobacter, and two are Nocardia. None of the isolates belong to any group of strict pathogens.

The identification of the predominant bacteria in the biological denitrification reactors has shown that there may be one opportunistic pathogen present but no strict pathogens. The bacterial population in the older reactor (D-713) is much more varied than in the younger reactor (D-712). Several species are common to both reactors. Pseudomonas stutzeri, which was used in the initial denitrification experiments, was present in the first sample from the D-713 reactor but has since disappeared.

REFERENCES

1. R. E. Buchanan and N. E. Gibbons, Ed., Bergey's Manual of Determinative Bacteriology, 8th ed., Williams and Wilkins, Baltimore (1974).

2. M. Goodfellow, G. H. Brownell, and J. A. Serrano, Ed., The Biology of the Nocardia, Academic Press, London (1976).

3. J. M. Larkin, P. M. Williams, and R. Taylor, "Taxonomy of the Genus Microcyclus Orskov 1928: Reintroduction and Emendation of the Genus Spirosoma Migula 1894 and Proposal of a new Genus Flectobacillus." International J. of Systematic Bacteriol, 27: 147-156 (1977).

4. J. M. Slack and M. A. Gerencser, Actinomyces, Filamentous Bacteria, Burgess Publishing Company, Minneapolis (1975).

5. M. S. Redfearn, N. J. Palleroni, and R. V. Stanier, "A Comparative Study of Pseudomonas pseudomallei and Bacillus mallei," J. Gen. Microbiology, 43: 293-313, (1966).

6. R. Y. Stanier, N. J. Palleroni, and M. Doudoroff, "The Aerobic Pseudomonas: A Taxonomic Study," J. Gen. Microbiol. 43: 159-271, (1966).

7. J. Rougl and S. R. Carr, "Variable Ammonia Production Among Smooth and Rough Strains of Pseudomonas pseudomallei: Resemblance to Bacteriocin Production," J. of Bacteriol. 112: 372-380 (1972).

RCW BLOWDOWN TREATMENT AT ORGDP
FOR WATER POLLUTION CONTROL*

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ABSTRACT

This paper will summarize projects at ORGPD for control of water pollution from RCW blowdown. Liquid chemical releases formerly associated with blowdown from the RCW system will be substantially reduced by new facilities for treatment of blowdown. Subjects discussed will include resoftening and recycling of RCW blowdown and electrochemical reduction of chromates.

*K/D-5097

RCW BLOWDOWN TREATMENT AT ORGDP FOR WATER POLLUTION CONTROL

B. M. Spann

INTRODUCTION AND BACKGROUND

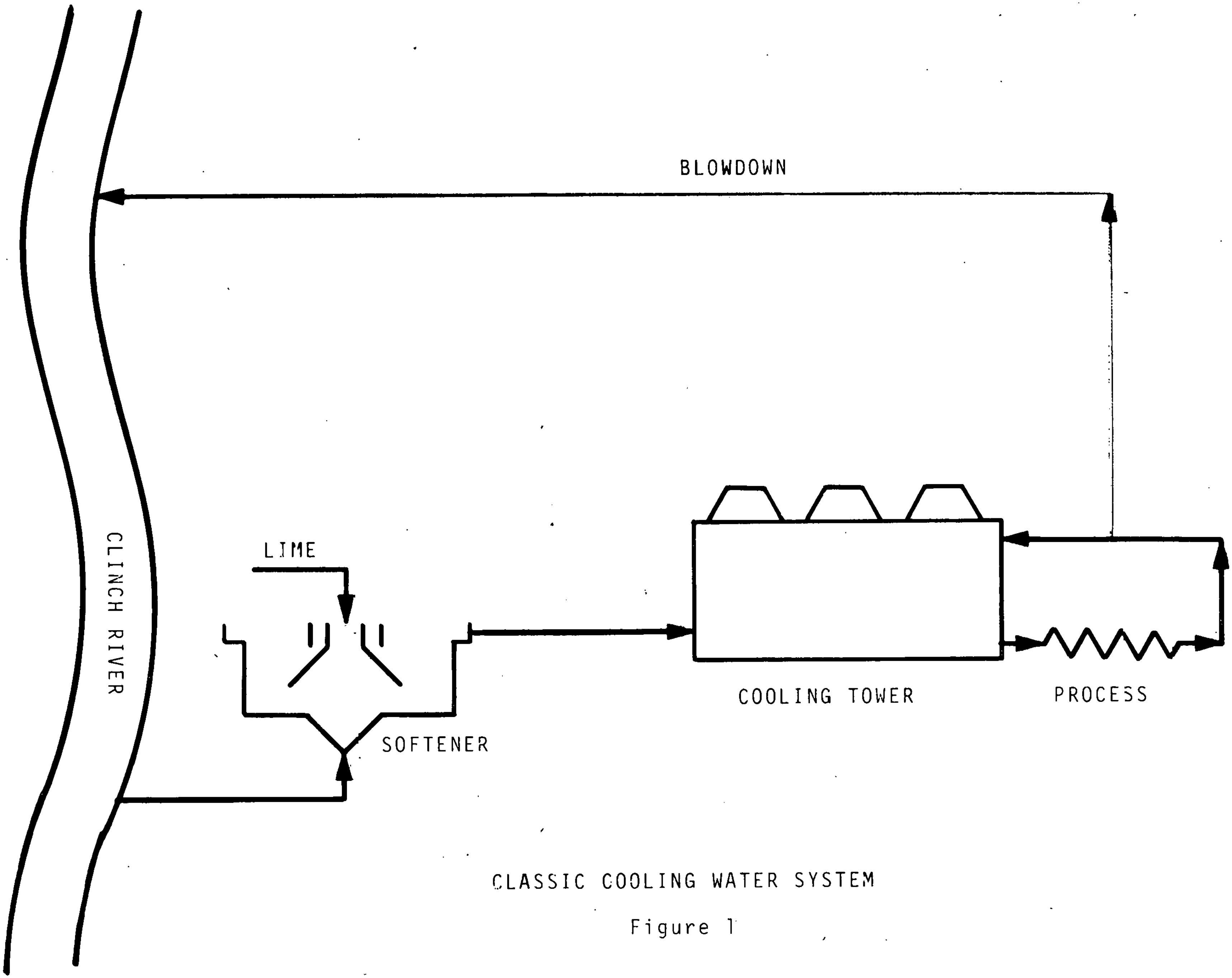
The Oak Ridge Gaseous Diffusion Plant (ORGDP) recirculating cooling water system will circulate 300,000 gallons per minute at CUP conditions, and require treatment of 12,000 gallons per minute makeup water. Evaporation from the cooling towers results in continuous concentration of substances dissolved in the RCW. To control corrosion and scaling of the heat exchanger tubing, it is necessary to remove part of the salt-laden recirculating cooling water (RCW) from the system as blowdown, and to replace it with softened makeup water. Proper disposal of blowdown water is required for all cooling tower operations. At ORGDP, the capability for either resoftening blowdown for recycling or treating it for discharge has been developed.

To protect copper heat exchange tubing in the RCW system, corrosion inhibitors are added to the RCW. The best known corrosion inhibitor agent for protection of copper at high temperatures is chromate. The corrosion inhibitor treatment presently used in the large RCW system at ORGDP consists of three proprietary materials. These materials, a blend of chromate, zinc, and polyphosphate, are metered separately and blended in-line in the proportions most advantageous to the operating conditions.

Recent Federal and State pollution control regulations have limited chromium discharge concentrations. The chromium level in the RCW is maintained at nine parts per million (ppm), or 18-20 ppm chromate. The current National Pollutant Discharge Elimination System (NPDES) permit limits discharge of this pollutant from the RCW system into the Clinch River to 0.05 ppm chromium, making removal or recycle of chromates necessary.

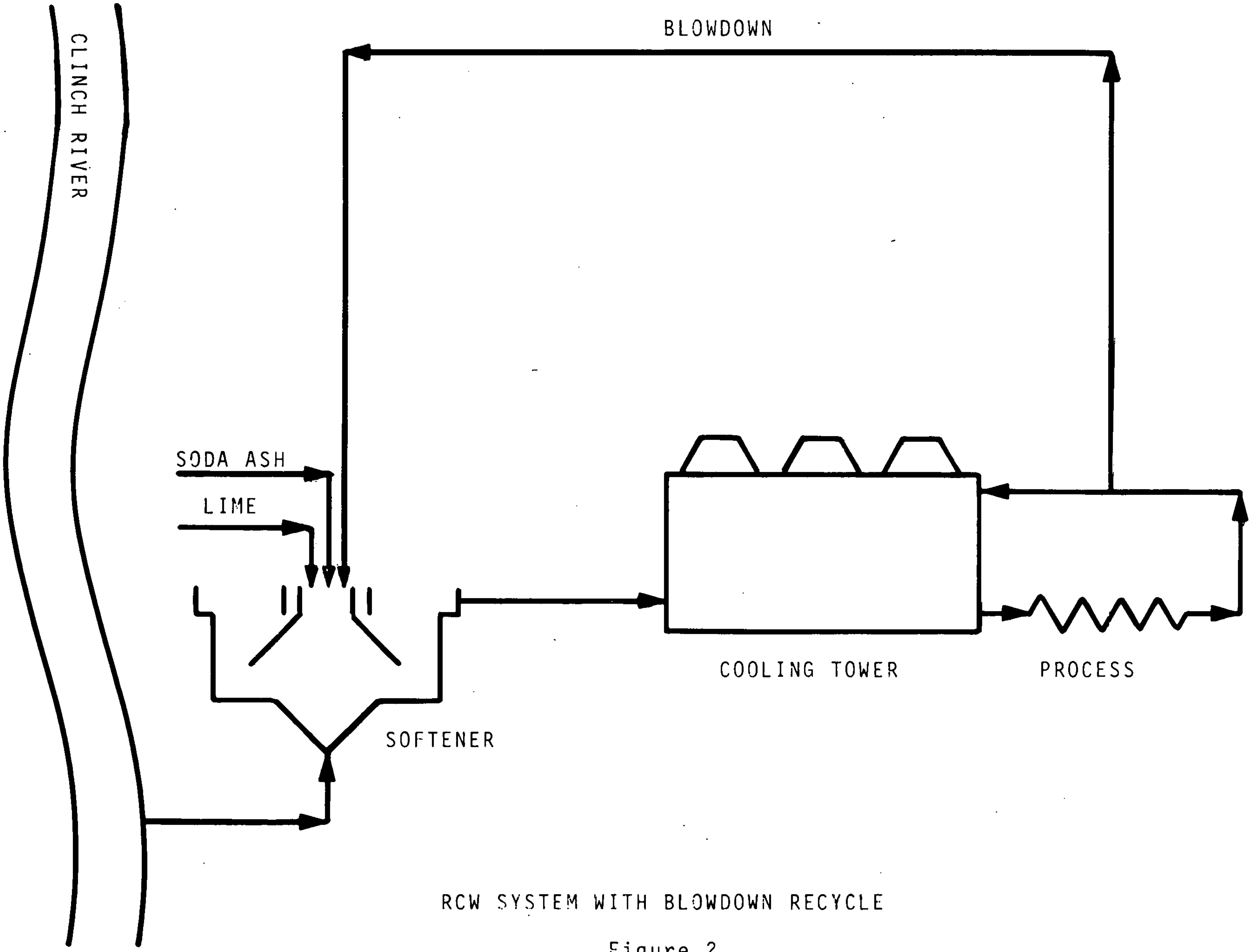
BLOWDOWN RECYCLE SOFTENING

The classic mode of cooling tower operation is to discharge blowdown, either continuously or intermittently, into a nearby stream (Figure 1). This was the method used during early years at ORGDP. In the late 1960's, laboratory tests were conducted which indicated that blowdown water could be successfully resoftened using lime and soda ash. In 1969, ORGDP added a soda ash feed system to the lime feed system at the makeup water softening plant and began recycling tower blowdown to the centerwell of the makeup softeners, where it was blended with raw water and the mixture softened (Figure 2). Chromates, being unaffected by the softening process, were recycled to the RCW system. Zinc and phosphorus were precipitated in the softening process as hydroxides and required replacement to main-



CLASSIC COOLING WATER SYSTEM

Figure 1



RCW SYSTEM WITH BLOWDOWN RECYCLE

Figure 2

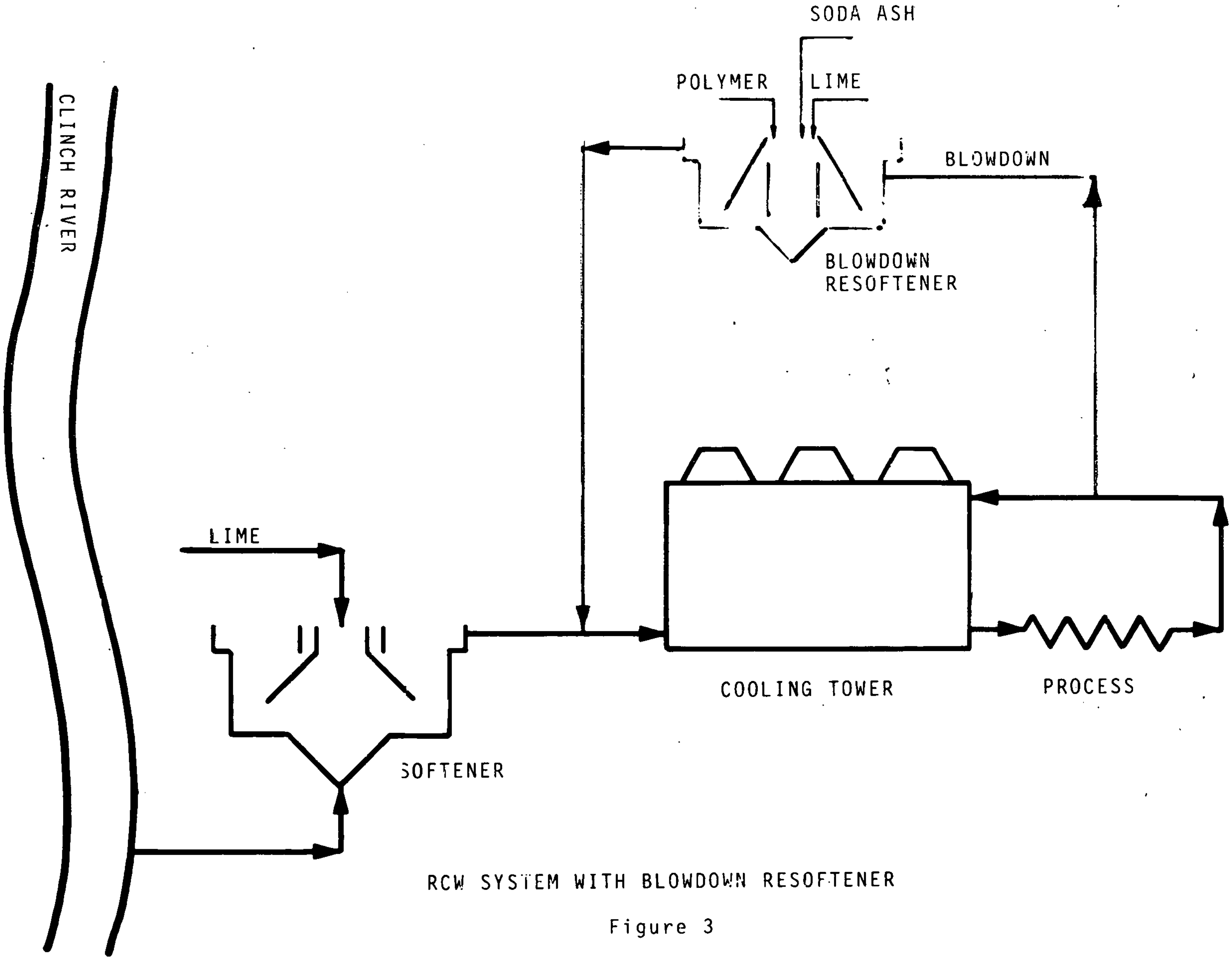
tain the necessary corrosion inhibition. The sludge from the softeners was removed and settled in a holding pond.(1)

A patent application on the concept of resoftening cooling tower blowdown, known as the Fowlkes-Webb Process, was filed by ORGDP in the spring of 1972.(2) A 2 1/2 year test was inaugurated to prove its feasibility, which was successful.(3) In fact, the additional softening provided by lime-soda ash improved makeup water quality compared to the softening attained previously with lime only. Prior to operation in the recycle mode, the calcium hardness of raw water was typically reduced from 74 ppm (as calcium carbonate) to 40 ppm. When operating in the recycle mode, the combined effluent contained about 21 ppm.(4)

Based on the results of the test, installation of a separate blowdown softener was proposed. Advantages of resoftening in a separate clarifier were that a temperature of 140°F rather than 60°F improved the efficiency of softening, and soda ash addition to the makeup softeners was eliminated. A purchase order was issued in the winter of 1974 for procurement of a blowdown recycle softener 35 feet in diameter (Figure 3). This unit went on-stream in the summer of 1976, and is presently in service for resoftening cooling tower blowdown using lime, soda ash, and a coagulant polymer. The unit has proven capable of resoftening blowdown (Table 1).(5)

The blowdown recycle softener is out of service periodically for maintenance and repairs, and the need for a backup unit was recognized. A second blowdown recycle softener was purchased in the fall of 1978, and is now under construction. Design improvements based on operating experience with the first unit have been incorporated into the design of the new blowdown recycle softener. The new blowdown resoftener is 45 feet in diameter, which will provide a 65% increase in retention time, and an equivalent decrease in rise rate. This should reduce sludge carryover into the effluent, which has been a problem in the existing unit, due to inadequate sizing.

The blowdown recycle softener now under construction is sized to treat 1.4 million gallons per day. It is of the upflow contact type, providing mixing, internal recirculation, flocculation, and clarification in a single basin (Figure 4). Operation will be similar to that of the existing unit. Blowdown will enter through a side inlet, and will be drawn upward by a turbine through a reaction zone, where it will be mixed with previously formed sludge. Metered quantities of anionic coagulant polymer, lime, and soda ash will be added. It will then enter a conical flocculation zone, where precipitates formed by chemical reaction with impurities in the RCW will be permitted to coagulate into larger particles. Part of the slurry will be drawn into the reaction zone, and the cycle repeated. The remaining slurry will flow into the clarification zone, where the sludge will separate from the RCW. Clarified water will percolate upward through a blanket of previously formed sludge to the outlet launderers and will be returned to the makeup water line. Excess sludge will be removed periodically through a timer-controlled desludging valve, and will be recycled to the makeup softener centerwells to act as "seeds"



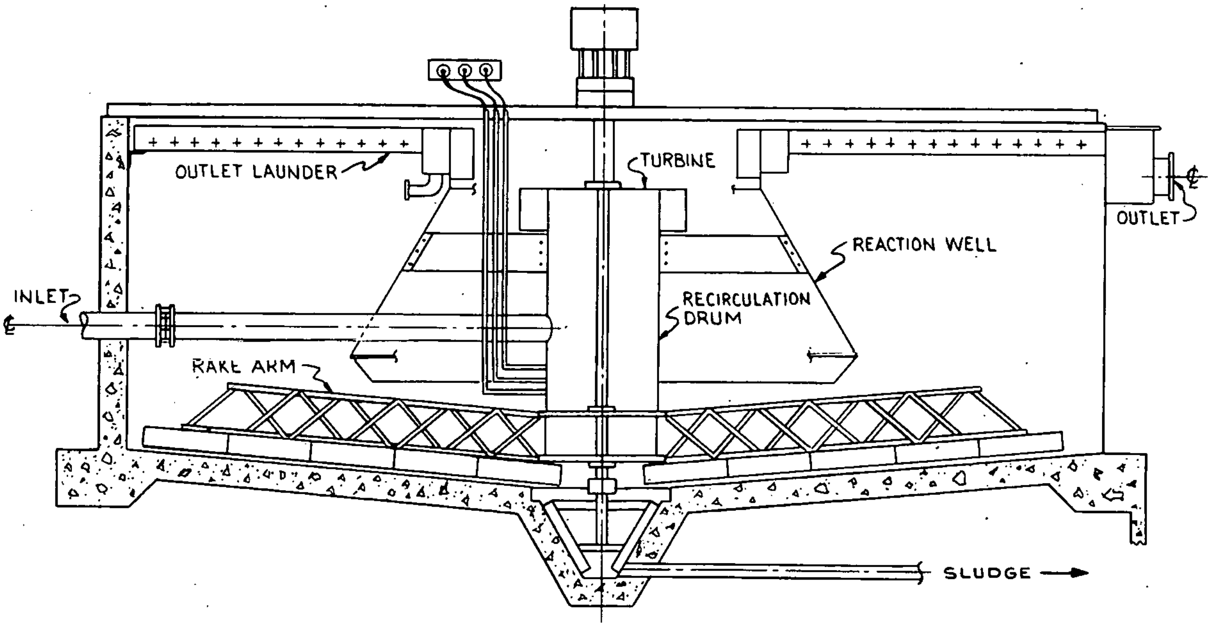
RCW SYSTEM WITH BLOWDOWN RESOFTENER

Figure 3

THE FEASIBILITY OF BLOWDOWN RESOFTENING HAS BEEN DEMONSTRATED

	INFLUENT	EFFLUENT
TOTAL HARDNESS, ppm	810	200
Ca HARDNESS, ppm	440	90
Mg HARDNESS, ppm	370	110
Total M alkalinity, ppm	20	90
pH	6.5	10.1

Table 1



The new blowdown recycle softener will treat up to 1.4 million gallons per day.

Figure 4

for additional sludge formation.

The blowdown resoftener now under construction will be located adjacent to the existing unit and connected in parallel with it, so each may be used alternately when the other is out of service. It is scheduled to go into service in June, 1980.

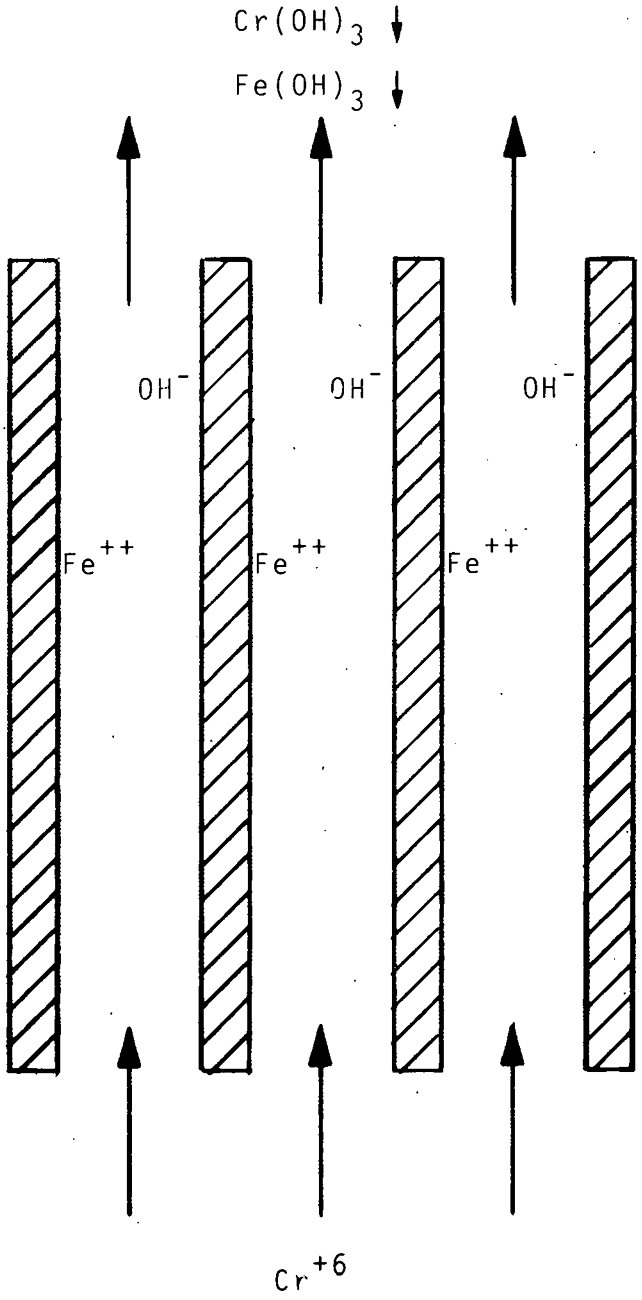
CHROMATE REDUCTION

While resoftening cooling tower blowdown is effective in eliminating chromate discharge to the surface stream, a substantial quantity of dissolved solids, such as sulfates, remain in the resoftened water. Sulfates are concentrated not only by evaporation, but also by the addition of sulfuric acid for pH control. To avoid exceeding the $[Ca^{++}]$ $[SO_4^{--}]$ product solubility limit and forming scale in the cascade heat exchangers, it may be necessary to discharge some of the RCW from the system and replace it with fresh makeup water. In order to meet NPDES discharge limitations, the chromate must be removed from this blowdown discharge.

Testing of an electrochemical metal reduction unit was begun in 1974.(6) This unit uses the principle of consumable iron electrodes (Figure 5). The blowdown passes between the electrode plates, where the soluble hexavalent chromium is reduced to insoluble trivalent chromium. A ferric hydroxide and chromic hydroxide sludge is produced, which can then be separated from the blowdown. Two electrochemical reduction units, each capable of treating 100 gpm blowdown, were put into service in 1977.

To increase blowdown treatment capacity, a 600 gpm electrochemical reduction unit, capable of being expanded to 800 gpm at a later date, was purchased in the Summer of 1978. The package unit consists of three 200 gpm capacity cells, a DC power source, and an acid wash system which cleans precipitates from the electrode plates. RCW line pressure is used to pass blowdown through the unit, and no surge tank or feed pump is needed. No pH adjustment or chemical addition is required. A drop in electric current between the electrodes stops the blowdown flow and sounds an alarm in the control room. The sludge produced is currently separated from the blowdown in a settling pond. A laminar settler and centrifuge will be added for sludge separation as part of a 1981 Line Item. The two smaller reduction units are being retained as backup.

The 600 gpm electrochemical reduction unit has been in service since August, 1979. As of March, 1980, twenty four million gallons of blowdown had been processed, with no discharge violations. Average chromium concentration in the settling pond discharge has been 0.04 ppm. Average electrode plate life has been three million gallons per set.



ELECTROCHEMICAL REDUCTION OF CHROMATE

Figure 5

In conclusion, water pollution is being controlled at ORGDP by facilities which permit RCW blowdown to be either resoftened and recycled to the system or chromates removed before discharge to surface water. Both systems have backup units which permit shutdown of the primary unit for maintenance and repair without loss of pollution control.

ACKNOWLEDGMENT

The valuable input of R. A. Koteski and B. E. Vaughn of ORGDP Utilities Operations Department is gratefully acknowledged.

REFERENCES

1. W. K. Simon, Recycling and Softening of Recirculating Water Blowdown for Reuse, K-P-4013. UNCLASSIFIED.

2. B. R. Webb and C. C. Fowlkes, Method for Maintaining Non-Corrosive Conditions in Recirculating Water Systems, January 17, 1975, Patent applied for and abandoned.

3. C. C. Fowlkes and B. R. Webb, Recycling and Softening of Recirculating Water Blowdown for Reuse, February 16, 1972, K-P-3944. UNCLASSIFIED.

4. C. C. Fowlkes, Softening of Cooling Tower Blowdown Water for Reuse, January 5, 1973, K-P-4023. UNCLASSIFIED.

5. R. A. Koteski and B. E. Vaughn, Recirculating Cooling Water Blowdown Treatment at the Oak Ridge Gaseous Diffusion Plant, March, 1979, K-P-6508. UNCLASSIFIED.

6. J. R. DeMonbun, Chromate Destruction, April 4, 1974.

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TREATMENT OF COAL YARD RUNOFF AT ORNL*

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ABSTRACT

At the present time the steam plant at the Oak Ridge National Laboratory (ORNL) is undergoing conversion from oil- to coal-fired boilers. To insure that rainwater runoff from the recently constructed coal storage yard meets current discharge standards, a three phase program was initiated. The first phase was a literature review which pointed out the great variability in chemical composition of runoff samples and demonstrated the site-specific nature of the problem. Next, a laboratory treatability study was conducted using samples of runoff from coal identical to that stored on the ORNL yard. In the last phase of the program, data from the study (i.e., chemical dosages, reaction rates, sludge characteristics) were used in the design of a treatment system. The project is currently in the final phase of detailed design.

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TREATMENT OF COAL YARD RUNOFF AT ORNL

INTRODUCTION

As a result of President Carter's April 1977 National Energy Plan (NEP), the steam plant located at the Oak Ridge National Laboratory (ORNL) is undergoing a shift from the consumption of oil and natural gas to more abundant supplies of coal. To ensure a sufficient stockpile during times when coal cannot be delivered, a 4 acre storage yard has been constructed with a storage capacity of 28,000 tons crushed stoker coal. All of the rainfall runoff from the newly constructed storage yard is directed into a 300,000 gallon leachate collection pond which overflows into White Oak Creek at mile 2.4.

The drainage from the coal storage yard is considered as material storage runoff and as such must meet the National Pollutant Discharge Elimination System (NPDES) standards for pH (6.0-9.0) and total suspended solids (TSS $\leq$ 50 mg/l) prior to discharge. The work described in this paper focuses on three major areas: 1) a review of the existing literature concerning leachate from coal storage areas, 2) laboratory treatability studies to provide necessary treatment design information, and 3) an engineering design effort to establish a leachate treatment scheme which will ensure that ORNL is in compliance with existing and future coal storage yard discharge standards.

LITERATURE REVIEW

Various water quality problems are reported as being related to the handling and storage of large volumes of coal. Precipitation in the form of rain or snow falling on the storage pile either penetrates the pile and is retained in the interior as interstitial water, evaporates, or is shed from the pile as direct runoff. Attempts have been made to estimate runoff quantities, but such estimates are highly dependent upon stockpile size and configuration, coal particle size, amount and intensity of rainfall, and moisture content of the coal being stored. It appears that runoff ranges from 50 to 95% of the rainfall on the pile, the remainder either evaporating or being held within the pile (Davis 1980; Cox, Chu, and Ruane 1979; Wachter and Blackwood 1978).

During the times when rainwater is in contact with the coal in storage, fine particulates and various inorganic and organic elements are leached from the pile to enter receiving streams. High concentrations of toxic inorganics, along with low pH values are reported as characteristic of the leachate from high sulfur eastern coals and present the major water quality concerns (Anderson and Youngstrom 1976; Chu, Ruane, and Steiner 1976; Brookman, Binder, and Wade 1977).

One of the most often quoted data sets concerning the quality of coal pile leachate is presented in the development document for proposed effluent limitations guidelines and new source performance standards for the steam-electric power generating industry (Nichols 1974). In this document, the Environmental Protection Agency (EPA) evaluated the coal pile leachate at several operating power plants in the United States. The results are summarized in Table 1.

TABLE 1

EPA SURVEY RESULTS - COAL PILE LEACHATE QUALITY

Parameter	Mean (mg/liter) pH = 2.7	Range (mg/liter) pH = 2.1-3.0
Iron	19,540	0.17-93,000
Sulfate	9,006	525-21,920
Zinc	3.64	1.6-23
Copper	2.10	1.6-3.4
Chromium	3.27	0-15.7

SOURCE: Nichols 1974.

This table demonstrates the low pH values and high concentrations of iron, sulfate, and dissolved solids which are encountered in coal pile leachate; but the table lacks information concerning the time period over which the samples were taken or what type of coal was being stored at each of the power plants. These types of data are presented frequently in the literature, but are of limited value for comparison purposes, unless accompanied by a more detailed analysis of coal type, leachate sampling procedure, and previous storage periods.

The review of previous work characterizing coal storage pile leachate has shown that the results of experimental analysis differ considerably from one group of researchers to the next. Data have been collected under a variety of experimental conditions and on many different types of coal, but the underlying theme is the same, that is, coal pile leachate is similar in quality to acid mine drainage, and thus, there exists the potential for a multitude of acid related problems. Sulfur-bearing minerals such as pyrite (iron sulfide), which are commonly associated with coal, are exposed to air and rainfall where they are oxidized to form sulfuric acid. Minute concentrations of salts of metals such as zinc, lead, arsenic, copper, or aluminum, when leached from the coal, may be toxic to plants, fish, wildlife, and aquatic insects. In addition, high concentrations of minerals may render many water bodies unsuitable as drinking water sources or recreation areas. Related to this acid formation are deposits of iron precipitates often found in streams that drain sulfur-bearing coal or mineral deposits (Kendrick 1977).

Because of their low tolerance levels in plants, animals, and man, the metal trace elements are of particular concern. Although the relative amounts of these elements per unit of coal are small, the total absolute amount of each available in a large coal storage pile could have important consequences in water, soil, or air quality (Wewerka, Williams, and Wanek 1976). These are the recognized problems associated with acid mine drainage and, more recently, with the storage of large quantities of coal.

LABORATORY STUDY

Knowing that the coal stored at the ORNL site would come from strip mining operations in the East Tennessee area, runoff from the storage yard was expected to be quite acidic with a pH value well below the 6.0-9.0 range. As a result, a leachate neutralization scheme was developed. The proposed treatment consisted of the following major steps: 1) runoff collection and primary settling to remove coal fines, 2) addition of 50% w/w sodium hydroxide (NaOH) to achieve neutralization, 3) secondary settling to remove precipitated metals, and 4) discharge of supernate into the receiving stream.

To begin the laboratory study, samples of runoff had to be collected which would have the same chemical and physical characteristics as the runoff expected at the ORNL storage site. This was accomplished by collecting runoff from the Y-12 plant coal storage yard which handles an identical supply of East Tennessee coal. In all, two 12 liter grab samples of runoff were collected. The first was taken on Wednesday, June 20, 1979 (approximately 11 days after a rainfall event) and is termed the dry weather sample. The second runoff sample, collected on Monday, July 9, 1979, (12 hours after a rainfall event) is termed the wet weather sample. The dissolved iron concentration of these two samples was found to be 9640 mg/l for the dry weather sample and 2270 mg/l for the wet weather sample. These two samples are believed to represent extreme and average iron concentrations, respectively.

Immediately after each runoff sample was collected, it was transported to the laboratory and allowed to stand (undisturbed) for 24 hours. This primary settling step corresponds to a 24 hour detention time in a runoff collection pond and allows suspended coal fines to settle out of the sample. The supernate from this primary settling step was analyzed for pH, total suspended solids, and iron concentration and results are shown in Table 2.

This data shows that after primary settling, the suspended solids are well below the 50 mg/l limit, but the pH must be raised from a value of approximately 2 to a value between 6 and 9. This pH adjustment was accomplished by instantaneously adding a volume of 50% NaOH to a 1 liter sample of the runoff and stirring the mixture for 5 minutes, followed by a 24 hour settling period. The caustic volume needed for neutralization was calculated by assuming that 1 mole of iron in the runoff

Table 2. ANALYSIS OF RUNOFF SAMPLES AFTER 24 HOURS SETTLING

Parameter	Dry Weather Sample	Wet Weather Sample
pH	2.1	2.3
TSS (mg/l)	0.0	3.8
Iron (mg/l)	9640	2270

sample would react with 3 moles of hydroxide. This relationship leads to 27 ml of 50% NaOH required by a 1 liter of the dry weather sample, and 6.4 ml required by 1 liter of the wet weather sample. Larger volumes of caustic were also added to additional 1 liter portions of each runoff sample to determine what effect this increase in hydroxide ion concentration has on leachate pH and sludge volume.

Figures 1 through 4 show the results of pH and sludge volume as a function of time for varying amounts of caustic added to each leachate sample. It is concluded from Figure 1 that 36-37 ml caustic (33% above stoichometric amount) is required to neutralize 1 liter of the dry weather sample and, similarly, Figure 3 shows that 8.5-9.0 ml caustic is required to neutralize 1 liter of the wet weather sample. Neutralization takes place within 5 minutes and there is a slight decrease in pH with settling time. This slight decrease in pH means that it is necessary to carefully adjust the leachate sample to a pH close to 9.0 to ensure not dropping below 6.0 before discharge. Volumes of caustic in excess of these amounts are shown to result in 24 hour supernate pH values above 9 while volumes of caustic less than these amounts yield supernate with 24 hour pH values below 6.

After caustic addition and a 24 hours settling time, the supernate was analyzed for pH, total suspended solids, sludge volume and iron concentration. Total suspended solids averaged about 10 mg/l after neutralization, and iron concentrations were in the same range.

The results of these laboratory experiments demonstrate that it is possible to achieve the NPDES pH and total suspended solids limits for coal pile runoff by simply adding an appropriate volume of 50% NaOH and letting the precipitated metals settle out for a 24 hour period. The major problem is the volume of ferric hydroxide sludge which is generated in the process. At best, (with the proper pH) the sludge volume after 24 hours settling is 71% for the dry weather sample and 43% for the wet weather sample.

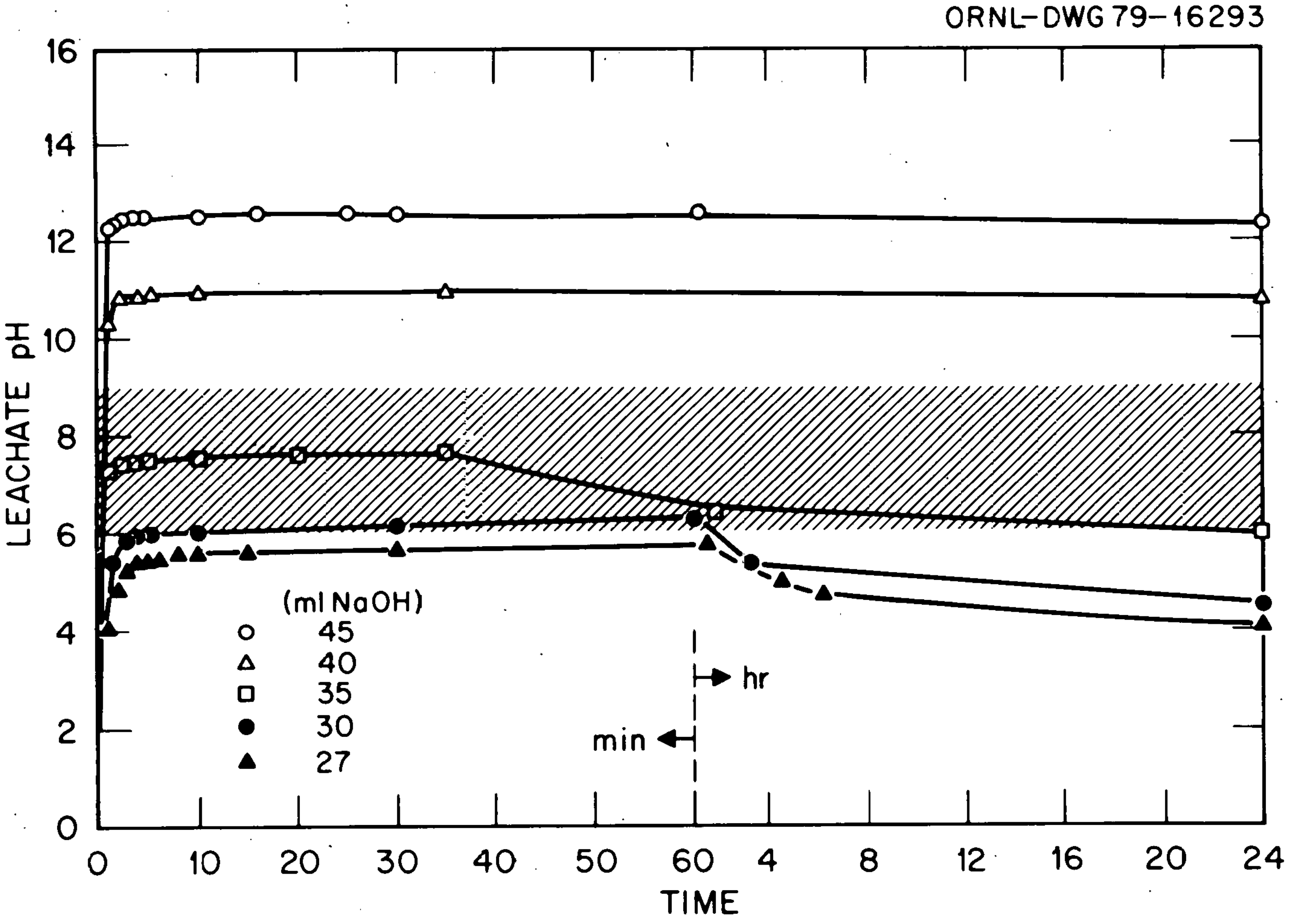

Fig. 1 Leachate pH versus time for NaOH addition to dry weather sample.

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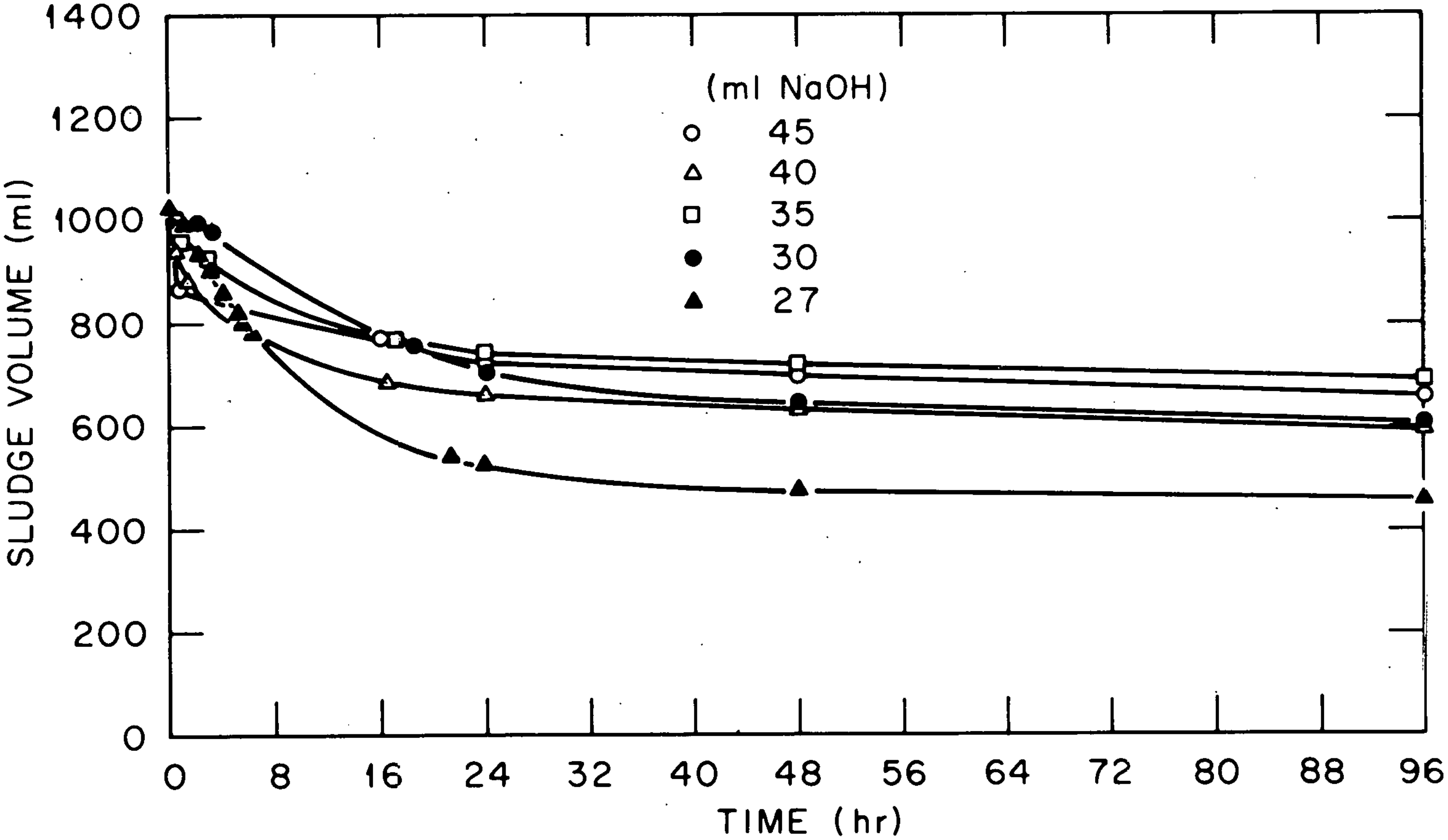


Fig. 2 Sludge volume versus time for NaOH addition to dry weather sample.

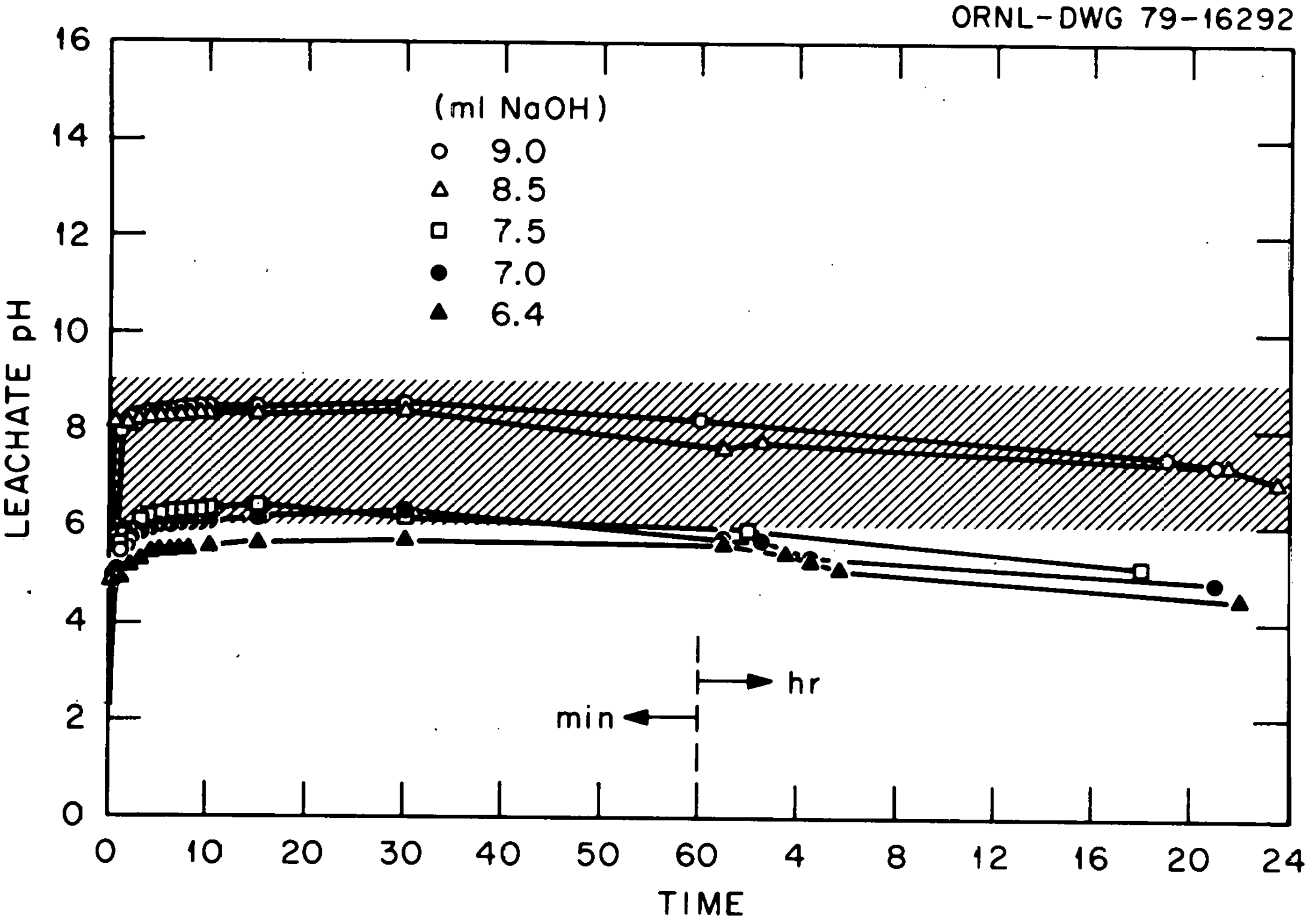


Fig. 3 Leachate pH versus time for NaOH addition to wet weather sample.

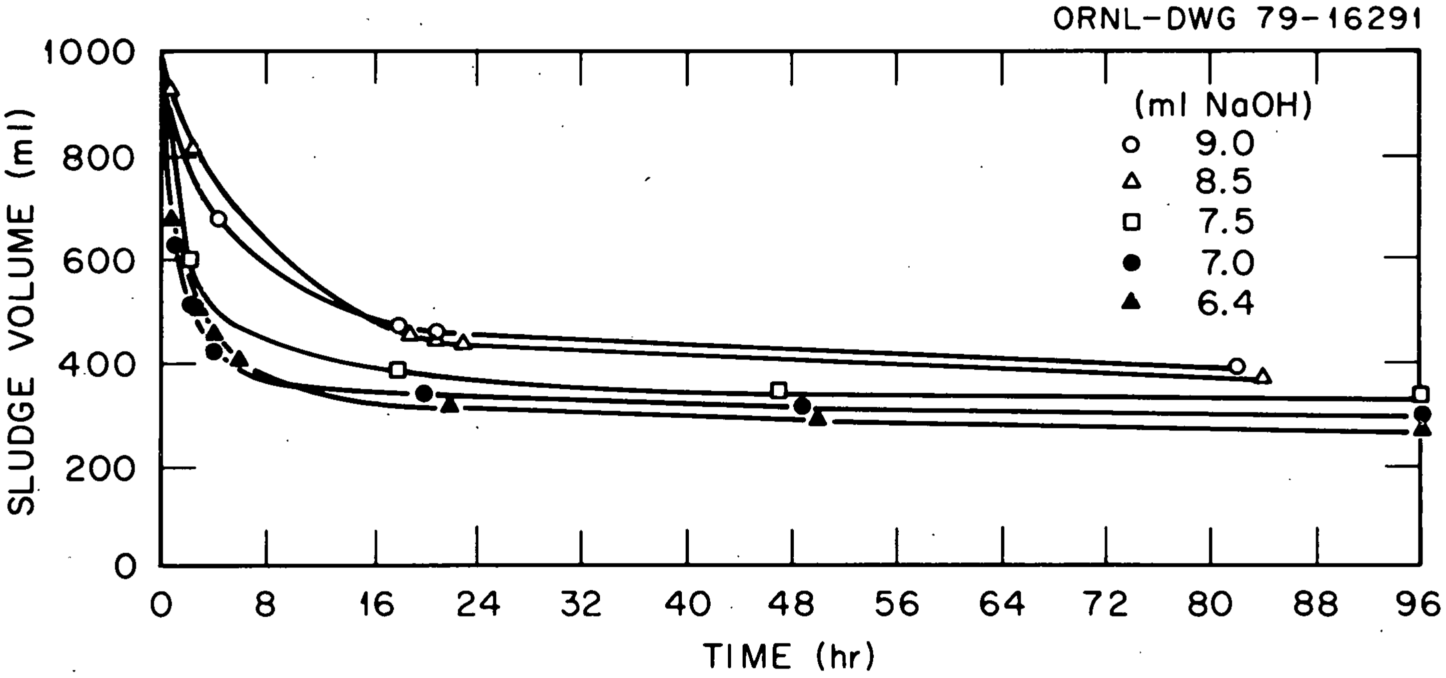


Fig. 4 Sludge volume versus time for NaOH addition to wet weather sample.

ENGINEERING DESIGN EFFORT

The Oak Ridge National Laboratory has identified two projects dealing with the coal yard runoff problem. The first is an interim system that is GPP-funded. The second is a comprehensive, long range solution included in a proposed 1982 Line Item.

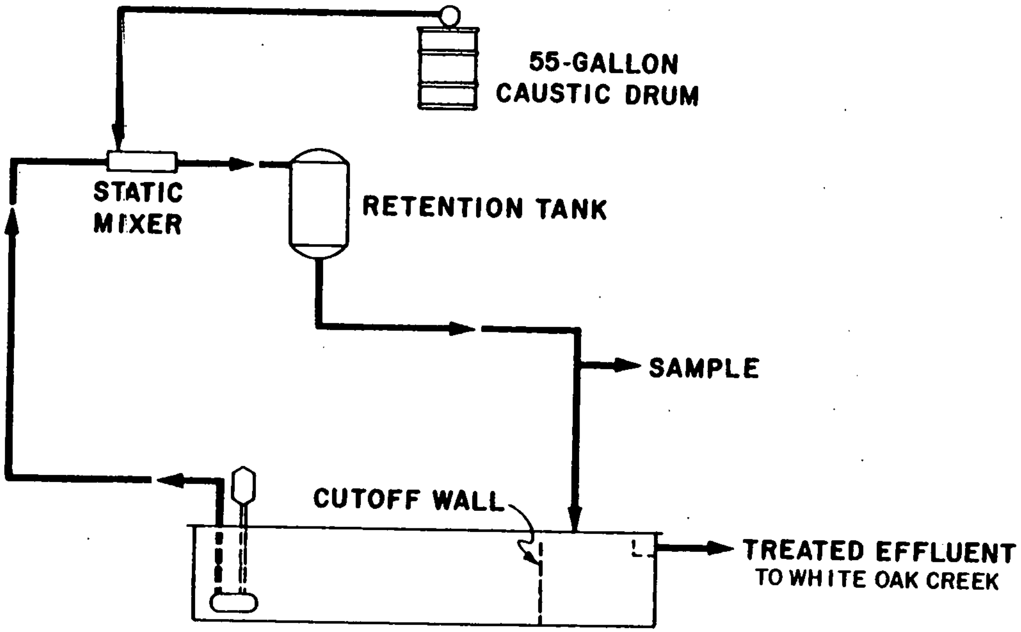
In February, 1979, a preliminary cost estimate was prepared for the interim system. Cost was an important consideration since it was assumed that a more elaborate system would replace this temporary one. To minimize cost, the following assumptions were made about the GPP project:

1. Caustic (NaOH) would be used to neutralize the acidic runoff.
2. Caustic would be supplied in 55-gallon drums to eliminate the expense of a storage tank.
3. A static mixer would be used to blend caustic with the runoff. This is a tacit assumption that neutralization occurs almost immediately.
4. An existing building would be used to store caustic drums and house processing equipment.
5. The system would be completely manually operated.
6. No provision would be made to dewater the sludge formed during neutralization.

The system identified for the estimate was very simple. The existing runoff retention pond (built during conversion of the steam plant to coal) would be divided into two sections. One portion would collect runoff and provide flow equalization. The other section would be used to clarify neutralized water and store sludge. The pond already has an overflow structure to release treated water to White Oak Creek. The estimated cost of the system was $200,000. It should be noted that this preliminary estimate was done before the laboratory treatability study.

As detailed design progressed, optional equipment was evaluated. The laboratory work showed that a five minute retention time was needed for the neutralization reaction to come to completion. Consideration was given to substituting an agitated vessel for the static mixer. It was determined that caustic soda could be purchased in bulk at only 65% of the cost of the chemical in drums. The savings would be enough to pay for the cost of a bulk storage tank and dike within a few years. A new building to house the process was also considered. Unfortunately, these desirable items could not be purchased, since the entire project was limited to $200,000.

The interim system now in Title II design is the one shown in Figure 5. A proposed polymer addition step has been eliminated. No suitable polymer could be found after some brief laboratory tests were conducted.



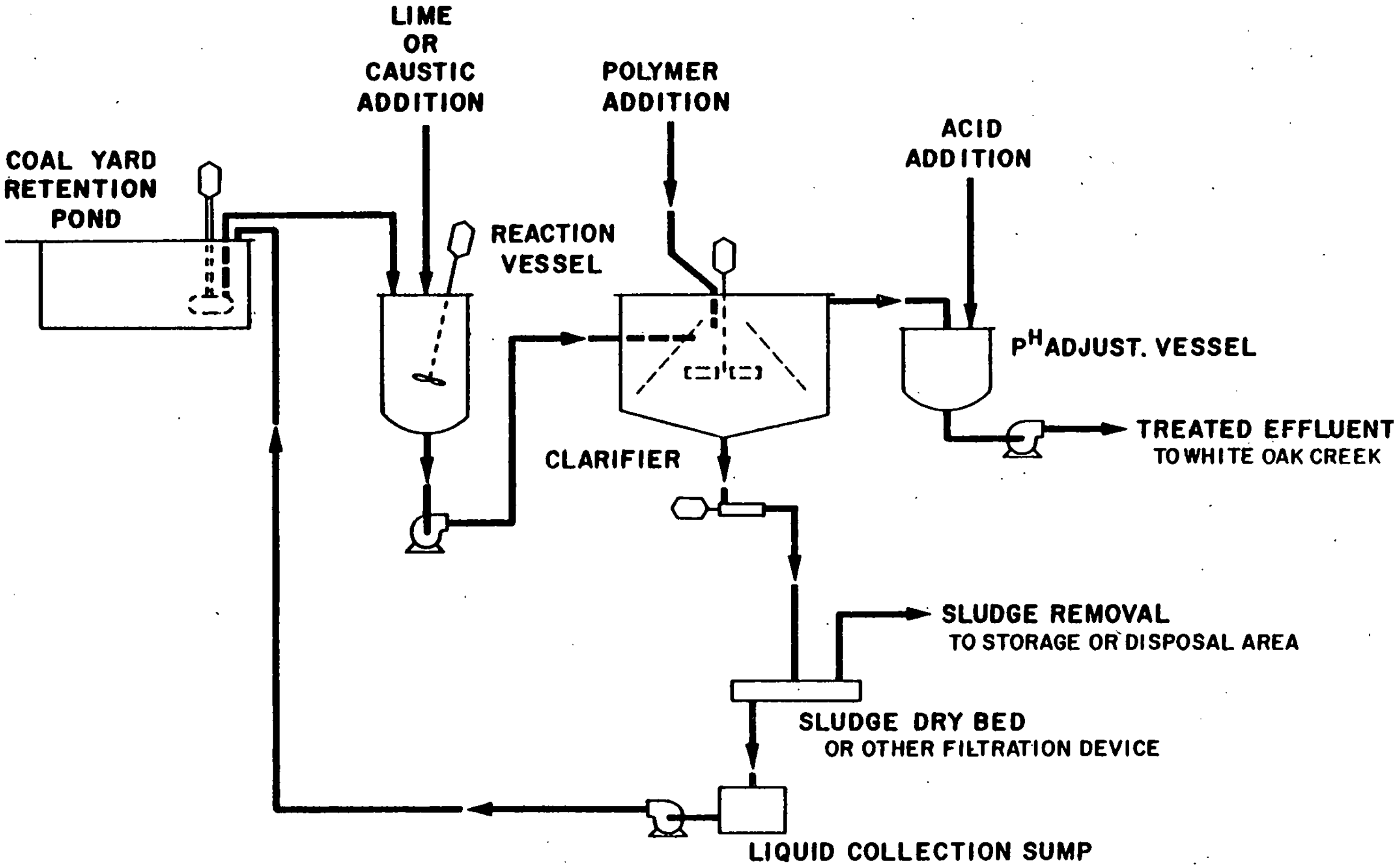
INTERIM TREATMENT SYSTEM FOR COALYARD RUNOFF

FIGURE 5

A pressurized vessel will be included to provide sufficient residence time downstream of the static mixer. This tank will not be agitated. Instead of in-line pH monitoring, a sample line will be installed for collecting grab samples. These design changes were made to keep the system controllable while staying within the budget.

It should be emphasized that the project now in detailed design is only a temporary measure. The proposed Line Item for Water Pollution Control at ORNL includes a more elaborate system to process coal pile runoff. A new building will be constructed specifically for the system. Either bulk lime or bulk caustic will be used for neutralization. Additional laboratory studies will be performed on neutralization and sludge settling and dewatering. Sludge processing will be an integral part of this Line Item-funded system. A solids-contact clarifier will be provided, and the portion of the retention pond used for clarification in the interim project may only be for sludge storage in the long range project. The system will be automated with signals telemetered to the steam plant control room (Figure 6).

As noted above, the justifications for two systems involve cost and schedule. The State of Tennessee has required that ORNL control coal pile runoff. The interim project is designed to control pH and suspended solids of the effluent with minimum capital investment. The decision to cut costs results in a process requiring the attention of a full-time operator. The long range system will eliminate most of the operating difficulties inherent in the short-term project. Controls and monitoring will be automated. Provisions will be made to condition and dewater sludge. In addition, special consideration will be given to the removal of heavy metals. This long term system will meet anticipated as well as existing regulations.



TYPICAL FLOWSHEET FOR LONG TERM COAL YARD RUNOFF TREATMENT

FIGURE 6

REFERENCES

Anderson, W. C., and M. P. Youngstrom. 1976. Coal Pile Leachate - Quantity and Quality Characteristics. J. San. Eng. Div. Proc. Am. Soc. Civil Engr. 102(EE6):1233-1239.

Brookman, G. T., J. J. Binder, and W. A. Wade, III. 1977. Measurement and Modeling of Storm Water Runoff from Coal Storage Piles and the Impact on Receiving Waters. Proc., Third Symposium on Coal Preparation NCA/BCR Coal Conference and Expo IV, October 18-20, 1977, Kentucky Fair and Exposition Center, Louisville, Kentucky. Sponsored by National Coal Association and Bituminour Coal Research, Inc. pp. 214-242.

Chu, T.-Y.J., R. J. Ruane, and G. R. Steiner. 1976. Characteristics of Wastewater Discharges from Coal-Fired Power Plants. Proc., 31st Industrial Waste Conference, Purdue Univ., LaFayette, Indiana. Ann Arbor Science, Ann Arbor, Michigan.

Cox, D. B., T.-Y.J. Chu, and R. J. Ruane. 1977. Quality and Treatment of Coal Pile Runoff. Proc., Third Symposium on Coal Preparation NCA/BCR Coal Conference and Expo IV, October 18-20, 1977, Kentucky Fair and Exposition Center, Louisville, Kentucky. Sponsored by National Coal Association and Bituminous Coal Research, Inc. pp. 252-277.

Davis, E. C. 1980. A Laboratory and Field Investigation of Factors Affecting Coal Storage Pile Leachate Quality. Ph.D Thesis, Vanderbilt Univ., Nashville, TN.

Kendrick, P. J. 1977. Acid Mine Drainage - An old problem with a new dimension. J. Water Poll. Cont. Fed. 49:1576-1581.

Nichols, C. R. 1974. Development document for the proposed effluent limitations, guidelines, and new source performance standards for the steam-electric power generating point source category. EPA, Washington, D.C., EPA 440/1-73/029.

Wachter, R. A., and T. R. Blackwood. 1978. Source Assessment: Water Pollutants from Coal Storage Areas. Industrial Environmental Research Laboratory, Office of Research and Development, U.S. EPA, Cincinnati, Ohio. EPA-600/1-78-004M.

Wewerka, E. M., J. M. Williams, and P. L. Wanek. 1976. Assessment and Control of Environmental Contamination from Trace Elements in Coal Processing Wastes. Proc., National Conf. of Health, Environmental Effects and Control Technology of Energy Use. U.S. EPA, Document No. 600/7-76-002. pp. 226-229.

INNOVATIVE ALTERNATIVES TO END-OF-PIPE TREATMENT

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ABSTRACT

Compliance with environmental regulations will require many pollution control projects and the expenditure of large sums of money. Because of limited resources, it is essential that priority be given to those projects with substantial environmental benefits. Less costly alternatives should be pursued to achieve compliance with regulations resulting in little environmental impact.

Examples are presented which illustrate how project costs were significantly reduced by obtaining clear problem definition and developing good communications with state and federal regulatory agencies.

(Paper not available for publication.)

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Nuclear Division

Paducah Gaseous Diffusion Plant
Paducah, Kentucky

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WASTE ACETONITRILE (CH_3CN) INCINERATION

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(Key Words)

(Acetonitrile, Incineration, Waste Disposal)

ABSTRACT

Waste acetonitrile (CH_3CN) from the production facilities at the Oak Ridge Y-12 Plant was investigated for possible recycle of the acetonitrile back to the production processes by removal of the contaminating material. Two recycle schemes using evaporation to remove the contaminating material and drying to remove water or distillation to remove water were designed and estimated on a preliminary basis. The results indicated that recycle of the decontaminated acetonitrile would be uneconomical, thus disposal of the contaminated acetonitrile was recommended.

This paper emphasizes the operational difficulties encountered during the start-up of an existing liquid injection incinerator (Prenco Pyro-Decomposition System) used for disposing of acetonitrile waste by burning without producing smoke and to completely oxidize the waste.

INTRODUCTION

Acetonitrile (CH_3CN) is a colorless, volatile liquid with similar odor to acetamide. It is highl flammable, presents a serious risk of poisoning by inhalation or swallowing and gives off poisonous vapors. Physical properties of acetonitrile are presented in Table 1. Acetonitrile has many industrial applications, including its use as a solvent in the production processes at the Oak Ridge Y-12 Plant.

Acetonitrile used in the production processes at the Oak Ridge Y-12 Plant(a) becomes contaminated as a result of contaminating materials introduced during processing. An investigation for possible recycle of the acetonitrile back to the production processes by removal of the contaminating materials was undertaken. Two recycle schemes using evaporation to remove the contaminating material and drying (molecular sieve) to remove water or distillation to remove water were designed and estimated on a preliminary basis. The results indicated that recycle of the

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(a) Operated by the Union Carbide Corporation's Nuclear Division for the Department of Energy.

TABLE 1

ACETONITRILE

PHYSICAL PROPERTIES

Molecular Weight	41.05
Boiling Point at 760 mm. Hg	81.6°C
50 mm. Hg	13°C
10 mm. Hg	-15°C
Vapor Pressure at 20°C	72.8 mm. Hg
dt/dp	0.042°C /mm Hg
Specific Gravity at 20/20°C	0.7868
Freezing Point	-45.7°C
True Density at 20°C	0.7857 gm/ml.
Coefficient of Expansion at 20°C	0.00137/°C
Solubility in water at 20°C	Complete
Solubility of water in at 20°C	Complete
Absolute Viscosity at 0°C	0.43 cps.
20°C	0.35 cps.
40°C	0.30 cps.
Refractive Index at 20°C, n/D	1.3441
Flash Point (Open Cup)	42°F
Specific Heat (21°to 76°C)	0.541 BTU/lb. /°F
Heat of Fusion at -46°C	94 BTU/lb.
Heat of Combustion at 25°C (liquid)	13,350 BTU/lb.
Heat of Vaporization at 80°C	313 BTU/lb.
Dielectric Constant at 0°C	42.0
20°C	38.8
81.6°C	26.2
Specific Conductance, OHM^{-1}	$5\text{-}9 \times 10^{-8}$ (25° C)
Surface Tension at 20°C	29.3 dynes/cm. air
Average Weight per gal. at 20°C	6.52 lb.
Evaporation Rate (Butyl Acetate = 100)	579
Nitrocellulose Dilution Ration - Toluene	2.0
Critical Constants	$t^{\circ}_{c} = 274.7^{\circ}$ C P_c=47.7 atm. d_c = 0.237 gm/cc.
Dipole Moment	3.2 Debye Units

decontaminated acetonitrile would be uneconomical, thus disposal of the contaminated acetonitrile was recommended.

PROPOSED RECYCLE BY DRYING (Molecular Sieve)

Waste contaminated acetonitrile was estimated to be generated at a rate of approximately 500 gallons per month. This accumulation of dirty acetonitrile is stored in a 500 gallon storage tank. The 500 gallons of dirty solvent is fed to a Solvent Recovery Evaporator with a continuous scraped heat transfer surface, this package unit would include the evaporator vessel, steam jacket, condenser, manual sludge cleanout, explosion-proof motor with the scraper assembly and an explosion proof motor on the product pump. All materials of construction in contact with the acetonitrile would be of 316 SS.

The 500 gallons of dirty acetonitrile is recovered through the evaporator at 15 gallons per hour in one week. The evaporator is started up and shut down daily. Once operating, the evaporator runs automatically and clean, wet solvent is pumped directly through a dual molecular sieve dryer to a 500 gallon storage tank. This tank would be sampled and tested prior to use. One molecular sieve dryer would absorb for 8 hours while the other molecular sieve dryer is being regenerated with nitrogen (N_2) or dry air. Figure 1 is a block flow diagram of the above process and Figure 2 is the process flow diagram.

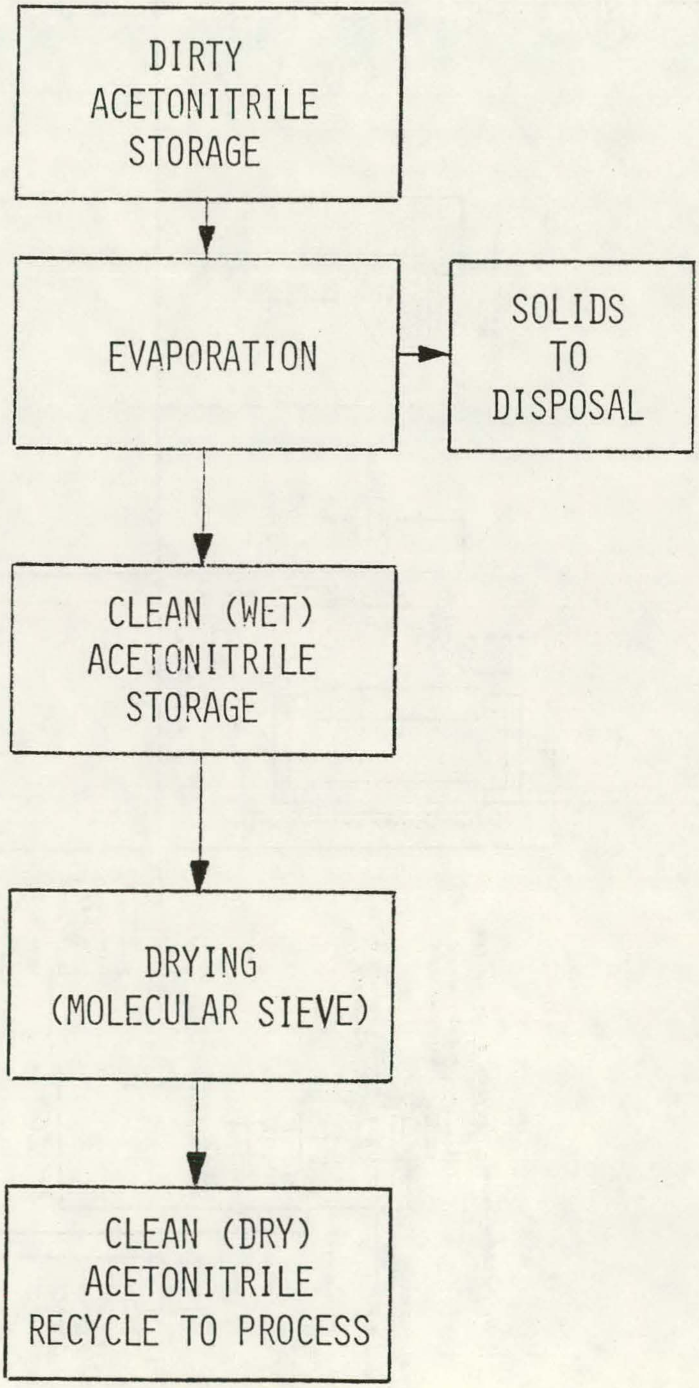
A conceptual cost estimate of the recycle process was prepared. This resulted in an estimate of $375,000 (1st Qr FY'80) for installation of the process. Thus, due to the high capital cost to install and operate the process, recycle by drying was deemed uneconomical.

PROPOSED RECYCLE BY DISTILLATION

When a 500 gallon production batch of acetonitrile becomes contaminated, it is sent to a 500 gallon feed tank as shown in the process flow diagram in Figure 3. Upon accumulation of an additional 500 gallon contaminated production batch in Tank F-1001 (Heated Solvent Dissolver Tank), evaporation of 500 gallon of ACN is accomplished by feeding contaminated ACN from the Feed Tank to Tank F-1001, thus maintaining a constant liquid level in Tank F-1001 while the liquid in the Feed Tank is spent. The evaporated 500 gallon ACN is condensed and stored in a 500 gallon Clean Solvent storage tank (F-403) for later purification by distillation. Concentrated contaminated ACN is filtered during evaporation to remove solids. The concentrated contaminated ACN is cooled after evaporation to facilitate additional removal of solids by filtration. This concentrated contaminated ACN is stored in the 500 gallon Feed Tank (F-404A) until another 500 gallon batch of contaminated production ACN is deposited in Tank F-1001.

FIGURE 1

BLOCK FLOW DIAGRAM



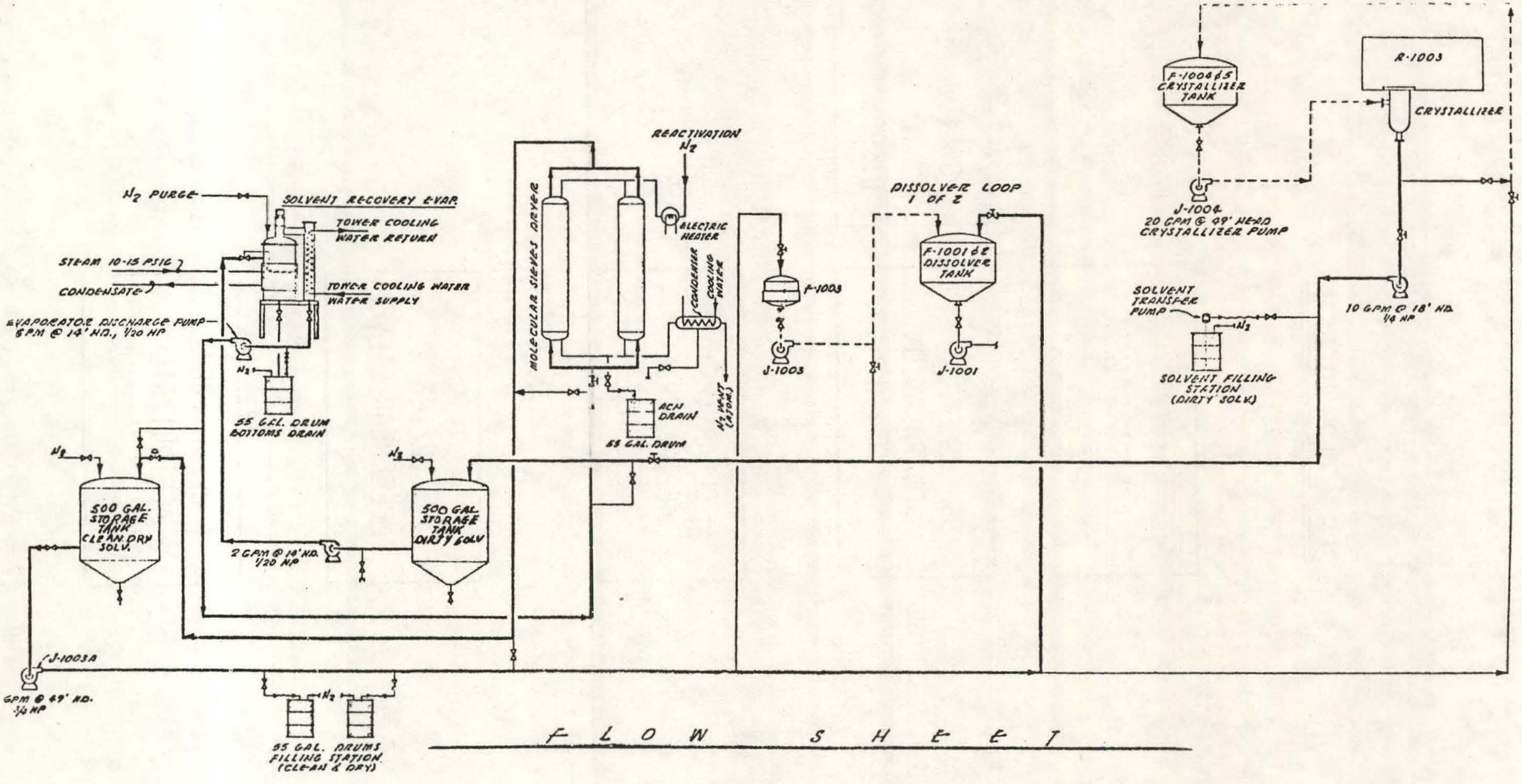


FIGURE 2: ACETONITRILE RECYCLE - DRYING (MOLECULAR SIEVE)

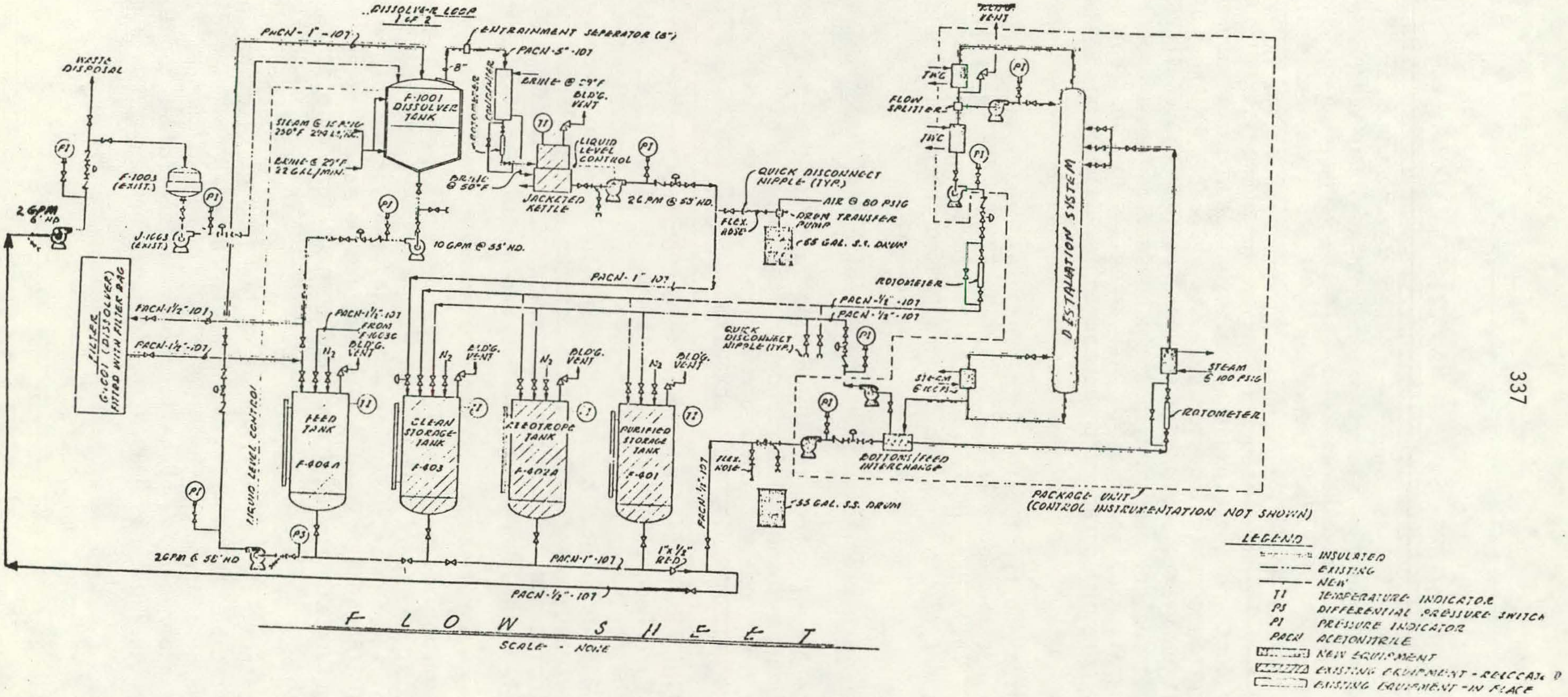


FIGURE 3: ACETONITRILE RECYCLE - DISTILLATION

The 500 gallon of ACN stored in the Clean Solvent storage tank (F-403) is the feed to the distillation systems where the overhead product is stored in a 500 gallon ACN-H_2O Azeotrope storage tank (F-402A) and the bottoms product is stored in a 500 gallon Purified ACN storage tank (F-401) for later reintroduction into the Production Facility. Figure 4 is a simplified block flow diagram of the above process.

Existing tank F-1001 (Dissolver Tank) would be revised to include an 8 inch vapor duct and entrainment separator. The four (4) storage tanks would be refurbished existing storage tanks relocated to the process. The distillation system would be a packaged packed column with feed preheater product cooler, reboiler, bottoms product cooler and controls for automatic operation of the system. All materials of construction in the process that come in contact with acetonitrile would be of 304 stainless steel.

A conceptual cost estimate of the recycle process was prepared. This resulted in an estimate of $692,000 (1st Qr FY'80) for installation of the process. Thus, due to the high capital cost to install and operate the process, recycle by distillation was deemed uneconomical.

ACETONITRILE DISPOSAL BY INCINERATION

Waste acetonitrile from the production facilities at the Y-12 Plant has been deemed uneconomical for recovery and recycle back to the process. Thus, complete disposal of the acetonitrile is desired, with incineration viewed as the complete disposal mechanism.

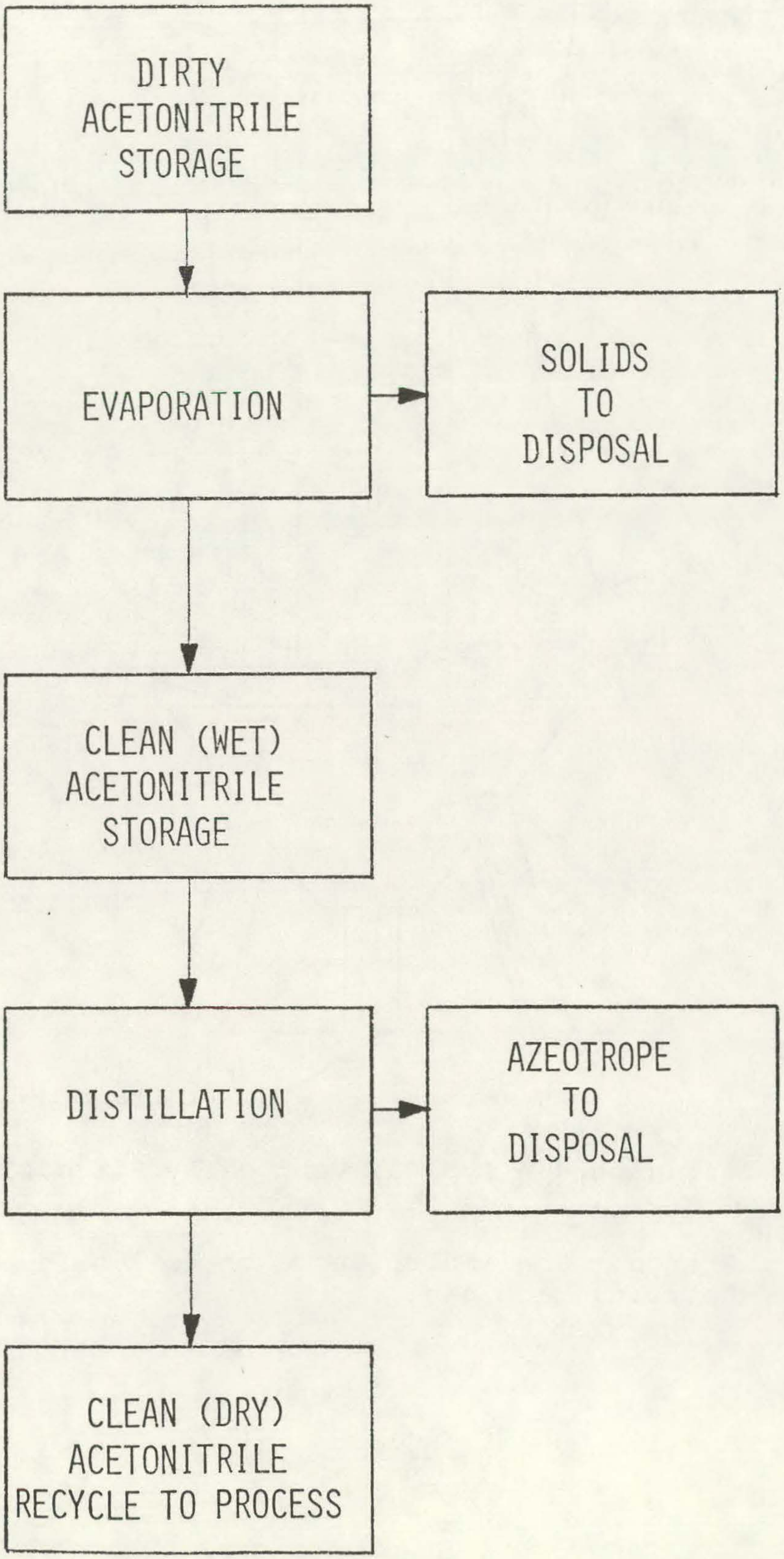
Utilization of an existing liquid injection incinerator (Prenco Corporation Pyro Decomposition System) shown in figure 5 was desirable, converting the contaminated acetonitrile to oxides, smokelessly. This incinerator was installed in the Y-12 Plant in 1973 for incineration of waste oil, but other means of disposing of the waste oil resulted in non use of the incinerator. Thus the incinerator remained unused for several years, resulting in degradation of many of the components of the incinerator.

Refurbishment of the incinerator included replacement of the gas pilot assembly, the spark plug assembly, the temperature indicating thermocouple, the burner nozzle assembly and the ultra violet flame detector. All piping and valves not replaced were sand blasted. All instrumentation and control equipment was checked for corrosion and cleaned or replaced.

Waste acetonitrile was introduced to the liquid injection incinerator by pumping from 55 gallon drums with an air operated positive displacement pump as shown in figures 6, the block flow diagram and figure 7, the process flow diagram. The 55 gallon drums are manifolded together such that after natural gas has heated the incinerator to a temperature of

FIGURE 4

BLOCK FLOW DIAGRAM



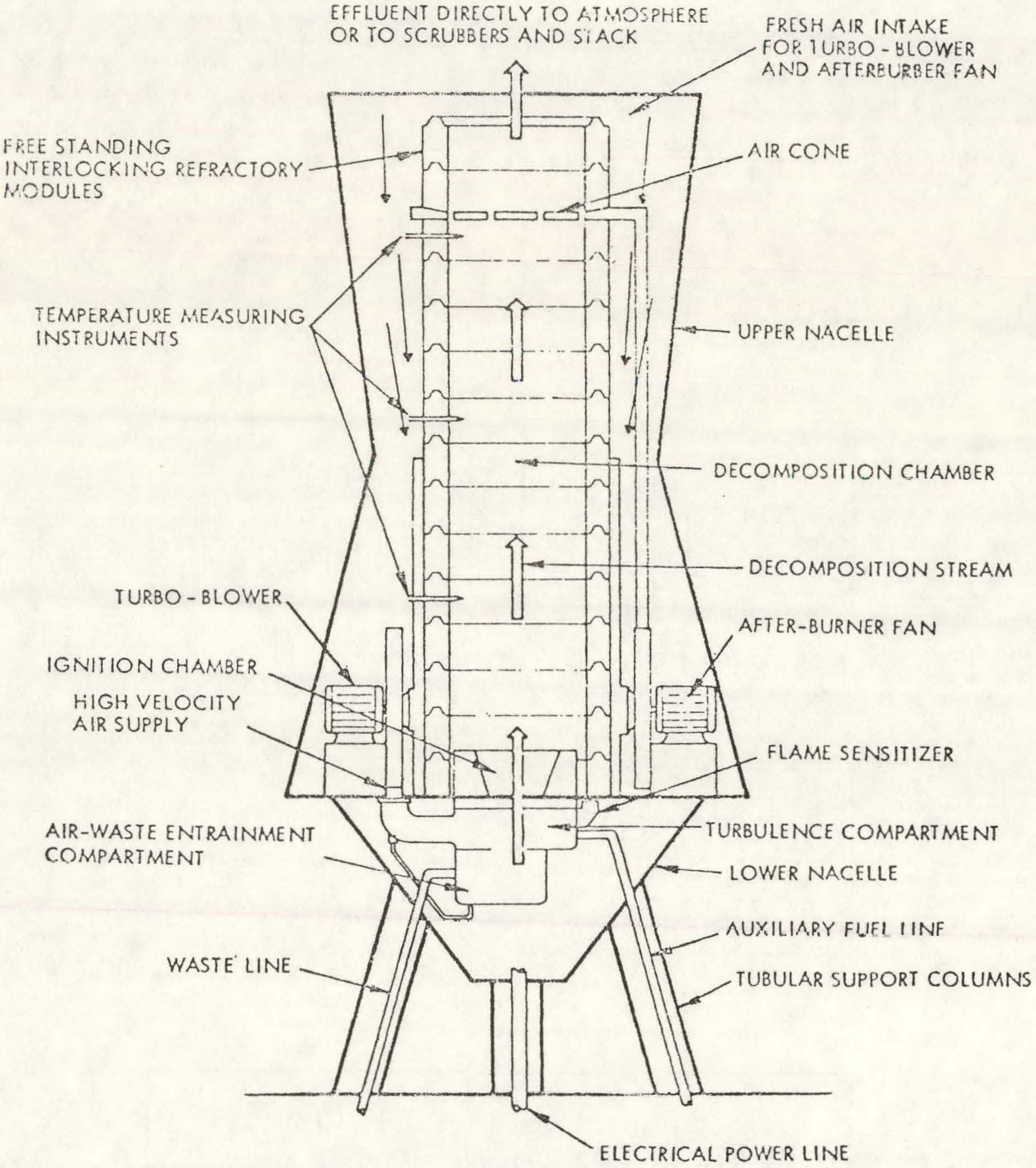
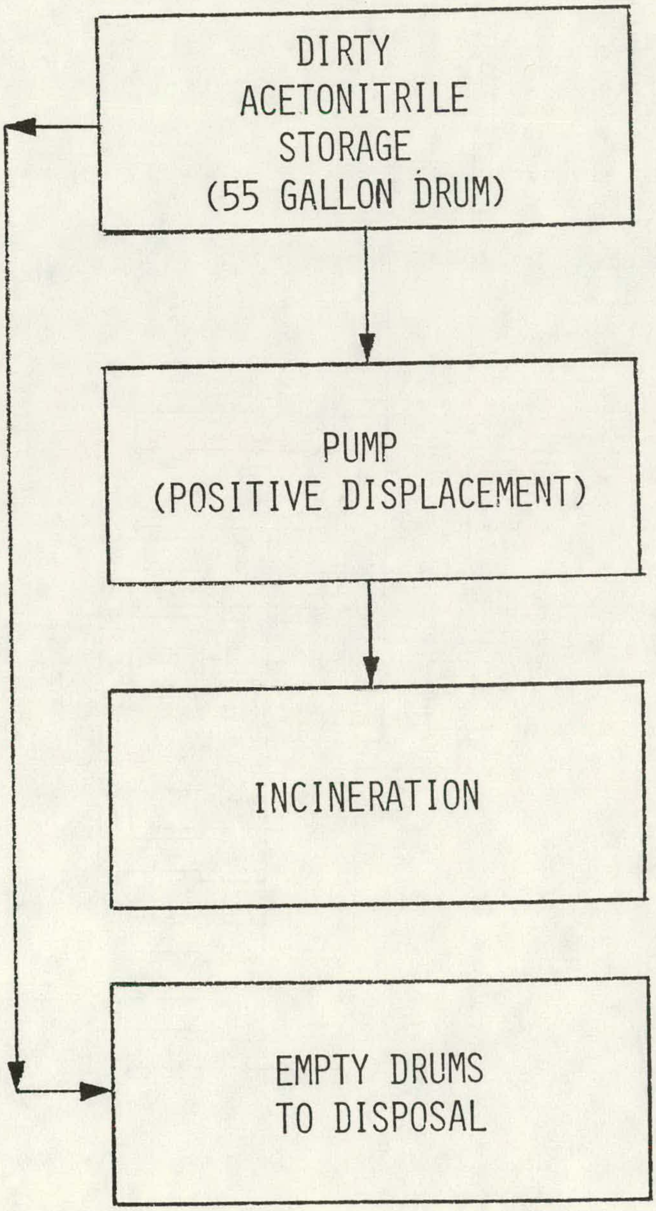


Figure 5: Typical Vertically Fired Liquid Waste Incinerator*

* Prenco. The modern approach to liquid pollution control. Detroit, Michigan

FIGURE 6

BLOCK FLOW DIAGRAM



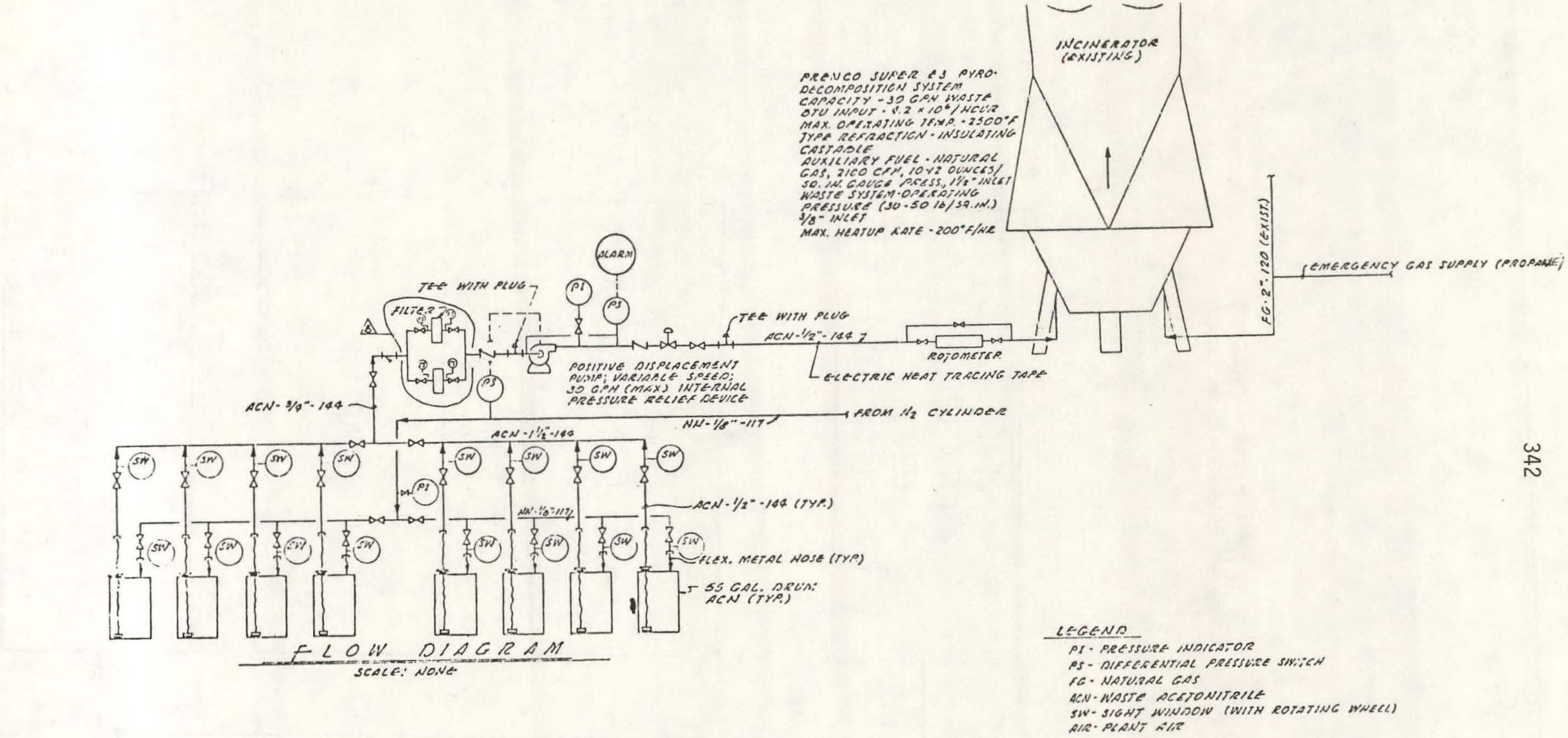


FIGURE 7: ACETONITRILE DISPOSAL - INCINERATION

2500°F, four (4) of the eight (8) drums manifolded together are fed to the incinerator at a rate of 30 gallon per hour. When the initial four (4) drums are spent, the remaining four (4) drums are fed to the incinerator while four (4) full drums replace the four (4) empty drums on the manifold. This procedure is repeated once every 7.5 hours until all the 55 gallon drums of waste acetonitrile have been incinerated.

During the incineration of acetonitrile the following combustion reactions will occur:

1. $CH_3CN + 3.75\ O_2 \xrightarrow[\text{(above 1500°F)}]{\text{heat}} 1.5\ H_2O + 2\ CO_2 + NO_2$ (Desired Reaction)

2. $CH_3CN + 1.63\ O_2 \xrightarrow[\text{(below 1500°F)}]{\text{heat}} 0.5\ HCN + 1.25\ H_2O + 0.5\ CO_2 +$
$0.5\ NO_2$ (Undesired Reaction)

3. $NO + 1/2\ O_2 \xleftrightarrow[\text{(max. at 600°F)}]{\text{heat}} NO_2$

These reactions result in the following material and energy balance on the incinerator:

Material Balance - Basis: Incineration at 30 gal/hr: 2,500°F

I. a. Desired Reaction
$CH_3CN + 3.75\ O_2 \xrightarrow[\text{(above 1500°F)}]{\text{heat}} 1.5\ H_2O + 2\ CO_2 + NO_2$

b. Desired Results
30 gal/hr acetonitrile (ACN) = 196 lb/hr ACN = 4.78 lb mole ACN/hr = 4.78 lb mole NO_2/hr = 220 lb NO_2/hr = 1760 lb NO_2/8 hr

II. a. Undesired Reaction
$CH_3CN + 1.63\ O_2 \xrightarrow[\text{(below 1500°F)}]{\text{heat}} 0.5\ HCN + 1.25\ H_2O + 0.5\ CO_2 + 0.5\ NO_2$

b. Undesired Reaction
30 gal/hr acetonitrile (ACN) = 196 lb/hr ACN = 4.78 lb mole ACN/hr = 2.39 lb mole HCN/hr = 64.5 lb HCN/hr = 516.3 lb HCN/8 hr and 2.39 lb mole NO_2/hr = 109.94 lb NO_2/hr = 879.5 lb NO_2/8 hr

Energy Balance on Waste Solvent Incinerator
Basis: 4.2×10^6 max. Btu/hr input @ 2500°F max. temperature

a. Btu/hr input by acetonitrile (30 gal/hr) - 2.60×10^6
b. Btu/hr input by natural gas (2100 SCFH) - 2.03×10^6
c. Total Btu/hr input by acetonitrile and natural gas - 4.64×10^6
d. Heat loss from refractory 9.28×10^5 Btu/hr

To insure that the reliability of the incinerator to incinerate the acetonitrile without producing toxic hydrogen cyanide (HCN), a test burn of the incinerator was conducted. The incinerator is heated at a rate of 100°F per hour until it reaches a temperature of 2400°F with natural gas for approximately six (6) hours to bake out the four refractory rings. The temperature is cut back to 2000°F, acetonitrile is pumped to the incinerator at a rate of 11.43 gph, the temperature is allowed to stabilize back to 2400°F by making air flow damper adjustments if needed. The acetonitrile flow is increased at 5% intervals and each time letting the furnace stabilize at 2400°F until the acetonitrile is flowing to the incinerator at a rate of 30 gph.

The incinerator was designed, for safety reasons, to operate at a maximum temperature of 2500°F. Some difficulties were encountered when trying to operate the incinerator above 2400°F. This was due to a 150°F variance of the set point on the automatic temperature controller, which would automatically shut the incinerator down when the operating temperature of the incinerator came to within the 150°F of the maximum operating temperature. Unfamiliarity with the operation of the incinerator caused an unscheduled flame out of the incinerator, resulting in the operator lowering his set operating temperature in the incinerator.

After the operating temperature stabilized at 2375°F, it was noted that automatic natural gas supply to the incinerator had reduced to less than 5% of its flow capacity, thus indicating that the heat of combustion of the acetonitrile at 30 gph was enough to maintain the 2375°F operating temperature.

Samples of the incinerator off gas were taken at a 30 minute interval and a 60 minute interval. The following results were obtained:

A. Sample 1 (30 minutes)

  i. Total Cyanide - $< 0.25 \mu g$
  ii. Sample Concentration - $< 9.3 \times 10^{-6}$ mg/l

B. Sample 2 (60 minutes)

  i. Total Cyanide - $< 0.25 \mu g$
  ii. Sample Concentration - $< 9.3 \times 10^{-6}$ mg/l

C. Work Area Limit for Cyanide - 10 mg/l

These results indicate that during the incineration of acetonitrile above 1500°F, there is no production of hydrogen cyanide (HCN) gas. Thus, the Prenco Corporation liquid injection incinerator has been deemed satisfactory for the incineration of acetonitrile. Therefore an Application for a Permit to Incinerate has been prepared and sent to the Tennessee Department of Public Health, Division of Air Pollution Control.

Dup

Chemical Treatments of Soil to Decrease Radiostrontium Leachability[1]

Brian P. Spalding[2]

ABSTRACT

The ready leachability of radiostrontium from radioactive waste is one of the most salient problems with shallow-land burial as a disposal method. The continuous leaching of buried waste at the Oak Ridge National Laboratory, for periods up to thirty years, has led to contamination of significant volumes of soil with ^{90}Sr. The goal of the present investigation was to evaluate methods to effect the in situ fixation or decrease the leachability of ^{90}Sr from soil. Small columns of three soils, collected from the solid waste disposal areas at ORNL, were labelled with ^{85}Sr as a convenient tracer for ^{90}Sr. After this labelling but prior to leaching, the soil columns were percolated with equivalent amounts of sodium salt solutions of hydroxide, fluoride, carbonate, phosphate, silicate, or aluminate. Leaching was then initiated with 0.1 *N* $CaCl_2$ (calcium chloride), and fractions of the leachate were analyzed for ^{85}Sr.

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[1] Contribution of the Oak Ridge National Laboratory (operated by U.S. Department of Energy, under contract W-7405-eng-26 with Union Carbide Corporation). Publication No. 1573, Environmental Sciences Division, ORNL.

[2] Research Associate, Environmental Sciences Division ORNL, P.O. Box X, Oak Ridge, TN 37830.

The $CaCl_2$ solution was selected to qualitatively simulate groundwater which contains Ca as the dominant dissolved cation. With two soils, which were high in indigenous exchangeable Ca, only 30 to 35% of the ^{85}Sr could be leached from the carbonate-treated columns. Presumably, the ^{85}Sr was coprecipitated with the nascent $CaCO_3$ formed during this treatment. In contrast, greater than 98% of the ^{85}Sr was readily leached from all untreated soils. Other anions fixed variable but generally less ^{85}Sr than the carbonate treatment. Thus, sodium carbonate appears to have potential application to immobilize ^{90}Sr in situ in contaminated soil.

INTRODUCTION

The disposal of low-level radioactive wastes by shallow land burial can pose potential problems due to the mobility of the long-lived fission product ^{90}Sr (Francis, 1978). The close chemical similarity of Sr to Ca, the dominant dissolved and mobile cation in most groundwaters, can facilitate the leaching of ^{90}Sr. Leaching of buried waste at the Oak Ridge National Laboratory has led to ^{90}Sr contamination of soils in and around disposal areas. It would be desirable in the management of these contaminated soils, as well as in the management of the waste itself, to have a method to fix or immobilize radiostrontium in soil. The present study was initiated to evaluate the in situ formation of insoluble calcium phases with which ^{90}Sr would coprecipitate. In addition, if such phases could be formed in situ, it was also desired to know how leachable or how well fixed the ^{90}Sr in these phases would be. Sodium salts of anions, including carbonate, fluoride, silicate, aluminate, and phosphate, were selected since all of these form quite insoluble Ca salts. The hydroxide was also studied because elevated soil pH can lead to enhanced radiostrontium adsorption via enhanced cation exchange selectivity (Spalding, 1980). The leachability of adsorbed radiostrontium induced by hydroxide has not been examined, and other more stable phases, such as the carbonate, are likely to form with aging of hydroxide-treated soils.

Several previous investigations have examined some of these precipitated phases in soil, although a systematic, comprehensive study of all of these phases has not been attempted previously. Gregers-Hansen (1964) achieved considerable Sr fixation in soil via heat treatment and, to a smaller extent, via phosphate addition. Phosphate fertilization of soil does lead to decreased plant uptake of radiostrontium through immobilization in calcium phosphates (Anderson, 1971). Sodium carbonate has been used to reduce plant uptake of radiostrontium from surface soil (Menzel et al., 1968); in this case, sodium carbonate was not employed to directly immobilize radiostrontium in $CaCO_3$ but rather to restrict rooting depth of field crops following deep plowing of contaminated surface soil with the alkaline carbonate. Mokady and Gal (1964) reported the fixation or radiostrontium by lime in soil due to isomorphic exchange of Sr with the indigenous $CaCO_3$ in soil using a $SrCl_2$ leaching solution; although this fixation mechanism has potential, the use of Sr as the leaching cation rather than Ca makes extrapolation of their findings most difficult to typical environmental conditions where Ca dominates the solution phase. Flocker and Fuller (1956) showed contrasting evidence in that ^{89}Sr was very slow in isomorphic exchange with $CaCO_3$ phases in calcareous soils.

MATERIALS AND METHODS

The collection, preparation, and characterization of the three soils used in this study have been described previously (Spalding, 1980). These soil characteristics are summarized in Table 1. Water was added in 1-mℓ increments, followed by shaking and mixing, to 150 g of air-dried (<5% moisture, dry-weight basis) soil contained in a 500-mℓ glass bottle; this wetting procedure was continued until sand-sized soil aggregates were formed and dust-free air was observed in the bottle. Wetting of soils to this moisture state produced an aggregate size distribution which yielded facile and reproducible leaching patterns from packed soil columns. The final moisture contents of soils BG4U, BG6U, and BG6N were 17.8, 16.5, and 13.3%, respectively, determined by drying at 100°C to constant weight. Nine grams of this moist soil were poured, with tapping, into 1-cm-diameter by 10-cm-long glass-barrel Econocolumns (Biorad Laboratories, Inc.). The soils subsided to within 0.5 cm of the top edge of the glass barrel, achieving calculated packing densities of 0.99, 1.01, and 1.05 g/cm^3, respectively, for the three soils.

To the top of each column was pipetted 1.00 mℓ of a stock solution of carrier-free ^{85}Sr (approximately 37 KBq/mℓ) in tapwater. The columns were allowed to age for 18 h before treating with one of six solutions. Solutions of NaOH, NaF, Na_2CO_3, $Na_3PO_4 \cdot 12\ H_2O$, $Na_2SiO_3 \cdot 9\ H_2O$, and $NaAlO_3$ were prepared to calculated Na concentrations of 1.56 *N*; actual Na concentrations, determined by atomic absorption of diluted solutions, were found to be 1.57, 1.57, 1.62, 1.70, 1.37, and 1.37, respectively. Two milliliters of a chemical solution or, for controls, tapwater were pipetted

Table 1 — Characteristics of three soils derived from Conasauga shale.

Characteristic	Units	Soil BG6U	 BG6N	 BG4U
Horizon	—	C	C	Ap
Organic matter	%	<0.1	<0.1	3.9
Fe_2O_3	%	2.66	1.14	2.04
MnO_2	%	0.64	0.22	0.09
Exchangeable acidity	meq/100 g	20.6	6.5	8.2
Exchangeable Ca	meq/100 g	2.4	17.2	12.6
Exchangeable Mg	meq/100 g	4.1	7.0	2.9
Exchangeable K	meq/100 g	0.1	0.2	0.8
Exchangeable Na	meq/100 g	0.1	0.2	0.0
Cation exchange capacity	meq/100 g	27.3	31.1	24.5
Exchangeable Sr	μeq/100 g	9	25	25
pH	—	4.4	7.3	6.5

on the top of a soil column and allowed to infiltrate by gravity; no leachate was produced by this treatment since the soils were still below their water-holding capacities. Duplicate columns were prepared for each chemical and control for each soil. After aging 18 h, leaching was commenced by pipetting 5 mℓ of 0.1 *N* $CaCl_2$ on each column twice daily. Generally, 12 to 16 h were required to percolate this 10 mℓ of leaching solution through each column. After 120 mℓ of total leachate were collected, the eluting solution was changed to 0.1 *N* HCl. Elution was then continued until ^{85}Sr activity could no longer be detected in the eluant.

Activity of ^{85}Sr in each 10 mℓ eluant fraction, contained in 25 mℓ plastic scintillation vials, was determined by counting with a well-type NaI(Tℓ) gamma scintillation detector attached to a multichannel analyzer. Five-minute counting times were employed and were generally adequate to achieve an uncertainty in the count rate of less than 0.1%. Activity of each fraction was expressed as a percent of the total activity applied to a column. The pH of each fraction was also determined with a pH meter using a combination reference-glass electrode.

RESULTS AND DISCUSSION

All of the chemical treatments effected two basic changes in the elution patterns of ^{85}Sr from the soil columns. Firstly, there was an increase in the volume of 0.1 *N* $CaCl_2$ required to leach the largest concentration or peak of activity. Secondly, there was often substantial reduction in the fraction of the total activity which could be leached following these chemical treatments. Considering the surface soil, BG4U (Fig. 1), approximately 26 mℓ were required to leach one-half the ^{85}Sr in the untreated soil, yielding a calculated column retention capacity of 28.8 meq/100 g (Table 2). With the fluoride and carbonate treatments, the volumes required to elute maximum activity with 0.1 *N* $CaCl_2$ yielded increased column retention capacities (Table 2). More importantly, although 98^+% of the ^{85}Sr could be leached by 100 mℓ of 0.1 *N* $CaCl_2$, only 60 and 27% of the ^{85}Sr could be leached by 120 mℓ from the fluoride- and carbonate-treated soils, respectively. In addition, the slopes of the elution lines or the rates of leaching of ^{85}Sr from the fluoride- and carbonate-treated columns had decreased substantially by 120 mℓ, indicating that numerous additional column volumes of 0.1 *N* $CaCl_2$ would be required to leach out the ^{85}Sr. In the case of the carbonate, this rate of leaching was so slow (Fig. 1) that the remaining ^{85}Sr could reasonably be considered fixed or unleachable.

The form of this fixed ^{85}Sr was most probably a coprecipitant or solid solution of ^{85}Sr with or in $CaCO_3$ and CaF_2. Such precipitated forms of Ca would be expected to readily dissolve in acid; changing the eluting solution to 0.1 *N* HCl led to the facile leaching of this fixed or

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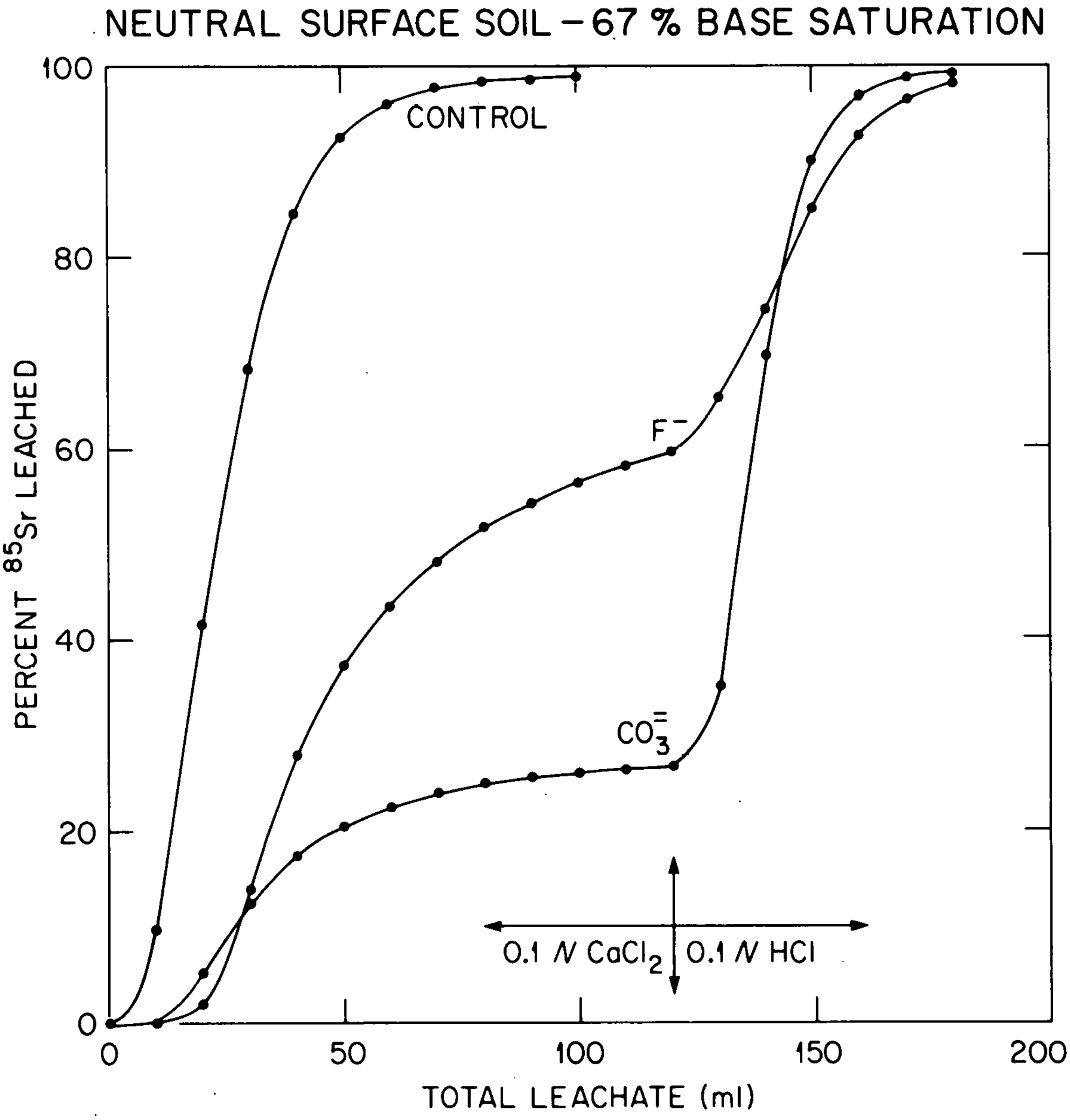

Figure 1. Elution of ^{85}Sr from columns of soil BG4U with 0.1 *N* $CaCl_2$ following chemical treatments.

Table 2 — Characteristics of ^{85}Sr elution from soil columns.

Soil	Chemical	Initial eluant pH	^{85}Sr elution model constants[†] A	B	C	Retention capacity[‡]	Average ^{85}Sr eluted for 100-120 mℓ
			(fraction/10 mℓ)	(mℓ)	(mℓ$^{-1}$)	(meq/100 g)	(%/10 mℓ)
BG4U	None	7.2	0.31	26	0.056	28.8	—
BG4U	CO_3^{2-}	9.4	0.07	32	0.054	36.9	0.43
BG4U	F^-	8.7	0.12	45	0.040	54.5	1.77
BG6N	None	6.7	0.35	27	0.066	29.8	—
BG6N	CO_3^{2-}	9.8	0.09	43	0.051	51.1	0.50
BG6N	F^-	9.2	0.21	45	0.047	53.7	1.20
BG6N	SiO_3^{2-}	11.4	0.10	59	0.028	72.4	3.15
BG6N	PO_4^{3-}	9.7	0.09	53	0.034	64.4	1.56
BG6N	AlO_2^-	11.2	0.12	50	0.034	60.4	2.00
BG6N	OH^-	12.7	0.12	62	0.028	76.4	3.48
BG6U	None	4.2	0.50	10	0.055	7.0	—
BG6U	CO_3^{2-}	9.5	0.35	41	0.075	46.8	0.59
BG6U	F^-	7.7	0.23	48	0.070	55.7	2.75
BG6U	SiO_3^{2-}	10.6	0.15	75	0.041	90.3	3.16
BG6U	PO_4^{3-}	7.6	0.33	46	0.082	53.2	1.45
BG6U	AlO_2^-	10.1	0.35	52	0.102	60.9	1.46
BG6U	OH^-	10.4	0.23	57	0.059	67.3	2.26

[†] Constants in Eq. [1].

[‡] Retention capacity = (B − column void volume) × *N* of $CaCl_2$/weight of soil (in hundreds of g).

precipitated ^{85}Sr as shown in Fig. 1. The soil columns of soil BG4U, which were treated with silicate, phosphate, aluminate, and hydroxide, could not be leached with 0.1 N $CaCl_2$ due to column plugging by these strongly alkaline chemicals, caused by dispersion of aggregates and soil organic matter. Such flow stoppages, induced by these chemicals, were not observed with the two subsoils with organic matter contents of less than 0.1%.

As shown in Fig. 2, the neutral subsoil, BG6N, exhibited almost identical elution patterns to BG4U for the control and carbonate treatments. The fluoride treatment of this soil, however, immobilized less ^{85}Sr than the surface soil (18 versus 40%, respectively). This soil did allow the comparison of all the Ca/^{85}Sr immobilizing treatments. As discussed above, there are several ways in which these treatments should be compared. These are by elution volumes of maximum leachable activity, by total amounts of leachable ^{85}Sr by the 120 mℓ of 0.1 N $CaCl_2$, and by rates of elution or slopes of the lines just before the leachate is changed to 0.1 N HCl. To estimate the first two of these characteristics, the elution curves were fitted to a general Gaussian equation:

$$\text{Fraction } ^{85}\text{Sr}/10 \text{ m}\ell = A \exp\{-[(B - \text{elution volume})\, C]^2\}\ , \qquad (1)$$

where the constants A, B, and C are estimates of the percent activity in the maximum or peak fraction, the elution volume of this maximum fraction, and a measurement of dispersion or width of the elution peak, respectively. These estimates of the three constants for each soil and chemical treatment were determined using a nonlinear least-squares regression computer

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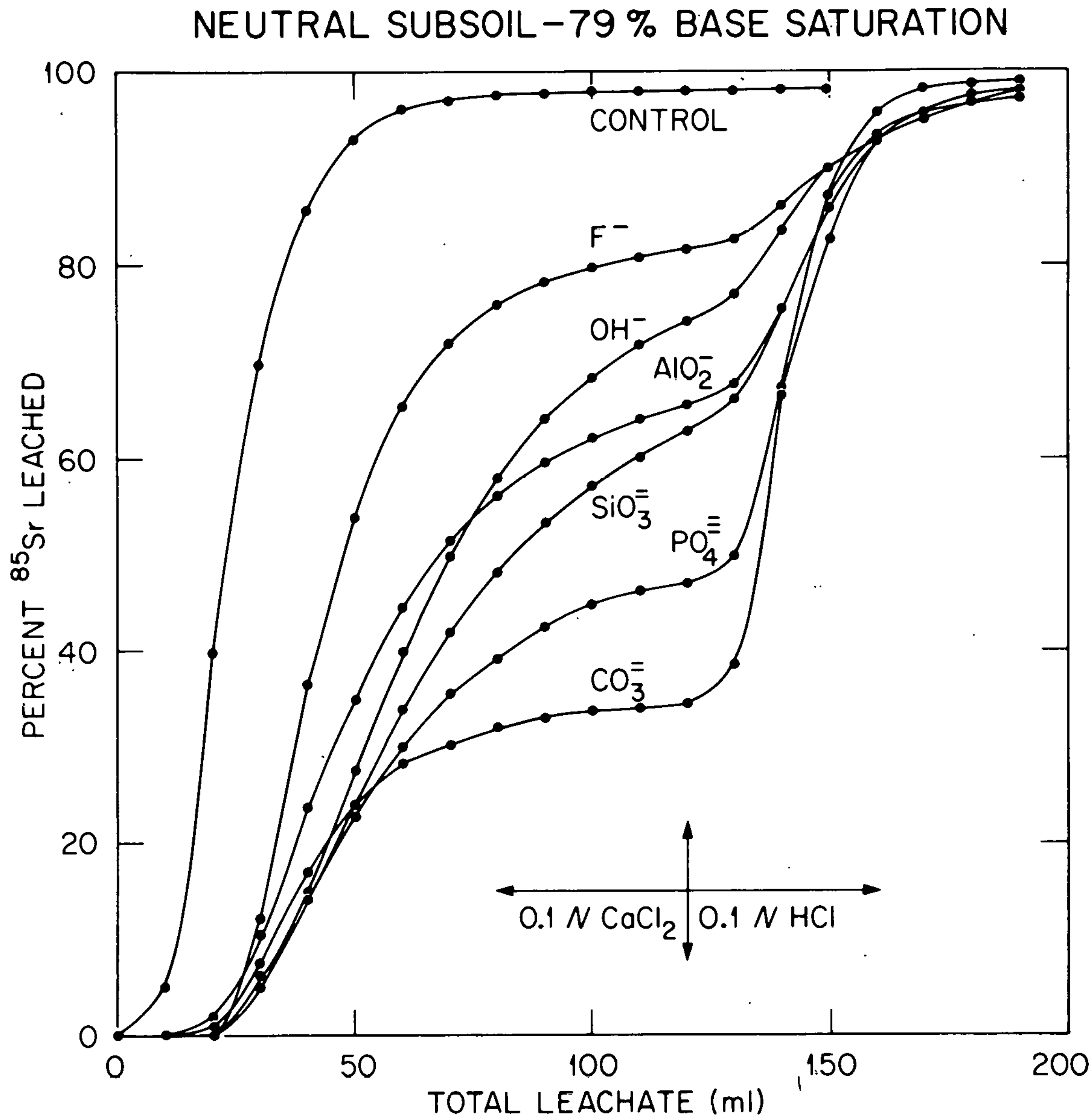

Figure 2. Elution of ^{85}Sr from columns of soil BG6N with 0.1 *N* $CaCl_2$ following chemical treatments.

program (SAS Institute, 1979). The model used actually explained an average of 92% of the variation in predicted elution in all cases.

It can be seen from Table 2 that all treatments raised the peak elution volume, B, by factors ranging from 1.2 to 7.5 and, consequently, led to increases in column retention capacities. All of the treatments resulted in elevating the pH of the initial leachate (Table 2). Such pH increases result in increases in pH-dependent charge on the soil particles as well as in a neutralization of exchangeable acidity. Since the newly created exchange sites, effected by these alkaline treatments, would contain Na as the charge-balancing cation, they will also exhibit selectivity for exchange by Ca and ^{85}Sr from the leaching solution (Spalding, 1980). This effect is clearly demonstrated in the case of soil BG6U, the acid (pH 4.2) subsoil; all treatments effected at least a four-fold increase in the soil retention capacities. The greater exchangeable acidity of this acid soil would lead to greater Na saturation following chemical treatment and, hence, lead to greater increases in Ca or ^{85}Sr retardation. Notably, the sum of exchangeable bases for soils BG4U, BG6N, and BG6U were 16.3, 24.6, and 6.7 meq/100 g (Table 1), which roughly correspond to the calculated retention capacities for untreated soils (28.8, 29.8, and 7.0 meq/100 g, respectively, Table 2). The two other near-neutral soils exhibited less increase in their retension capacities.

This acid subsoil was not, in general, able to immobilize as much ^{85}Sr in response to the chemical treatments as were the other two soils (Fig. 3). One interpretation of this behavior can be seen from the nature of the indigenous cations on the soils (Table 1). Whereas soils

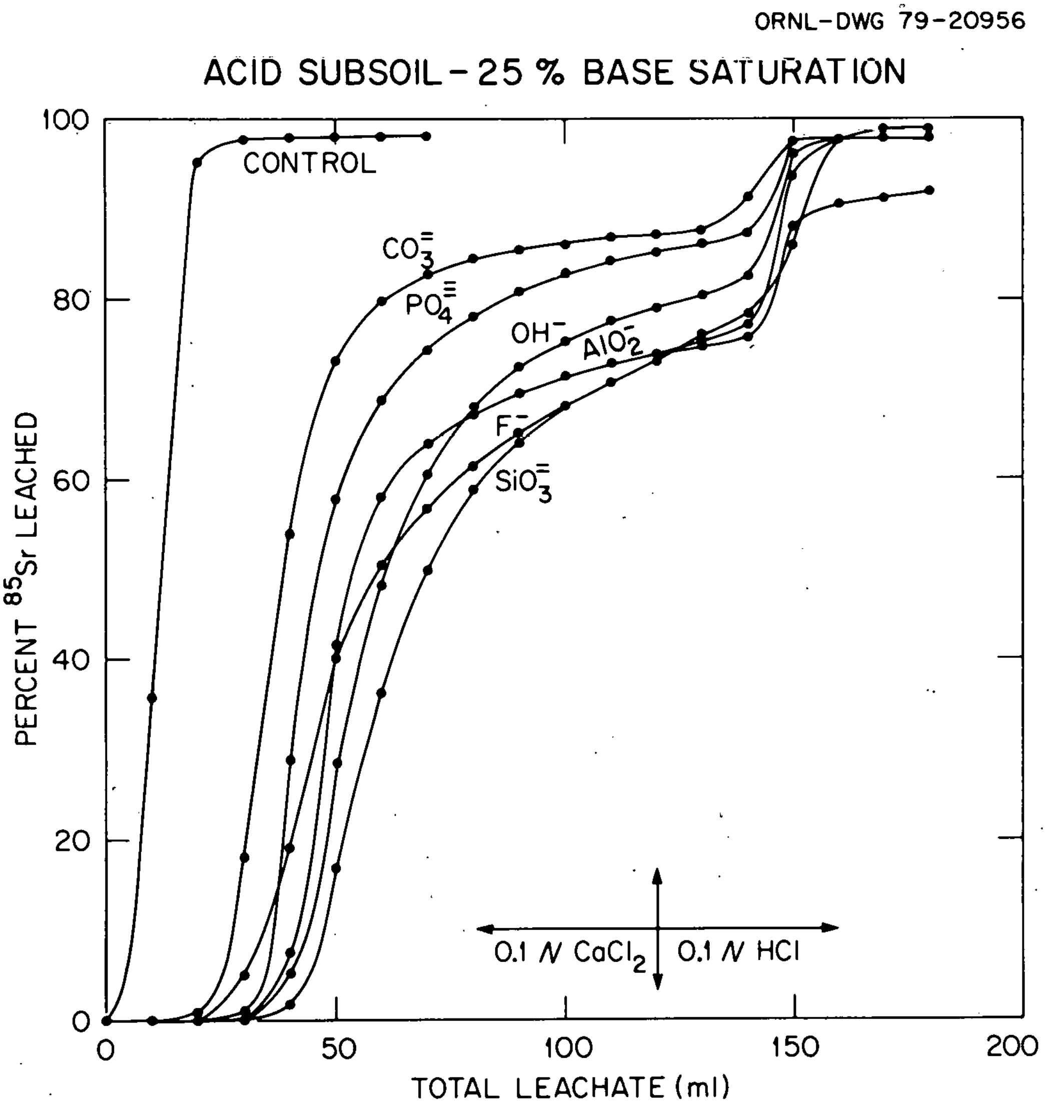

Figure 3. Elution of ^{85}Sr from columns of soil BG6U with 0.1 *N* $CaCl_2$ following chemical treatments.

BG4U and BG6N contained 15.5 and 24.2 meq/100 g indigenous exchangeable Ca and Mg, soil BG6U contained only 6.5 meq/100 g. There would be, therefore, less Ca and Mg present in this soil to form the precipitated phases with the various anions. In addition, much of the added anion would be consumed in neutralizing the exchangeable acidity in this acid soil. The exchangeable acidity (to pH 8) of soil BG6U would require 1.55 meq or 50% of the added alkalinity of each chemical. However, BG4U and BG6N, with their lower exchangeable acidities would require only 19 and 16%, respectively, of the applied alkalinity. Apparently, both the consumption of precipitating anions and the smaller amounts of Ca and Mg indigenously present led to the decreased amount of precipitated phases in soil BG6U.

The actual amount of ^{85}Sr, which can be precipitated in a given soil, can be considerably varied by operating parameters. The addition of more chemical for acid soils, the addition of more Ca in those soils low in indigenous amounts, or the use of longer columns would all be expected to lead to greater fixation of ^{85}Sr. Factors which cannot be manipulated by operating variables and, hence, are more fundamental from the point of view of the in situ immobilization of ^{90}Sr in soil, are the rates of isomorphic exchange of the precipitated activity with the Ca in the leaching solution or groundwater. These rates of the isomorphic exchange of the coprecipitated ^{85}Sr activities can be calculated, in comparative units, from the slopes of the elution lines in the final fractions of leachate. The average percent activity, eluted in the final three fractions with 0.1 *N* $CaCl_2$, is presented in Table 2. Notably, the carbonate phase exhibited the lowest isomorphic exchange rates of any of the precipitated phases. Even in the case of soil BG6U, where the carbonate treatment immobilized the least amount of activity after 120 mℓ of leaching (Fig. 3), that immobilized fraction was much slower to exchange than those of other treatments. The pH's of all the final leaches for all chemically treated columns were the same; the mean of all 32 treated columns was 7.2 ± 0.4(1σ). This condition would obviate pH differences among treatments affecting the solubilities of precipitated phases.

The 0.1 *N* $CaCl_2$, employed as the leaching solution in this study, simulates groundwater only in the sense that Ca is the dominant dissolved cation. The concentration of Ca in a typical groundwater would be at least an order of magnitude lower and would have bicarbonate rather than chloride as the anion. The higher concentration of Ca was employed here to speed up the elution from these columns; three weeks were required to obtain the total leachate volume in this study, while a tenfold longer time would have been required to achieve the equivalent amount of leaching using 0.01 *N* $CaCl_2$. Some precipitated phase likely formed during the initial leaching with 0.1 *N* $CaCl_2$, before excess anion was leached out, which would not have formed had a lower Ca concentration been employed. In terms of developing a technique for the in situ fixation of ^{90}Sr, however, this does not pose too much difficulty since supplemental Ca could be added after chemical treatment if the indigenous Ca groundwater concentration were inadequate to effect the desired level of fixation. On the other hand, since the diffusion coefficient of ^{90}Sr in soil increases exponentially with increasing Ca concentration in the soil solution (Prokhorov and Frid, 1965), the leachability of ^{85}Sr from the various precipitated phases by 0.1 *N* $CaCl_2$ would be faster than that with more realistic Ca concentrations. Thus the 0.1 *N* $CaCl_2$ used in this study provides a more rigorous test of the fixation of Sr in the various precipitated phases, assuming that diffusion limits isotopic and isomorphic exchange between solution and solid.

Although the solubilities and coprecipitations with various Ca(Sr) phases have been investigated intensively in the course of developing radiochemical separation techniques (Sunderman and Townley, 1960), the ability of these phases to form in situ in soil has not been investigated systematically previously. Although solubility products did provide a basis for selecting the various precipitated phases for investigation, they do not provide a basis to predict either the rates of precipitation or the degree of isomorphic exchangeability of the precipitated activity once formed. It would appear from this study that nascent $Ca(Sr)CO_3$ can be formed in soil in situ and lead to a marked reduction in the leachability of radiostrontium. This conclusion is supported by the observations of Flocker and Fuller (1956) that $CaCO_3$ in calcareous soils was very poorly available to plants because it would not isomorphically equilibrate in several months with spiked ^{89}Sr used as a tracer for Ca. Other immobilized phases in soil have been investigated even less, although it has been known for some time that heavy application of phosphate can reduce plant uptake of ^{90}Sr from soil (Anderson, 1971); presumably, this effect was due to precipitation of some species of Ca phosphate. Notably, the facile leachability of Sr by $CaCl_2$ in untreated soils provides a convenient method to decontaminate a given soil rather than fix the radiostrontium present. Such methods for decontaminating soils of radiostrontium have been proposed previously (Lagerwerff and Kemper, 1975). In the case of waste disposal, in situ fixation would seem more desirable since in situ decontamination would require the thorough collection of leachate; otherwise, accelerated contamination of groundwater would result.

CONCLUSIONS

The in situ treatment of soil with sodium carbonate can immobilize up to 70% of the radiostrontium present. In addition, the nascent coprecipitated $Ca(Sr)CO_3$ was in very slow isomorphic exchange with Ca in the leaching solution. Other chemical treatments including silicate, aluminate, fluoride, phosphate, and hydroxide produced precipitated phases which, by comparison with the carbonate, were in more rapid isomorphic exchange with Ca in solution. In addition to producing insoluble phases in situ, all six chemical treatments retarded the leaching of that fraction of nonprecipitated radiostrontium by increasing the cation exchange capacity of the soil as well as the soil's selectivity for radiostrontium. Sodium carbonate treatment of soil appears to have potential for immobilization of radiostrontium in contaminated soils.

LITERATURE CITED

1. Anderson, A. J. 1971. Influence of phosphorus and nitrogen nutrition on uptake and distribution of strontium and calcium in oat plants. Soil Sci. Soc. Am. J. 35:108-111.
2. Flocker, W. J., and W. H. Fuller. 1956. Availability of calcium in calcareous soils. Soil Sci. Soc. Am. Proc. 20:387-391.
3. Francis, C. W. 1978. Radiostrontium movement in soils and uptake by plants. TID-27564. NTIS, Springfield, Virginia. 131 pp.
4. Gregers-Hansen, B. 1964. Fixation of radioactive strontium in soil. Nature 201:738-739.
5. Lagerwerff, J. V., and W. D. Kemper. 1975. Reclamation of soils contaminated with radioactive strontium. Soil Sci. Soc. Proc. 39:1077-1080.
6. Menzel, R. G., H. V. Eck, P. E. James, and D. E. Wilkins. 1968. Reduction of strontium-85 uptake in field crops by deep plowing and sodium carbonate application. Agron. J. 60:499-502.
7. Mokady, R., and M. Gal. 1964. Strontium fixation by lime contained in soils. Science 145:154-155.
8. Prokhorov, V. M., and A. S. Frid. 1965. Effect of salt concentration of the soil solution on the diffusion rate of microamounts of strontium in soil. Sov. Radiochem. (Engl. Transl.) 7:496-498.
9. SAS Institute. 1979. SAS User's Guide. 1979 ed. SAS Institute Inc., Raleigh, North Carolina. 494 pp.

10. Spalding, B. P. 1980. Adsorption of radiostrontium by soil treated with alkali metal hydroxides. Soil Sci. Soc. Am. J. 44:in press.

11. Sunderman, D. N., and C. W. Townley. 1960. The radiochemistry of barium, calcium, and strontium. Office of Technical Services, Dept. of Commerce, Washington, D.C. 118 pp.

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Session VI

ENVIRONMENTAL AND EFFLUENT MONITORING

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PURGE CASCADE URANIUM MONITORING*

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M. J. Stephenson

Systems and Equipment Technology Department
Enrichment Technology Division
Oak Ridge Gaseous Diffusion Plant

Uranium 235--Gamma Emission
Uranium Hexafluoride--Containment--Sorption

ABSTRACT

Advanced analytical instrument techniques and procedures can provide support to ensure reliable and efficient operation of the purge cascades. This information can be used, for example, to allow more effective utilization and selection of chemical trap sorbents for removing uranium hexafluoride and other purge gas components. Initial investigations indicate that gamma monitoring can be effectively used to provide unique analytical data that can aid in the overall management of uranium control processes. The preliminary results of the Oak Ridge uranium monitoring effort are summarized.

INTRODUCTION

The removal of uranium hexafluoride from various enrichment plant effluent streams is necessary to prevent the loss of uranium. The removal process is the final barrier in several cases between the process and the environment. Chemical traps employing sodium fluoride or alumina are particularly effective for this application and are commonly used. Reliable and efficient operation of chemical traps in general requires an accurate knowledge of the kinetics and loading capability of the particular system. In the case of sodium fluoride and alumina, the trap performance is widely variable and dependent upon specific pellet properties, trap operating conditions, and uranium concentration in the feed gas. Process contaminants can also play a major role. Unfortunately, the uranium content of the gaseous diffusion plant purge streams is widely variable and it is nearly impossible to ascertain the remaining chemical

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*K/ET-5015

trap life at any given point in the loading cycle once the trap has been put into service. At present, chemical trap operating philosophies are based primarily upon prior operating experience. Trap breakthrough is established by sampling of the trap effluent and subsequent external chemical analysis. This method is adequate, but does not allow much room for error because sorbent breakthrough cannot be detected until after it has already occurred. Consequently, a conservative approach has to be adopted in order to ensure uranium containment. Traps are pulled off-stream prematurely, for example, or a backup removal system is incorporated into the operation. Furthermore, overall effluent analysis yields very little diagnostic information that can be used to provide quantitative guidelines for better sorbent management.

The Enrichment Technology Division is engaged in a comprehensive technological program aimed at assuring the adequacy and overall reliability of the purge cascades to support continuous, efficient, and safe cascade operation. This effort includes the development of more comprehensive uranium and fission product monitoring techniques, and the generation and implementation of better operating procedures to allow more effective utilization and selection of chemical trap sorbents for uranium hexafluoride and other purge gas components. Preliminary field studies indicate that external gamma scintillation can be used to accurately measure chemical trap uranium-235 loading profiles *in situ* and trap breakthrough can be predicted without effluent chemical analyses. This monitoring method can also provide information concerning the kinetics and length of the mass transfer zone, and even pinpoint bed regions with diminished sorbent capacity. The effect of regeneration can also be studied. The results of the Oak Ridge uranium monitoring effort are summarized in this paper. It should be noted that this program is relatively new and only preliminary data are given. Detailed results will be made available as the program proceeds.

NUCLEAR SPECTROSCOPY

The required components for nuclear spectroscopy include a detector sensitive to the particular radiation, spectroscopy amplifier, pulse height analyzer, and pulse counter with controlling timer. Thallium-activated sodium iodide crystals are commonly used in gamma scintillation detectors. This crystal produces a pulse of light for each gamma photon absorbed. The intensity of the light is proportional to the characteristic energy of the particular isotope. The light pulses are then focused on the cathode of an integral photomultiplier tube, which, in turn, produces pulses of electrons that are proportional to the gamma energy. The electron pulses are amplified and passed into an analyzer which is able to distinguish between various energy levels. Radioactive decay is a random phenomenon and, consequently, there is no way to specify the exact number of disintegrations that will occur from a given source in any time interval. The uncertainty introduced by random disintegration rates has to be taken into account, along with the other sources of experimental error.

DEVELOPMENT OF GAMMA SCANNING TECHNIQUE

Application of nuclear measurement techniques to perplexing and often unique engineering problems is primarily limited only by the ingenuity of the experimenter. External gamma scintillation has been used as an analytical tool for process analysis at the ORGDP for several years. The performance of a development pilot plant was first determined by fixed position gamma monitoring of process gas and liquid streams*. The removal of noble gas was being measured in this case and, appropriately, krypton-85 and xenon-133 radioactive tracers were used. Later, a portable gamma scanner was fabricated after large radiation buildups were detected at intermediate points along a packed column. It became very clear that the column operation was not straightforward in this case and column end point analysis simply would not suffice to establish the column performance well enough to allow quantitative modeling. The portable scanning technique enabled direct measurement of complex two-phase column concentration patterns and was, needless to say, instrumental to the success of the earlier project. The method was subsequently used for the analysis of other engineering scale equipment, including the determination of the solids loading profile in a krypton cold trap**.

Figure 1 shows a photograph of the gamma scanner installed next to a packed column. The lead shield is mounted on a carriage that rides up and down the face of the intermediate column on vertical tracks. A carriage marker is provided on the left side of the track to reference each count position. A small horizontal slit is machined through the end cap of the shield next to the column to allow collimated counting of the column activity. The detector is placed inside the lead shield pointing toward the column as shown in Figure 2. The detector assembly weighs about 300 pounds and is lifted by an overhead electrical hoist. A lead backstop is installed behind the column where stray radiation might interfere with the column count determination.

APPLICATION TO CHEMICAL TRAP MONITORING

Uranium-235 has characteristic gamma energies at 0.143 and 0.185 Mev. Figure 3 shows a photograph of a uranium-235 profile taken with a sodium iodide detector. The height of the characteristic peak is proportional to the amount of uranium present in the sample. Field experiments were subsequently conducted with several of the purge facility chemical traps to establish whether or not the chemical traps typically contain sufficient gamma activity to allow the use of the gamma scanning method to accurately follow sorbent loading. These tests showed that the uranium profiles could be well defined in both sodium fluoride and alumina traps. Uranium loadings as low as 0.001 lb U/lb pellet were detected in a 10-inch alumina trap with the present gamma detection system. The gamma scan of a sodium fluoride trap which had seen extended service in the K-27-8 pigtail operation is shown in Figure 4 plotted against the uranium content found

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*Stephenson, M. J., *Analysis of a Fractional Gas Stripper*, K-1895, December 1978.

**Eby, R. S., *The Desublimation of Krypton for a Noncondensable Carrier Gas*, K-1896, September 1978.

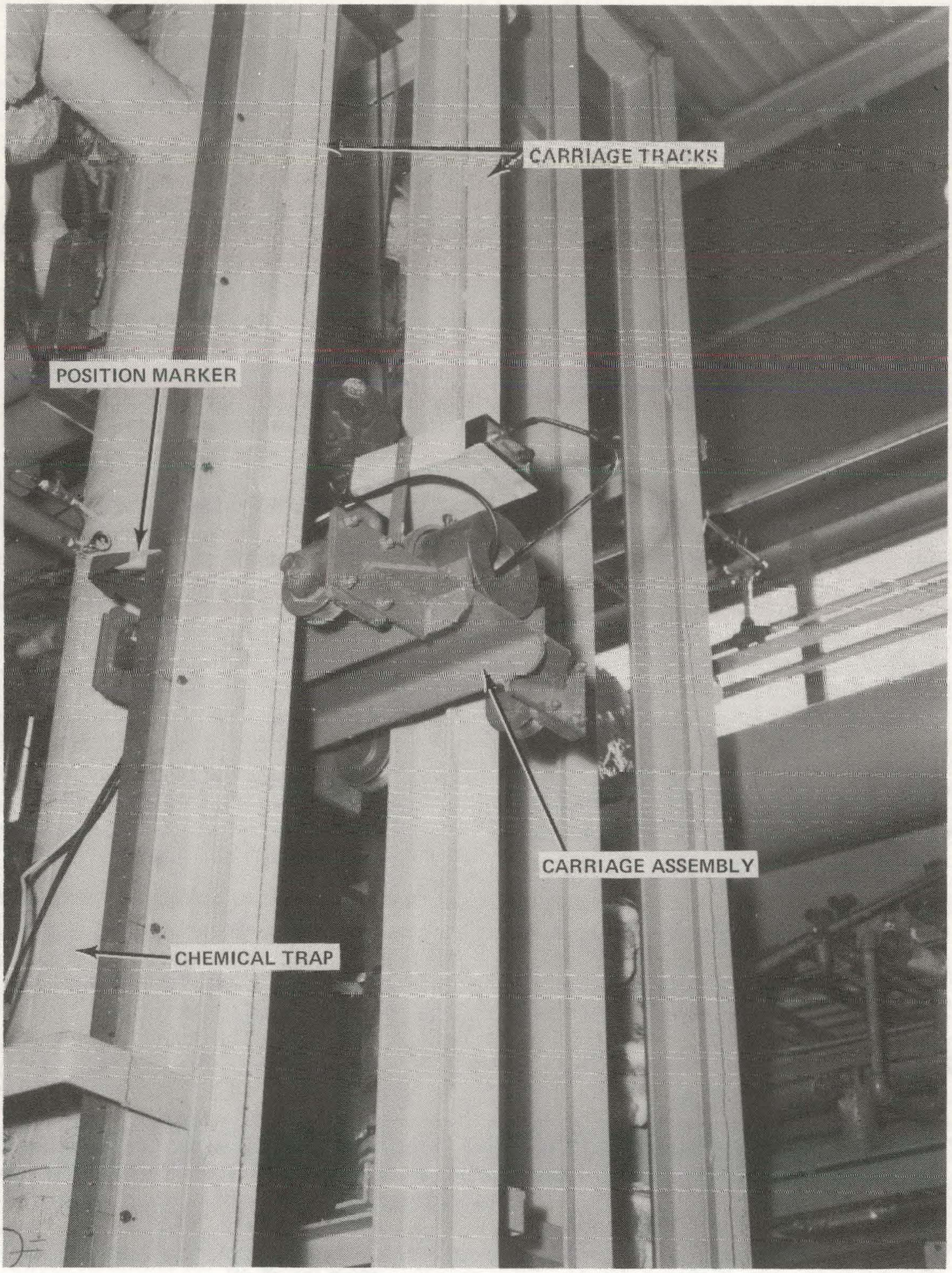

Figure 1

PACKED COLUMN GAMMA SCANNER

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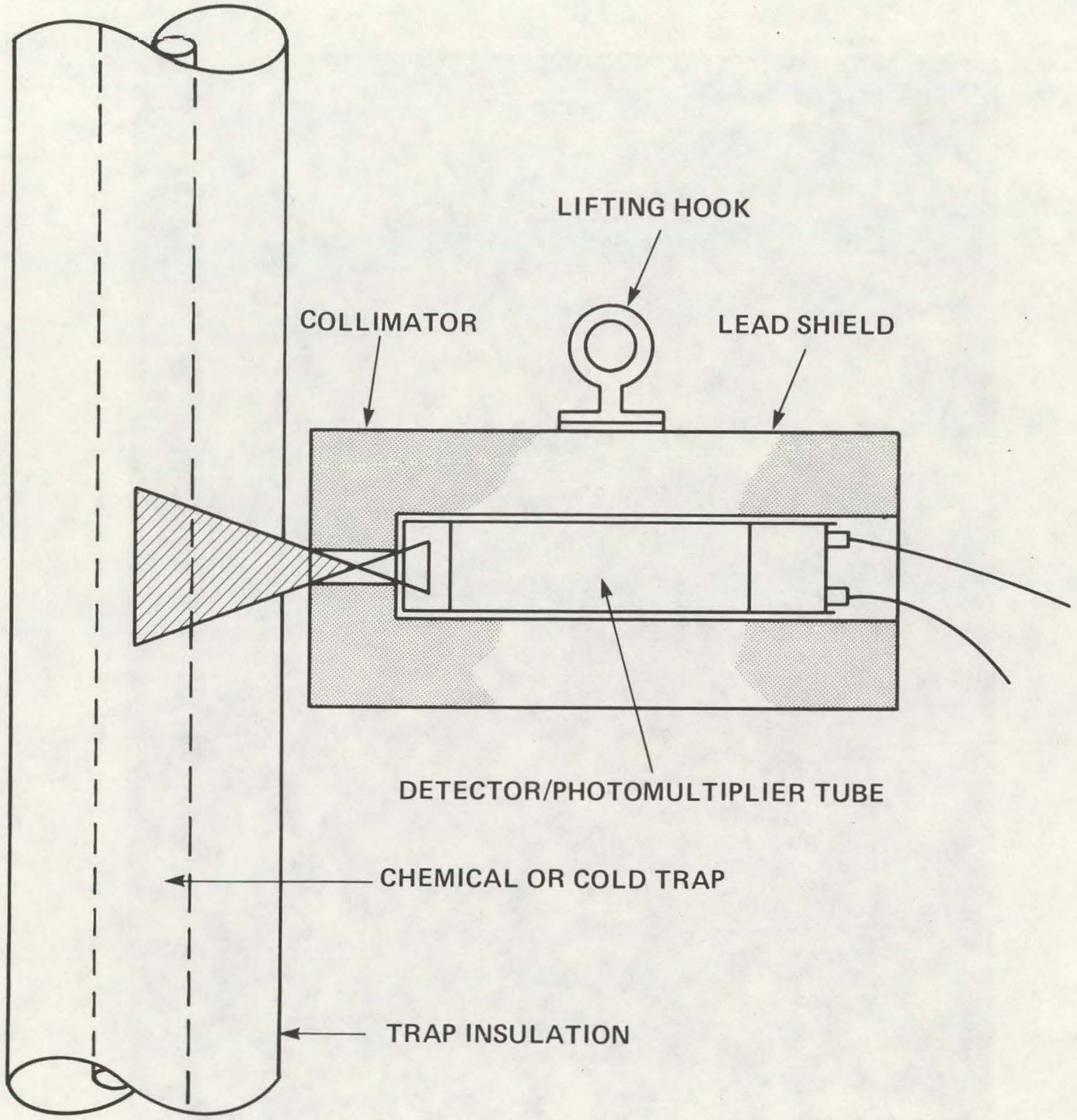

Figure 2

SCHEMATIC OF GAMMA SCANNER

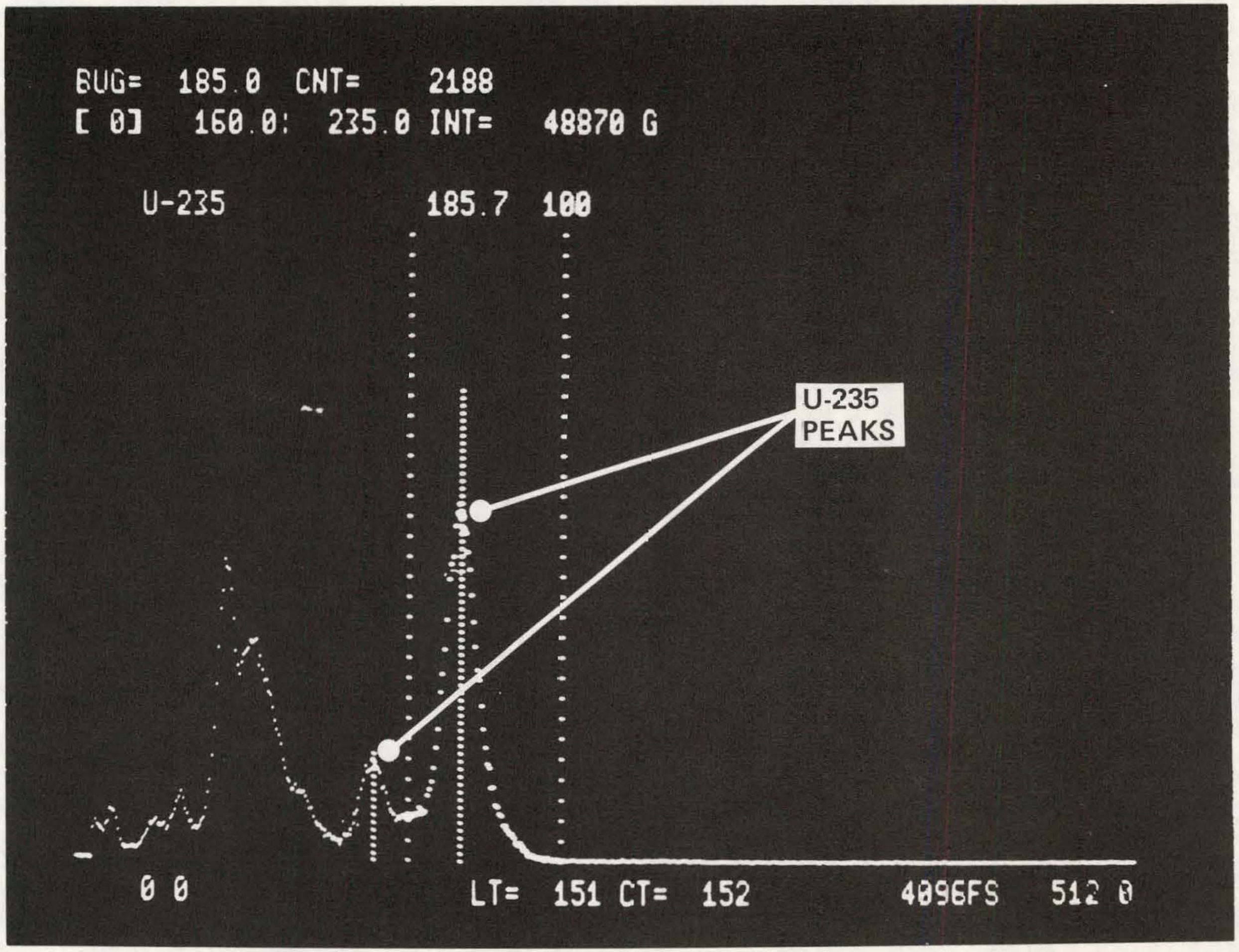

Figure 3

CHARACTERISTIC NaI PROFILE OF ^{235}U

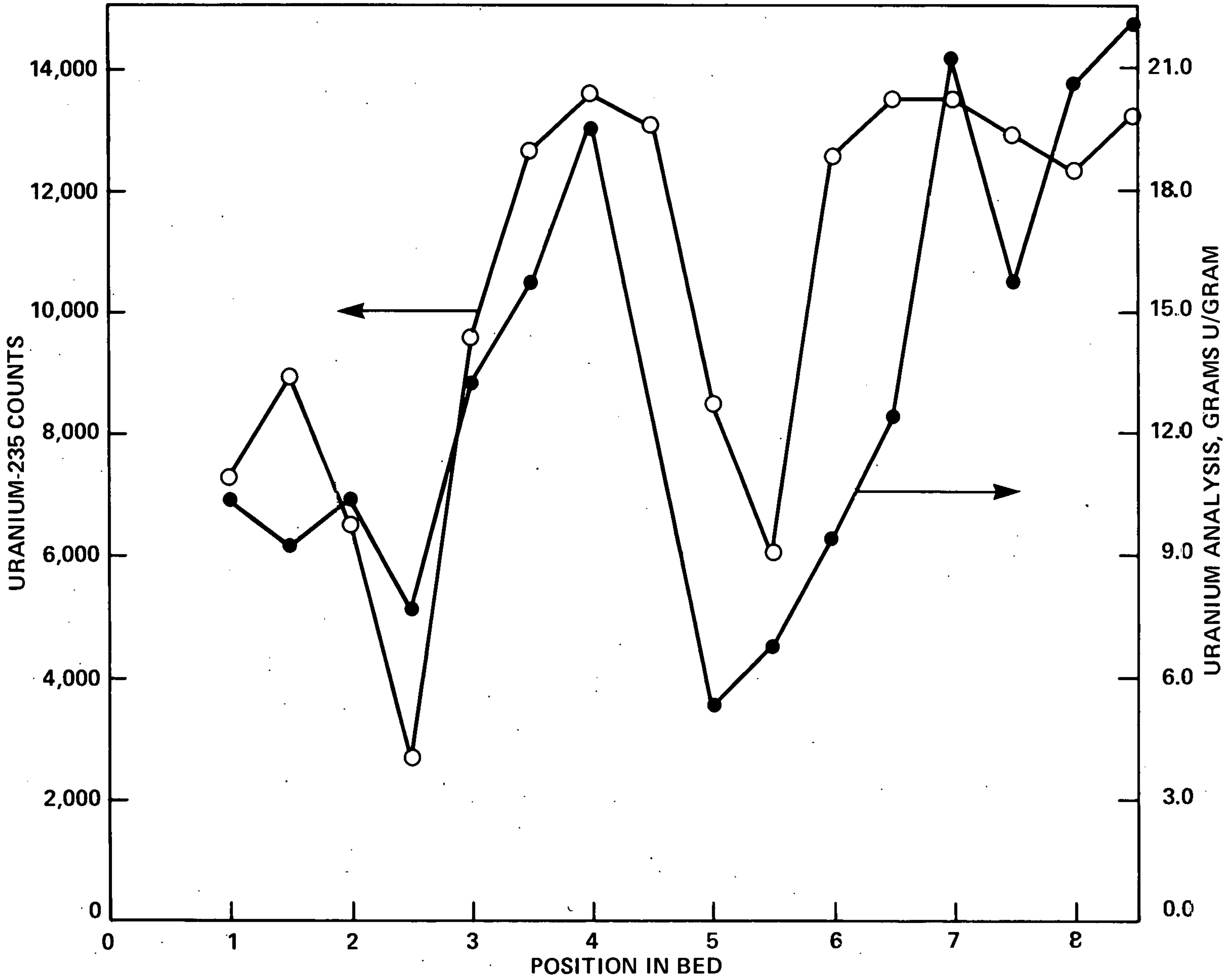

Figure 4
COMPARISON OF URANIUM-235 BED PROFILE AND QUANTITATIVE ANALYSIS OF NaF

by external chemical analysis. It was nearly impossible to obtain pellet samples in the exact bed location as the corresponding radiation measurements because of the physical construction of the trap but, nevertheless, an excellent comparison can be seen.

In the course of monitoring the uranium movement, other gamma emitting radionuclides were observed in the chemical traps. These measurements were made while the trap was still in service. So far, only uranium-235 and -238 daughter products have been positively identified, including protactinium-234m, thorium-234, thorium-231, and uranium-234. Additional identification work is in progress. Technetium-99 is a beta emitter and cannot be detected with the external monitor. A unique in-line beta cell has been developed at ORNL*, however, which might be adapted for this use.

GAMMA SCANNING FIELD STUDIES

Chemical traps are used extensively in the enrichment complex as shown in Figure 5 as an integral part of the purge system to assure uranium containment. Clearly, the function and integrity of the traps have to be guaranteed in these locations. Sodium fluoride, H151 alumina, and F1 alumina are three of the more common uranium trapping materials. The NaF trapping mechanism involves reaction of the uranium to form a solid $NaF-UF_6$ complex. The reaction can be readily reversed by heating the complex to around 650°F. Consequently, the spent NaF bed can be regenerated in place. The effectiveness of alumina, on the other hand, apparently relies upon hydrolysis of the UF_6 to UO_2F_2 by residual pellet water. The hydrolysis reaction in not easily reversed and the uranium must be recovered chemically by aqueous processing at the expense of the alumina. Gamma scanning of cascade chemical traps has been initiated to gain a better understanding of the life cycle characteristics of the uranium sorbents in the real purge environment and, ultimately, to identify obvious cause-and-effect relationships that bring about loss of pellet capacity with extended pellet use and regeneration.

SODIUM FLUORIDE TRAPS

The sodium fluoride traps located above the K-27-8 pigtail operate in an absorb-desorb cycle. Three of the six traps are valved in series for an adsorb cycle. When the first trap in line shows breakthrough, it is removed from service and another trap is valved in series. Breakthrough is again determined by external chemical analysis. The first NaF trap is then regenerated by heating the solid $NaF-UF_6$ complex to around 650°F. New NaF pellets can load greater than 0.5 lb UF_6/lb pellet. After several cycles, the physical pellet structure deteriorates and the uranium capacity drops to around 0.25 lb UF_6/lb pellet. Eventually, the pellets have to be replaced.

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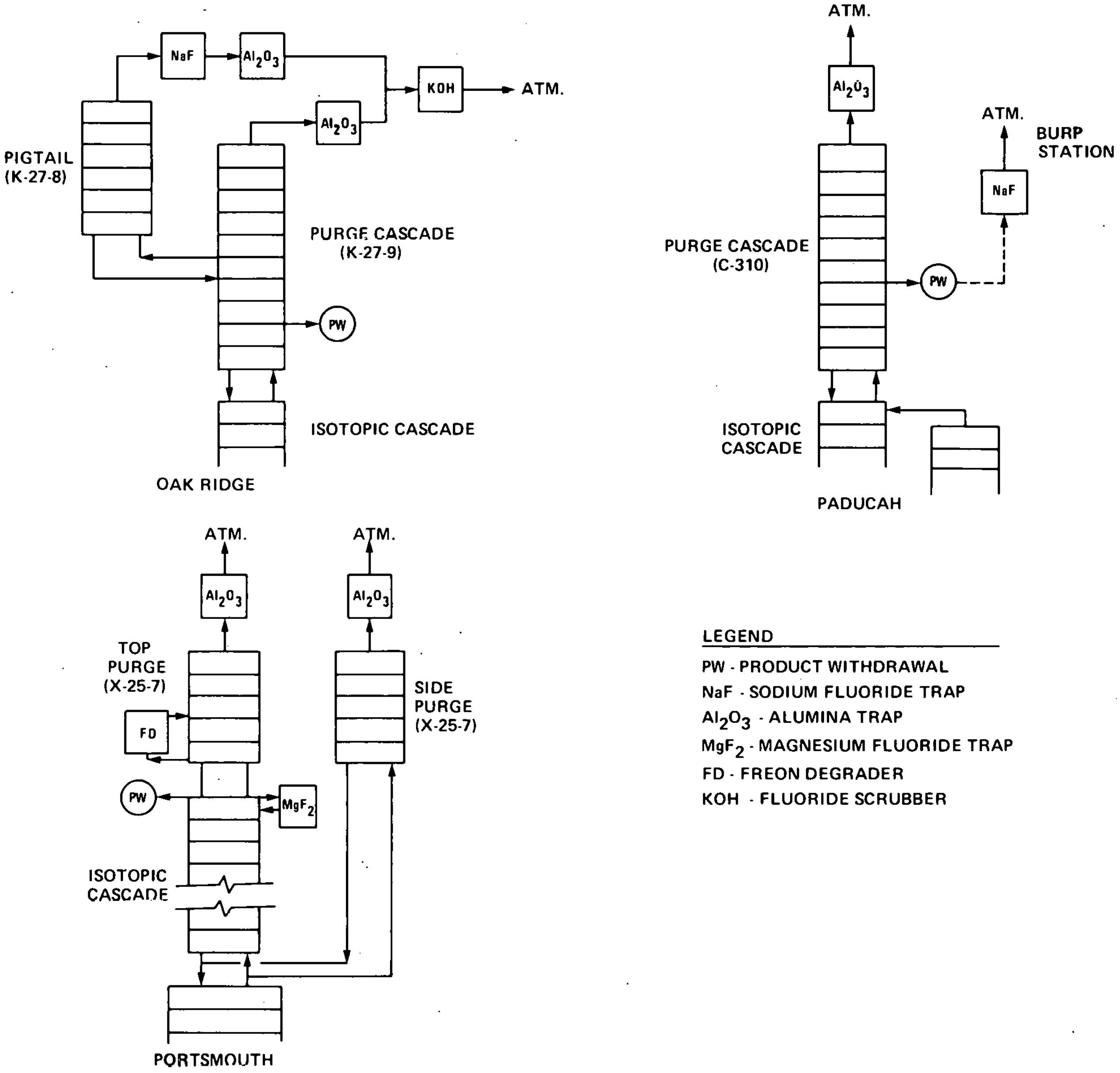
*Levins, D. M., et al., *Monitoring and Analysis of Process Streams in a Krypton-85 Off-Gas Decontamination System*, USDOE Report ORNL-TM-4923 (1975).



LEGEND

PW - PRODUCT WITHDRAWAL
NaF - SODIUM FLUORIDE TRAP
Al_2O_3 - ALUMINA TRAP
MgF_2 - MAGNESIUM FLUORIDE TRAP
FD - FREON DEGRADER
KOH - FLUORIDE SCRUBBER

Figure 5
SCHEMATIC OF THE THREE PURGE FACILITIES

Figure 6 shows the loading cycle of a new purge cascade, NaF trap taken by external gamma scanning. The trap was operated at a pressure of around 4 psia and temperature near 250°F. Scans were taken each day for 4 days. It is particularly striking to note how well the uranium movement can be followed through the bed. Breakthrough occurred shortly after the last scan. The length of the sorption zone appears to be around 3 feet for the particular operation. Once established, the sorption zone moved around 1 foot per day. As expected for a new bed, the uranium loading in the saturated part of the bed appears to be relatively uniform.

It is interesting to compare the profile of the new bed with one that has undergone numerous sorption-desorption cycles. Figure 7 shows the uranium profile of a trap removed from the cascade because of sharply declining performance. This particular scan was taken without insulation and the gamma detector was considerably closer to the bed in this case than the scan of the new bed. Consequently, the counts of the used bed are generally higher than those for the new bed. Only the loading shapes can be compared without a calibration factor to compensate for the relative difference in the probe location. While the loading profile in the saturated section of the new bed is relatively uniform, several regions of significantly reduced loading can be observed in the old bed. A very important conclusion can be drawn from this comparison: bed deterioration is grossly nonuniform. The uranium loading at the upper peaks of the bed was found to be a respectable 0.2 lb U/lb pellet. The low values, however, were around 0.05 lb U/lb pellet. High silicon contents were found in the regions of low uranium loading.

ALUMINA TRAPS

Alumina traps are used at the top of all three diffusion plant purge cascades. Oak Ridge uses two banks of four traps each, one in line and one in reserve. Breakthrough is determined by external chemical analysis of the trap effluent gas. The traps are then dumped and recharged. Alumina can load between 0.2 and 0.4 lb UF_6/lb pellet at saturation. The kinetics of the alumina/uranium trapping reaction are so slow, however, that the alumina traps contain only a small fraction of the saturated amount at breakthrough. Average loading values at breakthrough are in the 0.01 lb UF_6/lb pellet range.

Gamma scans of the four K-27-9 alumina traps are given in Figure 8. These traps are operated in parallel. It is particularly interesting to note the relative differences in the uranium contents of the beds. It is obvious that the parallel piping arrangement does not allow uniform flow distribution: the first trap in the arrangement appears to be receiving substantially more process flow, and hence uranium, than the second; the second more than the third; and the third more than the last. Breakthrough of the first trap will result in premature replacement of the other three beds in this case.

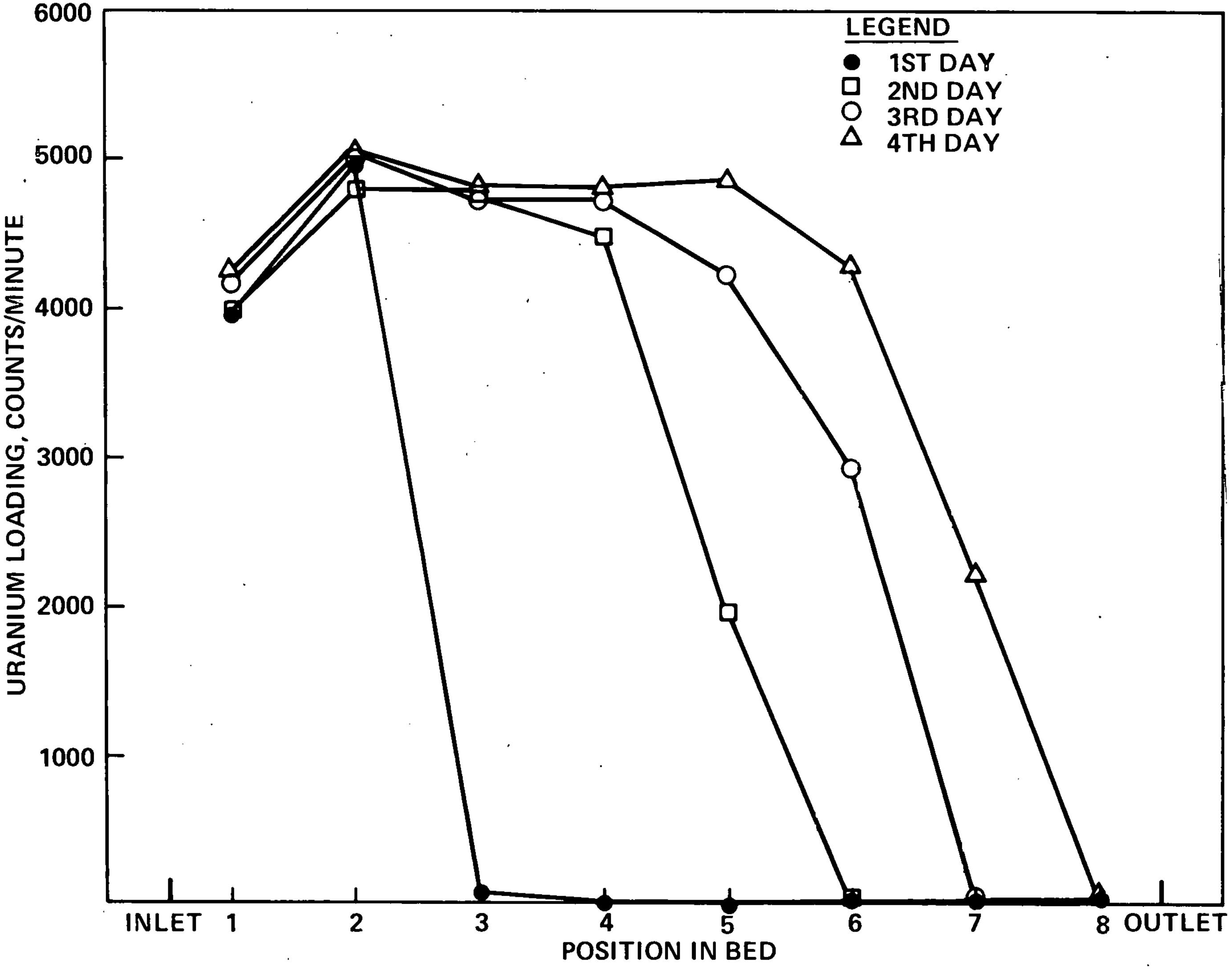


Figure 6

URANIUM LOADING PROFILE FOR A NEW NaF PURGE FACILITY CHEMICAL TRAP

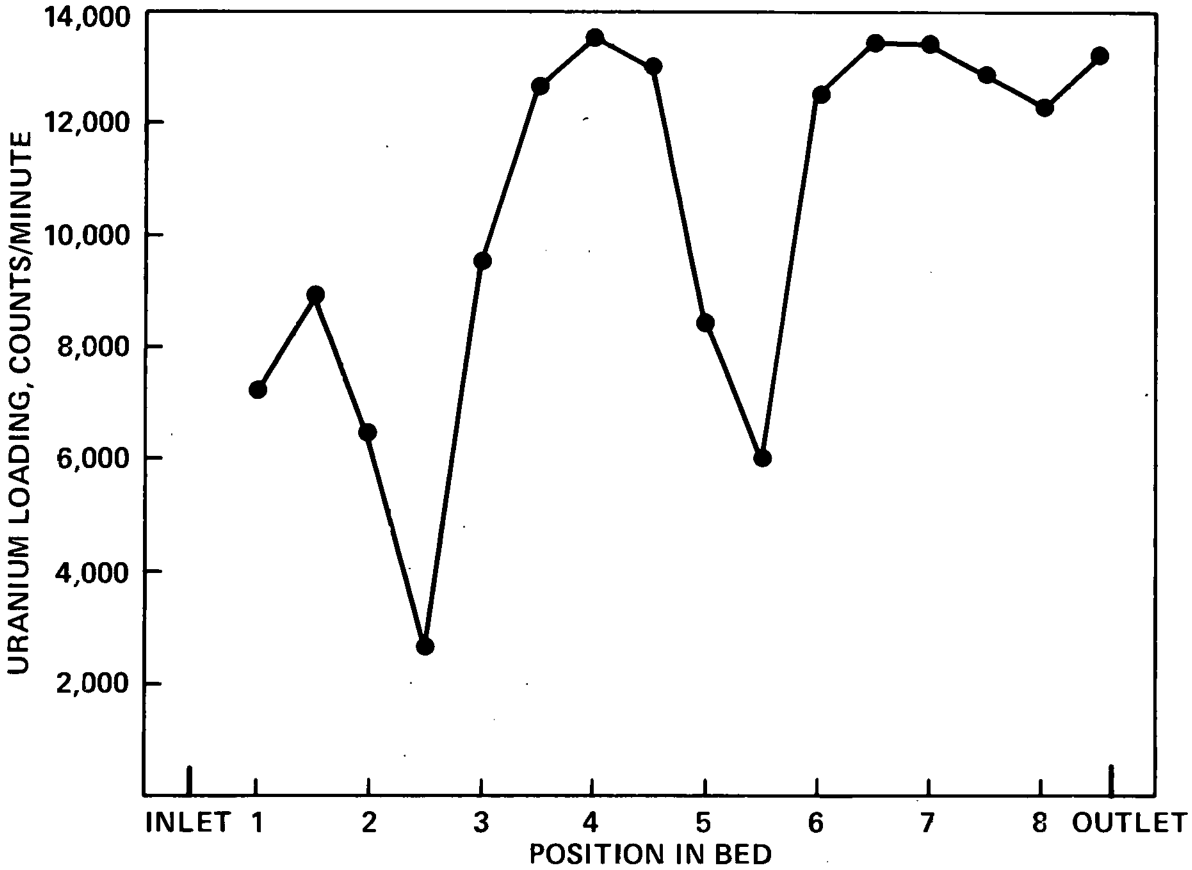


Figure 7

URANIUM LOADING PROFILE FOR A CHEMICAL TRAP REMOVED FROM SERVICE AFTER NUMEROUS CYCLES

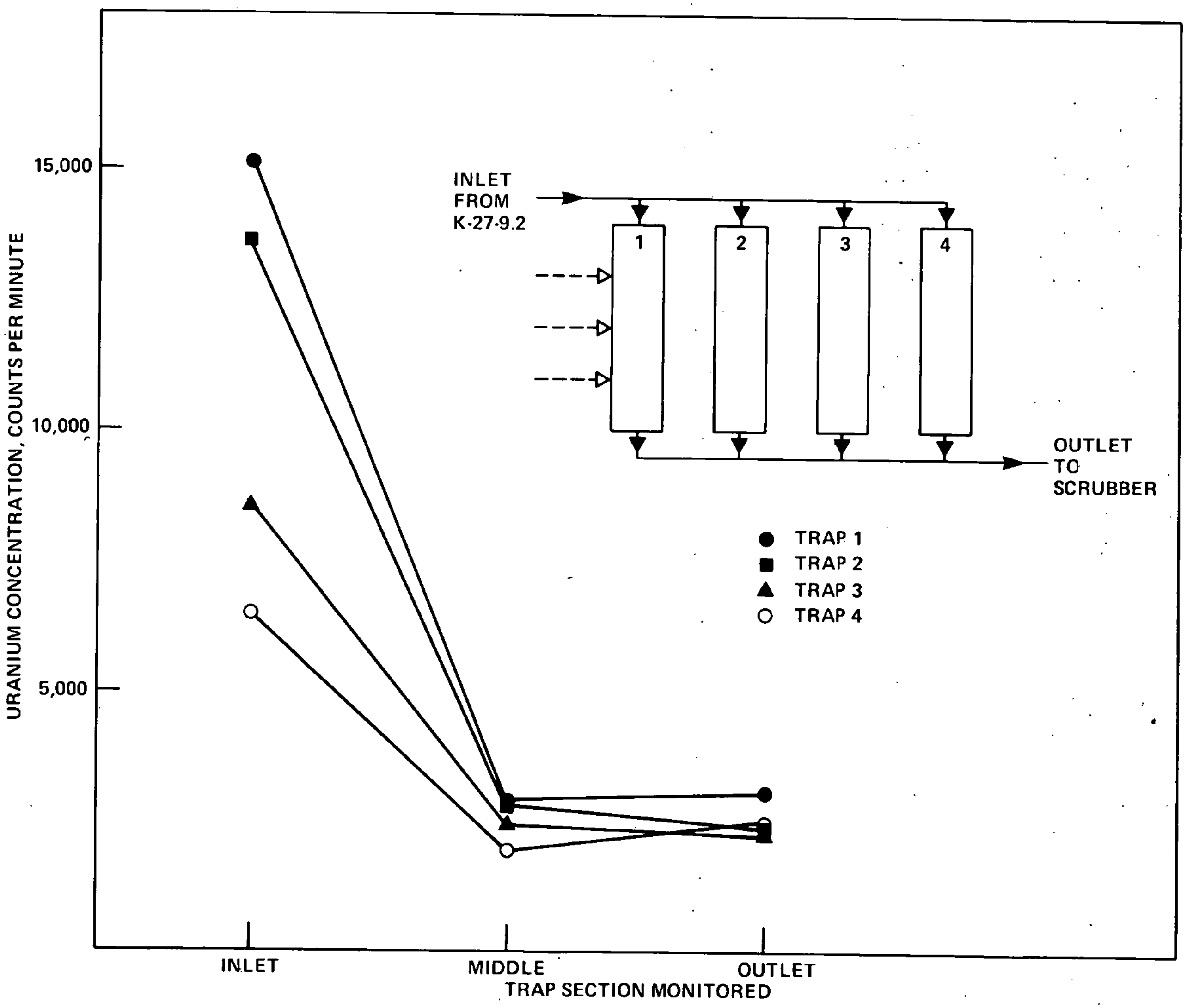


Figure 8

URANIUM LOADING COMPARISON OF FOUR-TRAP ALUMINA BANK IN PARALLEL FLOW

CONCLUSION

As shown by the initial investigations, gamma monitoring can be effectively used to provide unique analytical data that can aid in the overall management of uranium control processes. This information in particular can be used to optimize chemical trap performance to meet the increasingly stringent environmental regulations. Additional monitoring obviously needs to be performed before a more complete understanding of the bed deterioration can be obtained. Specifically, the trap loading profiles need to be followed through successive sorption-desorption cycles to ascertain where and when the diminished performance occurs, how fast the performance is lost, and whether or not the losses can be minimized or partly recovered through special treatment. All trap deteriorations ultimately will have to be correlated with the various activities of, and changes in, the diffusion cascade operation. Sufficient information has been obtained to show that gamma scintillation can be employed to provide other analytical services such as measuring cold trap loading profiles, detecting uranium deposits, and monitoring the movement of other gamma emitting components. When the field studies have been completed, the possibility of a continuous monitoring system with alarm and/or control capability for various enrichment plant effluent streams will be considered.

REFERENCES

1. R. S. Eby, *The Desublimation of Krypton for a Noncondensable Carrier Gas*, K-1896, September 1978.

2. D. M. Levins, et al., *Monitoring and Analysis of Process Streams in a Krypton-85 Off-Gas Decontamination System*, USDOE Report ORNL-TM-4923 (1975).

3. M. J. Stephenson, *Analysis of a Fractional Gas Stripper*, K-1895, December 1978.

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COOLING TOWER WINDAGE: A NEW ASPECT TO ENVIRONMENTAL ASSESSMENT[1]

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ABSTRACT

During the past decade the environmental impact of cooling tower drift on terrestrial environments has been a major consideration. Recent studies at the Paducah, Kentucky, Gaseous Diffusion Plant suggest that there is also a significant potential for aquatic impacts. Blowdown at the Kentucky and Oak Ridge Gaseous Diffusion Plants (ORGDP) is engineered for zero chromate discharges to receiving streams by either chromate reduction or chromate recovery procedures. Past operating experiences at the Paducah facility without chromated discharges resulted in violations of National Pollutant Discharge Elimination Systems (NPDES) permit standards for hexavalent chromium for which remedial action has since been taken. These episodes of noncompliance have been associated with high winds, cold weather, and tower operation without fan-induced draft. Under these circumstances, cooling water is lost from the sides of the tower instead of from the top as with drift, and transported to streams as runoff. This loss of cooling water, termed

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[1] Research sponsored by the Office of Health and Environmental Research and the Office of Uranium Resources and Enrichment, U.S. Department of Energy, under contract W-7405-eng-26 with Union Carbide Corporation. Publication No. 1549, Environmental Sciences Division, ORNL.

[2] Thermal Systems Development Section, Oak Ridge Gaseous Diffusion Plant, Oak Ridge, Tennessee 37830.

"windage," may impact the water quality of the regulated streams. Operating experiences at Paducah provided the impetus to quantify windage losses from the ORGDP cooling towers. Data are presented for the K-861 and K-892J towers under varying meteorological conditions, and the potential for NPDES noncompliance is discussed. Windage was measured volumetrically (effective windage) and calculated (true windage) from the total chromium residue present in each sample and the measured chromium concentration in the recirculating water system. A comparison between the two methods indicates that effective windage may introduce a significant bias due to evaporation (up to 30%) in assessing the chemical mass deposited. In a worst case example (wind gusting from 4 to 7 meters/second) windage losses from the new 78,000 gpm "J" tower ranged from 108.4 liters/m^2/hr at 0.5 meters distance to 0.9 liters/m^2/hr at 4 meters. This represents approximately 4500 gallons per hour. Estimates of true windage are derived from measured windage by correction for evaporation and thus is the more appropriate parameter for estimating total chemical release and for determining possible noncompliance with NPDES standards. Results of the research also have implications for power utilities since a common practice to prevent cooling tower icing is to operate without fan-induced draft.

INTRODUCTION

Recirculating cooling water (RCW) systems at Department of Energy (DOE) contractor-operated gaseous diffusion plants in Kentucky, Ohio, and Tennessee require the addition of a chromate, zinc-phosphate corrosion inhibitor for protection of copper in cooling condensers. For optimum protection a 20 ppm chromate concentration is maintained. During evaporative cooling cycles dissolved solids concentrate in the recirculating cooling water and must be removed to prevent scaling and deposition on heat exchangers. This is typically accomplished by periodic blowdown to receiving streams. Since the blowdown stream contains the same chemical concentrations as the recirculating cooling water system, cooling tower effluent constitutes a potential for impacts on water quality and stream biota.

In 1974 plant liquid effluents from DOE facilities were regulated to meet the National Pollutant Discharge Elimination System (NPDES) permit limits for hexavalent chromium by 1977. Before July of 1977 blowdown from the several cooling towers at the Paducah facility was discharged to Big Bayou and Little Bayou Creeks, and to the Clinch River at Oak Ridge. At that time (1977) blowdown treatment was engineered for zero chromate discharges through a recovery-recycle softener procedure at Oak Ridge and a chromate reduction procedure at Paducah (C-616 Plant Liquid Effluent Pollution Control Facility). The recovery-recycle system uses lime and soda ash (softening) to reduce calcium hardness and ionic polymers for clarification. Chromate concentration is unaffected by the softening with the resultant sludge returned to make-up clarifiers for recycle (Koteski and Vaughn, 1979). At Paducah hexavalent chromium is reduced to trivalent chromium by addition of ferric sulfate to the blowdown effluent and subsequently precipitated in a clarifier using lime. The clarified water is discharged to a settling lagoon before releasing to Big Bayou Creek.

In September of 1977 chromium concentrations in Little Bayou Creek occasionally exceeded permit limits (0.05 ppm Cr^{+6}), even though there were no discernable chromate discharges to the creek (Conrad, 1979). These episodes of non-compliance with NPDES standards were associated with high winds, cold weather, and tower operation without fan-induced draft. Operation of the cooling towers without fans is sometimes effected to maintain a minimum required temperature for the enrichment cascade. Under those conditions, it was noted that the loss of cooling water from the sides of the towers was detectably greater than during operation with fans on. Water lost in this manner, termed "windage" (Conrad, 1979), was found to be greater from newly constructed towers (counterflow) designed for high performance fill, than from the older, cross-flow towers. Windage water was subsequently transported to streams as runoff where water quality was adversely impacted. As an abatement strategy, wind screens were placed in the new towers and concrete aprons were constructed to reduce windage losses.

The results of the field studies at Paducah provided the impetus to determine if windage was also a problem at Oak Ridge and to assess the potential for compliance with NPDES standards. A series of field studies were conducted at the Oak Ridge K-25 plant's new 78,000 gpm K-892J tower and the new cell added to the K-861 tower during varying meteorological conditions. Aside from being site-specific, the data have generic application for power utilities since a common practice to prevent cooling tower icing is to operate without fan-induced draft.

METHODS

In studies conducted at the Paducah site, windage water was collected as wetfall along a distance gradient from the tower base and the results were expressed as precipitation (cm depth per hour). Sample collections were made at Oak Ridge by placing 50 ml of distilled water in glass collectors (12 cm dia. x 6 cm deep) at distances of 0.5, 2, 4, and 10 meters from the K-892J tower (Fig. 1) and at 0.5, 2, 4 and 8 meters from the K-861 tower. In a test of cell 17 only (add-on to K-861) sampling stations were arranged to 10 meters distance. The blank solution was added to each collector to prevent adherence of the chromium residue to the collector surfaces and possible error in subsequent chemical analyses. Depth (height of the water column) was calculated from the relationship of the volume, less than 50 ml blank, to the diameter of the collector, and termed effective wetfall windage. Pilot studies indicated that evaporation might be an important consideration in volumetric determinations. Since evaporative processes would not affect the total chemical residue in the samples, true windage volume was calculated from the total chromium present in each sample, and the measured chromium concentration of the recirculating water system. Each water aliquot was analyzed by atomic absorption spectrophotometry with graphite furnace attachment for microdeterminations. Results were expressed as true wetfall windage (cm depth/hr) and windage flux (liters/m^2/hr).

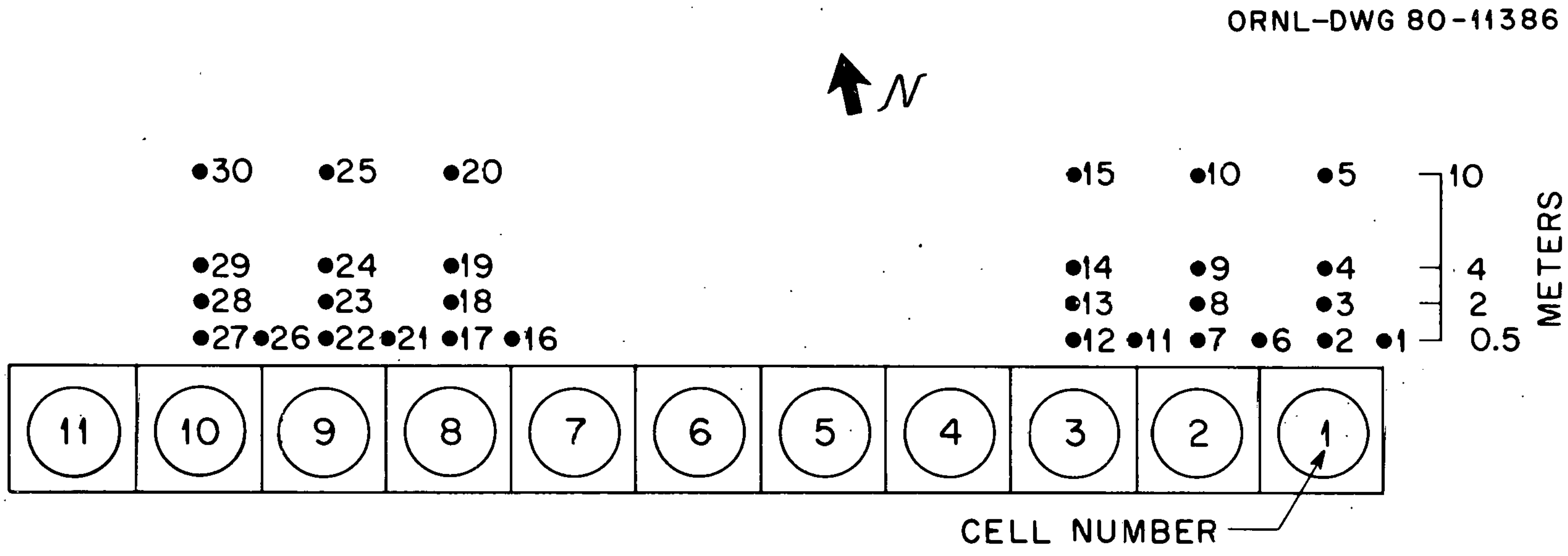

Figure 1. Windage sampling locations adjacent to the K-892J cooling tower. Drawing is not to scale.

RESULTS

The initial windage study was conducted in December 1979 at the newly constructed K-892J tower, which is of a counter-flow design, and consists of eleven cells utilizing high performance fill packing. The long axis of the tower is oriented east and west. The tower is 100 meters long, 12.8 meters wide, and 7.6 meters high. Diameter of the air exits is 7.3 meters. On the day samples were collected, three cells were operated without fans while three additional cells operated normally (fans on). Five cells were not in operation. The wind was from the south, southwest with gusts from 4 to 7 meters per second (10 to 16 mph). After nearly four hours exposure, it was noted that collectors adjacent to cells operating with fans on contained less water than the initial volume (50 ml blank). This suggested that evaporation was a significant consideration. The collected volume was measured, depth (wetfall) calculated and the results tabulated as effective windage volume. Samplers adjacent to cells operating without fans collected water very rapidly. In addition to the volumetric measurements, windage was also calculated from the total chromium residue present in each sample and the measured chromium concentration of the recirculating water system. Since evaporative processes would not affect the chemical residue in the samples, windage determined chemically was considered representative of true windage. A comparison of results from the two methods (Table 1) indicates that estimates of effective windage contain a significant negative bias (30%) in assessing the magnitude of the wetfall. Maximum effective windage (10 cm/hr)

Table 1. Comparison Between Effective and True Windage Volume and Wetfall from the K-892J Tower and with Fans Off.

Station	Distance (meters)	Exposure (hrs)	Effective Windage Volume (ml)	True Windage Volume (ml)*	Evaporation (%)	Effective Wetfall (cm/hr)	True Wetfall (cm/hr)
16	0.5	0.57	395	420	5.95	6.13	6.52
17	0.5	0.37	430	576	25.35	10.28	13.77
18	2.0	2.67	195	201	2.99	0.65	0.67
19	4.0	3.28	5	22	77.27	0.01	0.06
20	10.0	3.33	—**	—	—	—	—
21	0.5	0.38	375	482	22.20	8.73	11.21
22	0.5	0.38	465	515	9.71	10.82	11.98
23	2.0	2.72	335	445	24.72	1.09	1.45
24	4.0	3.32	23	38	42.11	0.06	0.10
25	10.0	3.35	—	—	—	—	—
26	0.5	0.42	470	624	24.68	9.89	13.14
27	0.5	0.43	335	423	20.80	6.89	8.71
28	2.0	2.77	320	288	—	1.02	0.92
29	4.0	3.37	30	36	16.67	0.08	0.09
30	10.0	3.38	—	—	—	—	—

*Calculated from the total chromium content of the sample and the known concentration in RCW system.

**Indicates no windage water collected.

measured adjacent to the tower (0.5 meters) was comparable to wetfall measured at the Paducah facility (Conrad, 1979), whereas true windage indicated a maximum of 14 cm/hr. Effective windage during operation with fans on was not measurable. However, windage calculated from the chemical residue indicated that a small quantity of water was falling. This small fraction was likely in the form of drift droplets of large diameters (500 to 2500 μm).

The data were further summarized as windage flux to the ground (liters/m^2/hr) and best fit curves plotted (Integrated Software Systems Corporation, 1970) using spline functions described by Reinsch (1967). Results from the K-892J tower during operation with fans on and fans off are depicted in Fig. 2. Wind was from the south, southwest from 4 to 7 meters/second ($\overline{X}$ = 5 m/s). The majority (>95%) of the windage water was deposited (fans off) within 5 meters from the tower base. Losses from cells operating with fan-induced draft depict water entrained in the exit air flow and deposited as drift. The point of intersection of the two curves (8 meters) represents the maximum distance windage was transported from the tower. At the K-892J tower the windage water drains to an open ditch and is transported to Poplar Creek. The windage runoff contains 9 ppm hexavalent chromium and therefore constitutes a violation of the National Pollutant Discharge and Elimination System as an unpermitted discharge. In order to estimate the total chromium deposited as windage (fans off), the areas under the curves were integrated over the distance from the tower (10 meters) and along the length (100 meters) of the tower, assuming no end effects. This represents a worse case example since all 11 cells would be in operation

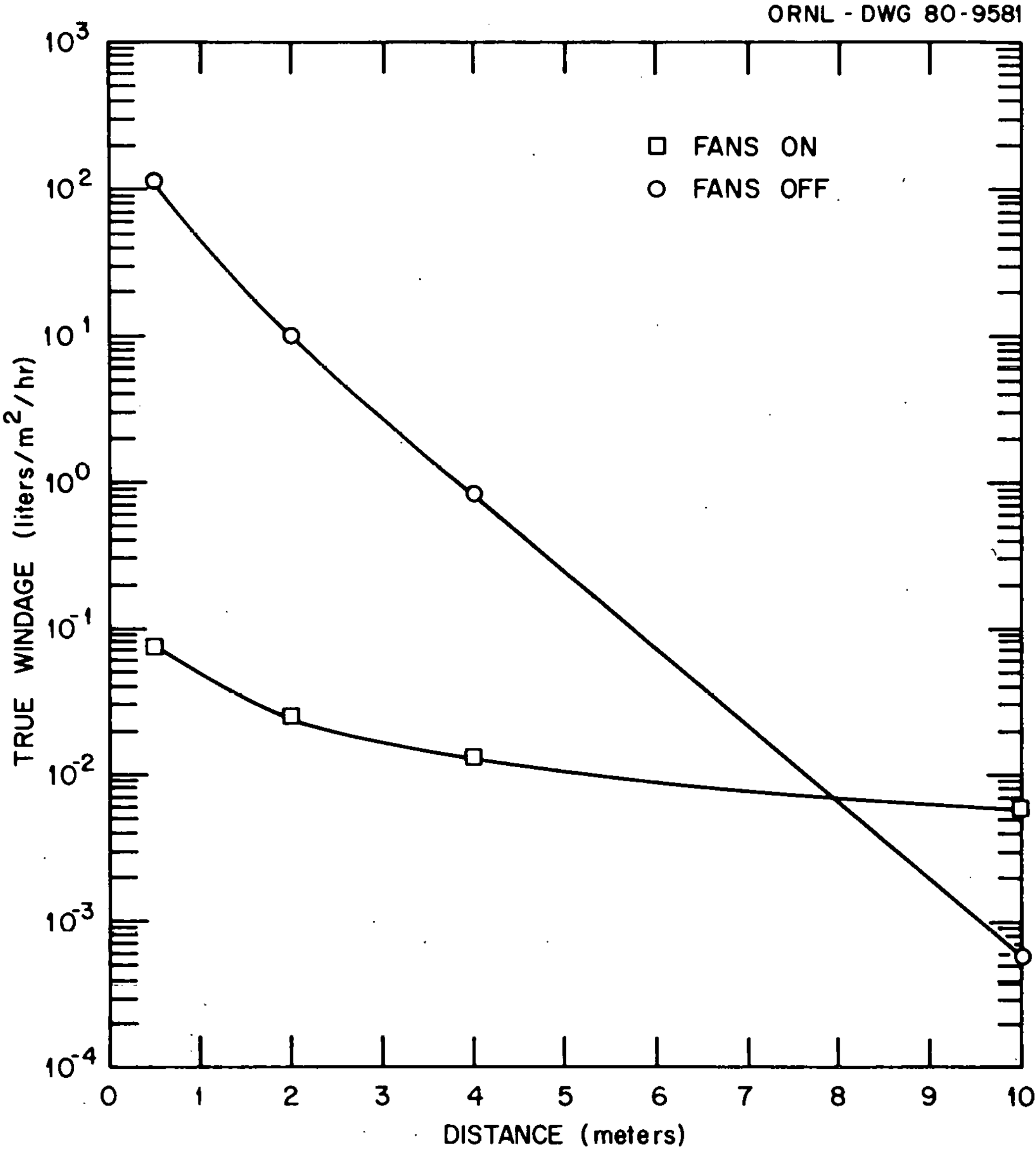

Figure 2. Windage from the K-892J cooling tower on December 7, 1979. Wind was from the SSW at 4 to 7 meters/second ($\overline{X}$ = 5 m/s).

without utilizing the fans. Total hexavalent chromium discharged through the windage was calculated by assuming a 9 ppm water concentration. Under the meteorological conditions of the first study (December) it is estimated that 1.7 x 10^4 liters of chromium laden water was lost per hour of operation. This represents approximately 153 grams of hexavalent chromium that may eventually impact water quality of Poplar Creek. The windage phenomena is primarily restricted to cold season months (November through March). After the chromium reaches Poplar Creek it is diluted well below EPA standards (0.05 ppm).

A second study was conducted on the K-892J tower in January during slightly different meteorological conditions. Winds were from the west, southwest at 2 to 6 meters per second ($\overline{X}$ = 3.5 m/s). The data were resolved as best fit curves by spline interpolation and yielded curves similar to the previous example. Average wetfall was calculated to be 12.24 ± 2.04 cm/hr at 0.5 meters. The greatest distance windage water was observed to be transported was 7 meters. Beyond that distance drift (fans on) was considered to be the major source of cooling water deposition (Fig. 3). Total windage water was estimated to be 1.5 x 10^4 liters/hour. This represents approximately 132 grams of hexavalent chromium which was transported to Poplar Creek as runoff.

In addition to studies at the newly constructed K-892J tower, similar investigations were conducted at the existing K-861 cooling tower and a newly constructed add-on cell (cell 17). The K-861 tower has been in operation for nearly three decades. It is 117 meters long, 7.4 meters high, and 19 meters wide. There are 16 cells with an

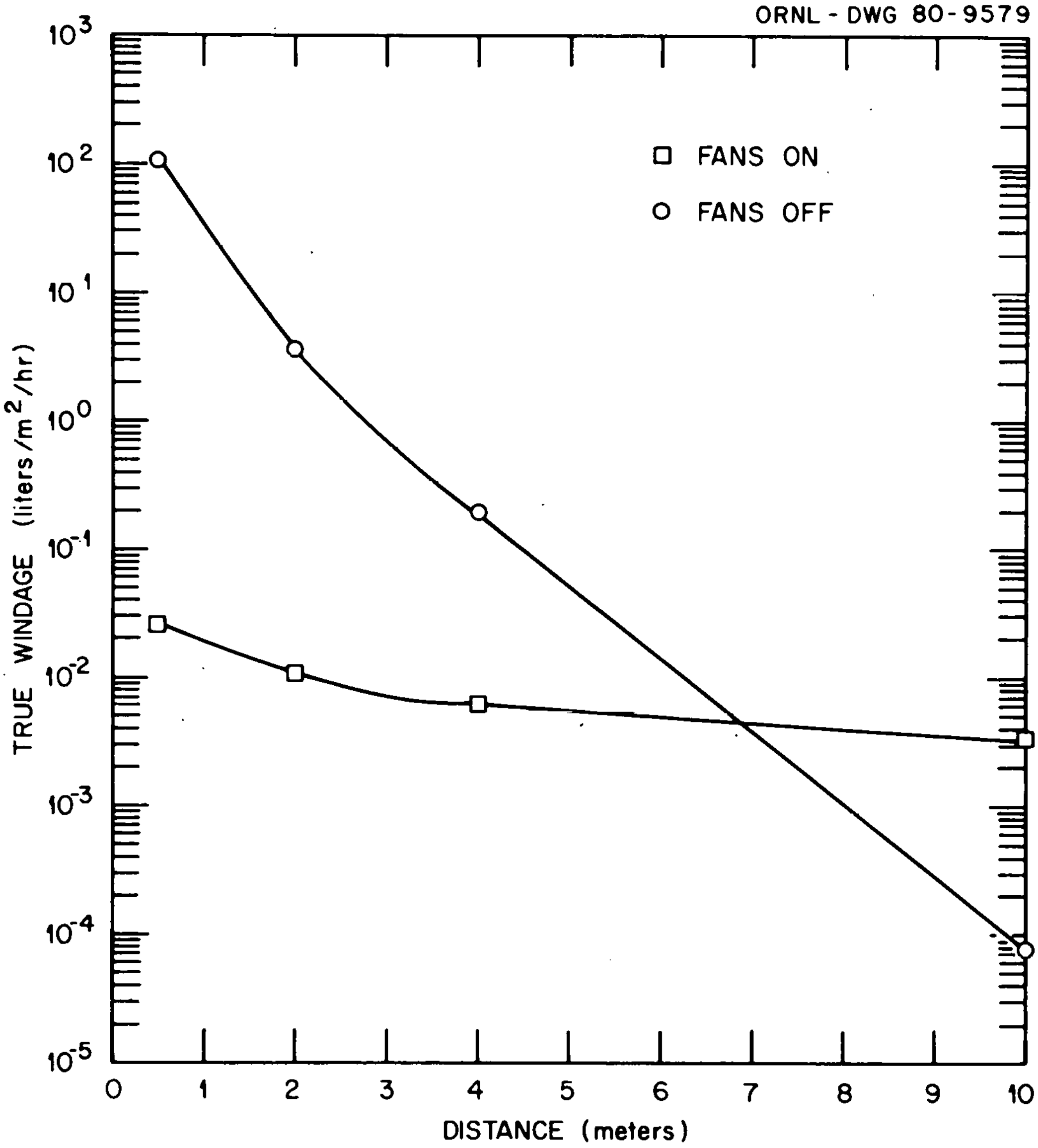

Figure 3. Windage from the K-892J cooling tower on January 25, 1980. Wind was from the WSW at 2 to 6 meters/second ($\overline{X}$ = 3.5 m/s).

air exit diameter of 6.8 meters. The cell 17 add-on tower has similar dimensions to individual cells of the K-892J tower. The add-on cell contains high performance fill material, whereas the older K-861 tower contains conventional splash bar (wooden) fill. Windage estimates during fans off operation (wind 2.4 m/s) depict the cell 17 add-on, whereas fans on data represent the older tower. Average wetfall was calculated to be 5.12 ± 1.37 cm/hr at 0.5 meters distance. Maximum distance of windage impact (4.7 meters) is indicated at the point where windage (fans off) and drift (fans on) loss curves intersect (Fig. 4). Total windage was estimated to be 1.33×10^3 liters/hr from the add-on cell.

A final test was conducted on January 16, 1980, at the cell 17 add-on tower during operation with fan-induced draft and without fans. Wind was from the southwest at 0.2 to 4 meters/second ($\overline{X} = 0.8$ m/s) during operation with fans off. Data with fans on operation depict drift losses whereas losses without fans represent windage. The maximum distance of windage transport was 2.5 meters (Fig. 5). Wetfall was < 0.5 cm/hr at 0.5 meters distance and total windage was estimated to be < 45 liters/hour.

Since drift does not contribute significantly to runoff, the point where windage flux is equal to drift flux becomes important to predict the greatest distance of windage transport. The relationship of windage transport (distance) to wind speed is described by the linear model, $Y = 1.6 + 1.36X$, and is depicted in Fig. 6.

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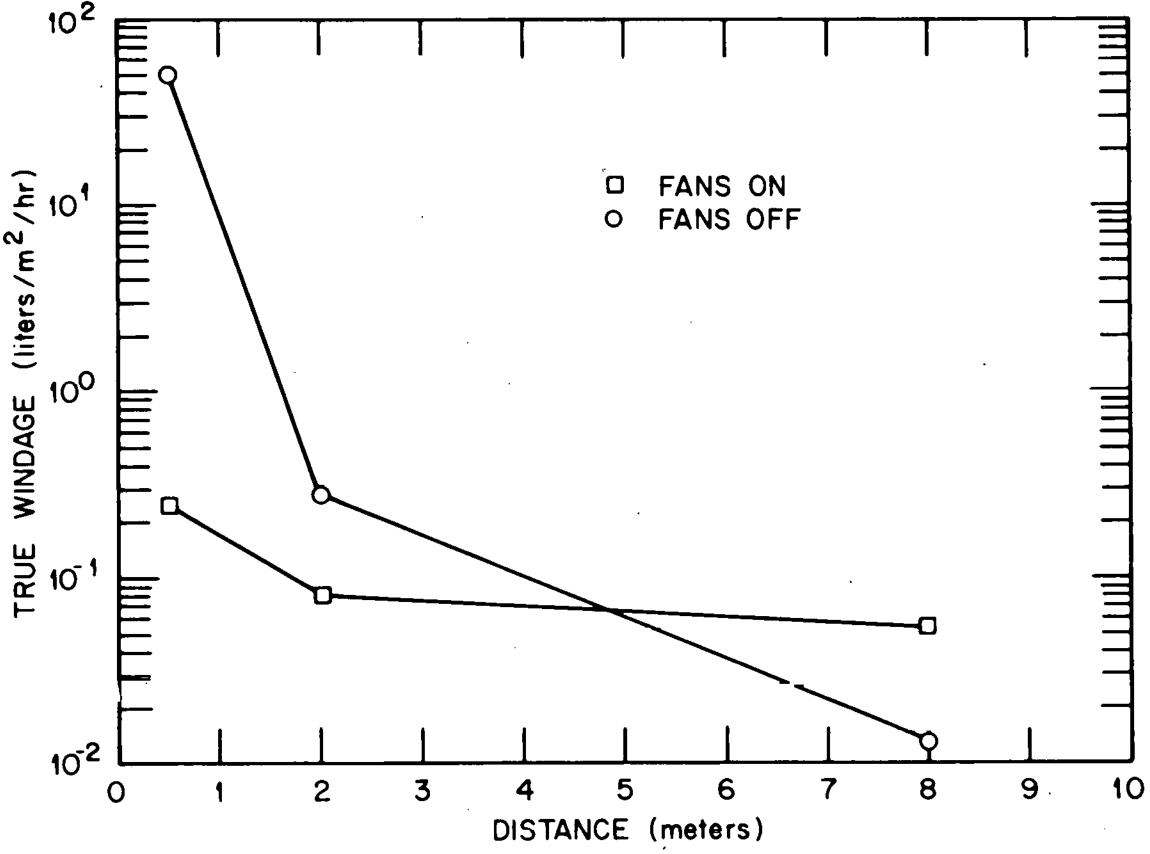

Figure 4. Windage from the K-861 cooling tower on January 8, 1980. Wind was from the NE at 1 to 3.5 meters/second ($\overline{X}$ = 2.4 m/s). <u>Fans off</u> operation is for the cell 17 add-on tower, whereas <u>fans on</u> operation represent the older tower.

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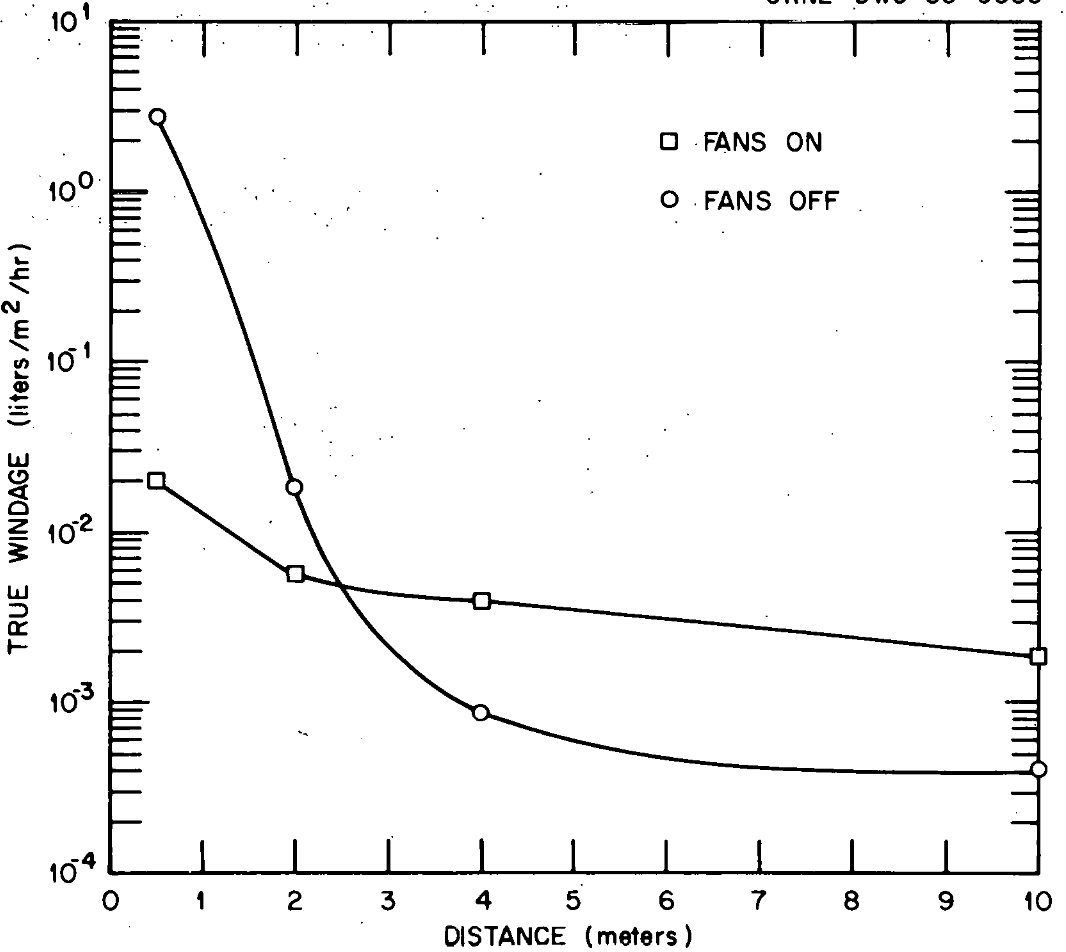

Figure 5. Windage from the cell 17 add-on tower (K-861) on January 16, 1980. Wind ranged from 0.2 to 4 meters/second ($\overline{X}$ = 0.8 m/s) from the SW during fans off operation, and from 0.2 to 3.3 meters/second ($\overline{X}$ = 0.4 m/s) from the West and the South during fans on operation.

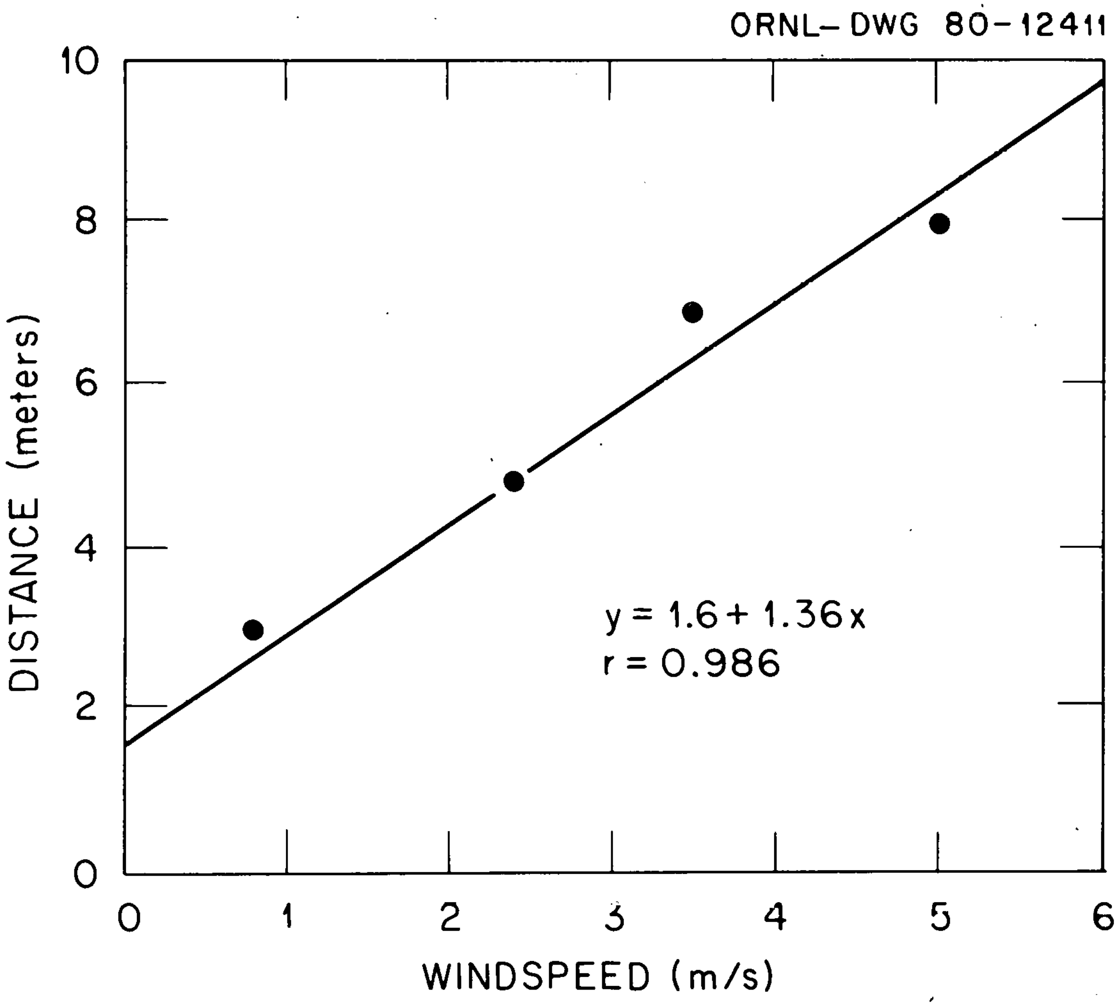

Figure 6. Relationship of windage transport (distance where windage flux is equal to drift flux) and wind speed.

CONCLUSIONS

Results of the several investigations presented herein have provided quantitative estimates of windage from Oak Ridge Gaseous Diffusion Plant cooling towers. Windage water deposited on the ground has the potential to reach nearby streams through runoff. Windage deposited on moisture depleted soils would not be significant. During winter months at Oak Ridge soils generally have a high moisture content such that windage deposition could be quickly transported as runoff. It is during this time that cooling towers are sometimes operated without fan-induced draft. Since windage water contains the same hexavalent chromium concentration (9 ppm) as the recirculating cooling water system, the runoff stream from the K-892J tower constitutes a NPDES violation as an unpermitted discharge. As a long-term abatement strategy, concrete aprons were constructed along each side of new cooling towers at the Paducah, Kentucky Gaseous Diffusion Plant. The maximum distance of windage impact is wind dependent. If apron construction is envisioned as an abatement strategy at Oak Ridge, the maximum distance of impact can be inferred graphically from the several points where windage (fans off) and drift (fans on) loss curves intersect under the different meteorological conditions. Once the hexavalent chromium laden runoff stream reaches Poplar Creek, it is diluted well below the standards for drinking water and poses little potential for biological effects to aquatic systems.

ACKNOWLEDGEMENTS

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LITERATURE CITED

Conrad, M. C. 1979. Chromium transport to surface streams from cooling tower windage. IN Compilation of papers presented at the 1979 UCC-ND Waste Management Seminar. Report Number K/C-1347, pp. 107-114.

Integrated Software Systems Corporation. 1970. *DISSPLA*: Display Integrated Software System and Plotting Language. Vol. 1, Beginners and Intermediate Manual. Vol. 2, Advanced Manual, San Diego, California.

Koteski, R. A. and Vaughn, B. E. 1979. Recirculating cooling water blowdown treatment at the Oak Ridge Gaseous Diffusion Plant. IN Compilation of papers presented at the 1979 UCC-ND Waste Management Seminar. Report Number K/C-1347, pp. 65-78.

Reinsch, C. H. 1967. Smoothing by spline function. Numerische Mathematik 10: 177-183.

EVALUATING FATE AND POTENTIAL RADIOLOGICAL IMPACTS OF ^{99}TC RELEASED TO THE ENVIRONMENT*

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J. W. Huckabce,[3] and T. G. Scott[4]

ABSTRACT

Tecnetium-99 (beta energy = 0.292 MeV and radioactive half-life = 2.1 x 10^5 years) is a major fission product contained within recycled uranium fuel. The use of plant/soil concentration ratios (CR) derived from laboratory pot experiments to assess the radiological impact of ^{99}Tc released from uranium enrichment facilities can result in estimates of potential dose which approach or exceed current U.S. EPA Uranium Fuel Cycle Standards. The appropriateness of adopting these laboratory derived values of CR for radiological assessment calculations needs to be tested against comparable field data on the behavior of technetium in soils and vegetation. To obtain information on the behavior of technetium under field conditions, we sampled soils and herbaceous vegetation, mostly fescue, near uranium enrichment facilities. The measurement of ^{99}Tc concentrations in soils and vegetation necessitated the development of techniques for radiochemical analysis which were checked for accuracy using isotope dilution mass spectrometry. We also evaluated the fate of ^{95m}Tc sprayed on bare soil and stands of mixed herbaceous vegetation in separate field experiments. In these experiments the CR value for technetium decreased with time, indicating a diminished availability for uptake into vegetation from soil. The transfer of technetium from soil to vegetation, determined from both ^{95m}Tc field exerpiments and the ^{99}Tc measurements near uranium enrichment facilities is approximately one to two orders of magnitude less than CR values obtained from laboratory experiments. Our data indicate that the radiological impact as a consequence of vegetation uptake of ^{99}Tc should be significantly less than indicated by assessments based on previous data.

(Paper not available for publication)

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UF_6 CONTAINMENT STUDIES: CONTROLLED RELEASES IN GAT ENVIRONMENTAL CHAMBER

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GOODYEAR ATOMIC CORPORATION

Uranium Hexafluoride - Releases
Uranium Hexafluoride-Cloud Formation
Uranium Hexafluoride-Containment Studies

ABSTRACT

Releases of gaseous UF_6 into static atmosphere at ambient environmental chamber test conditions with relative humidities varying from of 9-90% and temperatures of covering range 0°-40°C, have shown that changes in temperature and humidity do not significantly affect UO_2F_2 particle size formation (1-3 micron diameter) or the slow release cloud settling time (0.1 mm/second). Typical gas release particulate clouds have been studied using sequential photographs and motion pictures.

The second stage of study, which involves gas release into dynamic airflow, is now underway. Experiments involving simulated liquid UF_6 container rupture, spill size exceeding the available UF_6/moisture hydrolysis capacity, and various cloud knockdown techniques are currently in the planning stages.

INTRODUCTION

One the of recommendations of the Three-Plant UF_6 Cylinder Handling Committee was that experimental studies be made to evaluate different procedures and methods for use in the containment of UF_6 releases.[1] Subsequent to this recommendation, a three-plant committee of development personnel determined that there was a need for basic development effort to evaluate UF_6 containment methods, and to provide design information for UF_6 containment systems.[2] UCCND-Paducah was assigned the responsibility of evaluating scrubbers to remove airborne UF_6 release products. A concurrent GAT line item technical support plan cited the following objective: "to test presently used methods of containing a UF_6 release and develop, if needed, alternative methods of containment." Included in this general objective are the following specific objectives: (1) characterize the reaction between UF_6 and water; (2) determine the effects of environmental conditions of UF_6 cloud formation and eventual fate; (3) analyze the effects of water and/or steam sprays for UF_6 containment and recovery with special emphasis placed on nuclear safety; (4) evaluate other proposed containment methods (e.g., carbon dioxide, non-aqueous solvents, other chemical treatments); and (5) determine the best methods of recovery or disposal of products resulting from containment efforts.[3]

Having completed phase one, UF_6 gas release tests into static atmospheres, the work is currently into phase two study of UF_6 releases into dynamic atmospheric conditions simulating wind effects on UO_2F_2 cloud dispersal. Releases simulating liquid UF_6 container rupture, spill sizes exceeding available UF_6/moisture hydrolysis capacity, and cloud knockdown experiments will follow.

ENVIRONMENTAL CHAMBER

A technical support project, "UF_6 Containment Studies," was approved on April 2, 1975. GAT representative made trips to Edgewood Arsenal, Maryland, and Baton Rouge, Louisiana to evaluate environmental chamber designs and to discuss operational problems. After numerous shipping delays, complicated by train wreck damage enroute, the enclosure was received from Scientific Systems of Baton Rouge, in late 1978. Assembly and testing were completed by April of 1979. Figure 1 is an overall view of the containment chamber as it appears today. The interior dimensions are nine feet by sixteen feet by eight feet high, giving an approximate volume of 1,160 cubic feet. The air handling system is capable of controlling temperature and humidity (dew point) independently in the range of -5 to 45°C controllable to within ±0.4°C. Within these temperature-humidity ranges (near zero to 100% relative humidity), any climatic conditions anticipated for a plant location can be simulated. Observation windows are located in the sides, the door, and the top of the chamber. Sealed fluorescent lights provide interior illumination. The air handling unit is protected

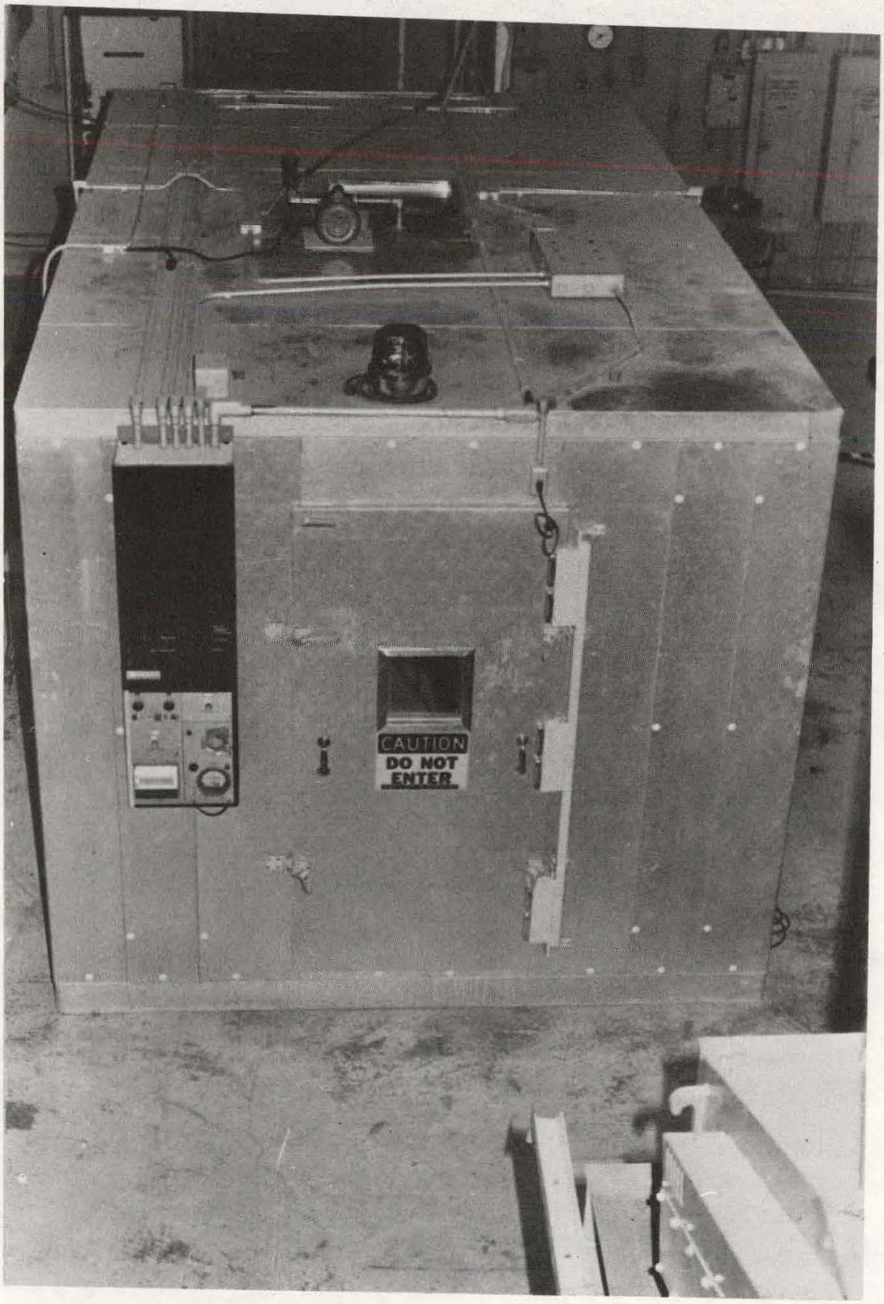

FIGURE 1 UF$_6$ CONTAINMENT CHAMBER

from contamination by the use of activated carbon and HEPA filters. All interior surfaces are constructed either of Type 304 stainless or of plexiglass for corrosion resistance. Decontamination is accomplished by pumping solution from a 50 gallon reservoir through a rotating spray nozzle mounted in the chamber ceiling. Figure 2 shows the decontaminating spray head inside the chamber. This spray system readily cleans interior chamber surfaces to background count.[4] Releases that are smaller than 20g tails assay UF_6 are flushed with 40-50 gallons of water to a neutralization pit having a limestone leach bed. Decontamination solutions from larger releases are pumped to drum storage and transferred to X-705 uranium recovery operations.

EXPERIMENTAL

Following a tails assay UF_6 release, samples of the resulting hydrolysis cloud are obtained at predetermined times on nucleopore filters housed and protected in plexiglass sampling boxes located inside the chamber. Sample box lids are vacuum operated, and controlled from outside the containment chamber. Figure 3A shows the sample boxes, while Figure 3B shows the box lids in the activated and deactivated states. After decontamination of the interior of the chamber, the filters are removed from their protective sampling boxes for particle size and composition analysis by scanning electron microscopy.

The first recorded release for which data were obtained, took place on May 10, 1979. 1.8 grams of UF_6 were released into the chamber with an air temperature of 22°C and a dew point of -2°C. This gives a relative humidity of about 20%. Samples were taken of the resulting particulate, and it was noted that the major portion of the particulate matter was in the 0.81 to 1.10 micron range. In eleven releases which have followed, we have found this general range of results to be representative. A number of these releases have been photographed both in still and motion pictures.

Figure 4 is a composite print of 35 mm stills, photographed in real time at a rate of 1 exposure per second. A layering effect, or stratification of the cloud, can be seen. It is most evident in later exposures of the sequence.

RESULTS

Twelve releases have been recorded, ranging in mass from just under two grams to just over 20 grams tails assay UF_6, into static atmospheric conditions with temperatures between 15° and 40°C, and dew points from -2° to 30°C. There were no significant differences found in the UO_2F_2 particle size formation (1-3 microns in diameter), or in release cloud settling rates (0.1 mm/sec.). Figure 5 is a representative bar graph indicating percent distribution vs. UO_2F_2 particle

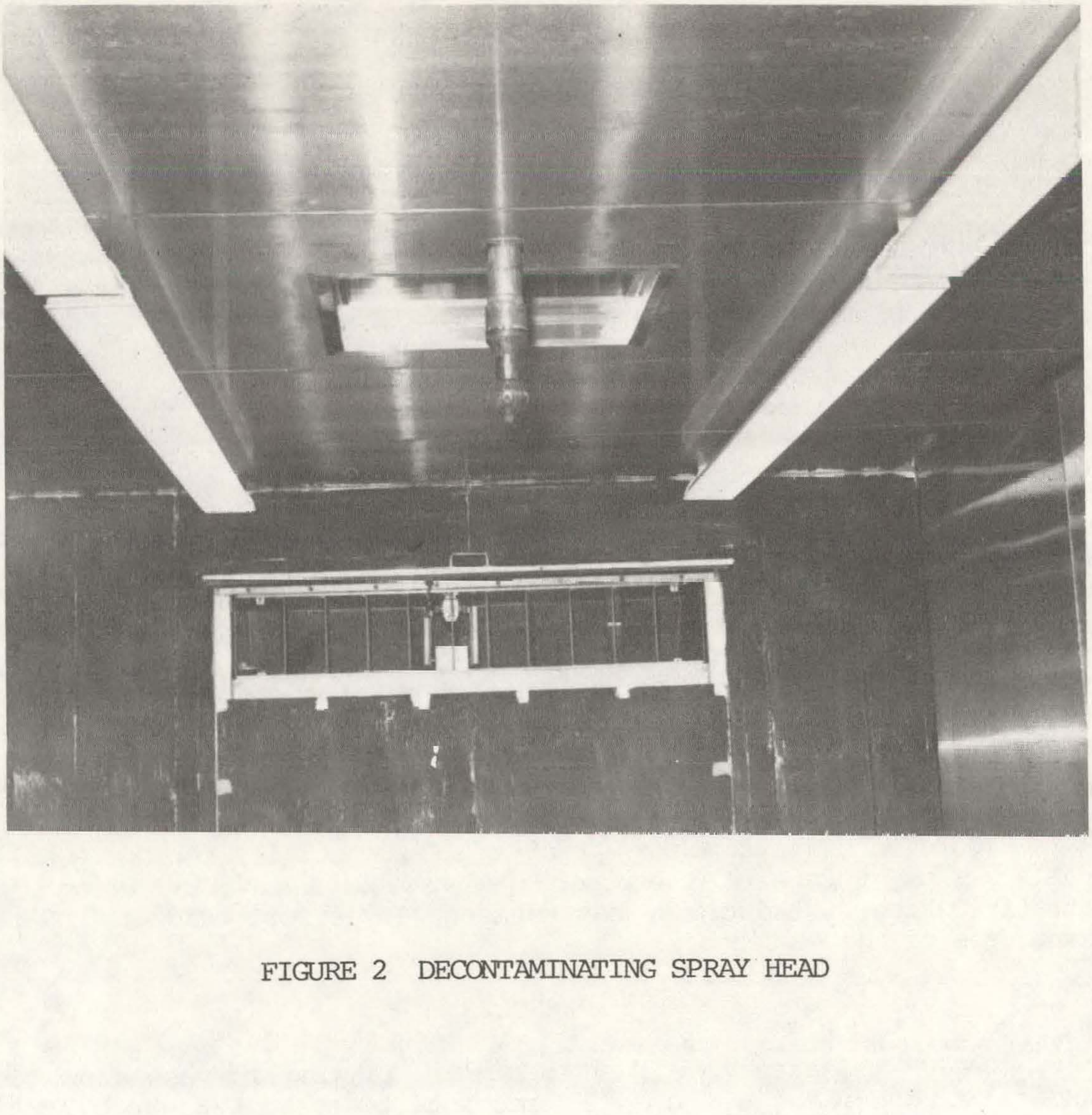

FIGURE 2 DECONTAMINATING SPRAY HEAD

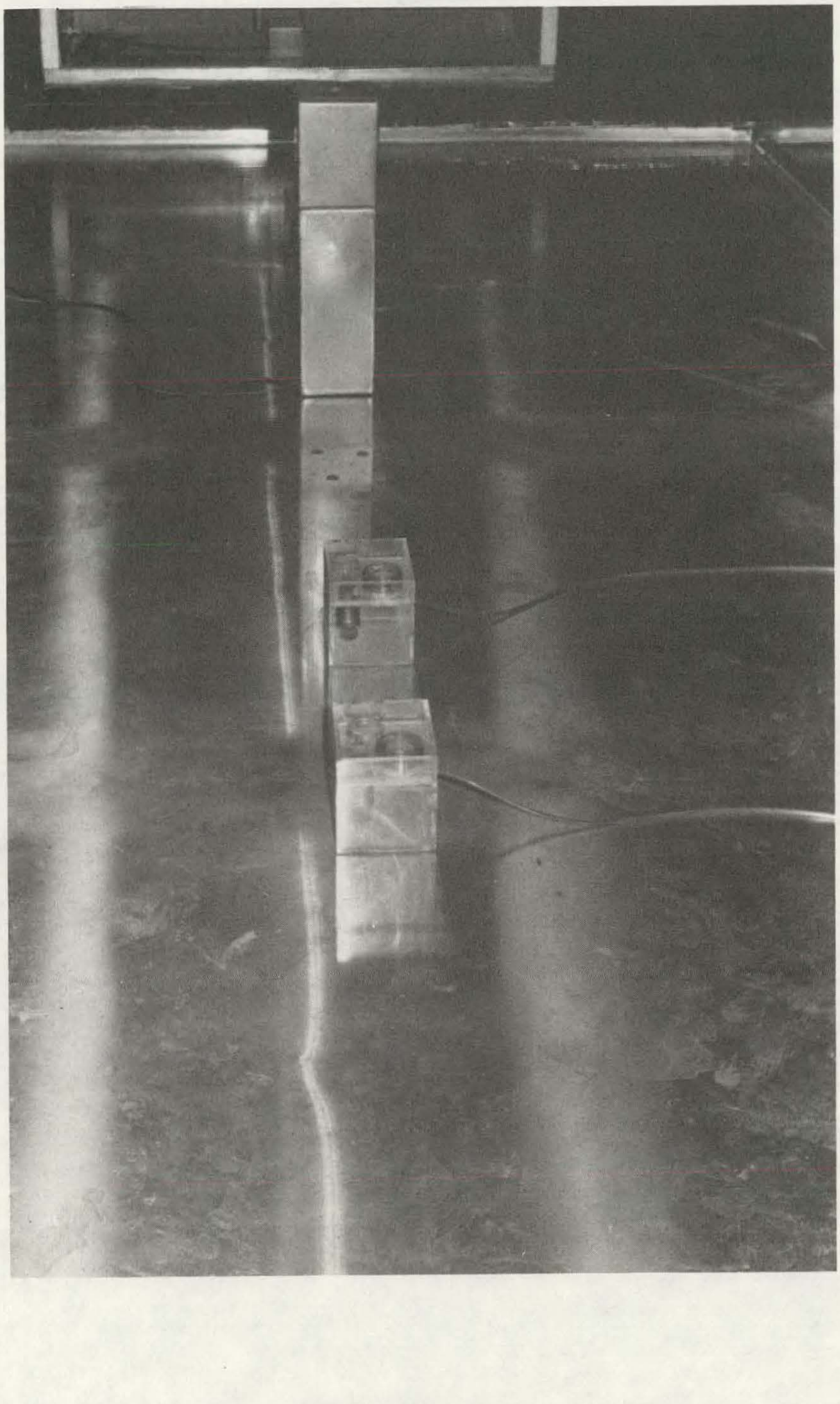

FIGURE 3A GAS RELEASE BOX (TOP) AND SAMPLE COLLECTORS (CENTER)

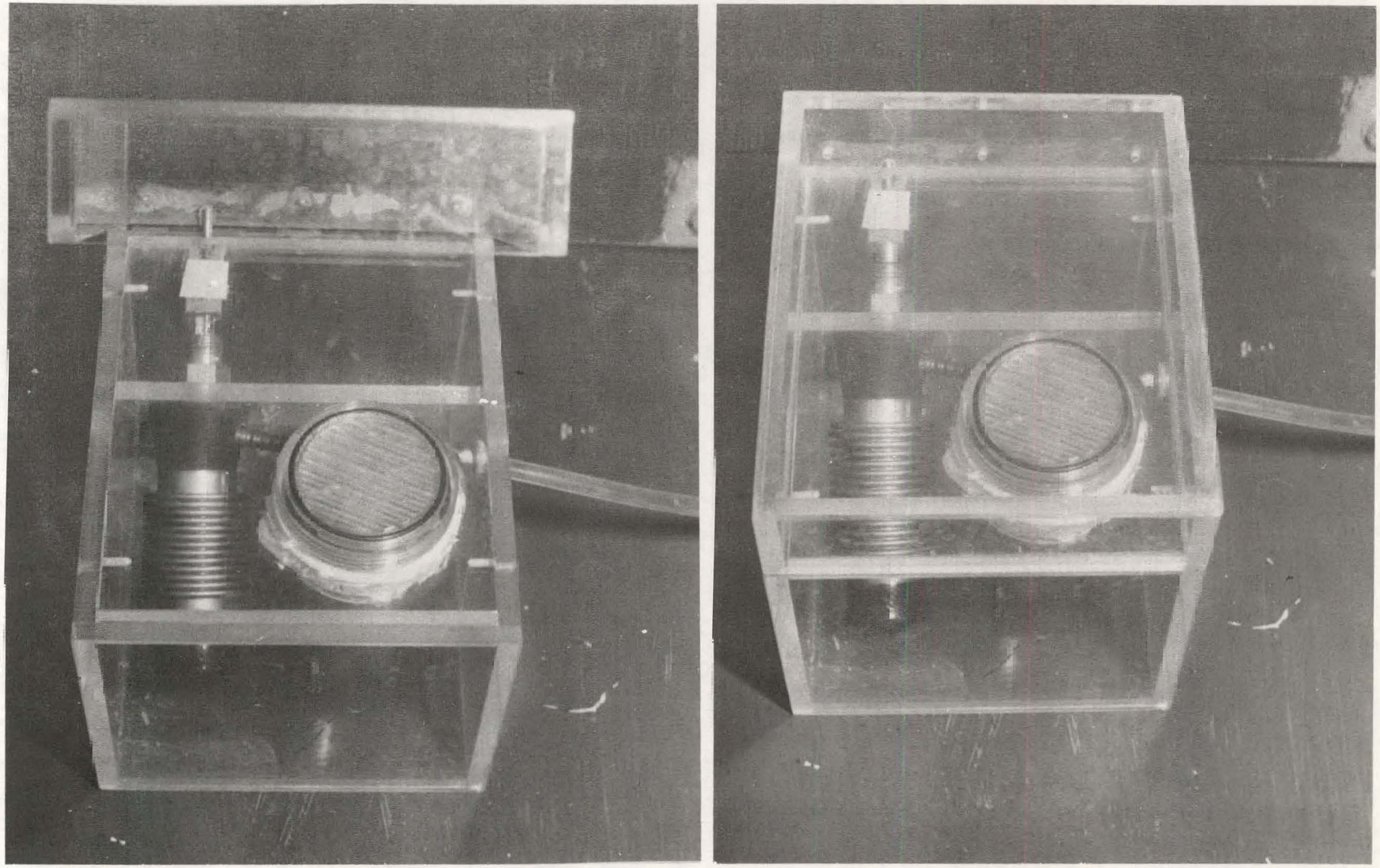

FIGURE 3B PARTICULATE SAMPLING DEVICE OPEN (LEFT) CLOSED (RIGHT)

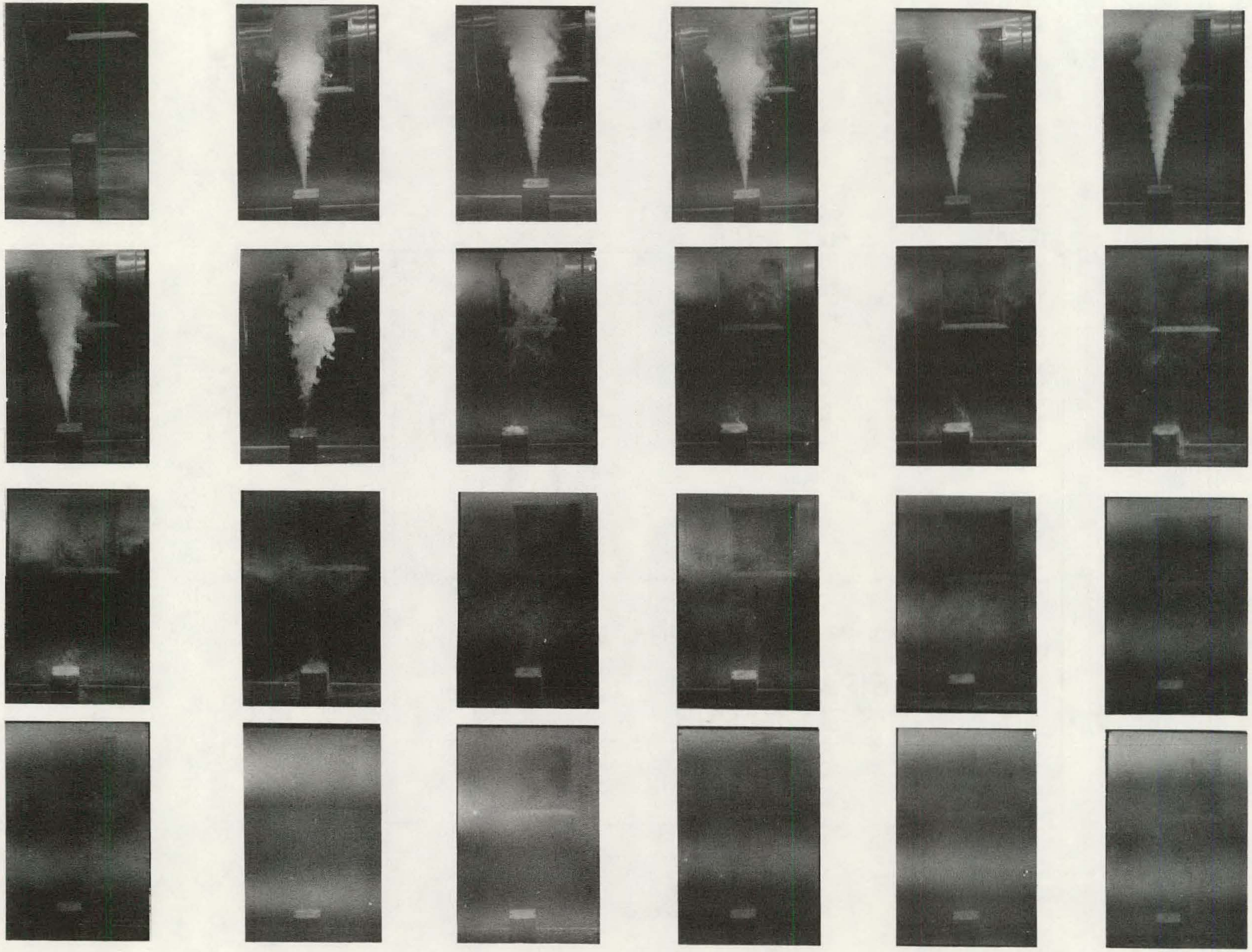

FIGURE 4 UF_6 CLOUD FORMATION

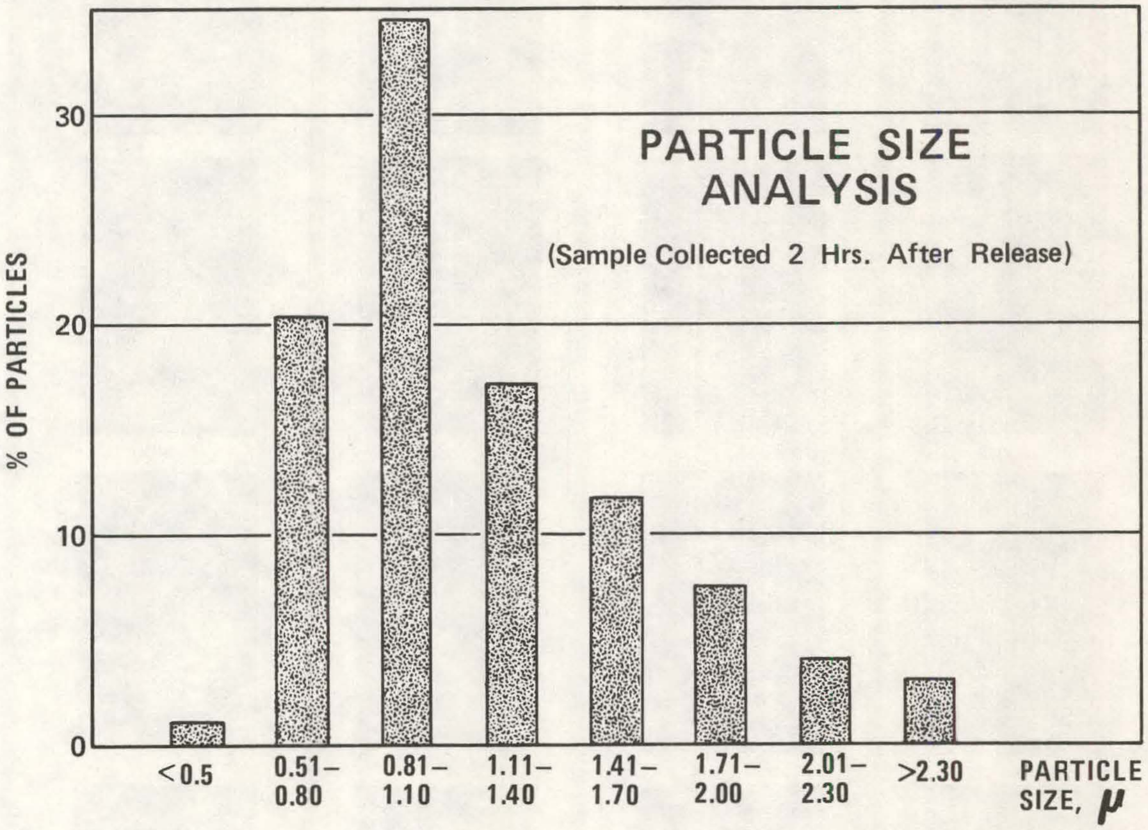

FIGURE 5 DISTRIBUTION OF PARTICLE SIZES

size. Very little difference was noted between particle size distribution results of the individual releases.

WORK IN PROGRESS

Work on the UF_6 containment project is currently directed toward studying the release of UF_6 into dynamic air flows. Installation of blowers, and air deflectors to establish the desired laminar type of air flow has been completed. "Wind" speeds of about 2 mph can be obtained. Smoke made up of ethylene diamine and acetic acid was used to observe particular air flow patterns prior to releasing UF_6. The smoke indicates air flow turbulence paths but does not necessitate decontamination before entering to adjust equipment. Operational evaluation of Pyr-A-Larms and alpha-air samples are now underway. The mathematical model for the UO_2F_2 plume dispersal studies being assembled by Battelle will be run concurrently with data from our studies on turbulence/laminar flow effects.

FUTURE WORK

As work progresses on the dynamic atmosphere UF_6 release studies, plans are being made to investigate "Zero Humidity" conditions, i.e., releases of UF_6 amounts in excess of available UF_6/Hydrolysis capacity. Need for such data was brought into focus in a recent controlled laboratory chamber release of small volume at ultra low humidity (0.05%), in which no visible UO_2F_2 cloud was formed. Liquid spill releases are also planned, and procedures for real time sampling of the atmosphere during a release by means of mass spectrometry are now being prepared. Cloud knockdown techniques, the ultimate project goal will be to evaluate the relative efficiencies of water or steam spray, fog, CO_2, and other chemical means which have not been devised at this time.

First phase testing, involving UF_6 gas releases into static atmospheres, under ambient conditions normally found in the gaseous diffusion plants, have indicated that between 9-90% relative humidity, and between 0-40°C, temperature and humidity effects do not significantly affect UO_2F_2 particle size formation (1-3 micron diameter), or release cloud settling rates (0.1 mm/sec.).[5]

REFERENCES

1. UF_6 Cylinder Handling Committee Report: Containment, September 20, 1974.

2. W. R. Golliher, "Development Work on UF_6 Containment," Letter to H. E. Trammell, January 31, 1975.

3. Technical Division Project Plan, UF$_6$ Containment Studies, Goodyear Atomic Corporation, Piketon, Ohio, April 2, 1975.

4. D. L. Williams, and S. W. Wohlfort, Personal Communication, to E. O. Sternberg, GAT-521-79-155, Goodyear Atomic Corporation, Piketon, Ohio, August 7, 1979.

5. S. W. Wohlfort, Process Technology - Mission IV Bimonthly Project Reviews (December - January), GAT-520-79-87, Goodyear Atomic Corporation, Piketon, Ohio, February 1, 1980.

QUALITY ASSURANCE IN ENVIRONMENTAL MEASUREMENTS

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Key Words

Quality Assurance, Environmental Monitoring, Control, Uncertainty

ABSTRACT

The following elements of a quality-assurance (QA) program as applied to environmental surveillance activities are presented: (1) a philosophical and conceptual framework for QA, with a detailed assessment of the sources of uncertainty in a monitoring program; (2) the requirements for the formulation of general and technical procedures of quality control; (3) the environmental QA activities implemented at Oak Ridge National Laboratory (ORNL), including details on record keeping, data reduction and compilation, auditing, analytical procedures, inter-laboratory sample comparisons and data interpretation; and (4) the role management must play to ensure a successful program. The QA principles developed here may be applied to any surveillance program.

Quality assurance (QA) can be defined as the planned and systematic actions necessary to ensure accuracy of techniques and analyses by determining errors and minimizing them.[1] A QA program should develop and implement procedures that will facilitate proper identification and evaluation of problem areas in order to give the user confidence that the system or component will perform satisfactorily. Many scientific and technical organizations and governmental agencies are committed to the continuous development of QA standards and procedures.

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The role of an environmental surveillance program is to provide qualitative and quantitative data on environmental pollution levels. Surveillance programs are operated by federal, state, local, and private agencies. The data from these programs are used for a wide variety of purposes, such as the establishment of guides and standards for enforcement activities. A QA program to ensure the reliability of the data is essential because of the importance of these values and the importance of these values and the importance of the actions which result from decisions that are made using these values and the importance of the actions which result from decisions that are made using these values. Therefore it is imperative that the precision and accuracy of the data be assured in order that policy decisions concerning environmental quality are based on valid and comparable data.[2,3]

GENERAL PHILOSOPHY AND QUALITY ASSURANCE CONCEPTS

Quality must be defined in terms of the parameter(s) being measured.[1] The measurement of a physical entity involves uncertainties which cannot be eliminated completely, but when the possibilities of uncertainties are recognized, they can often be reduced to acceptable limits.[4] Reduction of these uncertainties can be achieved by proper attention to detail and close control of the significant variables. Control must be related to the source of variation, which can be either random or systematic in nature.[5] Examples of unrecognized sources of uncertainties are interferences in chemical reaction systems and the appearance of undesirable physical or chemical effects. Absolute analytical values are not directly attainable; there standards from which the desired result can be derived by comparison must be established. Uncertainties cannot be reduced to zero; but methods, such as standards from which the desired result can be derived by comparison must be established. Uncertainties cannot be reduced to zero; but methods, such as standards and cross-checking, are available for obtaining reliable estimates of a given value; thus a range of acceptable errors can be estimated.[6]

Since QA is concerned with detecting determinable errors and preventing their recurrence, a systematic QA program must be followed. Such a program must include:[7]

1. Good physical facilities and equipment.
2. Adequately trained and experienced personnel.
3. Procedure verification.
    a. Use of standard methods.
    b. Routine analysis of control samples.
4. Frequent calibration and servicing of instruments and equipment.
    a. Calibration to maintain accuracy.
    b. Correlation of quantitative tests to confirm accuracy.
5. A knowledgeable and supportive management.

Sources of Uncertainty

The first objective in the development of an overall QA program is to identify the sources of uncertainty throughout the surveillance program. Most efforts in the past have stressed only the analytical uncertainties. However, the following expression, which is an expansion of the work of Johnson,[6] lists other sources of uncertainty. The dots indicate that other sources of uncertainty may be important.

$$T_u = N_u + C_u\,(s_u,\ l_u,\ f_u\ .\ .\ .) + A_u(st_u, p_u,\ al_u, m_u, co_u\ .\ .\ .) + D_u + .\ .\ .\ .$$

where

T_u = total uncertainty associated with a surveillance program,

N_u = uncertainty associated with the natural nonuniformity of the sample population,

C_u = total uncertainty associated with collection strategies,

- s_u = error associated with a limited sample size,
- l_u = uncertainty associated with the choice of sample location with respect to the source,
- f_u = uncertainty associated with the sample collection frequency,

A_u = total uncertainty associated with analytical processing,

- st_u = variability associated with sample storage,
- p_u = variability associated with sample preparation,
- al_u = variability associated with aliquoting,
- m_u = uncertainty associated with instrument variability,
- co_u = estimate of error associated with counting statistics,

D_u = total uncertainty associated with data treatment and interpretation.

Natural Nonuniformity (N_u)

Probably the greatest source of variability is in the natural distribution of radionuclides. For example, in studying the distribution of natural ^{40}K in soils, it was noted that the values ranged over two orders of magnitude in central and eastern Tennessee.[8] This large variation was found to be due to the multiple geologic formations in central and eastern Tennessee.

There are many other factors that influence the distribution of radionuclides in the environment.[9] Weathering and sedimentation of soil are important, and the radioactive content of soil will vary with seasonal and climatic conditions. Radionuclide concentrations will also vary with depth. Further, side-by-side sites may experience different rainfall or wind patterns (perhaps due to a local obstruction). These factors must be analyzed simultaneously along with the collection strategy.

Collection Strategy (C_u)

The objective of sample collection (C_u) strategy is to obtain a portion of material small enough in volume to be easily transported to and processed through the laboratory while accurately representing the material being sampled. Often, it is much more difficult to formulate and validate sample collection procedures than those related to analytical processes.[10,11]

One of the important considerations in the determination of sample size (s_u) is the desired minimum detectable concentration (MDC) of the radionuclide of concern.

In addition, in the formulation or planning stage of a surveillance program, sampling location (l_u) and collection procedures are established. Procedural variations are often necessary in order to collect representative samples in those circumstances where the original procedure might yield a nonrepresentative sample. Selection of approximate sampling locations should be based on air and water circulation patterns, land and water usage, population distribution, and availability of land. In selecting sampling locations one must avoid local concentrations of natural radioactivity, building wake effects, dripping and puddling of precipitation, heavy dust-raising activities, backwater areas in streams, riverbank springs, and atypical vegetation patterns. One solution to the problem of selecting representative sampling sites and decreasing the location (l_u) uncertainty is increase the number of sampling stations.

Finally, in order to reduce f_u to a minimum, it is necessary to tailor the collection frequency to the expected variations in discharges, to the half-life of the released radionuclides, and to the nature of the environmental media.

Analytical Uncertainty (A_u)

Quality assurance procedures in the radiochemistry laboratory are designed to complement the overall objectives of the environmental surveillance QA program. The sampling regime produces a wide variety of materials (soils, vegetation, water, air filters, etc.), each requiring specialized procedures for analysis and each having an analytical processing (A_u) uncertainty. One of the best ways to reduce A_u is to use standardized methods, such as those of the American Society for Testing and Materials (ASTM),[12] American National Standards Institute (ANSI),[13] National Academy of Sciences (NRC Monographs on Radiochemistry),[14] and the collection of procedures of the Environmental Measurements Laboratory.[15] One major problem in many environmental monitoring programs is that of inadequate coordination of the sampling and analytical programs. Also nonhomogeneity in sample media contributes possible large uncertainties. For example, replication of 10-g aliquots for plutonium analysis from kilogram soil samples containing discrete particles can easily vary several orders of magnitude.[15]

The uncertainty associated with sample preparation (p_u), storage (st_u), and aliquoting (al_u) is very difficult to estimate. When a sample is received in the analytical laboratory, it is often not in the proper physical form for analysis. The sample may require concentration (water samples), drying (biological samples), or homogenization before aliquots can be processed by a suitable chemical procedure. The sample must be handled and processed in such a way that no significant changes in composition occur before the analysis is performed. Sample storage prior to analysis requires some thought and care to avoid loss of certain radionuclides or to avoid spoilage or sample decomposition. Generally, the shorter the time that elapses between collection of a sample and its analysis, the more reliable will be the analytical results. It is difficult to state exactly the maximum allowable time between collection of a sample and its analysis; this depends on the character of the sample, the particular analysis to be made, and the conditions of storage.

Nondestructive methods of analysis are used in all applicable situations. Gamma-emitting radionuclides are determined in many surveillance samples by the use of high-resolution gamma-ray spectrometry with a minimum of sample treatment. Calibration sources for the spectrometer are obtained from the National Bureau of Standards (NBS) to reduce measurement uncertainty (m_u). One of the most useful calibration sources is the NBS Mixed Radionuclide Gamma-Ray Emission-Rate Standard (SRM-4216) that is issued annually. Other extended sources in the series are described by Coursey.[16] Many calibrations for natural radioelement determinations are performed with standards from the New Brunswick Laboratory, now located at Argonne National Laboratory.

Many environmentally important radionuclides (^{90}Sr, ^{99}Tc, ^{239}Pu, etc.) require specific radiochemical separations prior to their final determination by counting or spectrometric measurements. Careful attention to fundamental principles by the chemist performing the separations is another facet of the QA program. Among these principles are complete dissolution of the sought radionuclide from the sample matrix, complete exchange with the isotopic tracers used for yield determinations, and complete removal of interfering radionuclides in the final isolation step.

Quality assurance is provided by technician training, use of replecate samples, use of reagent blanks, use of standard samples, use of quality control "blind" standards, and the participation in "round-robin" exercises. Among the important interlaboratory comparison programs useful in this connection are those of the AIF-NBS,[17] EPA,[18] and the quarterly distribution provided by the Department of Energy's Environmental Measurements Laboratory.[19]

In addition to specific quality-assurance techniques for general analytical procedures, quality control must be exercised on all instruments used for radioactivity measurements.[20] Radioactive decay, by its fundamental nature, is a random process resulting in uncertainty due to counting statistics (co_u). Matuszek[21] presented quality-control charts for the background and standard deveiation values for a commercial low-background beta-particle counting system showing significant differences from predicted statistical behavior. An important concept for all environmental programs is that of minimum detectable activity (MDA). Lochamy[22] provided a detailed discussion and methematical derivation of four different types of MDA implications.

Data Interpretation (D_u)

The data treatment (D_u) incorporates all the sources of uncertainty. Matuszek[21] indicated that some laboratory staffs normally report all errors. The treatment of environmental data is complex in that skewed and mixed distributions, along with the presence of "outliers" and "less than" values are generally prevalent. Generally, when these "out-of-fit" values are examined, it is found that the majority are obvious computation, measurement, or processing errors. One of the most common problems facing environmental surveillance programs is the problem of handling "less than detectable (LD)" values. To be conservative, many organizations make the assumption that all LD values actually have concentrations equal to the detection limits, and the group average is computed accordingly; other organizations set the LD values to zero. Both methods, however, bias the averages given. A more correct way is through the use of probability plotting.[9]

QUALITY ASSURANCE AT OAK RIDGE NATIONAL LABORATORY

A QA program has been initiated at ORNL in order to ensure that a high degree of accuracy and reliability is maintained in its surveillance activities. The program at ORNL consists of QA techniques and procedures and includes written descriptions of:

1. Quality-assurance organizational structure (including a QA coordinator) and identification of the role, responsibilities, and authority of each staff member as related to QA.
2. Operating procedures for each activity.
3. Inspection lists of operating and maintenance activities.
4. Quality control in sampling and radioanalytical laboratory procedures.
5. Analysis of QC samples.
6. Participation in intralaboratory and interlaboratory sample-exhchange programs.
7. Evaluation of the adequacy of sample preparation work and data analysis.
8. Procedures for review, analysis, and reporting of data.

Operating procedures for each type of sample collected at ORNL are given in Report ORNL/TM-7212 (Ref. 23).

A schematic diagram showing a flow chart of ORNL's quality-assurance program is given in Fig. 1; a more detailed discussion of the program is given in Report ORNL/TM-7213 (Ref. 24). The relation between sample flow, QA program, and impact of failure is shown in Fig. 2.

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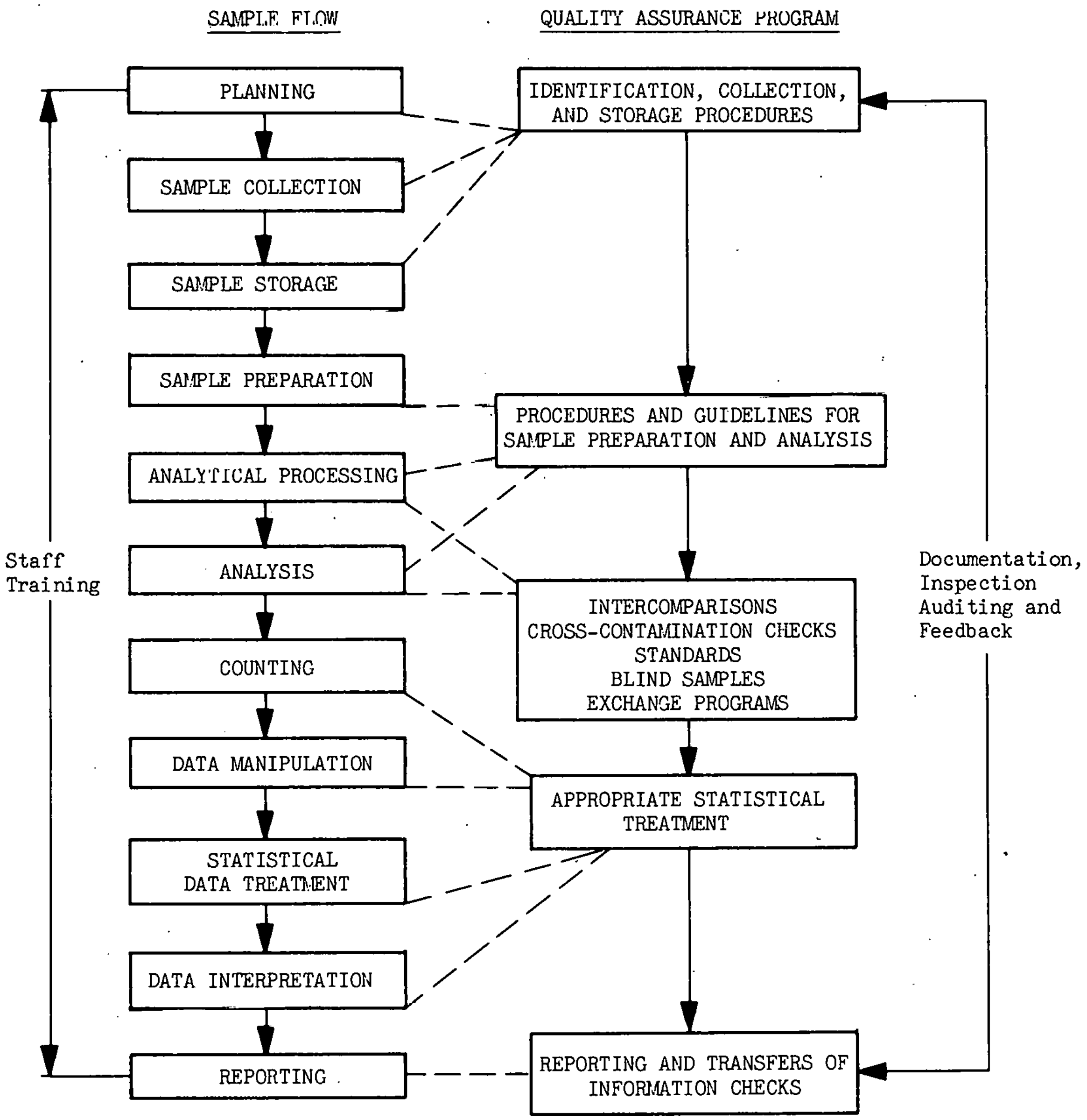

Fig. 1. Flow chart of QA program at Oak Ridge National Laboratory.

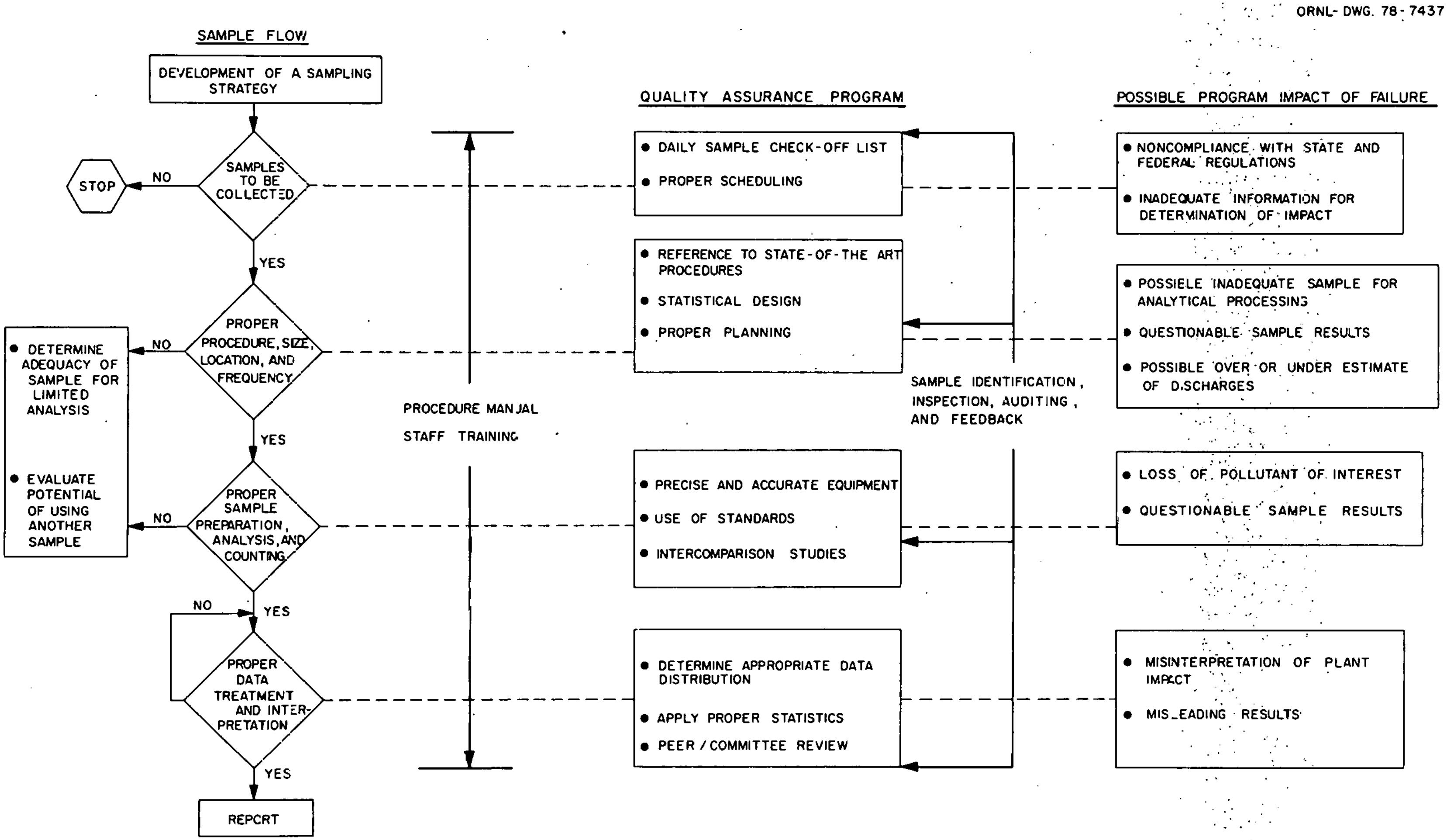

Fig. 2. Interrelations between sample flow, QA program, and the possible impact of failure.

Record Keeping for Environmental Data

The importance of record keeping cannot be overemphasized. It is important not only from a QA standpoint, but also from a regulatory point of view, for legal confrontations, for visualizing changing trends in the environment, for optimizing environmental monitoring procedures, for research studies, and for other purposes.

Record keeping for environmental monitoring at ORNL has been in existence since the formation of the Laboratory (∿ 35 yr). Permanent records are kept of routine monitoring of radioactivity present in the environment, and routine assaying for both specific and nonspecific radionuclides present in a wide variety of samples (e.g., biological, soil, rainfall, etc.).

Most routine environmental data are stored on computer printout. Since many samples require rather extensive analyses, specific treatment of each sample for sequential analysis is done by various groups at ORNL. Samples must be properly labeled when being routed through these groups in order to maintain an accurate record for each sample. Special forms and data cards have been developed which greatly facilitate accurate record keeping. The advantages of these computer cards are:

1. The card is routed along with the samples each step of the way.
2. All information related to the sample is on one card.
3. The information can be easily computerized.
4. Short-term turnaround for data is provided for all samples in the system.
5. Traceability of samples as they are routed through the system is provided.
6. Documentation of data related to the sample is provided.

Computer Aid for Monitoring Sample Flow

A computerized scheme for monitoring the sample flow has also been developed at ORNL.[25] The monitoring of sample flow is simply keeping track of the various samples as they progress through the steps shown in Fig. 1. This is an important aspect of QA, because sample loss and mix-up in the past has been one of the major problems facing the surveillance activities at ORNL. Cards corresponding to collection, sample storage and preparation, analytical processing and analysis, and data interpretation are used. Those specially designed cards are turned in to the sample coordinator following completion of each step. Special sample coding has been established for this program to expedite sample flow. For example (see Fig. 3), the collection card has spaces for the sample number step ("C" for collection); type of sample ("AF" for air filter); count rate of

C

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Sample No.					
1	2	3	4	5	6

ENVIRONMENTAL MONITORING QA

Step		Type		Location					Count Rate								Time In										Time Out									
									On				Off				Yr.		Mo.		Day		Hr.		Min.		Yr.		Mo.		Day		Hr.		Min.	
7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30	31	32	33	34	35	36	37	38	39	40	41	42	43
C																																				

Flow Rate						Comments																									Special	Tech.		Init.		
On			Off																																	
44	45	46	47	48	49	50	51	52	53	54	55	56	57	58	59	60	61	62	63	64	65	66	67	68	69	70	71	72	73	74	75	76	77	78	79	80

Figure 3. Environmental Monitoring QA Card for Collection Sample.

the air filter on and off the pump in counts per minute (CPM); routine or special sample designation; techniques used (continuous, grab, etc.); and initials of the person performing the particular operation. After this information has been transferred onto computer cards, it is processed and assembled on a computer printout. From this printout, one can determine which steps in the sample flow have been completed. A warning signal has been built into the program: when the time in any one period exceeds a preset time for each sample, that sample is flagged. This is very useful for samples with short-lived isotopes. This program has proven to be a very useful tool for the management of sample flow.

Quality Assurance in the Analytical Chemistry Division

Members of the Analytical Chemistry Division (ACD) at ORNL have tested and documented the radiochemical methods being used for the environmental samples. The ACD has acquired a Nuclear Data 6620 Analyzer, featuring on-line data reduction, which has decreased turnaround time for gamma spectrometry and improved reliability. The germanium—lithium (GeLi) detectors have been recalibrated, using National Bureau of Standards (BNS) Mixed Radionuclide Standards. The internal consistency between detection methods has been tested by sample comparison using independent measurement methods. Improvements in the ACD QA program are planned through increased documentation and a more rigorous routine QA schedule. The analytical methods used for environmental samples are described in Report ORNL/TM-6372 (Ref. 26), Union Carbide Corporation, Nuclear Division's *Environmental and Effluent Analysis Manual,*[27] and the *ORNL Master Analytical Manual*.[28]

Intercomparison studies are performed quarterly by the Analytical Chemistry Division for radioactive samples distributed by the Environmental Measurements Laboratory (EML) of the Department of Energy (see Tables 1 and 2).

The NPDES analytical techniques are also checked quarterly by samples distributed by the Environmental Resource Associates. For 1979, 37 parameters were checked with an excellent range of measured to standard ratio of 0.82 to 1.17.

Audits

Written procedures and scheduling plans for audits are given in Report ORNL/TM-7213 (Ref. 24), and audits are performed in accordance with these procedures. Such procedures include items as checking the air monitors bi-weekly, analytical balances semi-annually, how to take and prepare soil samples to avoid cross-contamination, etc. The Environmental Surveillance and Evaluation Section at ORNL is committed to taking the action necessary to correct the deficiencies identified by these audits. The audit structure is divided into three sections: (1) procedures and documentations, (2) special investigations, and (3) maintenance schedules.

Table 1. Ratio of ORNL results to EML and other laboratories that participated in the exchange program; 1979 yearly averaged results for all radionuclides

Sample Media	ORNL/EML	ORNL/Other Labs
Air	1.03	0.85
Soil	0.96	0.78
Tissue	1.73	0.95
Vegetables	1.02	0.65
Water	1.00	0.92

Table 2. Ratio of ORNL results to EML and other laboratories; 1979 yearly averaged results for all sample media

Sample Media	ORNL/EML	ORNL/Other Labs
^{137}Cs	1.01	0.89
^{239}Pu	1.14	0.75
^{90}Sr	0.86	0.68

The structure and scheduling are reviewed monthly to identify areas where changes are needed. When the audit information is evaluated, analyzed, and tabulated, it is passed on to management so that the appropriate action can be taken. The QA coordinator keeps track of the information received from the audits and makes sure that corrective action is taken.

Data Treatment

Plotting data on probability paper is a very good technique to calculate averages and standard deviations, to quickly show whether the distribution choice was correct (i.e., Gaussian vs. log normal), to determine whether the data belong to one of the two statistical populations, and to permit the confident reporting of averages when the values are close to or below the detection level.[9] An example of this technique is shown in Fig. 4, where ^{234}U soil data from perimeter air-sampling stations at ORNL in 1977 are plotted on probability paper. Figure 4 shows that the concentration of ^{234}U in soil at station 32 belongs to a higher distribution than the other stations.

As shown in the above example, such graphic presentations are very useful. Indeed, through the use of this technique, a visual indication can quickly be assessed to determine the plant's impact. To arrive at a more quantitative decision, however, one must employ standard statistical tests. These tests are usually performed on the central or mean values of the respective distributions; the most common test is the Student's t test.[29]

The Role of Management

A strong QA program must include a management system to control operations and specialized techniques to facilitate beneficial decisions. Proper organization for the flow of information is a key factor in ensuring that corrective action is taken in the proper time frame. The management elements and corresponding elements of QA are (1) Plan: quality assurance programs, instructions, and procedures; (2) Organize: organization; (3) Execute: procedural control, document control, control of purchased materials, equipment and services, and identification and control of sample flow; and (4) Monitor: inspection, test control, corrective action, and audits.

Management needs to identify the program objectives and take the steps necessary to attain these objectives. Management should work together with the working staff to plan and organize the program; this makes it possible for the staff to know what is required of them and gives them the opportunity to participate in the feedback loop. The working staff must be encouraged to identify problems affecting quality.

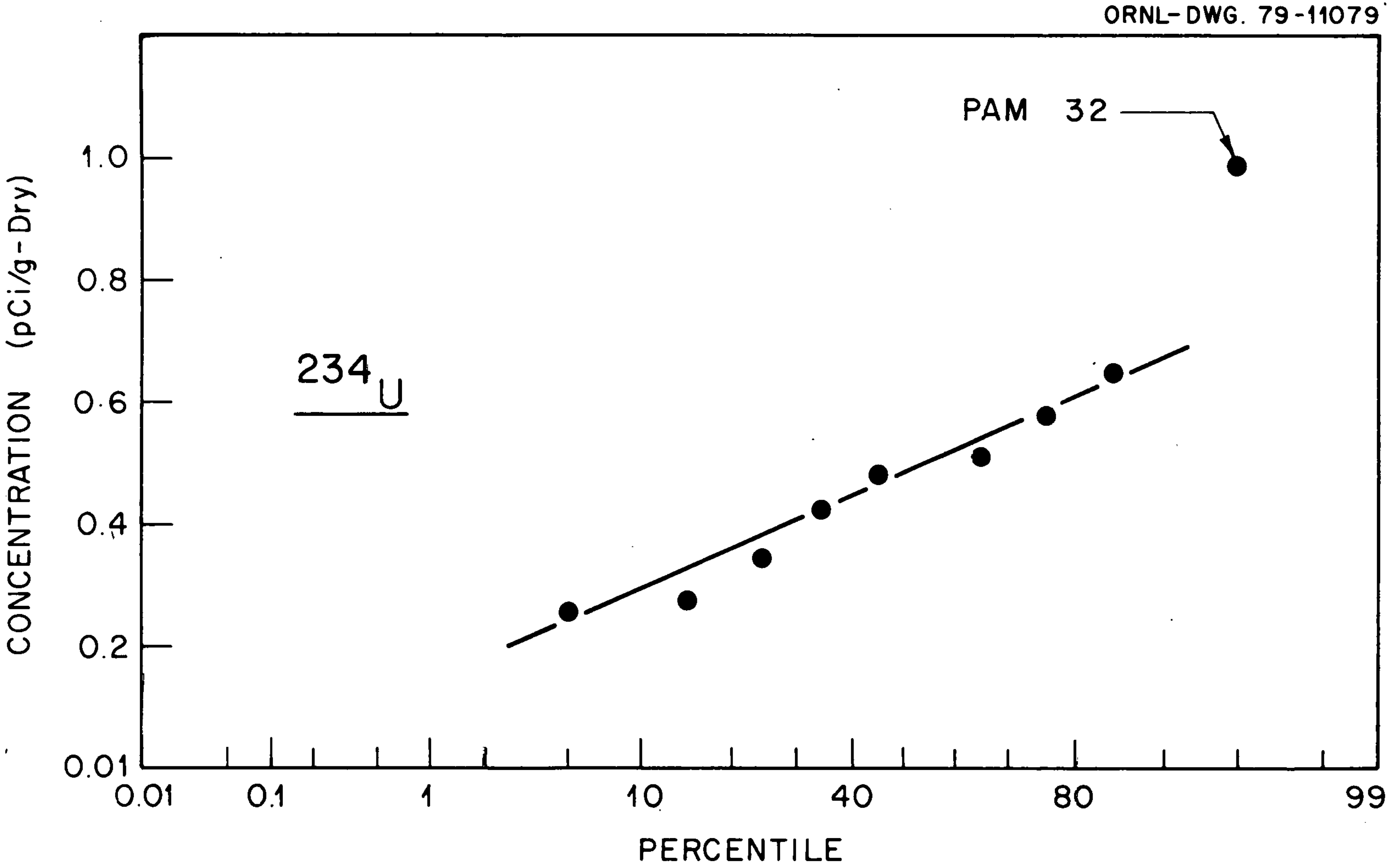

Fig. 4. Distribution plot of uranium-234 in soil.

CONCLUSIONS

Our experience has demonstrated the necessity of a complete QA program for improving environmental monitoring. A QA program provides a mechanism for ensuring efficiency in everyday activities. Further, the QA approach could and should be used as a basis for establishing regulatory guides for a monitoring protocol requiring the regulated facilities to collect and analyze samples with comparable procedures. Such a QA program would require regulated facilities to review monitoring procedures and methods rather than collect information for the sole purpose of compliance with regulatory guides. In addition, such a program would be beneficial to regulatory agencies by identifying nonessential collection requirements. Although the development of a QA program could initially increase operating expenses for environmental surveillance, we believe that, once fully implemented, a well-designed program will be cost effective.

For example, at ORNL sample loss has been reduced following implementation of the QA program. Sample loss is reduced because the QA program requires management to keep track of the QA information received from audits and to make sure any needed corrective action is taken. Also, technical procedures are updated and tested for effectiveness. As part of this process, feedback loops should be established and used by all staff members and management for an effective QA program. The QA program at ORNL has identified many areas in the environmental surveillance program that needed improvement and has been very successful in ensuring more reliable data from the environmental surveillance program. The confidence of all groups involved in the surveillance activities at ORNL has been imporved, and the program has helped identify common problems. The QA program at ORNL has provided the staff members with a vehicle for better communication about program policy input and has also given management at better overview of the sample flow and the impact of changes in program direction on the quality of environmental surveillance.

REFERENCES

1. A. L. Linch, "Quality Control for Sampling and Laboratory Analysis," in *The Industrial Environment: Its Evaluation and Control*, M. O. Amdur (Ed.), pp. 277-297, National Institute for Occupational Safety and Health, GPO, 1978.

2. Nuclear Regulatory Commission, Regulatory Guide 4-15, *Quality Assurance for Radiological Monitoring Programs (Normal Operations) —Effluent Streams and the Environment*, December 1977.

3. National Environmental Research Center, *Environmental Radioactivity Laboratory Intercomparison Studies Program 1973—1974*, Report EPA/680/4-73-001-B (PB-240 962), NTIS, February 1974.

4. M. Katz (Ed.), *Methods of Air Sampling and Analysis*, 2nd ed., American Public Health Association, Washington, D.C., 1977.

5. "Quality Control in Chemical Analysis," in *Standard Methods for the Examination of Water and Wastewater*, American Public Health Association, American Water Works Association, and Water Pollution Control Federation, 14th ed., pp. 26-33, American Public Health Association, Washington, D.C., 1976.

6. L. J. Johnson, "Elements of Quality Assurance in Environmental Surveillance," in *Proceedings of the Third Environmental Protection Conference, Chicago, Illinois, September 23—26, 1976*, ERDA Report ERDA-92, Vol.1, pp. 77—88, NTIS, December 1975.

7. National Environmental Research Center, *Handbook of Radiochemical Analytical Methods*, Report EPA/680/4-75-001 (PB-240 621), NTIS, February 1975.

8. T. W. Oakes, K. E. Shank, and C. E. Easterly, *Natural and Man-Made Radionuclide Concentrations in Tennessee Soils*, ERDA Report CONF-761031-3, Oak Ridge National Laboratory, NTIS, 1976.

9. J. P. Corley et al., *A Guide for Environmental Radiological Surveillance at ERDA Installations*, ERDA Report ERDA-77-24, Battelle Pacific Northwest Laboratories, NTIS, March 1977.

10. T. W. Oakes, K. E. Shank, and J. S. Eldridge, *Quality Assurance Applied to an Environmental Surveillance Program*, USDOE Report CONF-771113-8, Oak Ridge National Laboratory, NTIS, 1977.

11. I. P. Murarka, "Environmental Monitoring and Statistical Considerations," in *Proceedings of the Third Environmental Protection Conference, Chicago, Illinois, September 23—26, 1975*, ERDA Report ERDA-92, Vol. 1, pp. 92—116, NTIS, December 1975.

12. American Society for Testing and Materials, *1977 Annual Book of ASTM Standards, Part 3: Steel Plate, Sheet, Strip, and Wire; Metallic Coated Products*, ASTM, Philadelphia, 1977.

13. C. W. Seidel and J. M. R. Hutchinson, "American National Standards Institute Quality Assurance Program in Radioactivity Measurements," in *Measurements for the Safe Use of Radiation, Proceedings of an NBS 75th Anniversary Symposium Held in Gaithersburg, Maryland, March 1–4, 1976*, S. P. Fivozinsky (Ed.), pp. 77-82, NBS Special Publication 456, National Bureau of Standards, Washington, D.C., GPO, November 1976.

14. National Academy of Sciences—National Research Council, "Nuclear Science Series: Monographs on Radiochemistry and Radiochemical Techniques (a series of monographs on the radiochemistry of essentially all the elements and on radiochemical techniques)," published by the U.S. Atomic Energy Commission, and later by the U.S. Energy Research and Development Administration, as NAS-NS publications.

15. J. H. Harley (Ed.), *HASL Procedures Manual*, USAEC Report HASL-300, Health and Safety Laboratory, NTIS, 1972.

16. B. M. Coursey, "Use of NBS Mixed-Radionuclide Gamma-Ray Standards for Calibration of Ge(Li) Detectors Used in the Assay of Environmental Radioactivity," in *Measurements for the Safe Use of Radiation, Proceedings of an NBS 75th Anniversary Symposium Held in Gaithersburg, Maryland, March 1–4, 1976*, S. P. Fivozinsky (Ed.), pp. 173–175, NBS Special Publication 456, National Bureau of Standards, Washington, D.C., GPO, November 1976.

17. R. Collé, "AIF-NBS Radioactivity Measurements Assurance Program for the Radiopharmaceutical Industry," in *Measurements for the Safe Use of Radiation, Proceedings of an NBS 75th Anniversary Symposium Held in Gaithersburg, Maryland, March 1–4, 1976*, S. P. Fivozinsky (Ed.), pp. 71–76, NBS Special Publication 456, National Bureau of Standards, Washington, D.C., GPO, November 1976.

18. A. N. Jarvis and D. G. Easterly, "Environmental Radioactivity Standards," in *Measurements for the Safe Use of Radiation, Proceedings of an NBS 75th Anniversary Symposium Held in Gaithersburg, Maryland, March 1–4, 1976*, S. P. Fivozinsky (Ed.), pp. 263–265, NBS Special Publication 456, National Bureau of Standards, Washington, D.C., GPO, November 1976.

19. Health and Safety Laboratory, *Quarterly Report of the Energy Research and Development Administration, Division of Safety, Standards, and Compliance—Quality Assurance Program*, ERDA Report HASL-319, NTIS, May 1977.

20. L. H. Ziegler and H. M. Hunt, *Quality Control for Environmental Measurements Using Gamma-Ray Spectrometry*, Report EPA/600/7-77/144 (PB-277 377), Environmental Monitoring and Support Laboratory, NTIS, December 1977.

21. J. M. Matuszek, "Environmental Measurements and Regulatory Responsibilities," in *Measurements for the Safe Use of Radiation, Proceedings of an NBS 75th Anniversary Symposium Held in Gaithersubrg, Maryland, March 1–4, 1976*, S. P. Fivozinsky (Ed.), pp. 249–261, NBS Special Publication 456, National Bureau of Standards, Washington, D.C., GPO, November 1976.

22. J. C. Lochamy, "The Minimum-Detectable-Activity Concept," in *Measurements for the Safe Use of Radiation Proceedings of an NBS 75th Anniversary Symposium Held in Gaithersburg, Maryland, March 1–4, 1976*, S. P. Fivozinsky (Ed.), pp. 169–172, NBS Special Publication 456, National Bureau of Standards, Washington, D.C., GPO, November 1976.

23. T. W. Oakes, K. E. Shank, M. A. Montford, and J. L. Danek, *Methods and Procedures Used in Environmental Surveillance at ORNL*, ORNL/TM-7212, in preparation.

24. K. E. Shank, T. W. Oakes, J. S. Eldridge, and M. A. Montford, *Quality Assurance Procedures for Environmental Surveillance at ORNL*, ORNL/TM-7213, in preparation.

25. R. L. Stephenson, T. W. Oakes, and K. E. Shank, *A Computer Program for Monitoring Sample Flow from Environmental Surveillance Activities at the Oak Ridge National Laboratory*, USDOE Report ORNL/TM-6599, Oak Ridge National Laboratory, NTIS, December 1978.

26. L. C. Henley, *Radiochemical Procedures*, USDOE Report ORNL/TM-6372, Oak Ridge National Laboratory, DOE-TIC, May 1978.

27. Union Carbide Corporation, Nuclear Division, *Environmental and Effluent Analysis Manual*, undated (updated periodically).

28. Oak Ridge National Laboratory, Analytical Chemistry Division, *ORNL Master Analytical Manual*, Report TID-7015, orginally published in 1953 and updated periodically.

29. N. M. Downie and R. W. Heath, *Basic Statistical Methods*, Harper and Row, New York, 1970.

Dup

COMPUTER MODEL FOR SELECTING FLOW MEASURING STRUCTURES IN OPEN CHANNELS

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(Computer Model Natural Stream Measuring Structures)

ABSTRACT

Quantifying various pollutants in natural waterways has received increased emphasis with more stringent regulations issued by the Environmental Protection Agency (E.P.A.). Measuring natural stream flows presents a magnitude of problems, the most significant is the type of structure needed to measure the flows at the desired level of accuracy.

A computer model designed to select a structure to "best fit" the engineer's needs is under development. This model, given the pertinent boundary conditions, will pinpoint the structure most suitable, if one exists. This selection process greatly facilitates the old selection process of trial and error.

Quantifying various pollutants in natural waterways has received increased emphasis with more stringent regulations issued by the Environmental Protection Agency (E.P.A.). Measuring natural stream flows presents a magnitude of problems, the most significant is the type of structure needed to measure the flows at the desired level of accuracy.

A computer model designed to select a structure and evaluate the necessary boundary conditions could be the fastest and most economical way for the engineer to evaluate all the structures available.

In selecting a structure, the overriding consideration is the hydraulics of the structure. The engineer's first choice should always be made on the best hydraulic structure. After this is accomplished, the structure should be evaluated on a number of other considerations. Standardization, ease of construction, and ease of both operation and

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maintenance need to be considered. These are engineering value judgments and will not be included in the computer model.

Requirements of the Structure

An appreciation for the computer model will be better understood if some of the major considerations are discussed first.

The first criterion an engineer needs to develop is the function of the structure. Is the structure's function to regulate the flow? This is the case in most irrigation systems. Or, is the structure's main use to measure flows? These types are commonly found in natural streams, where various pollutants need to be quantified. Other types of structures are flow dividers and flow totalizers. These structures have special applications and will not be included in the model.

The second criterion to be evaluated is the energy required to drive the system (the head differential). Accurate head measurements require that modular flow be maintained across the measuring device. The minimum head required (ΔH) to operate in the modular flow range can be defined as $(H_I-H_2)/H_1$ (equation 1).

The modular limit is defined mathematically by rearranging equation 1 to read $1-H_2/H_1$ (equation 2)[1]. The modular limit is defined as the value of the submergence ratio (H_2/H_1) at which the real discharge deviates by 1% from the discharge calculated by the head-discharge equation.[2] This concept comes into play when an engineer must evaluate the effects of tailwater or the available head at low flows. This concept implies a flow pattern across the measuring structure. The limit is basically the degree of stream line curvature at the control section. Therefore, the modular limit is lower for measuring structure where the stream lines are more curved (a sharp-crested weir) and higher for a structure where the stream lines are more parallel (a Parshall flume).

Possibly, the toughest decision the engineer has to make is the range of flow to be measured. For a meaningful evaluation, the engineer should know what pollutant or pollutants the measuring structure is helping define. Once this background information is defined, either by the customer or the engineer, a relatively simple expression can be developed. This expression is based on the maximum and minimum flow range the structure will see and may be expressed by the ratio: $\gamma = Q\ max/Q\ min$ (equation 3).

Evaluating the limits of application for each measuring structure reveals a maximum attainable γ-value. A round-nosed, horizontal, broad-crested weir will illustrate the concept. The application limits for the weir show that H_1/L (the total available head divided by the length) range between 0.05 m to 0.50 m. Applying equation 3, the maximum γ-value is obtained:

$$\gamma = \frac{Qmax}{Qmin} = \frac{(0.50)^{1.5}}{(0.05)^{1.5}} \simeq 35$$

Thus for flow ranges above 35 the horizontal broad-crested weir cannot be used. Similar data are available for the other structures.

The next demand the engineer should evaluate is the accuracy and/or sensitivity of the structure. The accuracy of any particular measuring structure depends on several factors. These factors include errors inherent to the structure, the approach velocity coefficient, the discharge coefficient or any combination of these. The sensitivity of any measuring structure is defined as the fractional change of discharge of the structure that is caused by the unit rise of the upstream water level (Δh).[3] During modular flow the sensitivity is defined as

$$S = \frac{\Delta Q}{Q} = \frac{(dQ/dh_1)\Delta h}{Q} \quad \text{(equation 4)}$$

Recognizing that $Q = \text{Constant } x h_1^{\mu}$ the sensitivity is as follows

$$S = \frac{\mu}{h_1}\Delta h^1$$

where Δh_1 can refer to a change in the water level, head reading error, or mislocation of the gauging station.[4]

Careful evaluation of the sensitivity is required for all measuring structures. It can be shown for measuring structures with high μ-values (2.2 to 2.5) and small heads the sensitivity is low. If your pollutant is associated with groundwater movement, thus low flow, extreme care must be taken if accurate discharge measurements are required.

These are just a few of the major considerations necessary in the proper selection of a measuring structure. Without going into lengthy discussions, other relevant factors to be considered are the structure flexibility, the sediment passing capability, and the ease by which it passes floating debris.

The Selection Process

Considering the many calculations and factors needed to select a proper structure, a computer model could expedite the selection process. The model under development, given the necessary boundary data, will evaluate the given conditions and select the best structure based entirely on hydraulic characteristics.

The first question the model will consider is a structure possible, based on initial boundary conditions. Assuming a structure is possible, the next step is to describe the main function of the structure discharge measuring versus discharge regulating. Once a decision is made, two main branches are established. The task evaluated next in both branches is the input γ-value and again, is a structure possible? After this decision, the branches become too numerous to describe in detail. In general, the branches become site and pollutant dependent. The model will consider the various factors involved in each, such as sediment passing capability, accuracy required, flexibility, etc.

After all the required tests, a structure or structures are presented for the engineer to evaluate. During this "reflective period," secondary boundary data should be considered. This data should include ease of operation and maintenance, the structure construction difficulty, etc. If the engineer is happy with the choice, the development of appropriate drawings and cost estimate data are the final step in the design procedure.

If the secondary boundary constraints rule out all selected structures, a reevaluation of the initial boundary condition is recommended. This iterative process will continue until a satisfactory solution is determined.

Once the program is up and running, various other features are planned. One such feature is a plot comparing the physical size of a structure for the various storm events. An example would be to compare the size, and thus the cost, of a structure for a 10 year storm versus a 25 year storm. Another anticipated feature is flow channel requirements (approach channel geometry) given initial hydraulic boundary data. Ultimately, the model will be able to size both the control section and the flow channel. These additional features should shorten the "reflection period."

This model is being developed in order to free the engineer from the tedium of countless calculations needed to determine an appropriate structure. A logical choice will be available in hours whereas it may require days for the engineer to reach the same conclusion.

REFERENCES

1. M. G. Bos (ed.), Discharge Measurement Structures, p. 85, International Institute for Land Reclamation and Improvements, Wagen, The Netherlands, 1976.

2. Ref. 1, p. 85.

3. Ref. 1, p. 92.

4. Ref. 1, p. 93

BIBLIOGRAPHY

M. G. Bos (ed.), Discharge Measurement Structures, International Institute for Land Reclamation and Improvements, Wagen, The Netherlands, 1976.

V. T. Chow, Open Channel Hydraulics, McGraw Hill, New York, 1959.

J. W. Clark, W. Viessman, Jr., and M. J. Hammer, Water Supply and Pollution Control, International Textbook Co., New York, 2nd ed., 1971.

R. L. Daugherty and J. B. Franzini, Fluid Mechanics with Engineering Application, MdGraw Hill, New York, 6th ed., 1965.

Y-12 DEVELOPMENT GOALS IN POLLUTANT DISCHARGE MONITORING

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Key Words
Laser, Infrared, Sulfur Dioxide, Perchloroethylene,
Hydrogen Fluoride, Oil

ABSTRACT

The Y-12 Plant Development Division is initiating activity in the areas of air and water discharge monitoring. The Environmental Monitoring Program (EMP) has been established to obtain and evaluate commercial systems for Plant use in monitoring specific pollutants and to develop new instruments and techniques in step with the latest technical advances and regulatory changes. A commercial system, the Infrared Oil Film Monitor has already been installed on Poplar Creek and is currently being tested for its ability to detect floating oil. Tunable diode lasers will form the basis for development of instruments to monitor ambient and stack gas emissions for a variety of pollutants by infrared absorption spectrophotometry.

INTRODUCTION

To an environmental chemist, the past decade was probably most notable for advances in pollutant analysis which now permit the detection of many common pollutants in extremely low concentrations. Such high sensitivity analytical instruments and methods are becoming increasingly more commonplace. In this period of rapid technological advance, regulations are subject to a corresponding amount of flux; as a consequence, careful attention must be given so that new or existing instrumentation and methods are not soon out-of-date. The Development Division at Y-12 has initiated an Environmental Monitoring Program (EMP) to develop promising new techniques in accordance with our own needs and to anticipate changes in State and Federal emission standards. Besides developing new methods and instrumentation, the EMP provides a focus for management when information about state-of-the-art commercial monitors is needed. During its first year, EMP has initiated contributions to the Y-12 Plant in both these areas. The Wright and Wright Infrared Oil Film Monitor represents a commercial instrument which was found to be particularly suited to a specific Y-12 Plant need. On the other hand, laser absorption spectrophotometry is a technique which is being developed for a variety of Plant monitoring requirements.

Infrared Oil Film Monitor

The Oak Ridge Y-12 Plant* is located in Bear Creek Valley, and all process water from the Plant drains to the East Fork of Poplar Creek. Poplar Creek is allowed to flow into New Hope Pond for mixing and sedimentation of settleable solids before release to the outside. Just prior to New Hope Pond, the top few inches of the creek are diverted to a smaller pond which drains from the bottom, retaining oil and floating debris for disposal.(1) The system provides considerable protection for New Hope Pond and biota downstream from the Y-12 Plant in the event that oil is accidentally discharged into Poplar Creek. Maximum effectiveness is realized when spills are detected and corrected quickly to prevent a particularly thick layer of oil from flowing under the skimmer, or to avoid exceeding the capacity of the oil holding pond. The current method of monitoring the creek for oil spills is an hourly visual inspection. These have not proved totally reliable - especially at night when lighting conditions are poor. A monitor was needed to continually inspect the stream and provide warning when the presence of oil was detected in excessive amounts.

The Wright and Wright Infrared Oil Film Monitor is an instrument which uses light reflected from the surface of a stream or pond to detect the presence or absence of floating oil (Figure 1). The detector is small, lightweight, and self-contained. Detection is achieved by a physical method so that no fouling occurs (the instrument never touches the water). It is insensitive to floating debris and responds only to the presence of oil. Temperature extremes pose no problem. And it is inexpensive: less than $7K. There are two limitations to this instrument: it responds only to oil floating on the water surface, and its response is only semi-quantitative.

The Infrared Oil Film Monitor consists of a lamp, detector, and control panel. The lamp and detector mount above the surface of the water to be monitored. The control panel may be remotely located. The lamp is a broad-band infrared (IR) source, and the angle of lamp and detector are such that light reflected from the water's surface falls on the detector. The detector determines the power ratio between two frequencies of the reflected beam in the 3 μm wavelength region of the spectrum. The ratio is different for clean water than for oil, and the detector circuitry notes the difference. Thicker oil films result in larger changes in the ratio, and at some preset level an alarm is tripped. Although the measurement is only semi-quantitative, the instrument may be preset to respond to thin oil sheens (~0.1 μm) or thick (~10 μm).

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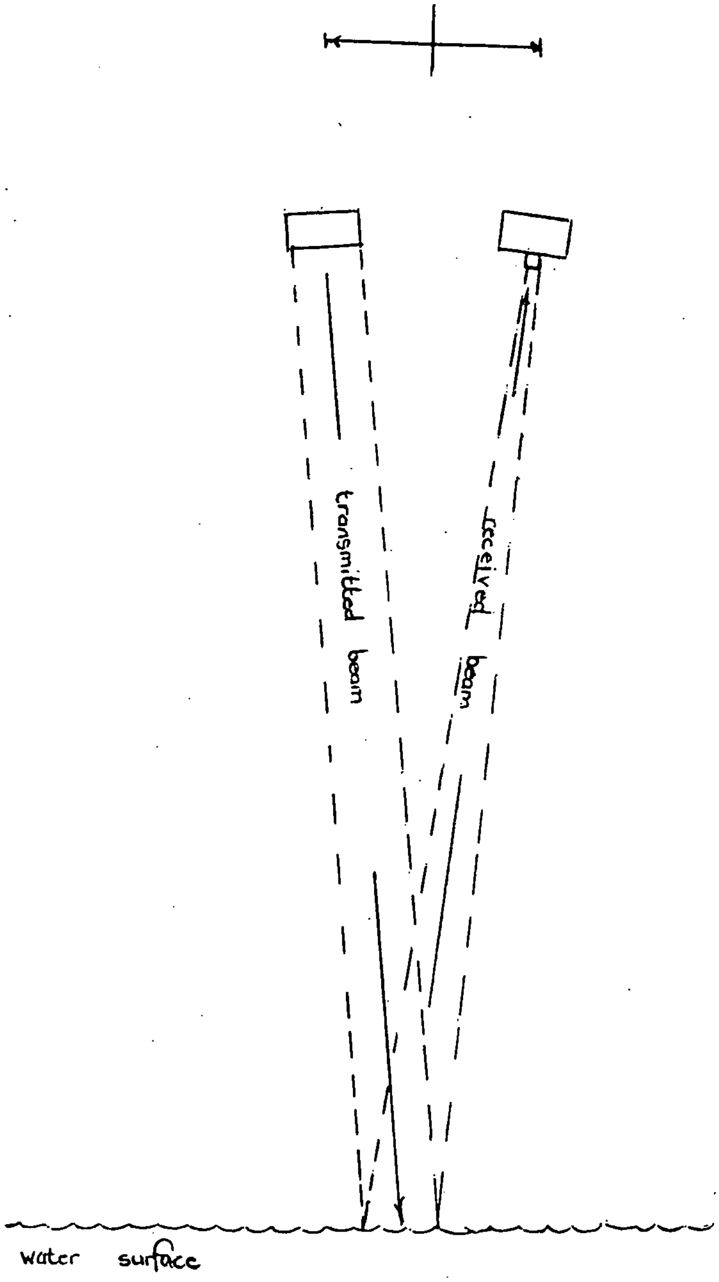

NORMAL INSTALLATION
INFRARED OIL FILM MONITORS

FIGURE 1: Detection of Surface Oil Using Reflected Infrared Radiation

The Infrared Oil Film Monitor was laboratory tested by mounting it over a 4 ft. x 10 ft. tank of water. Cutting oil was dropped onto the surface of the agitated water and instrument response was noted as a function of the thickness of the resulting oil film (Figure 2). In the thin-film mode, the alarm was activated for an amount of oil necessary to provide a 0.05 μm film (2 drops of cutting oil). In the thick-film mode, a 5 μm film was required to trip the alarm. Internal amplifier gain adjustments can be set to correspond to the user's needs. These tests were performed using the instrument as it came from the manufacturer.

The Wright and Wright Infrared Oil Film Monitor has been mounted over Poplar Creek and is currently undergoing field testing and evaluation. After its performance has been shown to be satisfactory, the alarm will be installed at the Plant Shift Superintendent's office, and automatic, continuous surveillance of the surface of the creek will help assure that the waters downstream remain oil-free.

Laser Detection of Pollutants

Infrared (IR) absorption spectrophotometry is a standard analytical tool in most laboratories. Any molecular species with a dipole moment (i.e. any heteronuclear material) will absorb IR at discrete frequencies which are unique to each material. Tunable diode lasers have recently been developed which emit in the infrared. They exhibit excellent frequency resolution ($< 10^{-3}$ cm^{-1}) and available power ($\sim$0.1 mW) at the center frequency not found with dispersion-type instruments. For these reasons, they have found use in the detection of atmospheric pollutants. The high resolution permits detection of a single species in a mixture of gases, and the high output power permits detection of some gases to parts-per-billion (ppb) concentrations.(2)

A tunable diode laser, power supply and cryogenics unit has recently been procured from Laser Analytics, Inc. The laser is tunable over the frequency range 1335-1385 cm^{-1}. This range encompasses absorption bands of both sulfur dioxide (SO_2) and perchloroethylene (C_2Cl_4) as illustrated in Figure 3. These spectra were obtained using a dispersion-type instrument. The unresolved individual contributions to the absorption bands will be detectable using the laser (see Figure 3 insert).

The detection of ambient levels of SO_2 and perchloroethylene will probably involve long-path absorption spectroscopy, as suggested in Figure 4. The long path length between laser and detector increases the absorbing volume, and hence the number of absorbing molecules, thereby increasing the sensitivity of the method. The concentration of a pollutant detected in this manner is an average of concentrations all along the path. Measurement of stack concentrations may be made by directing the beam through the stack gases.

A second laser which emits in the region around 3700 cm^{-1} is being prepared by Laser Analytics for use at Y-12. A quantitative method for determining both ambient and stack concentrations of hydrogen fluoride (HF) gas will be developed using this laser to probe the P(5), P(6), and P(7) branches of the HF ($V = 1 \rightarrow 0$) transition.(3)

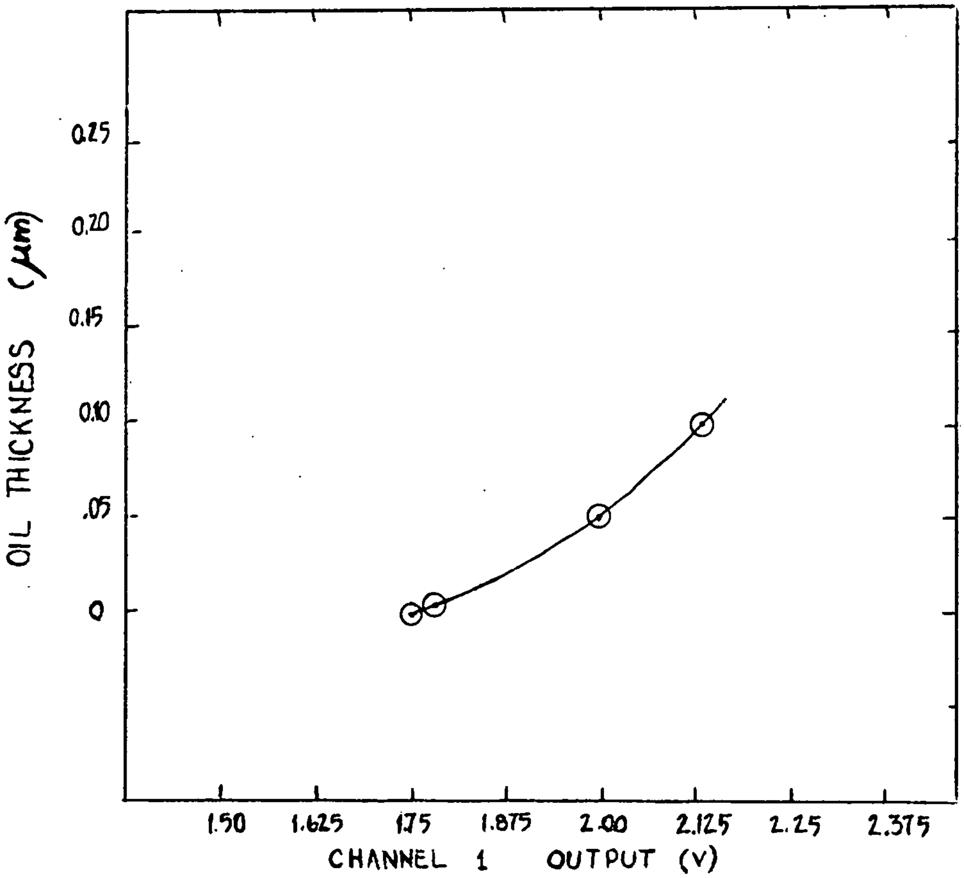

FIGURE 2: Infrared Oil Film Monitor Response to Cutting Oil on Water's Surface

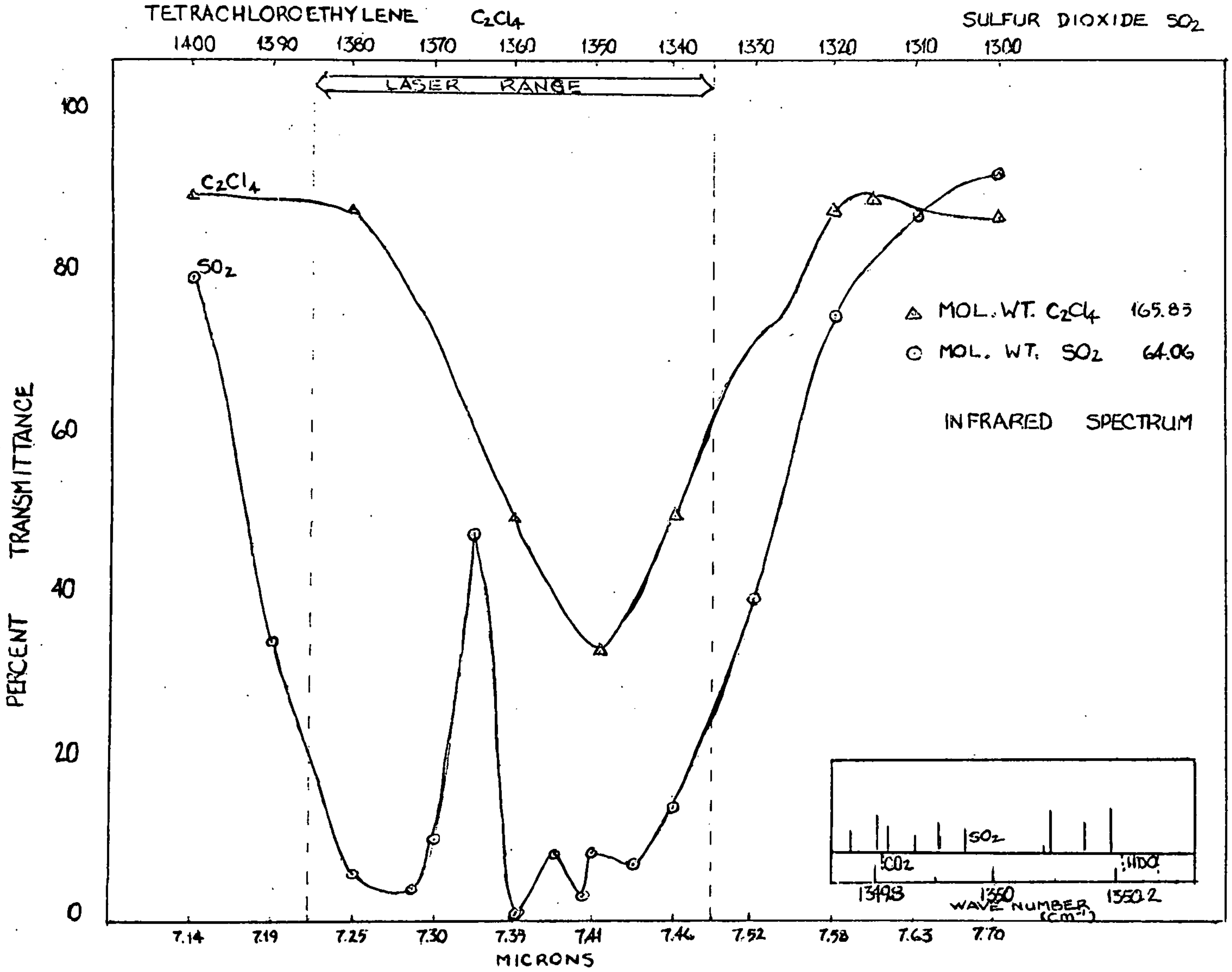

FIGURE 3: A Portion of the Infrared Spectra of Sulfur Dioxide and Perchloroethylene

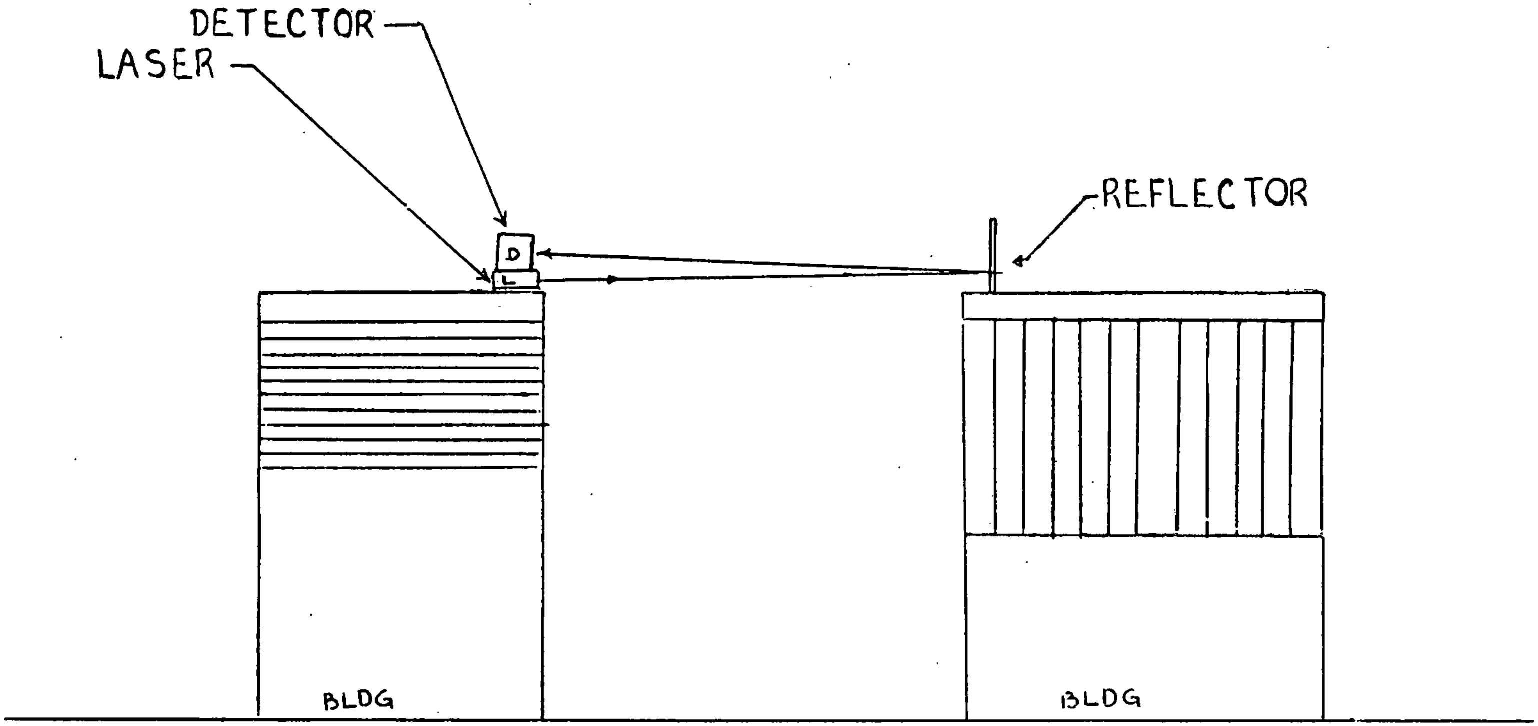

FIGURE 4: Long-Path Infrared Absorption Spectroscopy for Ambient Pollutants

REFERENCES

1. M. Sanders, "Spill Prevention Control and Countermeasure (SPCC) Plan for Oil at the Oak Ridge Y-12 Plant", Y/DD-242 (December 1977).

2. a. J. Reid, B. K. Garside, J. Shewchun, "Detection of Sulfur Dioxide at, and Below, the Part per Billion Level Using a Tunable Diode Laser", Optical and Quantum Electronics, 11, 385-391 (1979).

   b. C. K. N. Patel, "Laser Detection of Pllution", Science, 202, 157-173 (October 13, 1978).

   c. J. Reid, et al., "High Sensitivity Point Monitoring of Atmospheric Gases Employing Tunable Diode Lasers", Applied Optics, 17(11), 1806-1810 (1978).

   d. R. L. Byer, E. Murray, "Remote Monitoring Techniques", from Handbook of Air Pollution Analysis, Eds. R. Perry and R. J. Young, 406-448 (1977).

   e. J. F. Butler and J. O. Sample, "Tunable Diode Laser Instruments", Instrument Society of America International Conference and Exhibit, Houston, Texas, October 11-14, 1976, No. 76-613.

3. G. Guelachvili, "Absolute Wavenumbers Measurements of 1-0, 2-0, HF and 2-0, $H^{35}Cl$, $H^{37}Cl$ absorption Bands" (Laboratoire d' Infrarouge, Paris, Unpublished results).

TECHNICAL SUPPORT INTERFACING FOR THE FY-1981 LINE ITEM PROJECT CONTROL OF WATER POLLUTION AND SOLID WASTE — PHASE I

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ABSTRACT

Present and future LIPs are and will be addressing the issues of operational requirements, energy management, and compliance with regulatory standards. The goals of environmental projects are directed toward meeting regulatory standards which often remain poorly defined well into the normal project budget cycle. Maintaining lines of communication between the technical, environmental, engineering, customer, and other interested groups is imperative from the time of project description and scoping studies through project authorization. A technology transfer process has been inacted at the PGDP to provide critical interdivisional project reviews and to identify and recommend appropriate technologies in a timely manner consistent with existing Plant and engineering procedures. The FY-1981 LIP Control of Water Pollution and Solid Waste — Phase I is the first project to receive full benefit of this process. A significant technical effort has been expended in resolving the uncertainties in recommended technologies that were defined in earlier project reviews. The benefits derived from the Technology Transfer process and the refinements to the system are presented with FY-1981 project as the subproject case.

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