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Chairman: T. W. Oakes

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## SAFETY ANALYSIS REQUIREMENTS

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Safety Analysis, CPCF, Hazards, SAR

## ABSTRACT

Waste management projects can be impacted as a result of the safety analysis process. Safety assessments, preliminary safety analysis reports, final safety analysis reports, and operating safety requirements: all of these documents may be needed to sufficiently evaluate both the probabilities and the consequences of safety risks identified in a process. The identification of high risk hazards during the safety documentation process can result in either the elimination or of corrective changes in portions of the process design. Based on the recent preparation of an FSAR for the Oak Ridge Y-12 Plant(a) Central Pollution Control Facility, this paper will summarize safety analysis requirements and will attempt to illustrate the reasoning behind these requirements.

INTRODUCTION

The primary purpose of the safety analysis process is to assure that a thorough review and documentation of safety concerns for all DOE operating activities are performed. The major emphasis lies with maintaining control over hazardous materials and operations that pose risks to the safety and/or health of operating personnel or the general public. Unique and unusual safety problems are highlighted. However, to prevent redundancy, routine industrial safety precautions are not

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(a) Operated for the U. S. Department of Energy by Union Carbide Corporation, Nuclear Division under Contract W-7405-eng-26.

addressed in the safety analysis literature. Five major objectives have been identified<sup>1,2</sup>, for the overall safety analysis process, to assure that:

1. Potential hazards are systematically identified,
2. Potential impacts are analyzed,
3. Reasonable measures have been taken to eliminate control, or to mitigate hazards,
4. There is documented management authorization of the operation, and
5. The funding level to accomplish an adequate level of safety is identified.

There is some interfacing in the material presented in a safety analysis document and in an environmental analysis document. Particularly in waste management projects, where the presence of potentially hazardous and/or toxic substances is likely, the same scenarios may be evaluated in both review processes: atmospheric releases of noxious gases, liquid spills, consequences of inadequate waste treatment, etc. The difference between the two reviews is that, generally, a safety analysis concentrates only on the personnel and public health hazard aspects, while an environmental analysis considers these aspects as well as the effects of wastes on the surrounding animal and plant life, climatic effects, aesthetic aspects, and the overall ecological balance.

In order to better understand the philosophy of safety analysis, the following basic definitions are presented:



Safety System: Generally consisting of equipment and/or hardware, a safety system is that component of the facility that assures that operation will not pose undue safety risks. The function of the safety system may serve to: maintain hazardous materials containment, prevent occurrences of nuclear criticality incidents, or generally preclude the occurrence of a significant process hazard.

Administrative Controls: Functionally similar to safety systems, administrative controls serve to prevent process hazards from occurring. However, personnel action is the catalyst of prevention rather than a piece of mechanical hardware.

Configuration Control: Configuration control is a procedure taken to identify and document all physical and functional safety characteristics of a facility and to ensure that all changes to these systems are controlled and documented.

Safety Assessment (SA): This brief document serves primarily as a screening process: to determine if significant safety hazards exist in a given project, and if so, to establish the need for further documentation in the form of a safety analysis report.

Preliminary Safety Analysis Report (PSAR): This document serves to identify the basic safety systems and administrative controls required in the facility design and operation, and to analyze the expected behavior of those safety systems for all reasonable accident situations.

Final Safety Analysis Report (FSAR): This document describes how the safety systems identified in the PSAR were incorporated into the design, provides detailed analyses showing that safety systems provide an acceptable level of safety, and establishes a basis for the preparation of the QSR. The FSAR becomes the SAR document of record.

Operations Safety Requirements (OSR): Based on the information presented in the FSAR, the OSR defines the operating conditions, safety boundaries, and administrative controls necessary for the safe operation of the facility. The OSR is also a document of record.

#### SAFETY ANALYSIS REQUIREMENTS

The effectiveness of the safety analysis effort is in some way related to its scheduling, relative to the facility design schedule. Figure 1 illustrates the preferred interaction between design and safety documentation schedules. Prior to submittal to DOE for review and approval, all forms of safety analysis documentation must be internally reviewed by the design team, and accepted by the Safety Analysis Committee. This committee, chaired by the Safety Department head, includes the Plant Emergency Director and representatives from the Operation, Engineering, and Radiation Safety Divisions.

Safety analysis documentation will be prepared for all new and existing facilities, and all modifications to existing facilities. In many cases, only a Safety Assessment will be required; in some cases, such as those listed in the October 1979 "Hawkins" letter<sup>3</sup>, exceptions are granted by the Safety Analysis Committee and a formal SA is not

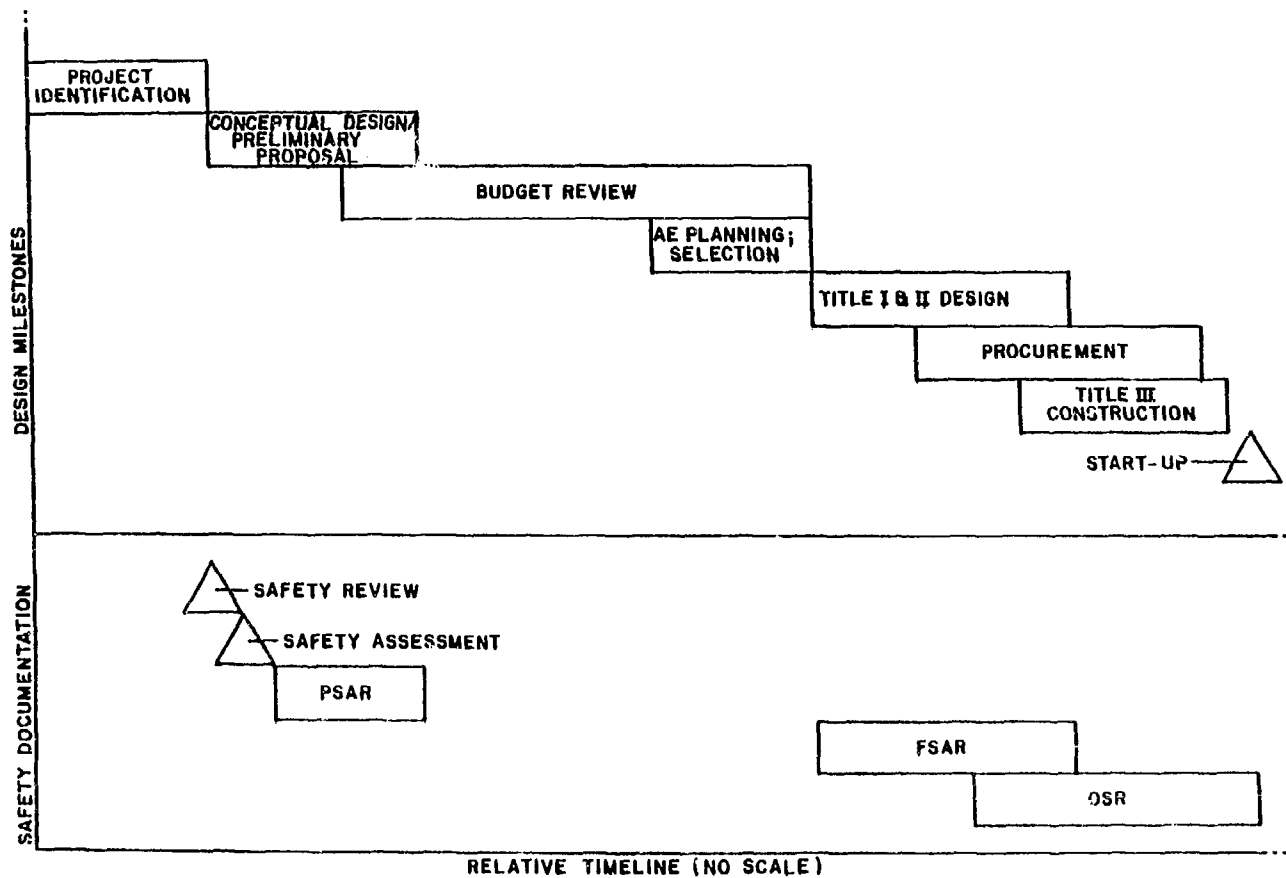


FIGURE 1: DESIGN/SAFETY SCHEDULE INTERLOCKS

required. In certain situations, where only small, predesignated quantities of hazardous materials are handled (e.g., in a laboratory), a limiting condition OSR can accompany the SA, and the requirement for the SARs can be waived<sup>4</sup>. Otherwise the PSAR follows the SA, and the FSAR and OSR are prepared to complete the safety documentation process. The PSAR step is not relevant for existing facilities, since the opportunity for design input at this point is nonexistent. The basic logic of determining what safety documentation is required is illustrated in Figure 2.

#### SAFETY ANALYSIS OF CENTRAL POLLUTION CONTROL FACILITY (CPCF)

A specific recent example of the safety documentation effort is the FSAR for the Central Pollution Control Facility, which is part of the 1981 line item, Control of Effluents and Pollutants, Phase I. Because of special DOE-ORO waivers, no PSAR was prepared for this facility; hence, some overlapping between PSAR and FSAR requirements resulted. Safety systems and administrative controls are identified, reasonable accident scenarios are presented, and detailed analyses of safety levels are performed. Following a brief description of the CPCF, a summary of the safety analysis effort will be discussed.

The CPCF will provide for the storage, treatment, and disposal of aqueous inorganic waste streams generated at the Y-12 Plant. These wastes, comprising approximately a 700,000-gal. annual demand on the CPCF, include pickling and plating shop liquid effluents, plating shop

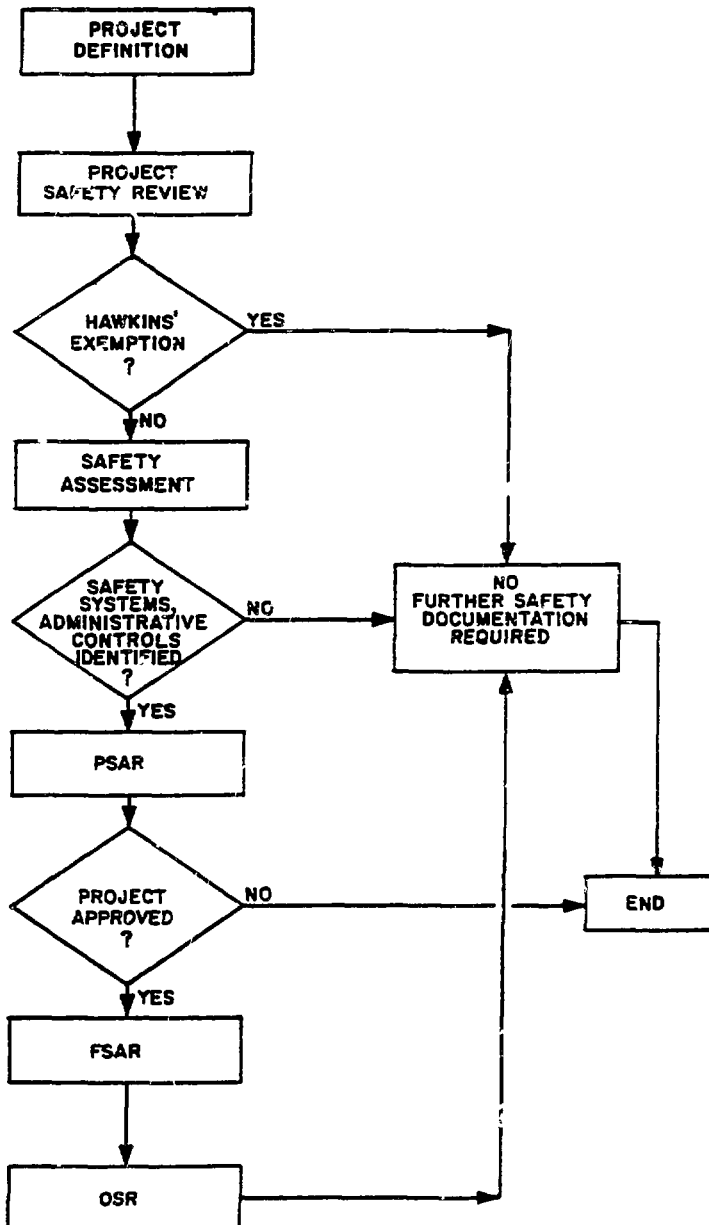


FIGURE 2: SAFETY ANALYSIS DECISION LOGIC

floor wastes, U/Be - contaminated wastewater generated in the fabrication areas of Buildings 9401-2 and 9201-5, and spent scrub solution from the HF Scrubber systems in Buildings 9206 and 9212 (part of the same line item).

A generalized block flow diagram of the CPCF is shown in Figure 3. Basically, there are two paths of waste treatment in the CPCF, with a certain amount of interaction between the paths. Dilute mopwater characterizes about two thirds of the incoming waste solutions, and will be treated primarily by flocculation in a reactor-clarifier system. The more concentrated incoming waste streams will be stored in the CPCF basement, tested in the CPCF laboratory to determine their optimum treatment method, and batch-treated in process reactors for neutralization and precipitation of heavy metals. The resulting reactor slurry will be settled, then dewatered via filtration. The liquid effluents from both the mop water treatment and the reactor/settler systems will be discharged to a set of effluent basins and sampled thoroughly before being released to the storm sewer as treated wastes. Sludges from the filtration units will be drummed for disposal in existing Y-12 burial grounds.

The CPCF will be housed in a new four story building situated within the security fencing of the exclusion area at the Y-12 Plant.

Inherent in the safety analysis process is the evaluation of accident scenarios with respect to their estimated probabilities of

FIGURE 3: CPCF BLOCK FLOW DIAGRAM

occurrence and their consequences if the event does occur. Four categories have been established for approximating accident probability: 1) probable - event will occur several times during the life of the facility; 2) likely - event is likely to occur sometime; 3) unlikely - event is unlikely to occur; and, 4) remote - the probability of occurrence is so small that it can be assumed it will not be experienced. To qualitatively evaluate the consequences of an occurrence, four categories are utilized: 1) catastrophic - may cause on-site deaths or severe impact on off-site personnel; 2) critical - may cause severe on-site injury, severe occupational illness, or major impact on off-site personnel; 3) low - may cause minor on-site injury, minor occupational illness, or minor impact on off-site personnel; and, 4) negligible - will not result in significant on-site injury, occupational illness, or provide a significant impact on off-site personnel. Several groupings of the probability and consequence categories can be made; the resulting combinations can be equated to several general levels of risk. An example of such a risk assessment is presented in Table 1; however, depending on the specific case in question, varying risk levels may be assigned to probability/consequence pairs.



Table 1: Risk Assessment Example

| <u>Probability</u> | <u>Consequence</u> | <u>Relative Risk Level</u>                                                                                                                             |
|--------------------|--------------------|--------------------------------------------------------------------------------------------------------------------------------------------------------|
| Medium             | Negligible         | Very low; not addressed in safety analysis documentation                                                                                               |
| High               | Low                | Low; discussed in SARs to demonstrate low consequence                                                                                                  |
| Medium             | Significant        | Significant; lower risks insignificant, higher risks unacceptable; analyzed at length in SARs to demonstrate the adequacy of/need for design features. |
| Remote             | Any level          | Low; not analyzed due to lack of credibility.                                                                                                          |
| Medium-High        | High               | Unacceptable; analyzed in detail in SARs to demonstrate necessity of prevention.                                                                       |

The accident scenarios addressed in the CPCF FSAR are those initiated by: failure of passive equipment when the design parameters are exceeded; failure of active equipment to perform as required; operator error; or, natural phenomena. Since the CPCF is by definition a chemical waste treatment facility, quantities of toxic or hazardous substances are usually present. Thus, in the consideration of facility hazards, the various aspects of toxic material safety was stressed. The significant accident scenarios were grouped in the following manner: 1) leaks, spills, and sprays of waste solutions; 2) explosions from either the too rapid addition of chemical reagents or the generation of explosive gases; 3) atmospheric releases of toxic or noxious substances; 4) building releases of toxic or noxious substances; 5) inadequate waste treatment;

6) the loss of utilities; 7) the occurrence of an earthquake, tornado, or flood; and, 8) the impact of adjacent facility operations. Each of these scenarios was evaluated, and the risk level was determined.

As a result of the evaluation, two safety systems were identified: 1) the sealed exhaust system for the chemical storage treatment equipment prevents noxious or toxic gases from entering the CPCF building; and, 2) the heating and ventilation system is relied upon to clear the building of any fumes resulting from a large spill. Administrative controls identified for the safe operation of the CPCF included recommendations to: require protective clothing in the process areas handling hazardous chemicals; assure communication between the CPCF laboratory and the operating area via written instructions for treating waste batches; adhere to restrictions on incoming waste composition; promptly clean up any chemical spills; prevent the sludge product from drying out and allowing dust to be a concern; and sample effluent basin solutions prior to storm sewer discharge.

### CONCLUSION

In summary, the safety analysis effort is generally documented by the production of a safety assessment, and if determined necessary, preliminary and final safety analysis reports and an operations safety requirements document. In the preparation of the FSAR for the Central Pollution Control Facility, both the probabilities and the consequences of various accident scenarios were evaluated, and the risks of operating

the facility were determined. Since the CPCF is a waste treatment facility, many of the accident scenarios considered, deal with potential waste releases, both to the immediate area and to the surrounding environment. While the safety analysis documentation evaluates the personnel health and safety aspects of such a release, often the same incidents must be analyzed from an environmental standpoint when determining the overall effectiveness of the treatment facility.

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1. Standard Practice Procedure, D-Series. No. D-5-29, Safety Review and Documentation Program. (March 31, 1981).
2. DOE Safety and Environmental Control Division. OR 5481.1, "Safety Analysis and Review System". (June 10, 1980).
3. C. C. Hawkins, DOE; letter entitled "Streamlining the Safety Documentation Process", (October 9, 1979).
4. DOE Branch Position Paper No. 4: Facilities and System Safety Branch. OSRs Without SARs.

**PREPARATION OF COMPUTER DATA BASES FOR  
ENVIRONMENTAL PROTECTION**

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**Key Words**

**Environmental, Data Bases, Computer, Programs, Data**

**ABSTRACT**

Organizations which handle massive amounts of environmental data must use computer data bases to keep record costs as low as practicable and to make possible the efficient and timely assessment of the environment. This paper will review the basic steps necessary for planning, programming, testing and documentation of a computer program.

**INTRODUCTION**

Computer based environmental data systems should be implemented before increasing data and reporting requirements cause breakdowns in data verification, report production, and manpower use. There are basic steps to be followed in this process and this paper will attempt to review each step. There are several reasons for advancing to computer data bases for environmental work and these include: greater quality assurance, savings of time and money, ease of complying with the many varied existing regulations, quick, convenient retrieval of specific and general environmental data by location, time interval or other parameter, and ease of data analysis (graphical or statistical).

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### PREPROGRAMMING STEPS

To begin computerizing any data, all data and information must be assembled for review. Collection information, parameters, locations, sample types, field and analytical analysis data must be determined by the environmentalist and the systems analyst for incorporation into the data base structure. All existing and proposed regulations that apply to the environmental system being computerized must be reviewed and incorporated either into the data base structure or the programs which run against the system. As requirements change, changes will be made to the data base structure, the programs, or both.

Inherent to environmental data are acceptable limits for each parameter measured since regulations that apply to specific environmental systems generally have rigidly defined compliance ranges. These limits can be incorporated into the data entry programs for earliest detection of violations and/or data entry error trapping. This facilitates a higher degree of quality control of environmental data and alerts supervision to problems that the field and lab technicians may be having.

The regular reporting programs can be structured such that they report the environmental data according to the needs of various user groups.

### PROGRAMMING

Generally, at this time the total package is ready for the computer programmer to begin programming. Intensive sessions occur among the systems analyst, programmer and generator reviewing data characteristics, present procedures and computerization objectives. The systems analyst and programmer must become as familiar with the procedures as the generator in order to create a useful and useable program. By understanding the data flow beginning with the laboratory analysis group's measurement processes, such problems as the resolution of standardized reporting units can be affected before actual data begins to flow through the system. Also, if the analysis group's data storage

media is computer oriented (tape, disk, etc.), the programmer may be able to take advantage of a direct transfer of the required data from system to system.

During the process of creating the system, the programmer generally uses real data to test the program modules. The generator will be asked to supply valid and invalid data and to operate the test program. At this time, most program problems will be uncovered and resolved. The generator and programmer must realize that they are developing a system highly subject to change for individuals who may be unfamiliar with the specific data, limits and units. The system should be given a trial run with real data, invalid data, noncompliance data and false data. If the programs operate efficiently using the above data, then a person unfamiliar with the data should try the programs. Usually, one or two entry type problems will occur. This happens because the programmer and generator are familiar with the data but others may not be aware of different facets inherent to the data. After all testing and debugging, the system is now ready for general use.

#### TRAINING AND DOCUMENTATION

Technicians will need to be trained to operate and use the computer programs. Documentation of the programs can occur before or after the technician has begun general use of the system. Documentation should include operator-user instructions, programming documentation and specific use and parameter limits used to develop the program.

#### SUMMARY

As can be seen by the steps involved in programming environmental data, greater quality assurance results from the computer program alerting the user to violations of entered data. Savings of time and money result from supervision being relieved of generating and calculating

data for report purposes. With parameter limits programmed into the computer program, complying with the many varied regulations is facilitated. Reports can be printed instantaneously of any violations and invalid or false data entered by technicians. This assures that supervision can review those specific occurrences instead of all generated data. More efficient data review can be accomplished by asking for a specific location or time interval, thus speeding the review process.

In general, computerizing environmental data results in increased quality assurance and control, better utilization of technician and supervision time, and overall savings of time and money. Any time a system can be accomplished more efficiently, the company involved reduces the risk associated with noncompliance of environmental regulations. Efficient computer utilization promotes better surveillance and immediate assessment of various processes occurring in the environment because of processes occurring internally or externally at the plant facility.

## THE USE OF DOE/RECON IN ENVIRONMENTAL PROTECTION

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### Key Words

DOE/RECON, Computer, Information Retrieval,  
Environmental Protection

### ABSTRACT

DOE/RECON is an interactive on-line information retrieval system which provides users rapid and easy access to a wide range of information. The DOE/RECON system is operated by the Technical Information Center in Oak Ridge, Tennessee for the United States Department of Energy. The Technical Information Center develops and manages the Department of Energy's technical information program which includes DOE-originated information as well as world-wide literature on scientific and technical advances in the energy field. To manage and make available this large amount of information, the Technical Information Center builds and maintains computerized data bases and disseminates this information via computerized retrieval systems. This system has been used to a great advantage in the field of environmental protection.

### INTRODUCTION

The Technical Information Center (TIC) in Oak Ridge, Tennessee is the national center for scientific and technical information for the Department of Energy (DOE). TIC develops and manages DOE's technical information program which includes DOE-originated information as well as world-wide literature on scientific and technical advances in the energy field. Also included is information related to socioeconomic, environmental, and policy-related subjects.

To manage and make available this large amount of information, TIC builds and maintains computerized data bases and disseminates this information via computerized retrieval systems. This retrieval system has been given the name DOE/RECON. Thus, DOE/RECON is an interactive

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on-line information retrieval system which provides users rapid and easy access to a wide range of information.<sup>1</sup>

### RECON

The acronym RECON stands for REMote CONsole, which signifies that the system can be utilized by users at various sites across the United States. Users can have access to RECON through telephone hookups with teletype-compatible terminals by using the the GTE telenet network or by dialing directly.<sup>2</sup>

DOE/RECON is relatively simple to use and requires only a small number of commands to search through a data base. Groups (or sets) of information related by subject, author, year of publication, etc., can be combined and the information can be displayed on a screen or printed on paper.

Instructions on the use of RECON can be obtained from the DOE/RECON User's Manual. There is also an on-line tutorial program which will provide instructions on the DOE/RECON system.

### DOE/RECON DATA BASES

Four major data bases created and maintained by TIC for the RECON system are the Energy Data Base (EDB), General and Practical Information Data Base (GPA), Research in Progress Data Base (RIP), and Issues and Policy Summary Data Base (ISP).<sup>3</sup>

The Energy Data Base contains scientific and technical information covering all areas of energy and other information in the areas of energy policy and management. GPA contains mass-distribution information on energy and other general energy information. RIP includes current DOE and other federal environmental research and development programs in the field of energy. ISP provides users an access to public statements on energy by DOE officials, the White House, Members of Congress, and others. Other data bases cover a multitude of subjects including oil and gas reserves, NASA technical briefs, radiation shielding codes, and many other subjects.

There are several data bases which contain environment-related information. The four major data bases discussed previously contain huge amounts of environment-related information. Other data bases which contain such information include the Environmental Mutagens, Environmental Teratology, Environmental Sciences Abstracts, and other data bases.

### SUBJECT SEARCHES

A search of a data base can be performed for information on a specific subject. When dealing with a broad topic, there will be produced a large volume of information. To make the information more specific, broad subjects are combined with narrower subjects to produce more specific information.

An example of a broad search would be to do a search for information on the environment. This type of search would provide thousands of articles, reports, etc. In the Energy Data Base alone, there are over 6,500 articles, etc., which contain information on the environment.<sup>4</sup> To reduce this volume of information to the more specific environmental information wanted, other narrower subjects are combined with the broad subject - Environment. In this same data base, there are over 2,400 references dealing with milk. When the subject of environment is combined with Iodine-131 the number of references is reduced to about 130, and with all three subjects combined, the number of references is reduced to about 40.

Information searches can also be limited by author, date, or other limiting factors.

### REFERENCES

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GERMINATION AND GROWTH EFFECTS OF HEXAVALENT CHROMIUM IN  
OROCOL TL (A CORROSION INHIBITOR) ON PHASEOLUS VULGARIS

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ABSTRACT

This research was designed to address the potential for germination and growth effects in bush beans (Phaseolus vulgaris L. var. Bush Blue Lake) from hexavalent chromium in Orocol TL, a proprietary chromated, zinc-phosphate compound added to DOE cooling water systems for corrosion inhibition. Studies were conducted at low and high Orocol TL concentrations in the soil by adjusting soil pH and the percent of organic matter.

Germination effects were determined for seeds germinated in soils adjusted to differing pH ranges (4-4.5, 5-5.5, and 6.5-7), levels of organic matter (1.8, 3, and 5%), and Orocol TL amendments (control of 0, 10, and 500  $\mu\text{g/g}$  chromium). Growth responses (effects) were determined from plants cultured in the same soil treatment combinations as described for the germination study.

High levels (500  $\mu\text{g/g}$ ) of hexavalent chromium in soil (as Orocol TL) affected germination and growth, while a high level of organic matter significantly reduced chromium toxicity on germination. At lower chromium concentrations there was significant uptake by all plant parts, with a corresponding reduction in biomass of leaves. Consequently, adjustments of soil pH from 4.0 to 7.0 appear to have no significant effect on chromium uptake in plants. Increasing the organic matter level to 5%, while decreasing the toxicity of high chromium levels to germinating seed, did not affect chromium uptake.

Key Words: Chromium, germination effects, growth effects, bush beans, corrosion inhibitor, hexavalent chromium

INTRODUCTION

Closed-cycle cooling towers, which involve the use of evaporative cooling to reject heat, have become increasingly popular as an alternative to once-through cooling for electrical generating stations because of

the reduced impact to aquatic systems by not returning hot water directly to the source. However, the operation of closed-cycle cooling has the potential for causing adverse effects to terrestrial biota from cooling tower drift. As the demand for electrical power increases, so will the need for cooling towers as a method of dissipating waste heat.

Depending on the quality of the makeup water and plant-specific operational procedures, constant water treatment may be necessary to decrease the possibility of corrosion within the cooling system. This often necessitates the addition of corrosion inhibitors and scale retardants. At the Department of Energy (DOE) uranium enrichment facilities in Oak Ridge, Tennessee; Paducah, Kentucky; and Portsmouth, Ohio; waste heat is dissipated by mechanical-draft cooling towers that use a proprietary inorganic chromated, zinc-phosphate corrosion inhibitor (Orocol TL marketed by Betz Laboratories, Inc.) in the recirculating cooling water systems (Fowlkes and Webb, 1972).

A fraction of the circulating water becomes entrained as small droplets in the exit air flow and is carried out beyond the towers as drift. The drift contains concentrations of dissolved minerals and chemicals similar, if not identical, to concentrations of the recirculating water (Laulainen, 1978), which is maintained at 20  $\mu\text{g/g}$  hexavalent chromium (as  $\text{CrO}_4^{2-}$ ) in the recirculating streams of the DOE uranium enrichment facilities. Loss of recirculating water (drift) presents a pathway for transfer of potentially toxic elements into the terrestrial environment.

Previous research at the Oak Ridge Gaseous Diffusion Plant (ORGDP) cooling towers provided quantitative evidence of the transfer of chromium from drift to vegetation (detectable above background to at least 1600 m from the towers) and to soil (with above background concentrations out to 180 m from the towers), and identified some effects of chromium in drift on vegetation (Taylor et al., 1975; Parr et al., 1976; Taylor et al., 1976; Taylor and Parr, 1978; Taylor, 1980). While contamination of vegetation from deposition of drift on aerial parts may produce a short-term effect, accumulation of chromium in the soil poses greater and potentially longer term consequences. Since the chromium in drift

is in water droplets, it was hypothesized that Orocol TL dissolved in a soil-water solution would be suitable to assess effects of chromated drift without sacrificing chemical composition.

The purpose of this research was to determine the potential for increasing or decreasing germination and growth effects in plants from chromium in Orocol TL at low and high concentrations in the soil by adjusting soil pH and the percentage of soil organic matter. In many studies (Shewry and Peterson, 1974; Dowdy and Larson, 1975; Dijkshoorn et al., 1979), chromium uptake by plants was found to increase in acidic soils. However, in the presence of organic matter, hexavalent chromium may be reduced to the less mobile trivalent form (Skeffington et al., 1976; Cary et al., 1977b).

#### METHODS

The design of the experiment incorporated three levels of three factors, organic matter, pH, and chromium concentration (added as Orocol TL), to determine what effects the treatments, either singly or in combination, would have on seed germination, chromium uptake, and plant growth. Soil used for the experiment was the lower A horizon (A<sub>2</sub>) of a Fullerton cherty silt loam. Organic matter treatments consisted of unamended soil (1.8%) and soil amended with peat moss to raise organic matter levels to 3 and 5%.

Soil pH was measured as 4.0 to 4.5 and was used as the low pH treatment. Soil was limed to raise pH to 5.0 to 5.5 and 6.5 to 7.0 for the other two treatments.

Hexavalent chromium amendments (as Orocol TL) to the soil were 0 (for control), 10, and 500 µg/g. In a separate study (Parr, 1981) it was determined that 25 to 35% of the hexavalent chromium remained mobile in the soil with the potential of plant uptake effects at 500 µg/g. Each treatment was replicated three times.

For the germination study, five bush bean seeds (Phaseolus vulgaris L. var. Bush Blue Lake) were planted in each pot which contained 300 g of the appropriate soil treatment. A layer of coarse silica was placed in the bottom of the pots to provide some drainage;

however, the pots did not have drainage holes in order to prevent the leaching out of the chromium through watering. Percent germination at the end of a 14-d period was recorded.

Treatment effects on seed germination were statistically analyzed by analysis of variance. The data were transformed to stabilize the variance using the arcsin transformation for binomial proportions (Snedecor and Cochran, 1972) before the analysis of variance calculations. To determine whether treatment combinations differed significantly from each other, a multiple comparison procedure (Fisher's Least Significant Difference Method) was used (Chew, 1977).

A separate growth effects study was conducted using the same treatments and levels as the germination study. Nine-day-old bean plants (Phaseolus vulgaris L. var. Bush Blue Lake) were transplanted in 1.9 kg of the appropriate soil mixture in pots without drainage to reduce loss of chromium through watering soil. Plants were then watered to the same moisture level and placed in the greenhouse.

Measurements of plant height were recorded every 2 to 3 d. Leaves, stems, and roots were harvested when the plant died or at the end of 8 weeks. Roots were carefully washed to completely remove all traces of soil. Roots of a separate group of bean plants grown in chromium-contaminated soil were washed once, twice, or three times, then analyzed for chromium content to determine if additional chromium was removed in the successive washings. The chromium concentrations did not differ significantly with the number of washes, indicating that surface contamination was removed in the initial wash.

Plant tissues were oven-dried (24 h) at 100°C, assessed for total biomass, then placed in a furnace for ashing (550°C) overnight. The ashed material was removed and cooled to room temperature and 2 mL concentrated nitric acid added to the ash for digestion (about 15 min). Using 0.1 N nitric acid, the solution was then washed into a funnel lined with Whatman No. 42 ashless filter paper and diluted in distilled water to 25 mL. Leaves, stems, and roots were analyzed for total chromium by atomic spectrophotometry using a Perkin-Elmer Model 403 Spectrophotometer.

The effect of Orocol TL on plant growth was determined by comparing chromium concentrations and biomass of leaves, stems, and roots. Statistical analyses of growth data determined that the interactive terms did not explain a significant amount of variation, so analysis of variance statistics were calculated using main effects only. To achieve a normal distribution of the estimated residuals from the analysis of variance model, a log transformation was used on each of the observed chromium concentration values. However, no transformation was necessary for the biomass data. After determining which main effects (chromium concentration in soil, organic matter content, and soil pH) differed significantly from each other, Duncan's multiple range test was used to identify significant differences within the main effects. The 0.05 level of probability was used as the criterion for accepting or rejecting null hypotheses in all statistical analyses.

## RESULTS AND DISCUSSION

### Germination Effects

Analysis of variance on germination results indicated significant main effects due to organic matter content and chromium concentrations along with their interaction (Table 1). Soil pH did not appear to affect the response. Results of multiple comparison procedures (Fig. 1) showed that seed germination between treatments containing 1.8 and 3% organic matter were similar, whereas seed germination in 5% organic matter was significantly higher. Germination of seeds planted in 500  $\mu\text{g/g}$  Cr-VI was significantly lower than germination in soils containing 0 or 10  $\mu\text{g/g}$  chromium; however, the germination within the 0 and 10  $\mu\text{g/g}$  treatments did not differ significantly from each other.

Although there was a definite inhibition of germination in all of the 500- $\mu\text{g/g}$  chromium soil combinations, the addition of organic matter to the 5% level significantly increased the probability of the seeds germinating. This indicated that the addition of organic matter might impart some ameliorating effect by reducing the hexavalent chromium to the less toxic, trivalent species.



Table 1. Comparison of seed germination (percent) at each treatment level\*

| Soil pH | Chromium concentration   |                  |                  |                           |                  |                  |                            |                  |                   |
|---------|--------------------------|------------------|------------------|---------------------------|------------------|------------------|----------------------------|------------------|-------------------|
|         | 0 µg/g<br>organic matter |                  |                  | 10 µg/g<br>organic matter |                  |                  | 500 µg/g<br>organic matter |                  |                   |
|         | 1.8%                     | 3%               | 5%               | 1.8%                      | 3%               | 5%               | 1.3%                       | 3%               | 5%                |
| 4-4.5   | 53 <sup>ac</sup>         | 73 <sup>ac</sup> | 93 <sup>bc</sup> | 67 <sup>ac</sup>          | 53 <sup>ac</sup> | 80 <sup>bc</sup> | 20 <sup>ad</sup>           | 40 <sup>ad</sup> | 100 <sup>bd</sup> |
| 5-5.5   | 80 <sup>ac</sup>         | 80 <sup>ac</sup> | 80 <sup>bc</sup> | 60 <sup>ac</sup>          | 27 <sup>ac</sup> | 93 <sup>bc</sup> | 20 <sup>ad</sup>           | 40 <sup>ad</sup> | 93 <sup>bd</sup>  |
| 6.5-7   | 47 <sup>ac</sup>         | 73 <sup>ac</sup> | 80 <sup>bc</sup> | 60 <sup>ac</sup>          | 67 <sup>ac</sup> | 93 <sup>bc</sup> | 13 <sup>ad</sup>           | 60 <sup>ad</sup> | 47 <sup>bd</sup>  |

\*Means superscripted by the same letter do not differ at the 5% error probability level.

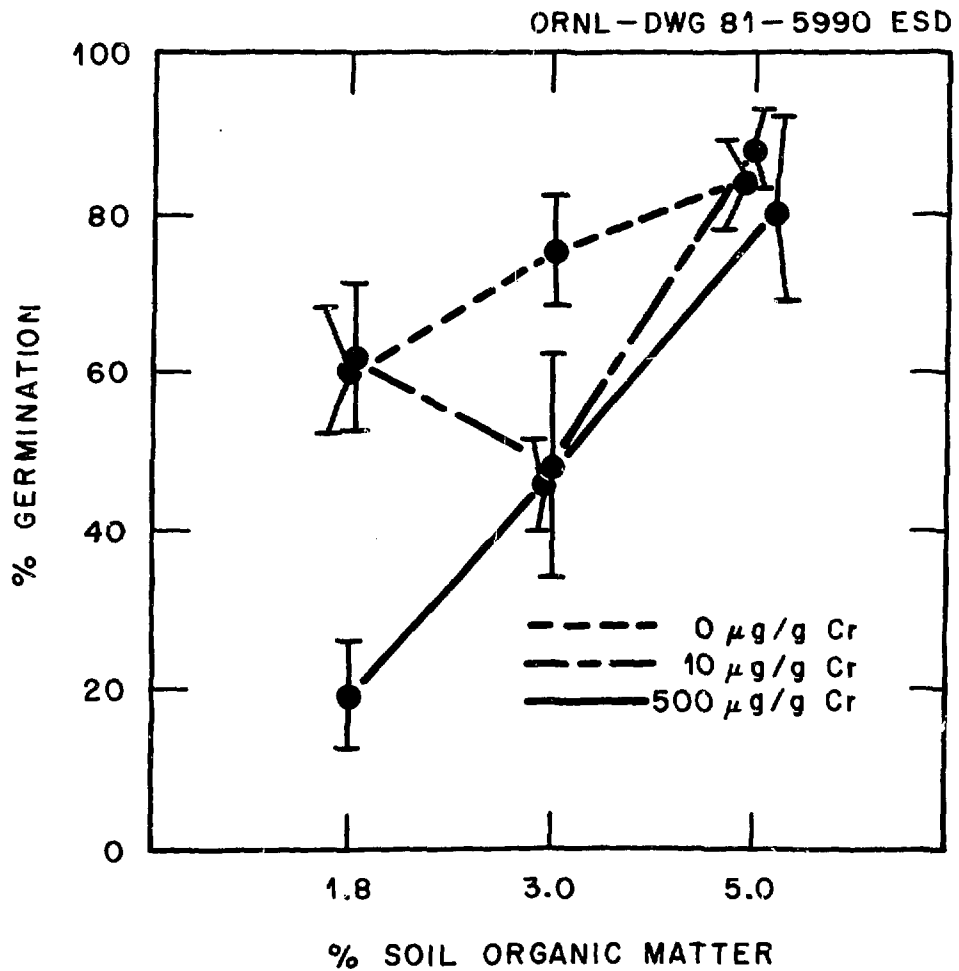


Fig. 1. Percent germination  $\pm$  SE of bush bean seed in soil amended with ORocol TL. Each point is the mean of nine pots.

## Growth Effects

### Effect of 500- $\mu$ g/g Cr-VI amendment

In order to assess growth effects, bush bean seedlings were transplanted into the same soil treatment combinations used in the germination study. Beans transplanted into the soil treatment combinations with 500  $\mu$ g/g Cr-VI died within 48 hours. Leaves, stems, and roots were collected and analyzed for chromium content. All plant parts contained extremely high amounts of chromium (Table 2). Plant roots in the 500- $\mu$ g/g Cr treatments with a pH of 4.0 to 4.5 contained significantly less chromium than the other treatments.

Of the 943 mg Cr-VI amended to the soil, 0.0004 to 0.110% was transported to the leaves and 0.003 to 0.016% remained in the roots. Concentration factors for leaves, stems, and roots of each treatment were determined on a dry weight basis from the ratio of the mean chromium concentration ( $\mu$ g/g) in the treated plant part, minus the mean chromium concentration ( $\mu$ g/g) in the controls to the chromium ( $\mu$ g/g) amended to the soil. A consistent trend is evident within the 500- $\mu$ g/g Cr treatment plants with the lowest factors in the roots (2.9-7.5), increasing in the stems (4.4-12.0), and highest in the leaves (8.1-19.1). The quantity of hexavalent chromium present in the soil evidently was sufficient to exceed the adsorbing and reducing capacity of the soil and roots (Bartlett and Kimble, 1976). Enough chromium, therefore, remained in the mobile, hexavalent state and was transported quickly throughout the plant.

### Effect of 10- $\mu$ g/g Cr-VI amendment

Bean plants grown in soil amended to concentrations at 10  $\mu$ g/g Cr-VI contained significantly ( $P < 0.05$ ) greater concentrations of chromium in all plant tissues when compared to those grown in non-amended soils, regardless of the percent of organic matter or soil pH treatment (Table 2).

Concentrations in leaves (Fig. 2) grown in nonamended soil ranged from 0.02 to 0.40  $\mu$ g/g chromium as compared to 0.16 to 21.77  $\mu$ g/g Cr in soil amended to 10  $\mu$ g/g Cr-VI.

Table 2. Mean chromium concentrations in leaves, stems, and roots\*

| Soil pH       | Chromium concentration   |                   |                   |                           |                   |                   |                            |                   |                   |
|---------------|--------------------------|-------------------|-------------------|---------------------------|-------------------|-------------------|----------------------------|-------------------|-------------------|
|               | 0 µg/g<br>organic matter |                   |                   | 10 µg/g<br>organic matter |                   |                   | 500 µg/g<br>organic matter |                   |                   |
|               | 1.8%                     | 3%                | 5%                | 1.8%                      | 3%                | 5%                | 1.8%                       | 3%                | 5%                |
| <u>Leaves</u> |                          |                   |                   |                           |                   |                   |                            |                   |                   |
| 4-4.5         | 0.12 <sup>a</sup>        | 0.11 <sup>i</sup> | 0.06 <sup>a</sup> | 2.70 <sup>b</sup>         | 1.27 <sup>b</sup> | 6.99 <sup>b</sup> | 6373 <sup>c</sup>          | 4030 <sup>c</sup> | 4853 <sup>c</sup> |
| 5-5.5         | 0.11 <sup>a</sup>        | 0.09 <sup>a</sup> | 0.15 <sup>a</sup> | 1.24 <sup>b</sup>         | 3.41 <sup>b</sup> | 0.98 <sup>b</sup> | 5046 <sup>c</sup>          | 4526 <sup>c</sup> | 6762 <sup>c</sup> |
| 6.5-7         | 0.11 <sup>a</sup>        | 0.12 <sup>a</sup> | 0.26 <sup>a</sup> | 0.58 <sup>b</sup>         | 1.67 <sup>b</sup> | 7.64 <sup>b</sup> | 7961 <sup>c</sup>          | 9523 <sup>c</sup> | 6586 <sup>c</sup> |
| <u>Stems</u>  |                          |                   |                   |                           |                   |                   |                            |                   |                   |
| 4-4.5         | 0.05 <sup>a</sup>        | 0 <sup>a</sup>    | 0.04 <sup>a</sup> | 0.26 <sup>b</sup>         | 0.74 <sup>b</sup> | 6.78 <sup>b</sup> | 3799 <sup>c</sup>          | 2505 <sup>c</sup> | 2184 <sup>c</sup> |
| 5-5.5         | 0 <sup>a</sup>           | 0.52 <sup>a</sup> | 0.02 <sup>a</sup> | 0.44 <sup>b</sup>         | 4.05 <sup>b</sup> | 0.44 <sup>b</sup> | 3880 <sup>c</sup>          | 3887 <sup>c</sup> | 5070 <sup>c</sup> |
| 6.5-7         | 0.08 <sup>a</sup>        | 0 <sup>a</sup>    | 0.09 <sup>a</sup> | 0.47 <sup>b</sup>         | 1.49 <sup>b</sup> | 8.24 <sup>b</sup> | 4937 <sup>c</sup>          | 5998 <sup>c</sup> | 3683 <sup>c</sup> |
| <u>Roots</u>  |                          |                   |                   |                           |                   |                   |                            |                   |                   |
| 4-4.5         | 1.73 <sup>a</sup>        | 2.07 <sup>a</sup> | 1.27 <sup>a</sup> | 21.0 <sup>b</sup>         | 16.9 <sup>b</sup> | 20.1 <sup>b</sup> | 1855 <sup>c</sup>          | 1518 <sup>c</sup> | 1429 <sup>c</sup> |
| 5-5.5         | 3.22 <sup>a</sup>        | 1.17 <sup>a</sup> | 1.35 <sup>a</sup> | 15.8 <sup>b</sup>         | 18.8 <sup>b</sup> | 16.4 <sup>b</sup> | 3035 <sup>d</sup>          | 3152 <sup>d</sup> | 3022 <sup>d</sup> |
| 6.5-7         | 0.85 <sup>a</sup>        | 1.19 <sup>a</sup> | 0.98 <sup>a</sup> | 24.9 <sup>b</sup>         | 17.1 <sup>b</sup> | 26.5 <sup>b</sup> | 3490 <sup>d</sup>          | 3742 <sup>d</sup> | 2392 <sup>d</sup> |

\*Means superscripted by the same letter do not differ at the 5% error probability level.

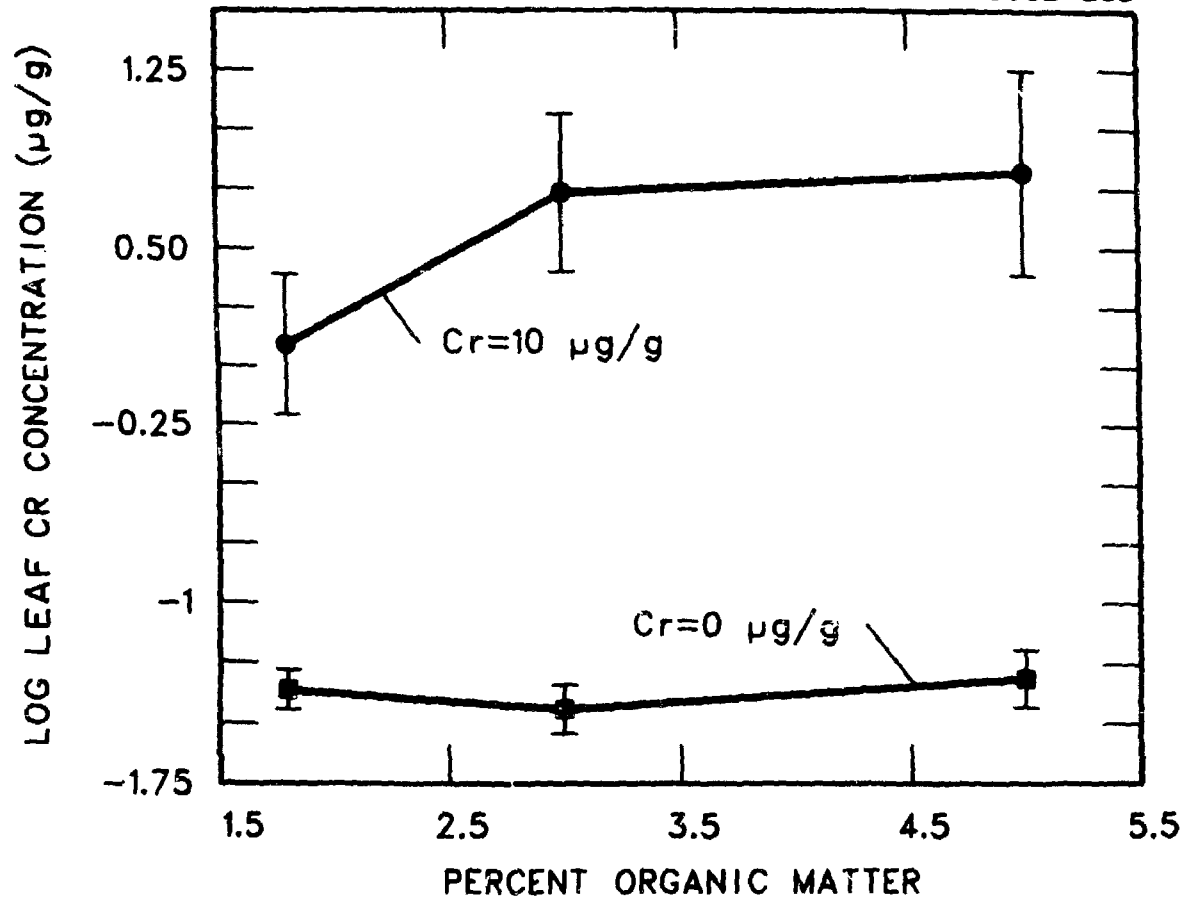


Fig. 2. Chromium concentrations + SE in leave of 0- and 10-µg/g treatment groups at the different organic matter levels.

In the stems, chromium concentrations in controls were below detection level to 1.70  $\mu\text{g/g}$ . Stem concentrations of plants in the 10- $\mu\text{g/g}$  Cr-VI soil ranged from not detectable to 24.64  $\mu\text{g/g}$  chromium.

Chromium concentrations of roots of plants in the 10- $\mu\text{g/g}$  Cr-VI treatment ranged from 6.56 to 33.83  $\mu\text{g/g}$  as compared to 0.26 to 7.35  $\mu\text{g/g}$  for plants in nonamended soil. Concentrations of chromium were significantly ( $P < 0.05$ ) higher than concentrations in the leaves and stems. Previous studies have shown that plants grown in chromium-contaminated soil or solution will take up chromium in the roots, but little, if any, is translocated elsewhere (Myttenaere and Mousny, 1974; Wallace et al., 1976; Cary et al., 1977a; Lepp and Eardley, 1978; Parr and Taylor, 1980).

Only a small fraction of the chromium added to the soil was transported to the leaves and stems, with 0.003 to 0.02% of the 18.4 mg Cr-VI added to the soil reaching the leaves and even less (0.0003 to 0.0107%) in the stems. Most (0.05-0.10%) of the chromium available to the plants remained in the root mass. Concentration factors were calculated for the 10- $\mu\text{g/g}$  treatment. Factors for stems and leaves were all less than one and similar to each other. Factors for roots were higher than for leaves and stems, but not much greater than one, indicating little magnification of chromium from the soil. It has been hypothesized that the roots of higher plants not only provide a barrier to translocation of some metals within plants but function as a mechanism for binding the chromium by absorption or adsorption (Wallace and Romney, 1977).

#### Biomass of plant tissues

Biomass effects due to soil treatments were significant in the roots and leaves but not apparent in the stems (Table 3). The organic matter content and the pH of the soil affected root biomass significantly. Bean roots grown in an organic matter of 5% had a significantly greater biomass than those grown in an organic matter of 3%.

Table 3. Mean dry weight biomass (g) of leaves, stems, and roots\*

| Soil pH       | Chromium concentration   |                     |                     |                           |                     |                     |
|---------------|--------------------------|---------------------|---------------------|---------------------------|---------------------|---------------------|
|               | 0 µg/g<br>organic matter |                     |                     | 10 µg/g<br>organic matter |                     |                     |
|               | 1.8%                     | 3%                  | 5%                  | 1.8%                      | 3%                  | 5%                  |
| <u>Leaves</u> |                          |                     |                     |                           |                     |                     |
| 4-4.5         | 1.00 <sup>cd</sup>       | 1.18 <sup>cd</sup>  | 1.25 <sup>cd</sup>  | 0.72 <sup>ce</sup>        | 0.95 <sup>ce</sup>  | 1.04 <sup>ce</sup>  |
| 5-5.5         | 1.38 <sup>ad</sup>       | 1.24 <sup>ad</sup>  | 1.61 <sup>ad</sup>  | 1.58 <sup>ae</sup>        | 1.42 <sup>ae</sup>  | 1.22 <sup>ae</sup>  |
| 6.5-7         | 1.25 <sup>bd</sup>       | 1.18 <sup>bd</sup>  | 1.58 <sup>bd</sup>  | 1.04 <sup>be</sup>        | 0.99 <sup>be</sup>  | 1.22 <sup>be</sup>  |
| <u>Stems</u>  |                          |                     |                     |                           |                     |                     |
| 4-4.5         | 0.30 <sup>a</sup>        | 0.28 <sup>a</sup>   | 0.27 <sup>a</sup>   | 0.21 <sup>a</sup>         | 0.39 <sup>a</sup>   | 0.22 <sup>a</sup>   |
| 5-5.5         | 0.28 <sup>a</sup>        | 0.24 <sup>a</sup>   | 0.41 <sup>a</sup>   | 0.31 <sup>a</sup>         | 0.31 <sup>a</sup>   | 0.22 <sup>a</sup>   |
| 6.5-7         | 0.26 <sup>a</sup>        | 0.25 <sup>a</sup>   | 0.31 <sup>a</sup>   | 0.29 <sup>a</sup>         | 0.26 <sup>a</sup>   | 0.26 <sup>a</sup>   |
| <u>Roots</u>  |                          |                     |                     |                           |                     |                     |
| 4-4.5         | 0.76 <sup>abcd</sup>     | 0.77 <sup>acd</sup> | 1.19 <sup>bcd</sup> | 0.51 <sup>abcd</sup>      | 0.64 <sup>acd</sup> | 0.77 <sup>bcd</sup> |
| 5-5.5         | 0.76 <sup>abc</sup>      | 0.54 <sup>ac</sup>  | 0.85 <sup>bc</sup>  | 1.05 <sup>abc</sup>       | 0.84 <sup>ac</sup>  | 0.78 <sup>bc</sup>  |
| 6.5-7         | 0.65 <sup>abd</sup>      | 1.07 <sup>ad</sup>  | 0.51 <sup>bd</sup>  | 0.53 <sup>abd</sup>       | 0.51 <sup>ad</sup>  | 0.66 <sup>bd</sup>  |

\*Means superscripted by the same letter do not differ at the 5% error probability level.

A soil pH of 5.0 to 5.5 produced significantly greater biomass than pH of 6.5 to 7.0. The significantly higher chromium accumulation in the roots of the 10- $\mu\text{g/g}$  treatment versus the control (0  $\mu\text{g/g}$ ) did not affect the root biomass significantly. Previous studies showed that one of the first effects of chromium was reduction of root growth (Shewry and Peterson, 1974), although small in some cases (DeKock, 1956). Other investigators (Hunter and Vergnano, 1953) reported poorly developed roots in chromium concentrations greater than 10  $\mu\text{g/g}$ .

Chromium concentration in the leaves significantly affected biomass. The level of organic matter in the soil did not have a significant effect on leaf biomass; however, the pH in the soil had significant effects at all three levels.

The significantly higher accumulation of chromium in the leaves of the 10- $\mu\text{g/g}$  Cr treatment corresponded with a significant decrease in leaf biomass when compared to controls in nonamended soil. Other investigators reported a reduction in yield for plants grown in 10  $\mu\text{g/g}$  chromium in soil culture or nutrient solutions (Turner and Rust, 1971; Shewry and Peterson, 1974; Davis et al., 1978).

It is apparent that many of the biomass effects were due not only to the Orocol TL amendment to the soil but to the condition of the soil. As was anticipated, plants grew best in soil conditions of high organic matter content and a soil pH of 5.0 to 7.0. Although chromium concentrations were significantly higher in all plant parts (leaves, stems, and roots) for the 10- $\mu\text{g/g}$  Cr treated group, only in leaf biomass was there a significant decrease in yield when compared to controls.

#### Effect of Cr-VI on rate of growth

The effect of the 10- $\mu\text{g/g}$  amendment of chromium to the soil on the rate of plant growth was calculated to determine if there were any significant differences due to treatment.

Growth of plants in all treatments appeared to level off around day 41 post-treatment. Rate of growth was calculated for each plant of each treatment by subtracting the first height measurement of the plant



from the height measured on day 41, divided by the number of days of growth (41). An analysis of variance comparison showed no significant ( $P < 0.05$ ) differences in the rates of growth due to treatment.

### CONCLUSIONS

Numerous investigations have been conducted at the DOE uranium enrichment facilities in Oak Ridge, Tennessee, and Paducah, Kentucky, to determine environmental effects of cooling tower drift, and, in particular, hexavalent chromium from Orocol TL on biological systems. This study was designed to answer specific questions concerning the effects of chromium in Orocol TL on the germination and growth of bush beans in soils of various pH levels and organic matter contents.

Statements of major findings are summarized below:

(1) The chromium (Orocol TL) in the soil had a significant effect on the germination of bush beans. That the effect was reduced with an increase in organic matter suggests that the chromium may have been tied up in the soil at exchange sites in the organic fraction.

(2) Excessive amounts of Orocol TL (500  $\mu\text{g/g}$  Cr) were immediately toxic to bush beans growing in all soil combinations, which may have been related to osmotic or salt effects but which probably indicates that the Cr-VI exceeded the reducing and adsorbing capacity of the soil.

(3) There was significantly greater chromium concentration in leaves, stems, and roots of the 10- $\mu\text{g/g}$  chromium soil amendments. However, concentration factors indicated the actual amount translocated was small and that most of the chromium remained in the roots, confirming previous studies. Although chromium concentrations were significantly higher in all plant parts, only in the leaves was there a corresponding reduction in biomass.

Based on the results of this study it appears that organic matter (1.8-5%) and soil pH (4-7) in ranges found in the ORGDP environs neither increase nor decrease significantly the uptake of chromium from the soil. However, chromium was taken up by all plant parts, and leaf biomass was significantly reduced. While this investigation was

specific for cooling towers and chromated drift, the results have generic application for any technology where the release and subsequent deposition of chromated residuals potentially interact with soils and vegetation.

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D. P.

STUDY OF TECHNETIUM UPTAKE IN VEGETATION IN THE VICINITY  
OF THE PORTSMOUTH GASEOUS DIFFUSION PLANT

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KEY WORDS: Technetium, Vegetation, Soil, Concentration, Uptake, Dose

ABSTRACT

Technetium-99 was measured in vegetation and soil collected on and near the Portsmouth Gaseous Diffusion Plant to obtain an estimate of the soil-to-vegetation concentration factors. The concentration factors appear to be lognormally distributed with a geometric mean of 3.4 (Bq/kg dry wt. tissue per Bq/kg dry wt. soil) and a geometric standard deviation of 4.7. A dose commitment was calculated using a hypothetical  $3.7 \times 10^{10}$  Bq Tc-99/year release and the actual CY-1981 concentration release of Tc-99. The radiological significance of Tc-99 in the terrestrial food chain is substantially less than previously believed.

INTRODUCTION

Technetium-99, a low energy beta emitter, is probably the most notable of the several isotopes of technetium, all of which are radioactive. Technetium-99 is a fission waste product that is present in spent nuclear reactor fuels. It has a half-life of  $2.12 \times 10^5$  years and emits a beta particle with an energy of 0.292 MeV. Approximately 0.84 kg of technetium-99 is produced per metric ton of reactor fuel in a typical pressurized water reactor.<sup>7</sup> The nuclear fuel cycle accounts for most of the technetium-99 released to the

environment and the reprocessing segment of the cycle is accountable for the majority of technetium released from this source. Other sources include medical diagnostic practices, atmospheric detonation of atomic weapons, and the natural fission of uranium-238 in the environment.

The atmospheric form of technetium will generally be as the pertechnetate ion,  $\text{TcO}_4^-$ . Although technetium will exhibit valencies of 0 to +7, the +7 valence state, the pertechnetate ion, is the most common and exists in aqueous solutions over a wide pH range. Pertechnetate is the basic chemical form of technetium used in nuclear medicine and the final form following the reprocessing of spent reactor fuel elements.<sup>2</sup>

There is relatively little information available concerning what happens to technetium in soils and plants. However, the literature does suggest a variety of mechanisms by which technetium may react with the organic and mineral components of natural soil systems. These mechanisms include ion-exchange, precipitation/coprecipitation and complexation/chelation.<sup>2</sup> Studies performed in soil systems have shown that precipitation may occur in soils with high concentrations of free iron, aluminum, and silica. Some of the studies were performed in non-soil systems and under somewhat idealized conditions, contributing to the difficulties in characterizing the fate technetium in soil and vegetation.<sup>2</sup>

#### Background

In 1975 and 1976, two studies were conducted and results published in an effort to characterize the uptake of technetium by plants. Wildung, et. al., presented the results of an experiment in which they studied the uptake of technetium in wheat and soybeans

(Table 1).<sup>1</sup> In the study, the soils were watered with solutions of various technetium concentrations. It was found that at low concentrations of technetium ( $\leq 0.01$  g Tc-99/g soil), the plants were similar in appearance to the controls. However, at higher concentrations ( $\geq 0.1$  g Tc-99/g soil) toxic symptoms began to appear. At the concentrations of technetium used, it was not clear whether the toxic symptoms were due to radiation effects or chemical effects. To gain some insight as to what produced the toxic effects, anion competition studies were performed and indicated that pertechnetate ions may be taken up as a nutrient analog. However, this does not eliminate radiation effects as the cause of toxicity.

Table 1 Concentration Factors of Wheat and Soybeans at Various Tc-99 Soil Concentrations

| <u>Soil Tc-99<br/>Concentration</u> | Concentration Factor<br>(Bq/kg dry wt. tissue per Bq/kg dry wt. soil) |                 |
|-------------------------------------|-----------------------------------------------------------------------|-----------------|
|                                     | <u>Wheat</u>                                                          | <u>Soybeans</u> |
| 0.001                               | 340                                                                   | 380             |
| 0.01                                | 145                                                                   | 138             |
| 0.1                                 | 173                                                                   | 67              |
| 1.0                                 | *                                                                     | 376             |
| 5.0                                 | *                                                                     | 380             |

\* No growth occurred.

In 1976 Gast, et. al.,<sup>2</sup> published the results of an experiment in which wheat seedlings were planted in various samples of Minnesota soils (Table 2). These seedlings were watered with technetium solutions ranging in concentration from 0 to 11.6 g Tc-99/ml of solution. Additionally, studies were performed to determine the toxic effects of technetium at very low concentrations, ranging from 0 to  $3.7 \times 10^4$  Bq Tc-99 per 50 ml of solution.

Table 2 Concentration Factors for Wheat Seedlings in Samples  
Minnesota Soils (Bq/kg dry wt. tissue per Bq/kg dry wt.  
soil)

| <u>Sample Locations</u> | <u>Concentration Factor</u> |                   |
|-------------------------|-----------------------------|-------------------|
|                         | <u>Unfertilized</u>         | <u>Fertilized</u> |
| Bearden                 | 830                         | 460               |
| Hegne                   | 1,120                       | 760               |
| Hibbing                 | 925                         | 715               |
| Nicollet (surface)      | 1,200                       | 875               |
| Nicollet (subsurface)   | 1,065                       | 995               |
| Omega                   | 655                         | 445               |
| Bergland                | 955                         | 800               |
| Arveson                 | 685                         | 250               |
| Waukegan                | 1,160                       | 875               |
| Zimmerman               | 1,055                       | 825               |

Because these experiments were inconclusive as to whether the toxicity was due to chemical or radiation effects, Gast made further efforts to determine the cause of toxicity. The dose rate was calculated at  $1.6 \times 10^{-1}$  Sv at the highest level of added technetium. These dose rates appear quite low when compared to the dose rates required in other species of plants to inhibit growth. Other studies have shown that x-radiation exposures of 4.0-5.0 Sv are required to produce a 20% growth inhibition.<sup>2</sup>

Prior to the mid-1970s when these two reports were published, most of the assessment literature had been using a concentration factor of 0.25 (Bq/kg wet weight plant tissue per Bq/kg dry weight soil). This value was based upon a series of assumptions relating the behavior of technetium to the behavior of iodine in the environment.<sup>7</sup> The concentration factors determined by Wildung<sup>1</sup> and Gast<sup>2</sup> were as much as three orders of magnitude greater than the assumed value of 0.25. These reports caused some concern among those agencies responsible for calculating dose assessments.

Two responses were forthcoming from this concern. One response was to get out into the field and actually take measurements from the vicinity of the reprocessing plants. The other response pointed out



some possible discrepancies between the laboratory experiments and field conditions.<sup>3, 7</sup> The three major discrepancies are: 1) In the laboratory experiments, the plants were not allowed to grow to maturity. 2) The concentration of technetium was significantly higher than one would expect to find in the vicinity of a reprocessing plant. 3) No effort was made to reach an equilibrium level between the soil and plant.

In 1979, a report<sup>7</sup> was written using the generally assumed concentration factor of 0.25 and an author-assumed factor of 50 (Bq/kg wet weight tissue per Bq/kg dry weight soil). The factor of 50 represented a middle-of-the-road value between 0.25 and the values found in the two previously mentioned laboratory experiments. A dose rate for individuals was calculated using both factors and an assumed release of  $3.7 \times 10^{10}$  Bq Tc-99/year. The dose rates calculated at a concentration factor of 50 were found to approach/exceed the dose rate limits promulgated by the US EPA in 40 CFR 190<sup>4</sup> for two target organs (Table 3).

Table 3 50 Year Dose Commitment (Sv)<sup>7</sup>

| <u>Organ</u> | <u>Concentration Factor</u> |                      | <u>US EPA<br/>Limit</u> |
|--------------|-----------------------------|----------------------|-------------------------|
|              | <u>0.25</u>                 | <u>50</u>            |                         |
| Total Body   | $8.6 \times 10^{-8}$        | $1.2 \times 10^{-5}$ | $2.5 \times 10^{-4}$    |
| Bone         | $1.5 \times 10^{-7}$        | $2.0 \times 10^{-5}$ | $2.5 \times 10^{-4}$    |
| Kidneys      | $1.9 \times 10^{-7}$        | $2.6 \times 10^{-5}$ | $2.5 \times 10^{-4}$    |
| GI Tract     | $1.3 \times 10^{-6}$        | $1.8 \times 10^{-4}$ | $2.5 \times 10^{-4}$    |
| Thyroid      | $5.7 \times 10^{-6}$        | $8.0 \times 10^{-4}$ | $7.5 \times 10^{-4}$    |

In 1980, the results of a study of the concentration of technetium in soils and vegetation in the vicinity of the three

gaseous diffusion plants were published (Table 4).<sup>3</sup> The gaseous diffusion plants are located at Paducah, KY; Oak Ridge, TN; and Portsmouth, OH. The concentration factors at the three plants ranged from 1.4 to 44 (Bq/kg dry weight tissue per Bq/kg dry weight soil). The data was lognormally distributed and had a geometric mean of 9.5 and a geometric standard deviation of 2.4. The mean concentration factor of 9.5 represents the concentration of technetium in the dry weight of tissue. If expressed as the concentration per wet weight of tissue the concentration factor becomes 2.4 (assuming 75% of the tissue weight is water). This factor alone would reduce the dose to the thyroid by approximately twenty times as compared to the concentration factor of 50.

Table 4 Statistical Summary of Soil-to-Plant Concentration Factors Combined from All Sampling Sites<sup>3</sup>

|                              |     |
|------------------------------|-----|
| Number of Values             | 24  |
| Maximum Value (Paducah)      | 44  |
| Minimum Value (Portsmouth)   | 1.4 |
| Arithmetic Mean              | 14  |
| Standard Deviation           | 10  |
| Standard Error               | 2.0 |
| Geometric Mean               | 9.5 |
| Geometric Standard Deviation | 2.4 |
| Geometric Standard Error     | 1.2 |

## RESULTS

The concentrations of technetium-99 in vegetation sampled at the Portsmouth Gaseous Diffusion Plant ranged from 34 to 27,200 Bq/kg dry weight tissue. The technetium concentrations in the soil ranged from 34 to 12,800 Bq/kg dry weight soil. The geometric means and standard deviations are 533 Bq/kg and 100 for vegetation, 145 Bq/kg and 52 for soil. The large standard deviations are influenced by the higher concentrations obtained from sampled points RIV-19 and RIV-26.

The concentration factors were calculated by dividing the soil concentration into the vegetation concentration. The highest concentration factors were associated with sample points 19 and 26, with the highest value at each point being 108 and 289, respectively. The concentration factors found at the Portsmouth plant ranged from 0.1 to 289 with a geometric mean of 3.4 (Bq/kg dry weight tissue per Bq/kg dry weight soil) and standard deviation of 4.7 (Table 5). The wide range of data accounts for the large standard deviation.

A histogram plot of the collected data is shown in Figure 1 and appears to most closely resemble an exponential curve.<sup>11</sup> If a exponential curve is the correct plot, one should be able to plot a straight line on logarithmic paper. A log-probability plot of the concentration factors is shown in Figure 2. The assemblage of factors appears to be reasonably lognormal. A correlation factor of 0.97 was obtained using a calculator program developed for normal and lognormal distributions.<sup>12</sup> A statistical summary is shown in Table 6.

Table 6 Statistical Summary of Concentration Factors  
at the Portsmouth Gaseous Diffusion Plant  
(Bq/kg dry wt. tissue per Bq/kg dry wt. soil)

|                                           |      |
|-------------------------------------------|------|
| Number of Values                          | 61   |
| Maximum Value (Point 26)                  | 289  |
| Minimum Value (Point 29)                  | 0.10 |
| Arithmetic Mean                           | 14.0 |
| Arithmetic Standard Deviation             | 40.1 |
| Arithmetic Error                          | 5.1  |
| Geometric Mean                            | 3.4  |
| Geometric Standard Deviation              | 4.7  |
| Geometric Error                           | 1.2  |
| Correlation Factor "r" for Lognormal Plot | 0.97 |

Table 5 Concentration Factors (Bq/kg dry wt. Tissue per Bq/kg dry wt. soil)

| SITE  | NOV  | DEC  | JAN  | FEB  | MAR  | APR  | MAY  | JUN  | JULY | AUG  | SEP   | OCT  | TOTAL |
|-------|------|------|------|------|------|------|------|------|------|------|-------|------|-------|
| 3     | 1.33 | 5.5  |      |      |      |      | 0.32 |      | *    | 0.67 | 2.23  |      | 5     |
| 5     |      |      |      |      |      |      |      |      | *    |      |       |      | 0     |
| 12    | 0.86 | 1.5  | 0.92 | 0.52 |      | 1.42 | 1.27 | 1.01 | *    |      | 4.6   | 0.87 | 9     |
| 15    |      |      |      |      |      |      |      |      | *    |      |       |      | 0     |
| 17    |      |      |      |      |      |      |      |      | *    |      |       |      | 0     |
| 19    | 9.09 | 2.71 | 20.4 |      |      | 35.3 | 4.7  | 29.6 | *    | 21.3 | 108.6 | 1.21 | 9     |
| 22    | 0.69 | 4.5  |      | 0.76 |      |      | 4.64 | 0.65 | *    | 0.04 | 4.29  | 0.96 | 8     |
| 25    |      |      |      | 10.0 |      |      |      |      | *    |      |       | 3.0  | 2     |
| 26    | 2.73 | 1.47 |      |      | 289  | 52.2 | 33.3 | 8.26 | *    | 3.96 | 19.7  | 59.1 | 9     |
| 26A   | 1.33 |      | 13.2 |      | 1.49 |      | 1.57 | 2.10 | *    |      |       | 4.81 | 6     |
| 29    |      | 5.5  |      | 1.31 |      |      | 9.52 | 38.0 | *    | 0.78 | 0.10  | 2.34 | 7     |
| 32    | 1.33 | 2.73 |      |      |      | 1.70 | 0.68 |      | *    |      | 1.35  | 1.62 | 6     |
| TOTAL | 7    | 7    | 3    | 4    | 2    | 4    | 8    | 6    |      | 5    | 7     | 8    | 61    |

\* No sample collected.

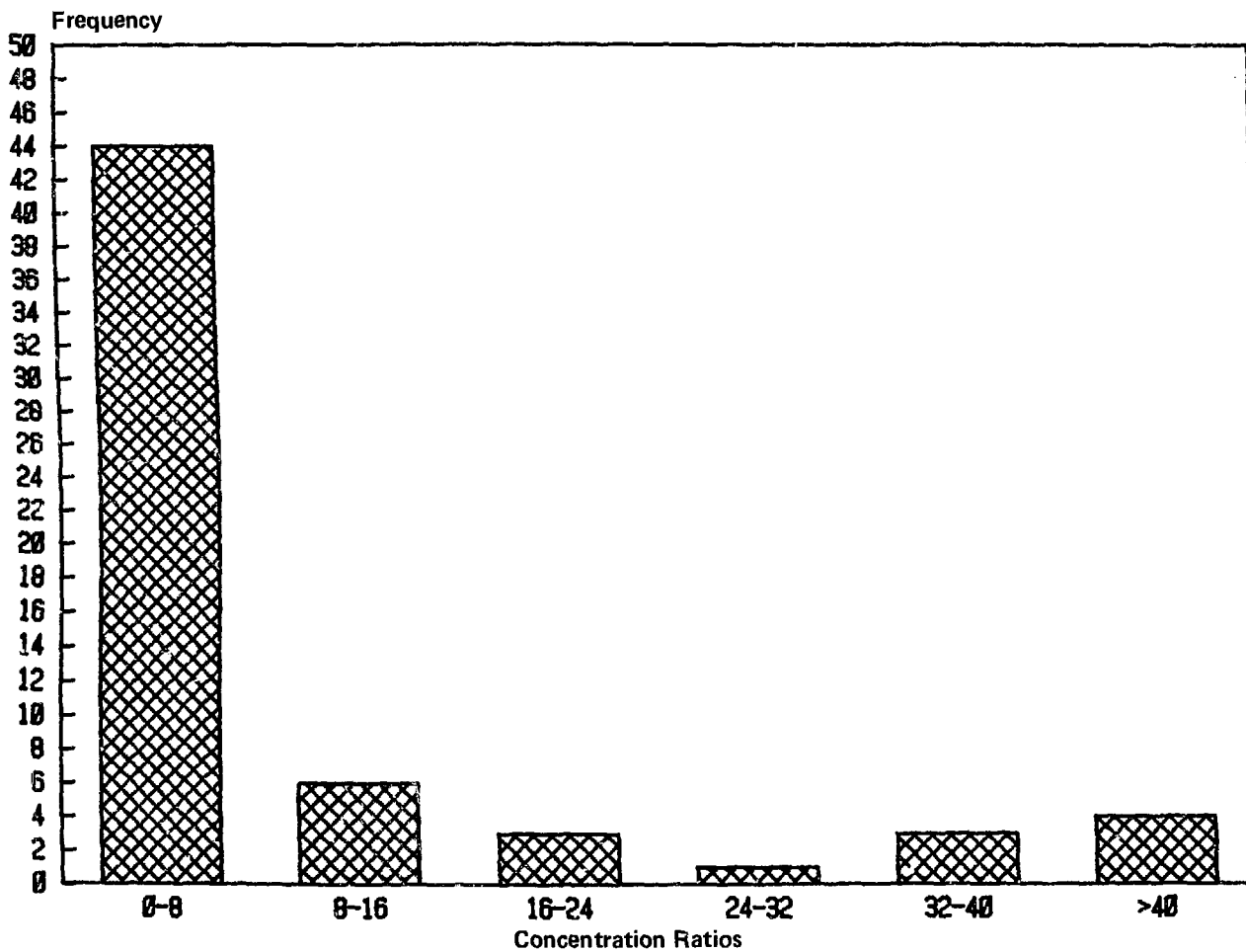


Figure 1 Distribution of Ratios

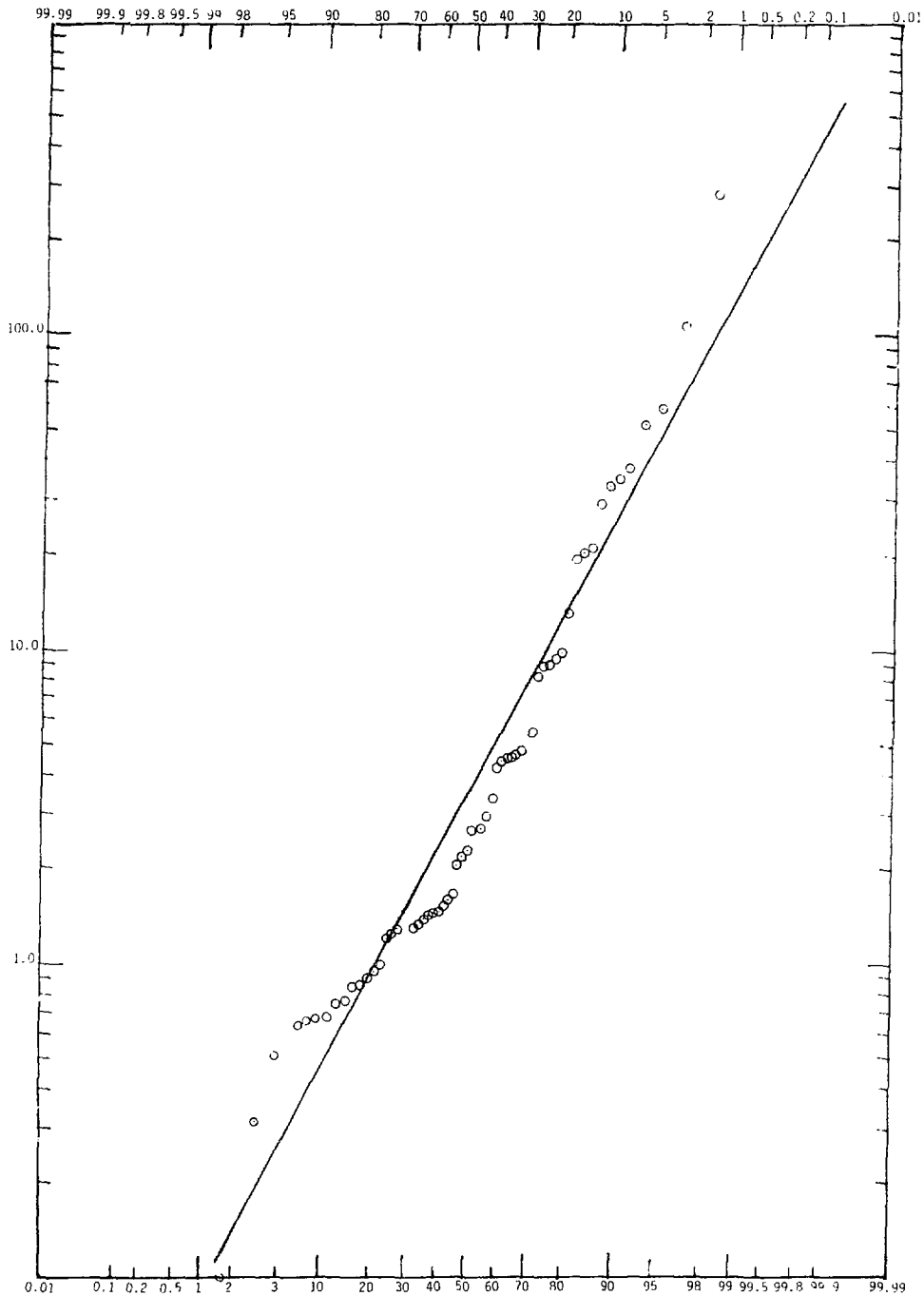


**Figure 2 Lognormal Probability Plot of Concentration Factors Found  
at the Portsmouth Gaseous Diffusion Plant**

## DISCUSSION

### Sampling and Analytical Procedures

At the Portsmouth GDP, the Environmental Control Department routinely samples vegetation and soil both on and off the DOE reservation. These samples are analyzed by laboratory personnel for various chemical and radiological parameters.

The routine vegetation and soil monitoring program consists of a series of monthly samples collected within the DOE reservation boundary. These samples are identified using Routine Internal Vegetation (RIV) and Routine Internal Soil (RIS) sample numbers. On a semi-annual basis, vegetation and soil samples are collected outside the DOE reservation boundary. These samples are identified using Semi-Annual Vegetation/Soil (SAV/SAS) sample numbers. The sample locations are shown in Figures 3 and 4.

The sampling of vegetation involved the collection of above-ground vegetation using shears to cut the sample. A minimum of 500 grams of wide blade grasses is collected. No soil, roots, or foreign matter are collected with the sample as these materials may contaminate the sample. As large an area as needed is sampled to provide the minimum sample quantity.

Soil samples are collected using a shovel to obtain a representative sample. The soil samples consist of approximately the top two inches of soil, as free of roots and stones as possible. The minimum sample consists of a 0.1 square meter area. Again, as large an area as needed is sampled to provide enough soil to fill two 1/2-liter containers.

A method was developed at Goodyear Atomic for the determination of technetium-99 in a variety of samples including vegetation and soils (Figure 5). The method includes destruction of the organic

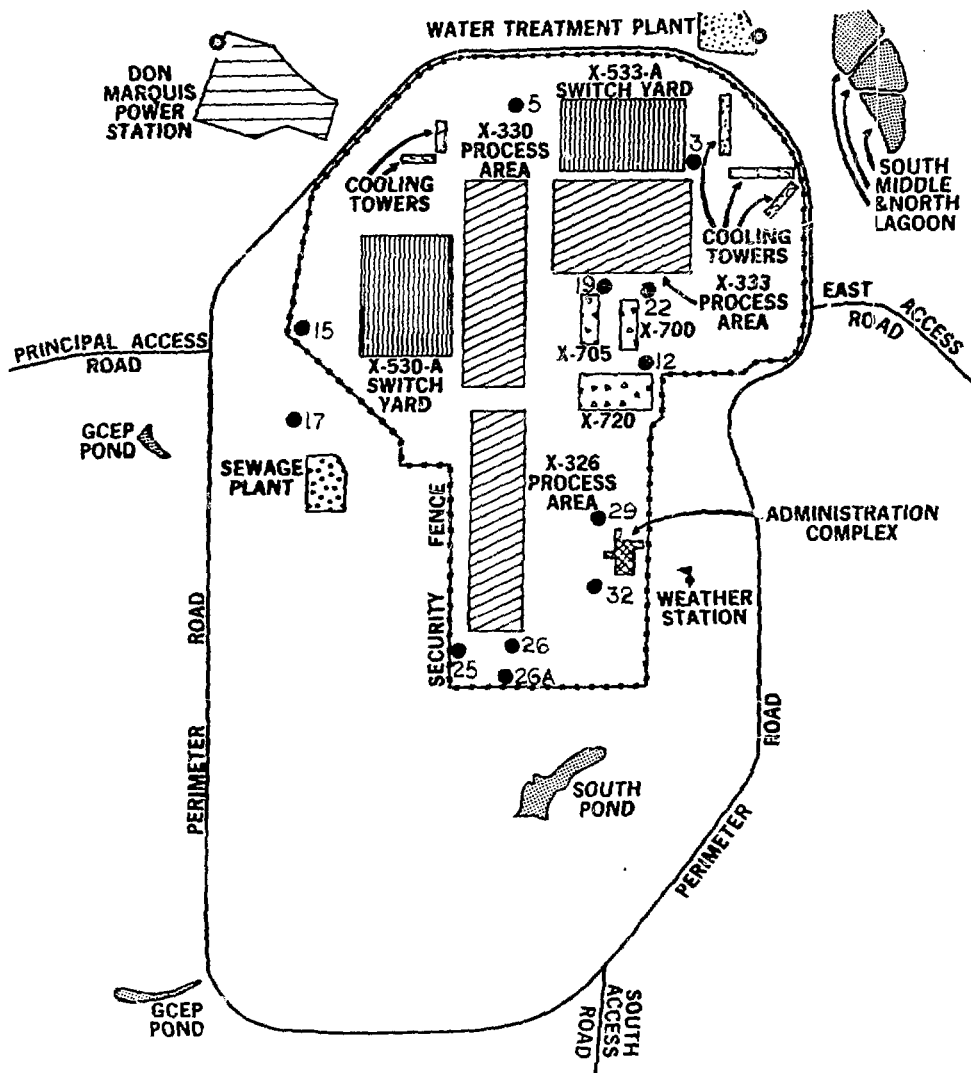


Figure 3 Vegetation and Soil Sampling Locations within the DOE Reservation (RIV and RIS)



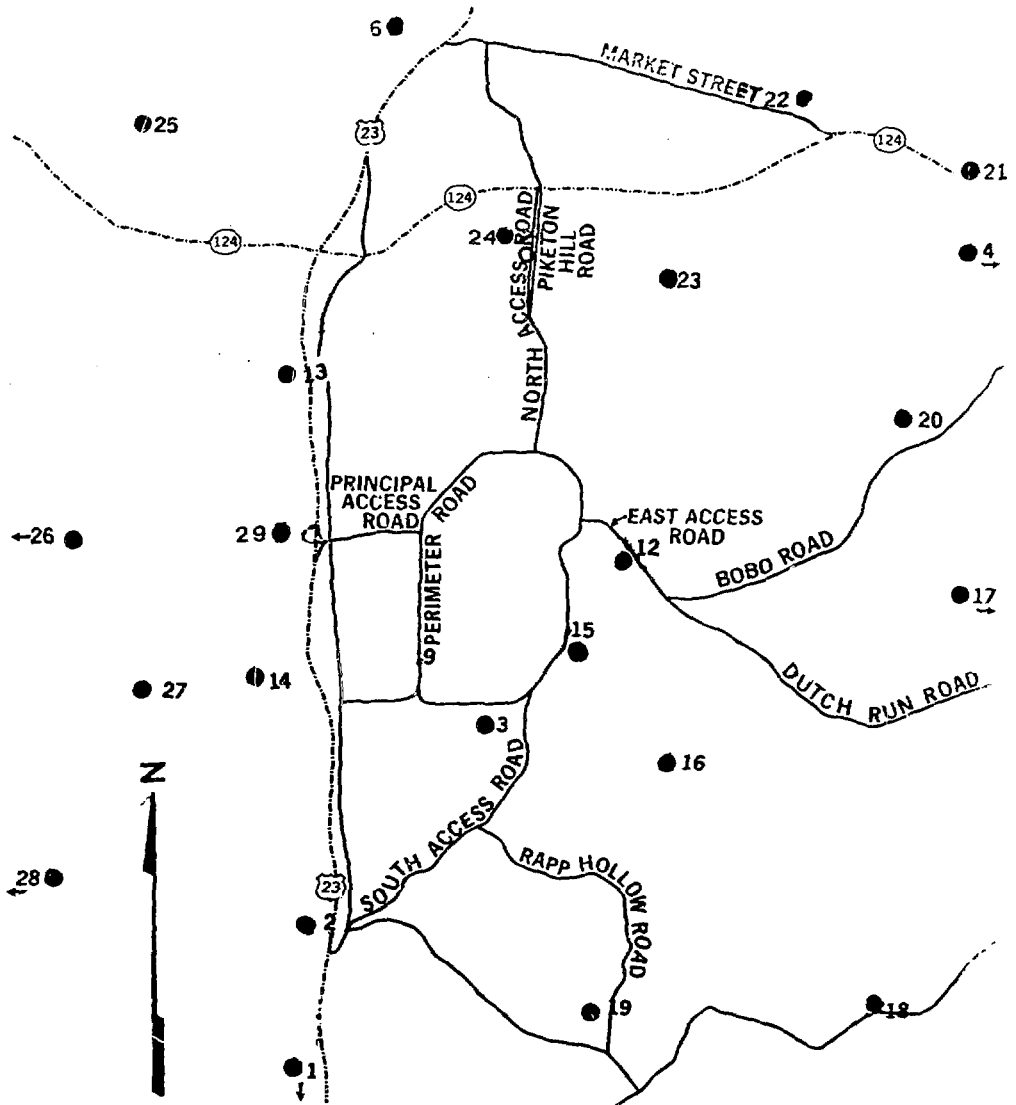


Figure 4 Offsite Vegetation and Soil Sampling Locations (SAV and SAS)

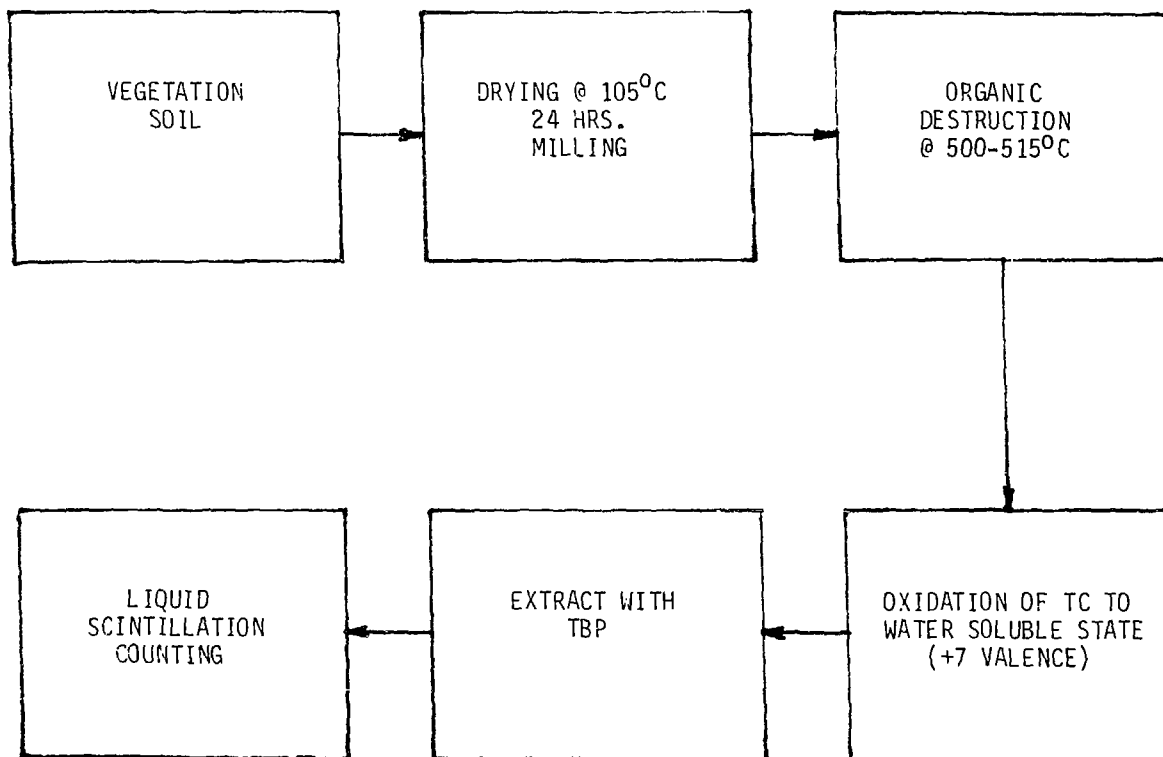


Figure 5 Basic Schematic for Determination of Technetium-99 in Vegetation and Soil

materials, oxidation of all the technetium to the +7 valence state and extraction of the technetium from the aqueous media with tributyl phosphate. A portion of the extract is added to a scintillation cocktail and technetium-99 activity is measured by liquid scintillation counting.<sup>5</sup>

#### Dose Assessment

In a study performed by Till, et. al.,<sup>7</sup> concentration factors of 0.25 and 50 were used in the calculation of a dose assessment. The atmospheric transport and deposition factors given in Table 7 are based on an assumed  $3.7 \times 10^{10}$  Bq technetium per year release. The calculated dose at each concentration factor was presented earlier. The dose commitment for an individual was recalculated using the same assumed release; however, the concentration factors of 9.5 (obtained from an earlier study) and 3.4 were used. But before being used in the calculations, the factors must be converted from the dry weight tissue factors to the wet weight tissue factors. Assuming the vegetation is 75% water, the concentration factors became 2.4 and 0.85, respectively.

Table 7 Atmospheric Transport and Deposition of Technetium<sup>7</sup>

|                                                                    |                                          |
|--------------------------------------------------------------------|------------------------------------------|
| Release Rate                                                       | $3.7 \times 10^{10}$ Bq/yr.              |
| Release Height                                                     | 20 m                                     |
| X/Q at 1600 m                                                      | $9.9 \times 10^{-7}$ sec./m <sup>3</sup> |
| Average Annual Deposition<br>Velocity for Wet and<br>Dry Processes | $1.1 \times 10^{-2}$ m/sec.              |
| Deposition Rate at 1600 m                                          | $1.12 \text{ Bq/m}^2 \text{ day}$        |

After these changes were made, the calculations to determine the dose were performed using the procedure outlined in USNRC Regulatory

Guide 1.109.<sup>8</sup> In calculating the dose commitment, the USNRC assumes a chronic buildup of technetium for fifteen years. However, recent evidence shows there may be an effective half-life of technetium in the soil and vegetation.<sup>3</sup> Forage, harvesting, wind, rain runoff and leaching would tend to remove technetium from the area in question. While these effects may not change the concentration factors, they would lower the dose received by an individual by lowering the amount of technetium received by the individual. However, for calculations, the fifteen year buildup has been assumed. Table 8 shows the calculated concentration of technetium in vegetables, meat, and milk and Table 9 shows the amount of technetium ingested by an individual over a period of one year. The dose commitment is shown in Table 10 for all concentration factors cited. At the assumed release rate, an individual would receive a fifty year dose of approximately 2-6% of the limits set by the US EPA.

Using the actual release rate of technetium at the Portsmouth Gaseous Diffusion Plant, the technetium concentration would be that shown in Table 11 along with the amount of technetium ingested by an individual in one year. Based on this data, an individual would receive the dose commitment shown in Table 12. Using the concentration factor and release rate at the Portsmouth plant, the average individual dose commitment would be less than 1% of the US EPA limits stated in 40 CFR 190.

All of the calculations, thus far, have been performed on vegetation found on the DOE reservation. Semi-annual soil and vegetation samples are collected from thirty locations at varying distances from the reservation. In the past three calendar years, only two semi-annual vegetation samples and three semi-annual soil samples have been found to have greater than 0.03 Bq/gram dry weight (0.03 Bq/gram is the detection limit). The maximum vegetation concentration is 0.07 Bq/gm dry weight and the maximum soil

Table 8 Concentration of Tc-99 in  
Vegetable, Meat, and Milk at 1600 m

| <u>Concentration Ratio</u> |                   | <u>Vegetable</u> | <u>Meat</u>  | <u>Milk</u> |
|----------------------------|-------------------|------------------|--------------|-------------|
| <u>Dry Tissue</u>          | <u>Wet Tissue</u> | <u>Bq/kg</u>     | <u>Bq/kg</u> | <u>Bq/l</u> |
| 1.0                        | 0.25              | 8.5              | 4.1          | 4.8         |
| 3.4                        | 0.85              | 24.0             | 11.0         | 13.0        |
| 9.5                        | 2.4               | 63.0             | 28.0         | 33.0        |
| 200.0                      | 50.0              | 1,250.0          | 560.0        | 630.0       |

Table 9 Intake Rate of Tc-99 (Bq/yr)

| <u>Concentration Ratio</u> |                   | <u>Vegetables</u> | <u>Meat</u>       | <u>Milk</u>       | <u>Total</u>      |
|----------------------------|-------------------|-------------------|-------------------|-------------------|-------------------|
| <u>Dry Tissue</u>          | <u>Wet Tissue</u> |                   |                   |                   |                   |
| 1.0                        | 0.25              | $5.6 \times 10^2$ | $4.4 \times 10^2$ | $5.2 \times 10^2$ | $1.5 \times 10^3$ |
| 3.4                        | 0.85              | $1.5 \times 10^3$ | $1.3 \times 10^3$ | $1.4 \times 10^3$ | $4.1 \times 10^3$ |
| 9.5                        | 2.4               | $4.1 \times 10^3$ | $3.1 \times 10^3$ | $4.1 \times 10^3$ | $1.1 \times 10^4$ |
| 200                        | 50                | $3.1 \times 10^4$ | $5.9 \times 10^4$ | $2.1 \times 10^5$ | $3.0 \times 10^5$ |

Table 10 50 Year Dose Commitment (Sv)

| <u>Concentration Factor</u> |                   | <u>Total Body</u>    | <u>Bone</u>          | <u>Kidneys</u>       | <u>GI Tract</u>      | <u>Thyroid</u>       |
|-----------------------------|-------------------|----------------------|----------------------|----------------------|----------------------|----------------------|
| <u>Dry Tissue</u>           | <u>Wet Tissue</u> |                      |                      |                      |                      |                      |
| 1.0                         | 0.25              | $8.6 \times 10^{-8}$ | $1.5 \times 10^{-7}$ | $1.9 \times 10^{-7}$ | $1.3 \times 10^{-6}$ | $5.7 \times 10^{-6}$ |
| 3.4                         | 0.85              | $2.3 \times 10^{-7}$ | $4.0 \times 10^{-7}$ | $5.1 \times 10^{-7}$ | $3.5 \times 10^{-6}$ | $1.6 \times 10^{-5}$ |
| 9.5                         | 2.4               | $6.3 \times 10^{-7}$ | $1.1 \times 10^{-6}$ | $1.4 \times 10^{-6}$ | $1.0 \times 10^{-5}$ | $4.2 \times 10^{-5}$ |
| 200                         | 50                | $1.2 \times 10^{-5}$ | $2.0 \times 10^{-5}$ | $2.6 \times 10^{-5}$ | $1.8 \times 10^{-4}$ | $8.0 \times 10^{-4}$ |
| US EPA Limits               |                   | $2.5 \times 10^{-4}$ | $2.5 \times 10^{-4}$ | $2.5 \times 10^{-4}$ | $2.5 \times 10^{-4}$ | $7.5 \times 10^{-4}$ |

Table 11 Yearly Intake of Technetium 99 by an Individual  
Concentration Factor - 0.85 Bq/kg Wet Wt. Tissue  
per Bq/kg Dry Wt. Soil Release Rate -  $8.5 \times 10^{-3}$   
Bq/yr.

|                           | <u>Vegetables</u>            | <u>Meat</u>                  | <u>Milk</u>                  | <u>Total</u>                 |
|---------------------------|------------------------------|------------------------------|------------------------------|------------------------------|
| Concentration<br>of Tc-99 | 2.56 Bq/kg                   | 1.24 Bq/kg                   | 1.42 Bq/l                    | NA                           |
| Intake<br>of Tc-99        | $1.63 \times 10^2$<br>Bq/yr. | $1.36 \times 10^2$<br>Bq/yr. | $1.55 \times 10^2$<br>Bq/yr. | $4.54 \times 10^3$<br>Bq/yr. |

\* Concentrations of Tc-99 were calculated using a concentration factor of 0.85 and the total CY-1981 release of  $4.0 \times 10^9$  Bq Tc-99.

Table 12 50 Year Dose Commitment (Sv)

|                     | <u>Total Body</u>     | <u>Bone</u>           | <u>Kidneys</u>        | <u>GI Tract</u>       | <u>Thyroid</u>        |
|---------------------|-----------------------|-----------------------|-----------------------|-----------------------|-----------------------|
| Calculated*<br>Dose | $2.58 \times 10^{-8}$ | $4.43 \times 10^{-8}$ | $5.66 \times 10^{-8}$ | $3.94 \times 10^{-7}$ | $1.72 \times 10^{-6}$ |
| US EPA<br>Limit     | $2.5 \times 10^{-4}$  | $2.5 \times 10^{-4}$  | $2.5 \times 10^{-4}$  | $2.5 \times 10^{-4}$  | $7.5 \times 10^{-4}$  |

\* Dose was calculated using concentration factor of 0.85.

concentration is 0.3 Bq/gm dry weight. These detectable concentrations of technetium did not occur at the same sample time nor at the same sample locations. Therefore, a concentration factor could not be calculated.

### CONCLUSION

There is no evidence that shows technetium has been found off of the DOE reservation. The dose commitment presented earlier indicates that there is no apparent risk to an individual as the result of the deposition of airborne technetium.

### ACKNOWLEDGMENT

Special acknowledgment should be given to the people in the Radiochemistry and Spectrochemistry Section and the Environmental and Industrial Hygiene Chemistry Section of the Chemical Analysis Department for their analytical work.

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D-42

THE QUANTITATIVE DETERMINATION OF CHRYSOTILE ASBESTOS IN BUILDING  
MATERIALS BY X-RAY DIFFRACTOMETRY

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Key Words: X-ray diffractometry, asbestos determination, building  
materials

ABSTRACT

An x-ray diffractometry technique using an internal standard has been developed for the quantitative measurement of the chrysotile asbestos content of a wide variety of construction materials. This technique is simple and cost effective compared with the usual need for combined x-ray powder diffraction patterns and optical or transmission electron microscopy to determine the asbestos content of materials. The diffractometry method is designed to differentiate between construction materials which are not asbestos contaminated and those which require costly special handling to ensure employee safety. The asbestos concentration range between 0.5 and 5.0 percent was initially investigated to meet the 1.0 percent asbestos Environmental Protection Agency National Emission Standards regulation, and has now been extended to determine as much as 50% chrysotile.



## INTRODUCTION

The Environmental Protection Agency issued a national standard in 1977 that limits the exposure of workers using building materials containing more than one percent asbestos (% of dry weight)<sup>1</sup> and also regulates asbestos emissions and the disposal of material which results from renovation or demolition of structures. Asbestos-contaminated materials removed during such renovation or demolition must be specially contained and buried in an approved landfill. Since numerous medical studies<sup>2-8</sup> have shown that inhalation of asbestos fibers greatly increases the probability of lung disorder, the protection of workers becomes a matter of concern. The construction industry utilizes a vast array of materials that may contain significant quantities of asbestos; these include gypsum, floor tile, wall-board, insulation batting, firebrick, mortar, cements, acoustic tile, and soundproofing compound.

A single method capable of quantitatively measuring chrysotile asbestos at the 1% level in such a variety of materials has been developed at the Oak Ridge National Laboratory; since 90% of the total asbestos used in the United States is chrysotile,<sup>9</sup> this method should be of great economic value to the construction industry in selecting raw materials which meet federal regulations, in differentiating between "clean" materials and those which require protective clothing and masks for workers, and the identification of materials which require special disposal.

Procedures for determining asbestos in water,<sup>10</sup> air,<sup>11</sup> dust layers,<sup>12</sup> and single fibers<sup>13</sup> have been described but are not applicable to this need. Taylor<sup>14</sup> described a diffractometer method for determining all major forms of asbestos, but the detection limit for chrysotile was 6%, and this concentration does not meet the EPA requirements. The ORNL has previously utilized a relatively standard analytical protocol to qualitatively detect the presence of asbestos in various materials:<sup>14</sup> polarized light microscopy is used to determine morphology, index of refraction and birefringence; then transmission electron microscopy may be employed to detect sub-micrometer sized fibers. Additional examination by either the Debye-Scherrer x-ray diffraction camera, diffractometry or scanning electron microscopy is frequently required to complete the fiber identification and

to estimate the concentration of asbestos. Problems with these techniques include sensitivity, specificity, fiber size, cost, length of time required to complete an examination and, above all, adequate standards and measurement techniques to ensure accurate quantitative analysis. The x-ray diffractometer technique described is accurate, quantitative and cost effective.

## EXPERIMENTAL

### Instrumentation

Measurements were performed with a General Electric XRD-5 air path diffractometer using a flat pyrolytic graphite monochromator in the optical path between the specimen and the detector. This simple optical modification provides a significantly increased signal-to-background ratio, compared to the normal system, which improves the detection limit for lower concentrations of asbestos. Instrument parameters used for these analyses were: copper target x-ray tube operated at 35 keV (constant potential), and 20 mA, graphite monochromator,  $1^\circ$  beam slit,  $0.2^\circ$  detector slit,  $4^\circ$  take-off angle, operating in a step scanning mode with step width of  $0.01^\circ 2\theta$ , and scanning speed of 50 sec per degree. The asbestos peak with a "d" value of 0.736 nm and the aspirin internal standard peak with a "d" value of 1.125 nm were used for the analysis. The net integrated intensities were measured, using counts at the base of each peak for background correction. The 1.150 and 1.300  $2\theta$  chrysotile and the 0.720 and 0.820  $2\theta$  aspirin settings were used for the background measurements. The total scanning time for a complete analysis is approximately 4 hours; but newer automated diffractometers can perform these same scans in much less time.

### Standards

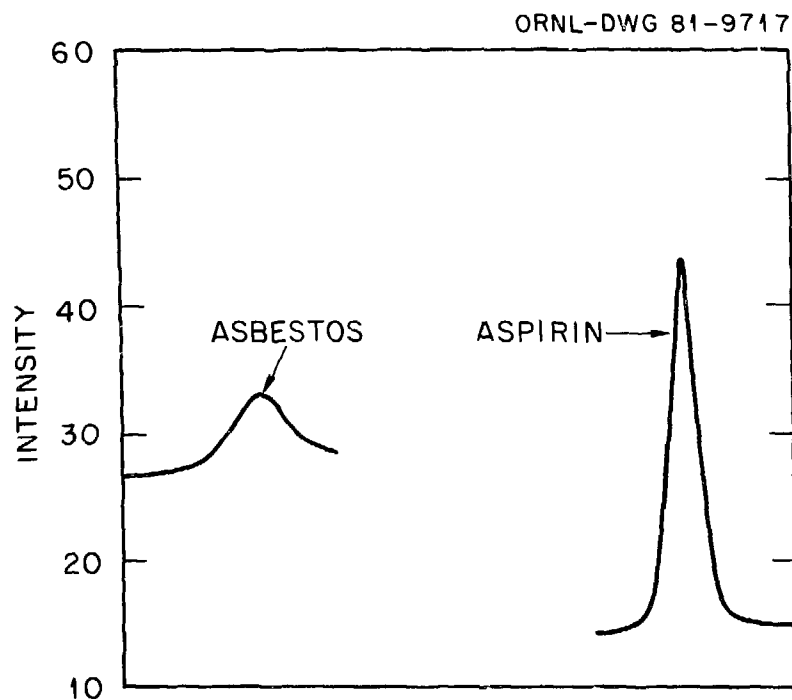
Matrix effects and differences in bulk density were expected to cause significant variations in the net counts obtained at the asbestos peak, based on data obtained during preliminary tests. Pressed pellet standards were prepared at the 1% asbestos level to simulate a wide range of common building materials:  $Al_2O_3$  to simulate ceramics such as

firebrick, dimethyl oxalate to simulate cellulose and organic materials, and gypsum to simulate wallboard and plaster. These 1% chrysotile standards were scanned and large variations in the net intensity of the asbestos 0.736 nm peak were noted. The typical alumina and dimethyl oxalate scans are shown in Figure 1. Comparison of these net accumulated asbestos counts to the talc-based pressed pellet calibration curve would have resulted in apparent concentrations of 0.1, 0.2 and 3.5% asbestos in the gypsum, alumina and dimethyl oxalate matrix standards containing 1% chrysotile asbestos. These data conclusively demonstrated the need for an internal standard to compensate for these effects.

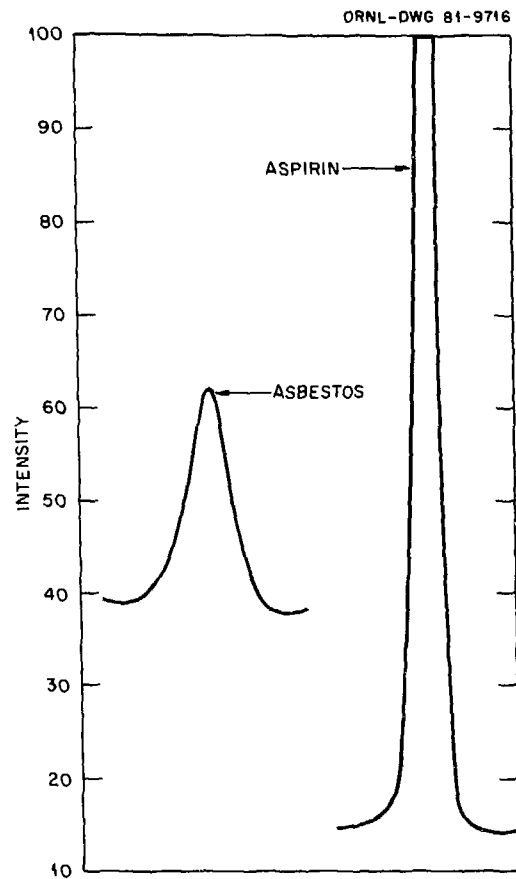
After examining several potential internal standard compounds and methods for introducing them into specimens, powdered acetylsalicylic acid (common aspirin) was selected. Grinding the powder into the solid specimen was found to be more satisfactory than addition as either aqueous or alcoholic solution. The asbestos-internal standard ratios obtained for these same test standard materials show that the aspirin internal standard provided excellent compensation for matrix and bulk density effects (Table 1). These ratios indicate a detection limit of 0.1%, and a quantitation limit of 0.5% chrysotile.

Reference standards were then prepared by hand grinding weighed quantities of Duke Laboratories chrysotile asbestos fibers with aspirin internal standard and talc to achieve concentrations of 0.5, 1.0, 2.0, 5.0, 10, 20, and 50% asbestos. The standards and specimens were hand ground to as near 200 mesh as possible (15 min) and pressed for 30 sec in a 2.54 cm diameter hydraulic press die at 5000 pounds ( $34.5 \times 10^5$  Pa) pressure. The resulting discs were scanned on both sides, to average side-to-side variability, by the procedure detailed below.

The chrysotile-aspirin internal standard ratio was first plotted versus chrysotile concentrations of 0.5, 1.0, 2.0, and 5.0 weight percent in talc to obtain the calibration curve (Figure 2), and a first order fit was obtained for the range of interest. Also shown in Figure 2 are the plotted ratios obtained for the alumina, gypsum, and dimethyl oxalate 1% asbestos standards showing the internal standard compensation for the matrix on asbestos counting rate. The calibration range was then extended to 50% chrysotile using additional standards of 10, 20, and 50% asbestos (Figure 3).



1% Chrysotile Asbestos in  $\text{Al}_2\text{O}_3$



1% Chrysotile Asbestos in Dimethyl Oxalate

Figure 1. Effect of matrix on asbestos counting rate.

TABLE 1

## ASBESTOS - INTERNAL STANDARD CALIBRATION DATA

| <u>Matrix</u>                  | <u>Weight %<br/>chrysotile<br/>asbestos</u> | <u>Net counts<br/>asbestos</u> | <u>Net counts<br/>aspirin</u> | <u>Asbestos-<br/>aspirin<br/>count ratio</u> | <u>Avg.<br/>Asbestos-<br/>aspirin<br/>count ratio</u> | <u>Corrected<br/>ratio<br/>(intercept<br/>.160)</u> | <u>% Asbestos<br/>from chart</u> | <u>Error</u> |
|--------------------------------|---------------------------------------------|--------------------------------|-------------------------------|----------------------------------------------|-------------------------------------------------------|-----------------------------------------------------|----------------------------------|--------------|
| Talc                           | 0.5                                         | 6427                           | 32000                         | 0.201                                        |                                                       |                                                     |                                  |              |
| Talc                           | 0.5                                         | 6026                           | 31934                         | 0.189                                        | 0.182                                                 | 0.022                                               | 0.46                             | 0.04         |
| Talc                           | 0.5                                         | 5050                           | 32540                         | 0.155                                        |                                                       |                                                     |                                  |              |
| Talc                           | 1.0                                         | 7612                           | 35929                         | 0.212                                        | 0.210                                                 | 0.050                                               | 1.00                             | 0.00         |
| Talc                           | 1.0                                         | 7298                           | 35298                         | 0.207                                        |                                                       |                                                     |                                  |              |
| Talc                           | 2.0                                         | 8720                           | 35414                         | 0.246                                        | 0.256                                                 | 0.106                                               | 1.96                             | 0.04         |
| Talc                           | 2.0                                         | 10352                          | 36148                         | 0.286                                        |                                                       |                                                     |                                  |              |
| Talc                           | 5.0                                         | 16802                          | 40352                         | 0.416                                        | 0.422                                                 | 0.262                                               | 5.00                             | 0.00         |
| Talc                           | 5.0                                         | 16954                          | 39573                         | 0.428                                        |                                                       |                                                     |                                  |              |
| Dimethyl<br>Oxalate            | 1.0                                         | 12018                          | 257579                        | 0.047                                        | 0.046                                                 | 0.046                                               | 0.94                             | 0.06         |
| Dimethyl<br>Oxalate            | 1.0                                         | 12007                          | 265193                        | 0.045                                        |                                                       |                                                     |                                  |              |
| Al <sub>2</sub> O <sub>3</sub> | 1.0                                         | 2531                           | 38826                         | 0.065                                        | 0.055                                                 | 0.055                                               | 1.08                             | 0.08         |
| Al <sub>2</sub> O <sub>3</sub> | 1.0                                         | 1844                           | 40980                         | 0.045                                        |                                                       |                                                     |                                  |              |
| Gypsum                         | 1.0                                         | 442                            | 19676                         | 0.022                                        | 0.045*                                                | 0.045                                               | 0.90                             | 0.10         |
| Gypsum                         | 1.0                                         | 1125                           | 16688                         | 0.067                                        |                                                       |                                                     |                                  |              |

\*Gypsum was hygroscopic and difficult to grind into a homogeneous standard.

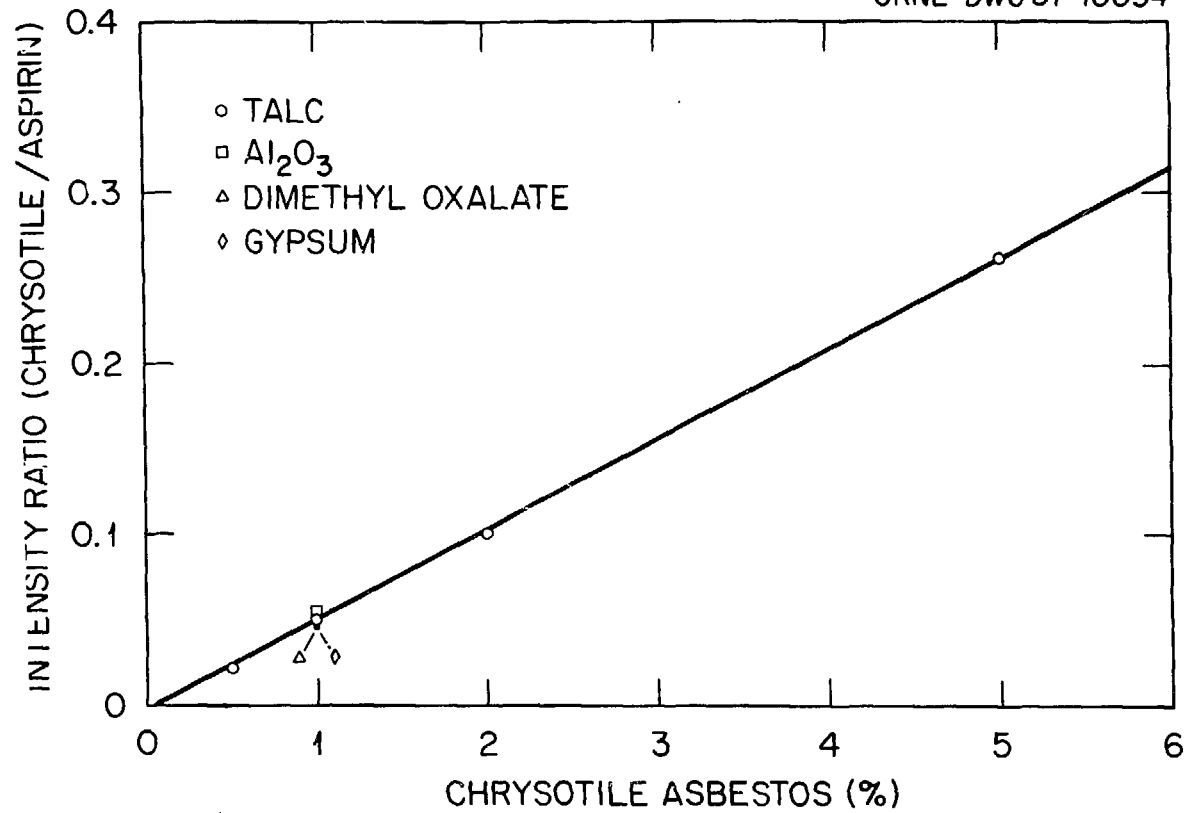


Figure 2. Low level chrysotile asbestos calibration curve.

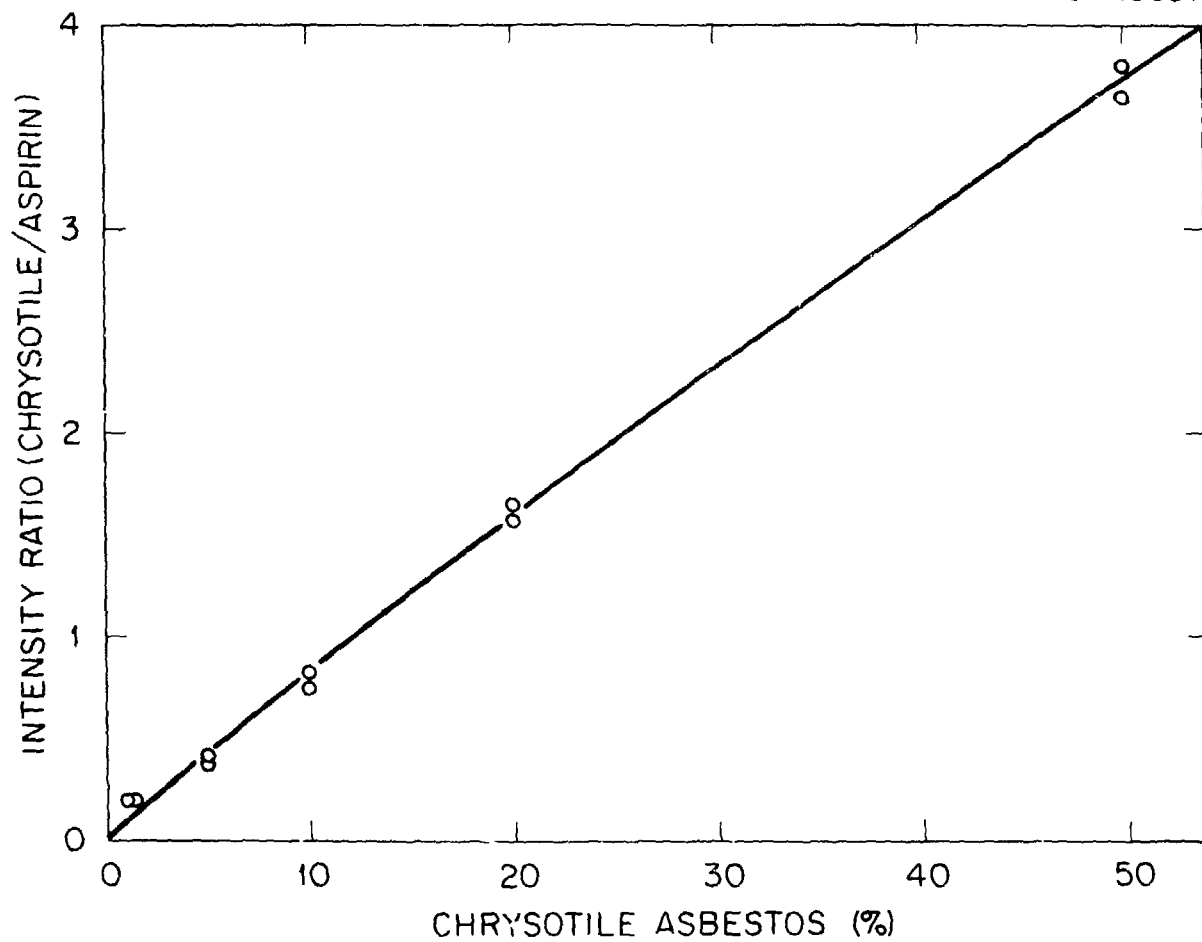


Figure 3. High level chrysotile asbestos calibration curve.

### Specimen Preparation

Since neither a gradient density column separation nor centrifugal separation of suspended asbestos fibers from talc, gypsum, or other mineral fibers was successful, we decided to develop a general preparative method, suitable for these varied materials, leading to final measurement by x-ray diffractometry. Organic specimens, sufficient to yield 1.00 g of ignited residue, were weighed into tared porcelain dishes. The specimens were ignited at 350°C for 3 hr, cooled and reweighed to determine weight loss on ignition. Specimens of adhesive, slurries, and wet material were similarly prepared. Ignition of the gypsum specimens at 350°C converted the gypsum ( $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ) to the hemihydrate ( $\text{CaSO}_4 \cdot 1/2\text{H}_2\text{O}$ ) form which does not interfere with measurement of the chrysotile asbestos peak (Figure 4). Careful ignition of the specimens at 350°C resulted in dry solids that were easily prepared for analysis and did not affect the chrysotile response.

Each dry specimen was hand ground in a mullite mortar to approximately 200 mesh and 1.00 gram was weighed into a clean container. Each specimen was then hand ground in a mullite mortar for 15 min with 0.30 grams of aspirin internal standard, this powder was then compacted into a 2.54 cm diameter pellet for analysis.

### RESULTS AND DISCUSSION

Major difficulties experienced in performing conventional quantitative analysis of building materials include the physical nature of the materials, the care needed to prepare them for analysis, interferent compounds, and bulk density variations.

The first full set of ORNL building material specimens received for analysis included tar-filled floor tiles, organic fiber acoustic panels, adhesive pastes and gypsum-filled wall boards, and indicate the difficulty in obtaining a quantitative analysis by conventional measurements. These specimens (Table 2) were analyzed by polarized light microscopy, transmission and scanning electron microscopy, and x-ray powder diffraction techniques to determine whether the chrysotile asbestos concentration exceeded one percent. Specimens containing asbestos near that level were measured by diffractometry.



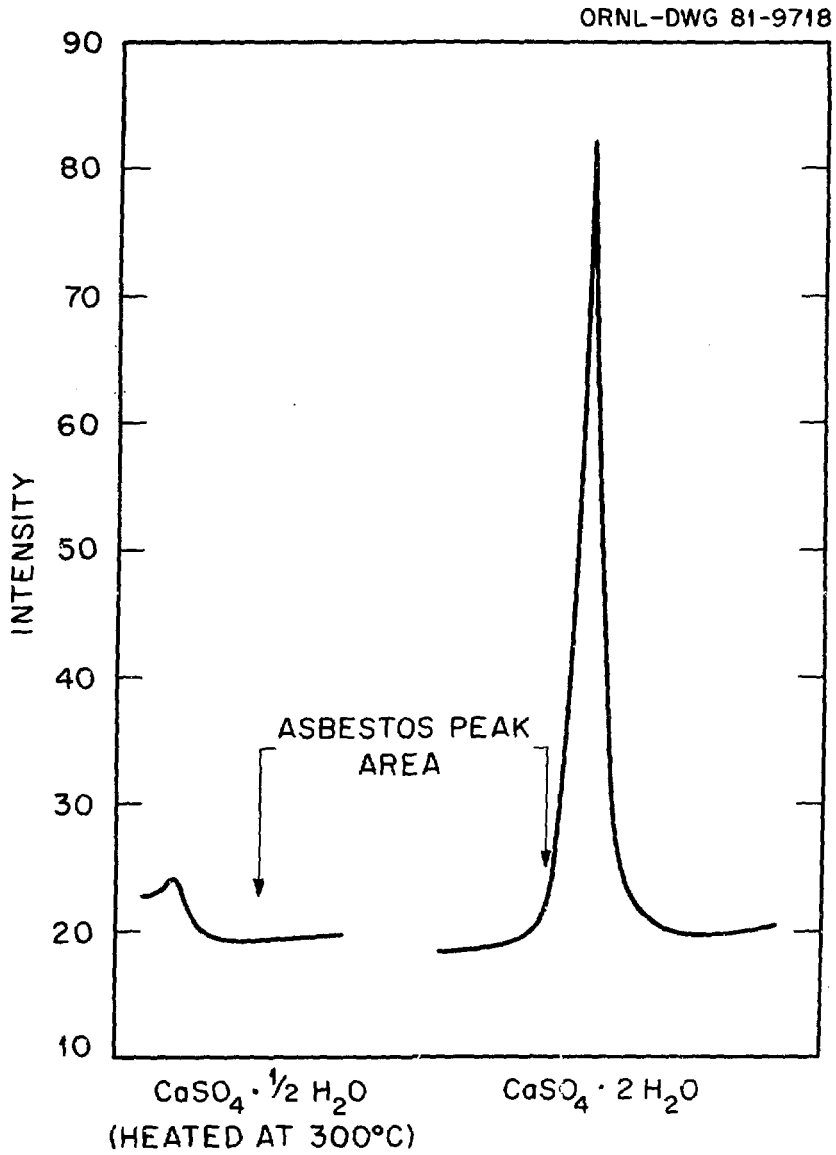


Figure 4. Removal of gypsum interference by heating.

TABLE 2  
DESCRIPTION OF BUILDING MATERIAL SPECIMENS

| <u>Lab. Ident.</u> | <u>Sample</u> | <u>Material Type</u>                   | <u>Reported<br/>% Asbestos</u> |
|--------------------|---------------|----------------------------------------|--------------------------------|
| 3885               | 1             | Acoustic plaster                       | >1                             |
| 3886               | 2             | #15 Tar saturated felt                 | >1                             |
| 3887               | 3             | #15 Asphalt asbestos felt              | >1                             |
| 3898               | 4             | Roofing material                       | >1                             |
| 3899               | 5             | Sheetrock wallboard (new)              | <1                             |
| 3900               | 6             | Vinyl asbestos floor tile (green)      | >1                             |
| 3901               | 6A            | Vinyl asbestos floor tile (gray)       | >1                             |
| 3902               | 6B            | Vinyl asbestos floor tile (black)      | >1                             |
| 3903               | 7             | Imperial plaster board (new)           | >1                             |
| 3904               | 8             | Vinyl asbestos floor tile              | >1                             |
| 3909               | 9             | Acoustic plaster (Central Auditorium)  | >1                             |
| 3910               | 10            | Plaster (J-241) brown coat             | >1                             |
| 3911               | 11            | Plaster (B3500W) white coat            | <1                             |
| 3912               | 11A           | Plaster - corridor brown coat          | <1                             |
| 3913               | 12            | Plaster - wall (B2010) white coat      | <1                             |
| 3914               | 12A           | Plaster - wall (B2010) brown coat      | <1                             |
| 3915               | 13            | Gypsum plaster, brown coat (new stock) | >1                             |
| 3916               | 14            | Gypsum block (J241)                    | <1                             |
| 3929               | 15            | Joint cement (T. texture)              | >1                             |
| 3930               | 16            | Joint cement (U.S.G.)                  | <1                             |
| 3931               | 17            | Synkloid cement                        | <1                             |
| 3932               | 18            | Acoustic tile (perforated)             | >1                             |
| 3933               | 19            | Acoustic tile (mineral)                | >1                             |
| 3948               | 20            | Roofing B7603                          | <1                             |
| 3949               | 21            | Firebrick - 3000°F                     | <1                             |
| 3950               | 22            | Mortar mix - 3000°F                    | >1                             |
| 3951               | 23            | Flashing (wing 1 - 4500S)              | <1                             |
| 3952               | 24            | Masonite (new)                         | <1                             |
| 3885(R)            | 25            | Acoustic plaster                       | >1                             |

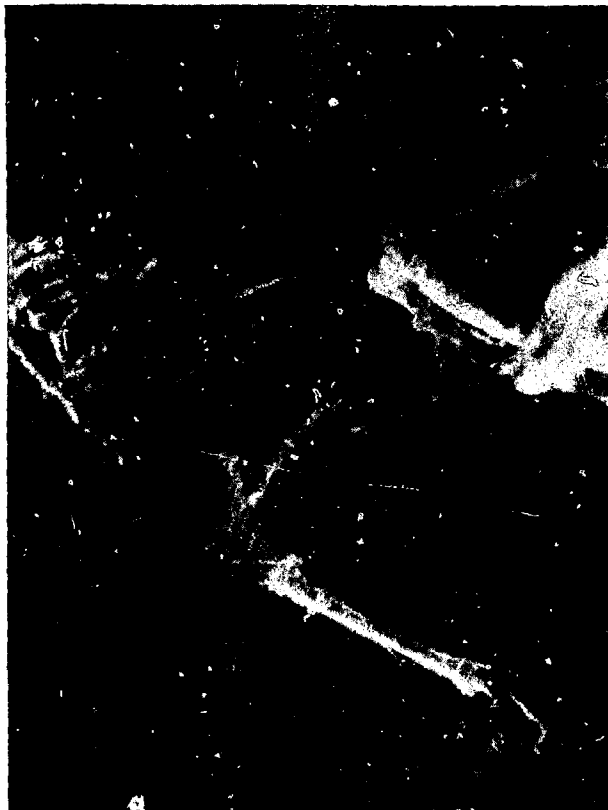
The plastered acoustic tile specimen from the ORNL cafeteria provided an excellent comparison of the standard protocol analyses with the new diffractometer method. Polarized light microscopic examination of the plaster was possible only after dilute HCl leaching to remove the bulk of the non-fibrous material. This examination and study of the fibrous filler in the tile detected chrysotile fibers by use of matching refractive index fluids, morphology, and the optical birefringence of the fibers.

Photographs of the specimens (Figure 5) were used to estimate the relative percentage of the specimen area covered by the fibrous material, and indicated that the tile contained 4-6% chrysotile. Debye-Scherrer x-ray diffraction powder patterns showed a definite serpentine pattern, and indicated the concentration to be in the 3-10% range. Fibers were also mounted and examined by scanning electron microscopy. The typical chrysotile morphology was evident, and the energy dispersive x-ray elemental analysis detected the characteristic elements magnesium and silicon. The result of ORNL diffractometer analysis of the material was 5.3%, in good agreement with the conventional methods. Other specimens noted in Table 2 were also analyzed with similar results.

Since the standards were all prepared from Canadian chrysotile, we prepared a 5% Rhodesian chrysotile standard in talc to test the reliability of the method. The analyzed value of 5.2% was in good agreement with the known value.

The possibility of direct line interferences, with either the asbestos or the internal standard line, must be considered whenever such diverse materials are analyzed. A very weak diffraction line is, in fact, observed in the talc standards at the 0.736 nm chrysotile region. While it is not significant in any but the lowest concentrations of chrysotile, use of the talc blank removes the 0.16 zero intercept. A study of the powder diffraction files<sup>15-16</sup> indicates only a few interferent compounds which may be logically expected to be present in the building materials of interest. The nonfibrous serpentine, antigorite, has a strong diffraction peak at 0.729 nm that is a direct interferent with the 0.736 nm chrysotile peak. The presence or absence of antigorite can be rapidly determined by scanning for the 0.217 nm peak. Absence of the 0.217 nm peak indicates that the

ORNL PHOTO 1492-83



ORNL PHOTO 1493-83



Figure 5. Scanning electron photographs of two randomly selected areas of ORNL acoustic tile specimen.

0.736 nm peak is chrysotile, while its presence would indicate that the 0.736 nm peak was due in part to the presence of antigorite. Examination of the specimen with polarized light microscopy will establish whether the serpentine is fibrous chrysotile or nonfibrous antigorite.

The Research Triangle Institute provided several samples for analysis by the ORNL diffractometer technique. The samples had been prepared for use in a quality assurance program administered by RTI under contract to the U. S. Environmental Protection Agency. The first four specimens were from public buildings and the other (#8) was a synthetic material formulated at RTI. Results of comparison analyses are shown in Table 3. The ORNL data was in good agreement with reference data provided by RTI. Typical diffractometer scans of sample #1, #2, and #3 (Figure 6) show the response of the chrysotile in both high and very low concentrations. The generic term "asbestos" peak in these figures refers to the 0.736 nm chrysotile diffraction peak area. These scans show that even 30-40% amosite does not interfere with the chrysotile measurement.

#### CONCLUSIONS

X-ray diffractometry offers a direct technique for the accurate quantitative determination of low levels of chrysotile asbestos in a complex variety of raw and finished building materials. While this method was developed to determine the chrysotile form of asbestos, it should also be applicable to other forms of asbestos. Potential uses of the technique include selection of construction materials and determination of the asbestos content of materials in existing structures prior to demolition or renovation, which may be of extreme economic importance in meeting asbestos ceiling regulations in public schools.

#### ACKNOWLEDGMENTS

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TABLE 3

COMPARISON OF THREE TECHNIQUES FOR DETERMINATION OF  
CHRYSTILE ASBESTOS IN BUILDING MATERIALS

| <u>Sample</u> | <u>Polarized Light Microscopy<sup>(a)</sup></u><br><u>(PLM)</u>       | <u>Thermogravimetric<sup>(b-d)</sup></u><br><u>Analysis (TGA-GCA)</u> | <u>X-Ray</u><br><u>Diffraction</u><br><u>(ORNL)</u> |
|---------------|-----------------------------------------------------------------------|-----------------------------------------------------------------------|-----------------------------------------------------|
| 1             | 25% Chrysotile<br>60% Fiberglass<br>15% Nonfibrous                    | 24% $\pm$ 4% Chrysotile                                               | 27% Chrysotile                                      |
| 2             | Trace Chrysotile<br>Trace Amosite<br>75% Fiberglass<br>25% Nonfibrous | 3% $\pm$ 4%                                                           | 0.4%                                                |
| 3             | 30% Amosite<br>60% Fiberglass<br>10% Nonfibrous                       | 1% $\pm$ 4%                                                           | 0.1%                                                |
| 4             | 30% Chrysotile<br>55% Fiberglass<br>5% Cellulose<br>10% Nonfibrous    | 26% $\pm$ 4%                                                          | 31%                                                 |

## RTI FORMULATION

| <u>Sample</u> | <u>Contents by Weight</u>                             | <u>TGA-GCA Analysis</u> | <u>ORNL Analysis</u> |
|---------------|-------------------------------------------------------|-------------------------|----------------------|
| 8             | 5% Chrysotile<br>15% Cellulose<br>80% Portland Cement | 7% $\pm$ 4% Chrysotile  | 6% Chrysotile        |

(a) Median values obtained in round-robin analysis.

(b) See Scalera, J. V.; "The Determination of Chrysotile in Insulation Samples Using Combined TGA-GCA," in Proceedings of the 11th North American Thermal Analysis Society Conference, (1981), 2 (No. 51), 303-309.

(c) Analysis for chrysotile only.

(d) Mean  $\pm$  1 standard deviation.

ORNL-DWG 81-19855

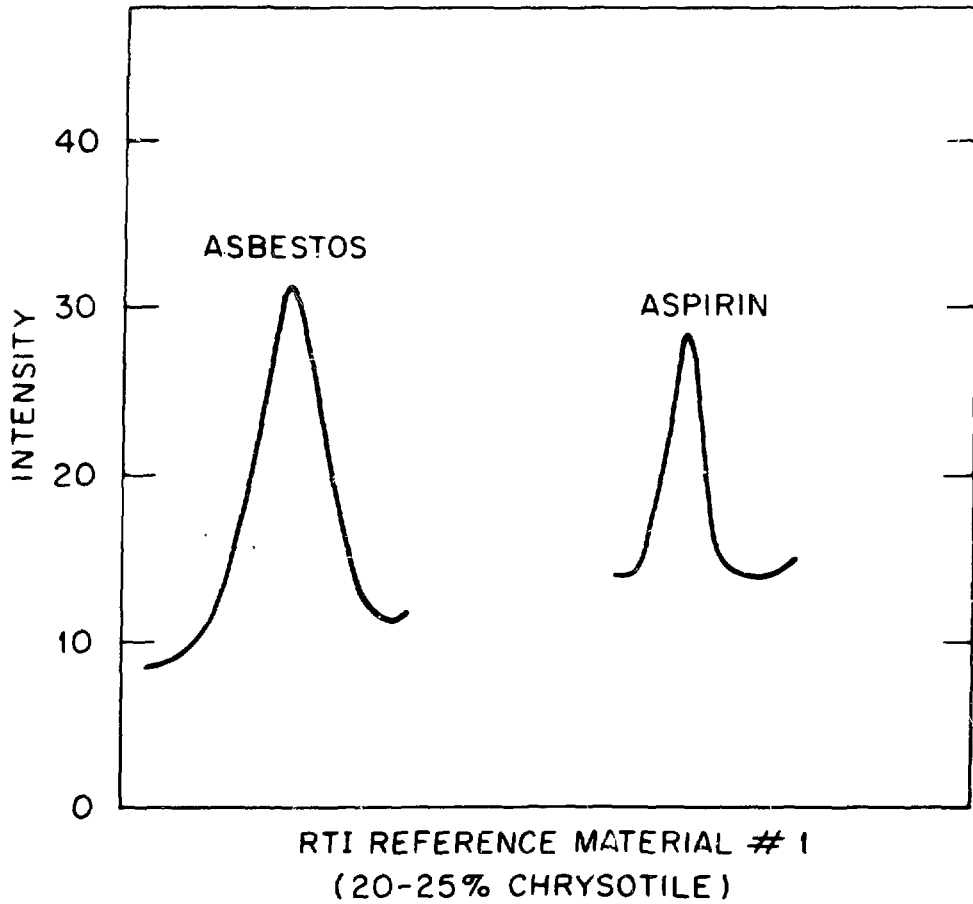


Figure 6a. Diffractometer scans of RTI specimen #1 containing 25% chrysotile.

ORNL-DWG 81-19856

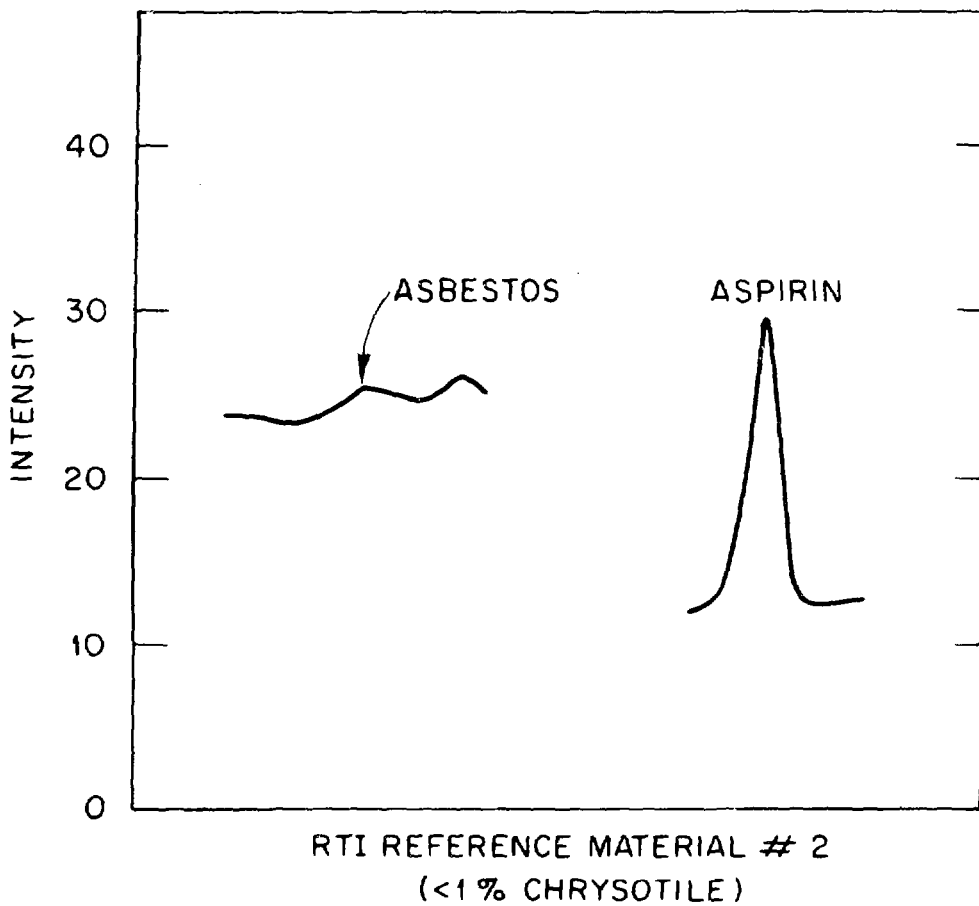


Figure 6b. Diffractometer scans of RTI specimen #2 containing <1% chrysotile.



ORNL-DWG 81-20720

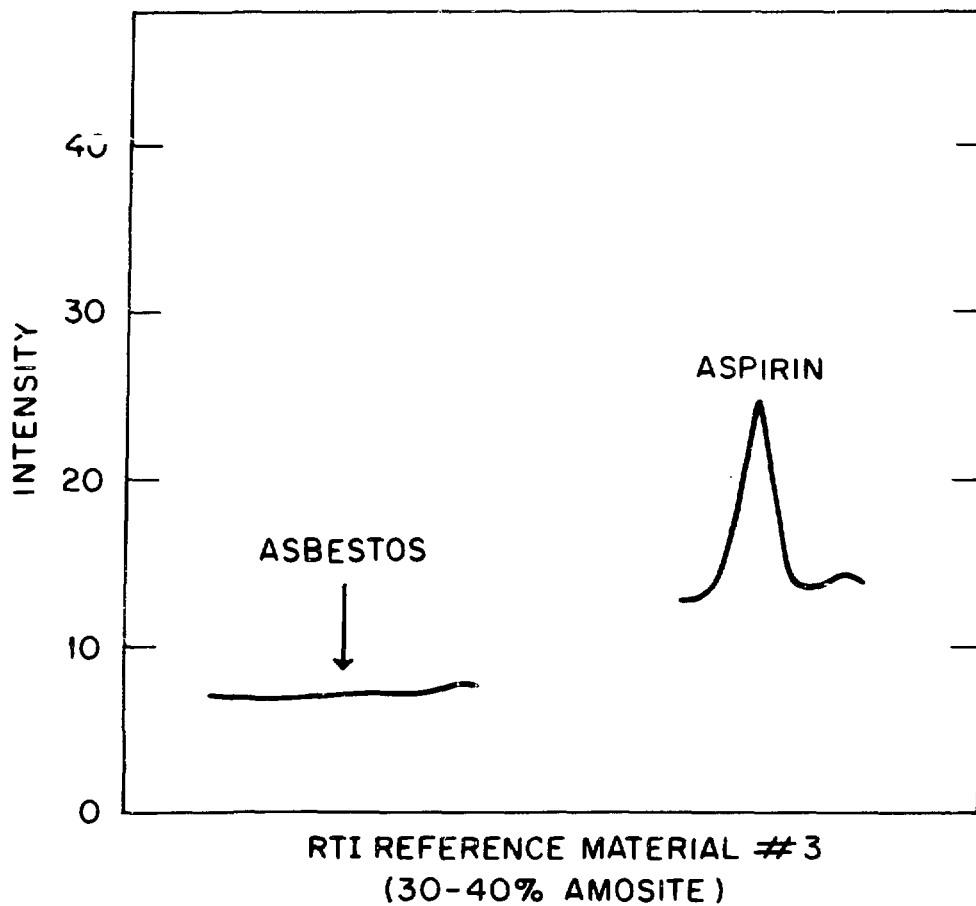


Figure 6c. Diffractometer scans of RTI specimen #3 containing <1% chrysotile and 30% amosite.

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FUNGICIDE TREATMENT FOR  
COOLING TOWER REDWOOD

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for the  
U.S. DEPARTMENT OF ENERGY  
Under Contract No. W-7406-eng-26

Key Words: Fungicide, Pentachlorophenate, Cooling Tower, Wood  
Preservation

ABSTRACT

The cooling tower cells at the PGDP are sprayed annually with a pentachlorophenate fungicide to protect the redwood members from fungal attack. Betz Corporation, the previous supplier of the fungicide, has recently discontinued marketing its pentachlorophenate product. This action instigated the search for an effective, EPA-approved alternative.

The EPA Position Document on pentachlorophenate states the pentachlorophenate will be classified as a restricted use pesticide with its application limited to certified applicators. Of the pentachlorophenate fungicides available, only Chapman Chemical Company's Napchlor G is licensed by the EPA for wood spraying. Charts reviewing the treatment parameters used in comparing and evaluating the fungicides, results of comprehensive laboratory and field tests used to determine operational efficiency, and comparative cost data for annual application will be presented.

### INTRODUCTION

Each cooling tower cell at the PGDP is sprayed annually, by personnel of the Cascade Operations Division, with a 10 weight percent solution of sodium pentachlorophenate (hereafter referred to as pentachlorophenate) to protect the redwood members of the top deck from fungal attack. Betz Corporation, the previous supplier of both the fungicide (Betz F-16) and periodic laboratory evaluation of the treated wood, has recently removed its fungicide and marking dye from the market. A two-phase program was initiated to evaluate the availability of environmentally acceptable fungicide treatments. The goal of phase one was to provide an alternative source formulation of pentachlorophenate for the near future. Phase two of this project is directed toward evaluation of alternative cooling tower treatments should the EPA ultimately disallow treatment with pentachlorophenate.

### EXPERIMENTAL

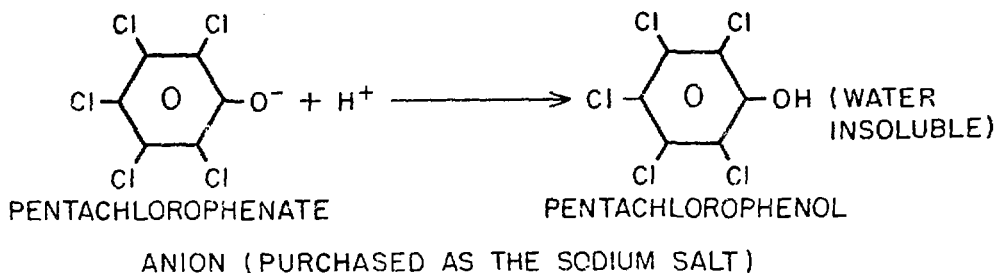
The protection of redwood from fungal attack, provided by solutions of pentachlorophenate, depends primarily upon the pentachlorophenate strength of the spray solution, the surface tension of the spray

solution, and the dryness of the wood to be sprayed. Surfactants may be added to solutions to reduce their surface tension and enhance penetration. Small air pockets within voids in the wood offer resistance to efficient penetration. As the surface tension of the penetrating solution is lowered, the resistance to penetration at the solution/air interface is lowered and the contact of these areas is facilitated. If the wood to be sprayed has been in service for extended periods, these voids will have been eliminated and as long as the wood is not allowed to dry out (cell off-stream 24 hours or more), the use of surfactants will not be required. It should be pointed out that the presence of the pentachlorophenate anion ( $C_6Cl_5O^-$ ) in water solution serves as a mild surfactant. This phenomena is addressed later in this section. Betz F-16, the fungicide formerly used at Paducah for spraying cooling tower redwood, contained dispersing agents and 20.7 weight percent pentachlorophenate. The Betz F-16 solutions were diluted with water to 10 weight percent and an acidic ( $pH = 3.3$ ) marking dye was added in the ratio of 1 gallon dye per 500 gallons of solution prior to spraying. An extensive vendor survey indicated only Chapman Chemical's Napchlor G as an EPA registered alternative source of pentachlorophenate for wood spray applications. Samples of Napchlor G were obtained and tests conducted to determine the impact of the following parameters on the preparation and use of this product at the PGDP.

1. Spray solution pH as a function of pentachlorophenate concentration.
2. Impact of an acidic marking dye on solution stability (i.e., tendency for pentachlorophenate/dye to precipitate).

3. Addition of surfactant to enhance penetration of fungicide into the redwood.

The final pH of the fungicide solutions as well as solution stability is directly related to the pentachlorophenate concentration. It was determined that reduction of the solution pH below 9.5 would result in partial precipitation of pentachlorophenate. The first particles were very finely dispersed as in a colloidal solution and would not freely settle. Precipitation of the water insoluble pentachlorophenol occurs via the following reaction:



Partial precipitation reduces the available fungicide for preservation of the cooling tower wood. During the initial field testing of the Napchlor G, at the 10 weight percent pentachlorophenate concentration, precipitation occurred due to the high concentration of the acidic marking dye. Increasing the pH by the addition of three pounds of sodium hydroxide flakes to 300 gallons of test solution has eliminated the precipitation. A fifteen-fold dilution of the original marking dye concentration achieved adequate coloration of the redwood for observation by the spraying personnel.

To determine the impact of fungicide solution surface tension on penetration, the reduction of surface tension provided by addition of an anionic surfactant was first examined. Solutions of Napchlor G varying from 10 to 12 weight percent pentachlorophenate were prepared. These solutions were divided into equal volume portions and a high foam surfactant\* was added to a concentration of 0.5% to one portion of each. These samples, along with a sample of Betz F-16, were submitted for analysis of surface tension. The data are recorded in Table 1. The Napchlor G samples without surfactants showed surface tensions equivalent to that of Betz F-16. While additional reduction of surface tension was supplied upon addition of the high foam surfactant, the improvement was minimal and upon standing a tacky residue formed which would be an operational problem on large scale operation. From this data and observations, the addition of a surfactant was deemed to be unnecessary and no further surfactants were evaluated. Penetration studies were then performed to further compare Betz F-16 and Napchlor G solutions without surfactant.

Samples of redwood (off stream 24 hours) were sprayed with a dosage calculated from the PGDP field spraying procedure and the surface area of the samples. The data are reported in Table 2 and no

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\*A low foam anionic surfactant, when added to solutions of Napchlor G in the recommended concentration of 0.5%, immediately formed an extremely tacky residue which would present very difficult operational problems upon use.

TABLE I

Surface Tension Data for Napchlor G and Betz F-16 Solutions  
Results of Surfactant Addition to Fungicide\*

Chapman Chemical Napchlor G

| Percent Pentachlorophenate<br>in Solution | With<br>Triton 770 Surfactant<br>dyne/cm | Without<br>Triton 770 Surfactant<br>dyne/cm | Betz F-16 Fungicide with<br>Solubilizing and Dispersing<br>Agents, dyne/cm |
|-------------------------------------------|------------------------------------------|---------------------------------------------|----------------------------------------------------------------------------|
| 10                                        | 38                                       | 46                                          | 48                                                                         |
| 11                                        | 37                                       | 46                                          |                                                                            |
| 12                                        | 37                                       | 45                                          |                                                                            |

\*Surface tension of water at 20°C is 73 dyne/cm.



TABLE II

Penetration Data\* for Laboratory Spraying of  
Redwood Samples

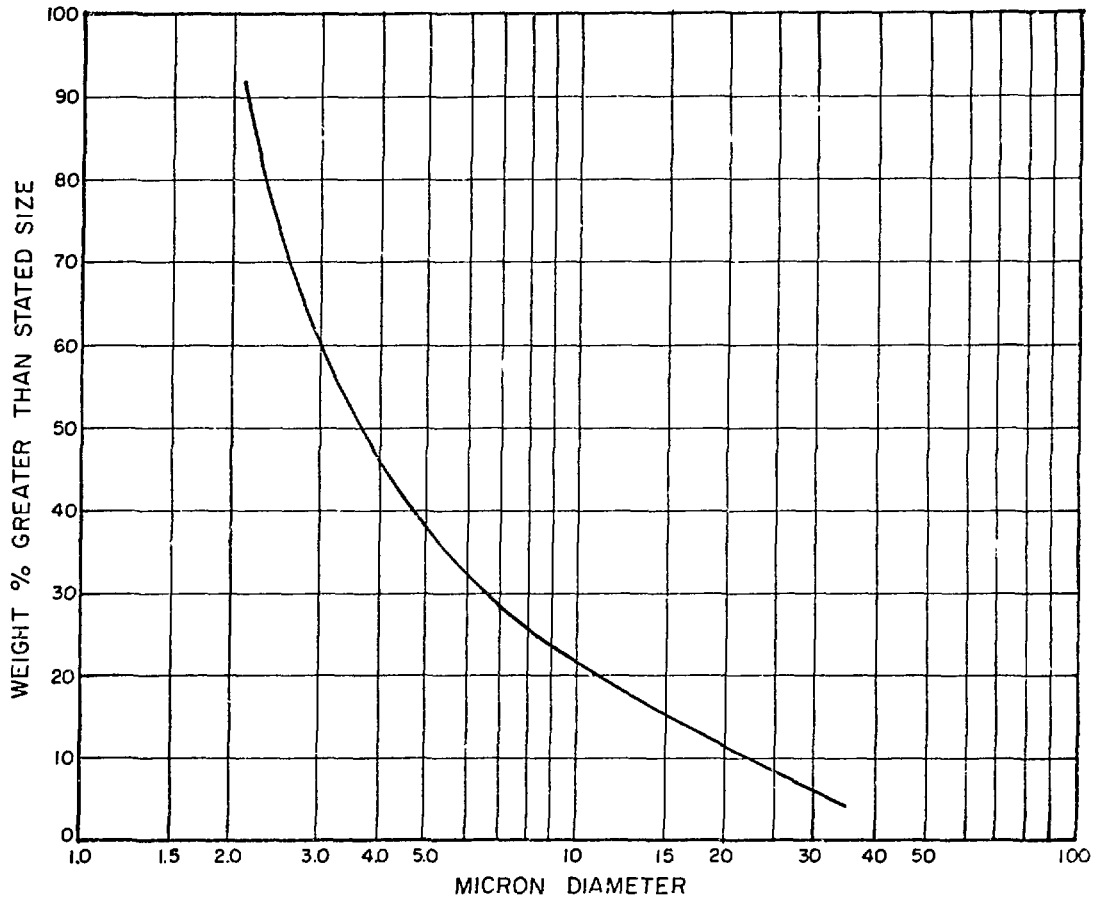
| <u>Depth of Sample Analyzed</u> | Betz F-16<br>Wet Wood<br>Pentachlorophenate, | Chapman Chemical Napchlor G<br>Wet Wood<br>Pentachlorophenate, |
|---------------------------------|----------------------------------------------|----------------------------------------------------------------|
|                                 | <u>ppm</u>                                   | <u>ppm</u>                                                     |
| 1/16-inch                       | 3,326                                        | 3,185                                                          |
| 1/16-inch to 1/8-inch           | 27                                           | 156                                                            |

\*Each data point represents a composite of two individual samples.

apparent difference between the products was noted for deposition of pentachlorophenate at the depths of penetration studied. Finally, dissolution of Napchlor G pellets was found to leave approximately 5% undissolved solids due to inerts in the formulation. The bulk of these solids were found to settle upon standing for 24 hours. Particle size data on these solids (Figure 1) indicate 5 weight percent of the particles are greater than 40 microns in diameter. To prevent build-up of solids on the spray wand nozzle, it was recommended that an in-line strainer be placed on the withdrawal line from the mixing tank to the solution storage tank.

#### CONCLUSIONS

The laboratory evaluation of Chapman Chemical's Napchlor G showed that it was as effective as the Betz F-16 in penetration and deposition of pentachlorophenate in redwood samples. The Napchlor G without a surfactant was recommended for use in spraying the cooling tower wood as a replacement for the Betz F-16 fungicide. The dye ratio has been lowered for the Napchlor G as compared to the Betz fungicide. The Napchlor G has been used during the 1981 fungicide spraying season. Operations has encountered no problems with the formulation and applicability of the fungicide. Use of the acidic marking dye represents a small cost savings and a significant savings in operator time when compared to the preparation and use of a dye of equivalent formulation to the Betz dye which is no longer available. It was recommended that a strainer mechanism be installed on the withdrawal



PARTICLE SIZE ANALYSIS  
FOR UNDISSOLVED SOLIDS IN NAPCHLOR G

Figure 1

line from the mixing tank to prevent the transfer of undissolved solids to the solution holding tank and ultimately the spraying wand nozzle. An operating procedure was formulated for the new material incorporating safety considerations and mixing instructions.

The continued usage of Chapman Chemical fungicide is dependent on federal guidelines pertaining to pentachlorophenate usage in spray applications. EPA's position document on the usage of pentachlorophenate has been examined and contact was made with the EPA's Special Pesticide Review Division for further clarification. Their position is that sodium pentachlorophenate will be classified as a restricted use pesticide and its application will be limited to certified applicators. Pending final EPA documentation, these findings indicate that long-term usage of sodium pentachlorophenate for spray application at PGDP may be anticipated. At the present time, the compound is not limited by EPA in our NPDES discharge permit. If the compound is banned, it appears that it will not be immediate, but rather a gradual phase-out with allowed depletion of accumulated stores. The second phase of the fungicide testing program calls for a long-term testing program of alternative fungicide compounds. However, the EPA registration number required for spraying the cooling tower wood is not available on the remaining products. Some manufacturers are striving for this acceptance, but the majority of products are for use as a supplement to the cooling tower water for fungal inhibition. The

Environmental Technology Section will periodically check the market for newly available fungicides. It should be pointed out that the legal usage of Napchlor G is dependent on the cell being offstream and no water flowing through the tower distribution system.

## OFF-SITE RESPONSE FOR RADIOLOGICAL EMERGENCIES

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Key Words: Radiological emergencies, mobile laboratory,  
environmental, accidents

## ABSTRACT

Environmental radiological surveillance under emergency conditions at off-site locations is one of the advisory functions provided by DOE within the ORO jurisdiction. The Department of Environmental Management of ORNL has been requested to provide sampling and analytical assistance at such emergency response activities. We have assembled and identified specific individuals and equipment to provide a rapid response force to perform field measurements for environmental radioactivity releases as a consequence of nuclear accidents. Survey teams for sample collection and field measurements are provided along with analytical assistance to operate the radioactivity measuring equipment in the DOE emergency van.

INTRODUCTION

The March 1979 accident at the Three Mile Island (TMI) Nuclear Power Plant served as a stimulus for reinforcing local emergency plans for response to radioactivity releases. A combined DOE-ORNL team participated in the initial response at TMI, providing assistance in the off-site surveillance activities.<sup>1</sup> Based on experiences gained

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\*Operated by the Union Carbide Corporation under contract W-7405-eng-266 with the U.S. Department of Energy.

at TMI, we have instituted an upgrading program for radiological emergency responses. A mobile laboratory outfitted with communications equipment and a small complement of radioactivity measuring devices presently serves as the command post for off-site responses. The Oak Ridge Operations Office (ORO) of DOE acquired the mobile lab principally for use following transportation accidents involving radioactive shipments.

Our ongoing programs of environmental surveillance for research and compliance programs have served as a framework for our emergency plans.

#### PLANNING PRINCIPLES

We have taken the position that emergency planning should be considered in a dynamic fashion. That is, we plan to implement state-of-the-art surveillance techniques and equipment into our emergency plans as soon as practicable. The Department of Energy's response to nuclear emergencies is governed in part by DOE Order 5500.2, "Emergency Planning, Procedures, and Response Program," August 13, 1981. Our assistance to DOE on off-site accidents is on an as-needed basis; however, planning for those needs encompasses principles in use at ORNL for onsite emergencies.

Because unplanned releases of radioactivity can vary widely from miniscule levels to that of widespread contamination, our emergency response personnel will vary in relation to the severity of the release. By incorporation of personnel, equipment and facilities of

our established environmental surveillance program into our emergency response system, we feel that many problems associated with identification of contamination sources will be alleviated.

In a broad sense, analytical radiochemistry (a measurement science for the qualitative and quantitative analysis of radioactive materials) plays an important role in environmental monitoring programs at all nuclear installations, and it is an essential feature of any emergency response system. The techniques of high-resolution alpha- and gamma-ray spectrometry, coupled with suitable radiochemical separation schemes for beta-emitter determinations are used in the environmental surveillance evaluation of liquid and airborne releases of radioactivity. These same techniques (possibly the same equipment) form an indispensable part of an emergency response capability. In emergency conditions, the analytical radiochemistry team of the environmental surveillance program is qualified to provide the rapid response necessary to achieve the desired analyses and identification of released radionuclides.<sup>2</sup>

Health physics instrumentation for field use is usually designed to determine the exposure rate of different radiation types, but it is not generally useful for determining the identity of radionuclides causing the exposure. Due to public concern over environmental levels of radioactivity deposited by the September 26, 1976 nuclear test by the People's Republic of China and concern over possible releases at the TMI accident, it is now deemed advisable to perform field measurements of radionuclide contamination with sophisticated laboratory equipment capable of measuring concentration levels at or slightly



above ambient levels. For  $^{131}\text{I}$ , this implies a capability of determining this nuclide at 0.04 to 0.8 Bq/l in samples of milk or at equivalent concentrations in vegetation, soil, or water and 4 Bq/l ( $10^{-7} \mu\text{Ci}\cdot\text{cm}^{-3}$ ) in air.

Low-level determinations at these concentrations requires the use of high-resolution, high efficiency detectors and computer-based spectrometer systems. We have identified such systems currently in use at ORNL and have implemented plans to move such laboratory systems to a field location when needed. Personnel qualified to operate the laboratory systems are identified and are on call to accompany the instruments to an off-site location if the need arises.

#### PRESENT CAPABILITIES

The present off-site emergency response capabilities are based on the use of the DOE mobile laboratory as a combined laboratory/field command post for minor contamination incidents and as a field laboratory for major incidents such as that tested by the annual Sequoyah exercise conducted by the Tennessee Valley Authority. The DOE laboratory is a medium-sized recreation type vehicle outfitted with a radiotelephone and two transceiver systems for voice communications. The radioactivity measuring equipment consists of a 1024-channel pulse-height analyzer coupled to a 3 x 3-in. NaI(Tl) detector housed in a lead shield. In addition, an alpha scintillation system for gross alpha measurements and an end-window G-M counter for gross beta determina-

tions comprise the fixed laboratory equipment. Storage lockers for portable survey instruments, TLD dosimeters, air samplers, etc. are provided in the mobile facility. Electrical power for the mobile laboratory is provided by an onboard gasoline-powered generator with sufficient output to operate all the equipment as well as the central air-conditioning unit.

The usual field operation requires an operating crew of 3 or 4, depending on the complexity of the exercise. The radioactivity measurements usually require two people for operation of the spectrometers and other measuring devices along with the data recording and calculational requirements. The third individual in the crew operates a sample receipt and screening station located outside the main facility. The fourth individual in the crew serves as the radio operator and performs other liaison as needed.

Field survey teams operate in support of the mobile laboratory, performing sample collections and field dosimetry at the direction of the main control center for environmental surveillance. Samples of air particulates, charcoal cartridges for  $^{131}\text{I}$ , vegetation, soil, or water collected by the field survey teams are taken to the mobile laboratory for analysis.

#### RECENT EXERCISES

Two field exercises have been conducted in which the entire response system was tested under actual conditions. The first exercise

consisted of a postulated release of  $^{131}\text{I}$  and noble gases from the High Flux Isotope Reactor (HFIR) at ORNL. The emergency command center was established at DOE headquarters in Oak Ridge and the mobile laboratory was sent to a site near the east end of Y-12 where it was to be operated as a field laboratory. Four teams of two surveyors each were directed to various locations in and around the path of the postulated plume of radioactivity. Air filters and grass samples were returned to the mobile laboratory for field assay. The exercise was the first joint one in which ORNL provided operational support to the overall DOE effort. This exercise was conducted on June 17, 1981, and gave valuable experience to the participants.

Figure 1 illustrates the initial phase of the exercise and shows the preparations of the field survey teams in assembling air sampling and portable survey equipment. Figure 2 shows the portable laboratory set-up at the Y-12 site during the course of the exercise. The photograph shows the arrival of the first set of grass and air filter samples by a field survey team. Preliminary screening and sample preparation takes place on the portable table outside the laboratory. Critique of the first exercise recommended, among other things, more reliable voice communications, more field team autonomy, and establishment of an exclusion area around the mobile laboratory. (Onlookers and visitors congregated around and in the mobile laboratory.)

A second joint exercise took place on July 7, 1981, in conjunction with the annual emergency drill at TVA's Sequoyah Nuclear Plant. In the emergency scenario, the reactor near Chattanooga had released

ORNL PHOTO 1573-83

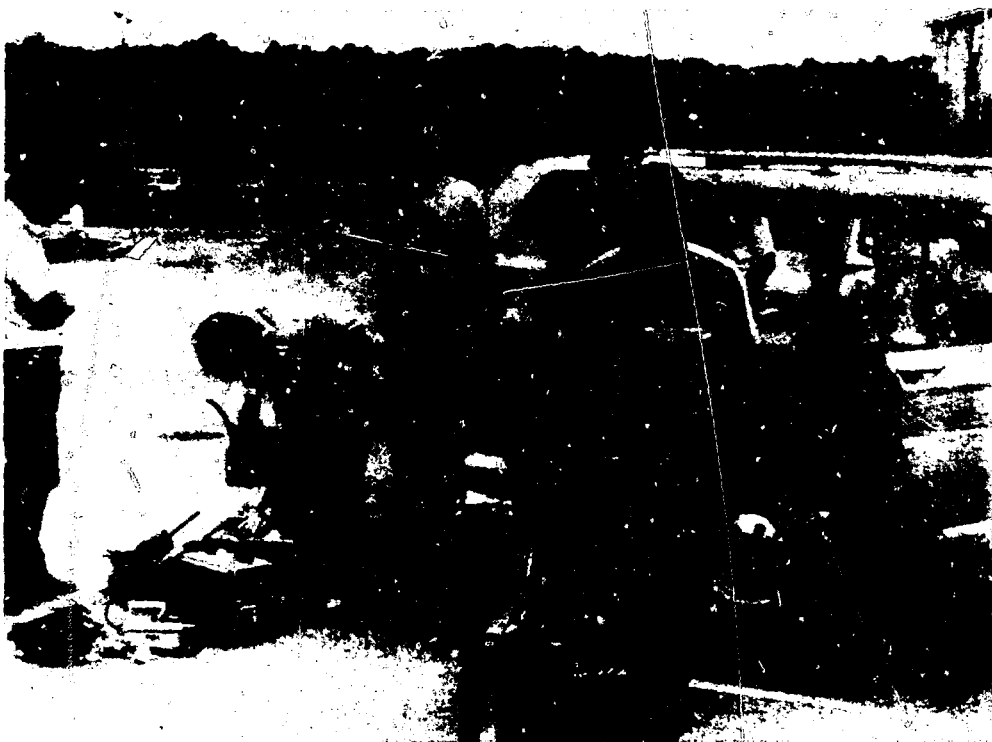


Fig. 1. Initial preparations for the June 17, 1981, emergency exercise. Equipment assembled includes portable survey devices, air samplers, and portable generators. The staging area was at the Federal Building, Oak Ridge, TN.

ORNL PHOTO 1574-83



Fig. 2. Mobile laboratory station at a field location during the June 17, 1981, emergency exercise. The photograph depicts the arrival of the first field survey team with air filter and vegetation samples.

$^{131}\text{I}$  to the environment, and radiological assistance from DOE-ORO was requested in the late afternoon. The response teams at ORNL were called by DOE at approximately 4 P.M. Within a period of approximately two hours, a response force of DOE-ORNL personnel in a convoy of four vehicles arrived at the Radiological Monitoring Control Center (RMCC) at Chattanooga's Lovell Field. Because of time restrictions and a shortage of mobile communications facilities, the mobile laboratory was dispatched to an elevated site at Huckleberry near Daisy, Tennessee. From that location, the mobile laboratory served as a relay station for communications from the RMCC to the field survey teams. Thus, it was possible to direct the DOE-ORNL survey teams to remote sampling points by means of the radio relay from Huckleberry. This arrangement was necessitated by the fact that the major communications from RMCC were conducted on a public service band that was not accessible in the DOE field units.

The Sequoyah exercise was deemed successful in spite of the inability to directly access the communication links of the TVA and state radio network. Test samples containing  $^{131}\text{I}$  were successfully analyzed under field conditions in the exercise. The major criticism of the second exercise was similar to that of the first: the need for improved mobile communications. During the two-hour transit time to the RMCC, the DOE-ORNL convoy had no contact with the emergency center. In addition, most government vehicles do not have ordinary radio receivers for commercial broadcasts. In a real emergency, the

other networks would be a valuable asset to the existing communication links. A scanner is to be placed in the van to alleviate some of these problems, and a portable repeater is being designed by the Y-12 Plant Radio Shop to expand the range of field team communications.

### FUTURE PLANS

The ability to provide a rapid response force to an off-site radiological emergency requires a dynamic emergency plan. This means that extreme flexibility must be available to tailor a response force to a variety of low probability accident scenarios. Economic considerations prevent the accumulation of sophisticated equipment dedicated to low probability emergency use exclusively. Therefore, we are planning to implement present and future instrument acquisitions into an overall emergency response scheme. We have identified three high-resolution gamma-ray spectroscopy systems that are transportable (in a configuration such that one or two people can load the system into an ordinary truck). Other detector systems (sodium iodide, plastic phosphors for beta measurements, and silicon diodes for alpha spectroscopy) have been identified for use with the transportable systems.

A state-of-the-art radiation monitoring cart has been ordered for routine service as an air monitoring station. This assembly weighs approximately 550 kg and is capable of measuring  $\alpha$ - and  $\beta$ -radioactive particulates,  $^{131}\text{I}$ , and radioactive noble gases in ambient air. The entire assemblage is mounted on a wheeled cart and is capable of

movement through standard doorways. In an extended off-site emergency, this monitoring station may be rapidly deployed to a remote site that contains electrical power. It contains CAMAC based electronics and can transmit measured response to a remote computer.

Other portable systems, including two complete battery-powered spectroscopy systems will be available for routine service as well as for emergency purposes within the next few months. A liquid scintillation counting system for tritium assays has also been identified and can be made available for transport within 1 or 2 hours.

The cadre of emergency response individuals consists of 8 to 10 specialists capable of performing a variety of emergency procedures including field sampling, dosimetry, and assessment. Personnel involved in the day-to-day operation of the sophisticated laboratory systems have been informed of possible emergency needs and are available on an emergency call list.

### CONCLUSIONS

A combined DOE-ORNL response force has been established for providing off-site assistance to radiological emergencies involving environmental contamination. Instrumentation and operational personnel have been identified and have participated in two field exercises during the summer of 1981. Continual upgrading of capabilities for assistance occurs with each new instrumental acquisition in the environmental surveillance programs within the Department of Environmental Management at ORNL.



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ENVIRONMENTAL LAWS AND REGULATIONS - POTENTIAL CHANGES

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Abstract

A review of the Clean Air Act, Clean Water Act, Resource Conservation and Recovery Act, Toxic Substances Control Act, and Comprehensive Environmental Response, Compensation, and Liability Act (Superfund) will be given. Recent congressional records will be analyzed as an indication of trends in these areas. Discussion on directions of environmental programs will be presented. A brief analysis of the potential effects on UCC-ND will be given.

(Paper not available for print.)

*Session 2: AIR AND WATER POLLUTION CONTROL*  
*Chairperson - R. G. Jordan*

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Def

## AN INITIAL EMISSION ASSESSMENT OF HAZARDOUS WASTE INCINERATION FACILITIES

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Emission, Fugitive, Incinerator,  
Hazardous Waste, Exposure, Dispersion

### ABSTRACT

Health and Safety Research Division, sponsored by EPA, conducted a study to quantify emission factors from stacks, spills, fugitives, storage, and treatment for a typical hazardous waste incinerator facility. Engineering participated in preparing flowsheets and providing calculations for fugitive emissions. Typical block-flow diagrams were developed for two types of hazardous waste incinerators (rotary kiln and liquid-injector) and for three capacities (small: 1 MM Btu/hr, median: 10 MM Btu/hr, and large: 150 MM Btu/hr). Storage requirements and support services were determined in more detail. Using the properties of a typical waste, fugitive emissions were determined, including emissions from pump leaks, valve leaks, flange leaks, and tank vents. An atmospheric dispersion model was then employed to calculate atmospheric concentration and population exposure estimates. With these estimates, an assessment was performed to determine the percentage of concentrations and exposure associated with selected emissions from each source at the incineration facility. Results indicated the relative importance of each source both in terms of public health and pollution control requirements.

### OBJECTIVE AND BACKGROUND

The objective of this study was to provide technical assistance in exposure and health risk assessment to the Incineration Branch of the Industrial Pollution Control Division, U.S. Environmental Protection Agency (EPA) by addressing the human health and safety issues associated with hazardous waste incineration facilities. To this end, fugitive

emissions from pre-incinerator process equipment were quantified, and atmospheric dispersion calculations and population exposure estimates were performed. The results were used to determine the percentage of concentrations and exposure associated with selected emissions and to estimate the importance of each source in terms of public health and pollution control. In other words, the goal was to produce generic source terms that made some sense and could be applied to assess the importance of emissions.

The Health & Safety Research Division (HSRD) of Oak Ridge National Laboratory (ORNL) conducted this study. Engineering Division at ORNL was requested to provide technical support in the form of design of typical facilities and calculation of fugitive emissions.

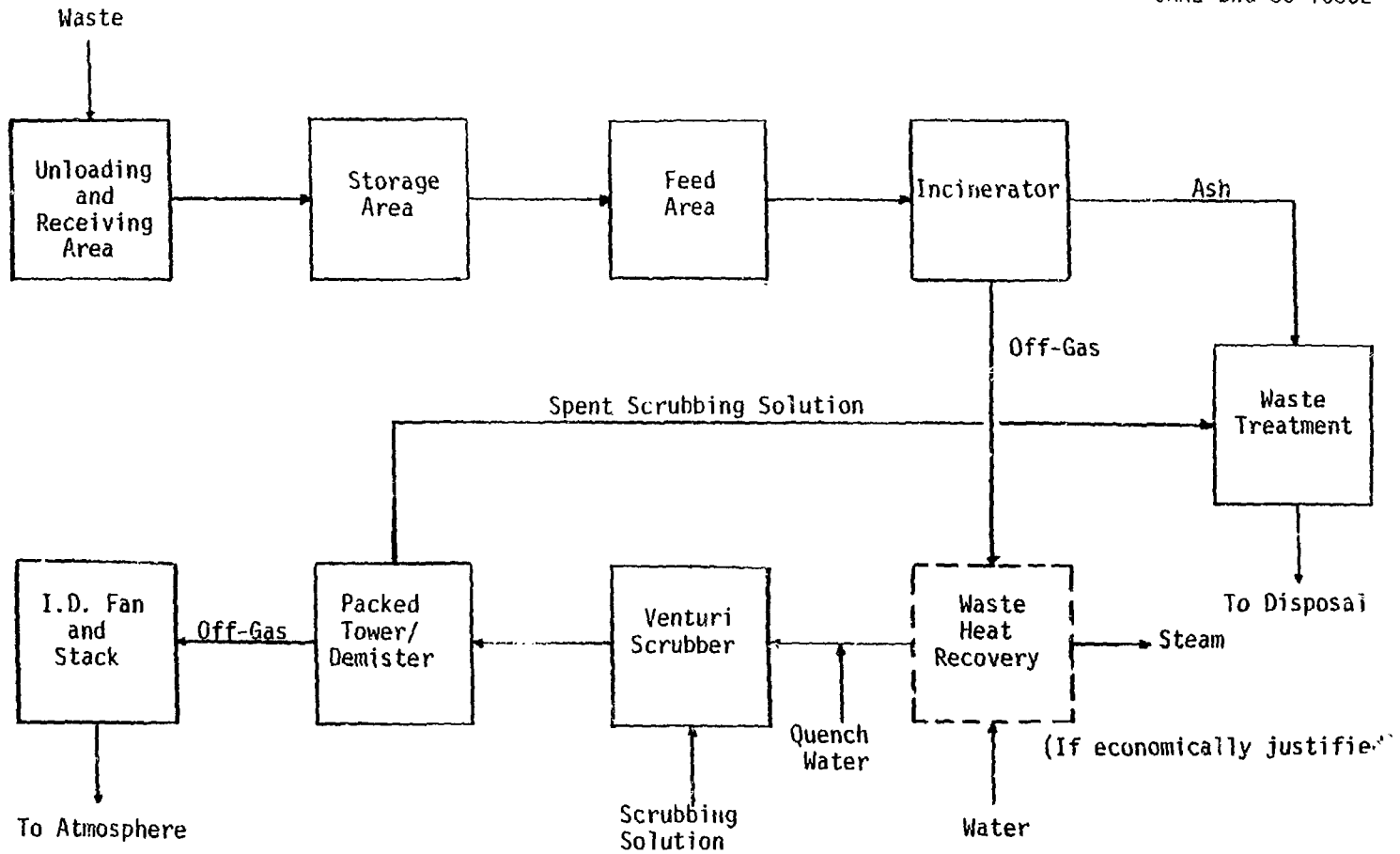
#### DESIGN OF TYPICAL FACILITIES

Six incineration facilities were designed. These included two incinerator types and three capacities. The chosen incinerator types were the rotary kiln and the liquid injector. The chosen capacities were 1 MM Btu/hr (small), 10 MM Btu/hr (medium), and 150 MM Btu/hr (large). These choices were based on a survey of operating incinerator facilities.<sup>1</sup>

A block flow diagram of a typical incinerator is presented in Figure 1. It includes the six basic areas of an incineration facility: unloading and receiving, storage, feed, combustion, offgas, and waste treatment (ash handling, etc.). The assumptions made in the development

FIG. 1: TYPICAL INCINERATOR BLOCK FLOW DIAGRAM

ORNL DWG 83-10862



of this diagram are as follows:

1. Waste heat recovery would be economically justified in all but the small capacity incinerators.
2. Typical off-gas systems would consist of a venturi scrubber and a packed tower/demister, followed by an induced-draft fan and stack.

From this block flow diagram, six process flowsheets were developed: one for each combination of the two incinerator types and three capacities. Figure 2 is a simplified version of one of the flowsheets: that of the 10 MM Btu/hr rotary kiln. Agitators, valves, instruments, etc., have been removed for the purpose of clarity. The major differences in the flowsheets were due to the different capacities. Only slight differences were due to the incinerator type.

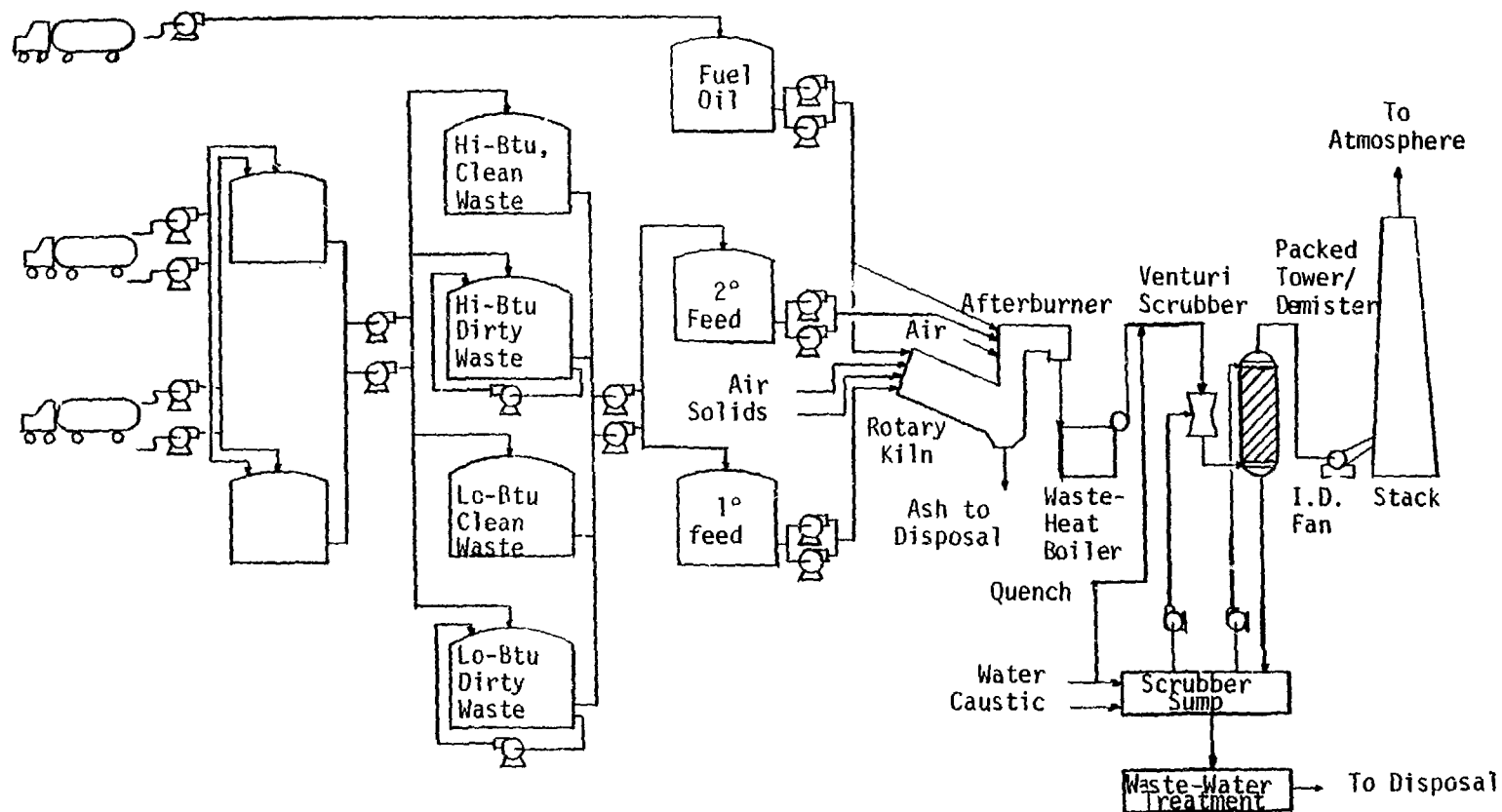
The unloading areas of the small, median, and large incinerators were designed to receive one tank truck, two tank trucks, and two tank trucks and a railroad tank car, respectively, at one time. Spered pumps capable of emptying the waste tankers in less than one hour and also capable of pumping to any receiving tank were provided for each unloading station.

Due to the small capacity, no receiving tanks were provided for the small incinerator. The storage tanks were assumed to also function as receiving tanks. Two tanks, one per unloading station, were provided for the large facility. This number would allow for segregation of the many kinds of waste such a large facility would expect to receive. All

FIG. 2: TYPICAL INCINERATOR PROCESS FLOWSHEET

10 MM BTU/HR ROTARY KILN

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the receiving tanks were sized to accommodate one tanker load. A pair of pumps capable of emptying these tanks in less than one hour were provided to transfer the waste to storage tanks.

Four storage tanks were provided for each incinerator, regardless of capacity. This number was chosen to allow for a simple segregation scheme. Wastes would be separated into high-Btu, clean or dirty waste, and low-Btu, clean or dirty waste. The tanks were sized to provide 14 days, 30 days, and 150 days storage for the large, median, and small incinerators, respectively. The 30 and 150 day figures were chosen to keep tank sizes reasonable. A pair of pumps capable of filling either feed tank in 8-12 hours (1-1.5 shifts) were provided.

Two feed tanks were provided for all facilities. For the rotary kiln, one tank was dedicated to waste to be fed into the kiln itself (primary chamber), and the second to waste to be fed into the after-burner (secondary chamber).

With the liquid injection, all the heat duty is in one chamber and from one feed, but in a rotary kiln, the heat duty must be distributed between the primary and secondary chambers, and between solid and liquid feeds. The duty was assumed to be split evenly between the two combustion chambers, and the primary duty was assumed to be split 2:1 between liquid feed and solid feed. For example, in the 10 MM Btu/hr rotary kiln, the duty in each chamber would be 5 MM Btu/hr. The liquid feed to the kiln would provide 3.3 MM Btu/hr and the solid feed would provide 1.7 MM Btu/hr. Only the large rotary kiln was designed to be able to accept whole drums due to the physical size of the incinerator.

Flow rates were determined by arbitrarily setting the heat content of the feed, making assumptions about the feed density, and utilizing the specified heat duties. The primary liquid feed to the rotary kiln was assumed to have a heat content of 8,000 Btu/lb, the solid feed to be 4,000 Btu/lb, and the secondary feed to be 14,000 Btu/lb. The feed to the liquid injector was assumed to be blended to 10,000 Btu/lb.

Liquids were assumed to have densities of 7 lb/gal.

Other features of the designs include the following:

1. nitrogen blanketing on the tanks to prevent contact of waste with air (explosion/fire hazard);
2. pump-around systems replacing agitators on tanks larger than 10,000 gallons for practicality;
3. tanks vented directly to the atmosphere; and,
4. redundant pumps to reduce downtime.

#### EMISSION FACTOR CALCULATIONS

The methodology for determining fugitive emissions from a typical hazardous-waste incinerator facility consisted of the following five steps:

1. determination of component properties;
2. determination of mixture properties;
3. determination of process operational parameters;
4. calculation of fugitive emission rates; and,
5. calculation of emission concentrations.

Although fugitive emissions were determined for eighteen cases (two incinerator types, three capacities, and three wastes), atmospheric dispersion and population exposure calculations were only performed for

one case: the median-size rotary kiln burning an average waste. The analysis of that waste, designated API Separator Sludge, is contained in Table 1. The analyses of the good and bad wastes are presented in Tables 2 and 3 respectively.

TABLE 1: ANALYSIS OF AVERAGE WASTE  
API SEPARATOR SLUDGE

| CONSTITUTENT         | MEDIAN CONCENTRATION (ppm) |
|----------------------|----------------------------|
| phenol               | 13.600                     |
| cyanide              | 0.001                      |
| heavy metals         | 642.873                    |
| ammonium salts       | 6.500                      |
| benzo (a) pyrene     | 0.004                      |
| crude oil (weight %) | 22.600                     |
| water (weight %)     | 53.000                     |

TABLE 2: ANALYSIS OF GOOD WASTE  
PHENOL/ACETONE DISTILLATION BOTTOM TARS

| CONSTITUTENT | MEDIAN CONCENTRATION (wt%) |
|--------------|----------------------------|
| acetophenone | 2.65                       |
| phenol       | 1.05                       |
| cumyl phenol | 1.15                       |
| total tars   | 95.15                      |

TABLE 3: ANALYSIS OF BAD WASTE  
TRICHLOROETHYLENE/PERCHLOROETHYLENE COLUMN BOTTOMS OR HEAVY ENDS

| CONSTITUTENT              | MEDIAN CONCENTRATION (wt%) |
|---------------------------|----------------------------|
| hexachlorobutadiene       | 33.8                       |
| 1,1,2,2-tetrachloroethane | 23.0                       |
| hexachlorobenzene         | 20.0                       |
| 1,1,1,2-tetrachloroethane | 6.3                        |
| hexachloroethane          | 4.0                        |
| ethylene dichloride       | 0.6                        |
| tetrachloroethene         | 4.5                        |
| beta-trichloroethane      | 4.5                        |
| pentachloroethane         | 3.3                        |

This discussion of emission factor calculations will be concerned with the median-capacity rotary kiln burning the average waste.

The basic physical properties (vapor pressure, density, etc.) of the individual waste components were obtained either from reference materials<sup>2,3</sup> or by calculation procedures presented in section 3 of Perry's Chemical Engineer's Handbook (Fifth Edition)<sup>3</sup>. The major problem with characterizing this waste was obtaining the properties of the component named as "oil". Having gained information on the process from which this waste stream arose, and having determined that "oil" meant "crude oil", Petroleum Refinery Engineering (Nelson)<sup>4</sup> was used to approximate the physical properties of a typical crude oil. This typical oil was assumed to be a typical U.S. crude.

Determination of the mixture properties (vapor pressure, density, molecular weight, and heat of combustion, was, in general, accomplished by utilizing simple mixing rules (such as  $P_{mix} = \sum x_i P_i$ ). Calculation of the vapor pressure allowed the classification of the waste as a light or a heavy liquid. If the waste's vapor pressure was less than 0.3kPa,

it was a heavy liquid. This stream was determined to be a light liquid. This classification was the basis on which the choice of emission factors was made, utilizing the information presented in Table 4.

TABLE 4: UNCONTROLLED FUGITIVE EMISSION FACTORS

| EMISSION SOURCE      | EMISSION FACTOR (kg/hr) |
|----------------------|-------------------------|
| pumps                |                         |
| light liquid         | 0.1200                  |
| heavy liquid         | 0.0200                  |
| valves (in-line)     |                         |
| light liquid         | 0.0100                  |
| heavy liquid         | 0.0030                  |
| flanges              | 0.0003                  |
| sampling connections | 0.0150                  |

Operational parameters that had to be determined were facility throughput, tank sizes and dimensions, pump operating times, and equipment quantities (valves, flanges, etc.). Facility throughput was calculated using the heats of combustion of the waste and #2 fuel oil to determine the proportions and amounts of waste and oil required to achieve the specified incinerator capacity. Nominal tank sizes had previously been chosen in this project's design phase, but actual capacities, heights, and diameters were chosen from vendor information provided by Bethlehem Steel Corporation's Buffalo Tank Division.<sup>5</sup> This information consisted of standard tank sizes and dimensions and guidelines for determination of tank dimensions for non-standard capacities. All tanks were assumed to be vertical and to have fixed roofs. Pump operating times (number of hours a pump would be in operation per year)

were calculated by dividing the throughput by the pump design capacity. Where two pumps were in parallel, it was assumed that each would operate half-time. The facility was assumed to be operational 300 days per year. Obtaining the different equipment quantities was accomplished using several ratios. These ratios were obtained from Organic Chemical Manufacturing, Volume 3: Storage, Fugitive and Secondary Sources,<sup>6</sup> UCC-ND TSCA incinerator designs, and this project's process flowsheets. The ratios are as follows:

|                                     |       |
|-------------------------------------|-------|
| valves to pumps                     | 15:1  |
| in-line valves to open-ended valves | 8:1   |
| flanges to valves                   | 1.6:1 |
| instrument connections to tanks     | 4:1   |
| sample connections to tanks         | 1:1   |

Equipment quantities were calculated for the facility as a whole and for the individual process areas (receiving, storage, feed, and fuel oil). The totals for each facility are presented in Table 5.

Emission rate calculations were divided into two parts: emissions from the various equipment types, and tank emissions. The former were based on emission factors presented in Table 4.<sup>6</sup> These emission factors were based on a survey of the synthetic organic chemical manufacturing industry (SOCMI). Utilizing the factors in combination with the previously calculated equipment quantities and pump operating times and previous characterization of the waste as a light liquid allowed the determination of the emission rates. Instrument connections were assumed to leak at the same rate as flanges, since no emission factor was specified. Emissions from tanks are separated into breathing and working losses. The former are affected mainly by the waste

Table 5  
Equipment

| Type                     | Rotary Kiln   |                |                   | Liquid Injector |                |                   |
|--------------------------|---------------|----------------|-------------------|-----------------|----------------|-------------------|
| Capacity                 | 1 MM          | 10 MM          | 150 MM            | 1 MM            | 10 MM          | 150 MM            |
| Pumps                    | 11            | 17             | 19                | 11              | 17             | 19                |
| In-line valves           | 78            | 130            | 143               | 78              | 130            | 143               |
| Open-ended valves        | 12            | 20             | 22                | 12              | 20             | 22                |
| Flanges                  | 144           | 240            | 264               | 144             | 240            | 264               |
| Sampling connections     | 6             | 8              | 12                | 6               | 8              | 12                |
| Instrument connections   | 24            | 40             | 44                | 24              | 40             | 44                |
| Tanks<br>(Total Gallons) | 7<br>(60,000) | 9<br>(145,000) | 13<br>(1,050,000) | 7<br>(72,000)   | 9<br>(170,000) | 13<br>(1,310,000) |

characteristics, tank geometry, and factors such as diurnal temperature fluctuations and paint condition. The latter is influenced in the most part by waste characteristics and the number of turnovers per year (throughput divided by capacity). The tank emissions were calculated using existing equations.<sup>6</sup> The total facility emissions were broken down by equipment type, process area, and component.

The last set of calculations involved determination of the concentrations of the various emissions components in the "boundary layer" above the liquid, be it a puddle on the ground or whatever. The boundary layer is that portion of the atmosphere immediately above the liquid. Its thickness is a few millimeters, at the most. In this layer, equilibrium exists between the gaseous and liquid phases. Therefore, Raoult's Law, one of the simplest equilibrium expressions, was used to calculate the concentrations. For these calculations, the only substances that were of significance were water and crude oil vapor (both from the waste), and #2 fuel oil vapor. All other components of the waste had negligible concentrations, negligible vapor pressures, or both. Many of the components, especially the heavy metals and salts, would be left as a solid deposit as the oil and water evaporated.

#### EMISSION FACTOR RESULTS

Results of the calculations for the particular case are presented in Table 6. It should be noted that these factors are for uncontrolled emissions.



Table 6  
Emission Factors

| Area                                         | Rate(lb/yr)      | Percent |
|----------------------------------------------|------------------|---------|
| unloading and receiving                      | 570.70           | 3.34    |
| storage                                      | 10,299.19        | 60.21   |
| feed                                         | 5,377.25         | 31.43   |
| fuel oil                                     | 860.89           | 5.03    |
| Equipment Type                               |                  |         |
| pumps                                        | 6,089.78         | 35.60   |
| in-line valves                               | 6,853.98         | 40.06   |
| open-ended valves                            | 1,442.27         | 8.43    |
| flanges                                      | 461.05           | 2.69    |
| instrument connections                       | 76.76            | 0.45    |
| sampling connections                         | 1,666.70         | 9.74    |
| tanks                                        | 517.56           | 3.03    |
| Constituent                                  |                  |         |
| water vapor                                  | 14,745.90        | 86.19   |
| crude oil vapor                              | 1,501.24         | 8.78    |
| #2 fuel oil vapor                            | 860.89           | 5.03    |
| Total = 17,108.03 lb/yr                      |                  |         |
| Initial atmospheric concentrations           |                  |         |
| considering entire facility as point source: |                  |         |
| water                                        | 1.245% by volume |         |
| crude oil vapor                              | 0.013% by volume |         |
| #2 fuel oil vapor                            | 0.017% by volume |         |

In terms of pollution control, these results show that the most significant area of the incinerator facility is the storage area. Controls in this area would be the most effective in reducing total fugitive emissions from the incinerator facility. Pumps and valves are the most important in terms of specific types of equipment, since they

account for over 80% of the emissions. Therefore, control of emissions from these items, often accomplished by improved maintenance programs, would be most effective. However, calculations for other cases show that the importance of tanks increases greatly as the capacity of the incinerator increases.

#### POPULATION EXPOSURE ASSESSMENT METHODOLOGY

Incineration of hazardous wastes produces stack and non-stack emissions. Because population exposure varies with emission type, understanding the relative contribution of each emission type is particularly important. Computer modeling is one way to estimate each contribution.

#### ATMOSPHERIC DISPERSION MODEL SELECTION

To calculate atmospheric concentration estimates due to emissions of a hazardous material, the Industrial Source Complex (ISC) Dispersion Model<sup>7</sup> was selected. This model is a U.S. Environmental Protection Agency (USEPA) recommended code which was readily available and fulfills all dispersion requirements of this study.

Industrial Source Complex Dispersion Model (ISC) is based on modified Gaussian plume assumptions and can be used to assess the air quality impact of emissions from a wide variety of sources associated with an industrial complex. ISC has been evaluated by the Office of Air Quality Planning and Standards, USEPA, and has been recommended for such applications.<sup>8,9</sup> The ISC computer code has many capabilities. Those employed in this study were: (1) the ability to specify receptor terrain

elevations, (2) use of two area-type sources to simulate fugitive emission releases, (3) the use of one point source to simulate stack emissions, (4) the use of city-specific meteorology employing local airport annual stability array (STAR) summaries, and (5) consideration of building-wake/stack-downwash effects on dispersion, developed from the actual incineration plant design. Using these ISC capabilities, ground level annual average downwind pollutant concentration estimates were calculated from fugitive and stack emission sources.

#### POPULATION SELECTION

The population base was selected to be that of the city of Cincinnati, Ohio, where a large incinerator facility already exists. To estimate the exposed population, the number of people per sector segment (Figure 3) had to be determined. This was performed by demographers at the Oak Ridge National Laboratory using a four-step procedure. First, based on preliminary 1980 Census data, numbers of people were assigned to 1970 block-group/ enumeration district centroids. Next, polygons were drawn around each centroid. In regions where many centroids existed, each polygon area was small; where few centroids existed, each polygon area was relatively large. Third, from the polygon area and the number of people assigned to each centroid, a population density was determined. These polygon population densities were then apportioned to a uniform 50 m x 50 m grid which covered the area of interest (a 15-km circle centered on the incineration facility). Fourth, the number of people per sector segment was calculated from the grid by a similar

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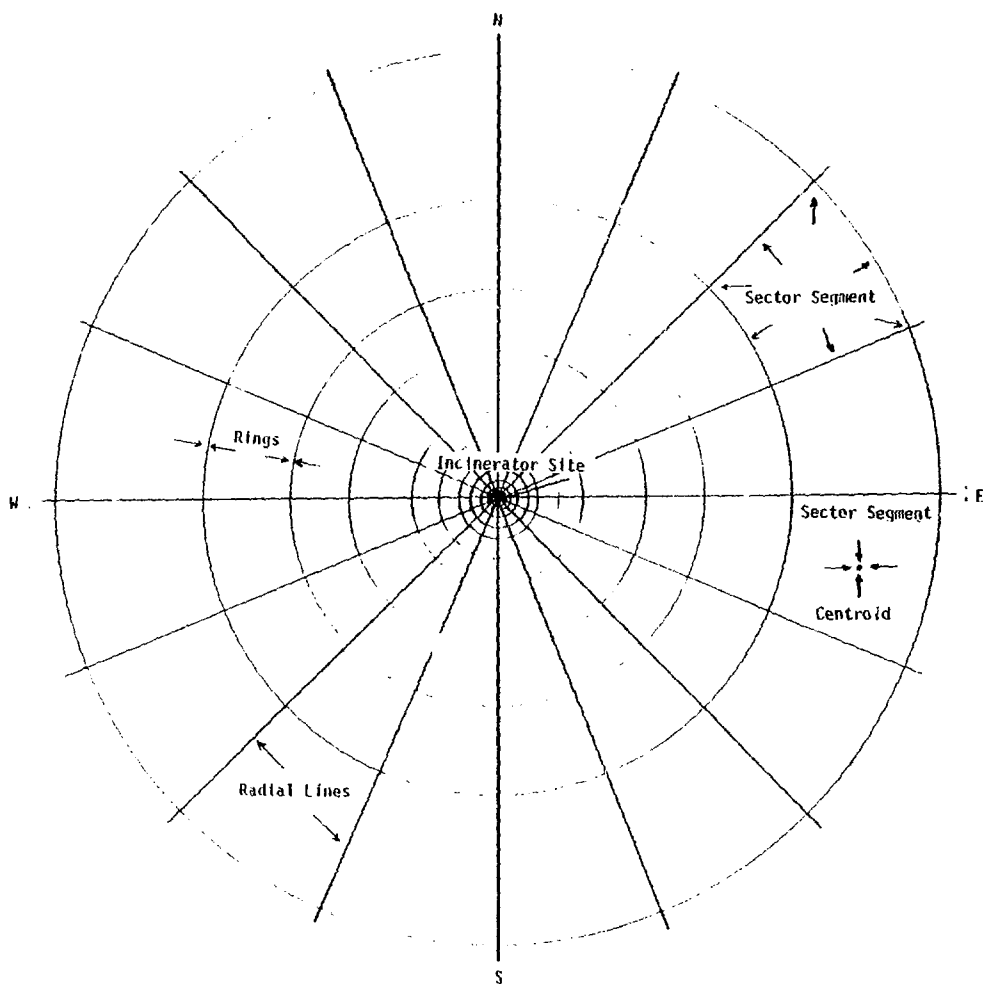


Figure 3. Parameters used to describe the study area.

area/density apportionment technique.<sup>10</sup> Table 7 contains these population estimates, referenced by each sector segment's geographic centroid, for the region surrounding the Cincinnati Municipal Sewer District (MSD) incinerator.

#### ATMOSPHERIC DISPERSION MODEL APPLICATION

Using meteorological data and incinerator design, operation, and emission release data (Table 8), the ISC computer model was run to estimate downwind concentrations at 176 receptors (16 directions and 11 distances). Each receptor point was defined by the intersection of one of eleven rings of various diameters centered around the incinerator and one of sixteen radial lines emanating from the complex center (Figure 3). Each radial was separated by 22.5° intervals beginning with due north (0°) and proceeding clockwise. The eleven ring diameters were 0.2, 0.3, 0.5, 0.7, 1.0, 2.0, 3.0, 5.0, 7.0, 10.0, and 15.0 km. These distances were chosen to span the greater Cincinnati metropolitan area.

Elevations of each receptor point were taken from topographic maps. Due to code limitations, at receptor locations where the elevation exceeded the stack height, the stack height elevation less 30.5 cm (1 ft) was used. Such treatment may be simplistic (as is the complex terrain calculation algorithm of ISC) but is more likely to overestimate actual concentrations than flat land assumptions; hence the elevated receptor assumption is conservative. For example, concentration estimates at 3.0 km are up to a factor of 2 higher for elevated receptors versus flat land receptors.

Table 7  
POPULATION DISTRIBUTION BY SEGMENT

| DIRECTION,<br>DEGREES<br>FROM NORTH | LOCATION OF SEGMENT CENTROID:<br>DISTANCE FROM ORIGIN, MILES |        |        |        |        |        |        |         |          |          |
|-------------------------------------|--------------------------------------------------------------|--------|--------|--------|--------|--------|--------|---------|----------|----------|
|                                     | 250.00                                                       | 300.00 | 400.00 | 500.00 | 600.00 | 750.00 | 850.00 | 1000.00 | 12500.00 | 15000.00 |
| 11.25                               | 11                                                           | 19     | 19     | 0      | 16     | 22     | 50     | 6804    | 7783     | 13304    |
| 33.75                               | 0                                                            | 0      | 0      | 0      | 10     | 27     | 37     | 1004    | 1643     | 14516    |
| 56.25                               | 0                                                            | 0      | 0      | 0      | 0      | 13     | 13     | 1003    | 1643     | 26218    |
| 78.75                               | 0                                                            | 0      | 0      | 0      | 0      | 4036   | 1372   | 1093    | 2520     | 21333    |
| 101.25                              | 0                                                            | 0      | 0      | 0      | 0      | 4262   | 7055   | 4030    | 12330    | 19421    |
| 123.75                              | 0                                                            | 0      | 0      | 0      | 0      | 2679   | 2512   | 4030    | 12330    | 19421    |
| 146.25                              | 0                                                            | 0      | 0      | 0      | 0      | 579    | 1178   | 10762   | 10687    | 8565     |
| 168.75                              | 0                                                            | 0      | 0      | 0      | 17     | 510    | 1494   | 754     | 1201     | 10436    |
| 191.25                              | 0                                                            | 0      | 27     | 25     | 00     | 310    | 2121   | 3225    | 2002     | 2531     |
| 213.75                              | 0                                                            | 0      | 51     | 51     | 91     | 3045   | 2236   | 244     | 2011     | 16304    |
| 236.25                              | 13                                                           | 51     | 70     | 70     | 13     | 3777   | 3010   | 7095    | 4293     | 14450    |
| 258.75                              | 11                                                           | 76     | 76     | 76     | 143    | 5675   | 4936   | 4505    | 7293     | 3492     |
| 281.25                              | 22                                                           | 35     | 52     | 52     | 44     | 1727   | 5200   | 6505    | 9939     | 3517     |
| 303.75                              | 21                                                           | 35     | 35     | 35     | 65     | 1260   | 2082   | 7726    | 10491    | 11504    |
| 326.25                              | 21                                                           | 32     | 32     | 32     | 00     | 1371   | 2506   | 6754    | 6809     | 14183    |
| 348.75                              | 21                                                           | 32     | 32     | 32     | 00     | 1125   | 2670   | 6754    | 6947     | 12097    |

Table 8  
Summary of Source Values

| Source Name                                   | Representation | Component Number | Size (m <sup>2</sup> )    | Coordinates of center (m) | Release height (m)      |                     |
|-----------------------------------------------|----------------|------------------|---------------------------|---------------------------|-------------------------|---------------------|
| Stack                                         | 1 stack        | 1                | 3.4 <sup>a</sup>          | 35.0, 0.0                 | 27.4                    |                     |
| Structure                                     | 2 area sources | 1                | 62.8                      | 26.5, 4.0                 | 20.1                    |                     |
|                                               |                | 2                | 62.8                      | 18.5, 4.0                 | 20.1                    |                     |
| Tank Farm                                     | 3 area sources | 1                | 455.2                     | -33.6, 9.5                | 6.1                     |                     |
|                                               |                | 2                | 455.2                     | -54.9, 9.5                | 6.1                     |                     |
|                                               |                | 3                | 455.2                     | -76.3, 9.5                | 6.1                     |                     |
| Pollutant Emission Rates (g/s) <sup>b,c</sup> |                |                  |                           |                           |                         |                     |
| Source Name                                   | Representation | Component Number | Uncontrolled <sup>d</sup> |                           | Controlled <sup>c</sup> |                     |
|                                               |                |                  | crude Hc <sup>f</sup>     | #2 oil <sup>g</sup>       | crude Hc <sup>f</sup>   | #2 oil <sup>j</sup> |
| Stack                                         | 1 stack        | 1                | .00639                    | .00397                    | .00639                  | .00397              |
| Structure                                     | 1 stack        | 1                | .0239                     | .0148                     | .00239                  | .00148              |
|                                               |                | 2                | .0239                     | .0148                     | .00239                  | .00148              |
| Tank Farm                                     | 3 area sources | 1                | .0524                     | .00413                    | .00524                  | .000413             |
|                                               |                | 2                | .0524                     | .00413                    | .00524                  | .000413             |
|                                               |                | 3                | .0524                     | .00413                    | .00524                  | .000413             |
| Total                                         |                |                  | .211                      | .0460                     | .0269                   | .00817              |

<sup>a</sup>Stack diameter 2.08m, release velocity 6.4 m/s, gas temperature 366.5 K.

<sup>b</sup>Stack emission rates calculated from source term methodology, assuming 99.9% control.

<sup>c</sup>Fugitive emission rate calculated from waste and fuel oil assumptions.

<sup>d</sup>Uncontrolled fugitive emission releases assumed.

<sup>e</sup>90% controlled fugitive emission releases assumed.

<sup>f</sup>Vapors from crude, sludge oil.

<sup>g</sup>Vapors from #2 fuel oil.

Another employed feature of ISC is the ability to estimate the effects of building-wake/stack-downwash phenomena on dispersion calculations using the overall dimensions of the incineration facility as input. The code estimates much higher concentrations (up to 300 times higher) at locations close to the incinerator but calculates little or no effect at distances of 2.0 km or more. Unfortunately, ISC performs these atmospheric concentration estimates assuming wake/downwash effects occur for all wind directions. This assumption introduces a conservative bias to the concentration estimates that is difficult to quantify. Nevertheless, we feel it is more prudent to include these effects on ground level concentration as estimated by ISC than to ignore them.

Downwind concentration estimates at 176 receptors were calculated for hydrocarbon (HC) vapor releases from the hazardous waste (crude, sludge oil) and the fuel oil (#2). An eleven by sixteen array of concentrations was calculated for each of three sources. The three sources were stack emissions, fugitive emissions from the incinerator structure, and fugitive emissions from the tank farm area. Two conditions were modeled: (1) uncontrolled fugitive and 99.99% controlled stack emissions; and (2) 90% controlled fugitive and 99.99% controlled stack emissions.

#### POPULATION EXPOSURE COMPUTATION

To calculate source contributions to receptor concentrations and population exposure, a separate computer program was written. Input for this program were the ISC computed eleven by sixteen concentration



arrays and the ten by sixteen arrays of population. By interpolation to the sector segment geographic centroids, the eleven by sixteen concentration arrays were converted to ten by sixteen arrays. These arrays were then matched to the population arrays to calculate various exposure results.

## RESULTS

### Hydrocarbon Vapor Air Concentrations

As described above, the ISC computer code was used to calculate ground level annual average air concentrations of HC vapor at sixteen directions and eleven distances downwind from the source. Concentrations were calculated for stack emissions, fugitive releases from the incinerator structure and the tank farm, and the sum of all emissions from all three sources. The ISC-estimated concentrations were then converted to sector-average or geographic centroid concentrations for releases from each source and the total. These centroid concentrations for all sources are detailed in Tables 9 - 12. Tables 9 and 10 contain HC crude vapor concentration estimates for uncontrolled and controlled fugitive emission conditions. Tables 11 and 12 contain HC #2 oil vapor concentration estimates for the same conditions. Comparison of maximum centroid concentrations shows that uncontrolled values are higher than controlled and that HC crude vapor values are higher than HC #2 oil vapor values. The maximum concentration occurred at the nearest centroid (250 m downwind), ranging, for example, from

Table 9

| ANNUAL AVERAGE GROUND LEVEL AIR CONCENTRATIONS (MICROGRAMS PER CUBIC METER) AT SEGMENT CENTRIDS,<br>CRUDE EMISSIONS FROM ALL SOURCES AT CINCINNATI MSD LOCATION, UNCONTROLLED AIR |          |          |          |          |          |          |          |          |          |
|-----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|----------|----------|----------|----------|----------|----------|----------|----------|----------|
| LOCATION OF SEGMENT CENTRIDS                                                                                                                                                      |          |          |          |          |          |          |          |          |          |
| DIRECTION,<br>DEGREES<br>FROM NORTH                                                                                                                                               | 250.00   | 400.00   | 600.00   | 850.00   | 1500.00  | 2500.00  | 4000.00  | 6000.00  | 12500.00 |
| 11.75                                                                                                                                                                             | 2.86E-01 | 4.04E-01 | 4.42E-01 | 5.79E-01 | 2.43E-01 | 1.38E-01 | 4.61E-02 | 3.67E-02 | 2.20E-02 |
| 33.75                                                                                                                                                                             | 2.08E-01 | 1.25E-01 | 7.92E-01 | 7.59E-01 | 1.12E-01 | 1.83E-02 | 4.01E-02 | 3.67E-02 | 2.20E-02 |
| 56.75                                                                                                                                                                             | 5.66E-01 | 9.12E-01 | 5.94E-01 | 3.45E-01 | 3.71E-01 | 5.71E-02 | 2.27E-02 | 1.70E-02 | 1.26E-02 |
| 78.75                                                                                                                                                                             | 9.06E-01 | 1.12E-01 | 6.94E-01 | 4.37E-01 | 1.37E-01 | 4.21E-02 | 3.37E-02 | 2.20E-02 | 1.26E-02 |
| 101.75                                                                                                                                                                            | 8.45E-01 | 1.11E-01 | 6.94E-01 | 4.37E-01 | 1.37E-01 | 4.21E-02 | 3.37E-02 | 2.20E-02 | 1.26E-02 |
| 123.75                                                                                                                                                                            | 1.45E-01 | 1.11E-01 | 5.50E-01 | 3.45E-01 | 3.64E-01 | 6.49E-02 | 3.37E-02 | 1.93E-02 | 1.26E-02 |
| 146.75                                                                                                                                                                            | 1.50E-01 | 1.11E-01 | 5.50E-01 | 3.45E-01 | 3.64E-01 | 6.49E-02 | 3.37E-02 | 1.93E-02 | 1.26E-02 |
| 168.75                                                                                                                                                                            | 2.10E-01 | 1.11E-01 | 6.66E-01 | 4.19E-01 | 1.72E-01 | 4.13E-02 | 3.37E-02 | 1.93E-02 | 1.26E-02 |
| 191.75                                                                                                                                                                            | 1.10E-01 | 1.25E-01 | 6.66E-01 | 4.19E-01 | 1.72E-01 | 4.13E-02 | 3.37E-02 | 1.93E-02 | 1.26E-02 |
| 213.75                                                                                                                                                                            | 1.31E-01 | 1.11E-01 | 5.50E-01 | 3.45E-01 | 3.64E-01 | 6.49E-02 | 3.37E-02 | 1.93E-02 | 1.26E-02 |
| 236.75                                                                                                                                                                            | 9.70E-01 | 5.17E-01 | 2.76E-01 | 1.70E-01 | 1.11E-01 | 4.61E-02 | 3.37E-02 | 1.93E-02 | 1.26E-02 |
| 258.75                                                                                                                                                                            | 4.45E-01 | 3.94E-01 | 2.76E-01 | 1.70E-01 | 1.11E-01 | 4.61E-02 | 3.37E-02 | 1.93E-02 | 1.26E-02 |
| 281.75                                                                                                                                                                            | 4.45E-01 | 3.94E-01 | 2.76E-01 | 1.70E-01 | 1.11E-01 | 4.61E-02 | 3.37E-02 | 1.93E-02 | 1.26E-02 |
| 304.75                                                                                                                                                                            | 1.10E-01 | 5.53E-01 | 4.47E-01 | 4.02E-01 | 3.64E-01 | 1.22E-01 | 6.49E-02 | 5.31E-02 | 3.15E-02 |
| 326.75                                                                                                                                                                            | 1.10E-01 | 9.45E-01 | 5.67E-01 | 5.20E-01 | 3.64E-01 | 1.22E-01 | 6.49E-02 | 5.31E-02 | 3.15E-02 |

Table 10

| ANNUAL AVERAGE GROUND LEVEL AIR CONCENTRATIONS (MICROGRAMS PER CUBIC METER) AT SEGMENT CENTRIDS,<br>CRUDE EMISSIONS FROM ALL SOURCES AT CINCINNATI MSD LOCATION, CONTROLLED AIR |          |          |          |          |          |          |          |          |          |
|---------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|----------|----------|----------|----------|----------|----------|----------|----------|----------|
| LOCATION OF SEGMENT CENTRIDS                                                                                                                                                    |          |          |          |          |          |          |          |          |          |
| DIRECTION,<br>DEGREES<br>FROM NORTH                                                                                                                                             | 250.00   | 400.00   | 600.00   | 850.00   | 1500.00  | 2500.00  | 4000.00  | 6000.00  | 12500.00 |
| 11.75                                                                                                                                                                           | 2.15E-01 | 1.35E-01 | 4.04E-01 | 4.29E-01 | 1.11E-02 | 1.42E-02 | 4.91E-03 | 4.70E-03 | 2.91E-03 |
| 33.75                                                                                                                                                                           | 1.66E-01 | 1.16E-01 | 3.64E-01 | 3.64E-01 | 1.44E-02 | 6.82E-03 | 1.67E-03 | 1.00E-03 | 6.71E-04 |
| 56.75                                                                                                                                                                           | 9.44E-01 | 1.15E-01 | 4.62E-01 | 4.62E-01 | 1.93E-02 | 6.82E-03 | 1.67E-03 | 1.00E-03 | 6.71E-04 |
| 78.75                                                                                                                                                                           | 1.44E-01 | 1.15E-01 | 4.62E-01 | 4.62E-01 | 1.93E-02 | 6.82E-03 | 1.67E-03 | 1.00E-03 | 6.71E-04 |
| 101.75                                                                                                                                                                          | 1.54E-01 | 1.15E-01 | 4.62E-01 | 4.62E-01 | 1.93E-02 | 6.82E-03 | 1.67E-03 | 1.00E-03 | 6.71E-04 |
| 123.75                                                                                                                                                                          | 1.44E-01 | 1.15E-01 | 4.62E-01 | 4.62E-01 | 1.93E-02 | 6.82E-03 | 1.67E-03 | 1.00E-03 | 6.71E-04 |
| 146.75                                                                                                                                                                          | 1.44E-01 | 1.15E-01 | 4.62E-01 | 4.62E-01 | 1.93E-02 | 6.82E-03 | 1.67E-03 | 1.00E-03 | 6.71E-04 |
| 168.75                                                                                                                                                                          | 1.44E-01 | 1.15E-01 | 4.62E-01 | 4.62E-01 | 1.93E-02 | 6.82E-03 | 1.67E-03 | 1.00E-03 | 6.71E-04 |
| 191.75                                                                                                                                                                          | 1.44E-01 | 1.15E-01 | 4.62E-01 | 4.62E-01 | 1.93E-02 | 6.82E-03 | 1.67E-03 | 1.00E-03 | 6.71E-04 |
| 213.75                                                                                                                                                                          | 1.44E-01 | 1.15E-01 | 4.62E-01 | 4.62E-01 | 1.93E-02 | 6.82E-03 | 1.67E-03 | 1.00E-03 | 6.71E-04 |
| 236.75                                                                                                                                                                          | 1.44E-01 | 1.15E-01 | 4.62E-01 | 4.62E-01 | 1.93E-02 | 6.82E-03 | 1.67E-03 | 1.00E-03 | 6.71E-04 |
| 258.75                                                                                                                                                                          | 1.44E-01 | 1.15E-01 | 4.62E-01 | 4.62E-01 | 1.93E-02 | 6.82E-03 | 1.67E-03 | 1.00E-03 | 6.71E-04 |
| 281.75                                                                                                                                                                          | 1.44E-01 | 1.15E-01 | 4.62E-01 | 4.62E-01 | 1.93E-02 | 6.82E-03 | 1.67E-03 | 1.00E-03 | 6.71E-04 |
| 304.75                                                                                                                                                                          | 1.44E-01 | 1.15E-01 | 4.62E-01 | 4.62E-01 | 1.93E-02 | 6.82E-03 | 1.67E-03 | 1.00E-03 | 6.71E-04 |
| 326.75                                                                                                                                                                          | 1.44E-01 | 1.15E-01 | 4.62E-01 | 4.62E-01 | 1.93E-02 | 6.82E-03 | 1.67E-03 | 1.00E-03 | 6.71E-04 |



2.86  $\mu\text{g}/\text{m}^3$  at 11.25 to 0.842  $\mu\text{g}/\text{m}^3$  at 281.25 for the "uncontrolled crude" model run (Table 9). Each table also shows that the downwind concentrations decrease rapidly with distance to less than 2% of the maximum at the 12.5 km centroid distance.

It is not surprising that the crude vapor concentration would be higher than the #2 oil vapor concentration because its emission value is much larger (Table 8). What is interesting from these tables is that the controlled fugitive emission air concentrations are uniformly about a factor of 10 less than the uncontrolled values, meaning that the constant stack emissions do not contribute significantly to downwind HC vapor concentrations and that fugitive emissions are the dominant source. An analysis of the fraction contribution to air concentrations at 250 m and 12.5 km for the "uncontrolled crude" model run, Table 13, shows this behavior. At 250 m, fugitive emissions from the tank farm dominate air concentrations for most directions while stack emissions are 1% or less. At 12.5 km, structure fugitive emissions contribute 20%, the tank farm contributes 77%, and the stack contributes only slightly more than 2%. Other conditions and modeling runs show similar dominance by fugitive emissions. Thus, for the sets of conditions studied, most downwind HC vapor air concentrations are due to fugitive emissions.

#### POPULATION EXPOSURES TO HYDROCARBON VAPOR

Population exposures to uncontrolled and controlled crude oil and #2 oil vapors are summarized in Tables 14-17. As expected, total population exposure decreases with fugitive emission control from 2.46 x

Table 13  
Fractional Contribution of Each Source to the Average  
Ground Level Air Concentration of Uncontrolled Crude Oil

| Centroid<br>Distance,<br>Meters<br>From Origin  | 250    |           |           | 12500  |           |           |
|-------------------------------------------------|--------|-----------|-----------|--------|-----------|-----------|
| CENTROID<br>DIRECTION,<br>DEGREES<br>FROM NORTH | STACK  | STRUCTURE | TANK FARM | STACK  | STRUCTURE | TANK FARM |
| 11.25                                           | 0.0042 | 0.0099    | 0.9259    | 0.0226 | 0.2041    | 0.7733    |
| 33.75                                           | 0.0042 | 0.0431    | 0.9527    | 0.0228 | 0.2052    | 0.7720    |
| 56.25                                           | 0.0034 | 0.0379    | 0.9586    | 0.0223 | 0.2048    | 0.7729    |
| 78.75                                           | 0.0033 | 0.0339    | 0.9628    | 0.0224 | 0.2045    | 0.7731    |
| 101.25                                          | 0.0033 | 0.0329    | 0.9638    | 0.0225 | 0.2044    | 0.7731    |
| 123.75                                          | 0.0029 | 0.0299    | 0.9672    | 0.0223 | 0.2042    | 0.7735    |
| 146.25                                          | 0.0031 | 0.0363    | 0.9606    | 0.0223 | 0.2052    | 0.7725    |
| 168.75                                          | 0.0025 | 0.0325    | 0.9649    | 0.0221 | 0.2047    | 0.7732    |
| 191.25                                          | 0.0013 | 0.0266    | 0.9716    | 0.0217 | 0.2034    | 0.7749    |
| 213.75                                          | 0.0014 | 0.0223    | 0.9763    | 0.0210 | 0.2019    | 0.7763    |
| 236.25                                          | 0.0029 | 0.0769    | 0.9202    | 0.0218 | 0.2029    | 0.7751    |
| 258.75                                          | 0.0087 | 0.3431    | 0.6462    | 0.0218 | 0.2033    | 0.7749    |
| 281.25                                          | 0.0116 | 0.5424    | 0.4460    | 0.0217 | 0.2026    | 0.7757    |
| 303.75                                          | 0.0120 | 0.6000    | 0.3823    | 0.0216 | 0.2022    | 0.7763    |
| 326.25                                          | 0.0153 | 0.6545    | 0.3303    | 0.0217 | 0.2029    | 0.7754    |
| 348.75                                          | 0.0078 | 0.2458    | 0.7464    | 0.0221 | 0.2034    | 0.7745    |

Table 14

| SUMMARY OF EXPOSURES TO 877641. PERSONS TO CRUDE<br>AT CINCINNATI MSD INCINER.: UNCONTROLLED OIL |                                                              |                                                               |
|--------------------------------------------------------------------------------------------------|--------------------------------------------------------------|---------------------------------------------------------------|
| SOURCE                                                                                           | COLLECTIVE EXPOSURE,<br>PERSON-MICROGRAMS<br>PER CUBIC METER | AVERAGE INDIVIDUAL<br>EXPOSURE, MICROGRAMS<br>PER CUBIC METER |
| STACK                                                                                            | 4.07E-02                                                     | 4.64E-04                                                      |
| STRUCTURE                                                                                        | 5.21E-03                                                     | 5.93E-03                                                      |
| TANK FARM                                                                                        | 1.90E-04                                                     | 2.15E-02                                                      |
| ALL SOURCES                                                                                      | 2.46E-04                                                     | 2.80E-02                                                      |

Table 15

| SUMMARY OF EXPOSURES TO 877641. PERSONS TO CRUDE<br>AT CINCINNATI MSD INCINER.: CONTROLLED OIL |                                                              |                                                               |
|------------------------------------------------------------------------------------------------|--------------------------------------------------------------|---------------------------------------------------------------|
| SOURCE                                                                                         | COLLECTIVE EXPOSURE,<br>PERSON-MICROGRAMS<br>PER CUBIC METER | AVERAGE INDIVIDUAL<br>EXPOSURE, MICROGRAMS<br>PER CUBIC METER |
| STACK                                                                                          | 4.07E-02                                                     | 4.64E-04                                                      |
| STRUCTURE                                                                                      | 5.21E-02                                                     | 5.93E-04                                                      |
| TANK FARM                                                                                      | 1.90E-03                                                     | 2.15E-03                                                      |
| ALL SOURCES                                                                                    | 2.82E-04                                                     | 3.22E-03                                                      |

Table 16

SUMMARY OF EXPOSURES TO 47501, PERSONS TO #2 OIL  
AT CINCINNATI MSD DETERMINED: CONTROLLED OIL

| SOURCE      | COLLECTIVE EXPOSURE,<br>PERSON-MICROGRAMS<br>PER CUBIC METER | AVERAGE INDIVIDUAL<br>EXPOSURE, MICROGRAMS<br>PER CUBIC METER |
|-------------|--------------------------------------------------------------|---------------------------------------------------------------|
| STACK       | 2.53E-02                                                     | 2.44E-04                                                      |
| STRUCTURE   | 3.22E-03                                                     | 3.57E-05                                                      |
| TANK FARM   | 1.40E-03                                                     | 1.70E-05                                                      |
| ALL SOURCES | 4.97E-03                                                     | 5.66E-05                                                      |

Table 17

SUMMARY OF EXPOSURES TO 47501, PERSONS TO #2 OIL  
AT CINCINNATI MSD DETERMINED: CONTROLLED OIL

| SOURCE      | COLLECTIVE EXPOSURE,<br>PERSON-MICROGRAMS<br>PER CUBIC METER | AVERAGE INDIVIDUAL<br>EXPOSURE, MICROGRAMS<br>PER CUBIC METER |
|-------------|--------------------------------------------------------------|---------------------------------------------------------------|
| STACK       | 2.53E-02                                                     | 2.44E-04                                                      |
| STRUCTURE   | 3.22E-02                                                     | 3.57E-04                                                      |
| TANK FARM   | 1.40E-02                                                     | 1.70E-04                                                      |
| ALL SOURCES | 7.25E-02                                                     | 8.25E-04                                                      |

$10^4$  to  $2.82 \times 10^3$  person- $\mu\text{g}/\text{m}^3$  for crude oil vapor and from  $4.97 \times 10^3$  to  $7.25 \times 10^2$  person- $\mu\text{g}/\text{m}^3$  for #2 oil vapor. The percentage decrease in response to 90% fugitive control is 80% for crude oil vapor and 85% for #2 oil vapor. Such near-linear population exposure decreases with control highlight the importance of fugitive emission control.

Tables 18 through 21 summarize population exposure by concentration level for the two HC vapors and conditions studied. These tables contain a wealth of information concerning the total population exposure at the Cincinnati site. For example, these data can be applied to either a threshold or non-threshold health effects model to predict health effects associated with the predicted population exposure. Both exposure and the population associated with each concentration level can be studied. Estimates concerning the health benefit from control of fugitive emissions can be calculated by comparing the controlled and uncontrolled values. These results show that public exposure to HC vapors from this incinerator is low in either case, with all locations receiving concentrations more than two orders of magnitude less than the National Ambient Air Quality Standard for HC. Nevertheless, should carcinogens be present in the HC vapors, the predicted population exposure decrease due to HC fugitive emission control may produce meaningful public health benefits through a reduction in cancer incidence.



Table 18

| SUMMARY OF EXPOSURES TO GROUND-LEVEL AIR CONCENTRATION LEVELS OF GROSS EMISSIONS FROM ALL SOURCES AT CINCINNATI AND IMCLER, UNCONTROLLED III |                              |            |            |            |
|----------------------------------------------------------------------------------------------------------------------------------------------|------------------------------|------------|------------|------------|
| AIR CONCENTRATION                                                                                                                            | NUMBER OF PERSONS EXPOSED TO | DESIGNATED | DESIGNATED | DESIGNATED |
| LEVEL, MINIMUM VALUE, % OF MAX. CURIC METER                                                                                                  | LEVEL                        | OR HIGHER  | LEVEL      | OR HIGHER  |
| 90-100                                                                                                                                       | 2,58E-00                     | 11         | 3.15E-01   | 3.15E-01   |
| 80-90                                                                                                                                        | 2,29E-00                     | 0          | 0.0        | 3.15E-01   |
| 70-80                                                                                                                                        | 2,00E-00                     | 21         | 4.42E-01   | 7.57E-01   |
| 60-70                                                                                                                                        | 1.72E-00                     | 0          | 0.0        | 7.57E-01   |
| 50-60                                                                                                                                        | 1.43E-00                     | 19         | 2.74E-01   | 1.03E-02   |
| 40-50                                                                                                                                        | 1.15E-00                     | 49         | 6.11E-01   | 1.64E-02   |
| 30-40                                                                                                                                        | 8.54E-01                     | 122        | 1.16E-02   | 2.80E-02   |
| 20-30                                                                                                                                        | 5.73E-01                     | 210        | 1.50E-02   | 4.30E-02   |
| 10-20                                                                                                                                        | 2.86E-01                     | 1603       | 9.64E-02   | 1.09E-03   |
| 0-10                                                                                                                                         | 0.0                          | 875606     | 2.35E-04   | 2.40E-04   |

Table 19

| SUMMARY OF EXPOSURES TO GROUND-LEVEL AIR CONCENTRATION LEVELS OF GROSS EMISSIONS FROM ALL SOURCES AT CINCINNATI AND IMCLER, UNCONTROLLED III |                              |            |            |            |
|----------------------------------------------------------------------------------------------------------------------------------------------|------------------------------|------------|------------|------------|
| AIR CONCENTRATION                                                                                                                            | NUMBER OF PERSONS EXPOSED TO | DESIGNATED | DESIGNATED | DESIGNATED |
| LEVEL, MINIMUM VALUE, % OF MAX. CURIC METER                                                                                                  | LEVEL                        | OR HIGHER  | LEVEL      | OR HIGHER  |
| 90-100                                                                                                                                       | 2.67E-01                     | 11         | 3.27E-00   | 3.27E-00   |
| 80-90                                                                                                                                        | 2.34E-01                     | 0          | 0.0        | 3.27E-00   |
| 70-80                                                                                                                                        | 2.04E-01                     | 21         | 4.73E-00   | 8.00E-00   |
| 60-70                                                                                                                                        | 1.78E-01                     | 0          | 0.0        | 8.00E-00   |
| 50-60                                                                                                                                        | 1.49E-01                     | 19         | 2.93E-00   | 1.00E-01   |
| 40-50                                                                                                                                        | 1.19E-01                     | 49         | 6.27E-00   | 1.72E-01   |
| 30-40                                                                                                                                        | 8.91E-02                     | 155        | 1.56E-01   | 3.20E-01   |
| 20-30                                                                                                                                        | 5.94E-02                     | 273        | 1.92E-01   | 5.20E-01   |
| 10-20                                                                                                                                        | 2.97E-02                     | 3622       | 1.31E-02   | 1.83E-02   |
| 0-10                                                                                                                                         | 0.0                          | 873452     | 2.60E-03   | 2.60E-03   |

Table 20

| SUMMARY OF EXPOSURES TO GROUND-LEVEL AIR CONCENTRATION LEVELS OF $\text{H}_2$ DII<br>EMITTED FROM ALL SOURCES AT CLEVELAND, OHIO, INCLUDING UNLIMITED OIL |                                                     |                                                              |                                                             |                                  |
|-----------------------------------------------------------------------------------------------------------------------------------------------------------|-----------------------------------------------------|--------------------------------------------------------------|-------------------------------------------------------------|----------------------------------|
| AIR CONCENTRATION<br>LEVEL, $\text{H}_2$ DII<br>% OF<br>MAX.                                                                                              | NUMBER OF PERSONS EXPOSED TO<br>DESIGNATED<br>LEVEL | EXPOSURE (PERSON-<br>CUBIC METERS) TO<br>DESIGNATED<br>LEVEL | EXPOSURE (PERSON-<br>CUBIC METERS) TO<br>OR HIGHER<br>LEVEL | DESIGNATED<br>OR HIGHER<br>LEVEL |
| 90-100                                                                                                                                                    | 43                                                  | 1.95E 01                                                     | 1.95E 01                                                    | 1.95E 01                         |
| 80-90                                                                                                                                                     | 0                                                   | 0.0                                                          | 0.0                                                         | 1.95E 01                         |
| 70-80                                                                                                                                                     | 43                                                  | 1.40E 01                                                     | 1.40E 01                                                    | 3.44E 01                         |
| 60-70                                                                                                                                                     | 41                                                  | 1.55E 01                                                     | 1.55E 01                                                    | 4.09E 01                         |
| 50-60                                                                                                                                                     | 13                                                  | 3.39E 00                                                     | 3.39E 00                                                    | 5.33E 01                         |
| 40-50                                                                                                                                                     | 95                                                  | 1.67E 01                                                     | 1.67E 01                                                    | 7.20E 01                         |
| 30-40                                                                                                                                                     | 351                                                 | 5.15E 01                                                     | 5.15E 01                                                    | 1.23E 02                         |
| 20-30                                                                                                                                                     | 875                                                 | 2.11E 01                                                     | 2.11E 01                                                    | 2.15E 02                         |
| 10-20                                                                                                                                                     | 3563                                                | 2.08E 02                                                     | 2.08E 02                                                    | 4.22E 02                         |
| 0-10                                                                                                                                                      | 872626                                              | 4.55E 03                                                     | 4.55E 03                                                    | 4.97E 03                         |

Table 21

| SUMMARY OF EXPOSURES TO GROUND-LEVEL AIR CONCENTRATION LEVELS OF $\text{H}_2$ DII<br>EMITTED FROM ALL SOURCES AT CLEVELAND, OHIO, INCLUDING UNLIMITED OIL |                                                     |                                                              |                                                             |                                  |
|-----------------------------------------------------------------------------------------------------------------------------------------------------------|-----------------------------------------------------|--------------------------------------------------------------|-------------------------------------------------------------|----------------------------------|
| AIR CONCENTRATION<br>LEVEL, $\text{H}_2$ DII<br>% OF<br>MAX.                                                                                              | NUMBER OF PERSONS EXPOSED TO<br>DESIGNATED<br>LEVEL | EXPOSURE (PERSON-<br>CUBIC METERS) TO<br>DESIGNATED<br>LEVEL | EXPOSURE (PERSON-<br>CUBIC METERS) TO<br>OR HIGHER<br>LEVEL | DESIGNATED<br>OR HIGHER<br>LEVEL |
| 90-100                                                                                                                                                    | 43                                                  | 2.34E 00                                                     | 2.34E 00                                                    | 2.34E 00                         |
| 80-90                                                                                                                                                     | 0                                                   | 0.0                                                          | 0.0                                                         | 2.34E 00                         |
| 70-80                                                                                                                                                     | 43                                                  | 2.60E 00                                                     | 2.60E 00                                                    | 4.95E 00                         |
| 60-70                                                                                                                                                     | 65                                                  | 1.07E 00                                                     | 1.07E 00                                                    | 6.00E 00                         |
| 50-60                                                                                                                                                     | 30                                                  | 1.38E 00                                                     | 1.38E 00                                                    | 7.34E 00                         |
| 40-50                                                                                                                                                     | 48                                                  | 1.42E 00                                                     | 1.42E 00                                                    | 8.80E 00                         |
| 30-40                                                                                                                                                     | 331                                                 | 6.47E 00                                                     | 6.47E 00                                                    | 1.55E 01                         |
| 20-30                                                                                                                                                     | 875                                                 | 1.14E 01                                                     | 1.14E 01                                                    | 2.07E 01                         |
| 10-20                                                                                                                                                     | 3526                                                | 3.63E 01                                                     | 3.63E 01                                                    | 6.30E 01                         |
| 0-10                                                                                                                                                      | 870963                                              | 8.62E 02                                                     | 8.62E 02                                                    | 7.25E 02                         |

### CONCLUSIONS

Based on these emission calculations, and the assumption of 99.99% destruction efficiency in the incinerator, the most important area of an incinerator facility in regard to pollution control is the storage area. Pumps and valves are the most important equipment types, although the importance of tanks increases with incinerator capacity. Therefore, control measures in these areas would be most effective.

The desire for generic emission factors reduces the accuracy of the calculations due to the fact that detailed design is impossible and local environmental effects cannot be considered.

Population exposure to HC vapors is dominated by fugitive emission sources in both the uncontrolled and controlled uses. This implies that control requirements for an incinerator facility should consider all pollutant sources, not just the stack emission values. However, assessing the public health significance of these HC exposures is hindered by incomplete knowledge of the emission composition. A detailed analysis of the HC vapor could improve this shortcoming.

The emission assessment used source term data developed for a typical incineration facility operating a 10 MM Btu/hr rotary kiln, burning a waste which was also chosen to be typical. The validity of applying this source term data for a generic site to a specific location to draw overall conclusions concerning relative emission importance needs to be studied.

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RELAXATION OF SO<sub>2</sub> EMISSION LIMITS  
FOR THE PGDP STEAM PLANT

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ABSTRACT

Kentucky sulfur dioxide emission standards for the C-600 steam plant stacks are very stringent and necessitate the burning of very low sulfur (0.8%) coal to meet standards. Dispersion calculations of PGDP effluents indicated that SO<sub>2</sub> emissions have only a minor effect on ambient concentrations and that the plant's emissions are overregulated.

A consultant was retained to explore the problem, and it appears that relief may be obtained by seeking a State Implementation Plan revision. This would allow the emission of more SO<sub>2</sub> from the coal-fired boilers within the applicable restrictions of National Ambient Air Quality Standards and the Prevention of Significant Deterioration regulation. The potential savings to the plant by burning higher sulfur coal could exceed \$250,000 annually.

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Paducah Gaseous Diffusion Plant  
Paducah, Kentucky

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

DESIGN OF A PARTICULATE MONITORING NETWORK  
FOR THE Y-12 PLANT

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Key Words

Air Quality Monitoring, Monitor Network Design,  
Air Pollutant Dispersion, Computers

ABSTRACT

An Air Quality Monitoring Network Design (AQMND) with multiple objectives is being developed for the Y-12 Plant production facilities. The objectives are: Y-12 facility surveillance; monitoring the transport of Y-12 generated airborne effluents towards either the Oak Ridge National Laboratory or the developed region of the City of Oak Ridge; and monitoring population exposure in residential areas close to the Y-12 Plant.

A two step design process was carried out, using the Air Quality Monitor Network Design Model (AQMND) previously used for the Oak Ridge National Laboratory network. In the first step of the design we used existing air quality monitor locations, subjectively designated locations, and grid intersections as a set of potential monitor sites. The priority sites from the first step (modified to account for terrain and accessibility), and subjectively designated sites, were used as the potential monitor sites for the second step of the process which produced the final design recommendations for the monitor network.

INTRODUCTION

In order to quantify the transport and distribution of certain particulates from the Y-12 manufacturing processes and possible resultant population exposures, the Radiation Safety Group at the Y-12 Plant and the Department of Environmental Management at the Oak Ridge National Laboratory (ORNL) have collaborated in the design of a new

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

of a new particulate monitoring network around the Y-12 Plant. This paper summarizes the work to date, including initial design recommendations and discusses possible extensions of the study to further refine the monitoring network design.

The Y-12 Plant is located in Bear Creek Valley, about three kilometers from the central business and population area of Oak Ridge. It is separated from that area by Pine Ridge, with the exception of a small gap in the ridge at the north-east corner of the plant reservation. Figure 1 is a three dimensional representation of the Y-12 and Oak Ridge area showing the complex ridge and valley terrain of the region.

#### STUDY METHOD

This study was conducted using meteorological and source data provided by the Y-12 Radiation Safety Group and an Air Quality Monitor Network Design Model (AQMND) developed for the design of the ORNL particulate and SO<sub>2</sub> monitoring network. The model has been fully described elsewhere.<sup>1,2,3</sup> The model is used to define a measure of the source to potential monitor site relationship for specified sources and potential monitor sites in the study area. The model is then used to choose a subset of the potential sites which maximizes a measure of the total network's ability to monitor these sources.

A two step procedure was used in the design process. In the first step, an arbitrary grid of 441 potential monitor sites was augmented by eight sites specified by Y-12 personnel. These sites are listed in the following table and are indicated on design plots by the associated acronyms.

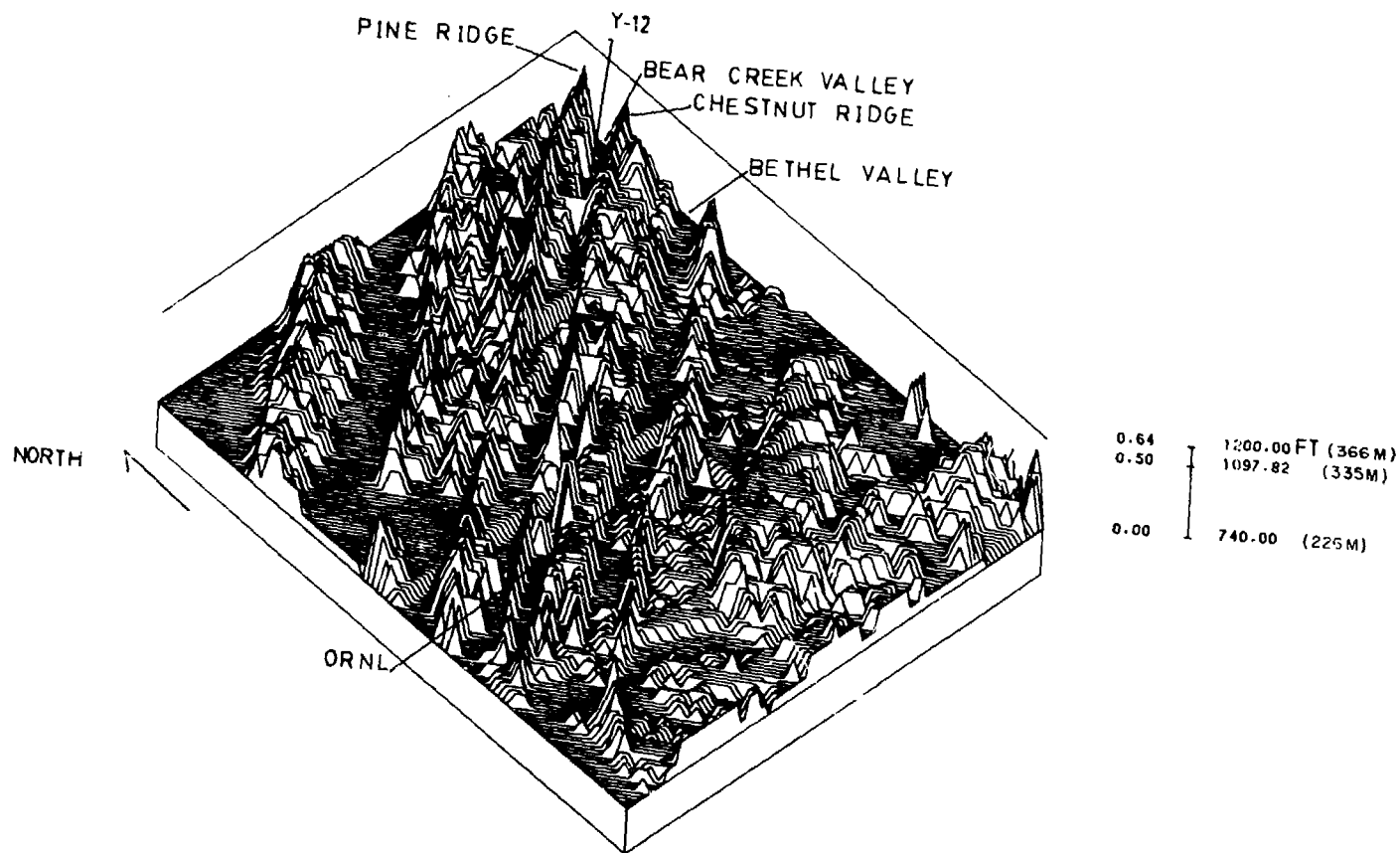


FIGURE 1. Y12 MONITOR NETWORK DESIGN, REGIONAL TERRAIN



TABLE  
Monitor Sites

| <u>Site</u>                    | <u>Acronym</u>    |
|--------------------------------|-------------------|
| Gamble Valley                  | GV                |
| Tank Farm                      | TF                |
| Water Plant                    | WP                |
| SO <sub>2</sub> Monitor - East | SO <sub>2</sub> E |
| - West                         | SO <sub>2</sub> W |
| South Patrol Road - East       | SPRE              |
| - Central                      | SPRC              |
| - West                         | SPRW              |

The Gamble Valley, Tank Farm and Water Plant sites were proposed for the purpose of monitoring transport across Pine Ridge towards the populated areas of Oak Ridge. The existing SO<sub>2</sub> monitors were proposed to monitor transport along the axis of Bear Creek Valley. The South Patrol Road monitors were proposed for the purposes of measuring Y-12 transport in the direction of ORNL and transport of ORNL material into Bear Creek Valley.

### RESULTS

The results of the initial design run, labeled in priority order, are shown in Figure 2. The locations of the two major particulate sources considered, Building 9212 and 9206, are shown by the underlined numbers 12 and 06 on the Figure. The recommended design is enumerated in Table 1. While none of the augmentation sites were chosen by the computer model, some of the chosen sites were so close to the augmentation sites that no practical difference would result from using either location. Also, reasons of security and power availability directed that several of the model's assignments be moved, usually to an augmentation site.

In the second phase of the design process, the chosen sites from the first phase computer results, the original eight augmentation sites, and other augmentation sites in suspected transport paths and in populated areas were used as input to the monitor network design model. Thirteen

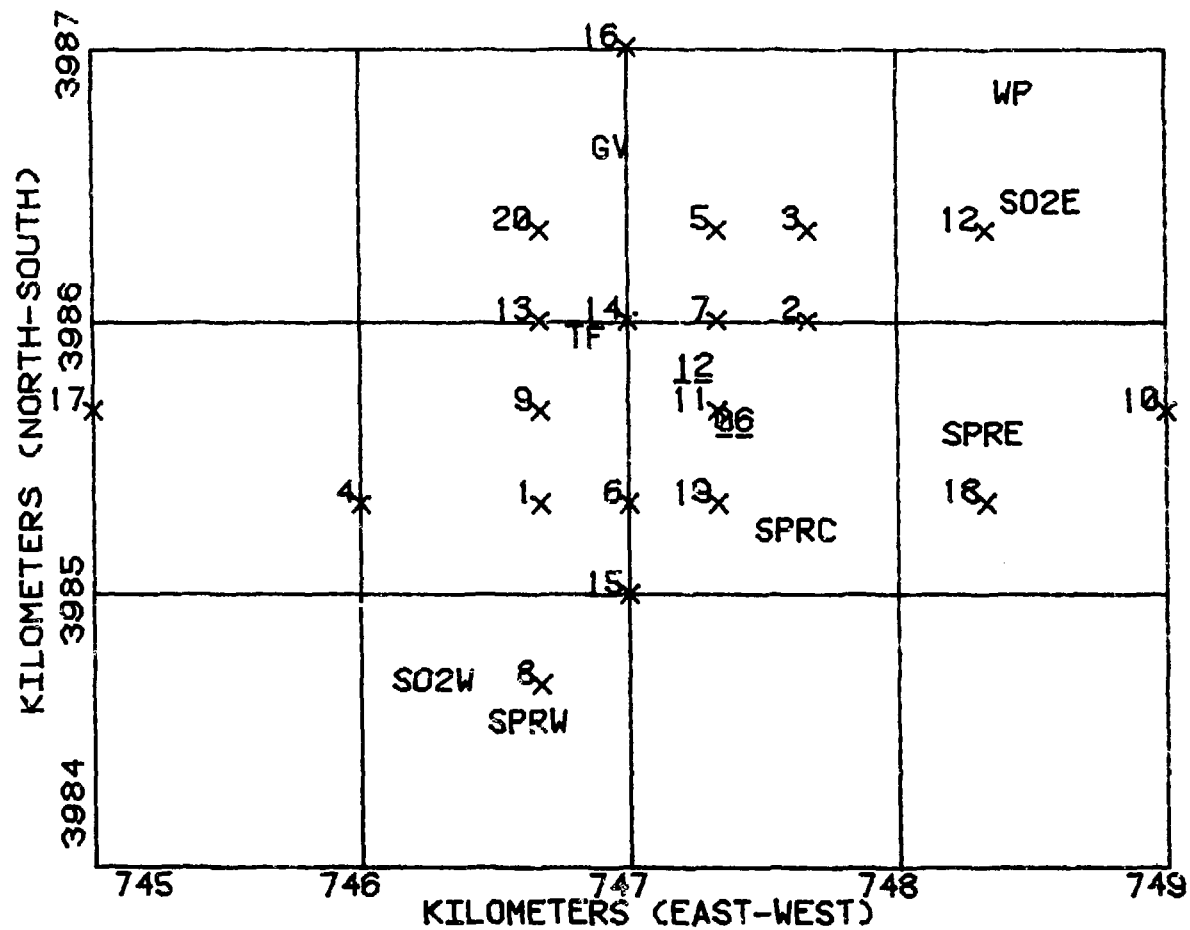


FIGURE 2. Y-12 MONITOR NETWORK DESIGN, RUN ONE.  
 TWENTY SITES, SCALE = 1:24000

sites, indicated in Figure 3, were chosen by the model. An eleven site network was recommended. Two recommendations of the model were not chosen. Computer sites 4, 5, and 12 were combined into one recommended monitor location.

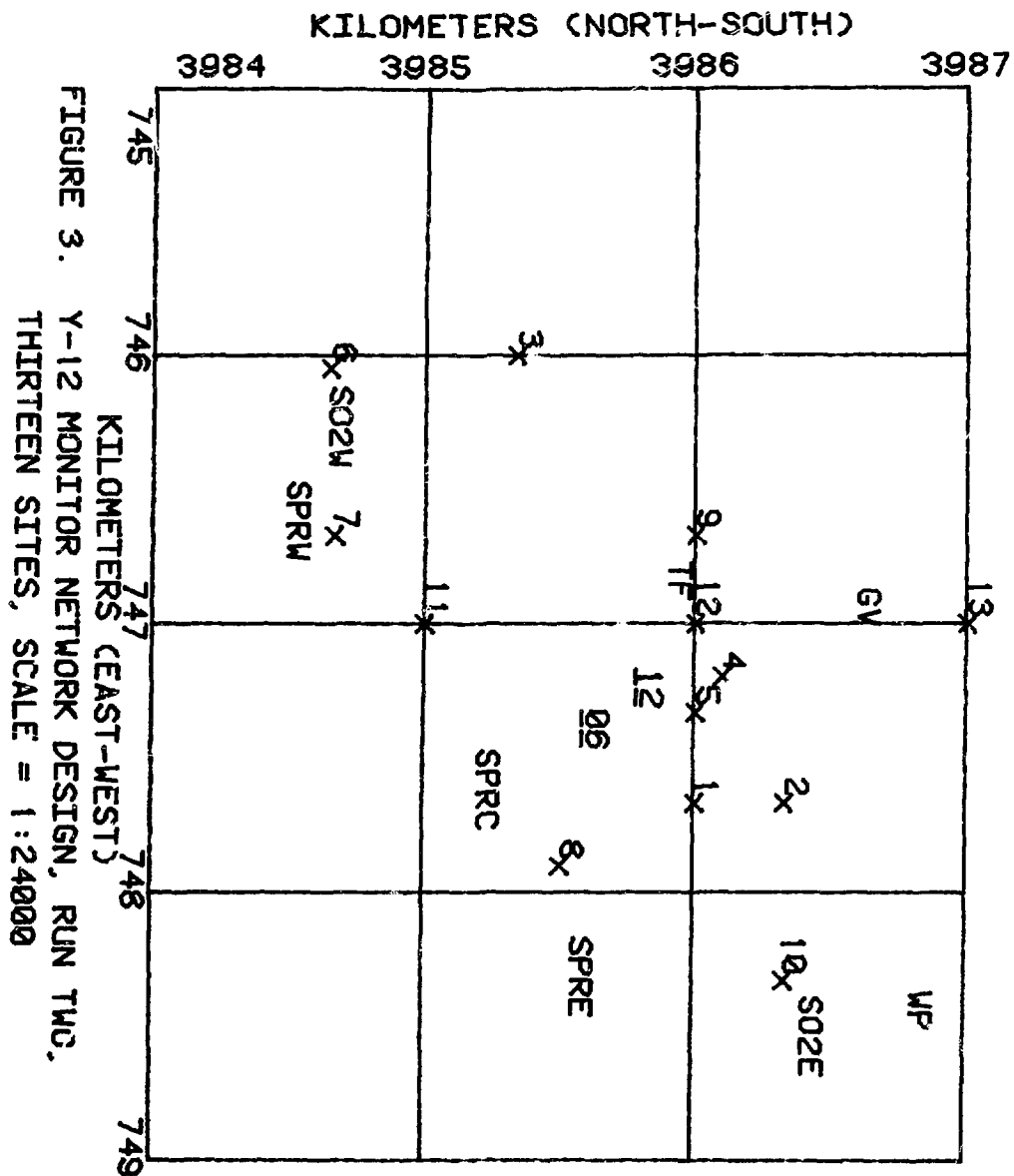
Ground reconnaissance of the potential sites has confirmed the suitability of the recommended sites and provided specific siting instructions based upon physical obstructions to air flow such as buildings, terrain and trees. Terrain features such as ridge gaps, which would channelize pollutant transport under stable inversion conditions at the ridge top, were also noted. The deletions of computer-recommended sites numbers 10, 11, and 17 of the first run for being inside the "street-canyon" of the Y-12 plant or being too distant and in the lee of a ridge were also confirmed.

### DISCUSSION

Extensions to this design effort hinge on the following question: Will the design be sufficiently improved by the time it must be implemented to make the effort worthwhile? Refinements can be made in the source data, meteorological data and in the atmospheric/diffusion model used in the network design process.

Each building, 9212 and 9206, was treated as an individual point source of equal strength with no appreciable plume rise. In fact, each building has multiple short stacks on its roof, some with the potential for plume rise due to air flow velocities. Treatment of individual stacks is possible at some increase in computer execution time.

Possible improvements in meteorological data and in diffusion model(s) used are related. The meteorological data used was a condensation of seasonal frequencies of wind speed, direction and "lapse" or "inversion" conditions into annual frequencies of stable (Pasquill "E") and unstable (Pasquill "C") categories for each wind speed and direction class. This was sufficient for the gaussian diffusion models used, but would not be satisfactory for a more sophisticated model of the type needed to simulate air flow in near calm, stable conditions of



the type that would lead to transport through the gap to the north-east of the Y-12 Plant or across Chestnut Ridge towards ORNL. Discussions with Y-12 personnel have also revealed the low frequency of fog, an indicator of stable atmospheric conditions, even when fog is present in most other valleys in the Oak Ridge area. This raises the possibility that the Y-12 Plant is creating a "Heat Island" effect, further complicating the modeling of diffusion of particulates in the region.

### CONCLUSIONS

A monitor network design has been developed for the Y-12 Plant which provides immediate guidance for the fulfillment of the monitoring requirement. Extensions to the design process to improve the design have been suggested herein. The decision of what further action to take is pending.

The two phase process with human participation is a vivid illustration of the way the computer model is intended to aid the human decision maker, not direct his actions.

TABLE 1  
Monitor Network Design Recommendations: Phase One

| <u>Site Number</u> | <u>Computer Priority</u> | <u>Comments</u>                               |
|--------------------|--------------------------|-----------------------------------------------|
| 1                  | 1                        | Inside plant boundary                         |
| 2                  | 2                        | "                                             |
| 3                  | (3, 5, 7)                | Install close to (5-7) line                   |
| 4                  | 4                        | Inside plant boundary                         |
| 5                  | 6                        | "                                             |
| 6                  | 8                        | SPRW probably equally good                    |
| 7                  | 9                        | Along Bear Creek Road                         |
| 8                  | 12                       | Effectively coincident with SO <sub>2</sub> E |
| 9                  | (13-14)                  | Effectively coincident with TF                |
| 10                 | (15-19)                  | Same area as SPRC                             |
| 11                 | (16-20)                  | Gamble Valley area                            |
| 12                 | 18                       | Off ridge line, use SPRE                      |
| 13                 | -                        | Use SO <sub>2</sub> N for completeness        |
| -                  | 10                       | NOT RECOMMENDED                               |
| -                  | 11                       | In Lee of Ridge Inside Y-12 Plant             |
| -                  | 17                       | Too distant                                   |

TABLE 2  
Monitor Network Design Recommendations: Phase Two

| <u>Site Number</u> | <u>Computer Priority</u> | <u>Comments</u>                                  |
|--------------------|--------------------------|--------------------------------------------------|
| 1                  | 1                        | Inside plant boundary                            |
| 2                  | 2                        | North of Bear Creek Road                         |
| 3                  | 3                        | "                                                |
| 4                  | (4, 5, 12)               | Just North of Bear Creek Road                    |
| 5                  | 6                        | Effectively coincident with<br>SO <sub>2</sub> W |
| 6                  | 7                        | SPRW 300 meters away                             |
| 7                  | 8                        | Between SPRC and SPRE                            |
| 8                  | 9                        | TF site                                          |
| 9                  | 10                       | Effectively coincident with<br>SO <sub>2</sub> E |
| 10                 | 11                       | On ridge top between SPRW<br>and SPRC            |
| 11                 | 13                       | Gamble Valley                                    |

REFERENCES

- <sup>1</sup>Hougland, E. S., Oakes, T. W., and Shank, K. E., "Design of the Sulfur Dioxide and Particulate Air Monitoring Network for the Oak Ridge National Laboratory Fossil Steam Plant," Presented at the 1980 Union Carbide Corporation-Nuclear Division and Goodyear Atomic Corporation Waste Management Seminar, (April 23, 1980).
- <sup>2</sup>Hougland, E. S. and Oakes, T. W., "Design of the Oak Ridge National Laboratory Steam Plant Air Quality Monitor Network in Complex Terrain," Presented at the 1981 Environmental Protection Seminar, Union Carbide Corporation, Nuclear Division, (April 22, 1981).
- <sup>3</sup>Hougland, E. S. and Oakes, T. W., (updated version of the previous paper), "Design of the Oak Ridge National Laboratory Steam Plant Air Quality Monitor Network in Complex Terrain," Presented at the Annual Meeting of the Air Pollution Control Association, Philadelphia, Pennsylvania, June 22, 1981.

EVALUATION OF TECHNIQUES FOR CONTROLLING  $UF_6$   
RELEASE CLOUDS IN THE GAT ENVIRONMENTAL CHAMBER

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KEY WORDS: Uranium Hexafluoride, Release, Control, Electrostatic

ABSTRACT

Studies designed to characterize the reaction between  $UF_6$  and atmospheric moisture, evaluate environmental variables of  $UF_6$  cloud formation and ultimate cloud fate, and  $UF_6$  release cloud control procedure have been conducted in the 1200 cu. ft. GAT environmental chamber. In earlier chamber experiments, 30 separate  $UF_6$  release tests indicated that variations of atmospheric conditions (0-40°C; 20-90% relative humidity; 2-1/2 - 5-1/2 mph wind speeds), and sample sizes (1.8-79.3 g  $UF_6$ ), had no significant effect on  $UO_2F_2$  particle size distribution (0.5-3.0 microns), release cloud formation (static/dynamic, gaseous/liquid release modes), or cloud settling rates (12-16 hours). During the past year, numerous procedures have been evaluated for accelerating  $UF_6$  cloud knockdown in a series of 37 environmental chamber releases. Knockdown procedures included: coarse water spray; air jet; steam spray (electrostatically charged and uncharged); carbon dioxide; Freon-12; fine water mist (uncharged); boric acid mist (charged and uncharged); and an ionized dry air stream.  $UF_6$  hydrolysis cloud settling rates monitored by a laser/powermeter densitometer, indicated the relative effectiveness of various cloud knockdown techniques. Electrostatically charged boric acid/water mist, and electrostatically ionized dry air were both found to be very effective, knocking down the  $UO_2F_2$  release cloud particles in two to five minutes. Work to adapt these knockdown techniques for use under field conditions is continuing, taking into account recovery of the released uranium as well as nuclear criticality constraints.

## INTRODUCTION

Tons of uranium hexafluoride ( $\text{UF}_6$ ) are involved in day-to-day operations of gaseous diffusion uranium enrichment plants. These plants are designed and operated within safety parameters that take into account the hazardous nature of  $\text{UF}_6$ ; and consequences to the work force and to the public should  $\text{UF}_6$  be released to the environment. Some systems within the plants have a greater potential for  $\text{UF}_6$  releases than others due to the nature of their operation e.g., sample withdrawal points, and  $\text{UF}_6$  feed and product withdrawal areas. Plant operations are therefore concerned with nuclear safety (both criticality as well as contamination from  $\text{UF}_6$  releases) throughout the process, and these potential problem areas should be addressed first in release control studies. Furthermore, since the Portsmouth plant produces highly enriched uranium material, accidental releases involve not only personnel safety, but are also of significant monetary concern.

The containment subcommittee of the  $\text{UF}_6$  cylinder handling committee (a joint three plant effort) met in June 1974 to review gaseous diffusion plant philosophy on  $\text{UF}_6$  outleakage control, to define current control procedures and practices, to establish areas where more experimental data were needed, and to submit recommendations which would lead to implementation of improved plantwide  $\text{UF}_6$  release control procedures. On the basis of these recommendations, technical support efforts were initiated, citing as primary objectives testing of presently used methods of controlling a  $\text{UF}_6$  release, and development as needed of alternative control procedures. The following tasks were defined: characterize the reaction between  $\text{UF}_6$  and water ( $\text{UF}_6 + 2\text{H}_2\text{O} \rightarrow \text{UO}_2\text{F}_2 + 4\text{HF}$ ); and determine the effects of environmental conditions on  $\text{UF}_6$  release cloud formation and eventual fate. These tasks were accomplished in the early phases of this work, and are included primarily as background information.<sup>1</sup> The status of the tasks remaining is reported in this paper. The remaining tasks are: analyze the effects of water and/or steam sprays for aiding  $\text{UF}_6$  release cloud knockdown and recovery, with special emphasis placed on nuclear safety; evaluate other release control methods (e.g., carbon dioxide, non-aqueous solvents, other chemical treatments); and determine the best methods of recovery or disposal of products resulting from release control procedures. While aqueous scrubbers (one suggested alternative) may in some instances be applicable, their use relative to high assay nuclear material containment at Portsmouth, would introduce a neutron moderator with attendant equipment sizing (always safe geometry) and cost factor problems.



## DESCRIPTION OF EQUIPMENT AND PROCEDURES

### Environmental Chamber

The GAT environmental chamber has been the basic test facility around which the bulk of activity in our containment efforts has been focused. As it appears in Figure 1, the chamber has an approximate internal volume of 1160 cu. ft., and measures nine by sixteen feet, by eight feet high. The air handler system is protected from contamination by the use of activated carbon and HEPA filters, and is capable of controlling temperature and humidity independently in the range of -5 to 45°C, controllable to within  $\pm 0.4^\circ\text{C}$ . Observation windows are located in the sides, the door, and the top of the chamber. Nine sealable ports are located at various positions around the chamber for passing tubes, control cables, power lines, etc., through the chamber walls. Sealed fluorescent lights provide interior illumination. All interior surfaces are constructed either of type 304 stainless steel, or of plexiglas for corrosion resistance. A self-contained decontamination spray connected to sanitary water supply readily cleans all interior chamber surfaces to background count. Representative samples of the particulate  $\text{UO}_2\text{F}_2$  fallout resulting from releases were obtained by means of a sampling device which may be opened or closed remotely and which permitted timed collection of fallout materials on inserted electron microprobe grids. Samples were subsequently examined by scanning electron microscope (SEM).

### Laser Densitometer

A laser densitometer device was constructed for measuring the opacity of the  $\text{UF}_6$  hydrolysis cloud formed within the chamber. A helium-neon laser and powermeter combination mounted on opposite sides of the chamber was coupled to a chart recorder and proved an effective means of comparing individual releases, and provided unbiased comparison of various cloud knockdown agent efficiencies.

### $\text{UF}_6$ Release Mechanism

Tests requiring a more non-directional type of release, gave rise to development of the present ampule type release. In this mechanism, (Figure 2) a pre-weighed sample of  $\text{UF}_6$ , sealed in a glass ampule, is placed on a heated aluminum V-block in the chamber. A thermocouple is attached to the ampule for external sample temperature readout, (visual observation was also employed to determine when the sample was completely liquified). A deadfall metal bar was released by a lanyard to break the ampule.

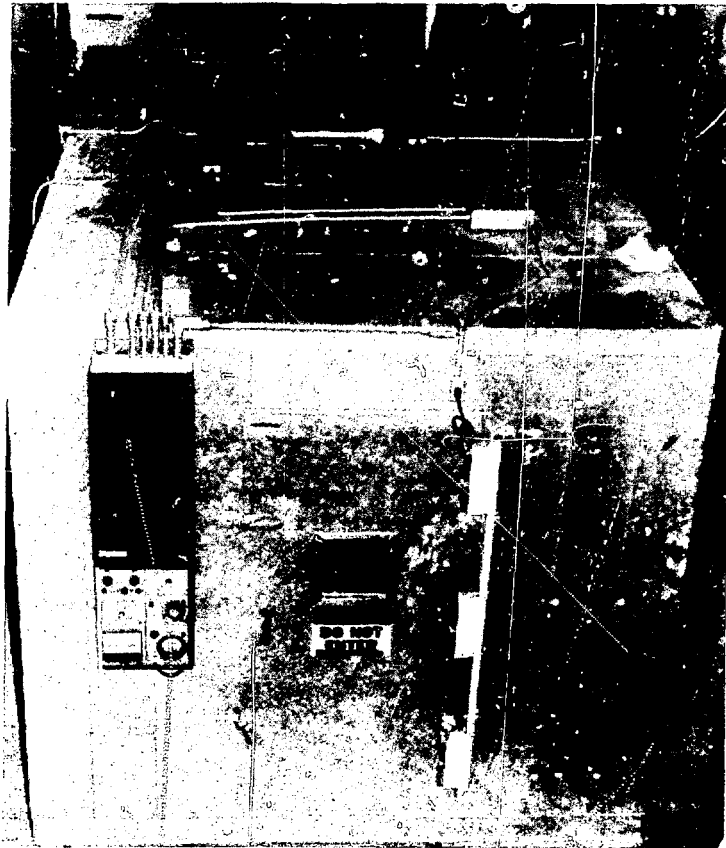


Figure 1 Environmental Chamber

### Cloud Knockdown Equipment

Initial experiments involving cloud knockdown attempts were carried out by the application of steam, or other chemicals through a delivery tube (fitted with a wide-area spray nozzle) extending into the chamber, and controllable by valving on the outside of the chamber. A number of innovations progressively ensued, beginning with isolation of the spray system from electrical ground in order to impose an ionizing charge on the system, and ultimately on the material being sprayed. A commercial electrostatic spray system was later obtained through which an electrostatic charge was imposed on boric-acid water solution. Further modification involved removal of the water spray system, and installation of electrically charged aluminum plates through which a stream of dry air was passed (Figures 3-6).

### EXPERIMENTAL

The experiments involved in the  $\text{UF}_6$  containment studies may be categorized under gaseous and liquid  $\text{UF}_6$  release modes,  $\text{UO}_2\text{F}_2$  cloud knockdown studies, and concurrent investigations.

#### Gaseous $\text{UF}_6$ Release Modes

Static Releases: Liquified  $\text{UF}_6$  was vaporized and remotely released from a heated sample bomb by means of a solenoid valve into a static air mass with the chamber.

Dynamic Releases: Liquified  $\text{UF}_6$  was vaporized and remotely released from a heated sample bomb into a moving air mass. The same release and sampling systems were used as in the static releases, but a blower with directing vanes was installed to provide a nearly laminar cross wind of up to five and one-half miles per hour across the release point.

#### Liquid $\text{UF}_6$ Release Modes

Liquid Spill Releases: Liquid spill releases were designed to simulate an accident in which a cylinder valve was knocked from a heated cylinder; resulting in a liquid  $\text{UF}_6$  spill. This was accomplished by inverting the heated pressure bomb, and allowing the nitrogen pressure in the bomb to force the liquified  $\text{UF}_6$  out through the solenoid valve.

Catastrophic Releases: Controlled releases attempted to simulate heated cylinder rupture accidents. The release mechanism employed in this series



Figure 2 Catastrophic (Ampule) Release

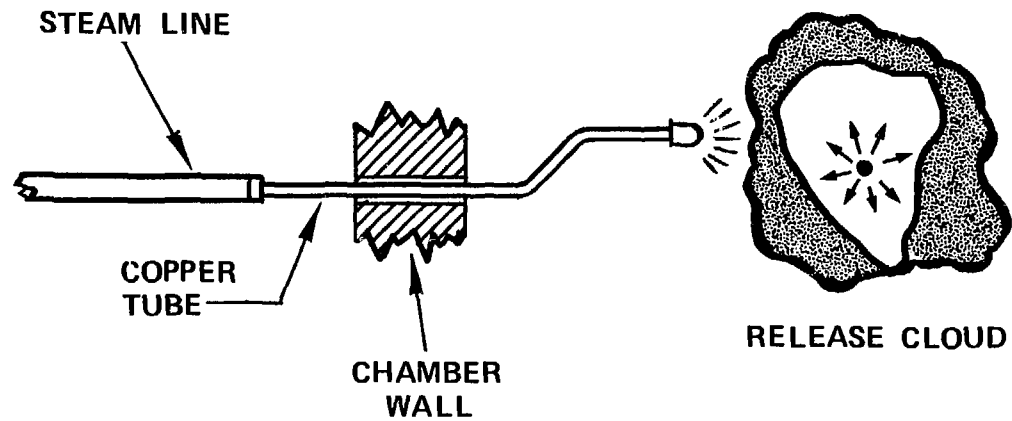


Figure 3 Development of Electrostatic Knockdown System

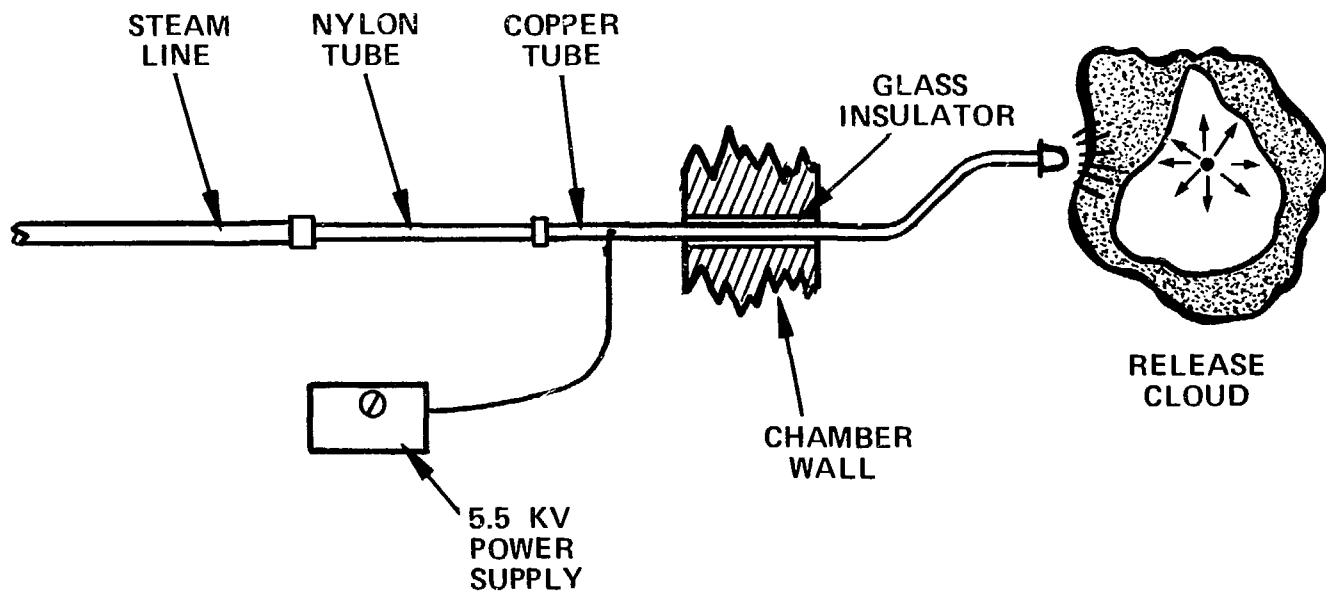


Figure 4 Development of Electrostatic Knockdown System

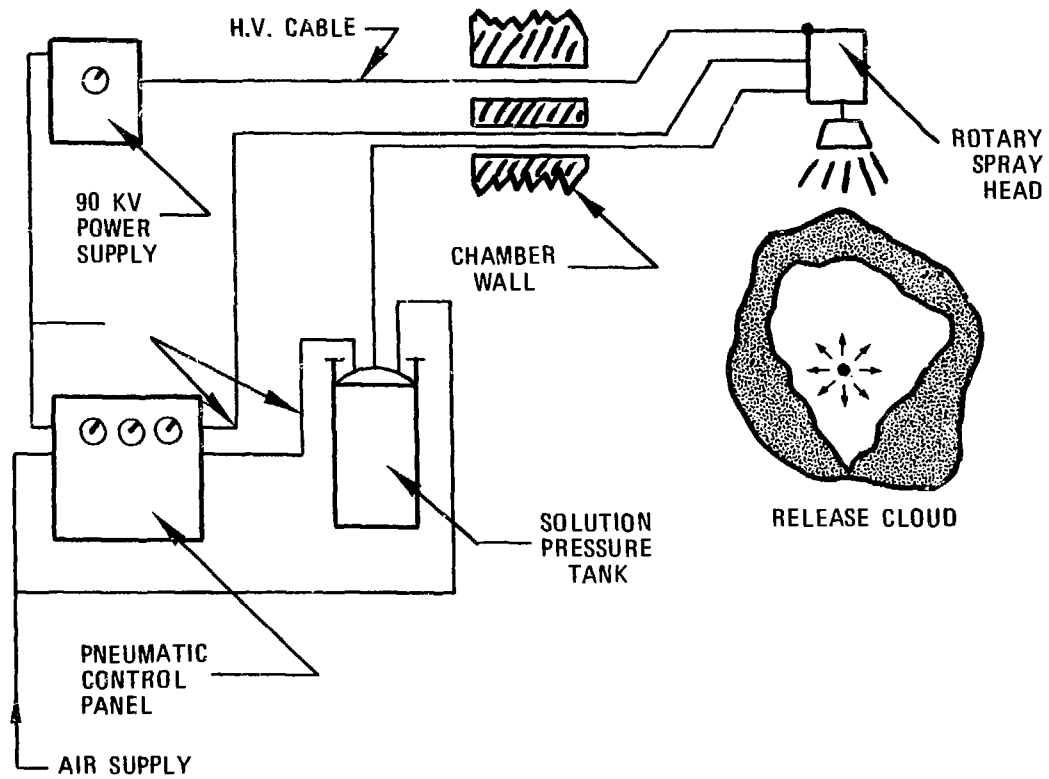


Figure 5 Development of Electrostatic Knockdown System

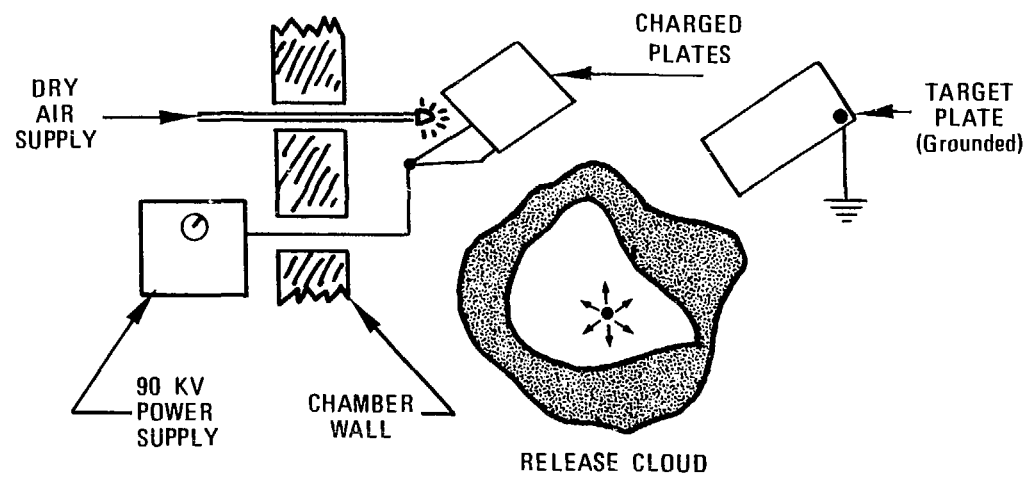


Figure 6 Development of Electrostatic Knockdown System



of tests was the ampule release device previously described. Ampule breakage proved to be very dependable and reproducible, as well as completely non-directional in releasing liquified  $\text{UF}_6$ .

#### $\text{UF}_6$ Cloud Knockdown Studies

Prior to commencement of the  $\text{UF}_6$  cloud knockdown studies, a number of potential cloud knockdown agents were considered. Since all work in the environmental chamber involved only tails assay material, criticality was not a concern, although ultimate results would necessarily have to consider nuclear safety as a prime factor. It was deemed necessary, therefore, to identify any knockdown media which could be effective, and then select only those which satisfied nuclear safety requirements for possible screening tests. Among the potential cloud knockdown agents screened were: coarse water spray, fine water mist, steam (charged and uncharged), electrostatically charged boric acid mist (90 kV), and an ionized dry air stream (90 kV). Relative success for each attempted knockdown procedure was monitored both by the laser densitometer previously described, and by light beam cloud penetration devices being tested by instrumentation development personnel in simultaneously-run experiments.

#### DISCUSSION OF RESULTS

##### Relative Effectiveness of $\text{UF}_6$ Release Cloud Knockdown Media

In the  $\text{UF}_6$  cloud knockdown studies, a total of thirty-seven releases were observed under various conditions of temperature and humidity (air temperature  $0^\circ$  to  $40^\circ\text{C}$ ; dew point  $-5^\circ\text{C}$  to  $25^\circ\text{C}$ ; sample release temperatures  $97^\circ\text{C}$  to  $190^\circ\text{C}$ ). Ten different knockdown agents were screened. Table 1 lists the knockdown agents tested with their relative effectiveness. Steam spray, electrically isolated from ground, and statically charged with a 5.5 kV power supply was found to be only minimally effective. Figure 7 is a composite picture of  $\text{UO}_2\text{F}_2$  particulate before and after injection of electrostatically charged steam, and indicates a large increase in particle size following steam treatment. However, this occurrence was only repeatable in two of a total of nine release control experiments using steam.

A 90 kV electrostatic paint spray system was obtained from the DeVilbiss Co., and filled with a boric acid/water solution. Boric acid was added to the water not only to provide the necessary conductivity so that the solution would accept an electrostatic charge, but also to provide a source of boron to simulate nuclear criticality control procedures. In

the first attempt, a dense release cloud was formed using a 20 gram sample of tails assay  $UF_6$  material. Timing was started with the activation of the spray, and in only two minutes, clear-chamber conditions were indicated by both the laser densitometer and the light beam penetration apparatus. In a total of eight release attempts, complete cloud knockdown was achieved each time. It was found, however, that the correct spray ratio of water to air to electrostatic charge was at best difficult to maintain. A very effective knockdown was subsequently obtained using only ionized dry air. This successful knockdown experiment demonstrated that a water moderated cloud knockdown spray would not be required. In a total of nine releases, complete cloud knockdown was achieved each time in a predictable five to seven minute period. This is compared to a static  $UO_2F_2$  cloud settling rate of twelve to sixteen hours when no knockdown media are used.

Table 1 Results of  $UF_6$  Release Cloud Knockdown Screening Studies

| Knockdown Media                                      | Results                         |
|------------------------------------------------------|---------------------------------|
| Coarse water spray                                   | Cloud intensified               |
| Fine water mist                                      | Cloud intensified               |
| Steam (uncharged)                                    | No change noted                 |
| Electrostatically charged steam (5.5 (kV)            | Only slight clearing            |
| Carbon Dioxide                                       | No change noted                 |
| Freon-12                                             | No change noted                 |
| Air jet                                              | No change noted                 |
| Boric acid mist (uncharged)                          | No change noted                 |
| Electrostatically charged boric acid<br>mist (90 kV) | Total knockdown time = 2 min.   |
| Ionized dry air stream (90 kV)                       | Total knockdown time = 5-7 min. |

#### $UO_2F_2$ Particle Size Variation

Particle size data accumulated from all tests run (63 combined total) have been reported in many forms largely dependent on the information required by specific inquiries. The most uniform set of data covering the work done thus far involves samples taken five minutes after  $UF_6$  release. Very little difference was noted between individual tests in a series, or between series compared as a group, as shown in Figure 8.

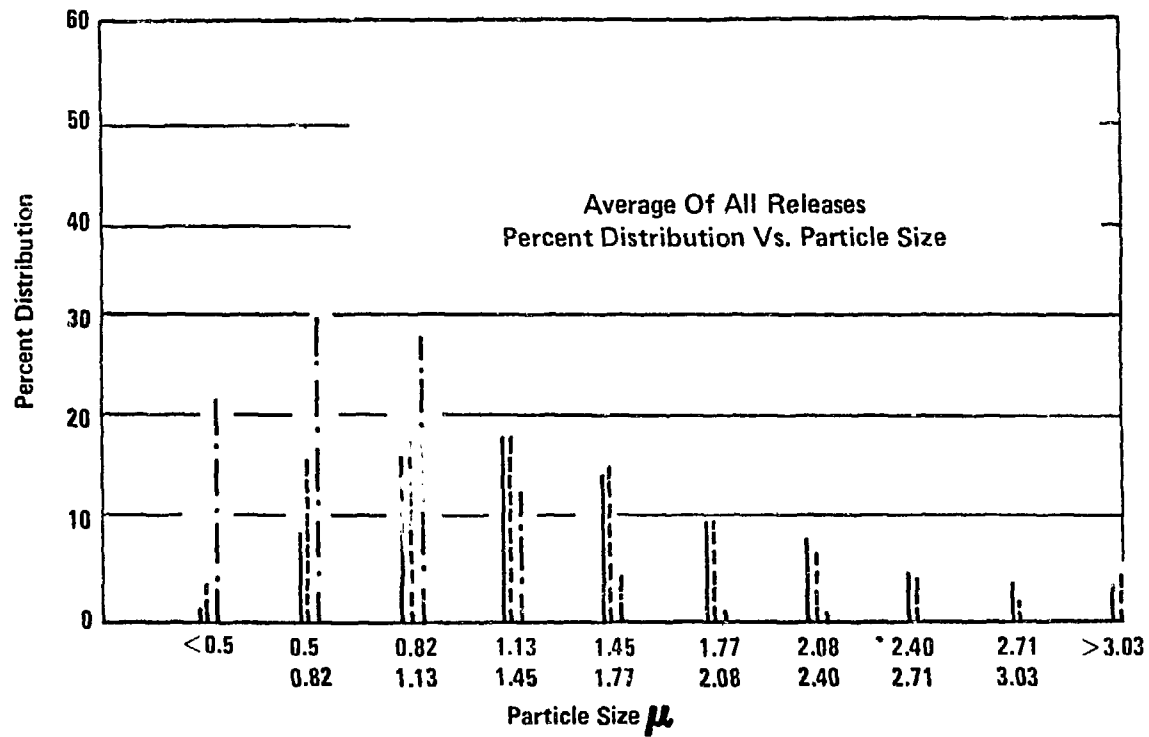
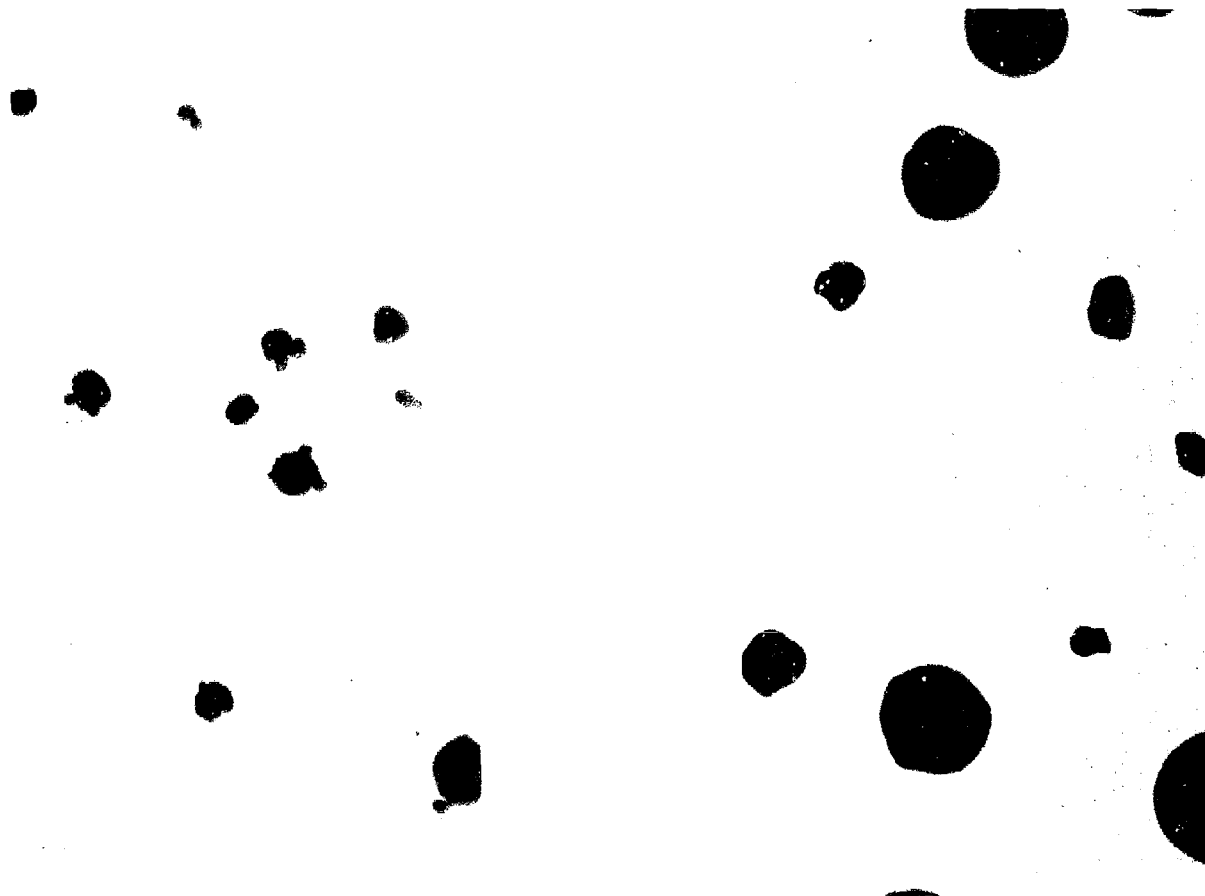


Figure 8 Comparison Chart: Static/Dynamic/Catastrophic Release Series Results Combined



Before Steam Injection (7000X)

After Steam Injection (7000X)

Figure 7 Comparison of UO<sub>2</sub>F<sub>2</sub> Particulate Before and After Steam Injection

### Atmospheric Effects on $\text{UF}_6$ Release Cloud Formation/Dispersal

It has been indicated that no relationship has been found to exist between conditions of temperature (0-40°C) and relative humidity (20-90% RH) on  $\text{UO}_2\text{F}_2$  particle size distribution at conditions normally encountered in work areas. Small chamber  $\text{UF}_6$  release experiments, however, have shown that at ultra low relative humidities (0.65% RH) unattainable in the environmental chamber, no visible hydrolysis cloud is formed.<sup>2</sup> Wind conditions within the confinement of the chamber have apparently aided cloud settling (at least minimally) by enhancing the opportunity for particle agglomeration. Similar findings may or may not occur, e.g., in an open field situation where continuous air turbulence combines with cloud dilution to separate the particles, diminishing their opportunity for agglomeration.

### Release Cloud Density Measurements

Cloud density measurements using a laser densitometer formed the basis for determining the degree of success attained by each knockdown attempt. Figure 9 is a reproduction of the cloud density chart obtained from the first successful electrostatic knockdown. Indicated on the chart are the times at which the samples were taken as well as the time the electrostatic spray was activated, and the diminishing level of chamber opacity as the cloud settled.

### Photographic Studies

Throughout the entire study, photographic recording has been considered an important segment of documentation. Normal and high speed movies of over 50% of the releases have been produced. Film segments spliced into longer photographic studies, have been used frequently as visual demonstrations during project review seminars. Rapid sequence photos have been studied in detail. An example of this work is included in Figure 10, which is a four-frame sequence from a high speed movie film showing what actually happens during the rupture of a glass ampule containing liquid  $\text{UF}_6$ .

### CONCLUSIONS

The following conclusions are based on studies of  $\text{UF}_6$  releases in the GAT environmental chamber:

- Reliable  $\text{UF}_6$  release cloud knockdown has been demonstrated (clear-chamber conditions re-established in five minutes after

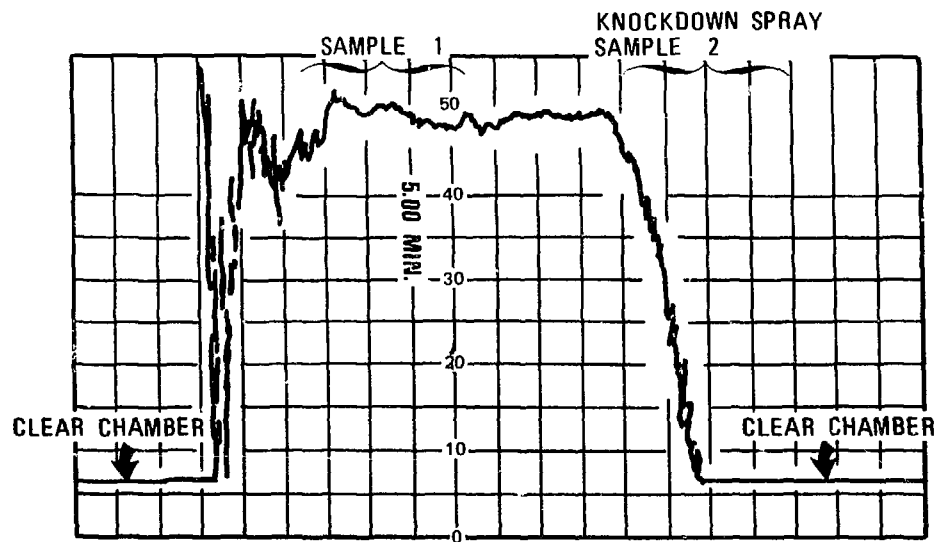


Figure 9 Laser Densitometer Chart Showing  $\text{UO}_2\text{F}_2$  Cloud Knockdown with Charged Boric Acid Mist

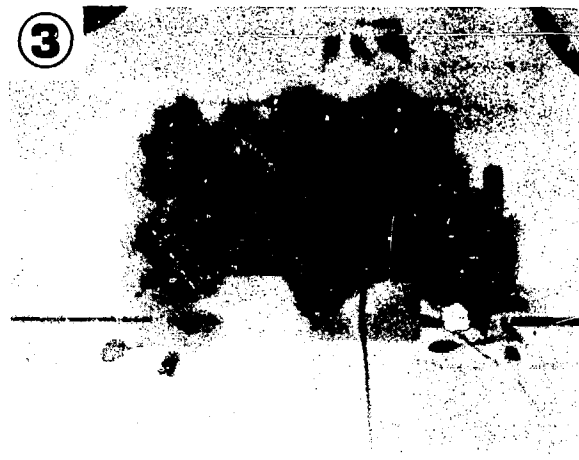
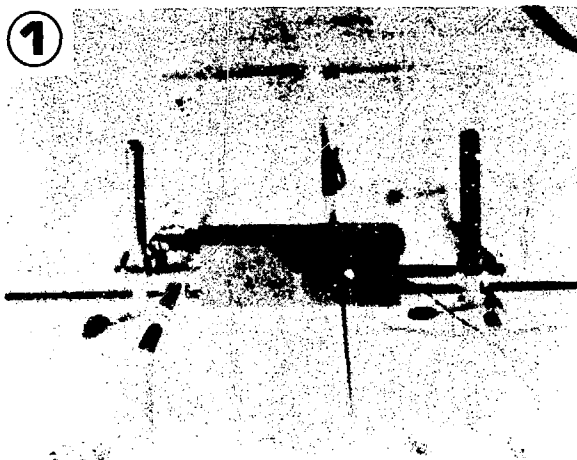


Figure 10 High Speed Photographs of Failed Vessel  $\text{UF}_6$  Release at 0.0012 Second Intervals

UF<sub>6</sub> release) by introduction of an electrostatic spray of ionized dry air. In comparison, an undisturbed cloud requires 12-16 hours to settle.

- No basis has been found for associating UO<sub>2</sub>F<sub>2</sub> release cloud particle size distribution with temperature or humidity effects at conditions normally encountered in GDP work areas. The majority of cloud particles fall in the range of 0.5 to 3.0 microns.
- Effects of turbulence encountered within an enclosure may under some conditions shorten cloud settling times by enhancing the possibility for particle agglomeration. The opposite may occur in open field situations where cloud dilution must be taken into consideration.
- In spite of the considerably higher density of UO<sub>2</sub>F<sub>2</sub> particulate matter (compared with the density of air) the UF<sub>6</sub> release hydrolysis cloud immediately rises to the enclosure ceiling followed by diffusion to fill the chamber. This is in contrast to widely held opinions that release clouds would tend to remain at floor level, as the relatively high density of UO<sub>2</sub>F<sub>2</sub> (6.37 g/cc) might suggest.

#### Future Efforts

A recirculating air system (Figure 11) is being constructed in the environmental chamber to draw in the UO<sub>2</sub>F<sub>2</sub> cloud, electrostatically trap the particulate matter, and return the cleaned air to the area. In addition to evaluation of this experimental unit, industrial electrostatic filters appear to have considerable potential for GAT application. One such unit will provide a complete air change every four minutes. These commercially available units are widely used in industries involving extensive welding operations. The most promising units will also be tested in the GAT environmental chamber.

Studies will be included in the next phase of experiments for airborne particle size measurements of UO<sub>2</sub>F<sub>2</sub> particulate materials as opposed to fallout material. The difference that has been indicated by outside consultants to exist between airborne and fallout modes of particulate sampling could cause significant variations in the design of cloud knock-down equipment for field use and in plume modeling analysis. Along the same line of investigation, the capability for measuring real-time temperature and pressure changes within the forming UF<sub>6</sub> hydrolysis cloud at ballistic speeds up to 2000 measurements per second will be acquired. These parameters have also been indicated as having possibly significant influences on the UF<sub>6</sub> release plume characteristics. Continued testing of



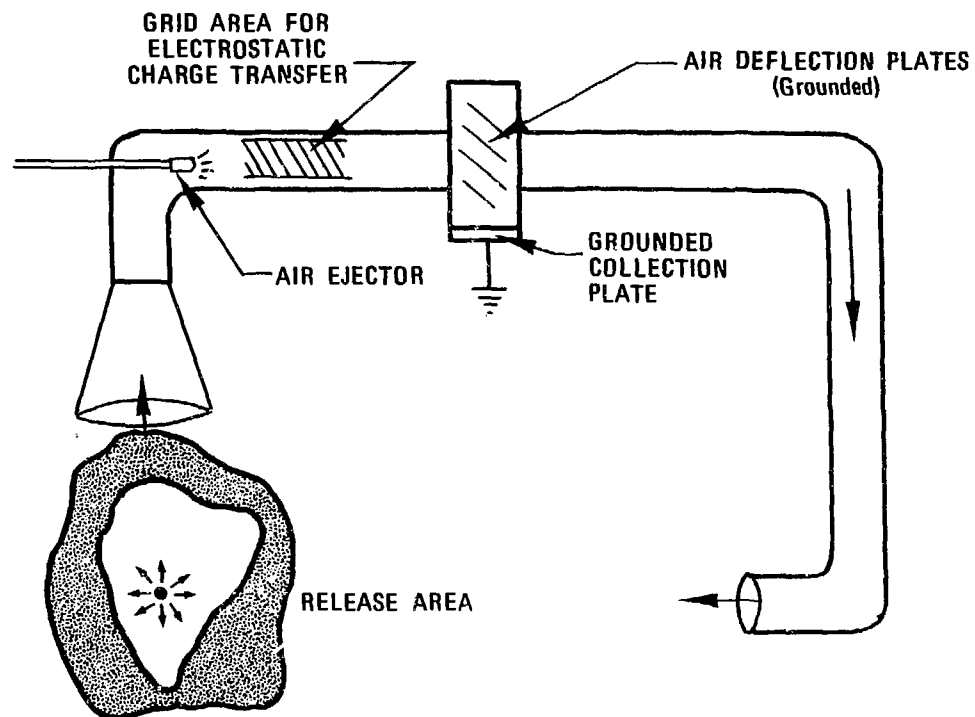


Figure 11 Concept of Proposed Recirculating Air System

new or improved alpha particle detection equipment is also planned. One such device, a continuous sampling strip filter, will give a measurement of increasing or decreasing alpha particle content of an air sample as compared to reading only the maximum accumulated reading. This device, when interfaced with the recirculating air/electrostatic precipitator system, should provide a completely automated  $\text{UF}_6$  release protection system, i.e., the alpha monitor set-point would trigger the electrostatic hydrolysis cloud knockdown system.

#### ACKNOWLEDGMENTS

The author wishes to acknowledge the contributions of D. L. Williams for his efforts in obtaining the environmental chamber and beginning the  $\text{UF}_6$  outleakage control studies; of D. L. Scott for his fine photographic documentation; and of D. L. Riepenhoff for his analytical support in SEM/TEM. Thanks are also due N. F. Reiter and R. L. Spaeth for supplying numerous gas and liquid phase  $\text{UF}_6$  samples used in environmental chamber release tests.

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SCALED-UP TESTING OF ALTERNATIVE TRAPPING AGENTS FOR RADIOACTIVE  
CONSTITUENTS IN PLANT VENT STREAMS

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KEY WORDS: Emissions, Radioactive, Gaseous, Technetium, Uranium, Removal

ABSTRACT

Radioactive discharges from the Portsmouth Gaseous Diffusion Plant vent streams are in compliance with present standards specifying radiation limits. Regulatory trends have become increasingly restrictive on the maximum permissible dose to a member of the public. This could mean more stringent controls for radioactive emissions in the future. Fixed bed activated alumina ( $Al_2O_3$ ) trapping is currently the principal method of limiting plant vent stream emissions of technetium and uranium to the atmosphere. Earlier small scale tests identified pure limestone ( $CaCO_3$ ) and soda-lime ( $NaOH-CaO$ ) as more effective than activated  $Al_2O_3$  for improved control of both radionuclides under top purge vent stream conditions. These same tests showed that soft sintered ( $400^\circ F$ ) sodium fluoride ( $NaF$ ) was best if only uranium is present. Scaled-up testing of these materials is being carried out, and preliminary data for technetium removal confirm the earlier results. Data for uranium removal efficiency are not complete as yet, but available results indicate the trapping process is capable of significant (80-85%) uranium reduction at the 0.5 ppm trap inlet level under prevailing test conditions. Removal efficiency for technetium is higher compared to uranium at on-stream trap times of approximately one month, irrespective of the type trapping agent examined. Factors affecting optimal control of radioactive constituents in plant vent streams by fixed bed trapping operations include: bed loading, 'ap change-out and recharging requirements; operating trap bank configurations in multiple-bed modes; and stability of sorbent materials. These factors will be studied, and results will be used to define available radionuclide emission control options.

## INTRODUCTION

Radioactive discharges from the Portsmouth Gaseous Diffusion Plant vent streams are in compliance with present standards specifying radiation limits (40 CFR, Pt. 190). Fixed-bed activated alumina  $Al_2O_3$  trapping has been and is currently the principal method of successfully controlling plant vent stream emissions of uranium and technetium to the atmosphere. Regulatory trends have become increasingly restrictive concerning the maximum permissible dose to a member of the public. This has required more stringent controls of airborne radioactive emissions. In anticipation of even tighter standards, investigations on fixed bed trapping of radioactive constituents started in 1979 with the goal of identifying improved trapping agents and/or optimizing operating criteria for the trapping systems that control uranium and technetium.<sup>1,4</sup> The multi-site Line Item Project (LIP), "Control of Radioactive Discharges," was recently advanced by DOE from FY 87 to FY 86. These trapping studies will provide part of the technology assessment LIP requirements.

### Regulatory Trends

Table 1 summarizes the regulatory trends with regard to radiation limits. In December 1979, annual allowable exposure limits for protection of the public residing adjacent to uranium fuel cycle facilities were tightened from the prior guideline contained in DOE MC 0524 to that specified in 40 CFR, Part 190 by the EPA. Portsmouth is still in compliance with the more stringent limits using existing radiation dose assessment models. Studies at ORNL<sup>2</sup> suggest that metabolic uptake factors on which compliance with existing limits is based should be increased by as much as a factor of 100 for certain isotopes of uranium. If these proposed factors are incorporated into dose assessment models, Portsmouth may have to

Table 1 Trend of Increasingly Stringent Radiation Limits (Standards)

| <u>Standard</u>                                                           | <u>Compliance Status for Portsmouth</u>                                                                               |
|---------------------------------------------------------------------------|-----------------------------------------------------------------------------------------------------------------------|
| Manual Chapter 0524 (DOE)                                                 | In Compliance                                                                                                         |
| 40 CFR, Part 190 (EPA, 1979)                                              | In Compliance                                                                                                         |
| New Limit Based on 100X Increase in Metabolic Uptake Factor - Anticipated | Would Not Be in Compliance Based on 1980 Data Using Current Models and Assumptions. Reductions by 90 to 95% Required. |

reduce radioactive airborne emissions by 90 to 95% to be in compliance, using 1980 data along with current models and assumptions.<sup>3</sup>

### Portsmouth Vent Streams

The four principal vent streams discharging low-level airborne radioactivity at Portsmouth are located at the top purge cascade, side purge cascade, X-330 cold recovery and X-333 cold recovery areas. The distribution of total radioactivity vented from these sources among the radioisotopes encountered is listed in Table 2. At Portsmouth, uranium-234 and technetium-99 accounted for 98.1% of the total airborne radioactive emissions in 1980, exclusive of daughter products. (The value is 83% of the total, if the Th-234 and Pa-234m daughter products of emitted uranium isotopes are included.) By far, the bulk of the annual radioactivity is discharged from the top and side purge cascade vent streams as outlined in Table 3. Continuing with 1980 data as an example, Table 4 lists the distribution of total curies and radioactivity due to uranium vented between the top and side purge cascade vent streams. Although annual total radioactivity (uranium and technetium) for those two vent streams is distributed approximately 44%-56% (top vent-side vent), the top purge radioactive emissions due to uranium alone are more than twice those discharged from the side purge vent.

Table 2 Distribution of Total Curies Vented Among Radionuclides\*  
(CY 1980 Data)

| <u>Isotope</u> | <u>Percent of Total</u> |
|----------------|-------------------------|
| U-234          | 49.7                    |
|                | } 98.1                  |
| Tc-99          | 48.4                    |
| U-235          | 1.6                     |
| U-236          | <.03                    |
| U-238          | 0.3                     |

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\*The uranium daughter products Th-234 and Pa-234m are not considered in calculating the distribution.

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Table 3 Contribution of Total Radioactivity From Vent Streams  
(CY 1980 Data)

| <u>Vent Stream Locality</u> | <u>Curies/Year</u> | <u>Percent of Total</u> |
|-----------------------------|--------------------|-------------------------|
| Top and Side Purge          | 0.498              | 96.8                    |
| X-330 and X-333 Areas       | 0.0165             | 3.2                     |
| Other                       | --                 | <0.01                   |

Table 4 Distribution of Radioactivity Between Top and Side Purge Vent Streams (CY 1980 Data)

| <u>Vent Steam</u> | <u>Percent of Total Curies</u> | <u>Percent of Total Curies Due to Uranium</u> |
|-------------------|--------------------------------|-----------------------------------------------|
| Top               | 44                             | 69                                            |
| Side              | 56                             | 31                                            |

If the ORNL findings on metabolic uptake factors are sustained, lower limits on radioactive constituents in plant effluents could result. Since inhalation is likely the principal route for biological intake, the top and side cascade vent streams, which discharge most of the radioactivity, are the likely candidates for improved control facilities. Compliance with stricter regulations would also require improvement in present sampling techniques, from a grab sample procedure to continuous monitoring. Under the assumption Portsmouth would not be in compliance with the new (40 CFR, Part 190) limit, a tentative listing of possible solutions for emission reductions is presented in Table 5. The studies described here focus on the fixed bed trapping option and specifically address Items 1(a), 1(c), and 4 as listed in Table 5.

Table 5 List of Alternative Solutions for Reduction of Airborne Radioactivity

---

1. Improve existing systems
    - a. Increase trap changeout frequency
    - b. Alter cascade operating procedures
    - c. Employ more efficient trapping agents
  2. Raise stack heights
  3. Increase purge capacity and/or lights storage
  4. Install additional banks of traps (parallel or series)
  5. Gas/liquid scrubbing processes
  6. Other
- 

#### Previous Studies

The composition of the top and side purge cascade vent streams consists mostly of low molecular weight gaseous impurities (principally air) which pass through  $\text{Al}_2\text{O}_3$  traps for final removal of traces of uranium and technetium. In addition, fluorine ( $\text{F}_2$ ) is present as a result of the R114 degradation process. The high exothermic reactivity of  $\text{F}_2$  with non-fluorinated type trapping materials is a factor that also needs to be considered in assessing trapping performance.

A schematic of the top and side purge vents in Figure 1 shows the mode of gas flow through fixed bed alumina  $\text{Al}_2\text{O}_3$  traps prior to atmospheric discharge. The  $\text{Al}_2\text{O}_3$  traps are arranged in banks each consisting of three parallel clusters that can be put into operation as a unit (Figure 2). There are multiple banks of traps operating in parallel with a typical arrangement involving three banks for the top purge vent and six banks for the side purge as illustrated in Figure 3. Standby banks of fresh  $\text{Al}_2\text{O}_3$  traps also serve as reserve and/or additional capacity to maintain continuity of operation. Although several varieties of  $\text{Al}_2\text{O}_3$  are available, the trapping agent in general use at these locations since plant startup is F-1 grade  $\text{Al}_2\text{O}_3$ , supplied by Aluminum Company of America, Pittsburgh, PA.

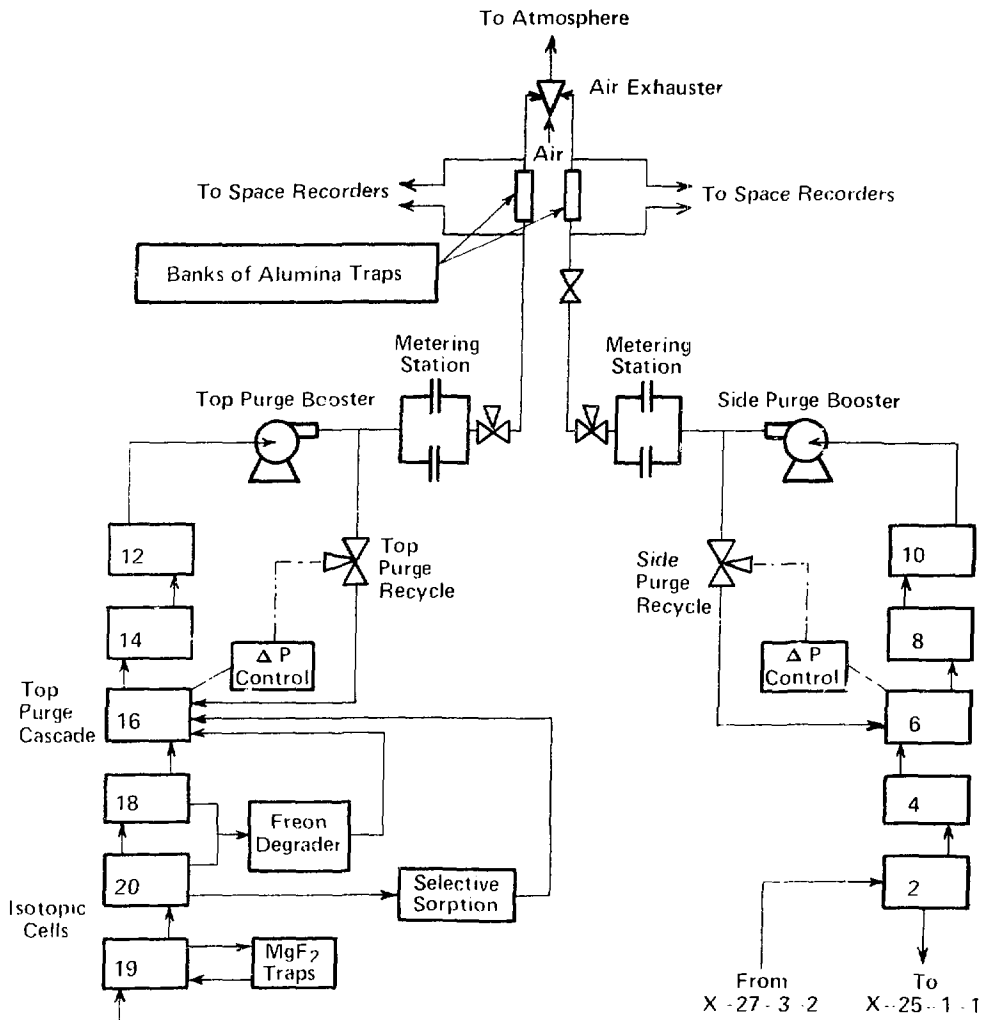


Figure 1 Schematic of the Top and Side Purge Vents



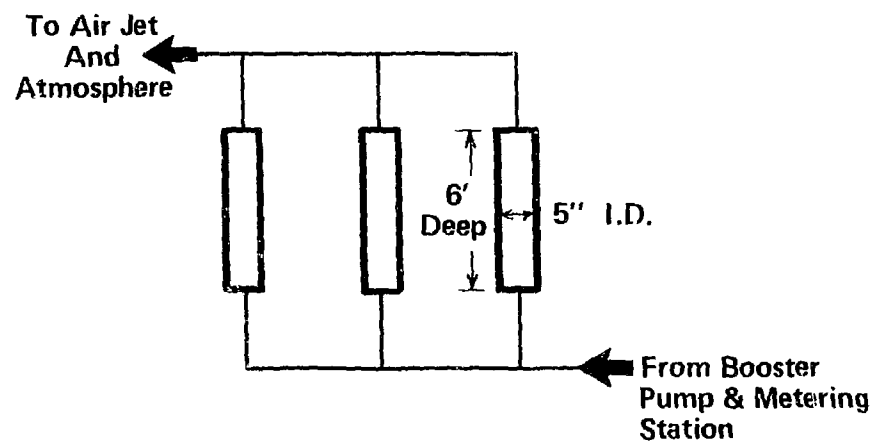


Figure 2 Single Bank of  $\text{Al}_2\text{O}_3$  Trap

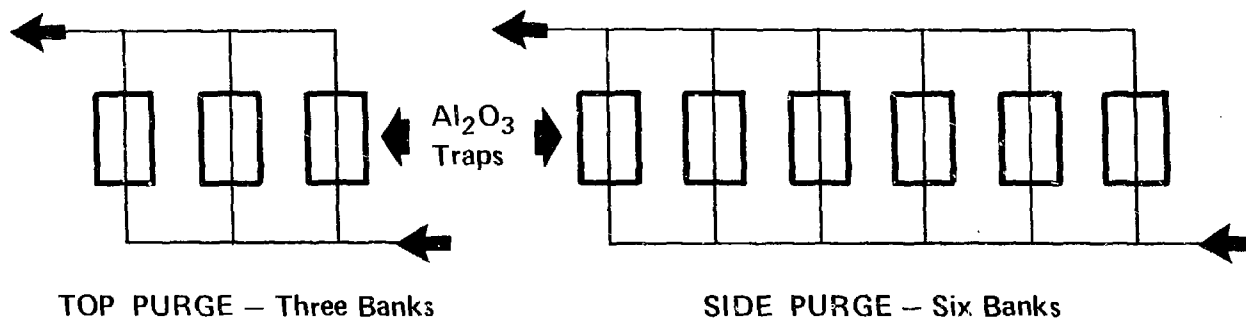


Figure 3 Typical Top and Side Purge Trap Arrangement

Fixed bed trapping studies completed and reported previously<sup>1,4</sup> demonstrate the following:

- The existing  $\text{Al}_2\text{O}_3$  plant trapping system is capable of good technetium control even though the installation was specifically intended for limiting uranium emissions.
- In small-scale side-by-side tests at the top purge vent, limestone ( $\text{CaCO}_3$ ) and soda-lime ( $\text{NaOH-CaO}$ ) perform better than F-1  $\text{Al}_2\text{O}_3$  for Tc-removal under the similar conditions of inlet gas composition, flow, and on-stream time which exist. Performance comparison is based upon the length of on-stream time during which technetium emission was held to less than the detection limit of 0.0007 ppm.
- In the small-scale tests, relative uranium removal efficiencies for limestone and soda-lime were also superior to F-1  $\text{Al}_2\text{O}_3$  as measured by maximum uranium trap loadings. On this basis, the most efficient material for uranium control is sodium fluoride ( $\text{NaF}$ , prepared by heating  $\text{NaHF}_2$  at  $400^\circ\text{F}$ ), which accumulated more uranium than any of 23 materials screened. Technetium control with  $\text{NaF}$  is relatively poor, however, in that  $\approx 90\%$  removal efficiency is observed versus  $>99\%$  with limestone, soda-lime, and alumina.

#### EXPERIMENTAL RESULTS

Recent work comprises:

- Additional small-scale side-stream trapping tests to screen dolomite-type limestones as trapping agents
- Initial efforts at evaluating the improved trapping agents on a scaled-up basis in full-size top purge cascade vent stream traps.

#### Small Scale Trapping Tests

Dolomite type limestone materials ( $\text{MgCa}[\text{CO}_3]_2$ ) that were examined compare poorly to "pure" limestone ( $\text{CaCO}_3$ ) in technetium removal capability as shown in Figure 4. On this basis, dolomite materials were excluded from further consideration; however, some grades of dolomite show better uranium loading than F-1  $\text{Al}_2\text{O}_3$  and may be recommended for full scale tests in mixtures with other materials. Table 6 provides a complete ranking of the best trapping materials identified for technetium control, with inclusion of the most recent data. Limestone (No. 8 Waterloo, Oak Hill, Ohio,

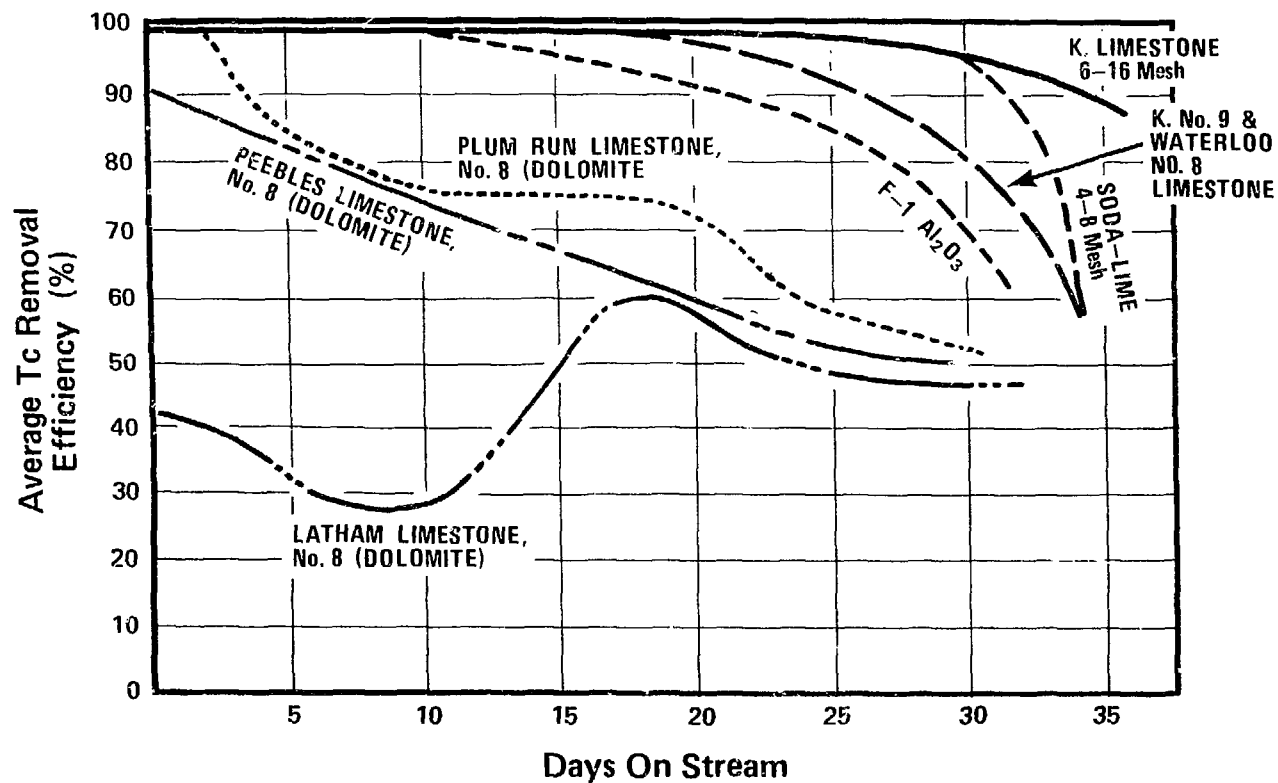


Figure 4 Comparative Performance of Trapping Agents at Top Purge Vent

or 6-16 mesh Valley Quarry Co., Fredonia, Kentucky) and soda-lime (4-8 mesh, Fisher) have significantly better potential for improved technetium trapping compared to F-1  $Al_2O_3$ .

Table 6 Trapping Materials Ranking for Technetium Control

| <u>Trapping Materials</u>        | <u>Relative Rank*</u> |
|----------------------------------|-----------------------|
| Kentucky Limestone (6-16 Mesh)** | 2.1                   |
| Soda-Lime (4-8 Mesh)             | 2.1                   |
| Waterloo Limestone (No. 8)       | 1.8                   |
| Kentucky Limestone (No. 9)**     | 1.5                   |
| F-1 Alumina (1/4"-10 Mesh)       | 1.0                   |
| Plum Run Dolomite (No. 8)        | <.5                   |

\*Based on side-by-side comparison of on-stream time with "zero" discharge. A value of one assigned to F-1 alumina corresponds to approximately ten days of trap operation at prevailing top purge vent stream conditions.

\*\*Valley Quarry Co., Fredonia, Kentucky

Trapping performance for uranium removal could not be readily measured by changes in the trap inlet/outlet stream concentrations because of inadequately sensitive detection limits for uranium. Therefore, for screening purposes, relative uranium loadings on the trap bed (obtained after completion of the trapping test) were used to compare potential uranium removal efficiencies of the various trapping agents. If near quantitative technetium removal was not simultaneously observed with high uranium loading on the bed, the material was generally eliminated from further testing. One notable exception to this screening process was made for NaF prepared at 400°F ("soft-sintered" NaF), which demonstrated the best relative uranium loading of any material tested so far. Table 7

ranks the best trapping materials identified in terms of these observed relative uranium loadings. The superior uranium-loading of NaF over F-1  $\text{Al}_2\text{O}_3$  is consistent with UCCND results on trapping studies of  $\text{UF}_6$  by these solid sorbents.<sup>5</sup>

Table 7 Trapping Materials Ranking for Uranium Loading

| <u>Trapping Materials</u>           | <u>Relative Loading*</u> |
|-------------------------------------|--------------------------|
| Sodium Fluoride (400°F Preparation) | 44                       |
| Kentucky Limestone (6-16 Mesh)**    | 11                       |
| Soda-Lime (4-8 Mesh)                | 4.0                      |
| Waterloo Limestone (No. 8)          | 3.6                      |
| Plum Run Dolomite (No. 8)           | 2.2                      |
| Kentucky Limestone (No. 9)**        | 1.1                      |
| F-1 Alumina (1/4"-10 Mesh)          | 1.0                      |

\*Value of one assigned to F-1 Alumina corresponds to 0.025 lbs/ft<sup>3</sup> after side-by-side exposure test at vent stream conditions.

\*\*Valley Quarry Co., Fredonia, Kentucky

#### Scaled-Up Testing

Scaled-up tests were conducted using standard plant trap equipment with appropriate modifications at the X-326 top purge vent. An existing standby bank (designated "F" bank) was equipped with flowmeters, pressure transducers, temperature sensors, and appropriate gas sample taps for each of the three-trap bank clusters. Although the bank operates at ambient temperatures, temperature monitoring is essential to establish absence of exothermic, rapid chemical conversion of the trapping materials to solid fluoride by-products, an occurrence that is of safety concern and might also affect trap efficiency.

Two traps contained the experimental trapping agents, while a third was filled with F-1  $\text{Al}_2\text{O}_3$  (Table 8). The top purge flow passed through the test bank connected in parallel with the remaining top purge bank traps. A front view of the modified three-cluster trap unit is shown in Figure 5, while a side view with adjacent bank units in the background is depicted in Figure 6. Operation, trap changeouts, and sampling of the inlet/outlet F-bank equipment are being performed by plant operations and support personnel.

Table 8 F-Bank Test Materials in Top Purge Vent Stream

| Trap No. | Run No. 1                   | Run No. 2                   |
|----------|-----------------------------|-----------------------------|
| 1        | F-1 $\text{Al}_2\text{O}_3$ | Limestone, Waterloo         |
| 2        | Limestone, Waterloo         | F-1 $\text{Al}_2\text{O}_3$ |
| 3        | Soda-Lime - NaF Mixture     | NaF                         |

Since concentrations of uranium and technetium in vent streams are quite low before trapping ( $\sim 0.1$ – $5$  ppm for uranium and  $\sim 0.01$ – $5$  ppm for technetium), characterization of accurate trap removal efficiency requires adequate detection sensitivities for the radionuclides.<sup>6</sup> A summary of gaseous uranium and technetium analytical detection limits, type of samples obtained and target limits is shown in Table 9. As previously stated in the discussion of small-scale trapping tests, uranium trap removal efficiency cannot routinely be measured because concentrations are very near uranium detection limits ( $\sim 0.3$  ppm) much of the time. By combining and concentrating the daily "grab" samples over a ten-day interval of trap operation, a tenfold increase in detection sensitivity ( $\sim 0.03$  ppm) was realized permitting reasonably accurate estimates of average uranium removal that can be expected. Uranium trap loading, which is determined at the end of a particular run, serves as another very important parameter of trapping agent performance. Relative uranium loading level was the basis for screening the trapping agents during the small-scale trap testing phase for uranium control.

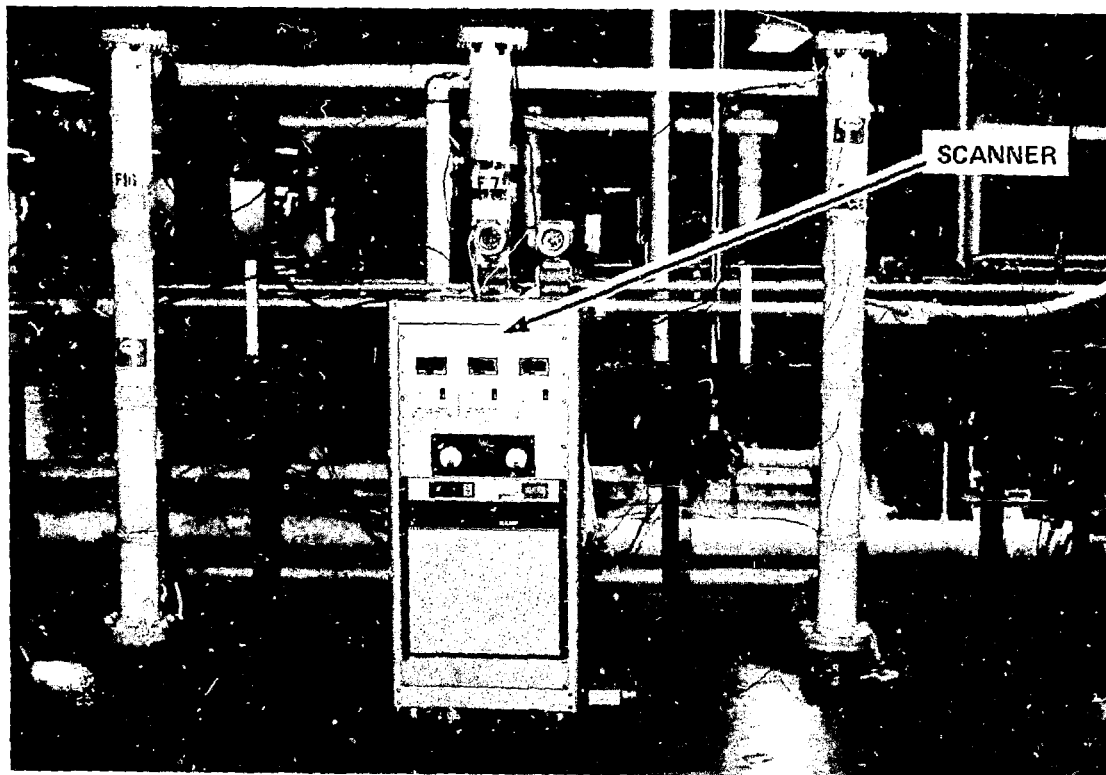


Figure 5 Front View of F-Bank





**Figure 6 Side View of F-Bank**

Table 9 Sampling Detection Limits (ppm)

| <u>Type of Sample</u> |                                           |                                                    |
|-----------------------|-------------------------------------------|----------------------------------------------------|
| <u>"Grab"</u>         | <u>Ten-Day Time -<br/>Averaged "Grab"</u> | <u>Possible Requirements<br/>for Target Limits</u> |
| Uranium: ~0.3         | ~0.03                                     | ~0.1                                               |
| Technetium: ~0.0007   | ~0.00007                                  | ---                                                |

For the initial two runs at F-bank, the materials listed in Table 8 were utilized. Technetium concentrations at the inlet and outlet to the traps versus onstream time are presented in Figure 7 for the first run. The average percent technetium removal efficiencies for the large and small scale runs are compared in Figure 8. Essentially, all data qualitatively concur with the small scale test results obtained in prior screening tests. Tc-removal in order of decreasing effectiveness follows: limestone > soda-lime/sodium fluoride mixture > F-1 alumina > sodium fluoride. Soda-lime presented the most significant problem during execution of this field test. Severe physical deterioration (powdering) was observed after completion of the first run and further use of this type soda-lime materials was abandoned.

Trap efficiencies for uranium removal, measured by composite ten-day, running-average grab samples beginning with the second test run, indicate 40-60% removal at 0.15 ppm and 80-85% removal at 0.50 ppm inlet uranium concentrations at on-stream times of 31 and 54 days, respectively. No significant efficiency trend is discernible between the three trap materials at this juncture of the testing. More data must be collected at longer onstream times to discriminate between the three trapping materials' efficiency for uranium removal from the gas phase at the concentration range (0.1-1 ppm) being encountered. On completion of the trapping operation, uranium loading profiles will be determined and compared with results from the small-scale tests as an additional performance criterion.

#### DISCUSSION AND CONCLUSIONS

The ranking of trapping agents based on small-scale test results serves as a guide for selection of potentially improved materials whose performance is being evaluated in scaled-up field tests. In general, the relative performance of the trapping materials for technetium control is

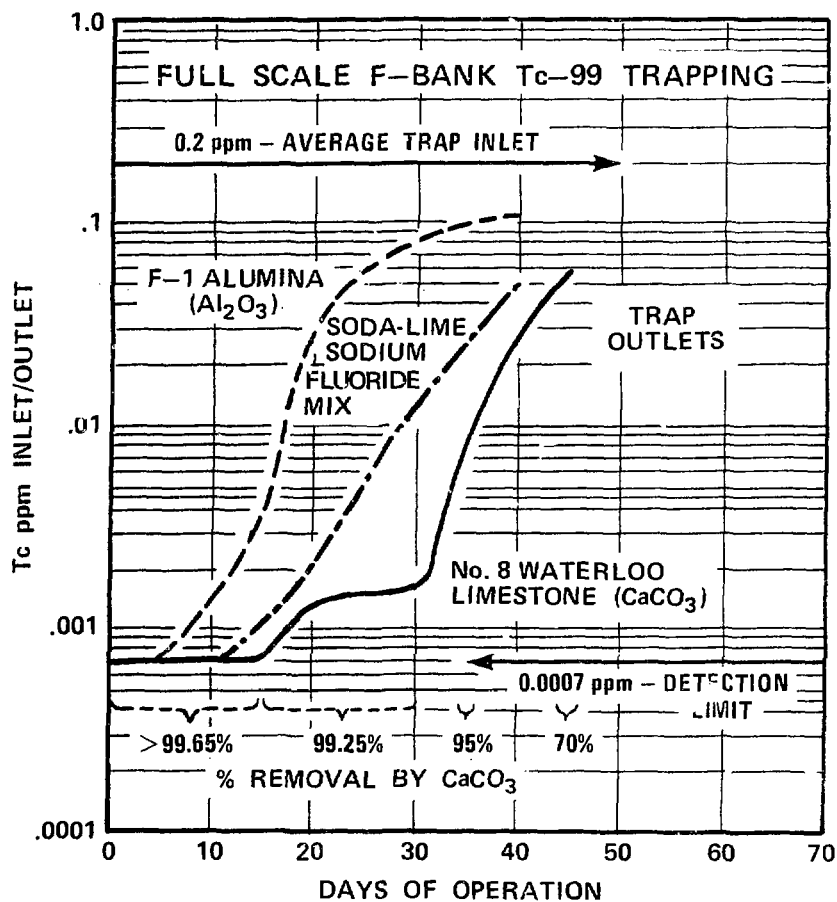


Figure 7 Technetium Concentrations (ppm) at the Inlet and Outlet to the Traps versus Onstream Time

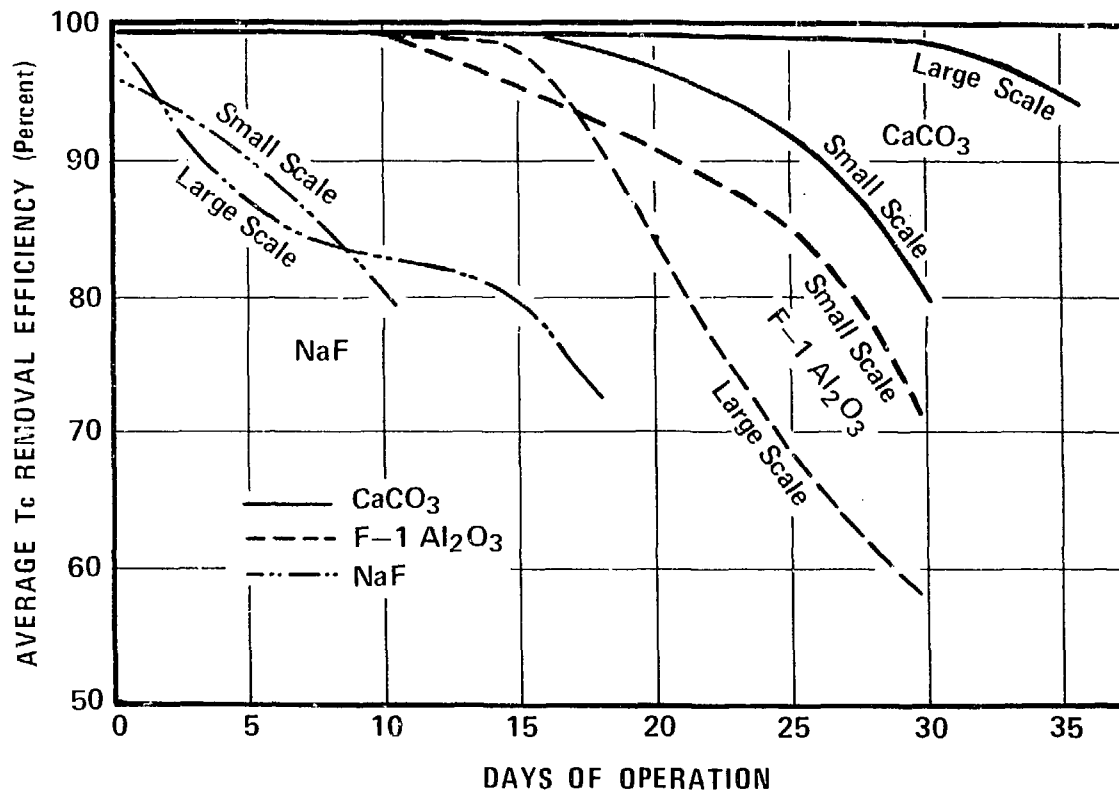


Figure 8 Comparison of Large and Small Scale Tests for Technetium Removal

being qualitatively reproduced in the scaled-up field testing phase compared to the small-scale side-stream test results obtained earlier. The major difference in operating experience is physical attrition of the soda-lime which was not observed during the small-scale tests. For uranium control, there currently are insufficient data on trap performance to allow detailed comparison of small-scale and full-scale test results. Although performance variations among F-1  $\text{Al}_2\text{O}_3$ , NaF, and  $\text{CaCO}_3$  are not being observed on the basis of uranium trap removal efficiency after onstream times of more than 50 days, this is not necessarily inconsistent with the ratings of Table 7 which are based on trap loading. Longer onstream operating times may reflect performance variations that may agree with the ratings based on relative loading. Overall, the bulk of the information does show that uranium control will be more difficult at the 0.1-1.0 ppm trap inlet concentration level than technetium control at the same concentration for any of the trapping agents tested. This likely reflects the general tendency of the chemical form of technetium to more strongly adhere on these solids compared to  $\text{UF}_6$ . Nevertheless, the extent of simultaneous uranium and technetium removal at the ppm level by a fixed bed trapping process, offers a possible option for cost-effective improvement in airborne radioactive emission control to meet more restrictive requirements.

In addition to trap performance (radionuclide removal), a potential trapping agent must (a) be commercially available in large-scale quantities and at reasonably low cost, (b) present no operational handling problems (deterioration), and (c) create no unmanageable spent waste disposal problem. At this time, the leading material having these attributes is limestone. However, more information must be collected to develop and/or define onstream trap operating times, optimum trap configurations and selection of most efficient and economical recovery and/or disposal procedures (particularly for uranium) before selections can be finalized.

The principal conclusions of this work performed to date are as follows:

- "Pure" limestone ( $\text{CaCO}_3$ ) appears much more effective than dolomite-type limestone ( $\text{MgCa}[\text{CO}_3]_2$ ) for efficient technetium control at the top purge vent based on small-scale side-stream trap equipment tests.
- Data obtained in scaled-up tests of trapping agents for Tc-control are consistent with prior results obtained in small-scale tests at the top purge with the following observed order of decreasing effectiveness: limestone > soda lime/sodium fluoride mixture > activated alumina > sodium fluoride. Pellet attrition for soda lime trap material occurs.

- At similar inlet concentrations (0.1–1.0 ppm range) uranium trap efficiency is lower, and consequently, removal of uranium appears to be more difficult to achieve compared to technetium at top purge vent conditions using either limestone, activated alumina, or sodium fluoride. The fixed bed trapping process still offers the potential of a viable option for improved simultaneous radioactive emissions control of both the uranium and technetium radionuclides.
- More data must be collected for extended onstream uranium trapping efficiency to confirm preliminary observations from the top purge vent tests.

#### ACKNOWLEDGMENTS

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## STUDY OF ORNL COAL YARD RUNOFF SLUDGE TREATMENT

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Coal, Runoff, Sludge, Treatment, pH, Flocculation

## ABSTRACT

The ORNL coal yard runoff treatment system being constructed as an ORNL GPP project is necessary for neutralization and removal of iron manganese, and suspended solids. Sludge handling is anticipated to be an operational problem; therefore, modifications and additions are necessary for the provision of a sludge treatment and disposal system. This paper will address alternative considerations, evaluations, and recommendations regarding sludge production, treatment and disposal.

INTRODUCTION

This document addresses potential modifications and additions to the ORNL coal yard runoff treatment system presently under construction. The system currently being constructed is located immediately southwest of the existing coal yard and consists of an equalization pond, chemical treatment, and a settling pond. The object of the treatment is to neutralize the runoff and to remove suspended solids and certain ions such as iron and manganese.

The presently designed system, which is approximately 80% complete, will remove solids through settling followed by neutralization with caustic soda and additional settling. Runoff from the coal pile is now



being channeled to a pond divided into two sections. The upper section acts as an equalization basin and sedimentation chamber to remove coal fines and other suspended solids present in the fluid. Water from the equalization section is pumped to Building 2536 and mixed with NaOH to provide for pH neutralization. After passing through a retention tank in Building 2536, the fluid will be discharged to the lower portion of the pond, where settlement will occur and the clarified liquid will be discharged.

The proposed modifications to the system would provide more efficient handling of the sludge created by chemical treatment.

### PROJECT PURPOSE AND JUSTIFICATION

#### Project Purpose

The purpose of this project is to provide a feasible treatment and disposal system for sludge that will be generated by the coal yard runoff treatment system currently under construction.

#### Justification

The existing system under construction is necessary to neutralize, remove iron and manganese, and reduce the suspended solids from the ORNL coal yard runoff to acceptable limits of the NPDES standards. However, neutralization through the addition of NaOH creates a substantial volume of solids with poor setting characteristics that cannot be easily removed from the settling pond. Drainage and manual removal of the sludge was originally planned.

The proposed modifications provide for more efficient sludge handling. Polyelectrolyte (flocculation aid) addition followed by agitation will provide better flocculation and settling. Preliminary tests performed by vendors<sup>4,5</sup> have shown that the volume of sludge can be substantially reduced by appropriate polyelectrolyte addition. After settling, the sludge solids are to be separated from the liquid phase through centrifugation to further reduce sludge volume and improve handling characteristics. Final disposal of centrifuged solids at the landfill will provide for an easy, permanent, and environmentally acceptable disposal.

#### DESCRIPTION OF PROJECT

*The proposed modifications, shown in Figs. 1 and 2 are as follows:*

1. As presently designed, water collected in the equalization pond (upper basin) will be pumped into Bldg. 2536, passed through an existing static mixer and dosed with caustic soda. At this point, it is proposed that a polyelectrolyte will be added to improve the characteristics of the chemical floc produced through the addition of NaOH. A new screw-type mini-feeder will be provided for the addition of the polyelectrolyte.
2. The existing holding tank will be modified by addition of an agitator and power source. This will serve to convert the tank into a flocculator to assist in the creation of floc with good settling characteristics. From the flocculator, the liquid will be conveyed to the lower part of the pond for settlement.

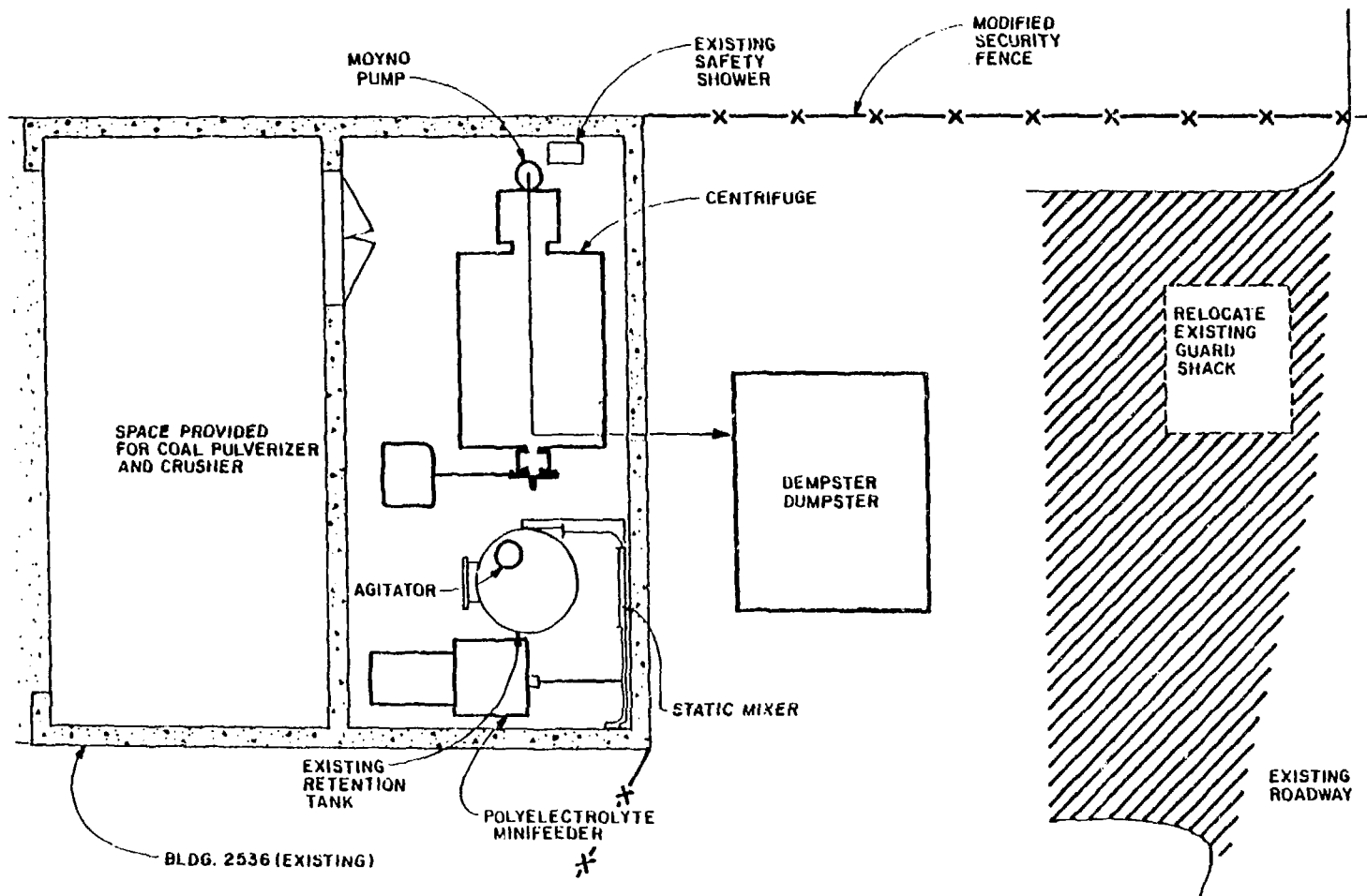


FIGURE 1

Proposed Equipment Modifications and Additions

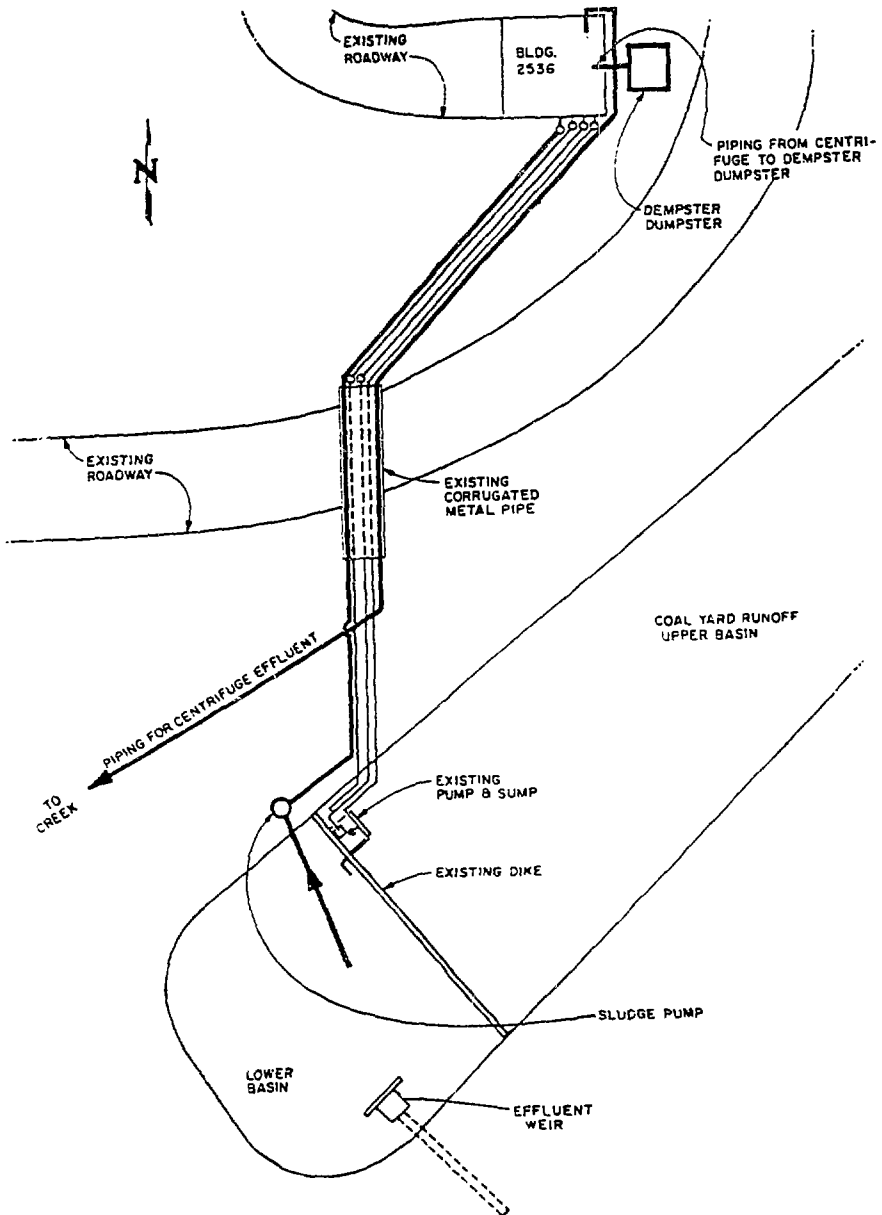


FIGURE 2  
PROPOSED PIPING MODIFICATIONS AND ADDITIONS

3. After settlement, the sludge will be pumped from the settling pond (lower basin) back to Bldg. 2536. A new sludge pump with appurtenances will be provided at the pond to accomplish the sludge removal. The pump or its intake will be mobile to enable sludge collection to occur at various points.
4. A scroll-type centrifuge will be provided to separate the solids in the sludge from the liquid phase. The clarified liquid will be discharged to the receiving stream.
5. The cake from the centrifuge will be pumped through the building wall and collected in a Dempster Dumpster located outside the building. The cake will be periodically trucked to the landfill for final disposal.
6. Other modifications required in the area include piping, fence modification, the relocation of a guard post, etc.

The total project cost for the proposed modifications identified above is estimated to be approximately \$300,000 (fiscal year 1981, 4th quarter dollars).

#### CONCEPT AND ALTERNATIVES

Other alternatives considered are as follows:

1. Modification of System for Lime Neutralization -

The modification of the system for lime neutralization would essentially be similar to the scheme herein proposed but with the addition of lime in place of NaOH. Automatic liming equipment and lime storage area would be required.

The modification to a lime system appears feasible from the technical standpoint. Lime is used more frequently for neutralization than caustic soda, because it produces sludge with better settling characteristics and is a cheaper material. Disadvantages would be that the lime addition and storage area would not fit in the existing building and building expansion would be required. In addition, the retention tank, as modified, would be too small and a new retention tank would have to be provided.

2. Provision of a Conventional Clarifier and Centrifuge -

A clarifier for treatment, sedimentation, and continuous sludge removal coupled with the automatic liming equipment identified above would be provided. This system would replace the existing treatment system and use of the lower pond for settling of sludge. Sludge removed from the clarifier would be further dewatered by the provision of a centrifuge.

This alternative is highly desirable from the efficiency standpoint in contrast to the existing system which may not meet the "best available conventional technology" requirement. This system, however, is the most expensive alternative.

3. Addition of Pressure or Vacuum Filtration Dewatering System -

Instead of using a centrifugation system as proposed, the dewatering systems primarily including either a vacuum filter or a pressure filter would be provided. The vacuum or pressure filter would be housed in Building 2536 and would use the same sludge collection/piping system as proposed (see Figure 2).

The technology of pressure and vacuum filtration has generally been established by the engineering community as an accepted conventional method for dewatering of sludges. However, in a pilot plant study performed concerning dewatering of similar sludges at K-25, it was found that pressure filtration and vacuum filtration were not suitable for their particular sludges. The following conclusions were drawn from the study.

- a. Vacuum filtration had high residual volumes, low throughput, cake cracking, and filter cloth blinding problems.
- b. Pressure filtration suffered from low throughput and filter cloth binding problems and is labor intensive.
- c. Both technologies tend to be more dependent on feed characteristics than is centrifugation.

#### Identification and Evaluation of Recommended Concept

The scheme recommended was selected because of the following:

1. It is the less costly alternative.
2. It fits the available space in Bldg. 2536.
3. It has the potential of providing the desired level of waste treatment (this needs to be confirmed through additional development work).
4. It utilizes the equipment and facilities which are already available.

#### UNCERTAINTIES

A number of uncertainties exist, as follows:

1. The utilization of the lower pond as a settling chamber is an open question. The pond lacks a proper sludge holding area at its

bottom and cannot be fitted with scraping equipment. The pumping of sludge from this pond might be an operational problem.

2. The use of a NaOH neutralization system is an area of uncertainty. Sodium sludge is usually more difficult to settle and centrifuge than calcium sludge. In addition, caustic soda is several times more expensive than lime.
3. The conversion of the holding tank into a flocculation basin is an area of uncertainty since it is an adaptation.
4. The type and dosage of polyelectrolyte has not yet been determined.
5. The final centrifuge specifications must wait until the sludge to be processed has been defined.

#### METHOD OF ACCOMPLISHMENT

The following development work is required:

1. The specific type of polyelectrolyte and the appropriate dosages must be determined. Polyelectrolyte vendors may assist in performing this service if requested to do so. This step is necessary because the characteristics of the sludge must be known prior to the issuance of final centrifuge specifications.
2. Once the sludge has been characterized, centrifuge tests must be performed to determine the type of centrifuge that will give the desired quality of solid-liquid separation. A desired cake moisture content of no more than 65% is desired. Centrifuge manufacturers may provide this type testing service through centrifuge renting arrangements or in their laboratories if the appropriate material is shipped.



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Df

COMPUTERIZED MANAGEMENT OF NATIONAL POLLUTANT DISCHARGE  
ELIMINATION SYSTEM (NPDES) DATA AT  
OAK RIDGE NATIONAL LABORATORY

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Key Words

NPDES, Computer, Data-base, Environmental, Monitoring

ABSTRACT

A program for computerized handling of information on quality of wastewater discharges at three Oak Ridge National Laboratory monitoring stations has been designed and implemented. This computer system analyses field and laboratory data and calculates water quality statistics appropriate for meeting National Pollutant Discharge Elimination System (NPDES) reporting requirements. The interactive nature of the program guarantees automatic identification of compliance violations for immediate notification of the responsible agencies. Reduction of manual processing has resulted in cost savings and greater reporting accuracy.

INTRODUCTION

Section 402 of the Federal Water Pollution Control Act as amended in 1977<sup>1</sup> established the NPDES permit process. This system requires monitoring of wastewater discharges, recording of measured water quality parameters and reporting of calculated statistics to the Environmental Protection Agency. Oak Ridge National Laboratory (ORNL) is presently reporting discharge data for three locations: White Oak Creek, Melton Branch Creek and the Sewage Treatment Plant.

Two types of reports must be submitted through the Department of Energy to the regulatory agency. These are Noncompliance Reports and

\*Research sponsored by the U. S. Department of Energy by Union Carbide Corporation Nuclear Division under Contract W-7405-eng-26.

quarterly Discharge Monitoring Reports (Figure 1). Noncompliance Reports identify violation of specific water quality limits. The Discharge Monitoring Report for each location contains minimum, maximum and mean statistics for each regulated parameter. These include measures of chemical, physical, and biological water quality aspects. Compliance with the NPDES program requires tabulation, calculation and reporting of daily, weekly, and monthly field and laboratory analyses. Data integrity is difficult to maintain in a manual system due to frequent processing and transcribing of data by personnel.

Recently an interactive computer system for storage and reporting of NPDES data (the NPDES File Maintenance and Reporting System) was designed and implemented on an ORNL computer. In comparison with prior manual procedures, use of the computer system has saved time and money in meeting permit requirements. The authors will describe the design and user view of the computer system.

### DISCUSSION

Prior to implementation of the computer system, a completely manual system was used for data generation, transcription and report production. This process required personnel activity at several levels to prepare the quarterly Discharge Monitoring Report:

- \* Technicians manually performed all calculations to determine daily quantities of chemicals.
- \* All records were handwritten.
- \* Senior staff reviewed and checked all records.
- \* Technician and senior staff assembled data necessary for reports.
- \* The Discharge Monitoring Report was typed.
- \* The final report was reviewed by senior staff.
- \* The report was submitted to Department of Energy (DOE).
- \* DOE reviewed, prepared, and submitted a final report to the regulatory agency.

NATIONAL POLLUTANT DISCHARGE ELIMINATION SYSTEM  
DISCHARGE MONITORING REPORT

TN 7N 000 2941 001 8922 35-54-40 84-18-55  
ST PERMIT NUMBER DIS SIC LATITUDE LONGITUDE

REPORTING PERIOD: FROM 10/01/1981 TO 10/31/1981

| PARAMETER              | QUANTITY |         |         | UNITS | CONCENTRATION |         |         | UNITS   | NO EX  | FREQUENCY OF ANALYSIS | SAMPLE TYPE |
|------------------------|----------|---------|---------|-------|---------------|---------|---------|---------|--------|-----------------------|-------------|
|                        | MINIMUM  | AVERAGE | MAXIMUM |       | MINIMUM       | AVERAGE | MAXIMUM |         |        |                       |             |
| FLOW                   | REPORTED | 2.80    | 4.35    | 9.82  | MGD           |         |         |         |        | CONT                  | N/A         |
| 50050 PERMIT COND.     |          |         | NONE    |       |               |         |         |         |        |                       |             |
| BOD                    | REPORTED |         |         |       |               | < 5     | < 5     | 5       | mg/l   | 1/7                   | WKLY COMP   |
| 00310 PERMIT COND.     |          |         |         |       |               |         | NONE    |         |        |                       |             |
| CONDUCTI-              | REPORTED |         |         |       |               | 3.20E-4 | 3.78E-4 | 4.40E-4 | MMH    | 1/7                   | GRAB        |
| VITY PERMIT COND.      |          |         |         |       |               |         | NONE    |         |        |                       |             |
| COD                    | REPORTED |         |         |       |               | 9       | 14      | 18      | mg/l   | 1/7                   | 24 HR COMP  |
| 00340 PERMIT COND.     |          |         |         |       |               |         | NONE    |         |        |                       |             |
| CR (TOTAL)             | REPORTED |         |         |       |               | < .01   | < .01   | .01     | mg/l   | 0                     | 24 HR COMP  |
| 01034 PERMIT COND.     |          |         |         |       |               |         |         | .05     |        |                       |             |
| C O.                   | REPORTED |         |         |       |               | 6.8     | 9.0     | 10.5    | mg/l   | 0                     | GRAB        |
| PERMIT COND.           |          |         |         |       |               | 5       |         |         |        |                       |             |
| DISSOLVED              | REPORTED |         |         |       |               |         |         | 280     | mg/l   | 0                     | 24 HR COMP  |
| 70300 SOL PERMIT COND. |          |         |         |       |               |         |         | 2000    |        | 1/31                  |             |
| OIL/GREASE             | REPORTED |         |         |       |               |         |         | < 2     | mg/l   | 0                     | GRAB        |
| 00556 PERMIT COND.     |          |         |         |       |               |         | 10      | 15      |        | 1/31                  |             |
| pH                     | REPORTED |         |         |       |               | 6.3     | 7.1     | 7.9     |        | 0                     | GRAB        |
| PERMIT COND.           |          |         |         |       |               | 6.0     |         | 9.0     |        | 7/7                   |             |
| SUSP. SOL.             | REPORTED |         |         |       |               | < 5     | < 5.0   | 5       | mg/l   | 1/7                   | 24 HR COMP  |
| 00530 PERMIT COND.     |          |         |         |       |               |         |         | NONE    |        |                       |             |
| TURBIDITY              | REPORTED |         |         |       |               | 3.50    | 3.80    | 4.00    | N.T.U. | 1/7                   | GRAB        |
| PERMIT COND.           |          |         |         |       |               |         |         | NONE    |        |                       |             |

PRINCIPAL EXECUTIVE OFFICER  
Wing, Jerome F.

\* TITLE OF THE OFFICER \*  
\* Chief, Environmental \*  
\* Protection Branch \*

\* DATE \*  
3/04/1982

\* I certify that I am familiar with the  
\* information in this report and to the  
\* best of my knowledge & belief such in-  
\* formation is true, complete, & accurate

\* SIGNATURE OF \*  
\* PRINC EXEC OFCR \*  
\* OR AUTHZD AGNT \*

Figure 1. Computer Generated Discharge Monitoring Report

By contrast, the present system requires the following steps:

- \* As field or laboratory data are received, a technician or staff member enters the data into the computer program from a terminal. Derived data are generated immediately.
- \* The data are verified during or shortly after entry using computer program functions.
- \* Discharge Monitoring Reports are generated on computer paper following an interactive request at the terminal.
- \* The reports are reviewed for any oversights.
- \* The reports are submitted to DOE.
- \* DOE reviews and submits reports to the regulatory agency.

Note that once data is entered and verified by the user, all further data manipulations are internal to the computer system. This dramatically reduces manpower costs and promotes quality assurance.

Early recognition of a noncompliance results from built-in program checking of actual parameter values against permit limits as data is entered. The program user is automatically notified of any non-compliance by both a visual message and an audible signal. This has resulted in rapid reporting of noncompliances to supervision for prompt corrective actions and in timely notification to the monitoring agency. Similar procedures identify data entry errors by alerting the user when entered values are outside valid limits or reasonable bounds.

Centralization of environmental data storage facilitates data retrieval and review. Requests for data values from a specific day or over any time interval can be made and answered with ease. Data centralization also aids generation of summary reports, easing the task of documenting massive amounts of information. Security measures control user access to the stored data. Potential destruction of stored data by fire or water damage is minimized by automatic generation of backup data files each night.

One disadvantage to a computer based system is down time on the computer. Our department's experience indicates that down time is minimal and has not caused significant delay. However, personnel must

be qualified to recognize raw data values indicative of problems in the event of computer failure.

### THE COMPUTER SYSTEM - BASIC DESIGN

The NPDES File Maintenance Reporting System is coded mainly in FORTRAN for use on the DEC PDP-10 computer; however, the major report generator modules are written in the DPL programming language. DPL is part of System 1022, a data-base management system, which handles the physical organization and retrieval details for the NPDES data.<sup>2</sup> The NPDES computer system provides for interactive data entry and retrieval through use of a computer terminal, typically a CRT.

The technology of data-base management systems makes possible the design of programs with the following desirable characteristics:

- \* New data types may be added and obsolete data types removed without major program changes.
- \* Data may rapidly be inspected or edited.
- \* Programs are immune to any changes in the physical organization of the data.

The NPDES computer system was implemented with these features, thus reducing program maintenance time and increasing its flexibility. The data-base consists of several permanent files (Figure 2):

- \* Parameter Files store all measured and calculated NPDES parameter values.
- \* A "Data Dictionary" contains text definitions, units, and bounds for each parameter.
- \* The Noncompliance File contains up-to-date and historical (since 7/1/81) records of each noncompliance.

The Parameter Files and the Noncompliance File are linked so that as parameter values are updated, the Noncompliance File is updated if necessary. The Data Dictionary ensures that the terminal user (1) has additional information about parameters if needed, (2) is prevented from entering invalid values, and (3) is warned immediately of a non-compliance entry.

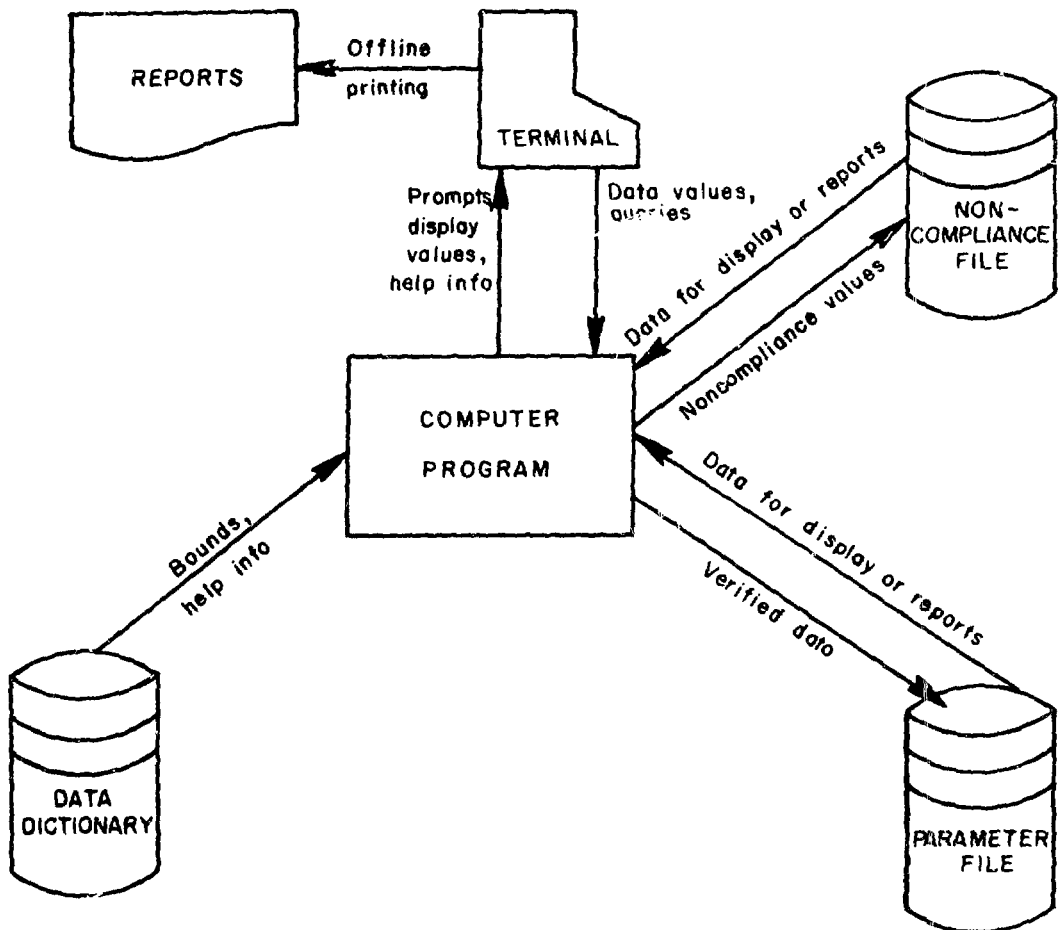


Figure 2. Schematic of Information Flow in the Computer System

### THE COMPUTER-USER INTERFACE

A major goal in designing a computer system for use by more than one person is that it be "user friendly." Such a system is easy to use, efficient in responding to requests, flexible enough to help confused users, and has enough safeguards to prevent the user from making mistakes with serious side effects. Often an expected consequence of such a design is use of the program not only by professional staff but also by technicians. Until now the NPDES code has been used only by the professional staff although we anticipate technician use in the near future.

Five features in the design of the NPDES program qualify it as a user friendly code: "decision tree" design, "HELP" information available at nearly every point, editing access to only one record at a time, special signalling for noncompliance entries, and flexibility of data entry.

The user's view of the system is a decision tree where a limited "menu" of choices is available at different levels of the program. This tends to be easier to use and less intimidating.

At each point at which the user must enter information (select from a menu or enter a value), the "Help Facility" may be invoked by entry of a question mark ("?"). This produces a message explaining the menu choices or describing the type of data required. Entering a double question mark ("??") produces up to two pages of generalized help information.

Several safeguards against user mistakes are provided. Changes to more than one day's set of values (one "record") at a time is impossible, dangerous requests such as deleting a record produce an extra prompt ("Are you sure...?") before executing, and entry of parameter values is immediately verified against up to three ranges: range of physical possibility, range of 98% likelihood, and noncompliance limits. Entry of data exceeding the first and broadest range produces a prompt for reentry. Exceeding the second range causes an "Are you sure?" type of prompt. As discussed earlier, exceeding a noncompliance



limit produces an "emphatic" message and an immediate noncompliance record.

Interactive computer programs must have sufficient flexibility of data entry to accommodate the individual styles of its users. If the user enters a parameter value without typing a decimal point, the NPDES program places it to the right of the last digit. However, if the user enters the number "12.8" for a parameter defined by accuracy considerations as an integer, the program does not reject the entry. Instead, it replies that the integer value "13" is stored. The user always has the option to change any prior entry, numerical or otherwise.

Special numerical forms are also considered. Procedures are included for entering and validating missing values and values of the form "mdl", where "mdl" is the minimum detectable level of a measured chemical.

#### SAMPLE TERMINAL INTERACTIONS

Figure 3 illustrates a typical parameter data entry operation. Note the output from the "Help Facility" and the data checking routines. Incorrect entry of the dissolved oxygen value was detected by the program and the user entered the corrected value below.

Figure 4 illustrates the procedure for generating the Discharge Monitoring Report displayed in Figure 1.

#### FUTURE WORK

Further automation of the NPDES system may occur within a year as bar code technology and word processing links are implemented. A bar code printer and reader may be used to log field data on site, then transfer it automatically to computer files; processing of samples which require laboratory analysis may be tracked by similar technology. Finally, the Department of Environmental Management anticipates use of a software link from the computer to a word processor for automatic generation of noncompliance reports.

## \*\*\*\* MENU \*\*\*\*

Enter P (parameter data),  
 V (violation data),  
 T (tabular output), or  
 Q (quit execution). ? P

Using station WOC Change to (or "X" to exit) ?

Using data type DAILY Change to ?

Using date= 1/ 1/81 Change to ? 12181

NO DAILY DATA EXISTS FOR WOC ON 1/21/81  
 TYPE E (enter data this date), N (do next date), or X (exit). ? E

Ready to enter new DAILY data for station WOC date= 1/21/81:

( 3) PH = ? 6.5

( 4) D O = ? 55

THE ENTERED VALUE (ABSOLUTE VALUE) OF 55.00  
 EXCEEDS THE VALID ABSOLUTE RANGE OF 0.1000E+00 TO 15.00

( 4) D O = ? 5.5

( 5) TEMP = ?

FULL NAME:Temperature UNITS:degrees C

NONCOMPLIANCE BOUNDS: NONE

To exit from this operation without changing the value, type X.

Hitting <RET> without any entry sets the parameter value to zero.

( 5) TEMP = ? 20

( 7) FLOSUM = ? 925

( 8) FLO 400000

DAILY DATA FOR STATION WOC DATE= 1/21/81:

|              |        |                  |         |
|--------------|--------|------------------|---------|
| ( 1) STATION | 1      | ( 2) SAMPLE_DATE | 1/21/81 |
| ( 3) PH      | 6.50   | ( 4) D O         | 5.50    |
| ( 5) TEMP    | 20.0   | ( 7) FLOSUM      | 925     |
| ( 8) FLO     | 400000 |                  |         |

Corrections to the 1/21/81 data may be made now:

TYPE L (list), C (change entry), D (delete), N (do next date)  
 LV or EV (list or enter violations) or X (exit) : ? X

Figure 3. Parameter Data Entry Operation

KEY: All user entries are underlined.

is a carriage return entry.

## \*\*\*\* MENU \*\*\*\*

Enter P (parameter data),  
 V (violation data),  
 T (tabular output), or  
 Q (quit execution).      ? T

## SELECT OUTPUT REPORT OPTION:

R Discharge Monitoring Report,  
 S Data Log Sheet, or,  
 X Exit to MENU point.      ? R

Specify the time interval for these calculations:

Type starting date of interest (mm/dd/yy): ? 10-1-81

Type ending date or hit return for end of month: ?

USING 10/ 1/81 thru 10/31/81

Before generating reports, do you want to check that all  
 noncompliances are recorded (esp. for data not entered) (Y/N) ? N

For all stations (Y/N) ?

For station WOC (Y/N) ? Y

For station MB (Y/N) ?

For station STP (Y/N) ?

Generate reports for other dates (Y/N) ? N

Compiling report programs... please stand by...

\*\*DEPARTMENT OF ENVIRONMENTAL MANAGEMENT\*\*

## NPDES DISCHARGE MONITORING REPORTS

REPORT TO TERMINAL? (Y/N) ? N

PRINT FILE NPDES.RPT TO GET A HARDCOPY LISTING OF THE MONTHLY REPORT

## SELECT OUTPUT REPORT OPTION:

R Discharge Monitoring Report,  
 S Data Log Sheet, or,  
 X Exit to MENU point.      ? X

Figure 4. Interactive Generation of Discharge Monitoring Report

KEY: All user entries are underlined.

↵ is a carriage return entry.

### SUMMARY

Computerization of the NPDES data has resulted in savings of time and money while improving data accuracy. The creation of a "user-friendly" computer system was critical to the success of this procedure. Inclusion of data-base organization concepts will reduce conversion costs for future changes.

### REFERENCES

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- <sup>2</sup>Martin, J., Principles of Data-Base Management, Prentice-Hall, Inc., Englewood Cliffs. New Jersey, pp. 48-49, (1976).

### ACKNOWLEDGEMENTS

Pamela Knight and Billie Masden designed and programmed the report writer modules. Walter Ohnesorge provided guidance on permit requirements and user needs throughout the project. Mary Montford supplied helpful information on report generation procedures.

PREDICTION OF LONG-TERM IMPACT  
OF PGDP CHROMATE SLUDGE LAGOON DISCHARGE

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Paducah Gaseous Diffusion Plant  
Paducah, Kentucky 42001

operated by  
UNION CARBIDE CORPORATION

for the  
U.S. DEPARTMENT OF ENERGY  
Under Contract No. W-7406-eng-26

ABSTRACT

An increased interest in non-chromate based corrosion inhibition systems has been fostered by EPA guidelines governing the disposal of chromium contaminated wastes. Several of the more promising non-chromate systems are being evaluated at K-25. Significant differences exist in the chromated water treatment systems used at the three diffusion plants. An area of common concern has been the long-term oxidation of trivalent chromium present in the respective sludge lagoons. Studies were initiated at Paducah to determine:

1. The discharge rate for the C-616 Sludge Lagoon.
2. The hexavalent chromium concentration in the discharge of the sludge lagoon.
3. The chemistry of trivalent chromium oxidation under sludge lagoon conditions.
4. The impact of the hexavalent chromium in the sludge lagoon discharge on the full flow lagoon.

Flow diagrams showing the basic differences in the chromate treatment systems at the diffusion plants are included.

INTRODUCTION

Recirculating cooling water (RCW) systems are used at each of the Gaseous Diffusion Plants to dissipate the excessive heat associated with the gaseous diffusion process. Periodic blowdowns (or removal of

portions of the RCW) from the cooling towers are required to control the concentrations of dissolved solids in the system. Hexavalent chromium ( $\text{Cr}^{+6}$ ) is maintained between 18 ppm and 22 ppm (as chromate,  $\text{CrO}_4^{2-}$ ) in the RCW for the purpose of corrosion inhibition. Currently, the National Pollutant Discharge Elimination System (NPDES) requires the concentration of hexavalent chromium to be less than 0.05 ppm in liquid effluents prior to their discharge into area surface waters.

A study of the PGDP C-616 Sludge Lagoon was prompted by several factors. Among these factors was the possibility of more stringent EPA guidelines on discharge levels of chromium and constraints on the use of chromium in RCW systems. The long-term availability of chromium for use as a corrosion inhibitor was also a factor.

In view of this, nonchromate based corrosion inhibitors are being considered for use in the RCW systems. ORGDP personnel are presently evaluating some of the more promising non-chromate systems. It is currently planned to field test the most promising non-chromate alternative in the K-29 RCW system.

An area of common concern at the three plants has been the long-term oxidation of trivalent chromium to hexavalent chromium in the respective sludge lagoons. With these points in mind, a study was initiated at Paducah to determine:

1. The discharge rate for the C-616 Sludge Lagoon.
2. The hexavalent chromium concentration in the discharge of the sludge lagoon.
3. The chemistry of trivalent chromium oxidation under sludge lagoon conditions.

### DISCUSSION

At this point, it is important to note that while the systems for treating chromated water at each of the three plants are basically similar, they do have some rather significant differences. The more important of these differences are the location of the NPDES permit point and the point of discharge of the sludge lagoon (accumulation point of trivalent chromium) in relation to the area surface waters. Simplified flow schemes for the chromated water treatment at each of the plants are shown in Figures 1-3.

At GAT, Figure 1, the soluble hexavalent chromium is reduced to insoluble trivalent chromium and precipitated as chromic hydroxide by the sulfur dioxide reduction/lime precipitation method. The insoluble trivalent chromium accumulates in the lagoons which have no direct discharge to area surface waters. The overflow from the lagoon is returned to the clarifier. The NPDES permit point for this system is located at the neutralization tank outfall to the Scioto River.

At ORGDP, Figure 2, the blowdown goes to two separate treatment systems. A large portion of the blowdown goes to the Recycle Softeners to remove calcium and magnesium hardness. The treated RCW is returned to the cooling towers and the sludge is sent to the clarifiers. The other portion of blowdown goes to electrochemical units where hexavalent chromium is reduced to trivalent chromium and precipitated as chromic hydroxide. It is then discharged to Lagoon K-901 A. A small portion of the soluble hexavalent chromium may be trapped in the sludge slurry

# FLOW SCHEME FOR CHROMATED WATER TREATMENT AT GAT

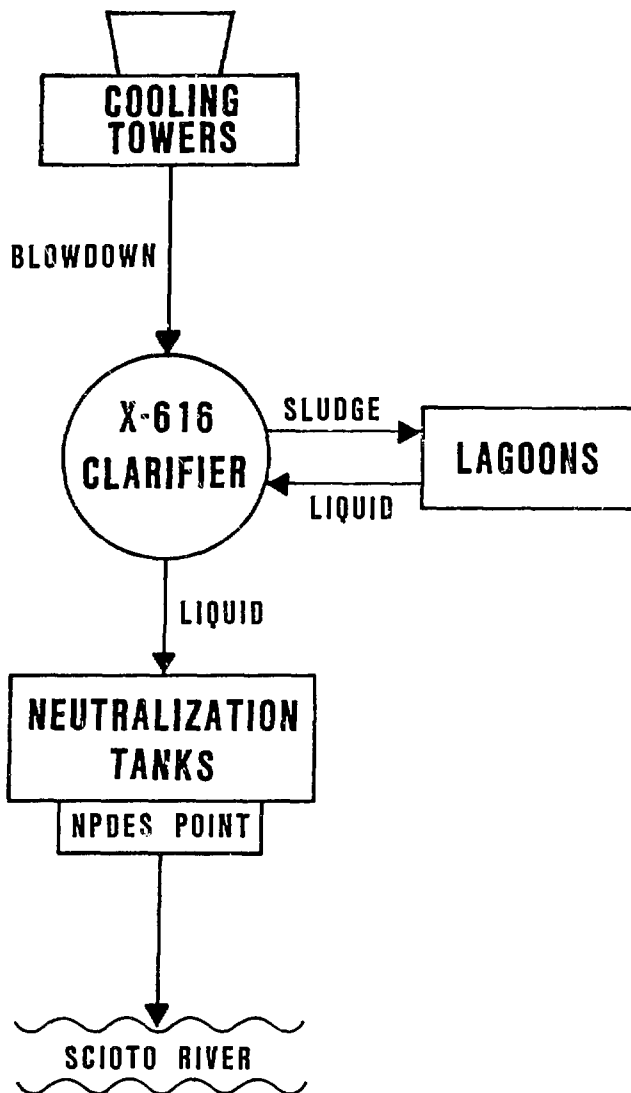


FIGURE 1



# FLOW SCHEME FOR CHROMATED WATER TREATMENT AT ORGDP

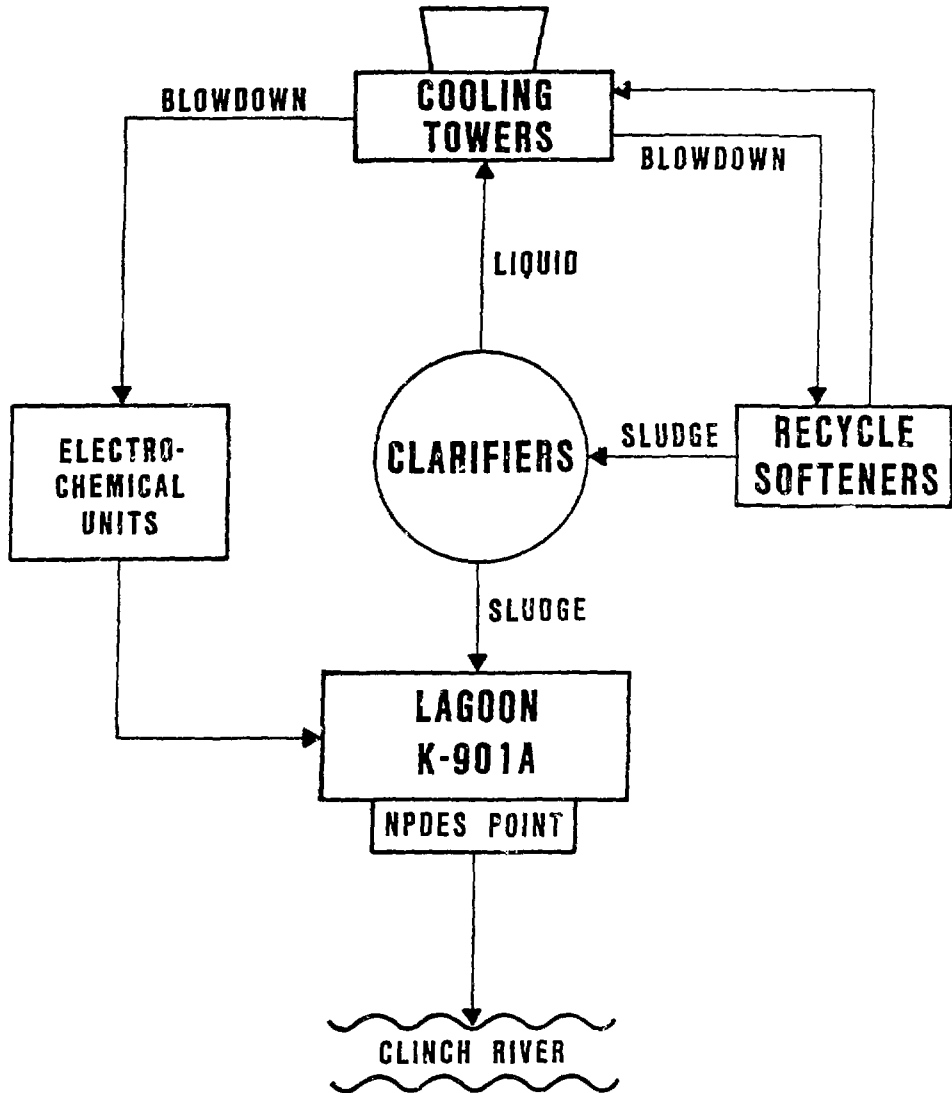


FIGURE 2

# FLOW SCHEME FOR CHROMATED WATER TREATMENT AT PGDP

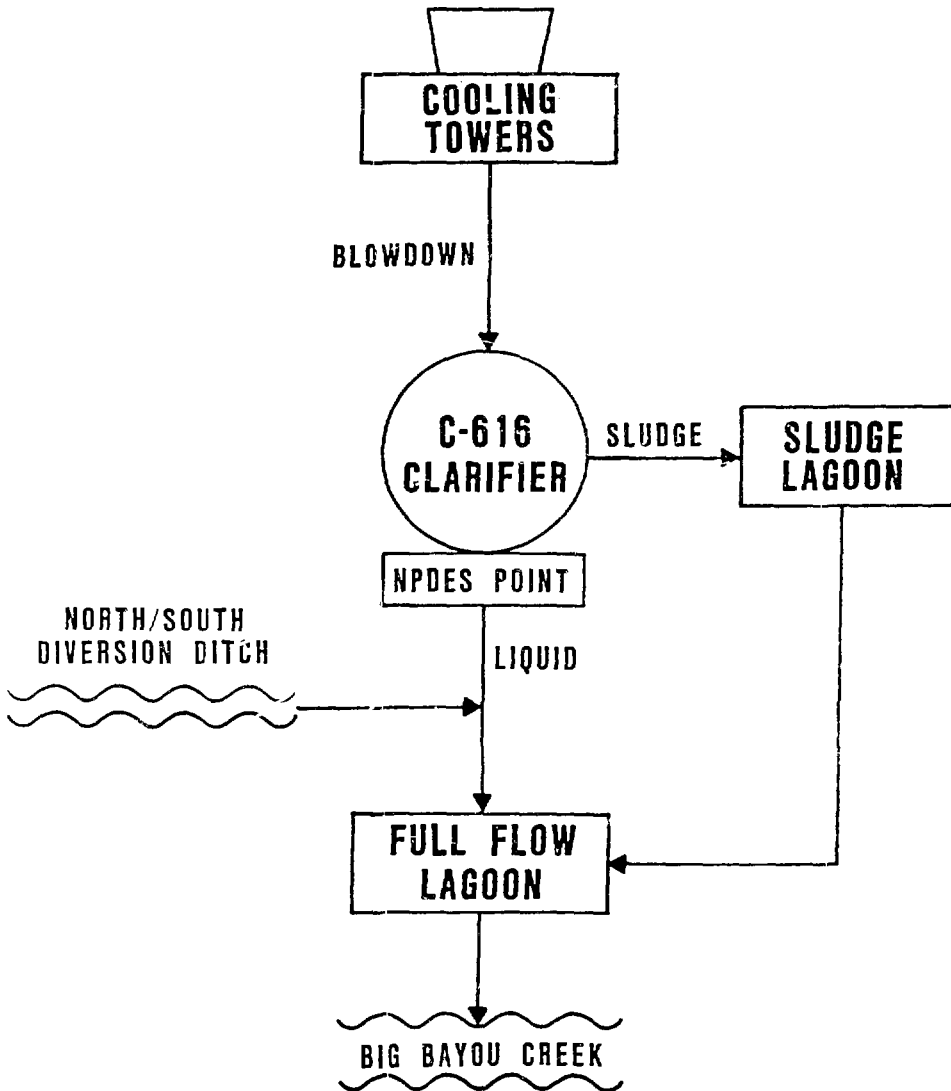


FIGURE 3

from the Recycle Softeners and clarifiers and also enter the lagoon. In this system, the NPDES permit point is at the lagoon discharge to the Clinch River.

The ferrous sulfate/lime precipitation method is utilized to reduce hexavalent chromium to trivalent chromium and precipitate the trivalent chromium as chromic hydroxide at PGDP, Figure 3. The trivalent chromium accumulates in the C-616 Sludge Lagoon. The NPDES permit point for the system is at the liquid effluent discharge of the C-616 clarifier to the full flow lagoon. This discharge is joined by the contents of the North/South Diversion Ditch (miscellaneous process discharges) prior to entering the full flow lagoon. The overflow from the full flow lagoon drains into Big Bayou Creek.

Flow measurements and sampling of the C-616 Sludge Lagoon overflow were initiated in July 1981. A normal flow of 17,000 gallons per day (GPD) was determined with the flow increasing for several days following a heavy rainfall due to increased rainwater run-off. The flow into the full flow lagoon was nominal compared to a flow of approximately 0.73 million gallons per day (MGD) from the clarifier liquid effluent and a flow of approximately 0.2 MGD from the North/South Diversion Ditch. Analysis of the samples showed existing levels of hexavalent chromium between 0.01 ppm and 0.02 ppm in the sludge lagoon overflow.

Trivalent chromium oxidation to hexavalent chromium was briefly examined as part of the study. Minor reactions between the chromic hydroxide (hydrated chromic oxide) and ozone or chlorine are possible

but probably occur to no appreciable extent. Ozone, which is present in air at approximately 0.02 ppm to 0.03 ppm, decomposes in water.

Chlorine reacts with the ferrous ion during treatment in the clarifier and is essentially at 0 ppm when discharged into the sludge lagoon. A 50 percent excess of ferrous sulfate is routinely added in the clarifier to ensure that all hexavalent chromium has reacted. This excess is more than sufficient to consume any chlorine present.

During precipitation of chromic hydroxide, side reactions, including olation and oxolation, often occur. Olation and oxolation reactions connect the  $\text{Cr}^{+3}$  ions in chains or rings via bridging hydroxide and divalent oxygen groups. These reactions are difficult to reverse and increase as the length of time from precipitation of the hydrated chromic oxide increases. Clay and dirt also bind the insoluble trivalent chromium and inhibit oxidation. This leads to the following assumption:

The kinetics of trivalent chromium oxidation are such that a hexavalent chromium equilibrium in the C-616 Sludge Lagoon has essentially been reached and the current hexavalent chromium concentration in the sludge lagoon overflow is approximately constant.

Sampling will continue periodically as a precaution.

To determine the impact of the hexavalent chromium in the sludge lagoon discharge on the full flow lagoon, all flows and concentrations were assumed constant except for the hexavalent chromium concentration in the sludge lagoon overflow. It was also assumed that the three influent streams (clarifier liquid effluent, North/South Diversion

Ditch, and sludge lagoon overflow) represent the only hexavalent chromium sources for the full flow lagoon. Calculations showed that for a concentration of 0.05 ppm  $\text{Cr}^{+6}$  to be observed at the full flow lagoon overflow, 10 to 100 times the present hexavalent chromium concentration in the sludge lagoon overflow would be necessary. An increase of this magnitude is highly improbable and, if occurred, would probably not be limited to a change in only one variable.

#### CONCLUSION

As a conclusion of the study, no problems with the present levels of hexavalent chromium in the sludge lagoon are seen. With oxidation of trivalent chromium to hexavalent chromium occurring to no appreciable extent and a safety margin of 10 to 100 times the existing level of hexavalent chromium, no problems are anticipated to develop with the hexavalent chromium levels in the sludge lagoon. Little variance from the present hexavalent chromium concentration in the C-616 Sludge Lagoon is expected in the future.

#### ACKNOWLEDGMENT

The author gratefully appreciates the information supplied by R. W. Anderson and L. E. Deacon.

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## ORGANIC PRIORITY POLLUTANTS IN WASTEWATER

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Oak Ridge Gaseous Diffusion Plant, Oak Ridge, Tennessee  
Operated by, Union Carbide Corporation, Nuclear Division  
for the U.S. Department of Energy  
under Contract W-7405 eng 26

Keywords: NPDES permits, priority pollutants, gas chromatography/mass spectrometry

ABSTRACT

Prior to June 1978, a collection of environmentally concerned groups brought suit against the Environmental Protection Agency (EPA) for failing to implement portions of the Federal Water Pollution Control Act (FWPCA). The court decision, which has commonly become known as the "EPA Consent Decree," required the EPA to publish a list of toxic pollutants to be controlled, discharge limitations for those compounds in water effluents, and methods for quantitating those compounds. Of the 129 compounds since designated as priority pollutants by the EPA, 114 are organic compounds. The gas chromatography/mass spectrometry methods of analysis, as proposed by the EPA (methods 624 and 625), have been applied to wastewater from the Oak Ridge Gaseous Diffusion Plant (ORGDP). All toxic pollutants identified in the ORGDP wastewater are from the volatile fraction. The concentrations of these organic pollutants ranged from < 10 ppb to ~ 2 ppm.

INTRODUCTION

Litigation brought against the Environmental Protection Agency (EPA) by several environmentally concerned groups (National Resource Defense Council, Environmental Defense Fund, et al) has resulted in the "EPA Consent Decree."<sup>1</sup> As a result of the Consent Decree, the EPA has designated 114 organic compounds and 15 metals as priority pollutants and has proposed a number of analytical methods for analysis of these pollutants in wastewater using what is known as the "Best Available Technology."<sup>2</sup>

As a means to expedite the control of these toxic chemicals in industrial effluents, the EPA has developed a comprehensive and complex strategy for issuing National Pollutant Discharge Elimination System (NPDES) permits to industrial sources. NPDES permits originated in 1973 as an amendment to the Federal Water Pollution Control Act (FWPCA).<sup>3</sup> The Oak Ridge Gaseous Diffusion Plant (ORGDP) was granted a NPDES permit in 1974, which is subject to renewal. With the advent of the Consent Decree, the guidelines for issuing NPDES permits have been markedly changed from those in effect several years ago.

The focus of the NPDES permits has shifted to toxic pollutants and the EPA is modifying the permit guidelines for primary industries. Thus, the Department of Energy (DOE) and the EPA are presently negotiating the general rules to be followed for the issuance of the ORGDP's "second round" NPDES permit.

Before establishing discharge limitations and other pertinent criteria, it was necessary to quantitatively scrutinize the plant's wastewater for conventional and toxic pollutants. The Environmental Management group at the ORGDP was responsible for coordinating the project, the results of which were transmitted to the EPA by DOE to assist in establishing specific NPDES requirements for the facility. Analytical testing was performed by the Analytical Chemistry Department of the Technical Services Division at the ORGDP.

This article is meant to offer a brief synopsis of the EPA proposed methods for analysis of organic priority pollutants in wastewater and their applications in this project. The analysis of conventional pollutants (pH, suspended solids, etc), nonconventional pollutants (color, non-toxic metals, etc), and inorganic toxic pollutants will not be presented here.



### PROPOSED METHODS OF ANALYSIS

As a result of the Consent Decree, 15 analytical procedures, utilizing the "Best Available Technology" have been proposed to analyze for the 114 organic priority pollutants. (See reference No. 2 for details of each procedure--GC conditions, columns, etc.)

#### Chromatographic Techniques

Twelve methods (methods 601-612) are chromatographic techniques utilizing gas and liquid chromatography (GC,LC) with specific detectors. The twelve methods are for the analysis of twelve different classes of organic compounds. These twelve compound classes can be further categorized according to the methodology used to isolate them from aqueous samples. Those compounds that are readily volatile can be removed from solution by purging with an inert gas. This method of sample concentration known as the Purge and Trap Technique will be discussed later. The remaining compounds are classified as "extractables" and may be removed from the aqueous matrix by routine liquid/liquid extraction techniques.

Table 1<sup>4</sup> summarizes the compound classes and the preferred detector for the GC analysis of volatile organics. Table 2 summarizes the compound classes and the necessary detectors for those organics amenable to liquid/liquid extraction.

In some cases, more than one detector may be employed depending on the degree of interferences. For example, interferences by phthalate esters can pose a problem in pesticide analysis when the electron capture detector is used. These interferences can be eliminated with the use of an electrolytic conductivity detector.

TABLE 1  
Gas Chromatographic Methods using Purge-and-Trap Concentration

| Method | Compound Class             | Det. Method <sup>a</sup>          |
|--------|----------------------------|-----------------------------------|
| 601    | Purgeable Halocarbons      | HSD                               |
|        | Bromoform                  | 1,1-Dichlorethene                 |
|        | Bromodichloromethane       | <i>trans</i> -1,2-Dichloroethene  |
|        | Bromomethane               | 1,2-Dichloropropane               |
|        | Carbon tetrachloride       | <i>cis</i> -1,3-Dichloropropene   |
|        | Chlorobenzene              | <i>trans</i> -1,3-Dichloropropene |
|        | 2-Chloroethyl vinyl ether  | Methylene chloride                |
|        | Chloroform                 | 1,1,2,2-Tetrachloroethane         |
|        | Chloromethane              | Tetrachloroethene                 |
|        | Dibromochloromethane       | 1,1,1-Trichloroethane             |
|        | 1,2-Dichlorobenzene        | 1,1,2-Trichloroethane             |
|        | 1,3-Dichlorobenzene        | Trichloroethene                   |
|        | 1,4-Dichlorobenzene        | Trichlorofluoromethane            |
|        | Dichlorodifluoromethane    | Vinyl Chloride                    |
|        | 1,1-Dichloroethane         |                                   |
|        | 1,2-Dichloroethane         |                                   |
| 602    | Purgeable Aromatics        | PID                               |
|        | Benzene                    | 1,4-Dichlorobenzene               |
|        | Chlorobenzene              | Ethylbenzene                      |
|        | 1,2-Dichlorobenzene        | Toluene                           |
|        | 1,3-Dichlorobenze          |                                   |
| 603    | Acrolein and Acrylonitrile | FID                               |

<sup>a</sup> Abbreviations for detectors: HSD, halide specific detector, Hall 700A or equivalent; PID, photo ionization detector; FID, flame ionization detector.

TABLE 2  
Gas Chromatographic Methods using Liquid/Liquid Extraction

| Method | Compound Class                     | Det. Method <sup>a, b</sup> |
|--------|------------------------------------|-----------------------------|
| 604    | Phenols                            | FID/ECD                     |
|        | 4-Chloro-3-methylphenol            | 2-Methyl-4,6-dinitrophenol  |
|        | 2-Chlorophenol                     | 2-Nitrophenol               |
|        | 2,4-Dichlorophenol                 | 4-Nitrophenol               |
|        | 2,4-Dimethylphenol                 | Pentachlorophenol           |
|        | 2,4-Dinitrophenol                  | Phenol                      |
|        |                                    | 2,4,6-Trichlorophenol       |
| 606    | Phthalate esters                   | ECD                         |
|        | Benzyl butyl phthalate             |                             |
|        | Bis (2-ethylhexyl) phthalate       |                             |
|        | Di- <i>n</i> -butyl phthalate      |                             |
|        | Di- <i>n</i> -octyl phthalate      |                             |
|        | Diethyl phthalate                  |                             |
|        | Dimethyl phthalate                 |                             |
| 607    | Nitrosamines                       | NPD                         |
|        | N-Nitrosodimethylamine             |                             |
|        | N-Nitrosodiphenylamine             |                             |
|        | N-Nitrosodi- <i>n</i> -propylamine |                             |

TABLE 2, Continued  
Gas Chromatographic Methods using Liquid/Liquid Extraction

| Method | Compound Class      | Det. Method <sup>a, b</sup> |
|--------|---------------------|-----------------------------|
| 608    | Pesticides and PCBS | ECD/HSD                     |
|        | Aldren              | Endrin                      |
|        | $\alpha$ -BHC       | Endrin aldehyde             |
|        | $\beta$ -BHC        | Heptachlor                  |
|        | $\delta$ -BHC       | Heptachlor epoxide          |
|        | $\gamma$ -BHC       | Toxaphene                   |
|        | Chlordane           | PCB-1016                    |
|        | 4,4'-DDD            | PCB-1221                    |
|        | 4,4'-DDE            | PCB-1232                    |
|        | 4,4'-DDT            | PCB-1242                    |
|        | Dieldrin            | PCB-1248                    |
|        | Endosulfan I        | PCB-1254                    |
|        | Endosulfan II       | PCB-1260                    |
|        | Endosulfan sulfate  |                             |
| 609    | Nitroaromatics      | FID, ECD <sup>c</sup>       |
|        | Isophorone          |                             |
|        | Nitrobenzene        |                             |
|        | 2,4-Dinitrotoluene  |                             |
|        | 2,6-Dinitrotoluene  |                             |

TABLE 2, Continued  
Gas Chromatographic Methods using Liquid/Liquid Extraction

| Method           | Compound Class                                                                                                                                                                                                                                                                                                                                                                                                                       | Det. Method <sup>a, b</sup> |
|------------------|--------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-----------------------------|
| 610 <sup>d</sup> | Polynuclear Aromatic Hydrocarbons                                                                                                                                                                                                                                                                                                                                                                                                    | FID                         |
|                  | <div>Acenaphthene</div> <div>Acenaphthylene</div> <div>Anthracene</div> <div>Benzo(a)anthracene</div> <div>Benzo(a)pyrene</div> <div>Benzo(b)fluoranthene</div> <div>Benzo(g,h,i)perylene</div> <div>Benzo(k)fluoranthene</div> <div>Chrysene</div> <div>Dibenzo(a,h)anthracene</div> <div>Fluoranthene</div> <div>Fluorene</div> <div>Indeno(1,2,3-cd)pyrene</div> <div>Naphthalene</div> <div>Phenanthrene</div> <div>Pyrene</div> |                             |
| 611              | Haloethers                                                                                                                                                                                                                                                                                                                                                                                                                           | HSD                         |
|                  | <div>Bis(2-chloroethyl) ether</div> <div>Bis(2-chloroethoxy) methane</div> <div>Bis(2-chloroisopropyl) ether</div> <div>4-Bromophenyl phenyl ether</div> <div>4-Chlorophenyl phenyl ether</div>                                                                                                                                                                                                                                      |                             |

TABLE 2, Continued

## Gas Chromatographic Methods using Liquid/Liquid Extraction

| Method | Compound Class            | Det. Method <sup>a, b</sup> |
|--------|---------------------------|-----------------------------|
| 612    | Chlorinated Hydrocarbons  | ECD                         |
|        | Hexachlorocyclopentadiene |                             |
|        | Hexachlorobenzene         |                             |
|        | Hexachlorobutadiene       |                             |
|        | Hexachloroethane          |                             |
|        | 1,2-Dichlorobenzene       |                             |
|        | 1,2,4-Trichlorobenzene    |                             |
|        | 1,3-Dichlorobenzene       |                             |
|        | 1,4-Dichlorobenzene       |                             |
|        | 2-Chloronaphthalene       |                             |

<sup>a</sup> Abbreviations of detectors: FID, flame ionization detector; ECD, electron capture detector;

<sup>b</sup> NPD, nitrogen-phosphorus detector; HSD, halide specific detector.

Where two detectors are separated by a slash (/), one or both may be required, depending on interferences. See specific method for details.

<sup>c</sup> Both detectors are required.

<sup>d</sup> This method also outlines an LC separation where resolution of all 16 is required.

Table 3 lists the two proposed LC methods. All sixteen polynuclear aromatic hydrocarbons are resolved by the LC method. GC cannot resolve certain isomeric pairs. Therefore, the chromatographic method of choice depends on the separation requirements.

The twelve chromatographic procedures presuppose a high expectation of finding the compound of interest. Thus a compound is considered to be detected if a peak falls at the retention time of an authentic standard. If the identity of a peak is questioned, confirmation by gas chromatography/mass spectrometry is required.

#### Gas Chromatography/Mass Spectrometry Techniques

The gas chromatography/mass spectrometry (GC/MS) methods take a slightly different approach to priority pollutant analysis. GC/MS is the only available technique that can readily identify a wide variety of organics in the presence of many interferences. Thus, for purposes of GC/MS analysis, the 114 organic priority pollutants may be divided into two major classes--volatiles or purgeables (method 624) and extractables (method 625). The GC/MS methods are shown in Table 4. It should be noted that the extractable fraction is further subdivided into acid and basic fractions. Furthermore, the basic fraction contains the pesticides and the polychlorinated biphenyls (PCBs). Method 613 presupposes the sample to contain trace levels of 2,3,7,8-tetrachlorodibenzo-p-dioxin (TCDD), the most toxic of the dioxins. The method details safe handling practices for TCDD.

Compound identification by GC/MS is quite specific. Detection is based not only on retention time data but also on individual ions, which are characteristic of the compound under investigation. A computer system is required for continuous acquisition of mass spectral data throughout the analysis.

TABLE 3  
Liquid Chromatographic Methods using Liquid/Liquid Extraction

| Method | Compound Class                                                                                                                                                                                          | Detector                                                                                                                                       |
|--------|---------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|------------------------------------------------------------------------------------------------------------------------------------------------|
| 605    | Benzidine derivatives<br>Benzidine<br>3,3'-Dichlorobenzidine                                                                                                                                            | Electrochemical                                                                                                                                |
| 610    | Polynuclear Aromatic Hydrocarbons (PAH)<br>Acenaphthene<br>Acenaphthylene<br>Anthracene<br>Benzo(a)anthracene<br>Benzo(a)pyrene<br>Benzo(b)fluoranthene<br>Benzo(g,h,i)perylene<br>Benzo(k)fluoranthene | UV/Fluor.<br>Chrysene<br>Dibenzo(a,h)anthracene<br>Fluoranthene<br>Fluorene<br>Indeno(1,2,3-cd)pyrene<br>Naphthalene<br>Phenanthrene<br>Pyrene |



TABLE 4

## Gas Chromatographic/Mass Spectrometry Methods

| Method | Compound Class                                                                                                                                                                                                                                                                            | Concentration Method                                                                                                                                                                                                                                                                                                                                     |
|--------|-------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| 613    | 2,3,7,8-Tetrachlorodibenzo- <i>p</i> -dioxin                                                                                                                                                                                                                                              | L/L Extraction                                                                                                                                                                                                                                                                                                                                           |
| 624    | Purgeables                                                                                                                                                                                                                                                                                | Purge/Trap                                                                                                                                                                                                                                                                                                                                               |
|        | Benzene<br>Toluene<br>Ethylbenzene<br>Carbon tetrachloride<br>Chlorobenzene<br>1,2-Dichloroethane<br>1,1,1-Trichloroethane<br>1,1-Dichloroethane<br>1,1-Dichloroethylene<br>1,1,2-Trichloroethane<br>1,1,2,2-Tetrachloroethane<br>Chloroethane<br>2-Chloroethyl vinyl ether<br>Chloroform | 1,2-Dichloropropane<br>1,3-Dichloropropene<br>Methylene chloride<br>Methyl chloride<br>Methyl bromide<br>Bromoform<br>Dichlorobromomethane<br>Trichlorofluoromethane<br>Dichlorodifluoromethane<br>Chlorodibromomethane<br>Tetrachloroethylene<br>Trichloroethylene<br>Vinyl chloride<br><i>trans</i> -1,2-Dichloroethylene<br>Acrolein<br>Acrylonitrile |
| 625    | Acid Extractables                                                                                                                                                                                                                                                                         | L/L Extraction, pH 2                                                                                                                                                                                                                                                                                                                                     |
|        | Phenol<br>2-Nitrophenol<br>4-Nitrophenol<br>2,4-Dinitrophenol<br>Fentachlorophenol                                                                                                                                                                                                        | <i>p</i> -Chloro- <i>m</i> -cresol<br>2-Chlorophenol<br>2,4-Dichlorophenol<br>2,4,6-Trichlorophenol<br>2,4-Dimethylphenol                                                                                                                                                                                                                                |

TABLE 4, Continued  
Gas Chromatographic/Mass Spectrometry Methods

| Method | Compound Class                      | Concentration Method                 |
|--------|-------------------------------------|--------------------------------------|
| 625    | Base Extractables and Pesticides    | L/L Extraction, pH 11                |
|        | 1,2-Dichlorobenzene                 | Fluorene                             |
|        | 1,3-Dichlorobenzene                 | Fluoranthene                         |
|        | 1,4-Dichlorobenzene                 | Chrysene                             |
|        | Hexachloroethane                    | Phrene                               |
|        | Hexachlorobutadiene                 | Phenanthrene                         |
|        | Hexachlorobenzene                   | Anthracene                           |
|        | 1,2,4-Trichlorobenzene              | Benzo(a)anthracene                   |
|        | <i>Bis</i> (2-chloroethoxy) methane | Benzo(b)anthracene                   |
|        | Naphthalene                         | Benzo(k)anthracene                   |
|        | 2-Chloronaphthalene                 | Benzo(a)pyrene                       |
|        | Isophorene                          | Indeno(1,2,3,-cd)pyrene              |
|        | Nitrobenzene                        | Dibenzo(a,h)anthracene               |
|        | 2,4-Dinitrotoluene                  | Benzo(g,h,i)perylene                 |
|        | 2,6-Dinitrotoluene                  | 4-Chlorophenyl phenyl ether          |
|        | 4-Bromophenyl phenyl ether          | 3,3'-Dichlorobenzidine               |
|        | <i>Bis</i> (2-ethylhexyl) phthalate | Benzidine                            |
|        | Di- <i>n</i> -octyl phthalate       | <i>Bis</i> (2-chloroethyl) ether     |
|        | Dimethyl phthalate                  | 1,2-Diphenylhydrazine                |
|        | Diethyl phthalate                   | Hexachlorocyclopentadiene            |
|        | Di- <i>n</i> -butyl phthalate       | N-Nitrosodiphenylamine               |
|        | Acenaphthylene                      | N-Nitrosodimethylamine               |
|        | Acenaphthene                        | N-Nitrosodi- <i>n</i> -propylamine   |
|        | Butyl benzyl phthalate              | <i>Bis</i> (2-chloroisopropyl) ether |

TABLE 4, Continued  
Gas Chromatographic/Mass Spectrometry Methods

| Method | Compound Class                   | Concentration Method        |
|--------|----------------------------------|-----------------------------|
| 625    | Base Extractables and Pesticides | L/L Extraction, pH 11       |
|        | A-Endosulfan                     | Heptachlor                  |
|        | B-Endosulfan                     | Heptachlor epoxide          |
|        | Endosulfan sulfate               | Chlordane                   |
|        | $\alpha$ -BHC                    | Toxaphene                   |
|        | $\beta$ -BHC                     | Aroclor 1016                |
|        | $\delta$ -BHC                    | Aroclor 1221                |
|        | $\gamma$ -BHC                    | Aroclor 1232                |
|        | Aldrin                           | Aroclor 1242                |
|        | Dieldrin                         | Aroclor 1248                |
|        | 4,4'-DDE                         | Aroclor 1254                |
|        | 4,4'-DDD                         | Aroclor 1260                |
|        | 4,4'-DDT                         | 2,3,7,8-Tetrachlorodibenzo- |
|        | Endrin                           | p-dioxin (TCDD)             |
|        | Endrin aldehyde                  |                             |

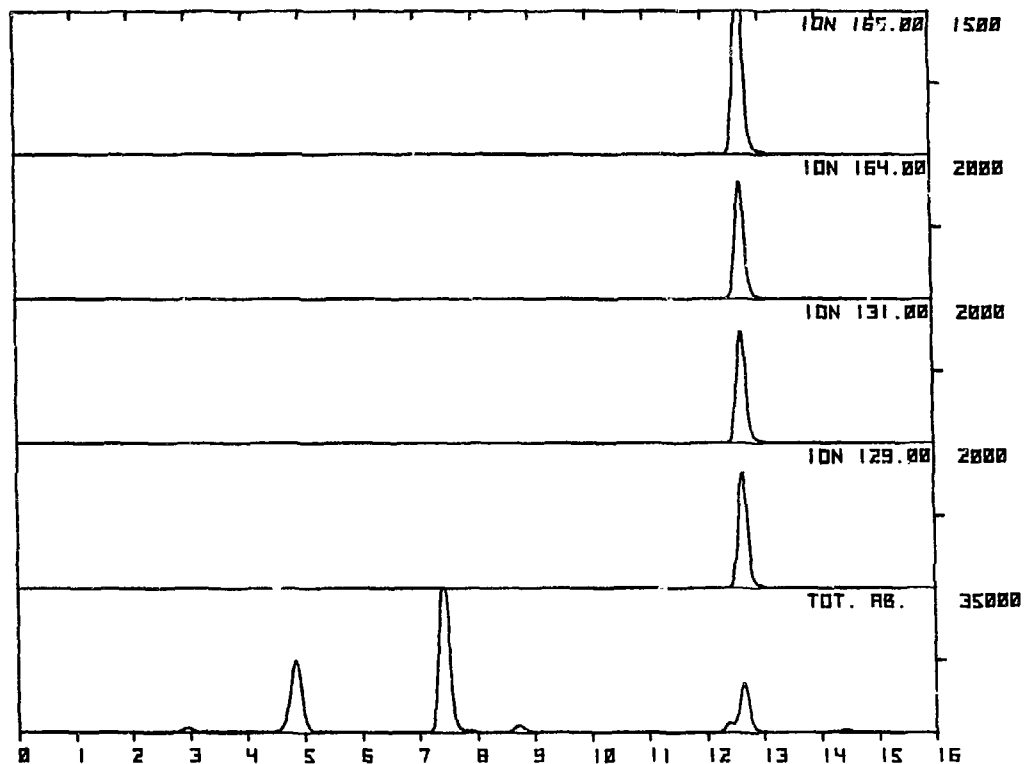
Figure 1 is an example of how an identification is made based on analysis by GC/MS. Mass spectral data was recorded throughout the run and stored on floppy disks. Under the conditions of the analysis, a retention time of 12.6 min was characteristic of tetrachloroethylene. The specific ions characteristic of tetrachloroethylene ( $m/z$ 's 129, 131, 164, and 166) were extracted from the GC/MS data and plotted as specific-ion-current profiles. These ions are present and maximize at the same retention time. Thus, tetrachloroethylene was determined to be in the water sample.

As previously stated, the chromatographic methods presuppose a high degree of certainty that the sample contains a pollutant from a particular compound class. The GC/MS methods 624 and 625 make no such supposition. The mass spectrometer is used as a universal detector and thus, may be used to screen for all chemicals on the priority pollutant list. For this reason, method 624 and 625 were used in the analysis of the ORGDP wastewater.

#### SAMPLING

Proper sample collection and preservation is critical and may affect the validity of data collected during the analysis. Samples to be analyzed for the volatile fraction (method 624) were collected as "grab samples." Sample vials were filled to overflowing (zero headspace) sealed, refrigerated, and analyzed within 14 days. The exclusion of headspace is imperative to assure the volatiles remain in the water until analysis.

Samples collected for liquid/liquid extraction were composite samples taken over a prescribed period of time and pooled. The samples were refrigerated until extraction, usually within seven days.



STORES #2 10/27/81  
TETRACHLOROETHYLENE MAJOR IONS

Figure 1

IDENTIFICATION BASED ON GC/MS ANALYSIS

## SAMPLE CONCENTRATION METHODS

### Purge-and-Trap Method

The purge-and-trap technique was developed by Eellar and Lichtenberg of the EPA and, in general, is applicable to the trace analysis of organic compounds that have a low solubility in water and a high vapor pressure.<sup>5</sup> The method uses an inert gas, such as helium, passing through the sample to transfer the organics from the aqueous phase to the gas phase. The organics are collected by adsorption on a porous polymer trap which is subsequently heated and backflushed with helium to introduce the organics to the chromatographic system. This sequence of events was automated by interfacing a Hewlett-Packard 7675A purge-and-trap sampler to the GC/MS system. The sequence of events for an analysis are illustrated in Figure 2 and are described below.

1. In the standby mode, cooling air is applied to the trap while the sample, in the purge chamber, equilibrates with room temperature. The trap is continually purged with helium.
2. With the rotation of the eight-port valve, the volatiles are purged from the sample to the trap.
3. After a prescribed purge time, the trap is thermally desorbed at a pre-set temperature and backflushed into the GC. This is the beginning of the chromatographic run.
4. After a prescribed desorption period, the trap heats to a temperature fixed at 50°C above the desorption temperature and is purged to vent.
5. After an appropriate vent period, the sampler returns to the standby position and is ready for another sample.

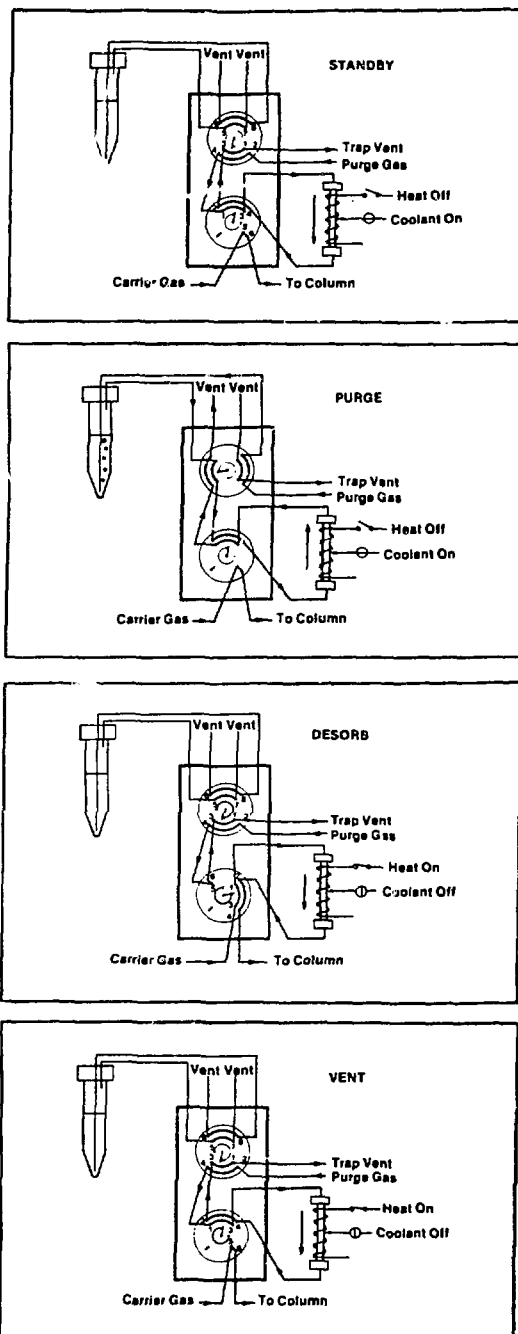


Figure 2

OPERATION OF PURGE-AND-TRAP APPARATUS

Steps 4 and 5 take place while the chromatographic run is in progress. Steps 1 and 2 occur independently of GC operation. Thus, the purge sequence can be initiated on a new sample while the current chromatographic run is in progress. Automated control of this process, not only decreases analysis time and manual errors, but also improves reproducibility.

This scheme of analysis has several potential problem areas. The carrier gas must be ultrapure. Low-level contaminants within the carrier gas will be concentrated on the trap and interfere with the analysis. A second source for contamination is the sample itself. Occasionally a sample will foam excessively when purged. If the foam enters the transfer lines and the trap, the system will be contaminated and must be cleaned before proceeding. A third source for error is cross contamination between samples. This is likely to occur after analyzing samples or standards with a high level (ppm) of volatile organics. After such an analysis, a sample blank (organic-free water) should be run to ensure the trap has been effectively desorbed.

The chromatographic column utilized for the volatile fraction was a 6-ft glass, packed column of Carboxpack C/O.1 percent SP-1000. The initial column temperature of 70°C was held for two minutes then programmed to 200°C at 8°C/min.

#### Liquid/Liquid Extraction

Liquid/liquid extraction with a low-boiling solvent is a time-honored technique in organic analysis. It is amenable to a wide variety of compounds and large concentration factors may be realized. The pH of the water is adjusted prior to extraction in order to obtain the acid or basic fraction. The 1 to 3-liter water sample is then extracted three times with methylene chloride. The combined extracts are dried and concentrated.



Methylene chloride is the recommended solvent for general purpose extractions. It is commercially available in very pure form (distilled in glass from Burdick and Jackson) has a low toxicity, a low-boiling point, and a polarity to attract a wide variety of organics.<sup>6</sup>

Glassware must be free of contamination. For each set of samples, a solvent blank is required for verification that, not only glassware, but solvents are free of organics. It is recommended that glassware used in this scheme of sample preparation be isolated in storage from other laboratory glassware.

Extreme care must be exercised to preclude the introduction of phthalate esters into the sample as a result of the extraction process. Phthalate esters are common plasticizers and are ubiquitous to the average laboratory environment.

The basic extracts were analyzed on a 6-ft glass, packed column of 3 percent SP-2250 on 100/120 Supelcoport. The column temperature was held isothermal for 4 minutes at 70°C, then programmed to 270°C at 8°C/min.

The acid fractions were chromatographed on a 3-ft glass, packed column of 1 percent SP-1240 DA on 100/120 Supelcoport held isothermally at 70°C for 2 minutes, then programmed at 8°C/min to 170°C.

#### INSTRUMENTATION AND CALIBRATION

All samples for this project were analyzed on a Hewlett-Packard 5992 GC/MS equipped with a dual floppy disk system for data acquisition and manipulation. The HP 5992 is equipped with software to automatically calibrate the mass spectrometer and to optimize sensitivity and resolution based on a perfluorotributylamine (PFTBA) standard. When using GC/MS as a quantitative tool, ion source tuning can affect response factors. The EPA

has suggested the use of decafluorotriphenylphosphine (DFTPP) as a convenient mechanism to evaluate ion source and detector response. For this purpose, an optional "Autotune" program is provided for the HP 5992, which will normalize all detected spectra to the DFTPP standard. Normalized spectra are achieved by multiplying the raw abundances by standardization factors in software during data acquisition.

#### QUALITY CONTROL MEASURES

Standard quality assurance practices were utilized in this project. These include method blanks, field replicates, field blanks, and surrogate standards.

A method blank is an aliquot of organic-free water which is subjected to the same extraction and analysis process as the samples. This is to ensure that the glassware, reagents, and extraction process are not contributing contaminants.

Replicate samples were periodically collected in the field. These replicates are analyzed to ensure the integrity of the sampling process.

Field blanks were used in method 624 to ensure that no volatile organics leaked through the sample vials. A field blank is an aliquot of organic-free water which is transported to the sampling site and back in the same type sampling vial used for sample collection.

Surrogate standards were used in method 624 to monitor the effectiveness of the purge-and-trap apparatus. Three compounds (bromochloromethane, 2-bromo-1-chloropropane, and 1,4-dichlorobutane) were spiked into each sample and standard solution analyzed by the purge-and-trap technique. These are the surrogate standards suggested in method 624.

Figures 3 and 4 are examples of fortified samples. A mixture of organics was spiked into a water blank and analyzed. It is interesting to note that in this scheme of analysis, N-nitrosodiphenylamine (NDPA) decomposes in the hot GC injection port to diphenylamine (DPA) and is detected as such. If the water sample to be investigated is suspected to contain NDPA, the analyst must utilize a clean-up procedure to remove potential DPA interference. Likewise, 1,2-diphenylhydrazine decomposes on column to azobenzene and is detected as such.

### RESULTS

#### Method 625

Figures 5 and 6 are typical of results obtained for the basic and acidic extractables. Each figure is a plot of the total-ion-current chromatogram (TOT.AB.) and specific-ion chromatograms (ION 43, etc.). In Figure 5, the baseline is an unresolved envelope under which many compounds lie. This chromatographic pattern is indicative of a hydrocarbon oil. Specific-ions 43 m/z and 57 m/z are characteristic of aliphatic hydrocarbons, and a plot of these individual ions duplicates the total-ion-chromatogram. To insure the absence of priority pollutants, the total-ion-current chromatogram is examined for specific-ions characteristic of those pollutants, as previously described.

Figure 6 represents the acid fraction of a water sample and contains a major peak. Although not a priority pollutant, mass spectral data suggests the peak to be diethylene glycol monobutyl ether (Butyl Carbitol), commonly used as a solvent for oils and a plasticizer intermediate.

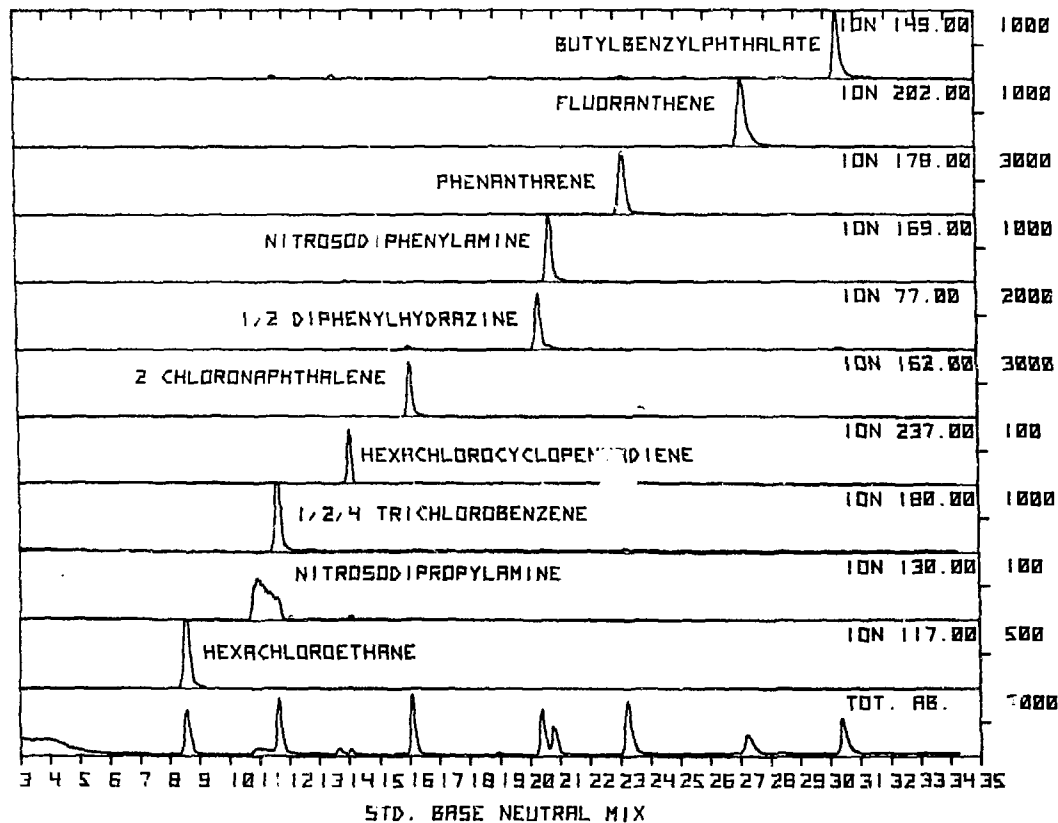


Figure 3

SPECIFIC IONS EXTRACTED FROM TOTAL-ION-CHROMATOGRAM FOR BASE NEUTRAL FRACTION

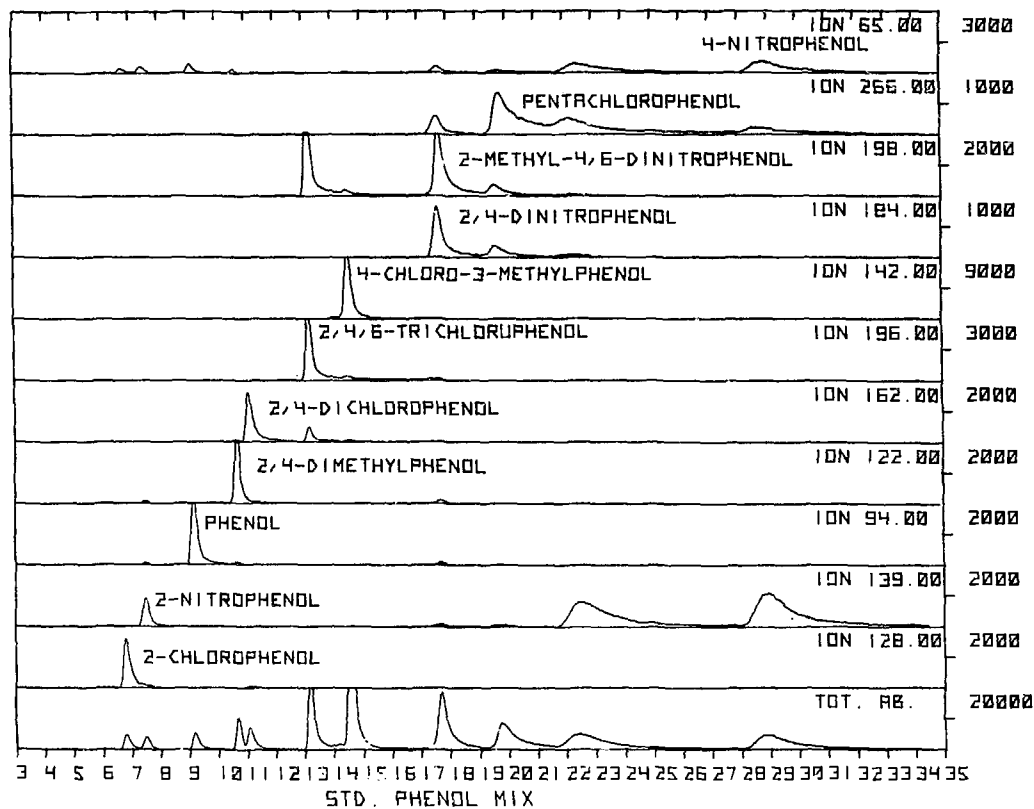
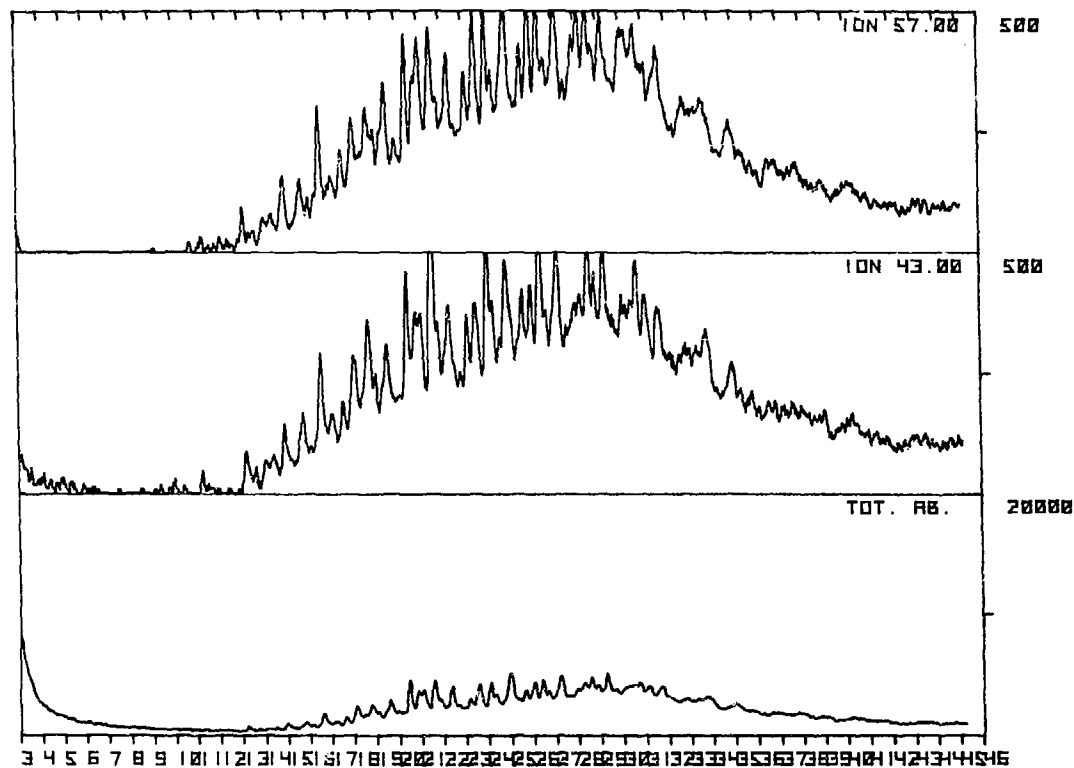


Figure 4

SPECIFIC IONS EXTRACTED FROM TOTAL-ION-CHROMATOGRAM FOR ACID FRACTION



81/10/4 K1407 10/1/81 BASIC FRACTION

Figure 5

EXAMPLE OF "SAMPLE" BASIC FRACTION

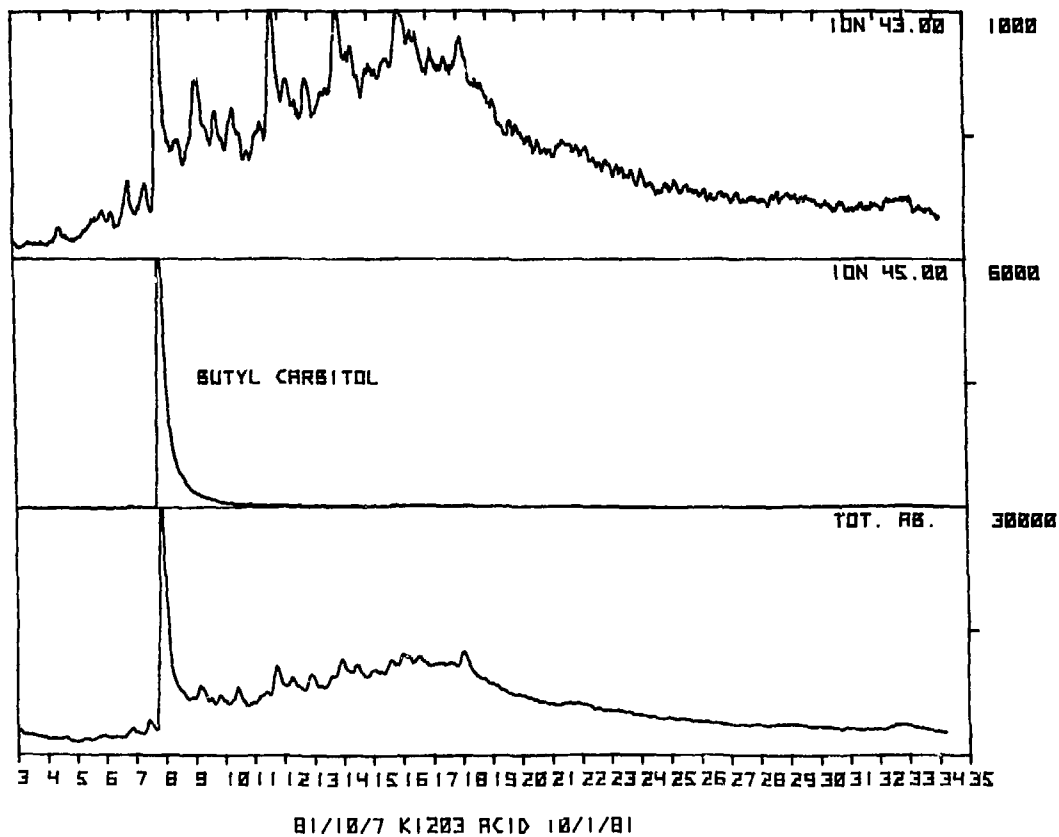


Figure 6

EXAMPLE OF "SAMPLE" ACID FRACTION

Although numerous organic compounds were detected in the acid and basic fractions of the ORGDP wastewater, no compounds from the priority pollutant list exceeded the minimum detection limits of the method. The minimum detection limits vary (10 ppb to 250 ppb) depending on the compound.

#### Method 624

Numerous organics were detected in the volatile fraction of the ORGDP waste water. These organics are listed in Table 5. The limit of detection for this method was 10 ppb for those organics reported.

TABLE 5

#### Organics in Volatile Fraction of the ORGDP Wastewater\*

| Compound              | Concentration<br>(ppm) | Compound                 | Concentration<br>(ppm) |
|-----------------------|------------------------|--------------------------|------------------------|
| Chloroform            | <.01 - 0.2             | Benzene                  | <.01                   |
| Trichloroethylene     | <.01 - >2.0            | 1,1-Dichloroethylene     | <.01 - 0.03            |
| 1,1,1-Trichloroethane | <.01 - >2.0            | Methylene Chloride       | <.01 - 1.0             |
| Tetrachloroethylene   | <.01 - 0.3             | \$Methyl Ethyl Ketone    | <.01 - 0.3             |
| Toluene               | <.01 - 0.2             | \$Methyl Isobutyl Ketone | <.01 - 0.1             |

\* Includes drainlines sampled after January 1982.

\$ Not on priority pollutant list.

Figures 7 and 8 are representative of the specific characteristic ions extracted from the GC/MS data. Also apparent in these figures is one of the spiked surrogate standards, bromochloromethane.



### CONCLUSIONS

The methods outlined in this paper are those proposed by the EPA and are subject to comment and modification. Present work by the EPA and EPA contractors is directed towards the applicability of multicomponent isotope dilution GC/MS for the determination of priority pollutants in industrial effluents.<sup>7</sup> An interesting and potentially useful aspect of this type of analysis is the ability to perform an important quality assurance/quality control activity using the labeled analogs of the compounds of interest. The close relationship between the recoveries of a naturally abundant compound and its labeled analog suggests the use of the labeled species as a check on absolute recovery.

Whatever form the final regulations take, we as waste dischargers must demonstrate our ability to monitor our effluents using the specified methods in order to obtain a NPDES permit. Therefore, the analyst must remain abreast with the proposed methodology and be prepared to implement them.

Laboratory personnel should also be made aware of their legal responsibilities. Knowingly falsifying data or misrepresenting a report in any way is a criminal act and punishable by fines of up to \$10,000 and/or six months imprisonment.

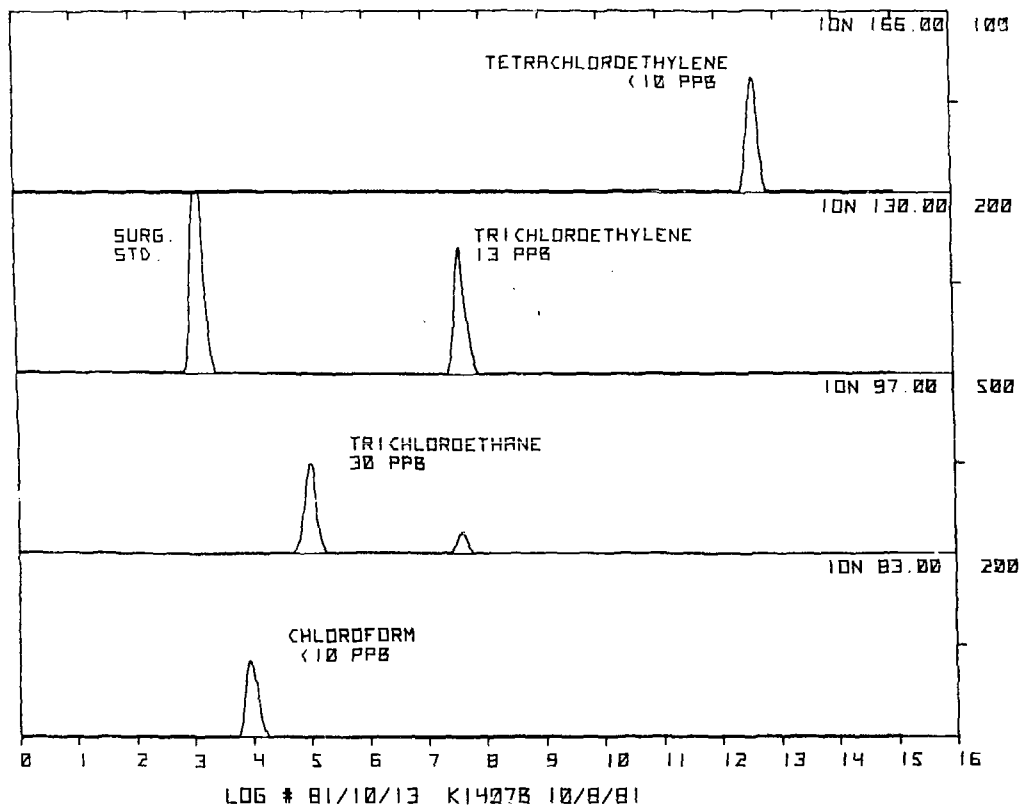


Figure 7

RESULTS FROM "SAMPLE" VOLATILE FRACTION

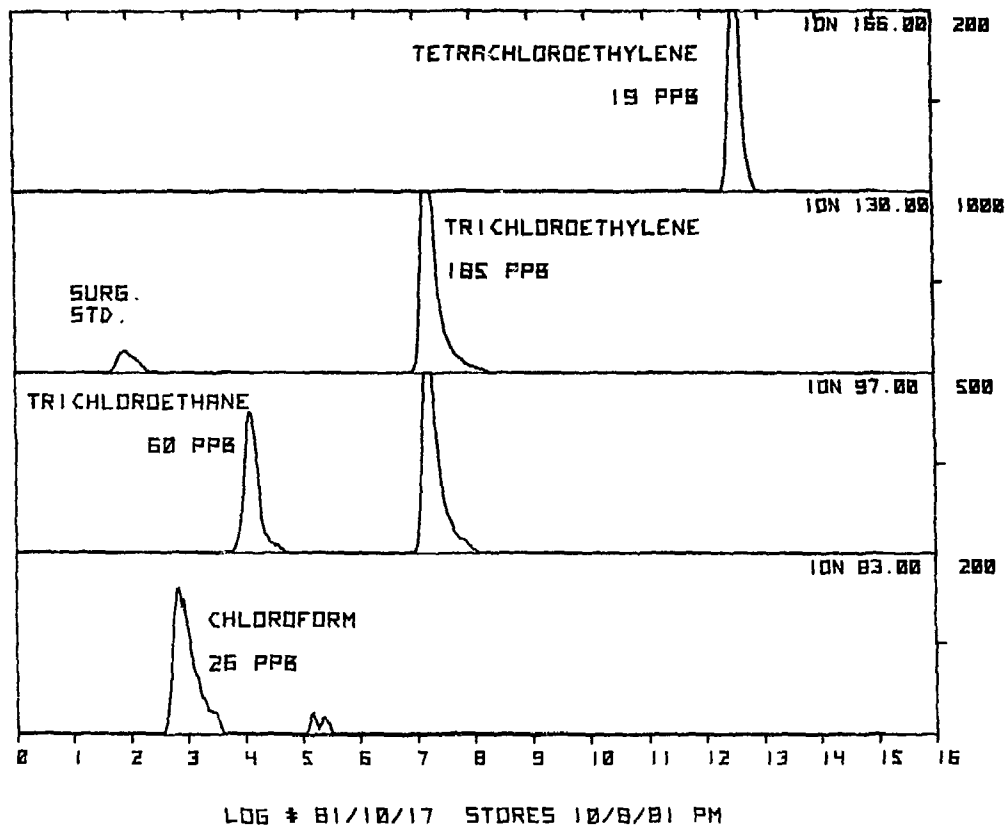


Figure 8

RESULTS FROM SAMPLE VOLATILE FRACTION

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*Session 3: SPILL CONTROL AND COUNTERMEASURES*

*Chairperson: R. C. Baker*

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## SPILL EXPERIENCE AT ORNL - 1978 to 1982

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## ABSTRACT

The history of oil and chemical spills at Oak Ridge National Laboratory for the past four years is reported, including their causes and the remedial measures taken. The organizational structure that has evolved for handling spills is described, including the role of each ORNL division in the program. Particular initiating events which have been characteristic of more than one spill have been identified and the preventive actions taken for them described. Finally, future plans to improve the timeliness and adequacy of spill response are discussed.

INTRODUCTION

During the four year period from 1978 to the present, ORNL's Department of Environmental Management has responded to 60 spills - 37 of these spills involved oil (Table 1) and 23 involved other chemicals (Table 2). While only a small fraction of these spills had any environmental significance, evaluations of the causes of spills and of ORNL's response to them have identified areas where improvements were needed. This paper will provide a description of these evaluations, describe the organization that has evolved at ORNL to respond to spills, and show how the evaluations have been and are being used to improve ORNL's performance in the area of spill response.

SPILL EVALUATIONS

An analysis of the causes of the spills listed in Tables 1 and 2 is shown in Table 3. For oils, the major cause for spills appears to be mechanical failures. This is probably true at ORNL for two reasons:

1. After a number of oil spills in late 1978 and early 1979, a Laboratory-wide Waste Oil Investigation Committee was established

\*Research sponsored by the U. S. Department of Energy by Union Carbide Corporation Nuclear Division under Contract W-7405-eng-26.

Table 1History of Oil Spills at ORNL (1978-1982)

| <u>Date</u> | <u>Location</u> | <u>Type of Oil</u> | <u>Quantity</u> | <u>Cause*</u> | <u>Reportable</u> |
|-------------|-----------------|--------------------|-----------------|---------------|-------------------|
| 7/14/78     | 4508            | Lubricating        | 10 gal          | C             | No                |
| 8/3/78      | 2528            | Coal Oil           | 1 lb            | C             | No                |
| 11/29/78    | 7000            | Diesel             | 4 gal           | O             | No                |
| 12/21/78    | 7000            | Mixed              | 50 gal          | C             | No                |
| 1/9/79      | 7802            | Lubricating        | 1 gal           | C             | No                |
| 3/4/79      | 2519            | Diesel             | 50 gal          | O             | NC**              |
| 3/6/79      | 3025            | Hydraulic          | 20 gals         | M             | Yes               |
| 3/15/79     | 6010            | Transformer        | Unknown         | C             | Yes               |
| 7/5/79      | 1503            | Lubricating        | Unknown         | O             | Yes               |
| 7/10/79     | 7005            | Gasoline           | 1 gal           | O             | No                |
| 7/16/79     | 2519            | Hydraulic          | 5 gal           | M             | No                |
| 7/26/79     | 2519            | Lubricating        | 1 gal           | C             | No                |
| 7/26/79     | 7822            | Diesel             | 30 gal          | M             | No                |
| 7/31/79     | 7000            | Diesel             | 2 gal           | C             | No                |
| 8/1/79      | 2519            | Diesel             | 15 gal          | C             | Yes               |
| 8/2/79      | 0954            | Hydraulic          | 5 gal           | M             | No                |
| 10/2/79     | 5000            | Lubricating        | 1 gal           | M             | No                |
| 10/15/79    | 7902            | Hydraulic          | 1 gal           | M             | No                |
| 10/26/79    | 2528            | PNA                | 1 gal           | C             | No                |
| 1/4/80      | 7602            | Lubricating        | 1 gal           | C             | No                |
| 2/25/80     | 7813            | Hydraulic          | 2 gal           | M             | No                |
| 4/16/80     | 1504            | Hydraulic          | 1 gal           | M             | No                |
| 4/29/80     | 7822            | Hydraulic          | 2 gal           | M             | No                |
| 5/18/80     | 2536            | Diesel             | 1 gal           | C             | No                |
| 6/2/80      | 7822            | Hydraulic          | 4 gal           | M             | No                |
| 9/26/80     | 6010            | Cooling            | 100 gal         | M             | Yes               |
| 2/2/81      | 1000            | Diesel             | 5 gal           | C             | No                |
| 3/4/81      | 2525            | Mixture            | 1 gal           | O             | No                |
| 5/6/81      | 3026            | Transformer        | 1 qt.           | M             | No                |
| 5/6/81      | 3044            | Mixture            | 20 gal          | C             | No                |
| 7/27/81     | 3012            | PCB                | 100 gal         | M             | No                |
| 7/27/81     | 2528            | Coal Oil           | 1 gal           | O             | No                |
| 8/3/81      | 6000            | PCB                | 1 gal           | C             | No                |
| 8/8/81      | 4500-S          | Hydraulic          | 5 gal           | M             | Yes               |
| 9/3/81      | 4500-S          | Mixture            | Trace           | C             | No                |
| 10/6/81     | 7822            | Hydraulic          | 1 gal           | M             | No                |
| 1/21/82     | 7000            | Mixture            | 10 gal          | C             | NC**              |

\*Causes of spills are as follows:

C = Container failure

M = Mechanical failure

O = Operator Error

\*\*Non-compliance - No visible sheen but a violation of NPDES permit for oil and grease



Table 2

History of Chemical Spills at ORNL (1978-1982)

| <u>Date</u> | <u>Location</u> | <u>Type of Oil</u>   | <u>Quantity</u>   | <u>Cause*</u> | <u>Reportable</u> |
|-------------|-----------------|----------------------|-------------------|---------------|-------------------|
| 4/27/79     | 2528            | Methyl<br>Napthalene | 10 gals           | C             | No                |
| 8/30/79     | 7001            | Amyl Acetate         | 1 pt.             | C             | No                |
| 10/17/79    | 3019            | Nitric Acid          | Trace             | C             | No                |
| 10/29/79    | 2519            | Flyash/Water         | 1000 gals         | D             | No                |
| 11/27/79    | 5500            | Drilling Mud         | Unknown           | D             | No                |
| 12/26/79    | 4500N           | Developer            | Unknown           | C             | No                |
| 2/4/80      | 1000            | Fluoroscein          | Trace             | C             | No                |
| 3/20/80     | 3103            | Sulfuric Acid        | 1 gal             | O             | No                |
| 3/24/80     | 3544            | Sulfuric Acid        | 16 gals           | O             | NC**              |
| 5/20/80     | 3019            | Paint/Water          | Unknown           | O             | No                |
| 7/21/80     | 4500-S          | Mercury              | 100 g             | U             | No                |
| 9/2/80      | 4500-S          | Mercury              | Trace             | M             | No                |
| 11/25/80    | 3592            | Calcium<br>Hydroxide | 15 lbs            | O             | NC**              |
| 12/4/80     | 1000            | Flyash               | 1 ft <sup>3</sup> | C             | No                |
| 2/13/81     | 6010            | Ethylene Glycol      | 3,000 gals        | M             | No                |
| 3/19/81     | 7013            | Sulfuric Acid        | 6 gal             | C             | No                |
| 5/5/81      | 3119            | Paint/Water          | 5 gal             | O             | No                |
| 5/13/81     | 3500            | Mercury              | Puddle            | O             | No                |
| 5/18/81     | 2525            | Mercury              | 3 lbs             | U             | No                |
| 5/27/81     | 3049            | Detergent            | 2 gals            | C             | No                |
| 10/26/81    | 4500-S          | Ethylene Glycol      | 20,000 gals       | M             | No                |
| 1/5/81      | 4500-S          | Fluoroscein          | Trace             | O             | No                |
| 2/4/82      | 7860            | Cement               | Unknown           | O             | NC**              |

\*Causes of spills are as follows:

- C = Container failure
- D = Design problem
- M = Mechanical failure
- O = Operator error
- V = Unknown cause

\*\*Non-compliance - Not reportable as a spill but as a NPDES permit violation for pH.

Table 3  
Causes of Spills at ORNL

A. Oil

| <u>Cause</u>       | <u>1978</u> | <u>1979</u> | <u>1980</u> | <u>1981</u> | <u>1982</u> |
|--------------------|-------------|-------------|-------------|-------------|-------------|
| Operator Error     | 1           | 3           | -           | 2           | -           |
| Container Failure  | 3           | 6           | 2           | 4           | 1           |
| Mechanical Failure | -           | 6           | 5           | 4           | -           |

B. Chemical

| <u>Cause</u>       | <u>1978</u> | <u>1979</u> | <u>1980</u> | <u>1981</u> | <u>1982</u> |
|--------------------|-------------|-------------|-------------|-------------|-------------|
| Operator Error     | -           | -           | 4           | 4           | 1           |
| Container Failure  | -           | 4           | 2           | 1           | -           |
| Mechanical Failure | -           | -           | 1           | 2           | -           |
| Unknown            | -           | -           | 1           | 1           | -           |
| Design Problem     | -           | 2           | -           | -           | -           |

to identify where oil was stored at ORNL and to ensure that it was contained adequately, and

2. A presentation to heighten environmental awareness was made by ORNL's Environmental Coordinator to all Laboratory personnel; this presentation specifically dealt with oil and its effects on the environment.

This second reason is also a likely cause for the dramatic increase in spills reported during 1979.

Of the mechanical failures reported, over half were caused by ruptured hydraulic lines. Spills caused in this way are particularly troublesome, since they generally occur in undeveloped areas (e.g., construction sites), where containment of the spill is difficult to achieve. In an attempt to prevent the recurrences of such spills, ORNL's Plant and Equipment Division (the division responsible for maintenance at ORNL) was requested in 1980 to institute an inspection and replacement program for hydraulic lines. The results of this request have been significant - in the 18 months since the request was made, only one hydraulic line failure has occurred.

For other chemicals, the pattern is completely different. In this case, two-thirds of the spills are due either to operator errors or to container failures. This pattern is consistent with the routine handling that these chemicals receive and their generally nonhazardous nature. Nevertheless, it pointed out an environmental problem which required addressing. ORNL's response has been both general and specific. To handle the problem of chemical storage and disposal in general, procedures either have been or are being written to cover storage of chemicals in laboratories, diking of storage tanks, and disposal of unwanted chemicals. Furthermore, in each specific spill event, the cause of the spill and its consequences are brought to the attention of the responsible division's management; in some cases, the division is also charged for the cost of the spill cleanup.

Experience gained from the spills described above has also been used in the continuing development of ORNL's spill response capability. The results of this development to date are discussed in the following sections.

### RESPONSE TO SPILLS AT ORNL

Responding to a spill involves three phases:

- identifying the source of a spill,
- stopping the spill at its source, and
- cleanup of the spill area.

Problems have occurred in identifying spilled materials, especially when the material is some form of oil. To address this problem, ORNL's Analytical Chemical Division has obtained a sample of each type of oil used at the Laboratory and obtained a "fingerprint" of it using gas chromatography. With this identification system in place, responding to an oil spill is assisted in two ways:

- when the spill is first discovered, a sample of the spilled oil can be analyzed to identify possible sources, and
- when a suspected source is determined, a second sample can be analyzed to see if the source oil matches the spilled oil.

This system has helped personnel responding to spills on numerous occasions.

Another useful lesson learned from previous spills has to do with dyes - cooling lines at ORNL contain fluorescein dye which help to identify leaks when they occur. Unfortunately, this same dye has also been used in tracer studies and in piping system tests. The coincidence has led, at times, to confusion about a spill's source. To avoid this problem, when a dye is required for testing, other colored dyes (e.g., rhodamine) are considered.

The experience gained in responding to spills listed in Tables 1 and 2 has also helped to streamline the process of obtaining assistance from other Laboratory divisions. To ensure a timely response, the divisions responsible for operations and maintenance at the laboratory have both appointed people to coordinate recovery from a spill and set up special accounts to accumulate their costs in this effort. ORNL's Analytical Chemistry Division has also appointed a coordinator to ensure that samples from a spill are expedited through the analytical process. Such cooperation is vital to the effective response to a spill situation.

### FUTURE WORK

While the above steps have helped both to reduce the number of spills and to improve ORNL's response to the spills that do occur, work is still needed, especially in two areas: inventorying storage sites around the laboratory and education on the prevention of and response to spills. Regarding the inventory of hazardous materials around the Laboratory, a system is being developed to track such materials from the time they arrive at ORNL to the time they are disposed of.

As can be seen from Table 3, more education is needed for the people handling chemicals regarding their environmental hazards. Plans for such training are currently being made. Training for people responding to spills is also important; to this end, a computer program which can either simulate a spill or be used as a resource in the event of a spill is being developed. This program is the topic of the next paper.

### CONCLUSIONS

Information on spills can be a valuable resource in the detection of environmental problems. This resource has been used at ORNL to prevent the occurrence of future spills and to enhance ORNL's spill response capability.

Ref

THE SPILLS PROBLEM  
AND  
APPLIED ARTIFICIAL INTELLIGENCE

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Key Words

Artificial Intelligence, Spills, Environmental Monitoring,  
Expert Systems

ABSTRACT

We describe an Artificial Intelligence program designed for assisting in the location, assessment, and cleanup of hazardous spills and for the training of spills personnel who must deal with these matters. Because the program is of a type which may be unfamiliar to the reader, we devote some space to a discussion of the general attributes of the class of Artificial Intelligence programs known as Expert Systems and still more to a description of the system we employ, Carnegie-Mellon's OPS5. We illustrate our discussion with a variety of rules, some taken directly from the SPILLS program.

INTRODUCTION

When it was announced during the spring of 1980 that a conference<sup>1</sup> was to be held devoted to the evaluation of the several so-called EXPERT systems programs, C. K. Johnson of the ORNL programmed reasoning methodology panel (PRM) was asked to prepare the test problem with which each system would have to deal. Perhaps because so much of the work in Artificial Intelligence (AI) has been so abstract in character, it was suggested that the test problem should be of a more applied nature than some of the problems with which the various Expert Systems might previously have had to deal. To that end C.K. Johnson spent considerable time searching

for a problem combining just the right proportions of elements from real world and pure research environments. His choice was the result in part of a desire to incorporate something of Laboratory interest and importance which could draw attention to the work then under way by various members of the PRM panel. The SPILLS problem satisfied these requirements admirably. There was a local body of spills experts willing to collaborate in the preparation of material for the problem, an endless pile of documentation and literature, and a willing and able assistant in Sara R. Jordan, one of the charter members of the PRM panel. In due time there emerged a truly massive document which would soon be the object of a week long assault by eight teams of AI researchers and their respective EXPERT systems.

Although not one of these eight systems emerged as clearly the best, one did prove itself so easy to use, so generally powerful, and so broadly applicable as to attract immediate and considerable attention. This was the Carnegie-Mellon OPS5<sup>2</sup> production rule system, the latest in a series of such programs based on the work of Forgy and McDermott<sup>3 4 5</sup>. In less than one week the OPS5 team produced a program which addressed a number of aspects of the spills problem and showed promise of dealing successfully with many of the others. It was in response both to the OPS5 success and to its apparent potential that the ORNL Spills group decided to investigate extensions to the CMU "kernel" program in the hope of producing a thoroughly competent artificial spills expert. In the next section we discuss some of the goals which were established for the program.

### SYSTEM GOALS

The initial goals of the SPILLS program are summarized by the flow chart of Figure 1a which represents in a somewhat abbreviated fashion the steps which a human spills expert would take from the moment of the first report of a spill up to, but not including, the completion of all appropriate documentation following its cleanup. Most of these goals have been implemented in the sense that the program has either methods of achieving them directly or sets of instructions for guiding a technician in the associated tasks. To facilitate the system's use by untrained personnel a "help" file is being implemented which will eventually embody tutorial information about all system functions. A user who gets "stuck" or who is unsure what the system is currently doing can easily invoke the help subsystem which will respond in a way and at a level suitable to the user's perceived needs.

Some care has been taken from the start to ensure that an

intermediate goal of the system, that of training, could eventually be satisfied. The intent here is to present a spills trainee with a fictitious spill, letting the program monitor his cleanup procedure and correct or advise him as necessary. This capacity to cast the program in the role of intelligent instructor should prove invaluable in a field where there are not enough experts to provide training for those who need it.

Farther in the future the system will be given the capacity to fulfill all the requirements for spills documentation automatically (Figure 1b). This attribute can be accommodated in part by providing a fill-in-the-blank mode of operation. For the full implementation of this goal, particularly its aspect of automatic report writing, the system will require the incorporation of advanced natural language processing techniques. One last goal, perhaps the hardest to achieve, is the implementation of a learning capacity which would permit the system to acquire knowledge from its experience in dealing with new spills situations and from stored data defining previous spills with which the system had yet not had to deal. This acquired knowledge would be incorporated as rules and methods for dealing with spill types which the system would previously have been unable to handle.

### EXPERT SYSTEMS

Expert Systems constitute the first broadly applicable products of applied Artificial Intelligence research. These systems take many forms and embody as many esoteric concepts but it is the function of each to bring these concepts to bear on problems in a manner which facilitates, rather than confounds its use. The principal characterizing attribute of all these systems is the capacity for assimilating to a greater or lesser degree the knowledge possessed by a human expert. It is not surprising that the implementation of this artificial intelligence capacity has provided much insight into the nature of human intelligence, particularly the sort by which we recognize the quality of expertise. It has proven remarkably difficult to extract from (even quite willing) experts just those attributes which so qualify them, perhaps because expertise is so elusive a characteristic. Far more than just the sum of one's acquired knowledge, it has been defined as the embodiment in varying degrees of instinct, rules of thumb, capacity for the educated (and sometimes inspired) guess, all able to draw in some not well understood but clearly synergistic way on the expert's accumulation of facts and relationships.

We tend to regard thinking, at least that of the



scientific sort, as a well structured and logical process but in fact, much, if not most, of the (creative) thinking which an expert does bears little resemblance to the clear and inexorable progression by which he may later express the results of his thought process, a process which, because of its free-ranging, conceptually unbounded, "approximate" nature has come to be referred to as "fuzzy reasoning". It is this "fuzziness" which, because it is so difficult to define, is so difficult to implement in a machine. Nevertheless, it is this characteristic which the best "Expert Systems" do attempt to emulate. Their success in so doing hinges pivotally on the observation that much of what the expert in any field does involves the (probably unconscious) manipulation of relatively small "chunks" of his knowledge. There may be (almost certainly are) enormously many of these "chunks" and the manipulations are surely complex and numerous, but there is here the clue which makes machine emulation possible. If a way can be found for representing to a computer the "chunks" as separate, easily manipulated structures, each of which was largely independent of the rest, and if a "manipulator" program could be written incorporating some general knowledge and some "chunk-dependent" knowledge about the kinds of manipulations which might prove useful, the emulation capability we seek should be realizable. In one way or another, Expert Systems support both of these functions to some degree.

Several schemes have been developed for performing the "chunking" and manipulation operations suggested above. The most "user-friendly" of these permit the construction of programs which at first glance seem to possess no recognizable structure at all. They appear instead to be collections of isolated facts united more by their relevance to the single program domain than to each other. The form of this "fact representation" depends of course upon the system in use but the apparent disjointed aspect characterizes them all. Nothing resembling the orderly (algorithmic) progression of Fortran or Basic programs can be discerned. To all appearances the Expert System programs have been assembled a few pieces at a time, each new piece having been added as it occurred to the "programmer". The pieces are our "chunks" and many of them probably have been added in just this seemingly haphazard fashion. Note, however, that there is no suggestion here that the "chunks" themselves are in any way haphazard. Upon examination, it would be discerned that each is a highly structured embodiment of some small facet of the human expert's knowledge. Some may represent rules of thumb, others may describe sophisticated mathematical concepts and the techniques for their implementation, still others might incorporate directions for modifying "chunks" or the building of entirely new ones. It is the function of the "manipulator" to bring order, direction, and purpose to this

formless mass of "incremental" knowledge. Since these concepts, "chunk" and "manipulator", will seem far more comfortable when viewed in the context of a specific "Expert System" than they can be in the abstract, we turn now to a brief description of one of the most widely used, the Carnegie-Mellon OPS5 system.

### THE OPS5 EXPERT SYSTEM

As suggested above, Expert Systems can be based upon any of several conceptual frameworks, each resulting in a subclass of the general type. The class of which OPS5 is a member is known by the term which describes its most characteristic feature, the production rule, or simply, the production. In production systems the "chunks" of knowledge are expressed by the production rules, the manipulation of which is managed by a (usually) distinct "interpreter". In OPS5 the rules are maintained in a part of memory called (reasonably enough) production memory. The facts or data (or anything else) upon which the rules may operate are stored in another memory section referred to as working memory. The interpreter provides the environment within which rules and working memory can interact with each other and with the world. A quick look at the general structures of a working memory element and a production rule will suffice to suggest how the two function together.

An OPS5 working memory element (WME) is a parenthesized list of quantities of the form,

(quantity1 quantity2 quantity3 .....quantityN) .

The quantities can be any numeric or natural language structures appropriate to the domain for which the system is intended. Since working memory elements can be quite long (several hundred components would not tax the system) it is often convenient to invoke a useful adjunct (which we discuss only in its simplest application), the "tab" function represented by the up-arrow symbol "^". Among other things this facilitates a bookkeeping feature which makes OPS much easier for most programmers to use. When this device is incorporated the resulting OPS5 structure is known as an "attribute-value" system. A working memory element in this representation has the form (where "att" abbreviates "attribute"),

(^att1 quantity1 ^att2 quantity2.....^attN quantityN) .

The "quantities" are still the entities of importance. The "attribute" entries serve only a place-holding function freeing the user from the necessity of keeping track of the

order of occurrence of quantities which comprise the WME. Thus, the above WME could just as well be written as

```
(^attN quantityN....^att2 quantity2...^att1 quantity1) .
```

Before continuing with a discussion of OPS5 rules we list a few specific examples of the working memory elements upon which they can act. Some of these are extracted from functioning Expert Systems, others are constructed simply for the purpose of illustrating one or another point. The simplest consists of but one quantity:

```
(start) .
```

A slightly more complex one which mixes "tabbed" and "non-tabbed" quantities might represent a member of a collection of elements representing the physical quantity temperature:

```
(temperature ^value 7) .
```

This example collects some of the physical attributes of a chemical compound:

```
(material ^name benzene ^molecular-weight 78 ^boiling-  
point ^80 ^molecular-formula C6H6 ^color clear  
^density .879) .
```

With this one we represent (part of) the formal structure of an algebraic expression:

```
(expression ^type quadratic ^string x * * 2 - 5 * x + 2  
= 0) .
```

In this last we establish a goal for a robot (to hold a technician at the door):

```
(goal ^status active ^want hold ^object technician  
^at door) .
```

These examples in no way exhaust the expressive power of working memory elements but they should be sufficient to illustrate something of their versatility. We will see how they are accessed, modified, and even constructed by OPS5 rules as we examine rule structure in the following several paragraphs.

An OPS5 rule, like an OPS5 working memory element, is a parenthesized list. Its structure is more extended and complex than that of the WME but can nevertheless be represented by the following simple, formal expression:

```

(p production-name
  (left-hand-side-condition-1)
  (left-hand-side-condition-2)
  :
  :
  (left-hand-side-condition-N)
-->
  (right-hand-side-action-1)
  (right-hand-side-action-2)
  :
  (right-hand-side-action-K)) ; K not necessarily=N.

```

We will not delve here into the intricacies of rule formalism but will instead attempt to illuminate rule structure by discussing a series of examples. We begin by considering the following very simple, almost self-evident one:

```

(p start-rule
  (start)
-->
  (write (crlf) now you've done it!)).

```

The `p` identifies this as a rule (or production). The production's name is "start-rule". The single left-hand-side-condition (LHS) requires that there be somewhere in working memory an element of precisely the form "(start)". The funny arrow lets the OPS5 interpreter separate the (LHS) part(s) from the right-hand-side-action (RHS) part(s). Everything to the right of the arrow is executed if the condition(s) of the LHS are satisfied and so the output device (printer, CRT, etc.) performs a carriage return line feed (crlf), and displays the indicated string. This scarcely constitutes a remarkable result; we could have accomplished the same thing in Basic. It is only when we begin to introduce more complicated left- and right-hand sides that things begin to get interesting. We expand our repertoire with the next example.

Let us suppose that the following items have been placed in working memory:

```

(number ^value 7)
(number ^value 2)
(number ^value 3)
(number ^value 15)
(number ^value -1)

```

We would like to find the element with the largest "value" entry. The following example introduces three new constructs which permit a single rule to accomplish our task.

```

(p find-largest
  (number ^value <v>)
  -(number ^value {<u> > <v>})
-->
  (write (crlf) the largest value in the set is <v>)) .

```

Again, the p identifies the entity as a production and the production's name is "find-largest". The second line requires that there be a WME whose first entry is the word "number" and whose second is some number to which the interpreter assigns our specified label "v". In the language of artificial intelligence this assigning function is known as binding. It is denoted in OPS5 by the first occurrence of a given variable (here "v") within the left and right angle brackets "<" and ">". Remember that the up-arrow is a bookkeeping convenience for the programmer. The OPS interpreter skips over the associated attribute listing to the adjoining quantity. Thus, as far as OPS is concerned, there are only two entries in the condition element, the word "number" and the variable <v>. Similarly, there are only two entries in each of our working memory elements, the word "number" and the number itself.

In the third line the prefix "-" indicates the negation of the following construct. Thus, there must not be a working memory element whose first entry is the word "number" and whose second is the quantity represented by the curly brackets. These brackets serve the function of imposing conditions on the quantity associated with a given attribute. Here we see that we bind the variable <u> (it is its first occurrence) to the quantity associated with the attribute "value" and compare (">") <u> with <v> to see if <u> is greater than <v>.

Finally, the last line (the single action for this rule) writes the indicated string, incorporating the value "v", only for the one v value (15) satisfied by the LHS conditions. An English paraphrase of our rule is,

```

If there is a WME whose entries are the word "number" and
  some number v,
and
If there is not a WME whose entries are the word "number"
  and some number u such that u is greater than v,
then
write "the largest value in the set is v" .

```

Those familiar with more algorithmic languages such as Fortran and Basic will recognize that a great deal of bookkeeping is being done here by the interpreter in order to execute the operations implied by our simple one rule search program. We can illustrate one or two more features of OPS

by noting two variations which result in an even simpler version. First, we can eliminate the curly brackets and the variable <u>. We included them simply to introduce the concept of conditional clauses. Since we do nothing later with the <u> we can rewrite the third line as

```
-(number ^value > <v>) .
```

OPS understands that we mean by this that there must not be a working memory element whose value entry exceeds the value already bound to v. A further simplification results from the elimination of the word "number" from our LHS conditions, for, as long as at least what is specified by them is found in the contents of working memory, the conditions are satisfied. Our simplified rule has the form,

```
(p find-largest
  (^value <v>)
  -(^value > <v>))
-->
(write (crLf) the largest value in the set is <v>)) .
```

Thus far we have seen that OPS possesses impressive bookkeeping power and have hinted at another aspect, that of pattern matching of LHS condition representations with working memory element representations. We have by no means completed a description of rule formulation nor can we hope to be exhaustive in our discussion of several important OPS attributes. We choose instead to illustrate with the following examples one of the most useful, the capacity for self-modification, a capacity which any system capable of supporting learning must surely possess. In the process we shall attempt to elaborate on one or two of the more important aspects of rule structure.

OPS5 supports several techniques for enabling a system (a rule set) to modify its structure in response both to its environment and to its assessment of its own state. The first of these provides a rule with the power to modify one or more of the working memory elements to which it has responded. Suppose that somewhere in working memory are the elements,

```
(goal ^want identify-chemical ^status active)
(actor ^name smiley ^role nil) ,
```

and that in production memory is the rule,

```
(p next-task
  (goal ^want <task> ^status active)
  (actor ^name <n> ^role nil))
-->
```

```
(modify 1 ^status pending)
(modify 2 ^role <task>)
(write (crlf) <n>: please <task>)) .
```

The first condition is satisfied by binding the variable <task> to "identify-chemical", the second by binding the variable <n> to "smiley". Thus, the rule "fires", modifying the status entry of the first WME to "pending" and the role entry of the second to the quantity bound to <task>, "identify-material". Finally the output device would display the string

```
smiley: please identify-chemical .
```

Out of the context of some other rules, this capacity to alter the contents of working memory may not seem as useful as it really is. Perhaps we can illustrate the point better by the following example involving a more extensive set of working memory elements and four rules which might respond to them.

We suppose that some hypothetical robot control OPS system has operated for a while, performing various tasks and depositing elements in its working memory. Among them are these:

```
(robot ^position x5-y7 ^on floor)
(object ^name wrench ^position x9-y5 ^weight light ^on
  floor)
(goal ^status active ^type move-to ^position x9-y5)
(goal ^status active ^type holds ^object wrench)
(goal ^status active ^type move ^object wrench ^to
  x2-y2) .
```

Among many others, these rules are found in production memory:

```
(p rob21
  (goal ^status active ^type move-to ^position <p>)
  (robot ^on floor ^position {<c> <> <p>} ^holds nil)
-->
  (write (crlf) move to <p>)
  (modify 1 ^status satisfied)
  (modify 2 ^position <p>))

(p rob31
  (goal ^status active ^type move-to ^position <s>)
  (robot ^on floor ^position {<c> <> <s>} ^holds {<w>
    <> nil})
  (object ^name <w>)
-->
  (write (crlf) move to <s>))
```

```

(modify 1 ^status satisfied)
(modify 2 ^position <s>)
(modify 3 ^position <s>))

(p rob70
  (goal ^status active ^type holds ^object <w>)
  (object ^name <w> ^position <q> ^on floor)
  (robot ^position <q> ^holds nil)
-->
  (write (crlf) pick up <w>)
  (modify 1 ^status satisfied)
  (modify 3 ^holds <w>))

(p rob90
  (goal ^status active ^type move ^object <o> ^to <r>)
  (object ^name <o> ^weight light ^position <> <r>)
  (robot ^holds <o>)
-->
  (make goal ^status active ^type move-to ^position
    <r>)) .

```

With the last of the above we introduce the second procedure for implementing self modification, the "make" command. We will discuss it when the rule which incorporates it fires. For the moment we put ourselves in the role of the OPS rule interpreter to better examine the system's behavior. We begin by looking to see which (if any) of the rules have left hand sides which could be directly, or by some binding of variable(s), matched to the contents of working memory. Emulating the interpreter we enumerate by rule the LHS conditions which are satisfied and the bindings (if any) which are implied:

```

rob21; condition 1, <p> bound to x9-y5,
      condition 2, <c> bound to x5-y7,

rob31; condition 1, <s> bound to x9-y5,

rob70; condition 1, <w> bound to wrench,
      condition 2, <w> bound to wrench, (forced by 1),
      <q> bound to x9-y5,

rob90; condition 1, <o> bound to wrench,
      <r> bound to x2-y2,
      condition 2, <o> bound to wrench, (forced by 1) .

```

The only rule for which all conditions are satisfied is rob21. Thus, the system writes,

```
move to x9-y5 ,
```

and modifies conditions (1) and (2) as indicated. Upon



completion of this "recognize-act" cycle the interpreter repeats the process, examining the new contents of working memory to see what to do next. We leave it to the reader to show that the next two rules to fire are rob70 and rob90 and that the result of firing rob70 is the writing of the string,

pick up the wrench .

With rob90 we do something entirely new. We "make" the new working memory element,

(goal ^status active ^type move-to ^position x2-y2) .

In our simple move-the-robot example we could have accomplished the same result by suitably "modifying" the first condition element. In a more sophisticated case, we might have wanted to construct a new goal only tenuously related to the conditions which prompted it, perhaps incorporating substantial computation based on left hand side variables. We might have wanted to store the state of the system with time tags in such a way that a simple rule could later recall those things which characterized the system at the earlier instant. The range of possibilities is limited only by the programmer's insight and imagination. In any event, with the "making" of the new goal, rob31 can fire. The system writes

move to x2-y2 ,

and modifies the left hand side conditions as indicated.

The preceeding extract from a "model" robot control system may seem to offer little that could not be managed with a clever Fortran program and indeed robotics programs have been written in such highly algorithmic languages. Since all machines are deterministic in nature there can be no question that as long as a machine's architecture permits a given set of actions, any language which gives access to these actions can be used for describing and controlling any process of which the machine is capable. The power of the languages of Artificial Intelligence lies in the range and freedom of expression which is their natural concomitant. It would be instructive for the reader familiar with Basic or Fortran to write a program to do just those things exemplified by our four rule set. It is likely that at just the point when success seems imminent a subtle, previously overlooked feature of OPS will be discovered which cannot yet be accommodated. Particular difficulty will be encountered in implementing the binding property of OPS. Even the ability of OPS to deal freely with character strings and numeric data will prove surprisingly frustrating. When it is realized that a full rule set for the control of even an only

moderately bright robot may consist of several hundred to several thousand rules the advantages of OPS-like languages loom strikingly.

The careful reader may have wondered what would happen if two or more rules were satisfied at the same time. Although there is insufficient space here to present an adequate discussion of what is known in OPS as "conflict resolution", it is through the effective treatment of the problem that OPS gains much of its power. Very quickly put, OPS generally chooses for execution the most specific rule of several which might apply and in this way attempts to insure the greatest relevance for the resulting action.

Our last approach to self modification invokes the OPS function "build", a right-hand-side-action which permits a rule to create (build) a new rule. Associated with its use are a number of subtleties, but all that need concern us here is the general form of a rule incorporating it. The following simplified example of the formal structure should suffice for our purposes:

```
(p evolve-1
  (left-hand-side-condition-1)
  (left-hand-side-condition-2)
  :
  :
  (left-hand-side-condition-N)
-->
  (build new-rule-name
    (new-rule-left-hand-side-condition-1)
    (new-rule-left-hand-side-condition-2)
    :
    :
    (new-rule-left-hand-side-condition-K)
-->
    (new-rule-right-hand-side-action-1)
    (new-rule-right-hand-side-action-2)
    :
    :
    (new-rule-right-hand-side-action-L))) ,

N not necessarily=K not necessarily=L .
```

The part of this rule appearing before the first "-->" has exactly the structure of a conventional OPS rule. Its entries can be any legitimate OPS quantities and may invoke arbitrarily complex combinations of conditional clauses, variables, and the like. All that is required is that any variable quantity which is to appear in the new rule must have appeared here first with some binding. The RHS action "build" constructs a new rule with the name "new-rule-name"

(which can be a system generated variable if desired) and new LHS and RHS components as indicated. These new components can be comprised of any legal OPS expressions and again can be of arbitrary complexity.

Although we could exhibit several examples of OPS rules which employ the "build" function it is likely that in isolation they would convey little of use. We choose instead to present some English language paraphrases of rule building rules which might be of use in the hazardous spills environment. Not only should these paraphrases be more readable than the OPS-coded versions, they may serve to illustrate a point often made about good Expert Systems, namely that if something can be expressed in a natural language (here English), it can be expressed in a computationally useful way in the language of the expert system as well. For our first example of a rule that "learns" we choose one which, having discovered that a spills technician persistently makes an error of a particular sort when performing a certain task, generates a new rule which will fire each time the technician undertakes this task to provide him with corrective guidance.

```

If there is a technician named <name>
And
If <name> is engaged in task <task>
And
If <task> has an associated error type <type>
And
If <type> for <task> has an associated error limit <limit>
And
If <name> has committed <type> <n> times
And
If <n> exceeds <limit>
And
If <task> has an associated help file <help>
Then
Build a new rule
  If there is a technician named <name>
  and
  If <name> is engaged in task <task>
  Then
  Output <help> to <name> .

```

At first glance it might seem that we have done little if anything which could not have been done just as well without building a new rule. But, note how very much shorter the LHS of the "new" rule is than the corresponding side of the "old" rule. The "new" rule subsumes a great deal and can respond to a much simpler set of conditions, conditions it now "knows" to be relevant to the situation with which it will, for a while, be concerned.

The reader who has assimilated the earlier remarks about OPS5 will perceive that even this simple example suffers from at least two serious deficiencies which illustrate the general difficulty of writing learning systems. First, nothing would prevent the "old" rule from firing in response to the very circumstances the new one is intended to subsume. Thus, not only would the "new" rule never have a chance to fire, it would in fact be in a constant state of regeneration! Second, we would like to assume that the technician will ultimately learn to do the job correctly so that the "new" rule was no longer required. The present rule makes no provision for detecting such advancement on the technician's part and so would endlessly remind him of his earlier sins long after he had mended his ways. Both of these problems can be resolved by the addition of a few simple conditions and actions. The interested reader will find enough detail in our abbreviated discussion of OPS5 to discover these for himself.

A particularly simple learning rule which could be invoked for training the system to respond to a new chemical can be represented in this way:

- (1) If there is a set of parameters denoted by <s>  
and
- (2) If no rule has responded to <s> to yield an  
identification  
and
- (3) If the instructor has identified the chemical as <c>  
then  
    Remove (3)  
and  
    Build a new rule  
        If there is a set of parameters denoted by <s>  
        then  
            Identify the chemical as <c> .

Several comments are in order here. First, the incorporation of the statement "remove (3)" is by itself sufficient to insure that the "old" rule will not endlessly re-fire. Second, our shorthand "<s>" for the set of parameters is deceptive. This set must be enumerated in such a way as to facilitate its incorporation into the LHS condition of the new rule. Note that conditional clauses can be incorporated into the left-hand-side elements to facilitate the accommodation of ranges within which the several parameters constituting <s> could fall for the chemical <c>. We suggest without further comment that rules can be so written as to learn with training to accommodate such "tolerance" ranges, even if the ranges are characterized by mutual functional dependencies.

We conclude our discussion of learning with the observation that one of the most useful techniques of the human expert, that of reasoning by analogy, can be implemented in OPS5<sup>6</sup>. A system embodying the capability is able to modify methods which have been provided for dealing with one set of tasks to permit it to deal with tasks about which it initially has little if any information. A principal prerequisite for the success of the analogical method is the existence of readily perceivable mappings between the two involved domains. An analogical reasoning system must be able to detect some similarity between at least one aspect of its domain of expertise and an aspect of the domain for which it is expected to generate new methods. We suggest that the various sub-domains of the spills problem constitute prime candidates for the application of this technique.

### OPS5 AND SPILLS

In this section we discuss the application of the techniques of the OPS5 expert system to the hazardous spills problem and attempt in the process to elaborate somewhat on the general methods of expert system programming. To these ends, we exhibit a few of the rules representing some of the major functions of the OPS5 spills program. We discuss these in the approximate order in which they would fire during a typical session with the program noting that in general this order is dependent upon the specific details of the particular spill.

We consider first the rule which is always the first to fire,

```
(p interrupt-0
  (spill)
-->
  (remove 1)
  (make goal ^id (gint) ^status active ^want
    initialize)) .
```

This rule fires if there exists in working memory a working memory element matching the single component LHS condition "(spill)". The actions invoked by the rule are twofold. First, the working memory element (hereafter WME) "(spill)" is removed from working memory (WM). This is done so that the rule will never refire (unless, of course, some other system action should create a new element "(spill)". Next, a new WME is created (by "make") to define the first system goal. This goal is assigned a unique numerical identifier, "id", by the function "(gint)", given an active status, and a goal object (want) "initialize". If there is

another rule in the system one of whose left hand side conditions matches this new WME and whose other conditions (if any) are similarly matched that new rule will fire. Such a rule is,

```
(p init-1
  (goal ^want initialize)
-->
  (remove 1)
  (make goal ^want library-data)
  (make staff ^name tom-oakes ^expertise expert)
  (make staff ^name brian-kelly ^expertise expert)
  (
    :
  )
  (
    :
  )
  (
    :
  )
  (make staff ^name annette-campbell ^expertise
    novice)) .
```

This rule fires in response to the goal established by the first and performs the indicated actions. The first again removes from WM the WME which triggered the firing, the second establishes a new goal, and the remainder generate WMEs defining the expert levels of staff members likely to use the system. Note that in a sense the LHS of this rule is "underspecified", that not everything included in the structure of the previously generated goal WME is found in the LHS of this rule. This illustrates a powerful feature of OPSS. If at least everything which is specified in a rule's LHS condition element can be matched by the components of some WME, the condition element is considered "instantiated" (an unfortunate example of AI jargon). If all condition elements appearing in the LHS are instantiated the rule can fire. Although we have so far discussed only Spills rules containing one LHS condition, these rules, of which there are ten, are exceptions most of which are devoted to placing into working memory various definitions and information which will be of use during the system's operation. The last of these "configuration" operations places in working memory the WME,

```
(goal ^status active ^want get-data ^data-pointer 1) ,
```

to which the following rule responds:

```
(p acquire-data-1
  (goal ^want get-data ^data-pointer <dp>)
  {<proplst> (property-list ^data-type reporter ^data-
    pointer <dp> ^attribute <att>)}
  -(given ^data-type reporter ^attribute <att>)
  -(help)
-->
  (write (crlf) enter the (substr <proplst> string3 inf))
  (make given ^data-type reporter ^attribute <att> ^value
```

(accept))) .

The first condition is satisfied by binding the variable "<dp>" to the number 1. The second is satisfied if there is a WME whose first entry is "property-list", whose value for the "data-type" attribute is "reporter" and whose values for the remaining attributes can be supplied by some binding of variables. The value for "dp" is forced by the first condition to have the value 1. The value of "att" is determined by the WME which this condition matches. The curious looking structure of this second condition exemplifies a very useful feature of OPS which permits the labeling of conditions so that they may be referenced by RHS actions. In this example the second condition is assigned the variable name "proplst". Note that although the RHS could also have referred to this condition by its numerical position (2), any editing which moved the condition statement from the second position would have necessitated a corresponding editing of the RHS.

The third condition is satisfied if there is not (-) a WME of the specified form, the fourth if there is not a condition with the entry "help". When the rule fires, the system executes a carriage return-line feed (crlf) and writes the words "enter the" followed by a substring (substr) which is extracted from the indicated portion of the WME bound to the variable "<proplst>". Note that it is not necessary to include "string3" in the LHS since no variable has been associated with it. Its existence has been "declared" by a mechanism we will not discuss further, that of "literalization" of attributes. The last action makes a new WME incorporating "reporter", the LHS quantity bound to the variable "<att>", and a new datum read from the terminal by the function "(accept)".

Assuming that the user has not requested help, acquire-data-1 continues to fire as long as there are "property-list" WMEs of "data-type" reporter for which associated "given" WMEs have not yet been constructed. When the rule (input-no-help) responsible for advancing the data pointer to the next occupied position (whether integer or fixed point number, it matters not) finally produces a "<dp>" value beyond the range of "reporter" property-list WMEs, a new acquire-data rule fires whose characteristics are tailored to the dialogue format suited to the text strings of the next class of property-list WMEs (in this case, "flow-data").

We referred earlier to the user-friendly characteristics which have been incorporated into the spills program. We exhibit next two of the rules which contribute to this aspect. The first of these,

```
(p input-help
  (goal ^want get-data ^data-pointer <dp>)
  (property-list ^data-pointer <dp> ^attribute <att>)
  (given ^attribute <att> ^value help)
-->
  (remove 3)
  (make help ^value <att>)) ,
```

fires if the user has responded to any request for data with the single word "help". The RHS action generates a new WME which incorporates the label "att" of the datum for which help is required. A second rule,

```
(p help-value
  (help ^value <value>)
  (library ^value <value>)
-->
  (remove 1)
  (write (crlf) (substr 2 string2 inf))) ,
```

can now fire if there is a "library" WME describing the desired quantity with the result that whatever help-file material the system has concerning "<value>" is printed on the users terminal.

When the system has satisfied its data acquisition requirements a rule sensitive to this condition (exit-get-data) fires producing a new goal which sets in motion a little bookkeeping (interview-2,-7). After taking stock of the situation, the system next asks the names of the people who are available to deal with the spill (allocate-1,-2) and begins assigning the existing tasks to them. It is at this point that system behavior begins to depend heavily upon the characteristics and location of the spill and upon the actions taken by the spill response team members. Since we cannot hope to address all possibilities here, we have included as Appendix I a partial listing of a session with the Spills program in the hope that this specific example may prove generally illuminating. In the remaining paragraphs of this section we discuss three of the more important rules from the more "intelligent" section of the Spills program.

The first of these is a member of a class of rules intended for performing simple material identification tasks. We introduce this rule by listing and describing the WMEs which must be present in (or in the case of the last, absent from) working memory for it to fire. In order, these are

```
(goal ^status active ^id <id> ^want quickcheck) ,
(material ^class nil ^color surface-sheen) ,and
```



- (suggestion ^status confirmed) .

The first implies that the system has established a goal with an active status, an identifying number "<id>", whose object (want) is the performance of a simple analysis of the spilled material (quickcheck). The second describes the spilled material as being of yet undetermined class (nil) and as having a color described (by the user during the data-taking phase) by the value "surface-sheen". The last requires that there not be in WM an element whose first entry refers to a form of prompting whereby the system assigns tasks to the spill team. The implication of the complete construct is that the system must not have issued a suggestion to which the response has been "confirmed". The rule embodying these components is,

```
(p quick-7
  (goal ^status active ^id <id> ^want quickcheck)
  (material ^class nil ^color surface-sheen)
  - (suggestion ^status confirmed)
-->
  (remove 1)
  (write (crlf) the spilled material may be oil.)
  (bind <newid>)
  (modify 2 ^id <newid>)
  (make goal ^id <newid> ^status active ^want advise
    ^father <id>)
  (make suggestion ^id <newid> ^number (gint) ^status
    active ^class oil ^string confirm oil spill by
    performing a gas chromatographic analysis.))
```

The first RHS action removes the "goal" WME to which the rule has responded thus ensuring that the rule cannot refire. The second writes the indicated string on the user's terminal. The third invokes a system function which generates a unique symbol and binds (assigns) it to the variable "<newid>". The fourth alters the "id" entry of the second condition assigning the new value "<newid>". The fifth RHS action generates (by "make") a new WME which establishes a new goal for the system. This goal is given the identifying symbol associated with the variable "<newid>", an active status, and a goal object (want) "advise". The bookkeeping attribute "father" is assigned the value bound by the LHS to the variable "<id>", thus establishing the ancestry of the new goal. The last action creates a new WME embodying the suggestion whose existence was denied by the third LHS condition. It is assigned the same "id" as the just created goal and a unique number (by the system function "gint") by which the suggestion will be referenced in subsequent dialogue with the user. An "active" status entry and an "oil" class value are assigned. The indicated "string" entry will be used by rules devoted to

interaction with the user and will ultimately be displayed on the user's terminal.

The last two rules we discuss are from part of a quite extensive set which define the ORNL storm drain system and permit automatic backtracking through it. Of necessity we exhibit the first of these in a highly abbreviated form.

```
(p woc-5
  (goal ^status active ^want see ^object woc-5)
-->
  (make flow-segment ^from-name woc-5 ^to-name m5-1
    ^to-type manhole ^segment-number 1 ^next-number
      nil)
  (make flow-segment ^from-name m5-1 ^to-name m5-2
    ^to-type manhole ^segment-number 1 ^next-number
      nil)
    :
    :
    :
  (make flow-segment ^from-name m5-40 ^to-name m5-41
    ^to-type manhole ^segment-number 1 ^next-number 2)
  (make flow-segment ^from-name m5-40 ^to-name m5-42
    ^to-type manhole ^segment-number 2 ^next-number
      nil)
    :
    :
    :
  (make flow-segment ^from-name m5-8 ^to-name bldg3517
    ^to-type building ^segment-number nil ^next-number
      nil)
    :
    :
    :
  (make flow-segment ^from-name m5-11 ^to-name sump02
    ^to-type sewer-sump ^segment-number nil
    ^next-number nil)) .
```

This rule responds to a system goal whose status is active and whose intent (want) is to examine the section of storm drain whose outflow is white oak creek number 5 (woc-5). When it fires woc-5 generates a long (!) sequence of WMEs of the indicated form. The "flow-segment" entry specifies the WME as a part of the storm drain tree representation. The value associated with the "from-name" attribute indicates the node of origin of the link being defined. The "to-name" value specifies the destination node of the same link, the "to-type" entry its nature. "segment-number" and "next-number" are bookkeeping attributes whose associated values indicate respectively which one of several links from a node is referenced by the WME and which link shall be considered next by the backtracking procedure.

Our last example is one of the several rules which

implement the backtracking process.

```
(p back-3
  (goal ^status active ^id <id> ^want backtrack)
  (actor ^name <a> ^role characterize-source ^at {}))
  (suggestion ^status followed ^value no ^string <>
    building <m> is contaminated ^who <a>))
  (flow-segment ^from-name <old> ^to-name <m> ^next-
    number { <=> 0 <next> } )
  (flow-segment ^from-name <old> ^to-name <new> ^to-
    type { <type> <> building } ^segment-number <next>))
  -(suggestion ^string <type> <new> is contaminated)
-->
  (modify 1 ^status pending)
  (modify 3 ^status old)
  (bind <newid>))
  (make goal ^id <newid> ^status active ^want interact
    ^father <id>))
  (make suggestion ^number (gint) ^status active ^who <a>
    ^id <newid> ^form determine ^string <type> <new> is
    contaminated)) .
```

The first LHS condition is similar to several previously discussed and requires no comment. The second requires that there be a WME whose first entry is "actor". Whatever the actor's (technician's) name, it will be bound to the variable "<a>" if the role entry is "characterize-source". The "at" entry may be anything. The curly brackets serve here only a place holding function. The third LHS condition demands that the "actor" has responded to a previously offered suggestion concerning the possible contamination of some building "<m>" and that the "value" of his response has been "no".

With the fourth and fifth LHS conditions we make the connection with the WMEs generated by the rule woc-5 discussed above. The fourth describes a flow-segment connecting some location "<old>" with the quantity bound to <m>. The next-number entry introduces the "same-type" qualifier denoted by <=>. Its use here requires that the "next-number" defined by the variable "<next>" be of the same type as the the quantity following the <=> symbol, 0. In other words, <next> must be a number. The fifth LHS condition requires that there be another flow-segment with the same "from-name" (<old>) but a different "to-name" (<new>). Its "to-type" can be anything except (denoted by <>) "building" and its "segment-number" must have the value bound to the previously defined "next-number" (<next>).

When the rule fires it modifies the "status" entries of the first and third LHS conditions and uses the "bind" function to generate a new symbol which is assigned to the variable "<newid>". Another goal of the suggestion type is

generated by the fourth RHS action which will eventually result in an interaction between system and user. The result of this interaction will be the writing of the string associated with the WME created by the last RHS action, "make". The inclusion of the "who" attribute will result in the direction of the suggestion to the actor "<a>".

If the foregoing examples only poorly represent the extent and complexity of the OPS5 SPILLS program, they do at least suggest its flavor and (we hope) something of the nature of Expert Systems programming methodology. Taken together with the examples of the preceding section and the dialogue listing of the Appendix they should offer some insight into the techniques which will be employed in satisfying the as yet unfulfilled goals of the Spills project, the implementation of a training mode, the incorporation of a capacity for learning, and the capability for generating Spills documentation. It is our view at the moment that training is best accommodated by writing a set of supervisory OPS5 rules which can present spills data both to the trainee and to the Spills program, monitor the performance of each, and offer (prepared) guidance upon the detection of various errors. It is clear that this supervisory program must embody considerable intelligence itself since it must account, among other things, for the fact that trainee and program may approach a given set of tasks in different orders neither of which is necessarily superior to the other. A very high priority has been established for this training facet of the project. When we are certain that the Spills program itself deals fully and correctly with the tasks for which it was intended we will begin our implementation of it.

The incorporation of a learning capability can profitably be approached at a succession of levels of increasing difficulty. It will be relatively easy to give the system the mechanism by which it can acquire new chemical identification knowledge. We alluded briefly (and superficially) in the previous section to the sort of OPS rule which would be required. It may also prove useful to write rules which give the system access to the results of well known Fortran programs designed for rapid and efficient execution of various algorithmic analytical and data-base management tasks. Although some would argue that this is not in the spirit of "proper AI", we would respond that humans make use of such facilities and that the machines which emulate human behaviour should do no less. A very useful learning capability would permit the automatic generation of back-tracking rules not only for as yet unmapped sections of the storm drain system, but for the several tens of miles of process piping with which the system must ultimately be able to deal. A mechanism may also be provided which will allow

Spills rules to survey working memory for information which has gone either unused or in some sense ineffectively used. Such information would be called to the attention of a human expert who would either write, or cause the system to generate, a rule (or set of rules) embodying it in such a way as to enhance system performance. The most useful learning process is likely to be the most difficult to implement. We refer to the techniques associated with analogical reasoning. The goal here is to give the system the ability to cope with spills situations with which it is only slightly familiar by providing rules for modifying "almost inapplicable" (as well as almost applicable!) methods to deal with the new situation. The key lies in finding some element in the new task domain which can be in some sense matched to an element in the old. An attempt is made to extend the mapping characterizing this match to existing rules in such a way as to make a new rule (or more likely, a set of rules) more nearly suited to the new task requirements. If this process is repeated in some iterative sense and if the old and new task domains are not too disparate there emerges a new set of rules constituting a method for dealing with the new task. (It is even harder than it sounds!).

We will comment on automatic documentation only to the extent of indicating that something considerably more sophisticated than a "fill in the blank" capability is implied. Our efforts here will almost certainly be based on work being done in the very active area of natural language understanding and may not involve OPS5 at all. The interested reader should consult one of the Artificial Intelligence journals cited in the references<sup>7 8</sup> for regularly occurring articles on this subject.

### CODA

It is our hope that we have communicated something of the AI style of dealing with problems of practical importance. It is a style very different from that of the highly structured algorithmic methods with which most of us have grown up and although at the most microscopic level it is as deterministic an approach as any other, its languages grant great freedom of expression, a freedom which, if well used, can lead to fresh insights and extraordinarily powerful solutions for problems in almost any domain.

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#### APPENDIX I

In the interest of keeping the Appendix of manageable length we do not exhaust the available program options, but leave several tasks pending and others yet to be generated. Numbers appearing at the left hand margin are sequence numbers and signify the firing of a rule. The associated string identifies the rule which fired at that point.

## PGDP DIKE TESTING PROGRAM

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operated by  
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for the  
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## SECONDARY CONTAINMENT, DIKES, CRITERIA, TESTING

## Abstract

Secondary containment is provided for major oil and chemical storage tanks at all UCCND facilities. This and other spill prevention efforts have been established to ensure compliance with environmental regulations and to maintain the favorable public image as a responsible industry.

Recent testing of PGDP secondary containment facilities indicates that a substantial number of dikes are inadequate for their intended purpose. This paper recommends dike performance criteria and describes a suggested testing program to document the adequacy of secondary containment facilities.

INTRODUCTION

Secondary containment for oil and chemical storage tanks is required by EPA regulations promulgated under Section 311 of the Clean Water Act. Nuclear Division facilities have inventoried storage tanks and secondary containment facilities over the last several years and have upgraded these facilities where they were found to be inadequate. Most major storage tanks have been diked for many years because of previous concerns regarding fire protection, loss prevention, and environmental protection.

Renewed emphasis on spill prevention was initiated at the Paducah Gaseous Diffusion Plant in 1979 after several oil spills which were reported to regulatory authorities. This spill prevention effort included the construction of oil retention structures (inclined pipe dams) on all major plant effluent ditches, a spill awareness effort, and the inclusion of spill prevention elements in the plant Quality Assurance Program.

#### PERFORMANCE CRITERIA

Dikes are the most common form of secondary containment used at the PGDP. Several types of construction materials are used for constructing dikes including poured concrete, gunite, dirt, concrete block, and metal. Regardless of the materials of construction, for a dike to perform its intended purpose of containing spills, certain criteria should be met.

Table 1 presents suggested design criteria for the construction of new dikes. During a recent QA audit of the PGDP Engineering Division with regard to spill control, it was recognized that dike design guidelines should be documented to ensure consistent design practices. It is now planned to incorporate dike design criteria in the UCCND Engineering Guidelines document. An important factor in the construction of new dikes is the inclusion of an acceptance test to document that the dike will perform as planned. Several newly constructed dikes at PGDP were found to have leaks which required maintenance repairs before they would perform their intended function.



Table 1

Suggested Guidelines for Design of Dikes  
Surrounding Oil and Chemical Storage Facilities

1. Dikes shall be sized to hold as a minimum the greater of:
  - a) 100% of the volume of the largest storage container and at least 6 in. (maximum expected 24-hr rainfall), or
  - b) 110% of the contents of the largest tank.
2. The floors and walls of each dike shall be constructed of (or coated with) materials which are impermeable to and nonreactive with the material being stored. Dike walls shall be designed to withstand a sudden, massive release.
3. It is preferable that loading and discharge piping not pass through dike walls. Where drainage pipes pass through the wall, an effective seal (chemically resistant to the stored material) should be installed to prevent leakage. Valves provided on drain lines will be resistant to the chemical(s) being stored.
4. Dikes should be located an appropriate distance from tanks and be high enough such that a leak on the side of the tank will not spray over the dike. Where this is not feasible, appropriate baffles should be designed to deflect potential leaks and cause them to drop within the contained area.
5. Dike walls generally should not exceed an average height of 6 feet above the interior grade. (This is to avoid potential safety problems such as oxygen deficiency and associated tank entry safety procedures.)
6. Completed dikes should be leak tested with sanitary water to at least 70% of dike capacity to demonstrate their integrity. Any visible leaks through cracks, etc. must be repaired. Overall leakage rates ideally should be in the order of  $10^{-7}$  cm/sec or less. Maximum acceptable leakage is  $10^{-5}$  cm/sec or less. This is equivalent to approximately 10 gal/hr for a dike surrounding a 1000 ft<sup>2</sup> area.

INSPECTION AND TESTING PROGRAM

During QA audits of each PGDP Divisional Spill Prevention Program, spill containment facilities were reviewed for adequacy. In a few instances, deficiencies were readily apparent. Either no secondary containment was available or dikes were obviously deficient. In the majority of instances, the dikes "looked" satisfactory. Suspicions regarding dike integrity were aroused during discussions on procedural controls for draining rainwater from diked areas. In many instances, rainwater rarely, if ever, required draining.

Two dikes near C-400 were selected for leak testing. This first tank was used for  $\text{HNO}_3$  storage and was surrounded by an earthen dike coated with gunite. The dike was filled to approximately 70% of capacity with sanitary water and was allowed to equalize for a short time before measurement of water level change. The leakage rate was calculated by multiplying the interior area of the dike by the change in elevation and dividing by elapsed time. The nitric acid tank dike was found to leak at approximately 1000 gallons per hour. Previous visual inspections had indicated no obvious routes for major leakage.

The second dike selected for testing had been constructed as a GPP project in 1976. The storage tank (11,000-gallon capacity) is used for trichloroethylene; and the dike was constructed of concrete blocks. The measured leakage rate was approximately 3000 gallons per hour.

After leak testing of these two dikes, it was apparent that systematic problems with dike integrity were a possibility. Each division was asked to prepare an action plan for inspection and leak-testing dikes and completing repairs on those found deficient. A typical action plan is shown in Table 2.

A leak rate of 10 gallons/hour was specified as being acceptable during the dike testing. Leak rates above this value required review with regard to (1) nature of the chemical, (2) available back-up containment, and (3) drainage or seepage paths. Because backup containment is available for oils and other immiscible low specific gravity chemicals, case-by-case exemptions seemed appropriate.

A few trends noted in the PGDP survey may be useful to others planning similar surveys: (1) Most dikes surrounding gasoline and diesel fuel tanks were originally constructed of permeable soil and gravel; these dikes were completely ineffective in containing spills. (2) Pipes underlying diked areas or passing through dike walls often acted as conduits for leakage. These pipes are usually backfilled with sand or gravel. (3) Concrete block dikes are fairly permeable if not coated with a sealant such as coal tar epoxy. They are also subject to cracks, especially in mortared areas. Cracks ranged from hairline size up to 1/4 inch. (4) Some dikes were constructed of impermeable sides but had relatively permeable dirt floors.

This dike inspection program emphasized actual leak testing using water where feasible. After all, if a dike will not hold

Table 2

## Dike Integrity - Action Plan

| <u>Step<br/>Number</u> | <u>Action</u>                                                                                                                                                  | <u>Accountability</u> | <u>Completion<br/>Date</u> |
|------------------------|----------------------------------------------------------------------------------------------------------------------------------------------------------------|-----------------------|----------------------------|
| 1.                     | Survey existing dikes on storage tanks used by your division. (Include gasoline and diesel fuel tanks.)                                                        |                       | 3/10/81                    |
| 2.                     | Inspect each dike for cracks, faulty drain valves, permeable materials of construction, etc.                                                                   |                       | 3/15/81                    |
| 3.                     | Prepare list of critical few dikes in need of immediate attention. (This decision should be based on storage volume, type of chemical, and condition of dike.) |                       | 4/3/81                     |
| 4.                     | Test integrity of these critical few dikes (using non-chromated water). <sup>1</sup>                                                                           |                       | 5/1/81                     |
| 5.                     | Complete repairs on dikes found deficient in step 4. <sup>2</sup>                                                                                              |                       | 6/30/81                    |
| 6.                     | Leak check other dikes.                                                                                                                                        |                       | 8/81                       |
| 7.                     | Complete repairs on dikes found inadequate in step 6.                                                                                                          |                       | 10/81                      |
| 8.                     | Schedule retests of dikes at intervals you consider appropriate.                                                                                               |                       | 10/81                      |

---

<sup>1</sup>Leak rates greater than 10 gallons per hour would indicate potential problem areas. Dikes should be filled to at least 70% of capacity in order to provide sufficient head pressure and give meaningful results.

<sup>2</sup>Leak testing all dikes may not be feasible. For example, for C-337 PCB transformer dikes, alternate inspection procedures and possible leak testing of a few dikes to identify systematic problems may be sufficient.

water, the capacity and ability to hold other liquids (such as acids or solvents) is irrelevant. However, dike capacity and material compatability should also be evaluated during the inspection program.

Secondary containment should perform as expected. Inadequate dikes are in some ways worse than no dikes at all. Inadequate dikes can result in a false sense of security because there is usually a lower sense of urgency in responding to a spill which is contained in a diked area. If the dike is inadequate, the leak or spill may escape to surface drainage or seep into the ground resulting in a reportable spill and associated environmental problems.

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FIELD TESTING OF PCB SORBENT MATERIALS  
FOR USE IN OUTSIDE CAPACITOR AREAS

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Under Contract No. W-7406-eng-26

Key Words: Sorbent Material, Capacitor Bank, Sorption  
Ratio, Containment System, Weathering Studies

ABSTRACT

During fiscal year 1982, the PGDP initiated a project to place approximately 6,000 sq. ft. of PCB sorbent material under 14 outside PCB-containing capacitor banks. The object of this project is to provide for PCB containment and prevent contamination of underlying ground during infrequent failures of outside capacitors at the PGDP. Earlier laboratory studies identified promising PCB sorbents from commercially available sorbent materials. As a long term field test, a prototype containment system was set up under an outside capacitor bank following laboratory recommendations for sorbent materials and their placement. In addition, weathering exposure studies were set up separately to monitor the long-term durability and sorptive capacity of the sorbent materials. An evaluation of data produced from these tests indicated a need for broadening the original vendor survey to include manufacturers of open cell foam weather resistant products. A second containment system has been prepared and includes the most promising of the foam products. Also, weathering exposures have begun to evaluate the long-term durability and sorptive capacity of the selected materials. Results from these studies and vendor survey will be presented.

## pH CONTROL IN RCW LOOPS AT ORGDP

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Key Words: Chemical feed systems, pH control, process design, RCW, sulfuric acid

## ABSTRACT

The pH of RCW is a vital parameter in limiting corrosion and scaling in cooling water systems. At ORGDP, pH has in the past been adjusted by the addition of sulfuric acid to makeup water from the softeners. Since each of the RCW loops is independent and operates at varying flow rates, temperatures, and cycles of concentration that require different quantities of sulfuric acid for pH adjustment, acid addition only to the makeup water header has resulted in unsatisfactory pH control. This has resulted in increased blowdown requirements to maintain acceptable sulfate levels in the RCW. To minimize blowdown, system improvements are to be provided by an FY 1981 GPP project which will permit independent pH adjustment in each of the six RCW and blowdown resoftening loops.

INTRODUCTION

The pH of the cooling tower water is a vital parameter in limiting corrosion and scaling in the piping and on heat transfer surfaces within the recirculating cooling water (RCW) system. A chromate-based corrosion inhibitor system is used at the Oak Ridge Gaseous Diffusion Plant (ORGDP). This corrosion inhibitor system is most effective at a pH of about 6.2. To maintain this pH, sulfuric acid is added to the RCW with the softened makeup water to the system. Since sulfuric acid is corrosive to the

\*Operated by Union Carbide Corporation for the United States Department of Energy.

steel RCW pipes and contributes to the  $[Ca][SO_4]$  solubility product of the RCW, it is essential that the sulfuric acid be accurately metered to the system in order to assure optimum function of the corrosion inhibitor system and minimize the sulfate level of the RCW.

### BACKGROUND

The pH of the six RCW loops at ORGDP has in the past been adjusted by a two step addition of sulfuric acid to the makeup water from the softeners. The sulfuric acid is fed by air pressure from two 500 gallon day tanks, and is metered by rotameters. The day tanks are refilled as required by transferring acid from a 15,000 gallon storage tank, using a 10 gpm pump (Figure 1).

pH of the makeup water is first adjusted to 7.6 at the makeup water softener effluent trough. Approximately five percent of the water is then withdrawn for use in the non-chromate treated "A" and "B" RCW loops. The pH of the remaining water is then adjusted by adding sulfuric acid directly to the 36 inch makeup header prior to distribution to "C", "E", "G", and "H" loops. In addition, the pH of the resoftened blowdown is adjusted by adding sulfuric acid to the resoftener effluent well.

This method of acid addition resulted in unsatisfactory pH control. Since each of the six RCW loops is independent and operates at a different flow rate, temperature, and number of cycles of concentration, a different quantity of sulfuric acid is required for pH adjustment in each loop. The resulting loop to loop variation in pH and sulfate level has resulted in the requirement for increased blowdown.

In order to minimize the necessity of adding sulfate to the RCW system, a hydrochloric acid feed system was added at the RCW softening plant in 1977. This permitted the substitution of hydrochloric acid for sulfuric acid for pH adjustment when the  $[Ca][SO_4]$  product approached the solubility limit.





FIGURE 1 EXISTING SULFURIC ACID FEED SYSTEM

Since the  $[Ca][Cl]$  solubility product is much higher than the  $[Ca][SO_4]$  solubility product, this pH adjustment method reduced the potential for scaling. However, since the usual limit for chloride discharge is much lower than the limit for sulfates, only a small quantity of hydrochloric acid can be used before chlorides become a problem.

A temporary system was installed in 1980 for pH adjustment of individual RCW loops. This system utilizes portable day tanks which are refilled as required from a centrally located 16,000 gallon storage tank. This temporary system has improved pH control of the loops.

#### SULFURIC ACID DISTRIBUTION SYSTEM

To alleviate the problems associated with the former two-point adjustment of pH in the RCW loops, a project was initiated which will provide pH adjustment in each of the six individual loops. The project is being funded as a 1981 GPP project.

The two existing 500 gallon tanks at K-892 will be used to supply sulfuric acid for pH adjustment at the makeup water softener effluent trough, "G" and "H" cooling tower centerwell, and the RCW blowdown resoftener effluent well. Refilling of the tanks by transfer of acid from a 16,000 gallon storage tank, using air pressure, will continue. Level sensing capacitance probes will be installed which will indicate to the operator when refilling of the day tanks is needed. Diaphragm-type pumps, with piped in spares, will meter acid to each of the three use points. New 316L stainless steel piping will be installed to replace the carbon steel piping now in use, which is badly corroded. Sample lines and pH meters presently in use will continue to be used with the new system.

For adjusting the pH of "C" and "E" cooling water loops, dedicated sulfuric acid feed systems will be installed at K-832 and K-862

respectively. New 4,000 gallon sulfuric acid storage tanks will be installed at these locations. The storage tanks will be refilled as required by truck deliveries. Level sensing capacitance probes in each acid storage tank will indicate to the operator when an acid delivery is needed. Acid will be metered from the tanks to the respective cooling tower wells by diaphragm-type pumps with a piped-in spare at each location.

A new sulfuric acid feed system will be installed at K-802 for adjusting the pH of "A" and "B" cooling water loops. One 4,000 gallon sulfuric acid storage tank will supply the acid requirements of both these loops. This storage tank will also be refilled by truck deliveries. Acid will be metered from the tank to the flumes supplying makeup water to each loop by a diaphragm-type pump with piped-in spare. Instrumentation at K-802 will be similar to that at the other locations.

Vent lines will be installed on each acid storage tank. In the event of an accidental overflow of the storage tanks or a build-up of gas pressure in the tanks, these vent lines will relieve the acid excess or pressure build-up. Since the corrosiveness of the sulfuric acid would be increased by moisture, the vent lines will be equipped with air dryers to prevent atmospheric moisture from entering the tanks.

To prevent a spill or leakage from a delivery truck or acid feed system resulting in an environmental insult, each acid feed area will be surrounded by a containment dike, sized to contain the entire contents of the acid storage tank. Truck ramps will be provided so that the delivery trucks will park inside the diked area while refilling the storage tanks. Sump pumps will be provided so that rain water and acid spills may be pumped from the diked areas after being neutralized. The diked areas will be lined with an impervious membrane and acid brick to protect the concrete pads from acid attack.

To aid in pH control and system monitoring, the flow of makeup water to each loop will be metered and recorded by new instruments. A

weir box will be installed to meter makeup water in the gravity flow line to "G" and "H" loop. Multiple headed averaging pitot differential pressure type flow meters will be used to meter flow to the other loops. Flow readout and recording will be at the control rooms of the respective cooling tower pump houses.

Total cost of this project will be approximately \$680,000. Design was completed in February, 1982, and construction will be completed in March, 1983.

In conclusion, pH control in the RCW loops at ORGDP will be improved by installation of individual acid addition systems for each of the six RCW loops. This will aid in minimizing corrosion and scaling in the cooling water system.

#### ACKNOWLEDGEMENT

The valuable assistance of J. L. McNelly of ORGDP Utilities Operations Department is gratefully acknowledged.

*Session 4: TOXIC MATERIALS CONTROL**Chairperson: B. M. Eisenhower*

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## SOLVENT EXTRACTION OF POLYCHLORINATED BIPHENYL

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Key Words: Polychlorinated Biphenyl, Extraction,  
Solvation, Pilot Plant, Process Flow

## ABSTRACT

Laboratory studies conducted at the Oak Ridge Y-12 Plant (which is operated by Union Carbide Corporation, Nuclear Division, for the U.S. Department of Energy, under U.S. government contract W-7405-eng-26) indicate that two solvent extraction processes for the removal of polychlorinated biphenyl (PCB) from mineral oil are effective in reducing the PCB concentration to less than 5 ppm. Both processes, with slight modifications, are capable of processing a variety of oil streams contaminated with either PCB or other chlorinated hydrocarbon contaminants as well as PCB-contaminated soil. Pilot plant data are being obtained to demonstrate the processes and to evaluate the economic feasibility. Preliminary estimates show the processes to be portable and comparable in cost to other removal processes.

INTRODUCTION AND MODEL

Numerous solvents were screened as potential candidates for extraction of PCB from mineral oil. The best solvents are found to have a higher affinity for the PCB than the oil, a limited oil solubility, and a low recovery cost to produce a small concentrated waste stream. To help in the choice of a solvent, a PCB solvation model was prepared.

At first glance, PCB appears to be a polar compound with considerable organic content. Therefore, the best solvents should be polar organics. Two factors though appear to go contrary to this inference. First of all, this does not explain why mineral oil was actually one of the best

solvents; and, secondly, why the dipole moment in PCB was much less than in a comparable allyl chloride. An explanation for this phenomena is that the chlorine atoms will double bond to the ring structure thereby increasing the ring stabilization. This would result in the chlorine atom assuming a positive charge and the adjacent carbon becoming negative. This orientation is opposite to the usual chlorine-carbon dipole. The result is that Van der Waals' forces are the predominant intermolecular attractive force. However, preferential solubility can be obtained by utilizing the negatively induced carbons adjacent to the chlorine atoms. Certain polar organics with a positively induced carbon surrounded by particular side groups do make better solvents than oil, and will satisfy the above criteria for a candidate solvent.

Solvent recovery can be accomplished in many ways, but two in particular appear to offer economic advantages. First, the solvent effect is neutralized by a stripping solvent which is highly soluble in the primary solvent and insoluble in the PCB. Inorganics that hydrogen bond are the best candidates. The hydrogen bonding will have the effect of reducing the PCB resonance stabilization by inhibiting the formation of the chlorine double bond and will also inhibit the formation of the positively polarized carbon of the primary solvent. Secondly, the PCB is stripped out of the primary solvent by a relatively insoluble low boiling solvent. Since nonpolar organics are excellent solvents and should also be relatively insoluble in the primary solvent as to meet a solvent selection criteria, the low molecular weight nonpolar organics should be the best candidates. Based on the above analyses, the solvent systems dimethylformamide (DMF)-water ( $H_2O$ ) and DMF-hexane offer the best capability.

## PROCESS

### DMF-H<sub>2</sub>O Solvent Extraction System

In this system, as shown in Figure 1, the DMF is contacted countercurrently to the PCB-contaminated oil producing a clean oil saturated with DMF and a PCB-rich DMF stream. The DMF is removed from the clean oil by a vacuum flash. The DMF-PCB is then contacted with water to liberate the dissolved PCB and oil waste streams. The DMF-H<sub>2</sub>O stream is then contacted with a clean oil stream that removes residual PCB and then distilled to recover the solvent and antisolvent.

### DMF-Hexane Solvent Extraction System

The system is shown in Figure 2. The PCB-contaminated oil is contacted countercurrently to the DMF producing a clean oil which is flashed to recover the dissolved solvent. The DMF-PCB stream is countercurrently extracted with hexane to remove the PCB. The clean DMF is recycled, and the hexane-PCB stream is stripped and flashed recovering clean hexane and concentrating the PCB in the stripper. The advantage of the DMF-hexane is that waste heat could supply most of the heat duty.

### Pilot Plant

Currently, a pilot plant is being built to demonstrate the extraction and stripping. Solvent recovery will be done with appropriate equipment as shown in the process flow diagrams.

The extraction pilot plant is composed of three 18-ft-high, 4-in.-diameter columns. The system is designed for an oil flow of about 40 L/hr. The columns will contain in-line phase separators at both the



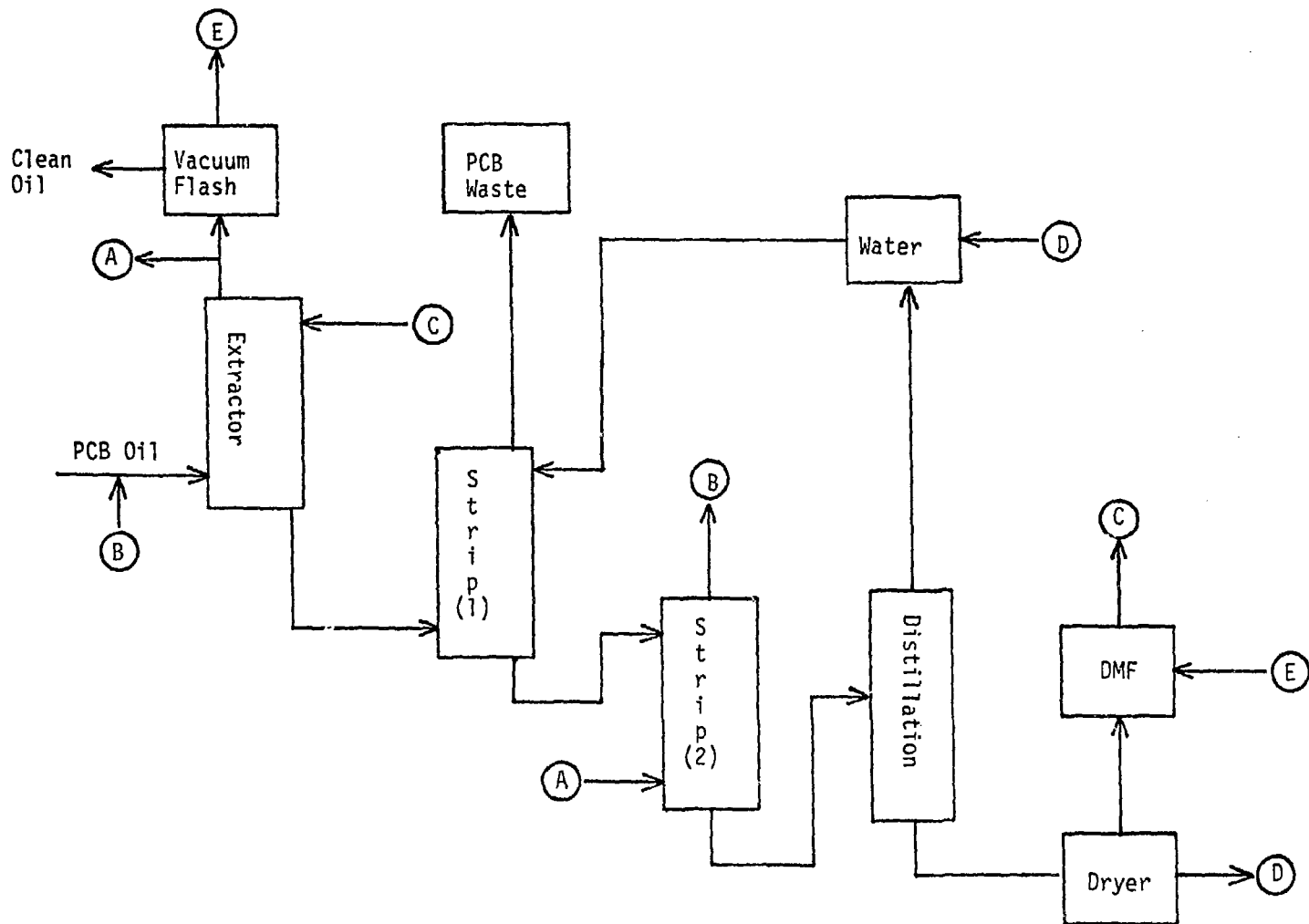


Figure 1. DMF-WATER-OIL SOLVENT EXTRACTION PROCESS.

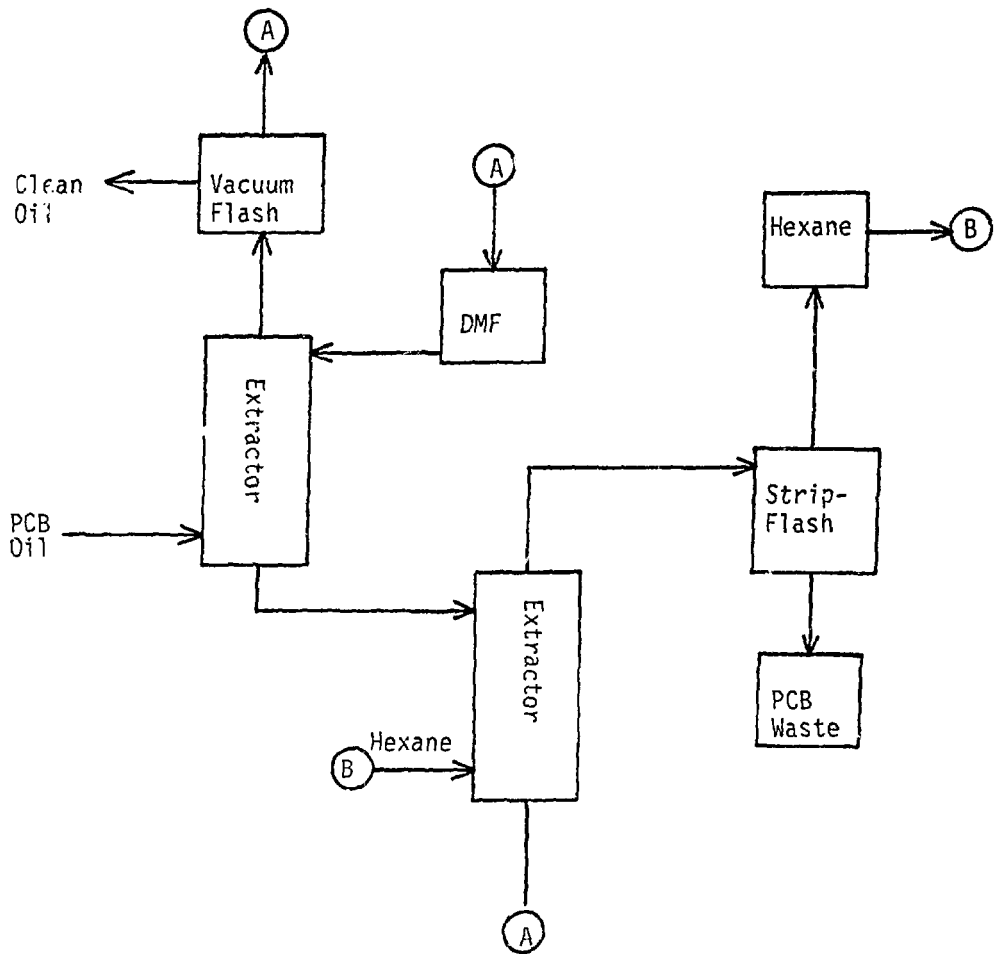


Figure 2. DMF-HEXANE SOLVENT EXTRACTION PROCESS.

top and bottom. Air-lift pumps are used for intercolumn flows and an in-line mixer is added for the water addition to DMF. Initial runs will be made with a chlorinated hydrocarbon that will simulate the PCB. A final demonstration run will use PCB. Based on data collected, an economic analysis will be performed to show the processing costs.

#### SUMMARY

Two processes for extraction of PCB from mineral oil are being developed. A pilot plant has been built and data are being collected. Based on pilot plant results, an economic feasibility study will be conducted.

## POLYCHLORINATED BIPHENYL CHEMICAL DESTRUCTION PROCESSES

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Key Words: Polychlorinated Biphenyl, PCBX, Chemical  
Destruction, Sodium Glycol, Sodium Naphthalide

## ABSTRACT

Laboratory studies have been conducted at the Oak Ridge Y-12 Plant (operated by Union Carbide Corporation, Nuclear Division, for the U.S. Department of Energy, under U.S. Government Contract W-7405-eng-26) to evaluate three chemical destruction processes for removal of polychlorinated biphenyl (PCB) from waste oils. These tests have shown that PCB can be destroyed using sodium glycol reagent, sodium naphthalide solution, and a proprietary process called PCBX. (PCBX is a service mark of Sunohio, a partnership of Sun Company and Ohio Transformer Corporation, Canton, Ohio.) In most tests, PCB was reduced to less than 5  $\mu\text{g/g}$  in a transformer oil, a lubricating oil, and a mixture of waste oils. Cost estimates for each process were not determined but are believed to be similar to the cost of the PCBX process which is in the range of \$0.80 to \$2.64 per L (\$3 to \$10 per gal), depending on the PCB concentration and other variables.

INTRODUCTION

In past years, several commercial firms produced industrial quantities of PCB for use as dielectric, lubricating, and industrial fluids. In 1976, the Toxic Substance Control Act (TSCA) was enacted, and PCB was the first chemical to have immediate restrictions placed on its manufacture, distribution, use, etc. The PCB regulations can be found in the Federal Register, Vol. 44, No. 106, May 31, 1979. Specific dates were established by this act to end all manufacturing, operations, distributions, etc. The TSCA regulations defined limits for disposal of PCB. Above 500  $\mu\text{g/g}$ , destruction using a special incineration process

was preferred. Special rules for disposing of liquids containing 50-500  $\mu\text{g/g}$  are defined by the TSA regulations, and liquids containing less than 50  $\mu\text{g/g}$  but above detectable are also regulated.

Most companies easily identified equipment containing concentrated PCB. The identification of equipment containing dilute amounts of PCB required a considerable sample program. As a result of data collected to date, large amounts of both concentrated and dilute PCB liquids have been identified.

Since the disposal options were limited to only incineration or special burial conditions, efforts to develop a cost-effective chemical process for destruction of PCB were begun by many investigators. Most chemical destruction processes have limitations, and studies to determine these limitations were initiated.

#### CHEMICAL DESTRUCTION TESTS

Several chemical processes for destruction of PCB have been reported, and sufficient information has been obtained to merit further investigations.<sup>1-4</sup> The primary purpose of our studies was to confirm that these reported processes would destroy PCB in three types of waste oils. The waste oils were a mineral oil commonly used in electrical transformers, a lubricating oil, and a mixture of lubricating and electrical oils. Brief analyses of these oils are shown in Table 1.

#### Sodium Glycol Reactions

The investigation of the glycol reactions was limited to laboratory beaker-sized experiments, and the chemical reactants were prepared in accordance with Pytlewski's published articles.<sup>1-2</sup> In brief summary, the reactant solution was prepared by adding sodium metal to a glycol solution; and above 60°C, a reaction occurred producing an amber-colored liquid.

Table 1

## Contaminated Oils

A. Mineral Oil Without Additives  
(electrical transformer fluid)

|                                       |               |
|---------------------------------------|---------------|
| Saybolt Universal Viscosity (37°C)    | 62 SUS        |
| Specific Gravity (g/cm <sup>3</sup> ) | 0.86-0.91     |
| Flash Point (minimum)                 | 143°C         |
| Pour Point                            | -40°C         |
| Dielectric                            | 30 kV minimum |
| Carbon, Sulfur, Ash                   | 0%            |
| Water (maximum)                       | 40 µg/g       |
| PCB                                   | 80 µg/g       |

## B. Mixed Waste Oils

Includes lubricating, electrical, etc.

Typical water content varies from 1 to 30 vol % and a PCB value of 3600 µg/g.

## C. Lubrication Oil

|                                    |                                                                          |
|------------------------------------|--------------------------------------------------------------------------|
| Saybolt Universal Viscosity (37°C) | 315-320 SUS                                                              |
| Viscosity Index                    | 85 min                                                                   |
| API Gravity                        | 26 min                                                                   |
| Flash Point                        | 218°C                                                                    |
| Fire Point                         | 252°C                                                                    |
| Carbon (%)                         | 0.03                                                                     |
| Water (%)                          | 0.03                                                                     |
| Other Data                         | Parafenic base, straight mineral oil, oxidation, and corrosion inhibited |

Several glycols, shown in Table 2, were investigated. In most cases, 2 g of sodium were added to 200 mL (0.05 gal) of glycol, and the stirred mixture was heated to 95°C-100°C in a nitrogen atmosphere until the sodium dissolved. The stirred mixture was then heated in air for one to two hours.

As shown in the Table 2 data, reactions with PCB only occurred with sodium polyethylene glycol 400. Some general comments on these tests are shown in Table 3. The equipment and operational costs have not been defined but are expected to vary depending on the PCB concentration, and removal cost associated with the excess glycol solution.

Table 2

## Contaminated Oils

|                                 |                                   |                |
|---------------------------------|-----------------------------------|----------------|
| Triethylene Glycol              |                                   |                |
| a.                              | PCB                               | No reaction    |
| b.                              | Mineral Oil - 60 µg/g PCB         | No reaction    |
| Tetraethylene Glycol            |                                   |                |
| a.                              | Aroclor 1260                      | 60% reduction  |
| 1,3-Butanediol Glycol           |                                   |                |
| a.                              | Aroclor 1260                      | 41% reduction  |
| Ethylene Glycol Monobutyl Ether |                                   |                |
| a.                              | Aroclor 1260                      | No reaction    |
| Polyethylene Glycol 400         |                                   |                |
| a.                              | Aroclor 1260                      | 98% reduction  |
| b.                              | Mineral Oil - 81 µg/g PCB         | 43% reduction  |
| c.                              | Mineral Oil - 72 µg/g PCB         | 69% reduction  |
| d.                              | Waste Oil Mixture - 3438 µg/g PCB | 24% reduction  |
| e.                              | Lubrication Oil - 76 µg/g PCB     | 100% reduction |
| f.                              | Mineral Oil - 80 µg/g PCB         | 37% reduction  |

## Sodium Naphthalide Reactions

This process has been investigated by two research and development groups,<sup>3-4</sup> and our studies used the reactant preparation formula described by the Goodyear Tire and Rubber Company. The reactant was made by mixing 50 mL (0.01 gal) tetrahydrofuran, 15.4 g naphthalene, and 2.3 g of sodium metal in a nitrogen atmosphere. The reactant was then mixed with the PCB solutions shown in Table 4. After a 1-hour contact, essentially all of the PCB was destroyed in three of the four tests.

Generally, the statements for sodium naphthalide noted in Table 5 are the same as the ones stated for sodium glycol reaction. The exact cost for the process was not determined, but it is estimated to be in the range of \$0.80 to \$2.64 per L (\$3 to \$10 per gal). The process would require removal of excess tetrahydrofuran and sodium naphthalide before recycle of the oil.

Table 3

## General Statements on Sodium Glycol Tests

1. Contact Times - one to two hours at 100°C.
2. Sodium-Chlorine Ratio - not determined but estimated to be greater than 10 to 1.
3. Reactant Products - not identified.
4. Reuse of Oil - purification cycle not defined.
5. Cost - not defined but estimated to be in the range of \$0.80 to \$2.64 per L (\$3 to \$10 per gal). Probably not cost-effective above 3000 µg/g PCB.

Table 4

## Sodium Naphthalide Reactions

|                                   |                 |
|-----------------------------------|-----------------|
| Arcolor 1260                      | 99.8% reduction |
| Mineral Oil - 80 µg/g PCB         | 94% reduction   |
| Waste Oil Mixture - 3438 µg/g PCB | 26% reduction   |
| Lubricating Oil - 76 µg/g PCB     | 93% reduction   |

Table 5

## General Statements on Sodium Naphthalide Tests

1. Sodium-Chlorine ratio - a reported ratio of 50 to 1 is needed.
2. Reactant Products - not identified.
3. Inert Atmosphere - reactant must be made in inert atmosphere.
4. Water - reactant is sensitive to water.
5. Cost - not defined but estimated to be in the range of \$0.80 to \$2.64 per L (\$3 to \$10 per gal).



Table 6

## PCBX Process

|              |                           |
|--------------|---------------------------|
| Original Oil | PCB 80 $\mu\text{g/g}$    |
| First Cycle  | PCB 8 $\mu\text{g/g}$     |
| Second Cycle | PCB < 5 $\mu\text{g/g}^*$ |

## PCBX Process

A proprietary process (PCBX) was licensed by the Environmental Protection Agency (EPA). The PCBX is limited to processing only transformer fluids containing less than 500  $\mu\text{g/g}$  PCB, and limited technical data on the process are available. The process is contained in a portable vehicle and can be piped to existing equipment. The PCB-oil is pumped from the process equipment through a chemical reactant in the truck and back to the equipment in a storage tank.

A contract was negotiated to process a demonstration batch of mineral oil containing 80  $\mu\text{g/g}$  PCB. The contract specified that the oil be cycled through the PCBX process until a level of 2  $\mu\text{g/g}$  PCB was obtained.

Results of the PCBX process are shown in Table 6. As noted, each cycle reduced the PCB by about 87%, and the demonstration batch was reduced to acceptable levels in two cycles through the unit.

The cost of this process varies depending on the PCB level, location of the contaminated oil, and volume to be treated. Typical cost should be in the range of \$0.80 to \$2.11 per L (\$3 to \$8 per gal) at PCB levels less than 500  $\mu\text{g/g}$ .

### CONCLUSIONS

Laboratory tests have shown that PCB can be destroyed by three chemical processes. The final choice for disposal of PCB wastes will probably be based on the disposal cost. The exact disposal cost of the chemical processes will vary depending on factors such as location, volume, etc. A specific disposal cost for most chemical processes can not be made, but an estimated range of \$0.80 to \$2.11 per L (\$3 to \$8 per gal) of contaminated liquid is probably valid, assuming that the PCB concentration is less than 500 µg/g.

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RECLAMATION OF PCB CONTAMINATED LUBRICATING OILS

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(Paper Not Available For Publication)

## RECLAMATION AND DISPOSAL OF WATER-BASED MACHINING COOLANTS

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Key Words: Machining Coolants, Reclamation, Disposal,  
Biological Degradation, Bacteria Identification, Biocide

## ABSTRACT

The Oak Ridge Y-12 Plant, which is operated by the Union Carbide Corporation, Nuclear Division for the Department of Energy under U.S. government contract W-7405-eng-26, currently uses about  $10^6$  L/yr (260,000 gal/yr) of water-based coolants in its machining operations. These coolants are disposed of in a 110,000-L (29,000-gal) activated sludge reactor. The reactor has oxidized an average of 38.6 kg of total organic carbon (TOC) per day with an overall efficiency of 90%. The predominant bacteria in the reactor have been identified once each year for the past three years.

Six primary types of water-based coolants are currently used in the machine shops. In order to reduce the coolant usage rate, efforts are being made to introduce one universal coolant into the shops. By using a biocide to limit bacterial deterioration and using a filter and centrifuge system to remove dirt and tramp oils from the coolant, the coolant discard rate can be greatly reduced.

INTRODUCTION

The Oak Ridge Y-12 Plant currently uses six major 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 paraffins, amines, polyglycols, and similar molecules. Many of the coolants also contain significant amounts of sodium nitrite.

These coolants will normally start deteriorating after 2-3 weeks due to bacterial action and are usually discarded about every four weeks. Coolants are also discarded when a change is made in the type of metal being machined, since each coolant has its own particular uses. If it can be determined that one coolant can be used for most of the metals machined at the Oak Ridge Y-12 Plant and that coolant can be protected with an effective biocide, the coolant discard rate would be significantly reduced.

#### COOLANT AND BIOCIDES DEVELOPMENT

A plan was established that listed all of the criteria a coolant had to meet before it could be introduced into the machine shops. These criteria included tests for machinability, corrosion protection, stability, and biological oxidation. Tests are also required to show that the coolant can be easily cleaned from the machined parts and that subsequent steps such as bonding or welding will not be adversely affected.

The coolant Trim-Sol (Master Chemical Corporation, Perrysburg, Ohio), which had previously been used for machining only aluminum, was also found to be suitable for machining iron, steel, stainless steel, and the various uranium alloys. The biocide Tris-Nitro (International Minerals and Chemical Corporation, Des Plaines, Illinois) (2-nitro-2-hydroxymethyl-1,3-propandiol) was found to be effective for preventing biological deterioration in Trim-Sol. The addition of 500 ppm Tris-Nitro stops all bacterial growth for an average of one month under machine shop conditions. Trim-Sol has been used almost exclusively in the general machine shop at the Plant for over two years. It is now being introduced into the various production machine shops.

### COOLANT RECLAMATION SYSTEM

After extended use, machining coolants will collect small particles of dirt and metal, and tramp oil which must be removed periodically. A coolant reclamation system has been installed in the general machine shop to clean the Trim-Sol coolant. The dirty coolant is pumped out of one of the machines, through a 40- $\mu$  filter, and into a portable tank. The coolant is then transported to the coolant reclamation system. The reclamation system consists of a 5- $\mu$  pressure filter and a liquid-liquid centrifuge. The centrifuge has a 17.5-cm-ID bowl and rotates at a speed of 9890 rpm. The centrifuge will separate tramp oil from the coolant up to a coolant input rate of about 200 L/min (50 gal/min).

The cleaned coolant is checked with a refractometer to measure the organic concentration, and then deionized water or Trim-Sol concentrate is added as needed to adjust the composition of the coolant. The coolants are processed through the reclamation system about once a month, and 500 ppm of Tris-Nitro biocide is added to each batch that is processed to limit bacterial deterioration.

Since starting up in April 1980, the reclamation system has processed a total of 230,000 L (60,000 gal) of coolant. No coolant has been purposely discarded from this shop, but some small losses are inherent in the machining operations. So far there is no evidence that the coolant cannot be recycled indefinitely, although it may eventually become necessary to replace some fraction of the used coolant with new coolant to maintain the needed quality.

### COOLANT DISPOSAL

The used coolants from the production shops are disposed of in a 110,000-L (29,000-gal) activated sludge reactor. An old concrete cooling tower basin was modified to serve as the reactor, and an adjacent 8,000-L (2,000-gal) basin serves as the settling chamber. Aeration and mixing

are supplied by four floating aerators, each with a capacity of 100 kg of oxygen per day. The effluent from the settling chamber is chlorinated and released.

During the past year, the concentration of the waste coolant entering the reactor has averaged 8,000 mg TOC/L (total organic carbon/liter), and the effluent has averaged 800 mg TOC/L before chlorination. The chlorination system has only been in operation for about one month, but it seems to reduce the TOC by about 50%. Chlorination reduces the turbidity of the effluent by about 70% and the viable bacteria concentration by 90%.

The reactor has oxidized an average of 38.6 kg TOC/day during the past year. The total volume of liquid processed through the reactor has been about  $10^6$  L/yr (260,000 gal/yr).

#### BACTERIA IDENTIFICATION

The predominant bacteria in the coolant degradation reactor have been identified once each year for the past three years by Dr. Bill Claus and Ms. Carol Baker of the Virginia Technological University's Biology Department. During the last two analyses, the proportion of the population represented by each predominant group was also determined. No strict pathogens were found in any of these analyses, but several genera were identified that contain opportunistic pathogens. The results of the last two analyses are shown in Table 1. Significant changes in the bacterial population have been found each year, but no changes in the operation of the bioreactor have been noted. In 1982, the bacterial analysis will consist of searching for specific pathogens that might be present in the reactor in low numbers.

Table 1

Population Changes Occurring in the Waste Coolant Bioreactor  
Between December 28, 1979 and January 29, 1981 Samples

| Genus                               | Percent of Total Isolated <sup>(a)</sup> |                  |
|-------------------------------------|------------------------------------------|------------------|
|                                     | December 18, 1979                        | January 29, 1981 |
| <u>Seliberia</u>                    | 21                                       | 0                |
| <u>Pseudomonas</u> <sup>(b)</sup>   | 20                                       | 37.7             |
| <u>Microcycclus</u>                 | 16                                       | 22.1             |
| <u>Sphaerotilus</u>                 | 4                                        | 2.6              |
| Coryneforms                         | 3                                        | 10.4             |
| <u>Listeria</u>                     | 3                                        | 0                |
| <u>Alcaligenes</u>                  | 0.5                                      | 6.5              |
| <u>Acinetobacter</u> <sup>(b)</sup> | 1                                        | 6.5              |
| <u>Nocardia</u> <sup>(b)</sup>      | 0                                        | 5.2              |
| <u>Aeromonas</u> <sup>(b)</sup>     | 2                                        | 1.3              |
| <u>Hyphomonas</u>                   | 1                                        | 0                |
| <u>Caulobacter</u>                  | 1                                        | 0                |
| Appendaged Bacterium                | 1                                        | 0                |
| <u>Moraxella</u>                    | 0.5                                      | 2.6              |
| <u>Flavobacterium</u>               | 0.5                                      | 0                |
| Unknowns                            | 26                                       | 5.2              |

(a) In the December 1979 sample, 184 isolates were examined; and in the January 1981 sample, 77 isolates were examined.

(b) Genus contains species that are opportunistic pathogens.



CONCLUSIONS

The coolant Trim-Sol has been found to be effective for machining most of the metals used in the Oak Ridge Y-12 Plant. Adding 500 ppm of Tris-Nitro biocide to the coolant each month will stop bacterial deterioration. Batch treatment has shown that filtration and centrifugation removes solid particles and tramp oils. The coolant then can be reused. The recycle system has reduced the purchase of new coolants and decreased the disposal cost. Savings noted to date are approximately \$60,000. The recycle system is adaptable to other machine coolant systems at the Plant.

*Session 5: HAZARDOUS MATERIALS CONTROL*  
*Chairperson: R. E. Anderson*

|                                                                                                                                                  |     |
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## TECHNICAL SUPPORT FOR THE HAZARDOUS WASTE INCINERATOR AT ORGDP

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for the United States Department of Energy

Keywords: TSCA, Incineration, Polychlorinated Biphenyls (PCBs),  
Hazardous Organic Disposal

## ABSTRACT

The 83 LIP - "Compliance with Toxic Substance Control Act" (83-N-402) - will provide the facilities that will enable the diffusion plants to comply with government regulations (TSCA). As a part of this project, an incineration facility will be built at ORGDP to destroy PCB-contaminated wastes that are generated by the three gaseous diffusion plants, Y-12, and ORNL. This presentation will cover the following topics:

1. OVERVIEW OF THE PROJECT - T. O. Rogers  
This will include the status of the project, including the CDR, EIS, and a discussion of the proposed flow sheet.
2. SUMMARY OF TECHNICAL SUPPORT - J. M. Kennerly  
The technical support being carried out to resolve the various design uncertainties associated with the project will be discussed.
3. RESULTS OF TEST BURNS AT C-E RAYMOND - D. H. Bunch  
This discussion will include the purpose of the test burns, a description of the pilot-scale equipment, the experimental conditions, and the findings of the study.

## OVERVIEW OF THE PROJECT

The project overview represents a summary of the TOSCA incinerator as presently designed and the Environmental Impact Statement<sup>1</sup> (EIS).

## INTRODUCTION

The 1983 Line Item Project, "Compliance With the Toxic Substance Control Act (TSCA)" (83-N-402), will provide facilities for the disposal of radioactively contaminated polychlorinated biphenyls (PCBs) and other hazardous organic wastes. Disposal of these wastes will be done in compliance with the Toxic Substance Control Act (TSCA). The conceptual design report recommended that the facility be located at the Oak Ridge Gaseous Diffusion Plant and that storage facilities be located at the Paducah and Portsmouth Gaseous Diffusion Plants. Although the project will not provide facilities at Y-12 and X-10, they too will ship wastes to the disposal facility at ORGDP.

The disposal of the radioactively contaminated wastes will be accomplished using a thermal oxidation method. This process will include a rotary kiln, afterburner, and required off-gas treatment equipment. Thermal oxidation was chosen as the most feasible method of destroying hazardous organic waste after an in-depth study of alternatives was made.

## Project Justification

In addition to the annually generated PCB waste, substantial quantities of PCB-contaminated wastes are stored at the gaseous diffusion plants. As part of the 1976 Toxic Substance Control Act, Congress banned the production of PCBs and commissioned the Environmental Protection Agency (EPA) to regulate the disposal of these substances.

Regulation 40 CFR 761,<sup>2</sup> was published by EPA in the Federal Register on May 31, 1979. Pertinent requirements, mandated by EPA in this regulation, follow:

1. A PCB-contaminated material contains 50 ppm or greater of polychlorinated bipheyls.
2. Material containing 500 ppm, or greater, of PCB must be incinerated or destroyed by an EPA approved process.
3. PCB material stored prior to January 1, 1983 must be disposed of before January 1, 1984.
4. Equipment retired from service and stored waste must be disposed of at an EPA licensed facility.

In addition, the following regulations concerning design and operation of a PCB incinerator were mandated in 40 CFR 761.

1. The following combustion criteria shall be followed:
  - ° 1200°C operating temperature must be met or exceeded.
  - ° 2-second residence time at 1200°C.
  - ° 3 percent excess air, minimum.
2. Combustion efficiency shall exceed or equal 99.9%.
3. The rate and quantity of PCBs fed to the incinerator shall be recorded.
4. The PCB feed shall stop whenever combustion temperature drops below 1200°C.

5. Stack gases shall be monitored and records kept on the oxygen, carbon monoxide (continuous), and carbon dioxide concentrations.

In addition to PCBs, the DOE-ORO plants have other radioactively contaminated hazardous wastes such as solvents, oils, and organic chemicals which will require their disposal in an environmentally acceptable manner.

Since most of the wastes are contaminated with trace quantities of radionuclides (primarily enriched uranium), commercial disposal of these wastes is not possible. Hence, DOE supports the PCB incinerator which will permit compliance with TSCA as quickly as the Federal budget cycle will allow.

#### Waste Characterization

Liquid, solid, and sludge wastes will be fed to the incinerator. The solids are mainly PCB-contaminated rubbish and dirt. The various liquids fed to the incinerator will include PCB liquids (concentration ranging from 50 ppm to 60%), chlorinated waste solvents, hydrocarbons, waste oils, and aqueous waste. Semi-liquid waste feeds will include paint, oil, and incinerator storage tank sludges.

Due to criticality concerns, the maximum uranium isotopic assay which will be incinerated is 1% U-235.

Table 1, taken from the EIS, shows the anticipated quantity of wastes to be stored in 1987 and their annual generation rate. Chemicals which represent major quantities of the numbers in Table 1 are as follows:

## Waste Solvents - Tetrachloroethylene

- Trichloroethylene

- Trichloroethane

- Acetone

- Varsol

- Methanol

Dilute PCBs - Kerosene

- Hexane

TABLE 1

## Waste Materials Inventory

| Waste Name                                                                                          | Annual Rate<br>1987<br>(liters/year) | Stored Quantity<br>1987<br>(liters) |
|-----------------------------------------------------------------------------------------------------|--------------------------------------|-------------------------------------|
| Liquid PCB <sup>a</sup>                                                                             | 11,800                               | 80,440                              |
| PCB contaminated oils and solvents <sup>a</sup>                                                     | 53,500                               | 1,110,000                           |
| Waste oils                                                                                          | 122,500                              | 550,000                             |
| Waste oils <sup>b</sup>                                                                             | 324,000                              | 425,000                             |
| Waste solvents                                                                                      | 160,000                              | 131,000                             |
| Waste solvents <sup>b</sup>                                                                         | 12,000                               | 90,000                              |
| Miscellaneous wastes (degreaser<br>sludges, photographic wastes,<br>biological wastes) <sup>a</sup> | 146,000                              | 77,000                              |
| TOTAL                                                                                               | 829,800<br>(219,200 gal)             | 2,463,440<br>(650,800 gal)          |
|                                                                                                     | <u>Kilograms/year</u>                | <u>Kilograms</u>                    |
| Solid wastes (PCB contaminated) <sup>a</sup>                                                        | 24,000                               | 6,400,000<br>(7040 tons/yr)         |
| Waste Fuller's earth <sup>a</sup>                                                                   | 10,900                               | 82,000                              |

<sup>a</sup>Portions of these materials contain uranium contamination.<sup>b</sup>These materials contain uranium contamination.

PROCESS DESCRIPTION

## Receiving/Storing/Blending

The project will provide for a total of 15 storage and blending tanks with a total waste storage of 85,000 gallons (322 m<sup>3</sup>). These tanks will provide the storage capacities as shown in Table 2.

Table 2

## Waste Liquid Storage Capacities

| <u>Receiving Tanks</u> | <u>Gallons</u> | <u>Meters<sup>3</sup></u> |
|------------------------|----------------|---------------------------|
| Primary Waste          | 5,000          | 19                        |
| PCB Concentrated Waste | 5,000          | 19                        |
| PCB Waste              | 5,000          | 19                        |
| PCB Aqueous Waste      | 5,000          | 19                        |
| Aqueous Waste          | 5,000          | 19                        |
| Secondary Waste        | 5,000          | 19                        |
| NaOH 50%               | 5,000          | 19                        |
| <u>Storage Tank</u>    |                |                           |
| Fuel Oil               | 2,000          | 8                         |
| Primary Waste          | 10,000         | 38                        |
| PCB Waste              | 10,000         | 38                        |
| Secondary Waste        | 10,000         | 38                        |
| NaOH 20%               | 3,000          | 11                        |
| <u>Blending Tank</u>   |                |                           |
| Primary                | 10,000         | 38                        |
| Secondary              | 10,000         | 38                        |
| Aqueous Waste          | 5,000          | 19                        |

These tanks will be diked and labeled in accordance with EPA regulations.

Materials when received at the facility will be compared to a previously received manifest. Also, prior to unloading, a laboratory analysis will be performed to insure that they are the proper materials.

Most of the solid wastes and some liquid wastes will be in drums. Drummed wastes will be processed through a lance station which will allow



the decanting of any liquids. Then the drum will be fed into a low-speed, high-torque shredder that reduces the drums and other solids to small pieces having a maximum width of 2 inches (0.05m). The shredded pieces will then be fed into a rotary kiln via a belt conveyor.

Liquid wastes will arrive at the facility in bulk tanks and in drums. The following characteristics will be determined on each waste:

1. Heat value.
2. Organic halogen content.
3. Ash content.
4. Water content and phases.
5. Viscosity.
6. Reactivity.
7. Compatibility.

Liquid wastes will be divided into three major categories. Primary waste will have a heat content greater than 7,000 BTU/lb ( $1.6 \times 10^7$  J/kg) but less than 10,000 BTU/lb ( $2.3 \times 10^7$  J/kg) and will be destroyed in the rotary kiln's master burner. Secondary wastes will have a heat value above 10,000 BTU/lb ( $2.3 \times 10^7$  J/kg) and will be destroyed in the secondary combustion chamber's master burner. Hazardous organic contaminated aqueous wastes will be destroyed in the rotary kiln's slave burner.

A compatibility test will be performed on each truck load of waste before the wastes are unloaded into storage tanks. This test will consist of a sample of waste from the receiving tank mixed with a sample of the new waste in a laboratory under carefully controlled conditions. This

test is necessary since the mixing of some materials might cause violent reactions, explosions, generation of dangerous gases, or polymers which would be difficult to handle.

The liquid wastes are blended in order to provide a consistent feed to the burners. By blending, the organic chlorine feed rate will be maintained below 30%, the secondary ash content below 0.5%, and the viscosity at less than 150 centistokes ( $1.5 \times 10^{-4} \text{ m}^2/\text{s}$ ).

### Incineration

The incinerator will be designed and operated to meet the 99.9% combustion efficiency for the destruction of liquid PCBs as required by TSCA. When burning solid PCB contaminated materials, the amount of PCBs discharged to the atmosphere will not exceed .001 gram of PCB/kg of solid PCB fed. Figure 1 shows the proposed incinerator and off-gas treatment.

The incinerator will consist of a rotary kiln and afterburner with a combined thermal capacity of 7.5 million BTU/hr ( $7.9 \times 10^9 \text{ J/h}$ ). The rotary kiln will be 8 feet (2.4 meter) in outside diameter and 20 feet (6.1 meter) long, with the afterburner designed to have a four second retention time. The rotary kiln can burn up to 700 lbs/hr (320 kg/h) of shredded solids and approximately 1 gpm (3.8 l/min) of liquid wastes at 1000°C. Natural gas or fuel oil can be used as supplemental fuel to obtain this temperature.

Upon entering the rotary kiln, the organic solids and liquids will be vaporized and the thermal oxidation reaction will start. Upon exiting the kiln, the solid and gaseous materials will go into a mixing chamber where the solids will fall into a wet ash handling system and the combustion gases will travel to the afterburner. The afterburner will operate at

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# TSCA INCINERATOR

DWG. NO. N/C-81-3867

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## INCINERATION

## OFF-GAS HANDLING

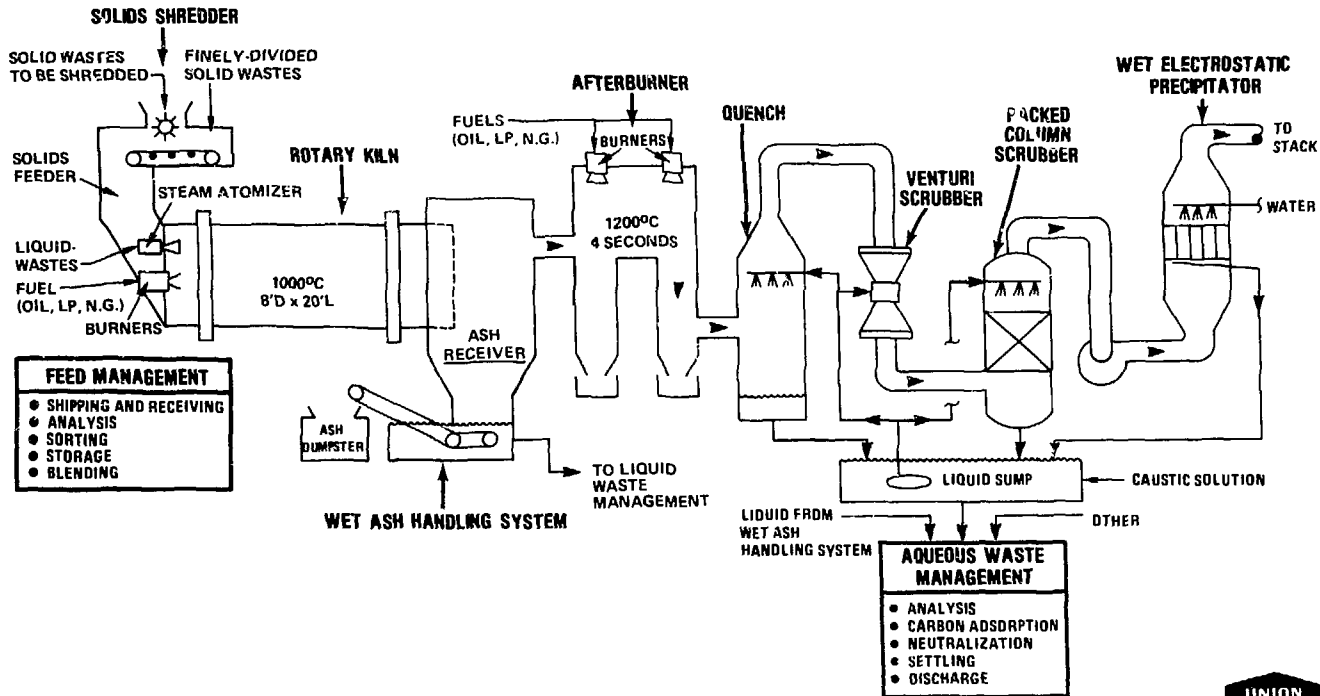


FIG 1



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1200°C and in the range of 3% to 10% excess oxygen. Natural gas or fuel oil can be used as supplemental fuel to maintain the temperature.

The wet ash handling system will be a water filled ash trough, and the ash will be pulled out of the trough by drag bars or similar equipment.

#### Off-Gas Treatment

After leaving the afterburner, combustion gases will pass through a refractory lined quench chamber. Here, the 1200°C combustion gases are cooled to adiabatic saturation (88°C) by water spray. The material of construction in the gas treatment system, after the quench, will be fiberglass reinforced plastic (FRP).

The cool gases will then pass through a medium energy venturi scrubber to remove large particles, followed by a packed bed scrubber to remove acidic gases. The induced draft fan will then force the material through a wet electrostatic precipitator to remove submicron particles. The clean gases will then exit to the atmosphere via a 100 foot (31 m) stack.

The total average volumetric design flow rate of gases emitted to the atmosphere is 3800 ACFM ( $1.8 \text{ m}^3/\text{s}$ ) which is 11,600 lb/hr (1.5 kg/s). This includes the primary combustion products ( $\text{CO}_2$ ,  $\text{H}_2\text{O}$ ) and excess air. The EIS estimated the emission rates of the gaseous effluents other than  $\text{N}_2$ ,  $\text{CO}_2$ ,  $\text{H}_2\text{O}$ , and excess air from the incinerator. These are shown in Table 3.

The water from the venturi and packed bed scrubber will be recirculated, and the pH will be controlled by NaOH. Addition of NaOH is necessary to neutralize the large amounts of HCl and other acidic gases generated.

TABLE 3

## Atmospheric Emissions Summary Estimate

| Pollutant                     | ppm or (gr/dscf)            | kg/hr                   | (lb/hr) | kg/yr                  | (lb/yr)                |
|-------------------------------|-----------------------------|-------------------------|---------|------------------------|------------------------|
| NO <sub>x</sub>               | 60.0                        | 0.31                    | (.68)   | 2300                   | (5060)                 |
| Particulates                  | (0.029)                     | 0.18                    | (.40)   | 1300                   | (2860)                 |
| HCl                           | 33.0                        | 0.14                    | (.31)   | 910                    | (2000)                 |
| VOC                           | 20.0                        | 0.038                   |         | 280                    | 620                    |
| CO                            | 10.0                        | 0.032                   |         | 230                    | 510                    |
| P <sub>2</sub> O <sub>5</sub> | (0.004)                     | 0.02                    |         | 160                    | 350                    |
| SO <sub>2</sub>               | 3.1                         | 0.02                    |         | 160                    | 350                    |
| F                             | 10.0                        | 0.02                    |         | 160                    | 350                    |
| Cl <sub>2</sub>               | 0.6                         | 0.004                   |         | 33                     | 73                     |
| U                             | (0.0003)                    | 1.2 x 10 <sup>-3</sup>  |         | 8.6                    | (19)                   |
| Pb                            | (7.5 x 10 <sup>-5</sup> )   | 4.5 x 10 <sup>-4</sup>  |         | 3.4                    | (7.5)                  |
| PCB                           | (3.7 x 10 <sup>-7</sup> )   | 2.2 x 10 <sup>-6</sup>  |         | 0.016                  | (.03)                  |
| HCB                           | 2.4 x 10 <sup>-5</sup>      | 7.7 x 10 <sup>-7</sup>  |         | 5.4 x 10 <sup>-3</sup> | 1.1 x 10 <sup>-2</sup> |
| Furans                        | 4.3 x 10 <sup>-10</sup>     | 2.7 x 10 <sup>-8</sup>  |         | 2.0 x 10 <sup>-4</sup> | 4.4 x 10 <sup>-4</sup> |
| Dioxins                       | 2.8 x 10 <sup>-10</sup>     | 1.7 x 10 <sup>-9</sup>  |         | 1.3 x 10 <sup>-5</sup> | 2.9 x 10 <sup>-5</sup> |
| Be                            | ( 9.4 x 10 <sup>-12</sup> ) | 5.9 x 10 <sup>-11</sup> |         | 4.3 x 10 <sup>-7</sup> | 9.5 x 10 <sup>-7</sup> |
| Fugitive VOC <sup>a</sup>     |                             | 0.12                    |         | 900                    | (1980)                 |

<sup>a</sup>VOC is volatile organic compounds.

Rain water and fire water will be collected in sumps and analyzed for designated pollutants. If acceptable, they will be discharged through the K-1700 (NPDES sampling point). If not acceptable, they will be pumped through carbon beds to remove the organics. Again, from the EIS, Table 4 shows the estimated contaminants in the purge water.

The ash from the incinerator will have a PCB level less than 50 ppm, or it will be recirculated into the incinerator. The ash will also have an estimated 60 mg of uranium/kg of dry ash. Other residues in the ash, such as lead and beryllium, are very small and not quantified.

The incinerator effluents will be disposed of as follows:

- ° Ash - Y-12 Radioactive Burial Ground
- ° Ash Water - Proposed Central Neutralization Facility (CNF) or K-1407A Pit
- ° Scrubber Water Blowdown - CNF or K-1407A Pit
- ° Rainwater and Firewater - K-1700 or Sewage Plant

The specific impact of this incinerator on the environment will be discussed in the report given by L. W. Long (Environmental Impact of Proposed Toxic Substance Incinerator).

TABLE 4

## Estimated Scrubber Purge Water Composition

| Parameter              | Concentration<br>g/l  | kg/hr                | (lb/hr)                | kg/hr                | lb/hr                 |
|------------------------|-----------------------|----------------------|------------------------|----------------------|-----------------------|
| Chloride               | 5.7                   | 24.1                 | (53)                   | 176,400              | (388,100)             |
| Fluoride               | $2.8 \times 10^{-1}$  | 1.2                  | (2.6)                  | 8,780                | (19,300)              |
| Sulfate                | $3.2 \times 10^{-2}$  | $1.4 \times 10^{-1}$ |                        | 1,020                | (2,240)               |
| Phosphate              | $1.6 \times 10^{-1}$  | $6.8 \times 10^{-1}$ |                        | 4,980                | (10,900)              |
| Sodium                 | 4.1                   | 17.3                 |                        | 126,600              | (278,520)             |
| Uranium                | $1.0 \times 10^{-2}$  | $4.0 \times 10^{-2}$ | $(8.8 \times 10^{-2})$ | 290                  | (640)                 |
| Lead                   | $2.4 \times 10^{-3}$  | $1.0 \times 10^{-2}$ |                        | 73                   | 161                   |
| Beryllium              | $3.0 \times 10^{-10}$ | $1.2 \times 10^{-9}$ |                        | $8.8 \times 10^{-6}$ | $1.94 \times 10^{-5}$ |
| Total Dissolved Solids | 10.9                  | 46                   |                        | 336,700              | (740,700)             |
| Total Suspended Solids | $8.3 \times 10^{-1}$  | 3.5                  |                        | 25,800               | 56,300                |

## SUMMARY OF TECHNICAL SUPPORT

During the early, planning phase of the TSCA Line Item Project, several uncertainties were identified which would need to be resolved before the final design of the project can be completed. While not altogether unique, these uncertainties are peculiar to the special requirements of the TSCA incinerator and therefore require special consideration aimed at overcoming potential problems that are expected in the ORGDP unit. As pointed out earlier, the TSCA unit is required to handle a special combination of feed materials that no other U.S. system is licensed to handle: PCBs and radioactive contaminated wastes. A further complication is imposed on this system by the wide range of feed materials having widely varying characteristics which must be processed under stringent emission guidelines. It is necessary that these widely varying feed materials must be managed and blended to achieve safe and efficient incineration and that the wastes generated (ash, scrubber liquor and sludges, and off-gases) can be handled satisfactorily in the existing and proposed ORGDP waste management facilities. The following discussion briefly outlines the technical support work that is being carried out by a team of technical personnel from the Process Support and Operations Divisions at ORGDP to resolve these uncertainties.

## Waste Characterization

Although the current level of waste characterization is sufficient for the present needs further studies of existing, as well as future, wastes are planned. The need is to determine if the blending of incompatible



materials could result in an undesirable criticality situation, precipitation, polymerization, explosion, or generation of an unexpected hazardous or toxic material. As part of this study, the quantities, heating values, and viscosities of the high heat content oils and organic liquids will be more closely evaluated. Having this information will permit the formulation of a plan for the efficient, safe and simultaneous incineration of low and high heat content materials with a minimum need for auxiliary fuel.

#### Shredder and Solids Feed

Because of size limitations, it will not be possible to feed intact, empty drums or capacitors into the rotary kiln. Therefore, a shredding system, in conjunction with a solids feeding system, will be required to achieve the needed size reduction. The most critical problem associated with the shredder is the potential for fire or explosion, caused either by explosive residues remaining in a pre-emptied drum or by the accidental placement of an unemptied drum of flammable liquid in the shredder. A comprehensive analysis of this system will be carried out to minimize these dangers and will include a survey of incinerator operators and manufacturers having experience in this area.

#### Selection of Refractory

The punishing environment that is expected in the rotary kiln (1000°C), the afterburner (1200°C), and quench chamber of the TSCA incinerator will, at best, result in slagging, breakdown, and spalling of the refractory materials which are used to line these areas. In addition to the deleterious effects of high temperatures, intermittent operation,

and abrasive solids, hydrogen chloride gas will be generated in significant quantities during the incineration of chlorinated organic feed materials: PCBs, trichloroethane, trichloroethylene, and methylene chloride. The hydrogen chloride, as well as small quantities of hydrogen fluoride which may be present, is expected to further accelerate the refractory breakdown. A survey of available refractory materials, augmented by the experience of the few operators of incinerator facilities which process chlorinated organics at these temperatures, will be the primary means of selecting the lining most applicable for the TSCA unit.

#### Ash Handling

The current design, as shown in Figure 1, proposes that ash falling out of the kiln will be quenched in water and handled wet. Data obtained on typical ash generated during the test burns will be used in determining whether a wet or dry ash handling system is most suitable for the wide range of solid material which will be generated in the TSCA kiln.

#### Behavior of Uranium

Very little information has been located which describes the behavior of uranium under the conditions that will exist in the rotary kiln and afterburner. Because of the absence of data, an attempt was made during the test burns to simulate the behavior of uranium in the kiln, afterburner, and off-gas treatment system by adding the element tungsten to the feed to the kiln.

## Adsorption of PCBs from Incinerator Aqueous Wastes

At the present time, the maximum allowable level of PCBs in waste water released to the environment through an NPDES discharge point is less than or equal to 1 ppb. Because unpredictable circumstances in the incinerator and/or off-gas treatment may occur which could result in the presence of undestroyed PCBs in the various aqueous waste streams generated by the facility, it is desirable that a standby system be provided which can scavage the PCBs sufficiently to meet the stringent discharge limits. A carbon adsorption system would be a more economical means of handling contaminated water than the alternative, which is processing the water through the kiln at a considerable energy cost.

A study is currently being directed at ORGDP to determine the effectiveness of activated carbon for removing trace quantities of PCBs from simulated waste water and to define the design parameter associated with this technology. During the initial equilibrium sorption study, Calgon F-300 powdered activated carbon demonstrated its strong sorption characteristics for the PCBs. However, in a subsequent column sorption study using the granular form of the Calgon F-300, premature breakthrough occurred because the sorption of the PCBs was severely reduced by the sorption limiting diffusion of PCBs into the granular carbon. During this first column study, the total Aroclor\* concentration in the feed was about 154 micrograms/liter (154 ppb). Based on analysis of the data from

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\* A trademark of the Monsanto Chemical Company for a general line of polychlorinated biphenyls.

the first column study, plans have been formulated for additional sorption studies using a more finely divided Calgon F-300 carbon which will pass through a 100-mesh screen. By reducing the feed concentration of total Aroclor to about 40 micrograms/liter (40 ppb), and by using a more finely divided carbon particle to minimize sorption-limiting diffusion, it is expected that from 150,000 to 400,000 bed volumes of feed solution can be processed before breakthrough, per volume of carbon bed. The amount of PCB adsorbed has been shown by the study to be dependent upon the degree of chlorine-saturation of PCB in the feed, as well as on the solution temperature. The analytical procedure developed during the study for analyzing the column effluent for PCBs is considered to be an invaluable aid in analyzing similar aqueous solutions.

#### Off-Gas Treatment

The current conceptual design, as shown in Figure 1, includes a medium energy venturi scrubber for removal of particles down to a few microns, a packed tower for efficient scrubbing of the acid vapors, and finally a wet electrostatic precipitator (WESP) for removal of a fraction of the submicron particles. To enhance the efficiency of acid scrubbing, caustic will be added to the recirculating scrubber liquors. An alternative to the WESP is a series of wet ionizing scrubbers (WIS). These units, as opposed to WESPs, are categorized as fractional collectors, and are known to improve overall collection efficiency as more units are added in series. WIS units also contain wetted packing, which improves acid scrubbing while performing particulate removal. A thorough comparison of the two technologies will be carried out by consulting with vendors and operators of installations using this equipment as part of the technical assistance before the type of final collector is chosen.

### TEST BURNS

Some of the major uncertainties which are peculiar to the types of feed materials to be burned, and to the resultant solids, liquids, and gases generated during the incineration of these feeds, are being resolved as a result of test burns conducted at C-E Raymond facilities in August of 1981. The following discussion summarizes some of the information which resulted from the series of tests.

The test burns were conducted at C-E Raymond's pilot plant incinerator in Springfield, Ohio, shown in Figure 2. The rotary kiln was manufactured by Bartlett-Snow, a subsidiary of C-E Raymond. Constant increments of the solid samples were fed into the front end of the kiln at regular time intervals. The liquid feeds were fed into the front end of the kiln through an air atomizing nozzle. The flow rate of the liquid wastes was determined from the weight change of the feed drum. Supplemental heat to the rotary kiln was provided by a natural gas burner located at the back end of the kiln and not visible in this picture (Figure 2). The solid wastes moved slowly through the kiln as it rotated at a slight incline. The ashes fell into a hopper located beneath the back end of the kiln.

The gases then passed up into an afterburner (also shown in Figure 2). Supplemental heat to the afterburner was supplied by a natural gas burner at the front end. The gases leaving the afterburner then passed through the off-gas treatment system shown in the schematic diagram, Figure 3. The gases were first cooled in a quench chamber and then passed through a venturi scrubber followed by a mist eliminator before being discharged out the stack by an induced draft fan.

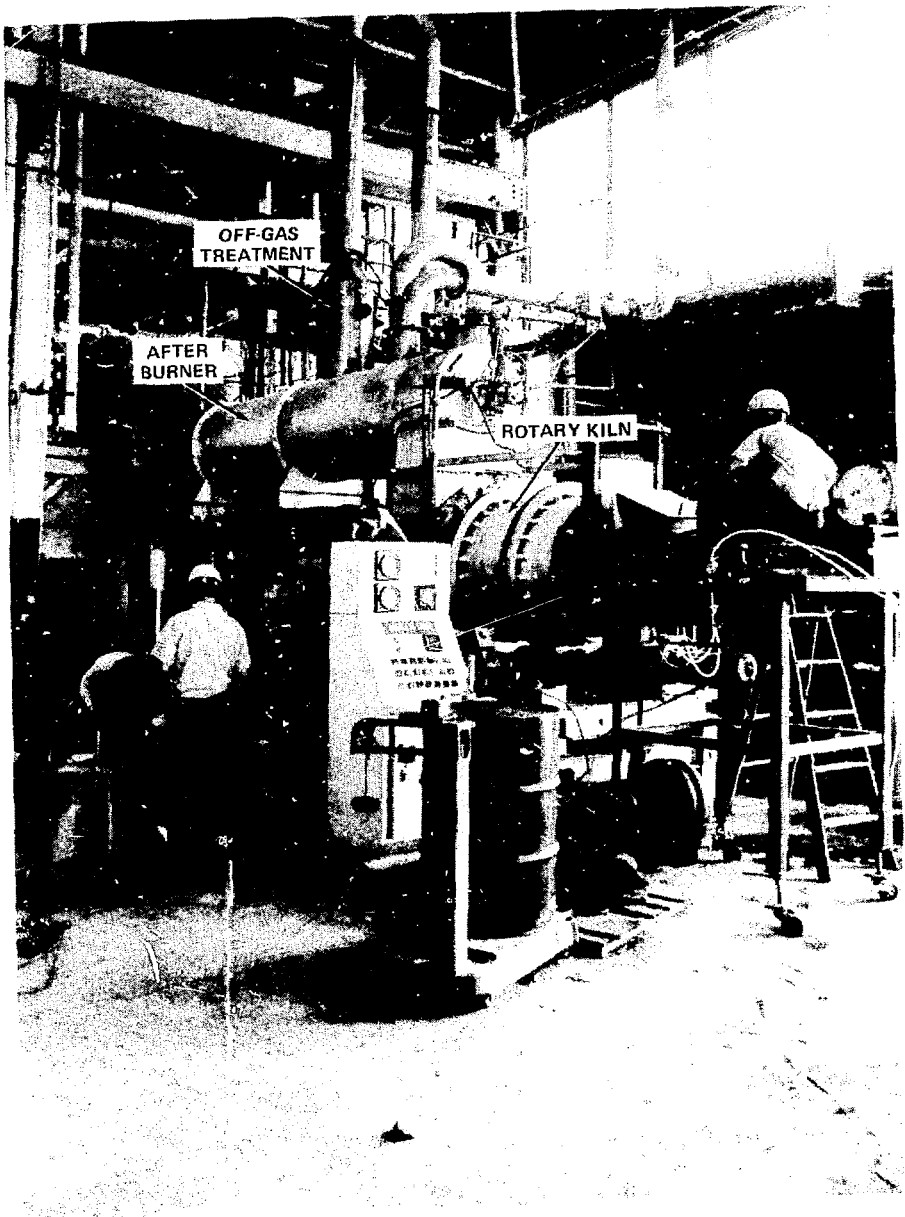


Figure 2  
C-E RAYMOND PILOT PLANT INCINERATOR

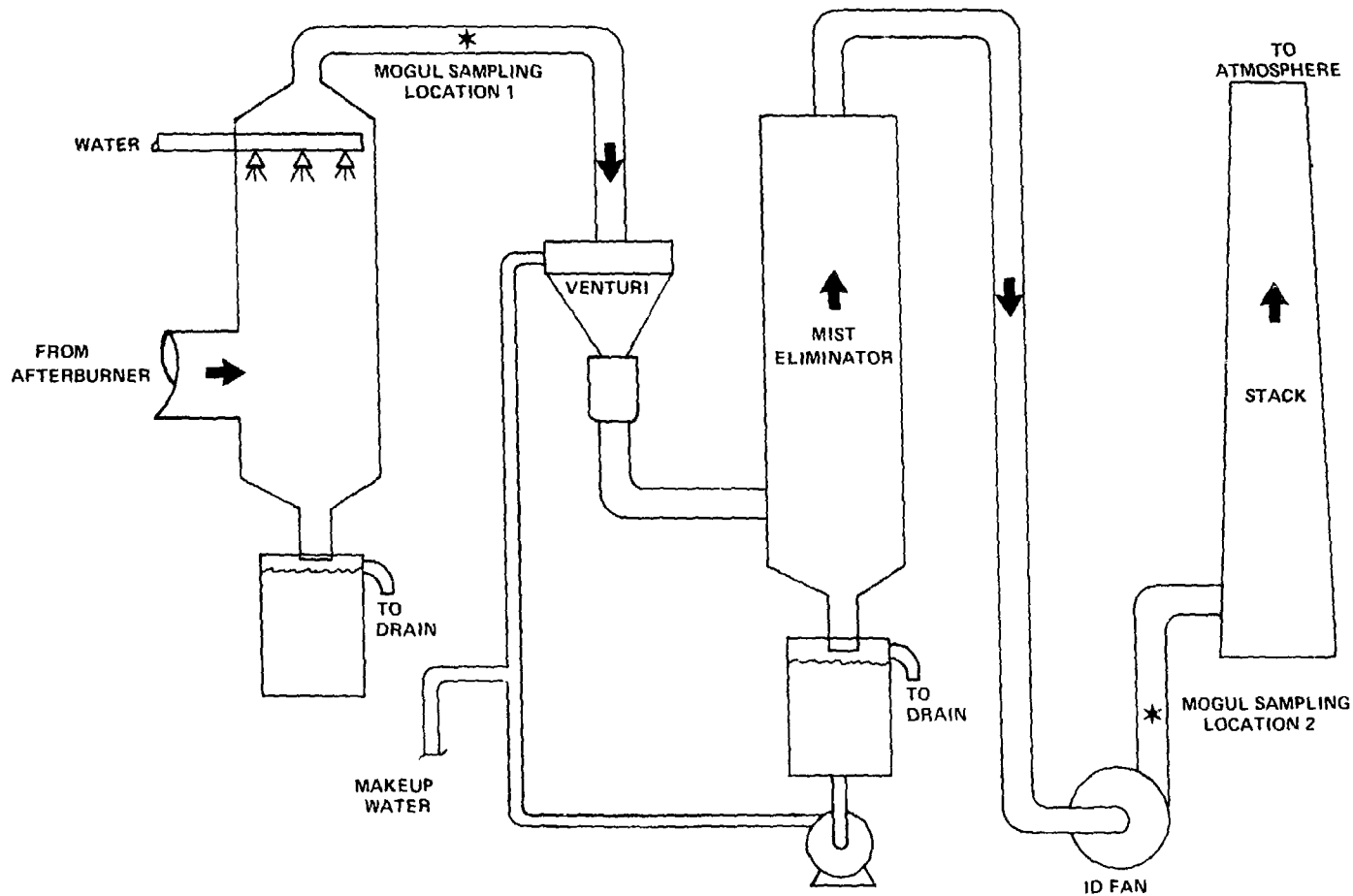


Figure 3  
C-E RAYMOND PILOT PLANT  
OFF-GAS TREATMENT SYSTEM

It was not possible to burn wastes contaminated with either polychlorinated biphenyls (PCBs) or uranium in C-E Raymond's equipment or in any other pilot plant incinerator in the United States. Because of this restriction, the test burn materials were carefully chosen to simulate the wide variety of wastes to be destroyed in the ORGDP incinerator. The test burn materials are listed in Table 5.

A chlorinated organic, 1,1,1-trichloroethane (TCE), was chosen because a large amount of this degreaser solvent will be fed to the ORGDP incinerator and because TCE, like PCBs, resists oxidation and produces substantial quantities of HCl when burned. Waste motor oil was chosen to represent BG oil, a type of lubricant used in the gaseous diffusion plants. Large quantities of BG oil will be burned in the ORGDP incinerator. Used oil from the ORGDP garage which contained sludge and metals was chosen in preference to clean, new BG oil or used BG oil with metals contamination. Solid materials - dirt, sand, and clay safety absorbent (Sorbal) - soaked in an oil/TCE mixture were also burned in the tests. These types of organic liquid-soaked materials would likely be generated during spills and would need to be fed to the ORGDP incinerator.

It was not possible to duplicate the planned operating conditions of the ORGDP incinerator in C-E Raymond's smaller incinerator which was built before the TSCA regulations were formulated. Temperatures and turbulences were controlled as closely as possible to the ORGDP operating values. Because of the physical restrictions of C-E Raymond's equipment, afterburner residence times of only 1/4 to 1/3 second were obtained instead of the 4 seconds planned for the ORGDP incinerator. The rotary kiln and afterburner temperatures obtained for each run are given in Table 6.



Table 5

## Burn Materials

| Run | Burn Material                                                                                      | Comments                                                                                                                                                          |
|-----|----------------------------------------------------------------------------------------------------|-------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| 1   | natural gas                                                                                        | Because natural gas was used as supplemental fuel during all of the test burns, this first test was a "blank" to determine background levels.                     |
| 2   | 91% Y-12 burial ground dirt, 4.5% waste motor oil, 4.5% tri-chloroethane                           | Large quantities of Y-12 oil landfarm dirt may be burned in the ORGDP incinerator.                                                                                |
| 3   | dirt from the ORGDP contractor's burial ground                                                     | Burned to determine the behavior of the ash formed by a different type of dirt. Contaminated dirt from any future spill site may be fed to the ORGDP incinerator. |
| 4   | 50% waste motor oil, 50% tri-chloroethane                                                          | Large quantities of waste oils and chlorinated organics will be burned in the ORGDP incinerator.                                                                  |
| 5   | waste motor oil                                                                                    | Waste motor oil containing sludge and metals was chosen in preference to clean, new oil or used turbine oil (BG oil) with possible uranium contamination.         |
| 6   | 65% Sorbal, 17.5% waste motor oil, 17.5% tri-chloroethane                                          | Similar wastes may be created during spill cleanup and fed to the ORGDP incinerator.                                                                              |
| 7   | 94% sand, 3% waste motor oil, 3% trichloroethane                                                   | Sand may be fed to the ORGDP incinerator to protect the refractory.                                                                                               |
| 8   | 91% Y-12 burial ground dirt, 4.5% waste motor oil, 4.5% tri-chloroethane (kerosene fed separately) | A repeat of Run 2 to study the effect of higher temperatures.                                                                                                     |
| 9   | 50% waste motor oil, 50% tri-chloroethane                                                          | A repeat of Run 4 to study the effect of a higher feed rate and higher temperatures.                                                                              |

Table 6  
Test Conditions

| Run | Burn Material                                                                       | Rotary Kiln<br>Temperature,<br>°C | Afterburner<br>Temperature,<br>°C |
|-----|-------------------------------------------------------------------------------------|-----------------------------------|-----------------------------------|
| 1   | natural gas                                                                         | 1040                              | 1080                              |
| 2   | 91% Y-12 dirt, 4.5% waste motor oil, 4.5% trichloroethane                           | 850                               | 920                               |
| 3   | ORGDP dirt                                                                          | 790                               | 890                               |
| 4   | 50% waste motor oil, 50% trichloroethane                                            | 900                               | 970                               |
| 5   | waste motor oil                                                                     | 1050                              | 1150                              |
| 6   | 65% Sorbal, 17.5% waste motor oil, 17.5% trichloroethane                            | 980                               | 1090                              |
| 7   | 94% sand, 3% waste motor oil, 3% trichloroethane (waste motor oil fed separately)   | 940                               | 1070                              |
| 8   | 91% Y-12 dirt, 4.5% waste motor oil, 4.5% trichloroethane (kerosene fed separately) | 970                               | 1040                              |
| 9   | 50% waste motor oil, 50% trichloroethane                                            | 980                               | 1090                              |
|     | Planned for ORGDP incinerator                                                       | 1000                              | 1200                              |

Samples of the waste materials were analyzed in detail by UCC-ND before shipment to Springfield. The flow rates of natural gas and air to the burners, as well as the rotary kiln and afterburner temperatures, were recorded during the test burns by C-E Raymond's operating personnel. The solids feed rate to the kiln was manually controlled by the addition of constant increments of solids at regular time intervals. Liquid flow rates to the kiln were determined by measuring the rate of weight loss from the feed drum. The temperature, pH, and flow rates of the quench and venturi scrubber liquors were measured at regular intervals by UCC-ND representative.

Extensive stack gas sampling was performed during each of the test burns by the Mogul Corporation of Chagrin Falls, Ohio, a subcontractor to C-E Raymond. Mogul sampled at two locations as shown in Figure 3: (1) between the quench and the venturi and (2) in the stack after the induced draft fan. A sample location before the quench would have been desirable, but there was not a sufficient length of straight pipe to obtain the flow conditions needed to obtain a representative sample. Mogul used EPA-approved methods to carry out the stack gas sampling. Mogul also recorded the temperature and flow rate at their sample location.

Samples of the quench and scrubber liquors and of the ash were shipped to ORGDP for analysis. In addition to the off gas analysis performed by Mogul Corporation, off-gas samples were collected on carbon tubes by the Mogul Corporation and shipped to ORGDP.

A list of the data collected during the test burns is given in Table 7 and a list of the analyses performed on the samples from the test burns is given in Table 8.

Table 7  
Data Collected During Test Burns

---

Visual observation of refractory lining of kiln

Visual observation of flame

Visual observation of discharge from the stack

Temperature of kiln

Temperature of afterburner

Temperature of off-gas after quench and before scrubber

Temperature of off-gas in the stack

Temperature of quench liquor

Temperature of scrubber liquor

Feed rate of waste to kiln

Feed rate of natural gas to kiln

Feed rate of natural gas to afterburner

Flow rate of off-gas after quench and before venturi

Flow rate of off-gas in stack

Pressure of off-gas after quench and before scrubber

Pressure of off-gas in stack

pH of quench liquor

pH of scrubber liquor

---

Table 8

## ANALYSIS OF SAMPLES

| <u>Sample</u>  | <u>Analyzed For</u>                                                                                                                                                                                                                                | <u>Analyzed By</u> |
|----------------|----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|--------------------|
| feed materials | heating value<br>ash content<br>moisture<br>carbon<br>hydrogen<br>nitrogen<br>oxygen<br>chlorine<br>sulfur<br>metals                                                                                                                               | UCC-ND             |
| off-gas        | particulate loading<br>particulate size<br>distribution<br>water<br>oxygen<br>carbon dioxide<br>carbon monoxide<br>nitrogen<br>hydrogen chloride<br>hydrocarbons<br>nitrous oxides<br>lead<br>zinc<br>tungsten (1 run)<br>chlorinated hydrocarbons | Mogul              |
| quench liquor  | pH<br>total organic carbon<br>total solids<br>suspended solids<br>dissolved solids<br>chloride<br>sulfate<br>nitrate<br>metals                                                                                                                     | UCC-ND             |

Table 8 (Continuation)

| ANALYSIS OF SAMPLES |                                                                                                    |                    |
|---------------------|----------------------------------------------------------------------------------------------------|--------------------|
| <u>Sample</u>       | <u>Analyzed For</u>                                                                                | <u>Analyzed By</u> |
| scrubber liquor     | pH<br>TOC<br>total solids<br>dissolved solids<br>chloride<br>sulfate<br>nitrate<br>metals          | UCC-ND             |
| ash                 | metals<br>chlorine<br>carbon<br>G-C analysis<br>particle size screening<br>EPA leachage extraction | UCC-ND             |

### Results

The remainder of this paper will discuss a few of the findings from the test burns. A comprehensive report on the results and conclusions from the test burns is being issued.

The current plans for the ORGDP incinerator specify that the ash from the rotary kiln will be quenched by discharging into a hopper of water as shown in Figure 4. The wet, cooled ashes will then be dredged from the bottom of the water hopper by conveying equipment and dropped into a dumpster. There has been concern about the behavior of the ashes upon being dropped into the water because large quantities of dirt from the Y-12 oil landfarm and dirt from the site of any future of spill of hazardous materials may be fed to the ORGDP incinerator. It is feared that ashes from the dirt might change to mud upon mixing with the water.

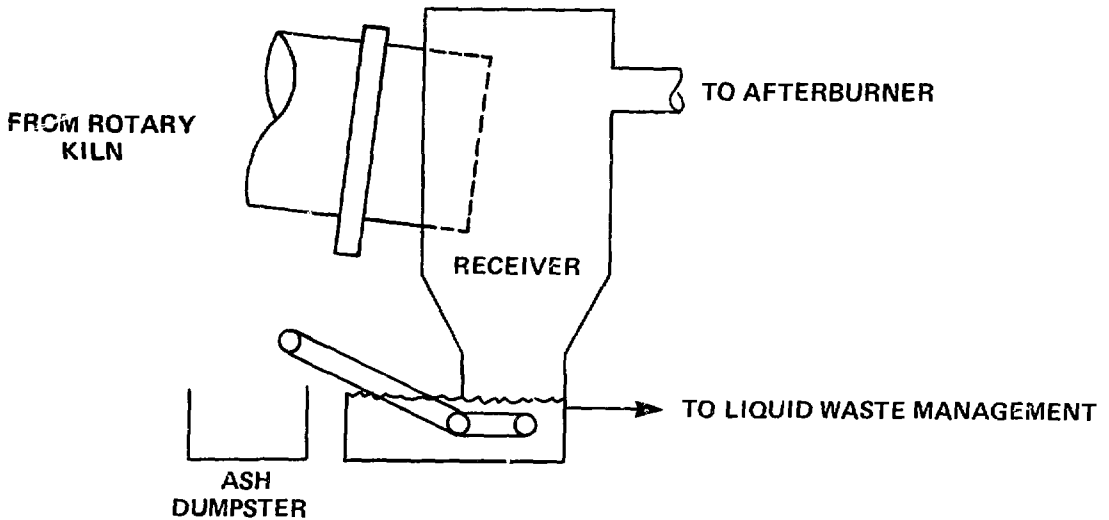


Figure 4  
TSCA INCINERATOR WET ASH HANDLING SYSTEM

The behavior of the ash formed from two different types of dirt when the ash was dropped into water was observed. The ash formed by red clay from the ORGDP contractor's burial ground formed durable chunks, similar to broken brick, which sank to the bottom of the water. The other type of soil used in the test burns was from the Y-12 burial ground near the oil landfarm and contained a large amount of chert. This dirt formed some small chunks during the test burn, but a significant amount of the ash remained as finely divided particles which caused the ash water to be turbid; however, the ash did not form viscous mud.

As shown in Table 9, more auxiliary fuel was used per kilogram of feed than is planned for the ORGDP incinerator. Less auxiliary fuel per kilogram of fuel may be needed in the ORGDP incinerator because it will be

Table 9  
TEST CONDITIONS

| Run | Burn Material                                                                           | Rotary Kiln<br>Temperature, °C | Afterburner<br>Temperature, °C | Auxiliary Fuel<br>J/kg Feed<br>(BTU/lb/Feed) |
|-----|-----------------------------------------------------------------------------------------|--------------------------------|--------------------------------|----------------------------------------------|
| 1   | natural gas                                                                             | 1040                           | 1080                           |                                              |
| 2   | 91% Y-12 dirt, 4.5% waste motor oil<br>4.5% trichloroethane                             | 850                            | 920                            | $7.65 \cdot 10^7$<br>(32,000)                |
| 3   | ORGDP dirt                                                                              | 790                            | 890                            | $7.65 \cdot 10^7$<br>(32,000)                |
| 4   | 50% waste motor oil, 50% trichloroethane                                                | 900                            | 970                            | $3.07 \cdot 10^8$<br>(132,000)               |
| 5   | waste motor oil                                                                         | 1050                           | 1150                           | $8.16 \cdot 10^7$<br>(35,100)                |
| 6   | 65% Sorbal, 17.5% waste motor oil<br>17.5% trichloroethane                              | 980                            | 1090                           | $4.63 \cdot 10^7$<br>(19,900)                |
| 7   | 94% sand, 3% waste motor oil, 3% trichloro-<br>ethane (waste motor oil fed separately)  | 940                            | 1070                           | $5.49 \cdot 10^8$<br>(236,000)               |
| 8   | 91% Y-12 dirt, 45% waste motor oil, 4.5% tri-<br>chloroethane (kerosene fed separately) | 970                            | 1040                           | $2.24 \cdot 10^8$<br>(96,500)                |
| 9   | 50% waste motor oil, 50% trichloroethane                                                | 980                            | 1090                           | $1.53 \cdot 10^8$<br>(65,800)                |
|     | Planned for ORGDP incinerator                                                           | 1000                           | 1200                           | $5.63 \cdot 10^7$<br>(24,200)                |



larger (have a lower surface area to volume ratio) and will be better insulated than the C-E Raymond incinerator, and because the low heating value wastes will be blended with high heating value wastes before being fed to the incinerator.

It is recommended that a detailed heat balance be performed during the design of the ORGDP incinerator to be sure that there will be sufficient input of energy in the form of the heat of combustion of the waste and auxiliary fuel to achieve the required combustion temperatures when all of the heat losses are taken into account.

In general, all of the wastes burned well. However, excessive amounts of fly ash resembling carbon black were formed during burns 4, 5, 8, and 9 when the pilot plant incinerator was operating far beyond its design conditions. During test burn 9 when the oil/TCE mixture was being forced into the incinerator at a high feed rate, the concentration of total hydrocarbons in the off-gas was about 10 times as large as in the other test burns. Better control of the air flow, the higher temperatures, and the longer residence times should prevent any incomplete combustion problems in the ORGDP incinerator. The use of a steam atomizing burner as planned for the ORGDP incinerator should give more complete combustion than was obtained with the air atomizing nozzle used in the test burns. Burner manufacturers recommend steam atomizing burners for incinerating chlorinated organic liquids.

Some of the other conclusions from the test burns are summarized in Table 10 and the other useful information gained from the test burns is listed in Table 11.

510-3-18

Table 10

## OTHER CONCLUSIONS FROM THE TEST BURNS

- 
- The refractory should be carefully chosen to withstand the severe operating conditions - halogenated compounds and high temperatures - in the ORGDP incinerator.
  - Even at the lower kiln temperatures used during these test burns, the organic materials were volatilized out of the dirt and sand.
  - The safety absorbant soaked in oil and TCE gave the poorest burnout of liquid organics. It is expected that the longer residence time and higher temperatures of the ORGDP incinerator will give a much more efficient burnout.
  - The ash from burning these materials passed the EPA leachate toxicity test and could be disposed of in the Y-12 landfill as proposed in the CDR.
  - The HCl removal efficiency of the venturi scrubber was higher during the one test when the pH of the scrubber liquor was controlled (pH control is planned for the ORGDP incinerator).
  - Some flocculation of the carbon soot in the scrubber liquor was observed when the pH was controlled at 9-10.
  - Except for the 2 burns of oil/TCE mixture, the total, dissolved and suspended solids in the waste water for each unit mass of feed were less than the average according to the current design.
  - A lower percentage of the chlorine in the feed was discharged to the atmosphere as HCl during the test burns than the percentage given in the current design.
-

Table 11

## USEFUL INFORMATION FROM THE TEST BURNS

- 
- Quantity of particulate in the off-gas streams by size range for each unit mass of feed.
  - Ash particle size distribution.
  - Quantity of waste water contaminants discharged for each unit mass of feed.
  - Quantity of off-gas contaminants for each pound of feed.
  - Effect of scrubber water pH control on the efficiency of the venturi scrubber.
-

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## ENVIRONMENTAL IMPACTS OF PROPOSED TOXIC SUBSTANCES INCINERATOR

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## ABSTRACT

A high-temperature incinerator has been proposed for construction at the Oak Ridge Gaseous Diffusion Plant (ORGDP) for the purpose of thermally destroying hazardous organic waste, including polychlorinated biphenyls, contaminated with radioactivity. The facility would handle waste from the Paducah Gaseous Diffusion Plant, the Portsmouth Gaseous Diffusion Plant, the Oak Ridge National Laboratory, and the Oak Ridge Y-12 Plant, as well as the ORGDP. In order to meet the requirements of the National Environmental Policy Act, an Environmental Impact Statement (EIS) has been prepared. The EIS was prepared for the Department of Energy by Battelle Columbus Laboratories with technical input being provided by Union Carbide Nuclear Division. The statement provides detailed evaluations of both construction and operating impacts of the proposed incinerator. In general, the environmental impacts associated with the proposed incinerator were determined to be insignificant relative to the benefits it will afford. This paper briefly summarizes the evaluations and conclusions presented in the EIS.

INTRODUCTION

The Department of Energy (DOE) has proposed to construct and operate an incineration facility at the Oak Ridge Gaseous Diffusion Plant (ORGDP) at Oak Ridge, Tennessee. The proposed incineration facility would provide a means of disposal for polychlorinated biphenyl (PCB) wastes and other liquid organic waste which are contaminated with very small concentrations of radionuclides (primarily low-assay

uranium). This facility would handle wastes from the Paducah Gaseous Diffusion Plant, the Portsmouth Gaseous Diffusion Plant, the Oak Ridge National Laboratory, and the Oak Ridge Y-12 Plant, as well as the ORGDP. DOE has determined that according to the National Environmental Policy Act (NEPA), this project would represent a major federal action and, therefore, requires a detailed report describing the environmental impacts of the proposed action.

The Environmental Impact Statement (EIS)<sup>1</sup> was prepared for the DOE by Battelle Columbus Laboratories with technical input being provided by Union Carbide Nuclear Division. This EIS was prepared in accordance with DOE's guidelines<sup>2</sup> for compliance with the NEPA as implemented by the regulations<sup>3</sup> promulgated by the Council of Environmental Quality. A notice of intent<sup>4</sup> to prepare an EIS was issued by DOE on February 10, 1981. Public scoping meetings to assist in determining the level of coverage of issues in the EIS were held in Oak Ridge, TN (February 24, 1981), Nashville, TN (February 25, 1981), Frankfort, KY (February 26, 1981), and Columbus, OH (March 3, 1981). The final EIS should be available to the public by May 1, 1982. The following sections have been extracted from the EIS and represent some of the evaluations and conclusions reached by the EIS.

#### CONSTRUCTION IMPACTS

Constuction of the proposed incinerator would have the potential to cause changes in the quality of the physical environment. Construction activities would result in emissions of dust and gases. Sources of these emissions would be land grading and excavation, storage of excavated materials, and equipment and vehicle operations. The quantity of dust emissions from construction operations would be dependent upon the area of land being worked. The construction activities for the proposed facility would involve only a small area (5 acres) and fugitive dust could easily be controlled by watering. The airborne emissions from contruction machinery would not result in a significant increase in the ambient air pollutant concentrations in the vicinity of the ORGDP

The primary effect on water quality from construction activities would be an increase in the sediment load to Poplar Creek. This increase in loading would result from erosion by precipitation on barren soils. Mitigation measures, such as the use of straw around disturbed soils or the use of ditches and dikes to curtail sediment run-off, should minimize potential impacts of soil erosion. Any unavoidable construction impacts would be of short duration and reversible.

#### AIR QUALITY IMPACTS

The combustion of the various waste materials would result in a flue gas containing small amounts of environmental pollutants of which hydrochloric acid, particulates, oxides of nitrogen, and volatile organic compounds are the most important in terms of emission rates. Estimates were made of the maximum ground-level concentrations of pollutants which would occur due to the proposed incinerator. Two types of events were analyzed, short-term concentrations and average annual concentrations. Analysis of pollutant dispersion from the proposed incinerator is complicated by the complex local terrain. Since there is no accepted model which can satisfactorily calculate the dispersion of airborne emissions from the proposed incinerator, given the complex local terrain, models were selected which result in overestimation of the concentrations. Based on this modeling, it was determined that the increase in the concentrations of these pollutants would represent an insignificant change in the environment. A summary of public exposures from stack emissions is presented in Table 1.

Table 1

| <u>Summary of Public Exposures From Stack Emissions</u> |                                                                          |
|---------------------------------------------------------|--------------------------------------------------------------------------|
| <u>Pollutant</u>                                        | <u>Annual Mean Exposure at Most Exposed Residence (ug/m<sup>3</sup>)</u> |
| Oxides of Nitrogen                                      | $1.0 \times 10^{-2}$                                                     |
| Particulates                                            | $5.8 \times 10^{-3}$                                                     |
| Hydrochloric Acid                                       | $4.4 \times 10^{-3}$                                                     |
| Volatile Organics                                       | $<1.3 \times 10^{-3}$                                                    |
| Carbon Monoxide                                         | $1.0 \times 10^{-3}$                                                     |
| Phosphorous Pentoxide                                   | $7.3 \times 10^{-4}$                                                     |
| Sulfur Dioxide                                          | $<7.3 \times 10^{-4}$                                                    |
| Fluoride                                                | $<7.3 \times 10^{-4}$                                                    |
| Chloride                                                | $<1.5 \times 10^{-4}$                                                    |
| Uranium                                                 | $3.8 \times 10^{-5}$                                                     |
| Lead                                                    | $1.5 \times 10^{-5}$                                                     |
| Polychlorinated Biphenyl                                | $6.7 \times 10^{-8}$                                                     |
| Hexachlorobenzene                                       | $2.4 \times 10^{-8}$                                                     |
| Furans                                                  | $8.8 \times 10^{-10}$                                                    |
| Dioxins                                                 | $5.6 \times 10^{-11}$                                                    |
| Beryllium                                               | $1.9 \times 10^{-12}$                                                    |

#### WATER QUALITY IMPACTS

Water quality effects on Poplar Creek were evaluated by using the direct discharge of treated facility effluents. These effluents may be generated by the normal facility operations or from fire or storm water discharges. Contaminants identified as being present in the effluent include chloride, fluoride, sulfate, phosphate, sodium, uranium, lead, beryllium, and suspended solids. Contaminants may also be contributed to water courses from erosion and the subsequent runoff of soil particles. Temperature and pH are not expected to be significant issues due to retention time and neutralization provided by the waste water treatment system. Unavoidable adverse impacts upon the water resources were determined to be minimal represented principally by the slight increase in dissolved solids from the waste water treatment facility. Table 2 shows the effects on water quality by the aqueous effluents.



Table 2

Effects of Facility Discharges on Water Quality in Poplar Creek

| <u>Contaminant</u>     | <u>Existing<br/>Concentration (mg/l)</u> | <u>Projected<br/>Concentration (mg/l)</u> |
|------------------------|------------------------------------------|-------------------------------------------|
| Chloride               | 6                                        | 8                                         |
| Fluoride               | <0.2                                     | <0.25                                     |
| Sulfate                | 34                                       | 34                                        |
| Phosphate              | 0.25                                     | 0.26                                      |
| Sodium                 | 7                                        | 8                                         |
| Uranium                | 0.006                                    | 0.007                                     |
| Lead                   | <0.01                                    | <0.01                                     |
| Beryllium              | <0.0004                                  | <0.0004                                   |
| Total Dissolved Solids | 186                                      | 188                                       |
| Total Suspended Solids | 7                                        | 7                                         |

PUBLIC HEALTH IMPACTS FROM RADIONUCLIDES

The EPA limits<sup>5</sup> for radiological doses to any off-site individual from uranium fuel cycle operations are 75 millirem per year for the thyroid and 25 millirem per year for all other organs. Exposures from liquid discharges of radionuclides were calculated using a computer data base which included internal and external dose conversion factors and bioaccumulation factors. It was assumed that 1.2 liters of water would be consumed per day from Clinch River; that 47 grams of fish from Poplar Creek would be consumed per day; and that 5 percent of the year would be spent swimming in Poplar Creek. This analysis represents a worst case and the results which are presented in Table 3 would therefore overestimate the dose which would be received by an individual.

Table 3

75-Year Dose Commitment Due to Liquid Discharges

| <u>Organ</u> | <u>Dose in Millirems</u> |
|--------------|--------------------------|
| Total Body   | 0.24                     |
| G.I. Tract   | 0.02                     |
| Bone         | 0.24                     |
| Thyroid      | 0.08                     |
| Lung         | <0.01                    |
| Liver        | 0.08                     |
| Kidneys      | 0.12                     |
| Testes       | 0.08                     |
| Ovaries      | 0.08                     |

Note: Computation by the Oak Ridge National Laboratory

Doses due to air emissions from the proposed facility were calculated for the nearest resident which would be about 3200 meters southwest of the ORGDP. Specific pathways for airborne exposures include direct irradiation, inhalation, and ingestion. It was assumed that this individual ate only food grown and processed in the same area. Since this is unlikely, the estimates are conservative and likely to be higher than would actually occur. The dose commitment due to air emissions from the proposed facility is presented in Table 4.

Table 4

50-Year Dose Commitments Due to Air Emissions

| <u>Organ</u> | <u>Dose in Millirems</u> |
|--------------|--------------------------|
| Total Body   | 0.28                     |
| Red Marrow   | 0.28                     |
| Lungs        | 0.03                     |
| LLI Wall     | 0.02                     |
| Thyroid      | 0.01                     |

Note: Computation by the Oak Ridge National Laboratory

ACCIDENT SCENARIOS

In the analysis of the proposed process design, numerous accident scenarios were postulated based on the historic record of chemical handling industries, incinerator facilities, and other facilities with handling, storage, or process similarities to the proposed incinerator. Safety features in the conceptual design were found to adequately reduce the risk associated with most of these accidents to an acceptable level. Of the numerous accidents evaluated only three were found to have a risk which was not clearly acceptable. These three accidents all involved fire at some point in the process. The adverse consequences resulting from an occurrence of one of these accidents would be the possible occupational exposure to workers in the immediate vicinity of the incinerator to PCBs. No other significant public exposure or environmental impacts were identified.

A severe transportation accident could result in a spill of PCB contaminated materials. However, the risk of significant public health or environmental impact is relatively low. The primary reason for this conclusion is that the quantities of materials to be transported are small, requiring only a few shipments per year. Also, the proper routing of shipments minimizes the potential for accidents in critical environments such as population centers or in water courses. In addition, the capability to quickly respond and clean up a spill will be an integral part of transportation activities, and finally, the spilled PCBs, with few exceptions, could be cleaned up to acceptable levels.

#### SUMMARY

Each of the many actions directly or indirectly involved in the construction and operation of the proposed facility may be potentially capable of causing changes in the existing conditions or characteristics of the environment at or near the proposed facility. The impacts of the proposed action have been analyzed in terms of the effluents and emissions expected from the facility and the impacts of those effluents and emissions on the chemical and physical quality of the environment. Also analyzed were the impacts upon the biota, upon human health, and upon the socioeconomic character of the area. Many of the analysis were based on conservative estimation procedures or worst reasonable case analysis. However, even with such approaches to the estimation of impacts, the projected consequences of the proposed facility are generally insignificant.

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HAZARDOUS MATERIALS MANAGEMENT AND CONTROL PROGRAM AT  
OAK RIDGE NATIONAL LABORATORY - ENVIRONMENTAL PROTECTION

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Key Words

Resource Conservation and Recovery Act,  
Hazardous Wastes, Hazardous Materials Coordinator

ABSTRACT

At a large research laboratory facility, the management and control of hazardous materials and their subsequent wastes can be a tremendous task. Environmental regulations mandated by the Resource Conservation and Recovery Act of 1976, established a Federal program to provide comprehensive regulation of hazardous solid waste materials from their time of generation to their disposal. In an effort to comply with these regulations, a Hazardous Materials Management and Control Program was created at Oak Ridge National Laboratory. The program provides personnel with specific guidelines for the procurement, use, storage, transportation and disposal of hazardous materials/wastes and ensures that they are managed in a manner which adequately protects all personnel, the general public, and the environment.

INTRODUCTION AND BACKGROUND

The Congressional enactment of the Resource Conservation and Recovery Act of 1976 (Public Law 94-5800) restricted what can be done with waste by-products with defined hazardous characteristics. Approximately 700,000 generators, transporters, and disposal site operators are affected by this law and the regulations contained in Subtitle C of the Act (i.e., those regulations dealing with the

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

management of hazardous wastes).(1) The complexity of these regulations has stimulated many questions, some of which will not be answered until time and human ingenuity change the circumstances, but because of the urgency of the problem, the proper management of hazardous wastes must be dealt with now.

Prior to enactment of RCRA in 1976, the management of hazardous wastes was closely integrated with the solid waste disposal industry. More often than not, local municipal landfills served as "dumping grounds" for both types of wastes. In many instances, this improper management of hazardous waste resulted in the leaching of toxic materials from these landfills and the contamination of groundwater -- the source of drinking water for about half of the U.S. population. The Environmental Protection Agency (EPA) has on file hundreds of documented cases of damage to life and the environment, resulting from the indiscriminate and/or improper management of hazardous wastes. EPA has identified 400 "top priority" sites designated for clean-up under Superfund. However, hundreds of other such sites are known to exist, and the numbers of unknown areas are even greater. The search for abandoned sites will be a continuing process.

In May 1980, the EPA, as required by RCRA of 1976, took steps to establish a national hazardous waste management system. Since November 19, 1980, the compliance date of these regulations, many problem areas have surfaced for individuals involved in the management of hazardous wastes. At Oak Ridge National Laboratory (ORNL), these problems are enhanced due to ongoing research activities at this facility. Many of the chemicals, utilized by the various laboratories at ORNL, are regulated by EPA/RCRA and are considered hazardous, either because they are listed wastes from nonspecific or specific sources or a commercial product. Other wastes may be considered hazardous if they exhibit specific characteristics (e.g., ignitable, corrosive, reactive, or EP toxicity). EP toxicity refers to waste materials found to contain quantities of toxic heavy metals or pesticides above specified limits. EPA/RCRA regulations outline a detailed procedure for these analyses. (2)

### HAZARDOUS MATERIALS PROGRAM

In an attempt to respond to the many definitions of hazardous materials and their ever increasing multitude of legal requirements in a uniform, orderly manner, a Hazardous Materials Management and Control Program was established at the Laboratory. Its mission is to simplify the responsibilities of the Laboratory staff when dealing with hazardous materials and to make every effort to comply with all applicable laws and regulations.

The Hazardous Materials Program is administered by two Hazardous Materials Coordinators -- a Hazardous Materials Coordinator for environmental protection (HMC-Environmental) and a Hazardous Materials Coordinator for health protection (HMC-Health). The HMC-Environmental is concerned with the storage, transportation, and disposition of hazardous materials/wastes, while the main areas of concern to the HMC-Health is the procurement and use of these materials. Prior to the establishment of the program, the user of hazardous materials at ORNL was required to make numerous personal contacts with the various Laboratory departments responsible for the materials: Health Physics, Fire Safety, Industrial Safety, Industrial Hygiene, Environmental Management, and others. With the implementation of this program, the user contacts only the Hazardous Materials Coordinators for any information he/she may require concerning hazardous materials. The other departments now serve as support groups and provide information in their areas of expertise to the Hazardous Materials Coordinators upon request (Figure 1).

In order to accomplish the above stated mission of the program, guidelines for the procurement, use, storage, transportation, and disposal of hazardous materials/wastes were established for the hazardous materials user. These guidelines have been incorporated into a manual (Hazardous Materials Management and Control Manual - ORNL) which is available to all Laboratory personnel.(3) To ensure that Laboratory personnel are familiar with and abide by the guidelines and procedures set forth by the program, each division at the

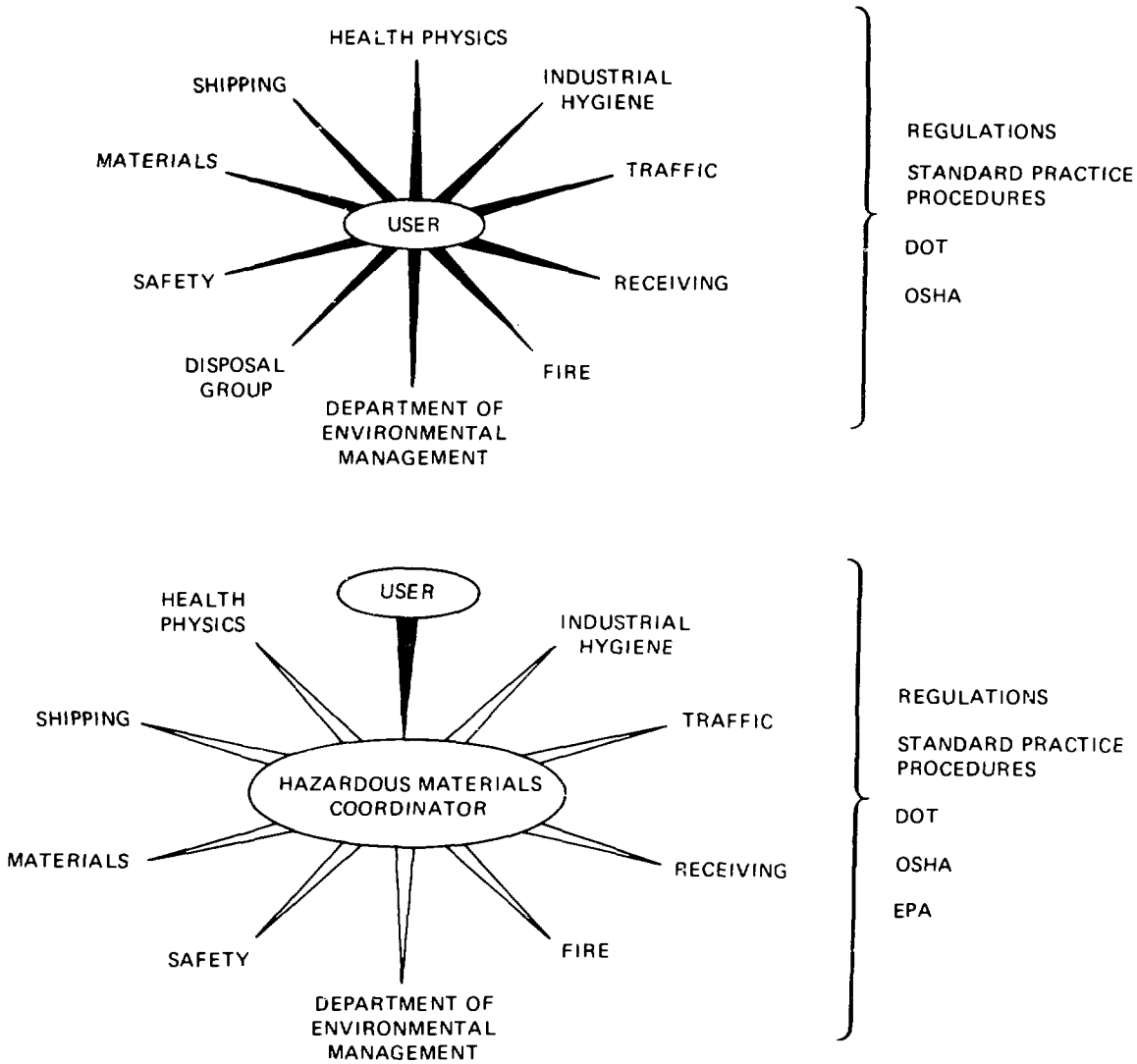


Figure 1. Former and Present User/Departmental Interaction



Laboratory has appointed an individual to serve as the Environmental Protection Officer (EPO) for his/her respective division. Via the EPO, the Hazardous Materials Coordinators (HMC - Environmental and HMC - Health) and their departments are kept informed of hazardous materials activities in all divisions at the Laboratory. This is very important since several divisions which are controlled by the program are not on-site, but at distant locations.

#### DISCUSSION OF PROGRAM - ENVIRONMENTAL PROTECTION

##### Storage of Hazardous Materials/Wastes

The HMC-Environmental ensures that hazardous materials/wastes are properly stored, transported, and disposed of at this facility. He/she is aided by the various support groups (i.e., Industrial Hygiene, Health Physics, Safety, Fire Safety, etc.) in fulfilling this responsibility.

At Oak Ridge National Laboratory, large numbers and quantities of hazardous materials and/or wastes must be retained for use or disposition at a later time. During this "holding period", precautions must be taken to protect Laboratory personnel and the environment. The HMC-Environmental ensures that hazardous materials are stored according to established guidelines (OSHA, RCRA, ORNL Safety Guidelines for Chemical Storage, etc.). Such parameters as material classification by hazard group (e.g., organic acids, inorganic acids, flammable liquids, reactive materials, etc.), separation based on chemical compatibilities, shelf life, and other special storage requirements are examined. Information found on the Hazardous Materials Control Card issued with each hazardous material, the Department of Transportation regulations, Union Carbide Corporation Nuclear Division Material Safety Data Sheets (Volumes I-III) and the EPA/RCRA hazardous waste regulations are used in obtaining the information for hazard classification.(4,5)

There are two areas of hazardous materials storage at ORNL which are of concern. One is the storage of hazardous chemicals within individual laboratories and the other is the storage of hazardous wastes, destined for off-site disposal, in a centralized facility. Hazardous materials stored in the typical research laboratory consist mainly of virgin laboratory reagent chemicals, both hazardous and nonhazardous. Improper storage of these chemicals with waste chemicals can create serious safety, health, environmental, and disposal problems. Additionally, improper waste storage can contribute heavily to unnecessary costs in clean-up, repacking, identification, and disposal. In an effort to deal effectively with the above-mentioned problems associated with chemical storage in the individual laboratory, a laboratory inspection program was initiated by the Department of Environmental Management. The inspection of individual laboratories is a means of ensuring that established storage guidelines set forth by the Hazardous Materials Program are followed. It also presents the opportunity to identify potential problems (e.g., possible spill areas within the lab; the identification of old, unused chemicals in need of disposal; proper storage of virgin chemicals; proper waste segregation and storage; and the identification of hazardous chemicals with expired shelf-life) which may be corrected before serious situations might occur.

The hazardous waste management program created by the RCRA of 1976, provides specific design and operating standards and permit requirements for the storage of hazardous wastes. The major portion of the regulations are contained in Parts 264 and 265 under Section 3004 of RCRA (2). At ORNL, the storage of hazardous wastes involves many of the safety considerations presented above for the storage of hazardous chemicals. In addition, specific RCRA requirements pertaining to storage building security, weekly inspections, and the development of plans for emergency response and spill clean-up, must be met.

After positive identification at the point of generation, hazardous wastes are transported to a centralized storage facility. Here

they are segregated into their particular hazard class (poison, corrosive, flammable liquid or solid, oxidizer, etc.) as specified in the U.S. Department of Transportation Hazardous Materials Table found in 49 CFR, Part 172.101 of the regulations.(6) The greatest majority of hazardous wastes remain in storage for a short time prior to being transported offsite for disposal in an EPA-approved chemical landfill. There are some waste streams generated at this facility for which no treatment and/or disposal method is currently available (e.g., co-contaminated hazardous wastes). These are RCRA-regulated hazardous wastes contaminated with low levels of radioactivity. A good example of this type of waste generated at the Laboratory is the "cocktail mixtures" used for scintillation counting. They are usually composed of a toluene base and have been "tagged" with a radioactive isotope such as  $^{14}\text{C}$ ,  $^3\text{H}$ , or  $^{32}\text{P}$ . Because of the low-level radioactivity, the waste material cannot be shipped offsite for disposal (Department of Energy policy). Currently, the co-contaminated wastes are being placed in retrievable storage where they can be removed when a treatment/disposal mechanism becomes available. The fact that some wastes must be stored indefinitely makes the aspect of proper storage all the more important.

#### Transportation of Hazardous Materials/Wastes

The movement of hazardous materials/wastes is governed by specific U.S. Department of Transportation (49 CFR 172) and EPA requirements (40 CFR 263). Compliance with these regulations must be met regardless of the mode of transportation (e.g., roadways, water, air). Under RCRA, EPA issued standards for hazardous waste transporters which prescribe procedures for recordkeeping, acceptance of waste, manifest system compliance, and delivery and spill clean-up. RCRA specifically notes that these standards are to be consistent with those developed by DOT under the Hazardous Materials Transportation Act of 1974 (49 CFR 100-199).(7) Although the DOT regulations were not intended to govern transportation of hazardous wastes, but

rather the shipment of pure, virgin hazardous materials, the EPA transporter regulations require that when a material is a hazardous waste as defined by EPA, then DOT regulations must be complied with for intrastate and interstate transportation of hazardous wastes.

The transportation of hazardous materials/wastes between ORNL and other Oak Ridge Operations facilities and to facilities outside the Oak Ridge Operations area is governed by regulations set forth by DOT and EPA and standard practice procedures mandated by Union Carbide - Nuclear Division management. Before a shipment of hazardous materials can be offered to a permitted transporter, it is the responsibility of the generator to identify his/her material. The majority of hazardous wastes generated at ORNL are general laboratory chemicals and can be identified by the manufacturer's label. Mixtures of hazardous wastes generated by research activities can be identified by the researcher. If these two avenues fail, waste materials are analyzed according to the EPA/RCRA testing criteria set forth in Part 261.20-261.24 of the regulations to determine their hazardous characteristic(s). Once identification is made the material is properly packaged, the appropriate hazard class and correct hazardous material shipping name is selected per DOT regulations contained in 49 CFR 172. No further information is required if only hazardous materials are being transported. The vehicle is placarded for the type material it is carrying, and the required shipping papers accompany the shipment during transport.

Materials considered to be hazardous by the EPA/RCRA guidelines, i.e., they are a listed hazardous waste or are hazardous due to some unique characteristic, require a detailed manifest shipping document for transportation (Figure 2). Besides the information that is needed for the shipment of hazardous materials (e.g., hazardous class, proper shipping name, etc.), the manifest also identifies the hazardous waste generator, the licensed transporter or carrier, and the treatment/storage/disposal (TSD) facility for which the waste is destined. By identifying all parties involved, the proper management of the hazardous waste can be better ensured.

# HAZARDOUS WASTE MANIFEST

OAK RIDGE NATIONAL LABORATORY

|                      |    |
|----------------------|----|
| MANIFEST DOCUMENT NO |    |
| PAGE                 | OF |

| GENERATOR/SHIPPER INFORMATION |  | TRANSPORTER INFORMATION |  | TREATMENT/STORAGE/DISPOSAL FACILITY |  |         |  |
|-------------------------------|--|-------------------------|--|-------------------------------------|--|---------|--|
| NAME                          |  | NAME                    |  | NAME                                |  |         |  |
| ADDRESS                       |  | ADDRESS                 |  | ADDRESS                             |  |         |  |
| EPA ID NUMBER                 |  | EPA ID NUMBER           |  | EPA ID NUMBER                       |  | CONTACT |  |
| CONTACT                       |  | CONTACT                 |  | CONTACT                             |  | CONTACT |  |

| WASTE INFORMATION |                          |              |                |                |                   |                  |                   |
|-------------------|--------------------------|--------------|----------------|----------------|-------------------|------------------|-------------------|
| HM                | PROPER DOT SHIPPING NAME | HAZARD CLASS | UN NO OR NA NO | TOTAL QUANTITY | TYPE OF CONTAINER | CONTAINER NUMBER | OTHER INFORMATION |
|                   |                          |              |                |                |                   |                  |                   |
|                   |                          |              |                |                |                   |                  |                   |
|                   |                          |              |                |                |                   |                  |                   |
|                   |                          |              |                |                |                   |                  |                   |
|                   |                          |              |                |                |                   |                  |                   |

COMMENTS/SPECIAL HANDLING INSTRUCTIONS

| SHIPPER'S CERTIFICATION                                                                                                                                                                                                                                             |           |      | T/S/D FACILITY CERTIFICATION                                                                                                                                                                                                                 |           |      |
|---------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-----------|------|----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-----------|------|
| <p>This is to certify that the above-named materials are properly classified, described, packaged, marked, and labeled, and are in proper condition for transportation according to the applicable regulations of the Department of Transportation and the EPA.</p> |           |      | <p>This is to certify that the above-named materials were delivered to this facility, and that any differences between manifest and shipment, or any rejected materials, have been indicated in the "Comments" section of this manifest.</p> |           |      |
| SHIPPER (GENERATOR) AUTHORIZED REPRESENTATIVE                                                                                                                                                                                                                       |           |      | T/S/D FACILITY AUTHORIZED REPRESENTATIVE                                                                                                                                                                                                     |           |      |
| NAME                                                                                                                                                                                                                                                                | SIGNATURE | DATE | NAME                                                                                                                                                                                                                                         | SIGNATURE | DATE |
| TRANSPORTER AUTHORIZED REPRESENTATIVE                                                                                                                                                                                                                               |           |      |                                                                                                                                                                                                                                              |           |      |
| NAME                                                                                                                                                                                                                                                                | SIGNATURE | DATE |                                                                                                                                                                                                                                              |           |      |

UCN 14352  
(3 481)

WHITE → GENERATOR (CONFIRMATION COPY)  
 GREEN → GENERATOR  
 CANARY → TRANSPORTER  
 PINK → T/S/D FACILITY  
 (RC DEPT OF ENVIRONMENTAL MANAGEMENT ORNL G-260 45005)  
 BLUE → CONTAINER

Figure 2. Hazardous Waste Manifest

### Disposal of Hazardous Waste

The final phase of the Hazardous Materials Management and Control Program is the disposal of the waste materials generated by the facilities. It is the responsibility of the HMC-Environmental to ensure that all hazardous wastes, which cannot be further utilized, processed, or recycled, be disposed of in an environmentally safe manner (Figure 3). RCRA regulations governing hazardous waste management established specific operating standards in 40 CFR Parts 264 and 265. Owners and operators of treatment, storage and disposal facilities (TSDF) are required to comply.(2)

ORNL has a permit under RCRA interim status, as a storage and treatment facility. Hazardous wastes which must be disposed of via the secure landfill route are transported off-site to a commercial facility for ultimate disposal. Approximately 75-80% of the Laboratory's total hazardous waste is general laboratory chemicals ranging from gram to gallon quantities.

The management of hazardous waste means more than careful disposal. It implies the consideration of alternate methods to reduce the amount and the hazard of the wastes. Reuse, energy recovery, and material recovery are desirable alternatives to chemical landfill disposal. In an effort to reduce the quantities of wastes requiring disposal offsite in commercial facilities, several programs have been established for recovering/ recycling usable and valuable materials from several waste streams. Current programs include the mercury recycling program, silver recovery from photoreproduction wastes, and recycling of noncontaminated waste oils.

Personnel of the Analytical Chemistry Division have a procedure for cleaning metallic mercury. Nonradioactively-contaminated waste metallic mercury is picked up by the Waste Disposal Group and submitted to analytical personnel for clean up. The "cleaned" mercury is turned over to Finance and Materials Division for resale on the open market.

Large quantities of wastes generated by the Laboratory's photographic and reproduction departments are classified as hazardous wastes by RCRA, either because of their corrosiveness (pH greater

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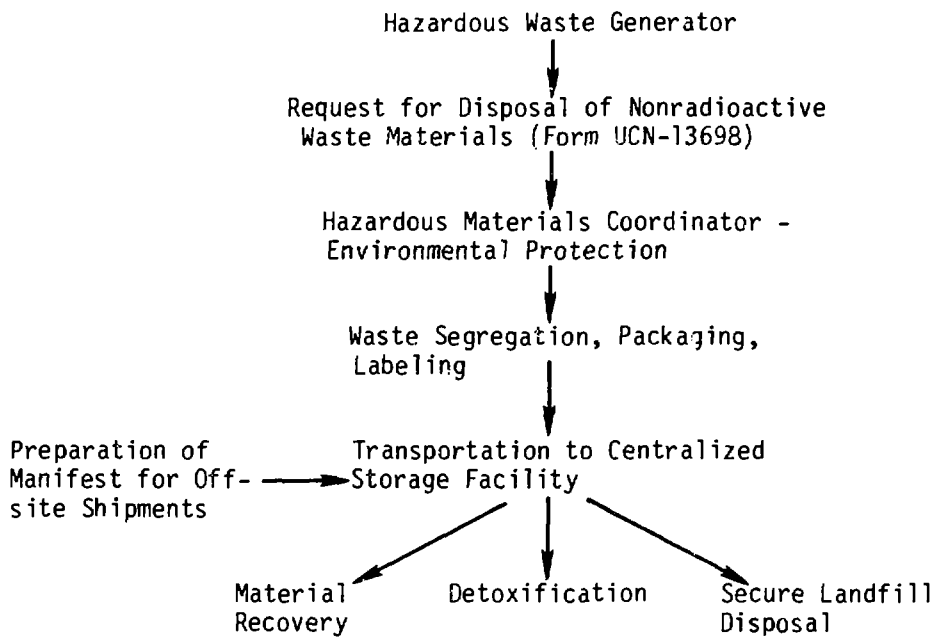


Figure 3. Management Scheme for Hazardous Wastes

than 12.5) or because of the concentration of silver (greater than 5.0 mg/L). Because of the significant amount of recoverable silver found in these waste solutions, they cannot be shipped offsite for disposal. Laboratory personnel from the Analytical Chemistry, Chemical Technology, and Chemistry Divisions in cooperation with the ORNL Department of Environmental Management have developed an effective method for recovering 99.999% of the silver from the wastes to achieve an effluent discharge containing less than 1 ppm of silver, with acceptable values for pH and biochemical oxygen demand (BOD). Following the silver-recovery phase of the operation, the waste is treated with commercial-grade sulfuric acid to adjust the pH before discharging the high BOD effluent to the ORNL Sewage Treatment Plant for final clarification. Recovered silver metal is turned over to the Finance and Materials Division for resale.

Approximately 20,000 gallons of noncontaminated waste oils are generated by Laboratory-wide sources annually. ORNL currently sells this oil to an offsite recycling company. All oils are analyzed for polychlorinated biphenyls (PCB's) and chlorinated solvent contamination before being placed in an underground 4,200-gallon storage tank until they are sold.

### CONCLUSIONS

The management of hazardous materials/wastes is very complex. The environmentally safe control of these wastes is now receiving attention at all levels of government and by the general public. Past episodes (e.g., Love Canal, Valley of Drums and numerous others) have focused attention on what can happen when hazardous waste is managed improperly. In many cases, the technology has existed for environmentally sound management, but because of high costs and/or no legal requirements, this technology has not been widely used.



At ORNL every effort is being made to comply with all laws and regulations governing hazardous materials/wastes with the least possible impact on research activities. The Hazardous Materials Management and Control Program has been instrumental in accomplishing this goal.

#### ACKNOWLEDGEMENTS

The authors would like to express their sincere thanks to Ms. Donna Slaughter and Ms. Annette Campbell for their excellent work in the editing and typing of this paper.

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HAZARDOUS WASTE MANAGEMENT  
ALTERNATIVES UTILIZED AT THE PGDP

P. A. Getz  
Paducah Gaseous Diffusion Plant  
Paducah, Kentucky 42001

operated by  
UNION CARBIDE CORPORATION

for the  
U.S. DEPARTMENT OF ENERGY  
Under Contract No. W-7406-eng-26

HAZARDOUS WASTE, CAPABILITIES, COMPLIANCE

ABSTRACT

The PGDP generates a diversity of hazardous waste material. Due to this diversity and limited storage capabilities, various modes of treatment, reclamation, and disposal of these materials, both on-site and off-site, have been utilized. Plant policies and procedures have been developed for the handling of these materials to help ensure compliance with federal, state, and DOE guidelines. As a result, several potential problem areas have been identified and resolved.

This report reviews these waste management alternatives with the associated problems which have been encountered to date.

INTRODUCTION

The Resource Conservation and Recovery Act (RCRA) requires that storage, treatment, transportation, and disposal of hazardous wastes be regulated to prevent adverse effects on health and the environment. Currently, the storage, treatment, and disposal of hazardous wastes comprise a significant portion of the overall waste disposal effort at the Paducah Gaseous Diffusion Plant. Due to the diversity of hazardous wastes generated and the presence of contaminants (i.e., low level radioactivity, PCBs), various storage, treatment, and

disposal methodologies are utilized. The lengthy budget cycle for line item and general plant projects necessitated modifications of existing facilities through the use of expense funding to meet the interim storage standards imposed by EPA as a result of RCRA. A new storage facility has been budgeted in the FY-80 Line Item Project, "Control of Water Pollution," to increase the hazardous waste storage capacity, as well as meet final facility standards as set forth by EPA. In addition, several sub-projects in the FY-83 Line Item Project, "Environmental Protection and Safety Modifications, Phase I" will address hazardous waste recovery and treatment which will reduce the needed storage capacity.

#### PROCESS

Initially, a waste characterization was necessary to identify the hazardous wastes generated at the PGDP, as well as any contaminants present in the wastes such as radioactivity (primarily depleted uranium) and polychlorinated biphenyls (PCBs). The results of this characterization can be found in Table 1.

Based on regulatory guidelines for the disposal of hazardous wastes and waste PCBs, internal guidelines<sup>1</sup> for the disposal of uranium-contaminated wastes, and data obtained from the waste characterization, decisions can be made concerning the storage and disposal methods to be used for hazardous, uranium-contaminated, and PCB wastes generated at the PGDP. Decision trees (Figures 1 and 2) have been developed to aid this process for routinely generated wastes, primarily PCB and PCB-contaminated wastes and waste organic solvents.

TABLE 1

## Hazardous and PCB Wastes Generated at the PGDP

| <u>Material Description</u>                         | <u>Contaminant</u> | <u>Annual Generation</u> |
|-----------------------------------------------------|--------------------|--------------------------|
| Paint Wastes/Mineral Spirits                        | None               | 1,000 gallons            |
| Trichloroethylene                                   | None               | 1,000 gallons            |
| Trichloroethylene                                   | Uranium            | 1,000 gallons            |
| 1,1,1 Trichloroethane                               | None               | 500 gallons              |
| Dibutyl Carbitol/Hexane Mixture                     | Uranium            | 25 gallons               |
| Tri (2-ethethyl hexyl) phosphate/<br>Hexane Mixture | Uranium            | 10 gallons               |
| Miscellaneous Laboratory Chemicals                  | None               | Varies                   |
| Nitrate Solution                                    | Heavy Metals       | 2,000 gallons            |
| Chromated Water                                     | Cr <sup>+6</sup>   | 150,000,000 gallons      |
| Metal Cleaning Solutions                            | Uranium            | 26,000 gallons*          |
| Hydraulic Fluid                                     | PCB                | 100 gallons              |
| Diesel Fuel                                         | PCB                | 200 gallons              |
| PCB-contaminated Solids                             | PCB                | 1.5 tons                 |

\*This is not generated on annual basis, but on a cycle of 4-5 years.

EPA regulations mandated by the Toxic Substances Control Act require that waste containing equal to or greater than fifty parts per million PCB be disposed of at an EPA permitted facility. Currently, commercial disposal methods are primarily dependent upon the concentration of PCB in the wastes, the physical characteristics of the wastes, and the waste description (i.e., capacitors, mineral oil, etc.). However, if greater than 50 parts per million depleted uranium or any enriched uranium is present in the waste, commercial disposal currently cannot be used. These wastes must be stored until a facility exists which is permitted to dispose of radioactively-contaminated PCB wastes. Decision tree #1 (Figure 1) has incorporated these criteria for the storage and disposal methodologies for PCB and PCB-contaminated wastes generated at the PGDP.

FIGURE 1

DECISION TREE #1  
DISPOSAL OF PCB-CONTAMINATED MATERIALS

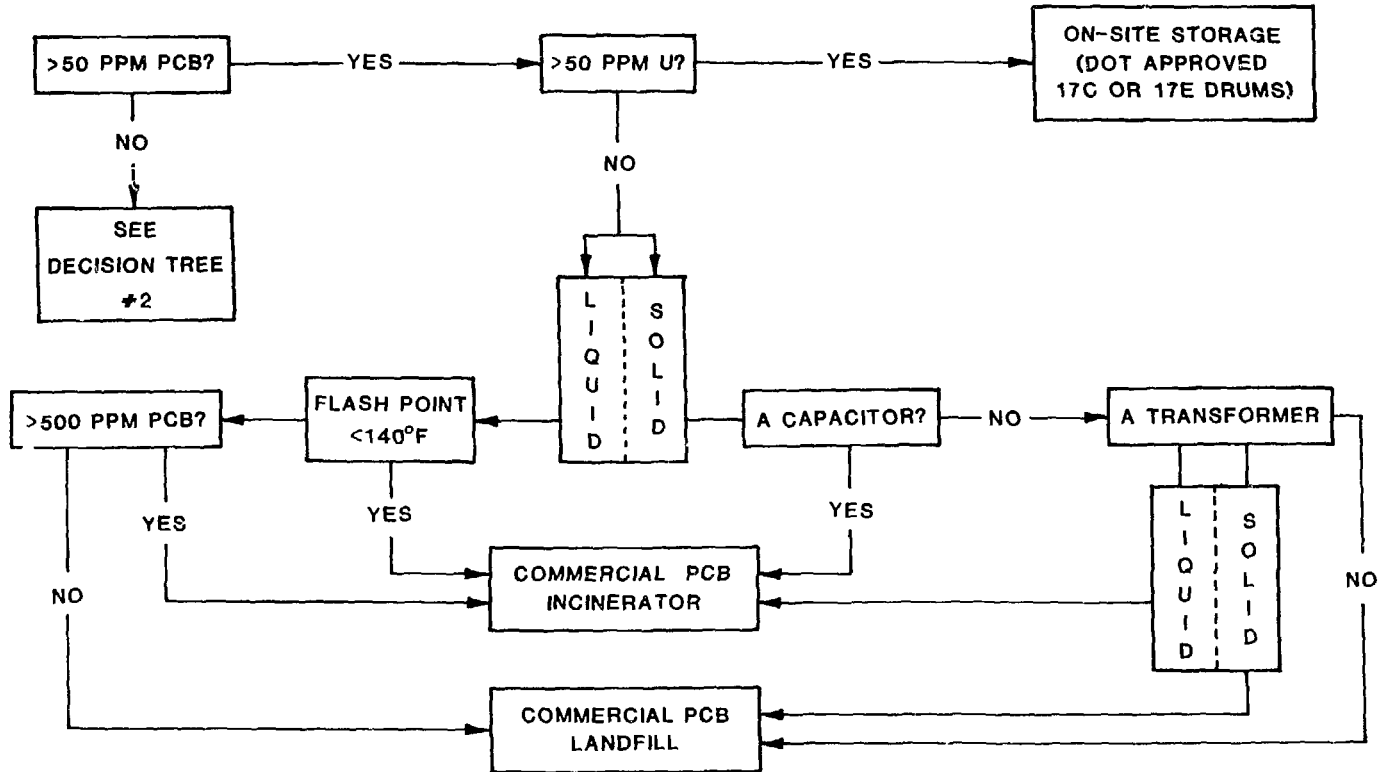
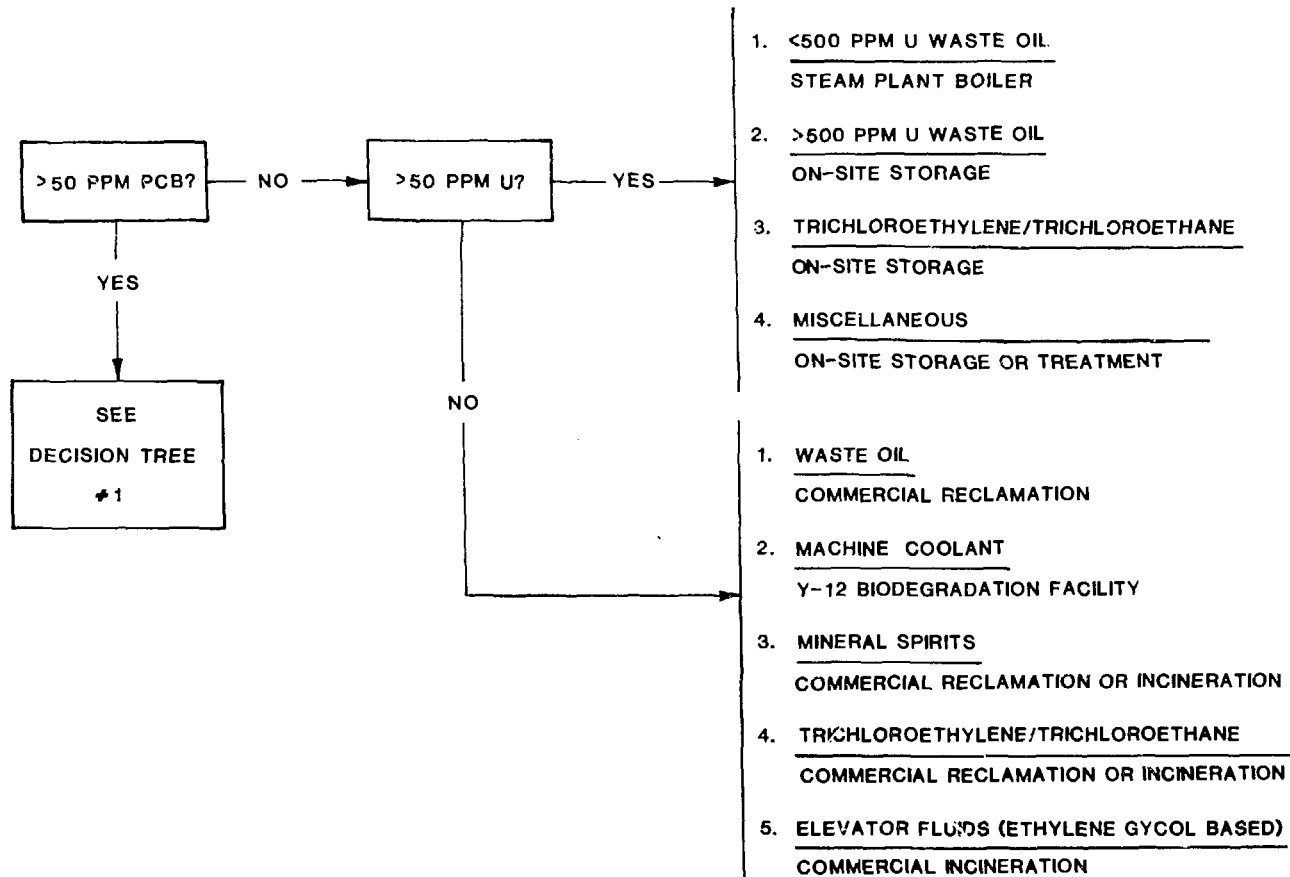


FIGURE 2

# DECISION TREE #2 DISPOSAL OF WASTE ORGANIC MATERIALS



As stated previously, RCRA requires that the storage, treatment transportation, and disposal of hazardous wastes be regulated. Most waste or spent organic solvents are classified as hazardous wastes because of characteristics which cause the solvent to be listed or which cause the solvent to fail the testing protocol as set forth in the EPA hazardous waste regulations. Because the PGDP currently has no treatment or disposal facilities for spent solvents, collection and storage of these solvents is performed. Decision tree #2 (Figure 2) can be used to identify the collection and storage location and mode for routinely generated, bulk solvents. Radioactively-contaminated solvents are to be stored until an incineration facility capable of handling radioactively-contaminated hazardous wastes is available. The remaining solvents are collected until truck-load quantities are available for commercial disposal or reclamation.

Miscellaneous laboratory wastes are generally handled on a case by-case basis. Most acids or bases are neutralized on-site at a permitted facility. Two laboratory solutions which consist primarily of solvents used for extractions are stored for future incineration in the Oak Ridge incinerator due to uranium contamination. Other chemicals generated at the PGDP are generally disposed of commercially in a hazardous waste landfill. They are packaged with compatible chemicals in "lab packs" according to Department of Transportation regulations.

Generally, treatment of the large volumes of hazardous liquid wastes is performed either on-site or at another UCCND facility. These wastes include chromated water, pipe cleaning solutions, and nitrate solutions.

Chromated water which is removed from the recirculating cooling water (RCW) system is treated at the C-616 Liquid Pollution Abatement Facility. The primary purpose of this facility is to reduce the hexavalent chromium ( $\text{Cr}^{+6}$ ) to trivalent chromium ( $\text{Cr}^{+3}$ ) in order to meet water quality standards for the NPDES permit. Approximately 450,000 to 500,000 gallons per day of chromated water are currently being treated at this facility by ferrous sulphate addition. The hexavalent chromium level is lowered from an average of 8.5 ppm to approximately 0.004 ppm. The resulting trivalent chromium is reacted with lime to form chromic hydroxide which is pumped to C-616-E Sludge Lagoon for storage. The effluent from the clarifier is pH adjusted and transferred to the full flow lagoon prior to discharge.

Another category of liquid hazardous waste which will be treated on-site prior to effluent discharge is the pipe cleaning solutions generated at the C-400 Cleaning Building. The tanks' contents are drained when the cleaning solutions become depleted and replenishment by addition of new chemicals is not effective. The total volume of all the tanks is approximately 26,000 gallons. This occurs approximately every four to five years. The four tanks contain chromic acid, troxide solution, hydrochloric acid, and an



alkali solution of sodium hydroxide, respectively. All the solutions except HCl are hazardous by testing; the HCl is a listed hazardous waste. Recent data also indicate most of the solutions, and particularly settled solids in the tanks, are contaminated with uranium. In view of the high potential for uranium contamination and the RCRA requirements which have evolved since the tanks were last drained, a system to treat these solutions on-site will be provided by the FY-83 Line Item Project, "Environmental Protection and Safety Modifications, Phase I." In addition, a process to physically "fix" the resulting sludge in concrete will be provided.

The final liquid hazardous waste which will be treated is the nitrate solution generated in the gold recovery process. This solution generally contains nitric acid, aqua regia, and several heavy metals such as lead, zinc, silver, and copper. The current treatment plan for this solution is precipitation of the heavy metals at the PGLP by sodium hydroxide addition after which the filtrate is shipped to the UCCND Y-12 installation for either biodenitrification or use as an electrolyte.

#### DISCUSSION

Due to the limited storage capabilities of these facilities, commercial disposal and/or reclamation capabilities have been utilized to the maximum extent possible. Plant policies for the commercial disposal of these materials are strictly enforced to help ensure compliance with federal, state, and DOE guidelines. As a

result, several potential problems have been identified and resolved.

For commercial disposal of hazardous wastes, a minimum time period to negotiate an initial contract of four to six months is needed from the time the purchase requisition is initiated. Delays can occur at every step in the process. Several actions can be taken to minimize these delays. First, the necessary packaging and marking for the waste should be determined in the early stages; therefore, if special containers are needed, they can be ordered and received so that the shipment will not be delayed. Another method to avoid unnecessary delays is to include very detailed information concerning the waste's description and characteristics in the initial bid package. This can avoid problems in two ways. First, if sufficient information is not included, the potential bidders will either request it, request a sample, or not reply to the bid. Secondly, not all disposal/reclamation facilities can handle all types of waste materials. Therefore, only companies capable of handling the materials specified should reply to the bid or indicate which materials in the bid package they can accept and not quote prices for those items. Once the bids have been received and evaluated, a site visit to the low bidder's disposal facilities is performed. If the visit indicates non-compliance with federal or state standards regarding storage, treatment, or disposal of hazardous wastes, a contract with the firm should not be initiated until actions to attain compliance are initiated by the disposal

firm. In some cases, if the firm is not willing to meet the requests, they will withdraw their bid so that other bidders can be considered. In the event that a firm is found to be out of compliance with EPA regulations, once a contract has been made, UCCND legal personnel<sup>2</sup> recommend that the firm be given approximately two months to attain compliance before the contract can be broken and a new purchase requisition initiated to negotiate a contract with another firm.

In conclusion, off-site disposal with commercial firms is a very acceptable disposal route if the necessary planning and precautions are performed. In most cases, commercial disposal offers an economic advantage over on-site disposal or treatment, particularly when low volumes of a variety of wastes are generated. However, due to uranium contamination present in some of the waste streams at the PGDP, some on-site treatment and storage is required.

particularly when low volumes of a variety of wastes are generated.

However, due to uranium contamination present in some of the waste streams at the PGDP, some on-site treatment and storage is required.

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## SOLID WASTE DISPOSAL SYSTEM

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Key Words: Uranium, Analysis, Disposal, Gamma Spectroscopy, Uranium-238, Radioactive Wastes

## ABSTRACT

This paper discusses progress to date in the Oak Ridge Y-12 Plant (operated by Union Carbide Corporation, Nuclear Division, for the Department of Energy, under U.S. government contract W-7405-eng-26) solid waste management program. The study on where waste is generated and the frequency of disposal will be presented. Utilization of a nondestructive gamma-ray analysis technique for measurement of the uranium in waste containers will be reviewed. Using current Nuclear Regulatory Commission (NRC) regulations and internal criteria as guidance, a scheme is presented for handling the solid waste disposal problem at the Plant.

INTRODUCTION

This paper presents an overview of development efforts for short- and long-range identification and solution of problems associated with unique wastes generated at the Plant. These efforts are aimed at better ways of identifying where waste is generated, how much and what type of waste is generated, where the waste is disposed now, and if that disposition is basically correct.

Sound, economical management of the solid waste disposal system requires that as much as possible of the waste be placed in the lowest cost component of the disposal system. Discussion is presented on development efforts to utilize a gamma-ray analyzer system, previously developed by Los Alamos National Laboratory (LANL) and field installed at

the General Electric Company (GE), Wilmington, North Carolina plant, for quantitative assay of low-enriched uranium in waste. This device will allow screening of waste to assure that goal.

### Study of Waste Generation and Collection

The basic waste collection system at the Plant consists of a numbered container or containers (dumpsters) placed near each building. These containers range from approximately 4 yds<sup>3</sup> to 12 yds<sup>3</sup>. Supplementary containers range from skid pans to 55-gal drums. The pickup and disposal of all these containers are managed by the Maintenance Division. Some pickups are routinely scheduled, others are when required.

All pickup and disposal data are maintained by the Maintenance Division on computer. The fact that these containers are specifically assigned a location and are picked up and returned to the same location helped facilitate the task of determining quantity and frequency of containerized waste disposal. Our study was limited to the numbered waste containers (dumpsters), because the frequency and quantity of disposal of the supplementary containers are very difficult to estimate due to lack of identification and standardization.

### RESULTS

Our study showed that for the 6-month period studied (October 1, 1980 through March 31, 1981), a very typical operating period, a total of approximately 36,000 yd<sup>3</sup> of waste was generated and disposed in Y-12 by way of the "dumpsters." Approximately 31,500 yd<sup>3</sup> (87%) were disposed in the sanitary landfill and about 3,500 yd<sup>3</sup> (10%) went to the burial grounds. Clean metals sent to the sale yard amounted to about 250 yd<sup>3</sup> (0.7%), with the remainder, approximately 750 yd<sup>3</sup> (2%), consisting of miscellaneous sludges, chemical disposals, etc.

Of the 214 "dumpsters" at the Plant, only 180 were in active use during the 6-month test period. Of these, 23 are identified as being routinely used for uranium contamination disposal. A significant number of these are used for disposal of depleted uranium chips, turnings, and bulk metal.

The Oak Ridge National Laboratory activities at Y-12 require in excess of 33% of the landfill operation with Biology requiring about 23%.

#### Gamma Ray Assay

A method based on detection of 0.767 and 1.001 MeV gamma rays from  $^{234m}\text{Pa}$  has been developed by LANL<sup>1</sup> for the assay of  $^{238}\text{U}$  in large containers of low-enriched uranium waste.

The decay chain series which produces  $^{234m}\text{Pa}$  is:  $^{238}\text{U}$  ( $4.5 \times 10^9$  yr)  $\rightarrow$   $^{234}\text{Th}$  (24.1 day)  $\rightarrow$   $^{234m}\text{Pa}$  (1.18 min)  $\rightarrow$   $^{234}\text{U}$  ( $2.5 \times 10^5$  yr).

Quantitative results can be obtained if the activity of this  $^{238}\text{U}$  daughter is in equilibrium, which requires an aging period of three months or more after purification of the uranium. Because of a low specific activity, a large NaI detector is needed to obtain sufficient sensitivity.

A field testing and application of the method were performed at the General Electric Fuel Fabrication Plant at Wilmington, North Carolina.<sup>2</sup> General Electric uses standard plywood boxes (4' x 4' x 4') for packaging of all their waste. These packages, after measurement by the "elephant gun," are shipped to burial at Barnwell, South Carolina.

The basic system consists of a lead collimated 5-inch-diameter by 5-inch-thick sodium iodide scintillating crystal optically coupled to an RCA model 8055 photomultiplier tube (PM). The GE application uses an Eberline Instrument Corporation Stabilized Assay Meter I (SAM-I).

The crystal, PM tube, and approximately two inches of lead are contained in a 10-inch x 26-inch-long steel pipe. The crystal is collimated to have a 36-degree viewing angle.

Los Alamos reported<sup>1</sup> that the detection limit with a 5-minute count is about 30 grams of  $^{238}\text{U}$  in a typical box of combustibles.

Because most of our containerized waste is in dumpsters (4-12 yd<sup>3</sup>) and the radioactive contaminant is exclusively depleted uranium, it appeared to us that this technique might be useful to make a decision on whether the contents of the dumpster goes to a sanitary landfill or requires being placed in the burial ground. Such an instrument could also be used for scanning scrap metal prior to sale to preclude unauthorized removal of contaminated scrap metal or solid depleted metal from Plant areas.

Evaluation of the effectiveness of this method for Plant use is in progress.

## PROPOSED SCHEME FOR HANDLING SOLID WASTES AT Y-12

In reviewing Part 61 and the NRC Uranium Fuel Licensing Branch Technical Position, it appears that these documents provide all the flexibility and guidance needed to adequately handle the solid waste problems at the Y-12 Plant. Only two areas need clarification:

1. At what uranium concentration level does sanitary waste require being placed in the burial ground?
2. Whether criteria stated in the Position Paper specifically for formerly utilized sites can also be applied to those production facilities currently in operation?

In scoping the Y-12 solid waste problem, it is apparent that much of the volume of waste generated is outside the production area (cafeteria, offices, Biology, paper shredder). These containers should always go to the sanitary landfill.

Several containers inside the production exclusion area always contain contaminated waste and always should go to the burial ground.

Some limited number of containers inside the production exclusion areas, which are normally used mainly for combustible office and general area trash, are the ones where a nondestructive screening instrument such as the "elephant gun" would be most useful.

SUMMARY

In summary, studies and evaluations have begun and are continuing. No conclusive data have yet been obtained, and no final decisions have been made.



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*Session 6: ENVIRONMENTAL PROTECTION PROJECT*  
*Chairperson: M. E. Mitchell*

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## CORROSION IN COAL-FIRED BOILERS

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KEY WORDS: Coal, Boilers, Corrosion, Dew Point, Fuel Additives

## ABSTRACT

The corrosive effect of the flue gas and the fly ash from burning coal on combustion and pollution control equipment has led to extensive research efforts aimed at solving this problem. A wide variety of chemical additives are offered by suppliers to perform corrosion reduction functions when added to the solid or liquid fuel. Protection of equipment by the use of corrosion resistant coatings and improved designs to prevent or reduce slag formation are also well known corrosion reduction techniques. However, the problem facing management is to evaluate the many different alternatives and to define the most effective one for their particular facility. Information gained from previous corrosion reduction attempts, and knowledge of factors which increase the  $\text{SO}_3/\text{SO}_2$  ratio in the flue gas have resulted in the investigation of methods of controlling the dew point and therefore, reducing the condensation of sulfuric acid. Various methods of avoiding the formation of acid are being evaluated.

INTRODUCTION

The steam plant provides heat for the process gas vaporization, heat to maintain the process temperature, and heat for the buildings and other miscellaneous processes. Each of the three independent systems of the Goodyear Atomic Corporation X-600 Steam Plant consists of a coal-fired boiler followed by an economizer, an electrostatic precipitator and finally an induced draft fan. The electrostatic

precipitators were added to the system to control particulate emissions in April, 1979.

In 1977, experimental work to study corrosion problems in the economizers was conducted using fuel additives. Firemate-8 is a chemical mixture which was used in these experiments. Although the experiment was inconclusive in determining whether the chemical reduced the corrosion rate in the economizers, the experiment was nevertheless extended to determine if the chemical would remove corrosive sulfur trioxide from the exhaust.

Addition of Firemate-8 has been experimented with for more than a year on a continual basis. The chemical was fed into the steam generating system through ports at different locations to neutralize the corrosive acid deposits. Apparently, the addition of Firemate-8 engendered a thick mud-like material which was collected from stack number two at the steam plant. It was reported that this white sludge included compounds of metals such as magnesium, aluminum, iron, and nickel.<sup>2</sup> The report stated that the chemical additive did not contribute iron to the sludge, thereby implying the iron's presence was an indication of corrosion. A couple of months later, corrosion was confirmed when boiler number two was shutdown.<sup>3</sup> Holes were found in the expansion joint on the outlet of ESP number two. The new induced draft fan which had been in service for a short time, showed that several blades were corroded as well and a hole was found in the fan housing. Repair was initiated and the system was put on line. The same system was shutdown again after three months, because of corrosion problems.

Test corrosion coupons were placed in the fan housing to measure the corrosion rate. Coupons removed from the number two fan housing were completely disintegrated; whereas, those removed from the number one fan housing showed small metal loss. Other test strips were placed in the housing of fan number three and showed a high corrosion rate as well.<sup>4</sup>

Along with the history of experimentation with Firemate-8 there was an attempt made to find some suitable type of stack coating. A vinyl ester called Plasite 4030 was applied. The polymer was degraded in approximately two months after the stack was put in service.<sup>5</sup> The texture and appearance of the failed coating indicated that Plasite 4030 was exposed to the destructive effect of elevated temperature and/or to heavy concentration of condensed sulfuric acid vapors.

### DISCUSSION

Magnesium oxide, aluminum oxide, and dolomite are components of mixtures which could be added to the fuel in an attempt to inhibit corrosion. The purported benefits of these chemicals include the reduction of  $\text{SO}_3$  emissions, and consequently, control of corrosion by reducing condensation of acidic vapors. Vendors claim that such additives increase the boiler efficiency by maintaining cleaner convection surfaces. A study conducted by ASME Research Committee on Corrosion and Deposits indicated that corrosion of the fireside is caused by molten alkali iron sulfates and that magnesium oxide powder prevents the corrosive attack by the acid-laden gases.<sup>6</sup>

Magnesium oxide is sold in a wide variety of mixtures under different commercial names. Vendors make extensive claims about their products' performance when added to the fuel during combustion.<sup>7</sup> Consequently, the selection of a suitable chemical additive is difficult. The choice depends on many factors such as the chemical and physical characteristics of the fuel, the usually encountered fireside problems, the operation and maintenance of the system, and cost effectiveness. Evaluation of performance of the chemical additives requires data such as  $\text{SO}_3$  concentration, acid dew point and operation data. Conclusions should not be drawn from

short test periods of one or two weeks because reaching equilibrium will be constrained by the ash inventory of the boiler and the boiler surface area.

Sulfur dioxide is an unavoidable product when any fuel containing sulfur is burned. The concentration of the sulfur dioxide is a function of the sulfur content in the fuel. Further oxidation of sulfur dioxide to sulfur trioxide proceeds under certain conditions. The following equations describe the two step oxidation of sulfur to the trioxide form.



Figure 1 shows that the  $SO_3/SO_2$  ratio increases as the temperature of the flue gas decreases. However, the reaction rate falls rapidly below 700°F. This explains why the major portion of the fuel's sulfur is discharged from the combustion equipment in the dioxide form.<sup>8</sup> Evidently, the rate of formation of  $SO_3$  in combustion equipment varies widely and is affected by several factors. Such factors include, but are not limited to, the size of the equipment, temperature of the firebox, catalytic agents, level of excess oxygen, and sulfur content of the fuel.

Table 1 presents a published range of  $SO_3$  as a function of sulfur content and excess oxygen in the flue gas of coal-fired boilers.<sup>9</sup> These ranges were estimated from research presented to ASME and to the National Research Council.<sup>18, 19</sup> Table 2 lists the concentration of  $SO_3$  in the exhaust from the Goodyear Atomic Corporation (GAT) steam plant and the percentage of S in the burned coal as determined by the GAT laboratory.<sup>10, 11</sup>

Since the validity of the data in Table 2 has not been established due to a limited statistical sample size, GAT laboratories are in the process of compiling more results. However, their results have been stated for the purpose of comparison with

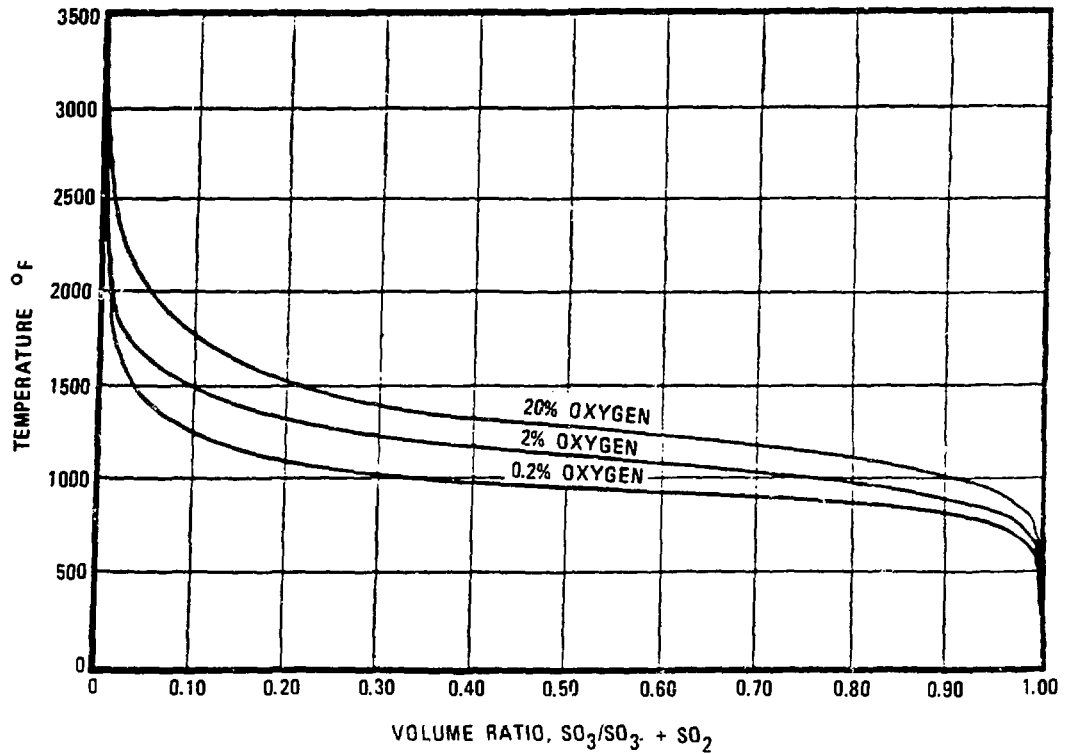


Figure 1 Equilibrium Concentrations of  $\text{SO}_3$ — $\text{SO}_2$  at Various Oxygen Concentrations as per the Reaction  $\text{SO}_2(\text{g}) + 1/2 \text{O}_2(\text{g}) = \text{SO}_3(\text{g})$  (Adapted from Haugen and Watson, 1945)

Table 1 Published Data of  $\text{SO}_3$  Estimated Concentrations from Coal-Fired Units

| % Sulfur in fuel              |                                                  | 0.5                                          | 1.0  | 2.0   | 3.0   | 4.0   | 5.0   |
|-------------------------------|--------------------------------------------------|----------------------------------------------|------|-------|-------|-------|-------|
| <u>% Excess</u><br><u>Air</u> | <u>%<math>\text{O}_2</math></u><br><u>in Gas</u> | <u>Sulfur trioxide expected in gas (ppm)</u> |      |       |       |       |       |
| 25                            | 4.0                                              | 3-7                                          | 7-14 | 14-28 | 20-40 | 27-54 | 33-66 |

Table 2 Concentration of  $\text{SO}_3$  in the Flue Gas from Coal-Fired Boiler as Determined by GAT Laboratory

| DATE     | %SULFUR | SULFUR TRIOXIDE |
|----------|---------|-----------------|
| 10-13-81 | 4.5     | 14              |
| 10-20-81 | 3.57    | 25              |
| 10-21-81 | 3.58    | 20              |
| 10-29-81 | 3.32    | 20              |
| 10-30-81 | 3.63    | 23              |
| 11-03-81 | 4.05    | 19              |
| 11-04-81 | 4.12    | 17              |
| 11-12-81 | 3.28    | 28              |
| 11-17-81 | 3.87    | 20              |
| 12-03-81 | 3.35    | 25              |
| 12-09-81 | 3.01    | 26              |



the concentration range of  $\text{SO}_3$  recorded in Table 1. Comparing  $\text{SO}_3$  concentrations in both tables it appears that the measured levels of  $\text{SO}_3$  are within the lower limit of published concentrations.

Sulfur trioxide reacts with moisture to form the corrosive sulfuric acid. The dew point of these acidic vapors can be calculated from equations published in several articles.<sup>9, 12, 13</sup> Figure 2 illustrates elevation of the dew point as a function of  $\text{SO}_3$  concentration whereas Figure 3 depicts the dew point in degrees centigrade versus the logarithm of  $\text{SO}_3$  concentration. It is believed that any significant disagreement of actual dew point with numbers from Figure 3 will be due to errors in the determination of the  $\text{SO}_3$  concentration. The results calculated from the cited equations and data obtained by scientists showed good agreement (within  $\pm 3^\circ\text{C}$ ). Below 10 ppm  $\text{SO}_3$  there could be significant disagreements. Also, some results showed dew points between  $130\text{--}150^\circ\text{C}$  ( $226\text{--}302^\circ\text{F}$ ) which are predicted by the curves for 5–50 ppm  $\text{SO}_3$ . These high temperatures were measured using a thermocouple. The thermocouple may record an integrated temperature composed of the gas temperature and the adjacent stack wall temperature. Such integrated temperatures are due to inadequate shielding of the thermocouple from the stack wall or inadequate exposure to the gas stream. Because of this problem, precise temperature readings are difficult to obtain and it is always recommended to calculate an arithmetic mean of a statistically valid sample size. Figure 4 is a schematic of the induced draft fan with its double inlet. Temperature was recorded for the inlet/outlet of ESP #2 and the inlet/outlet of induced draft fan number two.<sup>14</sup> Table 3 displays the arithmetic mean of these temperatures which were measured over ten consecutive days by taking three readings per day (one reading per shift).

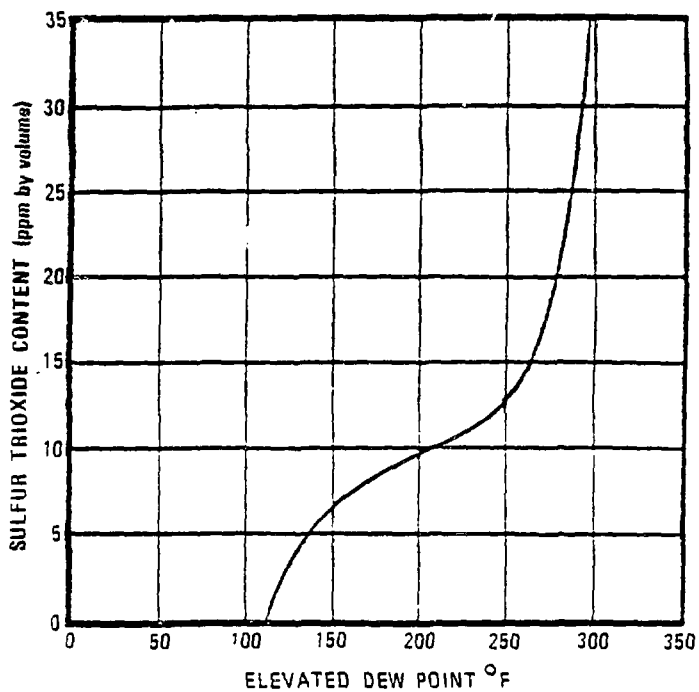


**Figure 2 Dew Point Elevation as a Function of Sulfur Trioxide Concentration**  
(Adapted from Rendle and Witsdon, 1956)

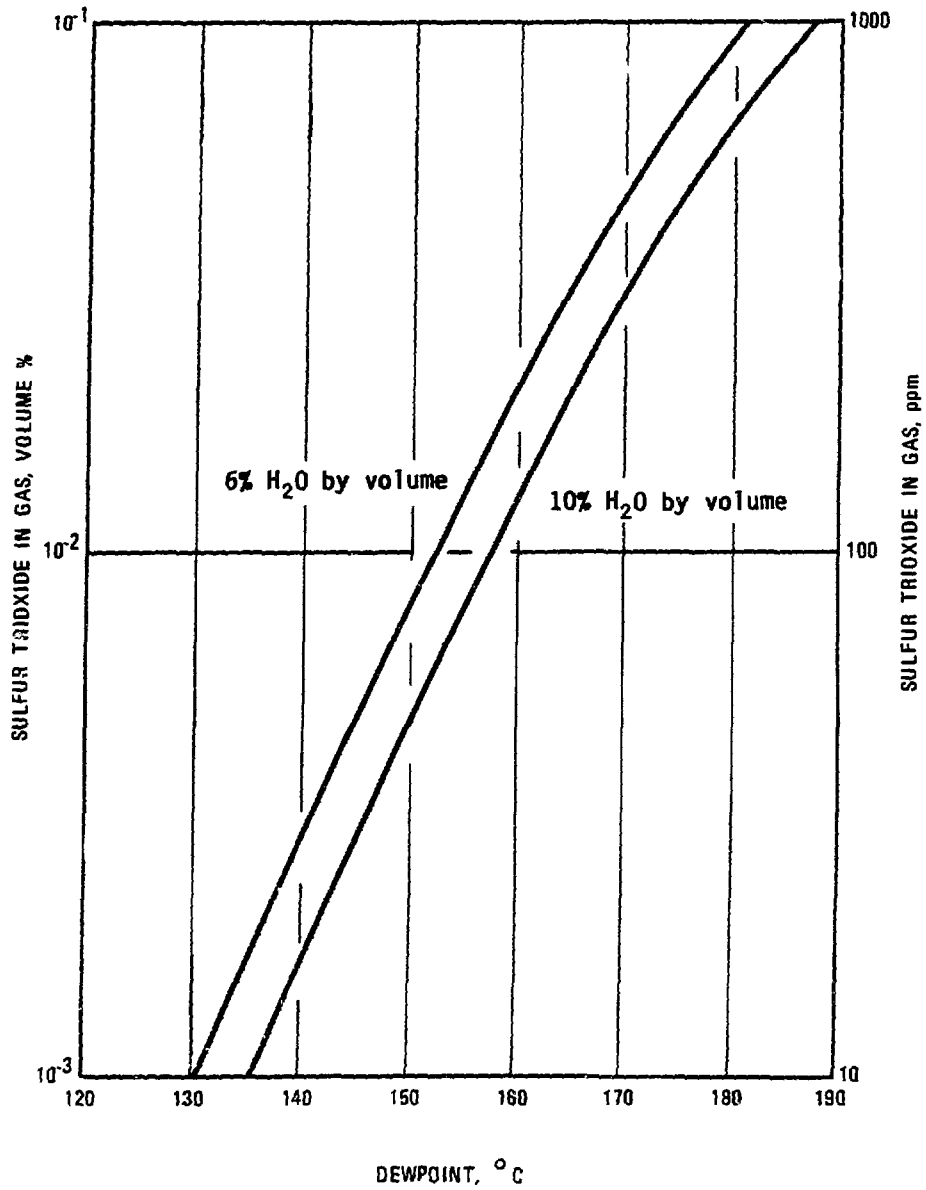


Figure 3 Calculated Dew Point versus Sulfur Trioxide Concentration

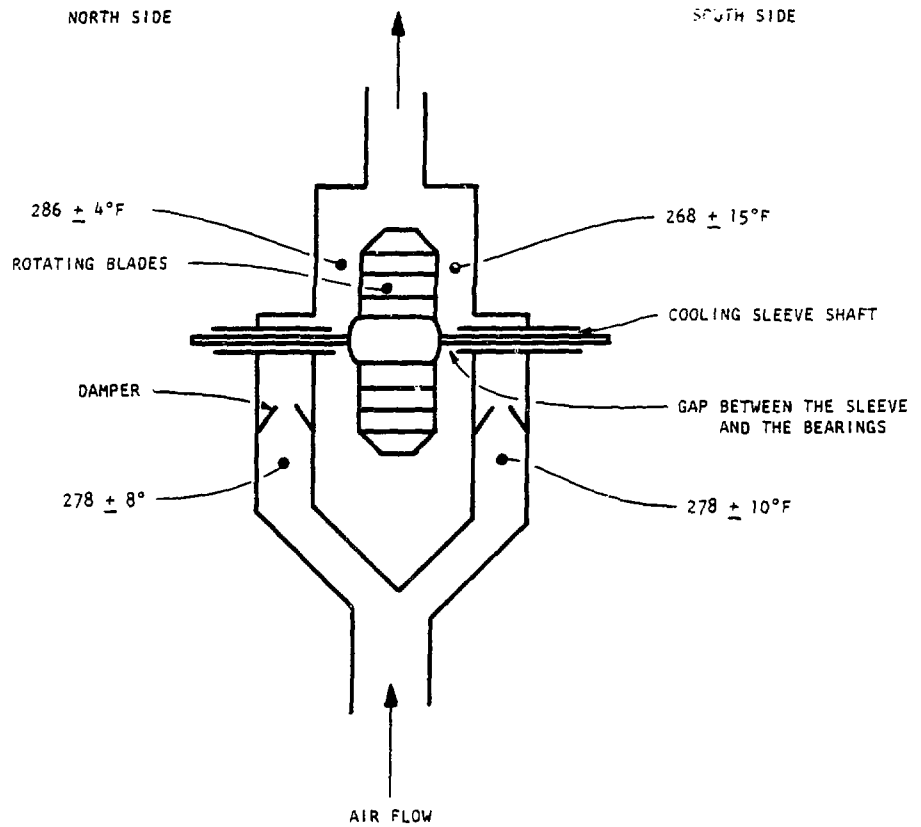


**Figure 4 Average Temperature at the Inlet and Outlet of Induction Draft Fan Number Two**

Table 3 Average Inlet/Outlet Temperature of Electrostatic Precipitator Number Two and Induced Draft Fan Number 2

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| Electrostatic Precipitator<br>Number Two               |                                                       | ID Fan #2                                               |                   |
|--------------------------------------------------------|-------------------------------------------------------|---------------------------------------------------------|-------------------|
| <u>Inlet/Outlet Temperature</u>                        |                                                       | <u>Inlet/Outlet Temperature</u>                         |                   |
|                                                        |                                                       | <u>North Side</u>                                       | <u>South Side</u> |
| $298 \pm 4^{\circ}\text{F}/272 \pm 10^{\circ}\text{F}$ | $278 \pm 8^{\circ}\text{F}/286 \pm 4^{\circ}\text{F}$ | $278 \pm 10^{\circ}\text{F}/268 \pm 15^{\circ}\text{F}$ |                   |

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A small temperature difference between the inlet and outlet of the ESP should be expected since the unit has been insulated and potential leakage of a cooling draft at the outlet of the electrostatic precipitator is not a valid assumption. However, the calculated average temperature drop to  $272 \pm 10^{\circ}\text{F}$  ( $T = 26^{\circ}$ ) at the outlet of electrostatic precipitator number two in Table 3 appears excessive and is probably due to some erroneous readings which affected the calculated mean. Cooling has reduced the flue gas temperatures to levels close to the dew point of acidic vapors, resulting in condensation which provided the conditions for corrosion to occur.

#### Possible Solutions

The introduction and discussion stated in this article show that corrosion problems in the steam plant may be divided into two sections. The first section is corrosion in the economizers and the second section is corrosion in the induced draft fan and the stack. Corrosion of the economizer tubes is either inside tube surface corrosion or outside tube surface corrosion.<sup>17</sup> The inside surface problems are related to the feed water characteristics. Such corrosive attacks are inhibited by the feed water treatment system in the steam plant. The outside surface corrosion of the tube is caused by condensed acidic vapors. Chemical additives have been used on an

experimental basis in the past in an attempt to reduce this corrosion but the results are inconclusive.

Efforts of primary focus in this paper are concerned with inhibiting corrosion by condensed sulfuric acid vapors in the induced draft fan and the stack. Raising the temperature of the flue gas after the electrostatic precipitator should be performed in such a way as to compensate for heat lost and thus maintain the temperature above the acid dew point. Calculations usually include a safety factor which considers fluctuations in the gas flow rate, changes in sulfur trioxide concentration, and variations in the dew point. One potential method is to install infra-red heaters in the duct connecting the electrostatic precipitator and the induced draft fan. With this system, a thermostat would regulate the operation of the heater and minimize energy utilization. Even by minimizing energy usage, however, costs and ESP environmental conditions may make this option impractical. Currently efforts at the Portsmouth site are directed at raising the temperature of the flue gas by either removing some tubes in the present economizers or designing a bypass. Figure 5 is a sketch of the proposed bypass. These modifications will reduce the efficiency of the economizers, however, and hence a larger amount of coal will be burned. Consideration will therefore need to be given to the impact of the resulting increase in  $SO_x$  emissions.

Parallel to the proposed solution of heating the gases above the acid dew point, other studies are being conducted. The objective of these studies is to protect the fan and stack from the condensed acidic vapors. Metallurgical studies are being conducted to characterize the type, the extent, and the probable causes of corrosion.<sup>16</sup> New types of materials to replace some of the components exhibiting the worst corrosion are being investigated. Initial tests included placing samples of corrosion resistant metals such as Hastelloy C-276 and Hastelloy G-3, and others into the induction fan housing.

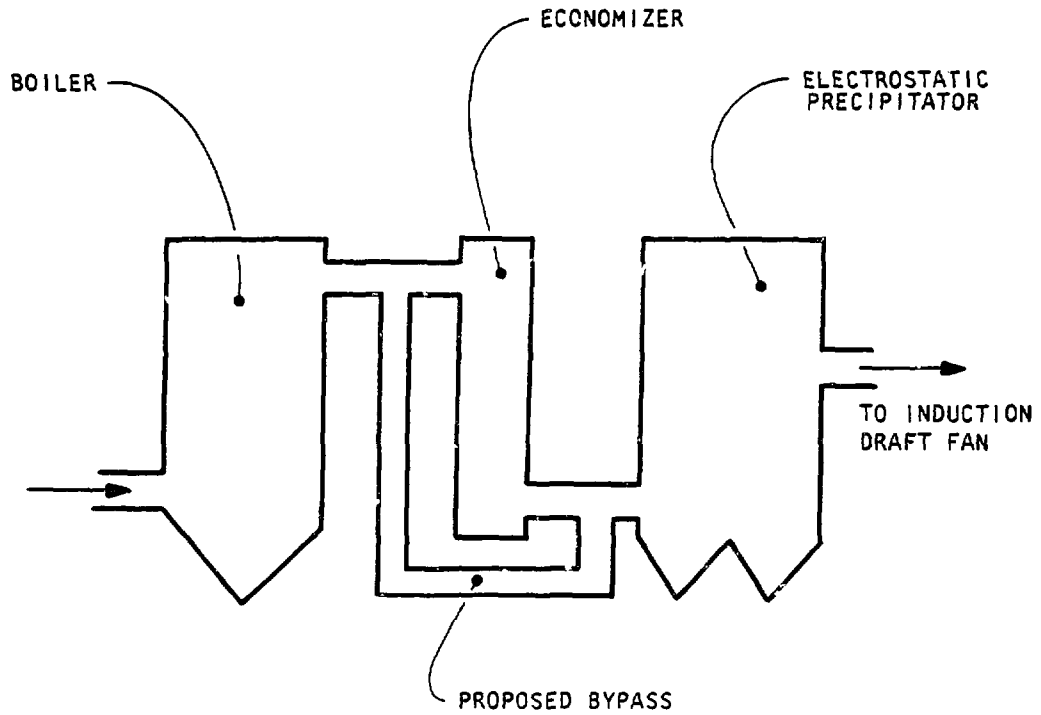


**Figure 5 Schematic Showing Proposed Bypass**

Application of corrosion resistant liners is one method used in industry as a corrosion control measure. Different types of liners are being evaluated for application to protect the inner surface of the stack and the fan housing.

#### ACKNOWLEDGMENT

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## METAL SMELTING FACILITY

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Contaminated Metal, Smelting, Low Level Radioactive Waste

## ABSTRACT

Currently there are 90,000 tons of contaminated ferrous and nonferrous scrap metal stored in aboveground scrap yards at the Department of Energy's Uranium Enrichment Facilities in Tennessee, Kentucky, and Ohio. This scrap is primarily contaminated with 100-500 ppm uranium at an average enrichment of 1-1.5%  $^{235}\text{U}$ . A study was performed that evaluated smelting of the ORGDP metal in a reference facility located at Oak Ridge. The study defined the process systems and baseline requirements, evaluated alternatives to smelting, and provided capital and operating costs for the reference facility. A review of the results and recommendations of this study will be presented.

INTRODUCTION

Large quantities of radioactively contaminated scrap metal are produced by activities at the DOE uranium enrichment plants. The scrap which cannot be sold on the commercial market (excluding NRC licensed facilities) due to the presence of enriched uranium and subsequent classification as special nuclear material is being stored at the DOE plants. A proposed smelter which would serve the dual purpose of reducing the volume of the scrap and decontaminating the metal by concentrating the uranium in the slag is described in this paper. The design of the smelter is generic in that it could be constructed and

operated at any of the DOE enrichment plants. However, to allow for conceptual level designs and cost estimates, it was assumed that the reference facility would be constructed at the Oak Ridge Gaseous Diffusion Plant (ORGDP). The information presented in this paper is preliminary and is subject to change based on refinements and changes to the facility design, operational requirements, and project constraints.

### PROJECT SCOPE AND PURPOSE

#### Project Scope

The scope of the project is limited to providing a Metal Smelting Facility (MSF) that is designed to process the radioactively contaminated ferrous scrap stored at the Power House Area of ORGDP. The smelter would be capable of smelting nonferrous scrap; however, smelting of nonferrous scrap is being performed at other DOE-ORO plants. This paper does not address the management of scrap stored at other DOE installations; however, in principle the MSF could be constructed at any of the DOE plants.

#### Purpose and Justification

There are approximately 90,000 tons of contaminated scrap metal stored at facilities operated by the DOE Oak Ridge Operations offices. Of this, nearly 28,000 tons contaminated with 100-500 ppm uranium are stored at ORGDP. A compilation of the metal listed by type and storage location is shown in Table 1. Table 2 illustrates the projected market value of the scrap on the 1982 scrap metal market.

Table 1

Nearly 90,000 tons of contaminated scrap metals are stockpiled, primarily at the enrichment plants

| Metal                           | Quantity, Mg (ton) |                    |                    |                  |                    |
|---------------------------------|--------------------|--------------------|--------------------|------------------|--------------------|
|                                 | PGDP               | ORGDP              | GAT                | NLO              | Total              |
| Ferrous<br>(misc.)              | 9,636<br>(10,600)  | 19,644<br>(21,630) | 20,000<br>(22,000) | 2,955<br>(3,250) | 52,255<br>(57,480) |
| Ni-plated steel<br>(classified) | 4,318<br>(4,750)   | 1,746<br>(1,921)   | 6,364<br>(7,000)   | 0                | 12,428<br>(13,671) |
| Subtotal                        | 13,955<br>(15,350) | 21,410<br>(23,551) | 26,364<br>(29,000) | 2,955<br>(3,250) | 64,683<br>(71,151) |
| Aluminum<br>(blades)            | 818<br>(900)       | 350<br>(385)       | 145<br>(160)       | 0                | 1,313<br>(1,445)   |
| Aluminum<br>(misc.)             | 1,336<br>1,250     | 412<br>(453)       | 0                  | 0                | 1,548<br>(1,703)   |
| Subtotal                        | 2,154<br>(2,150)   | 762<br>(838)       | 145<br>(160)       | 0                | 3,061<br>(3,148)   |
| Nickel<br>(classified)          | 3,296<br>(3,626)   | 3,241<br>(3,565)   | 1,917<br>(2,109)   | 0                | 8,455<br>(9,300)   |
| Copper                          | 0                  | 0                  | 0                  | 3,153<br>(3,468) | 3,153<br>(3,468)   |
| PLANT TOTALS                    | 19,405<br>(21,126) | 25,413<br>(27,954) | 28,426<br>(31,269) | 6,107<br>(6,718) | 79,352<br>(87,067) |

Table 2.

Total inventory value at current scrap market values

| Metal                  | Market Value |         | Scrap Inventory |        | Scrap Value<br>(\$ million) |
|------------------------|--------------|---------|-----------------|--------|-----------------------------|
|                        | (\$/kg)      | (\$/lb) | (Mg)            | (tons) |                             |
| Nickel                 | 1.85         | 4.07    | 8,455           | 9,300  | 75.7                        |
| Copper                 | 0.56         | 1.23    | 3,153           | 3,468  | 8.5                         |
| Steel                  | 0.06         | 0.13    | 64,683          | 71,151 | 18.5                        |
| Total inventory value: |              |         |                 |        | 102.7                       |

The majority of the scrap at ORGDP was produced during the Cascade Upgrading Program and Cascade Improvement Program. The generation ate from routine activities at ORGDP is 200 tons/year. Current handling procedures provide for above ground storage of the scrap in a designated 50 acre area at ORGDP.

The purpose of the MSF is to provide a mechanism that would be capable of smelting the scrap. The smelting process would provide for significant volume reduction of the metal and would produce a metal ingot that, after NRC's establishment of de minimus levels for low enriched uranium and technetium-99, might be suitable for unrestricted release to the public. Results from ongoing smelting experiments at the Paducah Gaseous Diffusion Plant will provide data for further evaluation of the potential for decontamination by smelting.

### FACILITY DESCRIPTION

#### General Requirements

The project includes the equipment for scrap handling and preparation in the storage yard, scrap transportation, processing in a smelting facility, ingot handling and storage, slag handling, and handling and disposition of non-usable scrap from the preparation and processing operation. The generic facility shall be sited approximately 500 ft. east of the scrap yard area of the ORGDP.

#### Scrap Preparation

Scrap preparation will include the sorting of material in the scrap-yard, preliminary size reduction, loading and transportation of usable

scrap to the MSF. The sorting operation will provide for separation of non-metals from metals and segregation of compatible metals for smelting, e.g., aluminum, stainless steel, iron, monel, copper, etc. Parallel with the sorting operation will be preliminary size reduction of scrap steel. The scrap to be processed will be loaded in the transport vehicles for delivery to the MSF.

#### Metal Smelting Facility

The MSF will be a new steel structure, with concrete foundations and flooring, divided into areas based on the processing systems required for the smelting operation. Typical of these areas are:

- Scrap receiving and separation area,
- Scrap reduction stations,
- Scrap storage and final segregation,
- Scrap weighing and drying area,
- Furnace operations and refractory repair,
- Slag processing,
- Flux storage and preparation,
- Mold preparation and cooling,
- Ingot cooling, dumping, and storage,
- Office, laboratory and control room,
- Air compressor and maintenance areas,
- Electric substation and standby power supply,
- Personnel convenience stations (wash rooms, toilets, Locker rooms, etc.).

Additional systems required for operation of the facility include water and wastewater, environmental control, personnel protection, emission control, metal handling and process cooling (cooling towers).

Scrap received at the rate of 40 tons/day will be transported by a 10 ton capacity overhead crane to the cutting/burning station for further size reduction, or, if properly sized, to the storage bins preliminary to drying.

These stations will be compartments of a size to facilitate manual cutting operations. Adequate ventilation and environmental control systems will be provided in each compartment to protect the personnel from fumes and dust generated by cutting the metal. After cutting, the overhead crane will remove the properly sized metal and place it in the storage bins.

After sufficient quantities of metal have accumulated, the scrap will be campaigned through the metal weighing and drying system. The dryer shall operate at 700-800 F with a throughput of approximately 6 tons/hr. The drying operation is required to remove oils, water, etc.

The metal exiting the dryer will fall into the charging bucket of approximately 40 ft.<sup>3</sup> capacity for transport to the furnace. A second overhead crane, also of 10 ton capacity shall be provided for moving the charge bucket to the furnace. Following assurance of proper exhaust hookups to the charging bucket, the charge will be fed by gravity into the furnace. The furnace, proposed to be an eight ton unit, will contain approximately two tons of molten metal at the time of the charge. The electric induction furnace for melting ferrous metals shall operate at



approximately 280 hertz. The melt rate of the furnace shall be 4-6 tons/hr. ferrous and roughly 1.6 tons/hr. non-ferrous (aluminum). The induction power requirements will be approximately 2000 kilowatts. Two furnace crucibles will be available to provide continuous operations. One furnace will be operational with the other on standby or under repair. Following the addition of fluxing agents and the removal of the slag, the molten metal (approximately 2/3-3/4 of the contents of the furnace) will be poured into the one ton molds. The molds will be positioned on a motorized cart that will travel past the furnaces for filling in series.

The full molds shall be individually removable by use of an overhead crane and placed into the mold cooling area for a period of 4-5 hours, following which the molds will be dumped in the ingot dumping area. The self-dumping molds shall have a taper to ensure easy removal of the ingot. Following adequate cooling, the ingots will be transferred to the ingot storage area.

Immediately preceding each pour, samples of the metal will be manually collected and analyzed and, if necessary additional slagging operations may be required to ensure that the ingot will not contain radioactive contaminants in concentrations exceeding prescribed limits. The sample will be analyzed by a spectrometer in the laboratory. Flux will be prepared (mixed) at the flux storage and weight station and then transported to and charged into the furnace.

It is estimated that approximately 50 lbs. of slag will be produced per ton of melt. The slag must be mechanically removed from the furnace, transferred to an adjacent room to minimize the spread of contamination, and placed into slag pots for cooling. An overhead jib crane may be required to perform the operation. A dry slagging operation is required to: 1) minimize criticality concerns, and 2) eliminate the potential for generation of waste water contaminated with radioactive materials. The electric furnaces shall include a closed loop water cooling system, water tanks, and evaporative cooling towers. Cooling capacities shall also be provided for the compressors and other pieces of equipment that may require supplemental cooling. Portable personnel protection shields shall be provided for placement between the furnaces at times when one furnace may need repairs while the other furnace is operating. Additional maintenance equipment for mold spraying and furnace relining shall be provided.

A standby power system shall be provided as a minimum to tilt the furnaces, power the crane, power the air compressor, position the molds and operate the air exhaust systems. The generating facilities may be diesel-electric or similar generation not necessarily free from short interruptions.

The air handling system shall have sufficient capacity to handle the exhaust produced in areas where a potential exists for airborne contamination. Because of the uranium and fluoride contamination of some of the scrap and the need to conform to fluoride emission

standards, emphasis shall be directed at control of the exhaust from the facility size reduction stations, the scrap dryer, the furnaces, the slag cooling area, and the mold cooling and dumping areas.

Adequate toilet, washroom, locker room and lunch room facilities shall be provided for the personnel.

#### Ingot Storage

Ingot storage includes the equipment to transport the ingots from several days production (approximately 100 ingots) to an off-site storage area and the equipment to locate (position) the ingots within the proposed storage facility. At present, the boiler rooms of the existing Power House, K-703, are proposed for this use.

#### Slag Storage and Disposal

A storage area of sufficient capacity will be provided so as not to impact the smelting operations by slag accumulation. This area will be separate from the main building to minimize the spread of contamination which will be concentrated in the slag. Equipment shall be provided for reducing the size of the slag, for packaging the slag in drums, and transporting the slag to a final disposal site, currently projected to be the Y-12 contaminated burial ground. The slag will require handling as special nuclear material (SNM).

#### Non-metallic and Miscellaneous Scrap Disposal

Equipment shall be provided for the packaging, temporary storage and final disposition of plastics and other combustibles segregated from the scrap in the scrap yard. The final disposal site is currently projected to be the Y-12 contaminated burial ground.

### CONCLUSIONS

The proposed MSF provides a mechanism for significantly reducing the volume of the contaminated scrap metal stored at the DOE plants. The resulting ingots being essentially decontaminated due to the transfer of uranium to the slag during the smelting process are more amenable to resource recovery or disposal. If NRC does establish de minimus levels for low enriched uranium and  $^{99}\text{Tc}$ , there exists a potential for recovery of both the capital and operating costs of the MSF through the sell of the ingots.<sup>1</sup>

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## ORNL PROCESS WASTE TREATMENT PLANT MODIFICATIONS

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Key Words: Low-Level Radioactive Waste, Ion Exchange

## ABSTRACT

The ORNL Process Waste Treatment Plant removes low levels of radionuclides (primarily Cs-137 and Sr-90) from process waste water prior to discharge. The previous plant operation used a scavenging precipitation - ion exchange process which produced a radioactive sludge. In order to eliminate the environmental problems associated with sludge disposal, the plant is being converted to a new ion exchange process without the precipitation process.

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## Introduction

The Process Waste Treatment Plant at Oak Ridge National Laboratory treats low-level aqueous waste collected from various locations at the laboratory. The current treatment plant was designed to use a scavenging-precipitation-ion exchange process and has been in operation since 1976. Prior to that a lime-soda-clay precipitation process was used. The scavenging-precipitation-ion exchange process has consistently produced an effluent well within the maximum permissible concentration limits for discharge to a public stream. The major disadvantage of the process is production of radioactively contaminated sludge. Disposal of the sludge in an environmentally acceptable manner is difficult and costly. For this reason alternate processes were investigated to eliminate the sludge production problem. The objective of this effort was to develop a process producing an acceptable effluent with reasonable capital and operating costs and no sludge generation.

## Description of the Process Waste Treatment Plant<sup>1</sup>

Figure 1 is a simplified process flow diagram of the existing treatment plant. The total treatment plant consists of: (1) the equalization basin; (2) the feed system, Building 3518; (3) process equipment, Building 3544; (4) the sludge disposal basin; and (5) radioactive-waste transfer piping. The first three components are located in the main ORNL area, the sludge disposal basin is located at Burial Ground No. 5 about 1.0 km south of the processing plant, and the waste transfer piping connects the processing plant with the disposal basin and the ORNL Intermediate-Level Waste System.

The equalization basin has existed for a number of years and has a capacity of  $3.8 \times 10^6$  liters of low-level waste ( $<1.0 \mu\text{Ci/liter}$ ), which is essentially  $^{90}\text{Sr}$  and  $^{137}\text{Cs}$ . Smaller quantities of  $^{60}\text{Co}$  and  $^{154}\text{Eu}$  are sometimes present.

Feed is pumped continuously from the basin through pipes, pumps, and valves located in Building 3518. Only minor modifications were made to this equipment to convert it from the previously used lime-soda process. Feed is pumped at a selected rate, usually between 175 and 375 liters/min, into the processing plant in Building 3544.

This building is divided into a control room, a chemical makeup area, and a shielded area containing regeneration-solution tanks, three ion exchange columns, an evaporator, a concentrated-waste tank, an acid off-gas scrubber, and pumps. The head-end treatment equipment, the sludge holdup and transfer system, and a concrete clearwell about 7 x 7 x 2 m are located on a concrete pad outside the building.

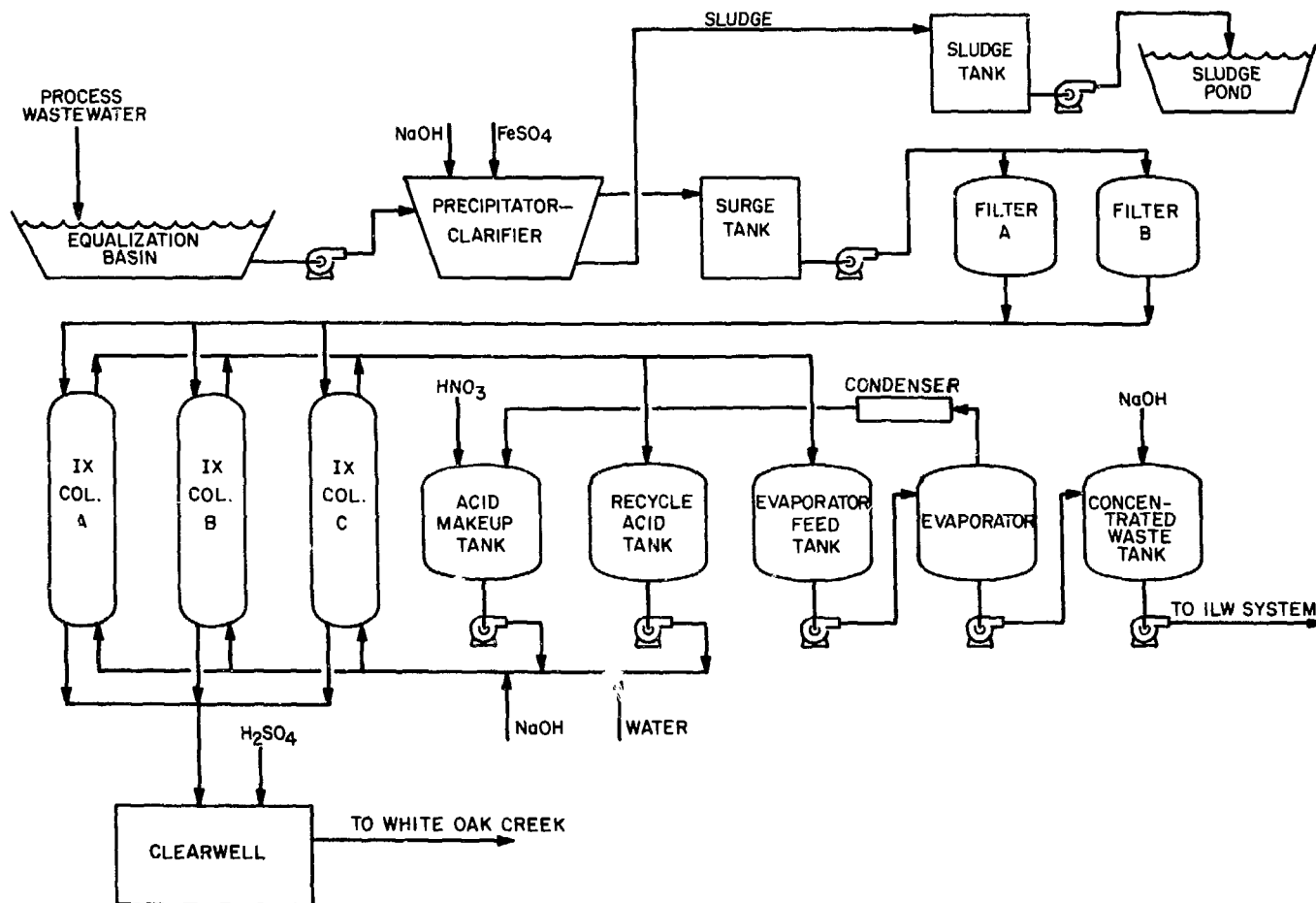


**FIGURE 1**  
**OLD PROCESS FLOW DIAGRAM**

The sludge that is generated in the precipitator-clarifier is periodically pumped to the sludge disposal basin as a slurry containing 2 to 4 wt% solids.

The line connecting the process building to the sludge disposal basin is constructed of 2-in. schedule 80, unplasticized PVC pipe and is laid underground. The concentrated liquid waste from ion exchange regeneration, evaporation, and neutralization is pumped through an underground pipeline constructed of 1 1/2-in. schedule 40, type 304L stainless steel to the existing intermediate-level waste collection system.

#### Previous Operations of the Process Waste Treatment Plant<sup>1</sup>

The Treatment Plant has been in continuous operation at an average flow rate of 300 liters/min. Occasionally, feed has been processed as fast as 565 liters/min. At no time has the plant effluent exceeded the maximum permissible concentration for water in public streams. The plant is designed for a maximum flow of 750 liters/min but has never operated at this rate.

The feed from the equalization basin is continually mixed with concentrated sodium hydroxide solution to give a pH of 11.8 and with a copperas ( $\text{FeSO}_4$ ) solution to give 5 ppm iron. The hydroxide addition rate is controlled by an electrode downstream from the addition point in the feed. The ferrous solution rate is controlled by the setting on the feed pump. The feed then flows through a static pipe-mixer. Coagulation of the precipitate into larger particles occurs in the flocculator section of the precipitator-clarifier, where the mixture is gently agitated as it flows down to the bottom. The floc enters the bottom of the clarifier section, where separation is achieved by upflow of the mixture through a sludge blanket, which consists of fluidized particles that trap the floc and continue the precipitation reactions by crystal growth. These particles agglomerate and settle to form a slurry in the bottom of the vessel. This action scavenges radionuclides, dirt particles, and algae, as well as most of the hardness, from the waste stream.

The slurry is periodically pumped to an agitated 23,000-liter sludge holding tank and then to the sludge disposal basin, as necessary. This step removes from one-half to two-thirds of the total radioactivity in the stream. The proper operation of the clarifier section is monitored by turbidity analyses of samples taken at appropriate points in the stream.

The effluent from the clarifier overflows to a 25,000-liter surge tank and then is pumped through one of two pressure-type polishing filters containing a bed of 0.6 to 0.8-mm anthracite. When pressure drop increases 5 to 6 psi, the flow is switched to the other bed and the first one is backwashed. Backwashing is done at 2000 liters/min for 10 min with water from the clearwell. The bed is then re-



washed at 650 liters/min for 3 min, after which the wash solution is pumped back to the equalization basin.

From the filter, the stream, which now usually has less than 5 ppm hardness, passes downflow through one or more of three ion exchange columns containing 1275 liters of sodium-form Duolite CS-100 resin. The beds are used consecutively; a switch is made after the passage of about 2000 bed volumes of feed. The maximum flow rate through a bed is 380 liters/min, but two beds may be operated simultaneously, in parallel. A movable beta-gamma probe is mounted on the exterior of each column. In the pilot-plant development of the process, it was found that such a probe could be used to follow a band of maximum activity from top to bottom as the column was used and thus to predict breakthrough of radionuclides. Since the readings from these probes in plant operation have never been of value, their use has been discontinued.

To regenerate a resin bed, the column is eluted upflow with two batches (five bed volumes each) of 0.50 M nitric acid. The first batch removes most of the radioactivity and hardness and is then concentrated by evaporation, neutralized with sodium hydroxide, and sent to the Intermediate-Level Waste Treatment Plant. The second batch is stored and used as the first batch for the next elution. After a water rinse, the resin is reconverted to a sodium form by passing 20 bed volumes of 0.1 M NaOH upflow through the bed. The caustic and water washes are sent back to the equalization basin.

After leaving the ion exchange bed, the stream passes over a beta-gamma probe and into the first compartment of the clearwell. The readings from this monitor apparently cannot be correlated with any variable in the process and are therefore generally ignored.

The clearwell, which contains 80,000 liters, is divided into two sections by an overflow weir. Water in the first section, which holds two-thirds of the volume, backwashes the filters and makes up the 0.1 M NaOH for resin regeneration. At the weir, where a pH electrode continuously measures the pH, sulfuric acid is added to reduce the pH to 7.0. The waste then flows into White Oak Creek.

### Description of Alternatives

Two process changes were considered. One concept would continue the precipitation-ion exchange process but substitute aluminum sulfate for ferrous sulfate as a flocculant. The sludge would be dissolved in nitric acid and discharged to the intermediate level waste ILW system. The second process eliminates the precipitation process and treats the waste after filtration with a strong acid cation exchange resin. In addition to the radionuclides, nonradioactive ions such as calcium, magnesium, and sodium would be removed by the resin. This would increase the resin loading and result in shorter run times and more frequent regeneration. The advantage of this process is that all of the radionuclides are dissolved in the

regenerant and are discharged to the ILW system. A separate sludge dissolution step is not required. Laboratory tests conducted by J. M. Chilton of the ORNL Chemical Technology Division confirmed the feasibility of the strong acid cation exchange process and established the process parameters. Since this process required fewer plant modifications and would be operationally simpler it was selected for further evaluation.

Two different approaches for modifying the treatment plant were considered. The first method involved using the three existing fixed-bed ion exchange columns refitted with strong acid cation exchange resin. A fourth column would be added to provide more capacity since the new process would have shorter service cycles.

Figure 2 is a process flow diagram of this system. For convenience wastewater will still flow through the precipitator/clarifier but no chemical additions will be made and no precipitation will occur. Wastewater is passed through the anthracite filters and then downflow through the ion exchange columns. Two columns in parallel will be run at the maximum flowrate of 750 g/min. Since the resin is run in the hydrogen form the ion exchange effluent will be acidic. The effluent will be neutralized with NaOH in the clearwell prior to discharge to White Oak Creek.

Regeneration of the ion exchange resin is accomplished by passing 6 resin bed volumes of 3 N  $\text{HNO}_3$  upflow through the columns followed by a water rinse. The first half of the acid regenerant is evaporated, neutralized and discharged to the ILW system. The second half is collected and reused as the first half of the next regeneration. The evaporator overhead is condensed and collected, brought up to 3N  $\text{HNO}_3$  by strong acid addition, and used for the second half of the next regeneration. This regeneration process results in recovery of a large quantity of  $\text{HNO}_3$  which would otherwise be wasted.

A second approach for modifying the process is to replace the existing fixed-bed columns with a single continuous, countercurrent ion exchange system. This would have the advantages of continuous operation and more efficient regeneration than the fixed-bed system. Operating cost savings would result from reductions in  $\text{HNO}_3$  usage, NaOH needed for neutralization, steam for evaporation, and final disposal volume.

A process flow diagram for the continuous ion exchange system is shown in Figure 3. In the continuous countercurrent ion exchange system, the resin is moved around a single loop of connected vessels providing simultaneous treatment, regeneration, backwash and rinse cycles in separate sections without interrupting flow. The resin is moved in one direction, and the influent and all other solutions (regeneration, rinse, backwash) move in the opposite direction. The system operates by continuously cycling between a "run mode" and a "pulse mode". During the run mode of 5 to 20 minutes duration,

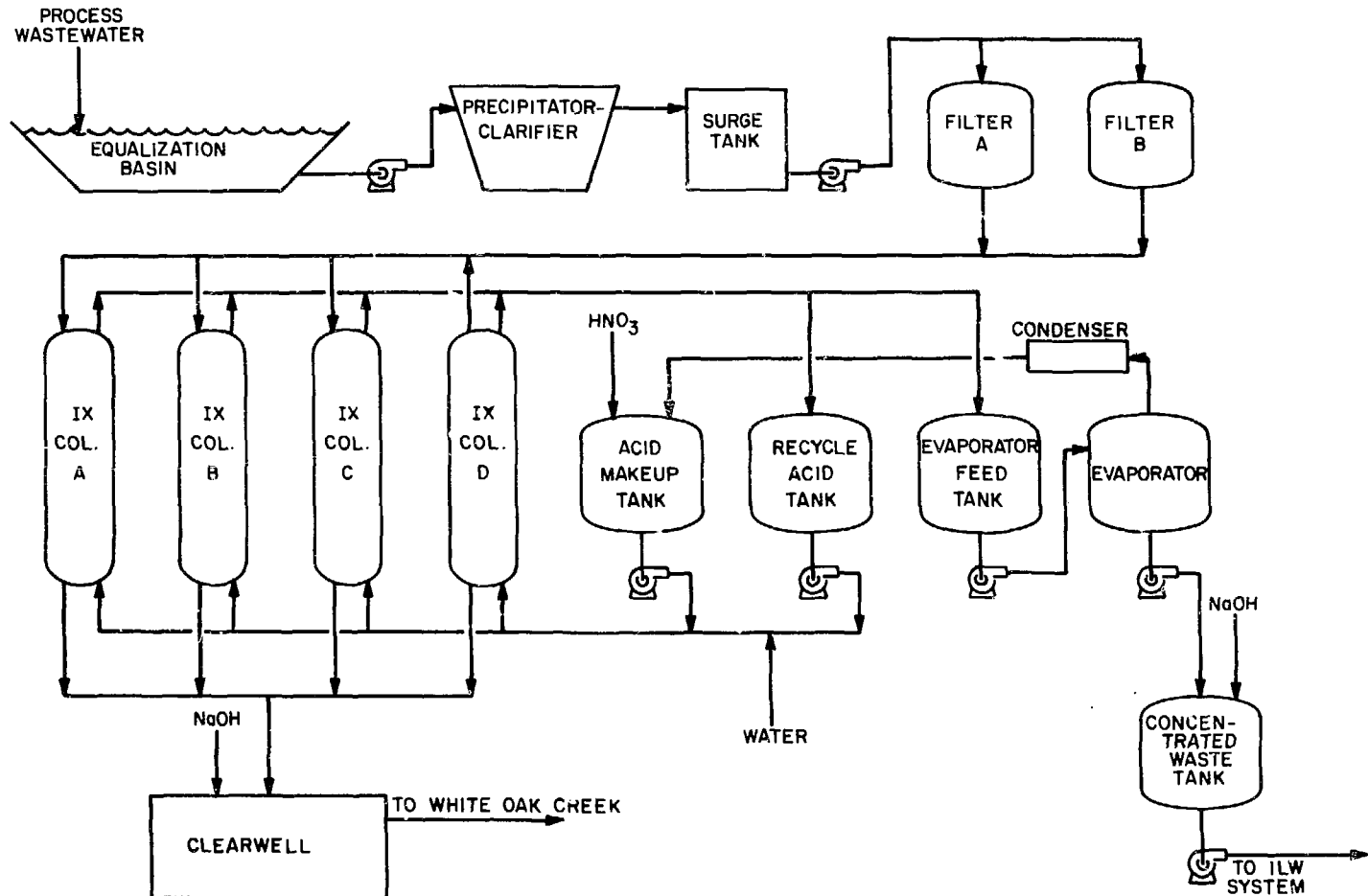


**FIGURE 2**  
**NEW PROCESS FLOW DIAGRAM**

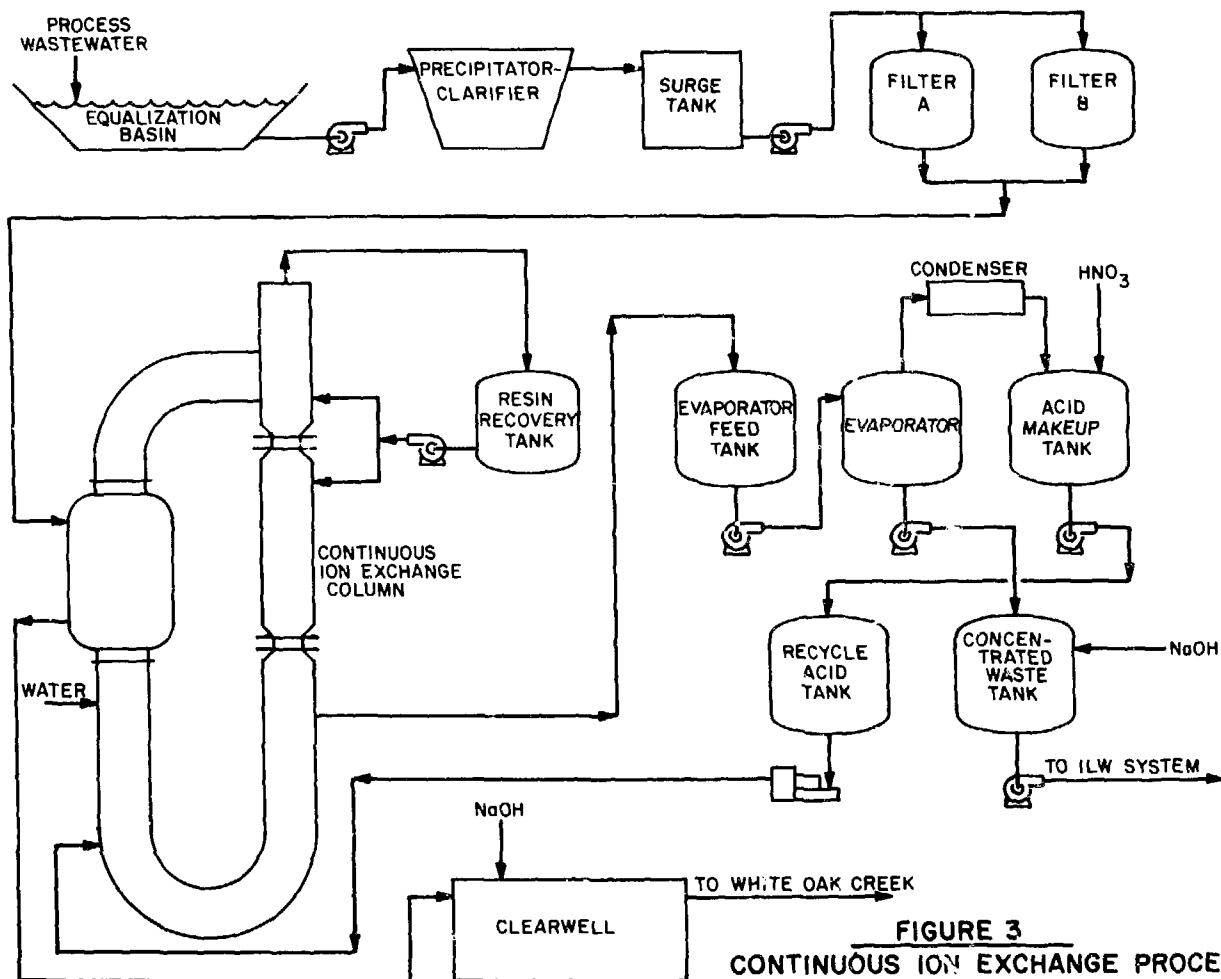


**FIGURE 3**  
**CONTINUOUS ION EXCHANGE PROCESS**  
**FLOW DIAGRAM**

three main valves of the contacting section and the regenerating section are closed. In the contacting section the waste feed stream is fed down through the resin bed and treated product water having a pH of 3 is delivered from the bottom of the bed.

Simultaneously, approximately 4N  $\text{HNO}_3$  regenerant is fed through loaded resin in the regenerating section at the bottom of the loop and exits as nitrate salts after stripping the resin free of the sorbed ions. Spent regenerant solution flows to the evaporator feed tank and to the evaporator. At the same time, loaded resin is dropping through an open valve into the pulse section. Positive pulse control sensors close this valve when the pulsing section is properly filled.

Clear rinse water washes regenerant traces from the stripped resin (next to enter the contacting section). The valve for the water rinse is operated by a conductivity controller that senses the interface of rinse and regenerant solutions to insure all regenerant traces are removed before rinsing is terminated. In the "pulse mode", during which process waste, regenerant, and rinse flows are halted for 15 to 30 seconds, main valves of the contacting section and the regenerating section open to allow the compacted resin bed to be pushed counter-current to the direction of flow. A hydraulic pulse of raw water transfers resin around the loop by a pre-selected distance. This movement puts loaded resin from the pulse section into position for regeneration while pushing stripped and rinsed resin into the contacting section and moving loaded resin from the contacting section around to the resin storage area. A water backwash cleans resin fines and foreign particles from the loaded resin which is fluidized at this point. Resin fines and the exit water rinse are pumped to the resin recovery tank.

After ion exchange, the process waste stream, now stripped of radioactivity and hardness, flows to the clearwell where it is neutralized by addition of Na OH solution. Spent regenerant solution is evaporated and the concentrate is neutralized and pumped to the ILW system. Overhead from the evaporator is condensed and collected for reuse to recover the  $\text{HNO}_3$ .

### Evaluation of Alternatives

Either of the two concepts would accomplish the project objective. Both options eliminate the production of sludge and will produce an effluent of acceptable quality for discharge. It is expected that operating labor requirements will be similar although maintenance costs may be slightly higher for the continuous column.

The primary advantage of the continuous column over the fixed bed system is that it can be regenerated more efficiently, resulting in less regenerant waste. The increased regeneration efficiency results

in the use of less  $\text{HNO}_3$  and  $\text{NaOH}$ , less steam for evaporation, and lower final disposal costs.

In order to determine the operating costs of the continuous counter-current ion exchange system and the four column fixed bed ion exchange column system, a series of calculations were made to determine the quantity of chemicals and steam used and the amount of concentrated waste created by each system on a daily basis. After computing the daily quantity of chemicals, steam, and waste used or formed, an annual operating cost was calculated for each system.

In making the calculations the following assumptions or data were used:

- The evaporator uses steam at 35 psig, which costs \$4.00 per 1000 pounds.
- All calculations are based on both systems having a design feed rate of 200 gpm.
- Chemical costs came from the July 13, 1981, edition of the Chemical Market Reporter while steam and final disposal costs were provided by L. C. Lasher of the ORNL Operations Division.
- Table 1 contains the data used in making the calculations.
- Only process chemical costs, steam costs, and final disposal costs are considered to be significant for the purpose of this study. All other costs remain approximately equal for both systems.
- Assumption was made that if the evaporator at the waste treatment plant was used and the regeneration waste was concentrated to a 7.0-7.4 N  $\text{NO}_3$  salt concentration, then significant further concentration of this waste would not occur in the ILW system.

Table 2 is a comparison of the costs of operating each system and shows that the continuous column can be operated for approximately \$127,000 less per year than the fixed bed system,

Table 1. Data elements used in cost calculations

| Item                 | Cost          | Quantity used per day |                   |
|----------------------|---------------|-----------------------|-------------------|
|                      |               | Fixed bed column      | Continuous column |
| 60% $\text{HNO}_3$   | \$8.75/100 lb | 173 GPD               | 58.5 GPD          |
| 50% $\text{NaOH}$    | \$300/ton     | 78.3 GPD              | 41.4 GPD          |
| Steam @50 psig       | \$4/1000 lbs  | 12216 lbs/day         | 2042.67 lbs/day   |
| Final Waste Disposal | \$0.70/gal    | 304.3 GPD             | 121.5 GPD         |

Table 2. Comparison of costs

| <u>Cost unit</u>   | <u>Fixed bed column</u> |              |             | <u>Continuous column</u> |              |             |
|--------------------|-------------------------|--------------|-------------|--------------------------|--------------|-------------|
|                    | <u>Day</u>              | <u>Month</u> | <u>Year</u> | <u>Day</u>               | <u>Month</u> | <u>Year</u> |
| Nitric Acid (60%)  | \$171.80                | \$5145.00    | \$61848.00  | \$ 58.08                 | \$1742.70    | \$20912.40  |
| Caustic (50% NaOH) | 149.50                  | 4485.00      | 53820.00    | 79.05                    | 2371.50      | 28458.00    |
| Steam @ 50 psia    | 48.85                   | 1465.80      | 17589.60    | 8.17                     | 245.10       | 2941.20     |
| Hydrofracture      | 213.00                  | 6390.00      | 76680.00    | 85.05                    | 2551.50      | 30618.00    |
| Totals             | \$583.15                | \$17494.80   | \$209937.60 | \$230.35                 | \$6910.80    | \$82929.60  |

Cost difference: \$352.80/day, \$10,584.00/month, or \$127,008.00/year in favor of continuous column.

Capital costs were estimated for both process modifications. Addition of the fourth fixed bed column was estimated to cost \$260,000. Addition of the continuous ion exchange column was estimated to cost \$860,000 or \$600,000 more than the fixed bed system.

Since the capital cost for the continuous column is greater than that for the addition of the fixed bed column, an economic analysis was made to determine whether additional capital could be justified by the operating cost savings.

The rate of return on the additional capital investment for the continuous column was computed using the discounted cash flow method. The initial capital outlay was taken as the difference between the costs of the continuous column system and the fixed bed system. The operating cost savings were taken as annual cash incomes. The operating cost savings were inflated at a rate of 10% per year. The life of the facility was assumed to be 10 years. The following is a summary of the economic data for this analysis:

|                                            |              |
|--------------------------------------------|--------------|
| Initial investment                         | \$600,000    |
| Annual operating cost savings (first year) | \$127,000    |
| Inflation rate for savings                 | 10% per year |
| Life of facility                           | 10 years     |
| Salvage value of facility                  | 0            |
| Rate of return                             | 25%          |

The 25% rate of return on the additional investment for the continuous column is marginally attractive. This investment, however, was considered in terms of the availability of capital and the competing uses of the available money. Since money for capital projects is limited, the lower cost option of adding the fourth fixed bed column was selected.

### System Performance

Two of the existing ion exchange columns were filled with strong acid cation exchange resin to test the performance of the new process. Table 3 gives the results of the performance tests. The new process produces an effluent well within the discharge requirements. The length of a service cycle on each column was 600-700 resin bed volumes, confirming laboratory test data. This compares to approximately 2000 resin bed volumes with the old process.

Before the full scale test it was assumed that breakthrough of Cs ion would closely follow Na ion breakthrough. In fact, a sodium ion detector was proposed to determine the end of a cycle. In practice it was found that Cs was removed for a significant period after Na breakthrough had occurred indicating a high selectivity of the resin for Cs over Na.

Table 3 - Test Data  
Average Concentrations Bg/l

|          | <u>Cs-137</u> | <u>Sr-90</u> |
|----------|---------------|--------------|
| Influent | 69            | 660          |
| Effluent | 4.3           | 1.3          |



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## THE NEW HYDROFRACTURE FACILITY AT ORNL

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Key words: waste disposal, permanent, cement, slurries, geologic fixation.

ABSTRACT

Hydrofracture, or shale fracturing, is the method currently being used at Oak Ridge National Laboratory (ORNL) for the permanent disposal of locally generated radioactive waste solutions. In this process, the waste solution is mixed with a solids blend of cement and other additives; the resulting grout is then injected into an impermeable shale formation at a depth of 200 to 300 m (700 to 1000 ft). The grout sets a few hours after completion of the injection, fixing the radioactive waste in the shale formation.

Since 1966, ORNL has disposed of more than 8 million L (2 million gal) of waste grout, containing over 600,000 Ci of radionuclides, via hydrofracture. A description of the process and its operational history are given. Disposal costs of the order of 25¢/L (\$1/gal) are reported. A new facility has been built and will become operational by the summer of 1982.

INTRODUCTION

The hydrofracture process was developed at ORNL for the permanent disposal of locally generated intermediate-level waste solutions. These solutions, which are alkaline, are about 1 M in  $\text{NaNO}_3$  and have a radionuclide content (predominantly  $^{137}\text{Cs}$ ) of about 0.25 Ci/L (1 Ci/gal). In this process, the waste is mixed with a blend of cement and other solid additives. The resulting grout is then injected into a nearly impermeable shale formation at a depth of 200 to 300 m (700 to 1000 ft), well below the level at which groundwater is encountered. During the course of the injection the injected grout forms a thin, approximately horizontal, grout sheet several hundred meters (up to 1000 ft) wide. The grout sets a few hours after completion of the injection, thus permanently fixing the

radioactive waste in the shale formation. This process has been in operational use for nearly 20 years at ORNL. It is an inexpensive process that is particularly suited for the permanent disposal of large batches of waste. A sketch of the ORNL disposal facility is shown in Fig. 1.

The essential feature of the shale fracturing process is the fixation of the radionuclides in a geological formation that is known to be isolated from contact with the surface environment. The permeability of the shale in the disposal zone is very low; the calculated rate of water movement is less than 1 cm per century. The process has additional features that would provide continued containment of the radionuclides even if the isolation of the disposal formation should be lost. For example, the leach rates of significant radionuclides from the set grout are quite low. In addition, any radionuclides that might be leached from a grout sheet would be retained in the disposal zone by the high ion-exchange capacity of the shale. Therefore, this process offers an exceptionally favorable approach to the permanent disposal of radioactive wastes.

#### PROCESS DESCRIPTION

The wastes that are disposed of by the hydrofracture process are generated in various facilities at ORNL. These wastes are first neutralized and concentrated by evaporation. The overhead from the evaporator is collected, treated by an ion exchange process to remove residual traces of radionuclides, and discharged. The concentrated bottoms from the evaporator are stored; this waste then becomes the feed stream for the hydrofracture process. A sketch of the liquid waste disposal system at ORNL is shown in Fig. 2.

Shale fracturing is operated as a large-scale batch process. Each injection is, however, a continuous operation designed to dispose of an annual accumulation of waste solution of about 350,000 L (100,000 gal). A flow diagram of the process is shown in Fig. 3. Prior to the injection, the waste solution is pumped to the waste storage tanks at the injection site. The dry solids are blended and stored in bins at the injection facility. A standby pump is rented for each injection; its function is to clean grout from the injection well in the event of failure of the main pump. During

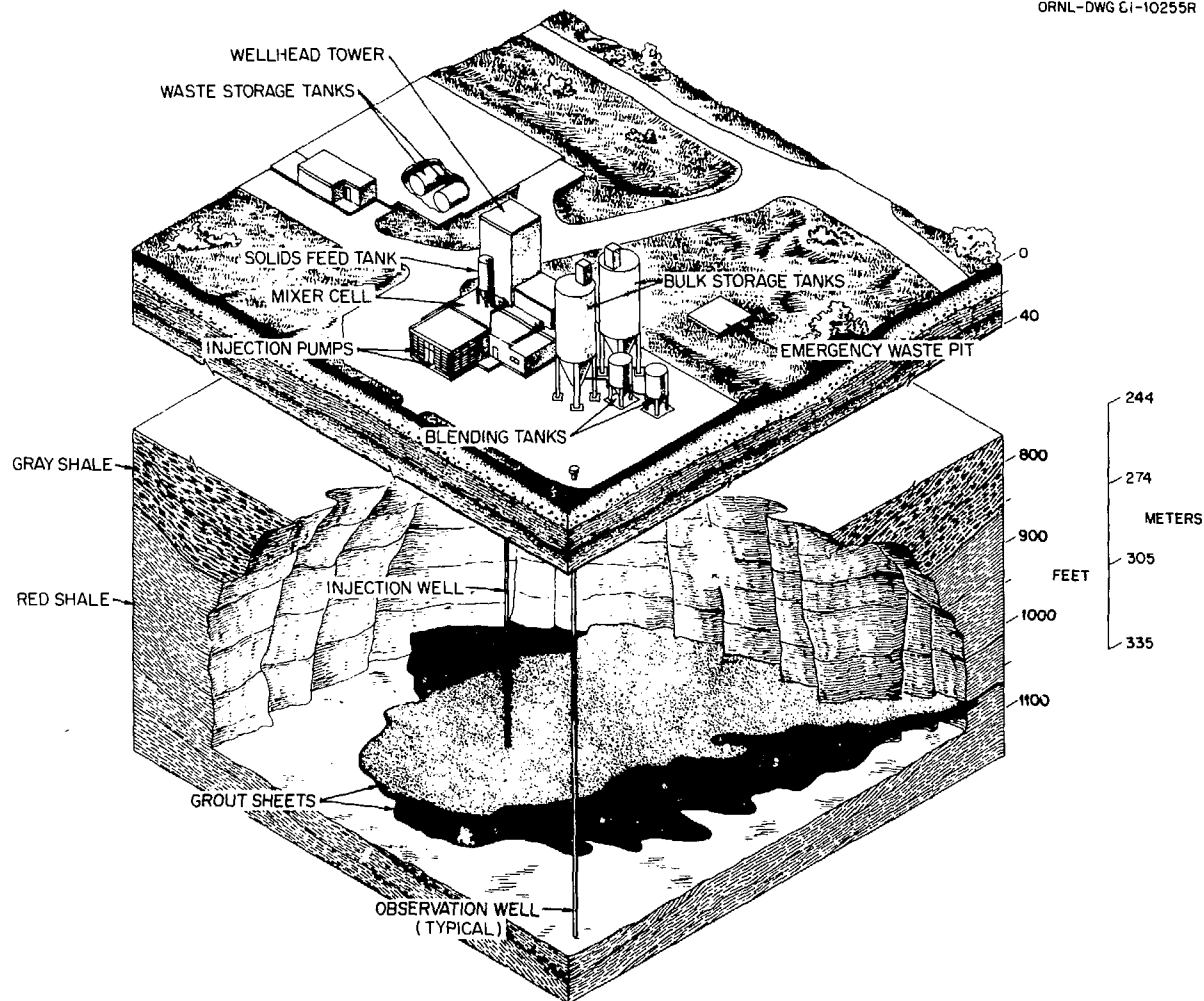


Fig. 1. Hydrofracture Disposal Facility at ORNL.

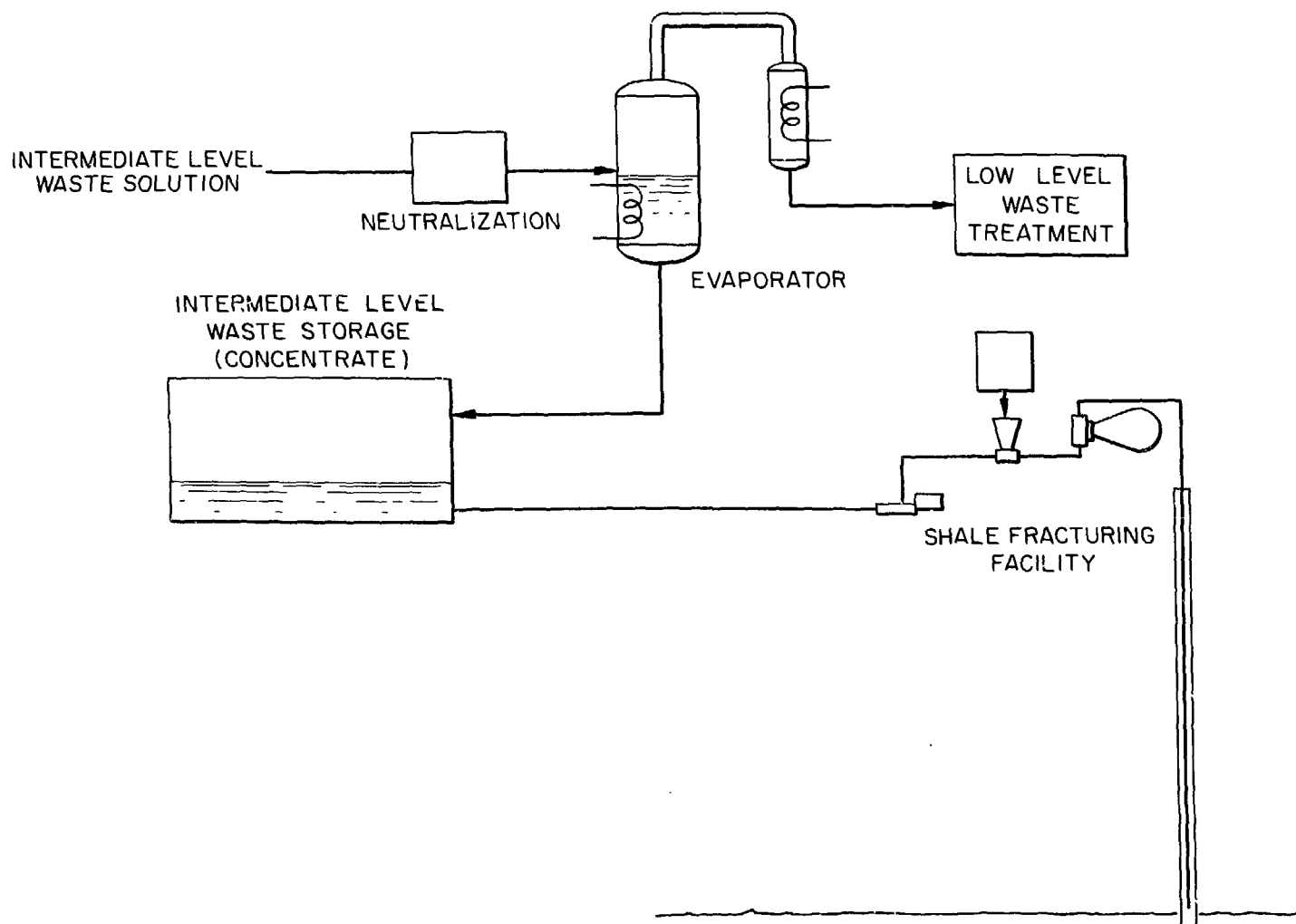
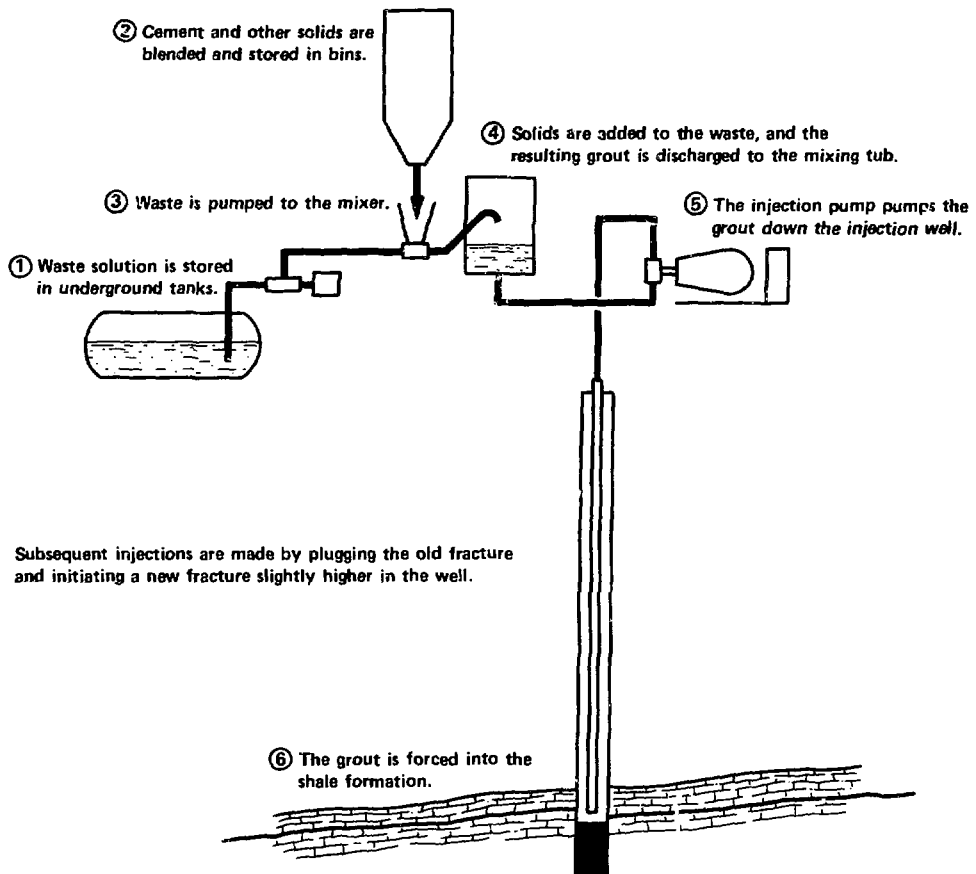


Fig. 2. ORNL Waste Disposal System.



EACH INJECTION IS A LARGE BATCH OPERATION  
THAT REQUIRES ABOUT 10 h TO COMPLETE

Fig. 3. Hydrofracture Process Description.

the injection, the waste solution is pumped to the mixer, continuously mixed with the preblended solids, and then discharged into the surge tank. From the surge tank, the grout is pumped down the tubing string in the injection well and out into the shale formation. The injection pressure is about 20 MPa (3000 psi). The normal grout injection rate is about 1000 L/min (250 gal/min); an injection requires about 8 to 10 h to complete. The grout sheet formed during the injection is approximately 1 cm thick and up to 300 m (1000 ft) wide. The fracture orientation generally follows the bedding planes in the shale, which are inclined about 10 to 15° to the horizontal.

Figure 4 shows a core sample, including part of a grout sheet and the adjacent shale layers. At the end of the injection, the well is flushed with water so that the slot in the injection well will be free of grout and can be reused for the next injection. Then a valve shuts the well until the grout has set. Subsequent injections are made through the same slot, forming grout sheets that are generally parallel to the first. After four injections have been made through the slot, the bottom of the well is plugged and a new slot is cut in the casing of the well 3 m (10 ft) above the old one.

A few days after the injection, the orientation of the grout sheet is determined by logging the network of observation wells that surrounds the facility. (These are cased wells that extend to the bottom of the disposal formation.) A gamma-sensitive probe lowered in these wells detects the presence of the grout sheet at a particular depth, thereby verifying the orientation of the grout sheet. A representative series of logs in one observation well is shown in Fig. 5. The intersections of the grout sheets of each of the two intervening injections can be easily determined. The permeability of the shale overlying the disposal zone is also periodically measured to verify that it has not been increased by the stresses generated by repeated injections. No change in the cover rock permeability has been observed to date.

The hydrofracture concept is attractive largely because the radioactive constituents of the waste solution are immobilized underground when the injected grout sets. For this concept to be realized in practice, the grout must have a number of unusual properties. It must be inexpensive, fluid, and pumpable for several hours, and must retain almost all of the associated water when it sets.

ORNL PHOTO 67950

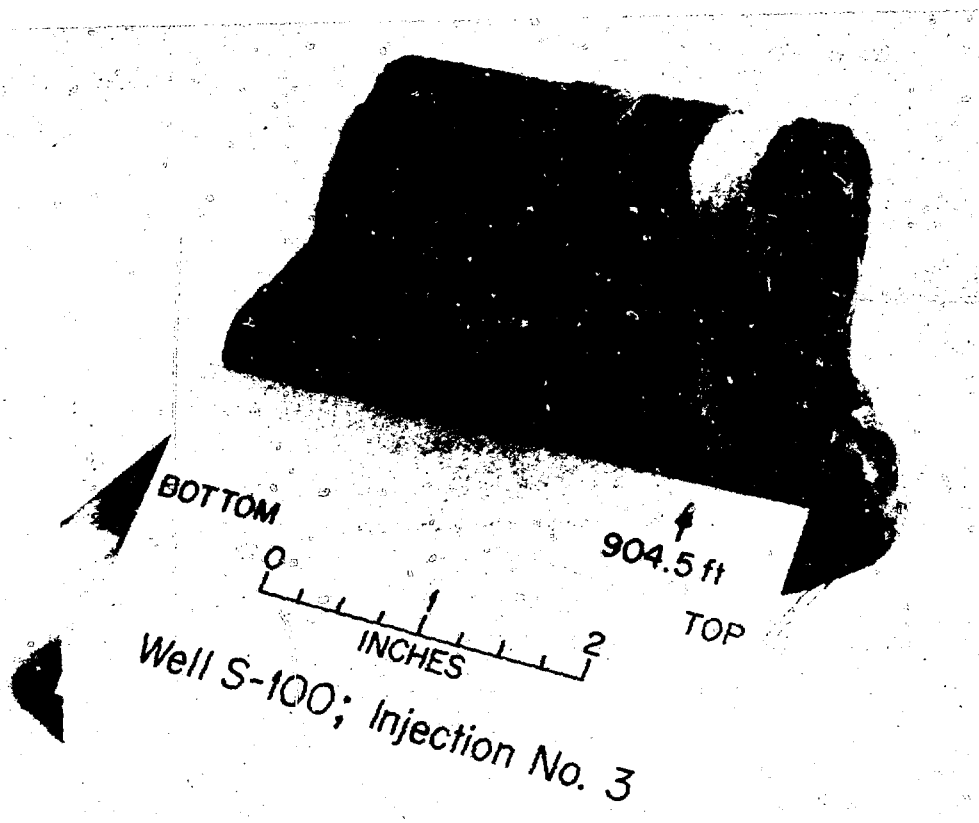


Fig. 4. Cored Sample of Grout Sheet.



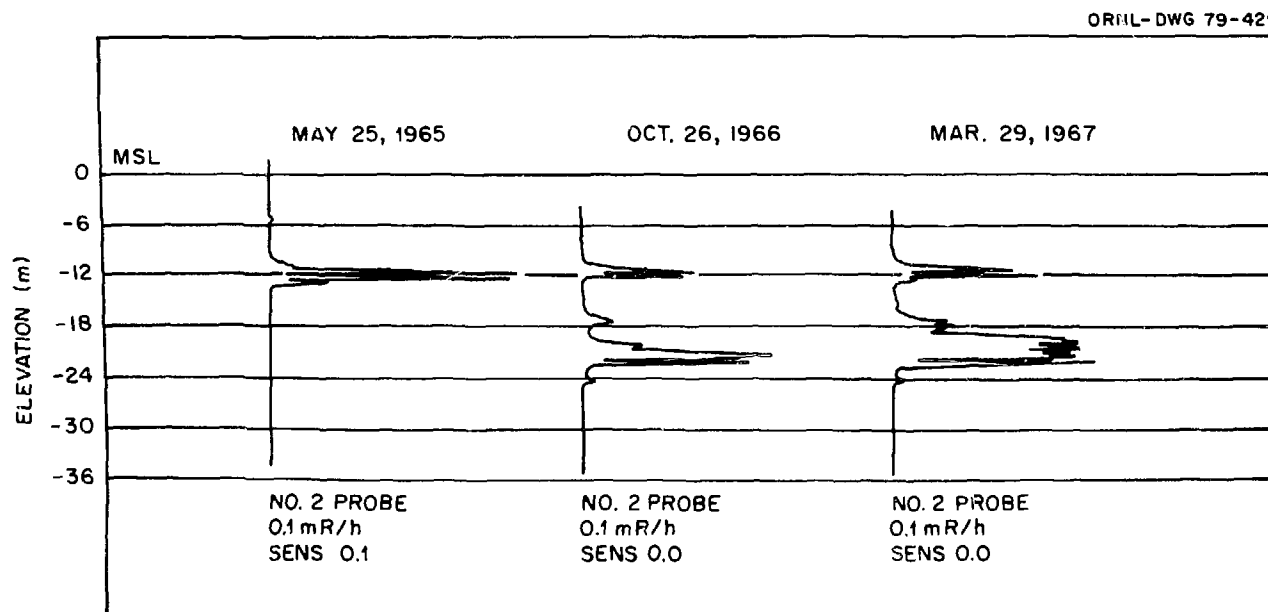


Fig. 5. Successive Logs in Observation Well.

The mix developed for this process consists of Portland cement, fly ash, drilling clay, pottery clay, and a retarder. The retarder delays the setting time of the mix, the pottery clay fixes cesium, the drilling clay retains excess water, the fly ash fixes strontium, and the cement is the overall binder. These various solids are blended shortly before each injection. This blend is subsequently mixed with the waste solution in a ratio of about 0.9 kg of solids per liter of waste solution (7.5 lb/gal). The resulting grout, which has an apparent viscosity of about 40 cP, remains fluid for about 24 h if kept in motion. Leach rates have been determined for four nuclides - cesium, strontium, curium, and plutonium.<sup>1</sup> Figure 6 shows measured leach rates for cesium with various fixers in the grout mix. The strontium leach rate is about the same as the lowest of the cesium leach rates. Curium and plutonium are much lower - about  $10^{-7}$  g/cm<sup>2</sup>·d. For reference, the leach rate for cesium from borosilicate glass is about  $5 \times 10^{-6}$  g/cm<sup>2</sup>·d.

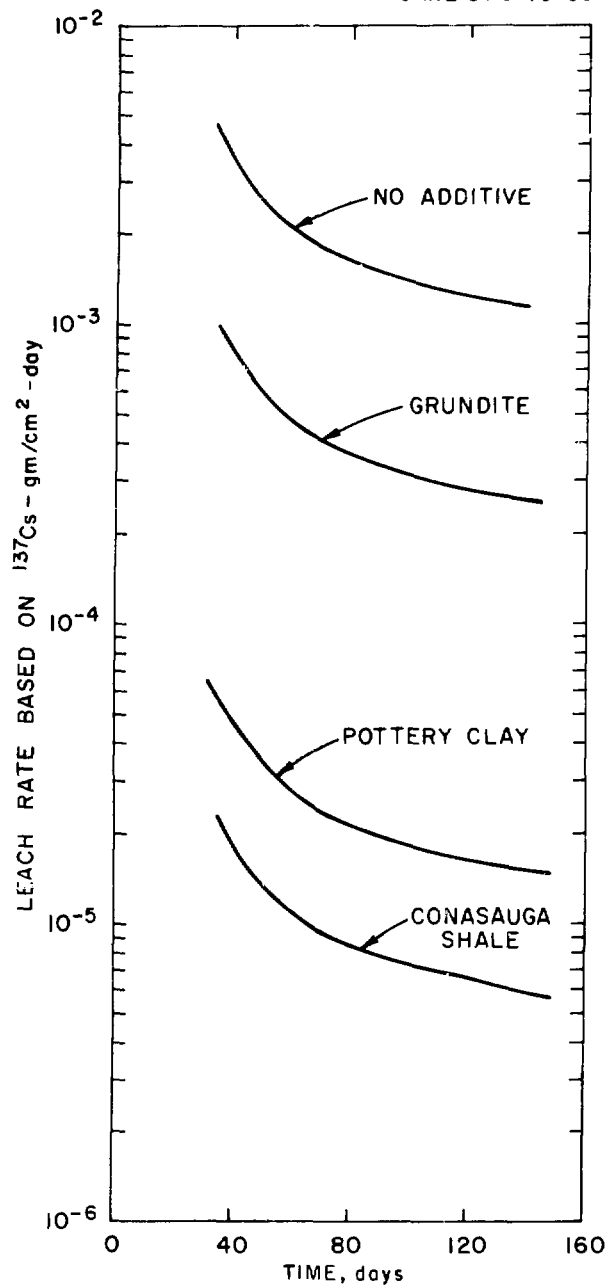
#### HOST ROCK CONSIDERATIONS

The properties of the host rock formations into which the injections are made should be such that the radionuclides will be completely contained for periods of several centuries. The most important of these properties is that the formation should have an extremely low permeability and should be located well away from any zones of circulating water, including both groundwater and underground aquifers. These two requirements will ensure that the radionuclides will not be leached from the grout and returned to the biosphere.

For the hydrofracture process, the orientation of the fracture formed in the host rock during the grout injection is clearly of concern. It is now generally agreed that the orientation of hydraulically induced fractures is controlled primarily by the state of stress in the earth at the point of fracturing. In the absence of other factors, the fracture will always be oriented perpendicular to the direction of the least compressive principal stress.<sup>2,3</sup>

One of the factors other than the state of stress that could have a major effect on fracture orientation is the existence of bedding planes

ORNL-DWG 75-86R1



Leach Rates of  $^{137}\text{Cs}$  From Grouts  
With Various Mix Additives.

Fig. 6. Leach Rates of  $^{137}\text{Cs}$  from Grouts with Various Mix Additives.

in certain rock types. At relatively shallow depths [up to about 400 m (1300 ft)], the fractures will tend to follow bedding planes despite any unfavorable overall earth stress pattern that may exist. This effect is discussed in Reference 4.

The geological formations that underlie the site of the fracturing facility at Oak Ridge were determined to be as shown in Fig. 7. The rock that was selected for the disposal zone for the injected grout is the Pumpkin Valley member of the lower Conasauga shale, which is a bedded shale formation that underlies most of Melton Valley. This formation is about 90 m (300 ft) thick and dips at an angle of about  $10^\circ$  to the south. The top of the disposal zone is a depth of 225 m (745 ft) at the injection well. Above the disposal zone is another zone of bedded shale with properties similar to those of the shales in the disposal zone. Above a depth of 45 m (150 ft), slowly circulating groundwater may be encountered.

The shale in the disposal zone has a permeability of less than  $10^{-5}$  millidarcy.<sup>5</sup> For any reasonable pressure gradient, the flow of groundwater through the shale will necessarily be very slow - of the order of 1 cm per century.<sup>4</sup> The isolation from the surface environment that results from this low permeability of the disposal zone provides long-term containment for the injected wastes. Secondary containment is provided by the high leach resistance of the solidified grout and the high ion exchange capacity for radionuclides of the shale.

The suitability of the bedded shales at Oak Ridge for waste disposal by hydrofracture was established by a number of tests that were made during the development of the process. These tests included:

1. Verification of the presumed subsurface lithography by a series of cores and logs taken from test wells.
2. Verification of the low permeability of the shale in the disposal zone. This permeability was determined (a) for individual core samples by laboratory measurements, (b) for the formation above the disposal zone by measuring the water acceptance rates of the rock core monitoring wells, and (c) for the rock in the disposal zone by measuring the rate of pressure decay after a large-volume water injection.<sup>4</sup>

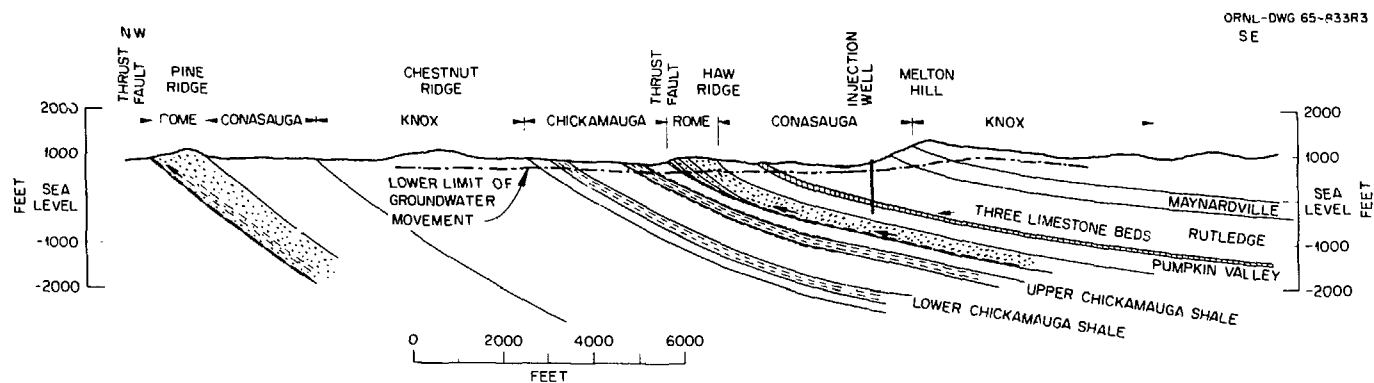


Fig. 7. Geological Formations Near Hydrofracture Site.

3. Verification that horizontal (bedding plane) fractures would be formed by a grout injection. This was done by making a large-volume grout injection with a radioactive tracer and subsequently locating the grout sheet at one or more observation wells.<sup>6</sup>

The potential applicability of the hydrofracture process to other sites was investigated in a series of tests at West Valley, NY, in 1977 and 1978. These tests demonstrated the generation of horizontal fractures in the shale beds at this location and suggested methods for verifying that the process would be suitable for use at other sites.<sup>7</sup>

#### PROCESS HISTORY

The hydrofracture process was developed at ORNL during the period 1959-1965; the experimental facility was modified in 1966 for the routine disposal of waste solutions. Since 1966, this facility has been used for 18 operational injections. More than 8 million L (2 million gal) of waste grout containing over 600,000 Ci of radionuclides have been injected. Although operational problems have been experienced, most have been comparatively minor and none have been severe; the general experience has been quite good. Cleanup of small waste spills has been found to be feasible, as has the direct maintenance of mechanical equipment.

The operational cost of an injection was approximately \$50,000 in about 1978. About \$10,000 of this was the cost of the dry solids, about \$25,000 was the service charge of an oil well cementing company for making the injection, and the remaining \$15,000 was for various maintenance and operations charges. Recent price quotations indicate that current charges will be about \$100,000 per injection.

#### PROJECT STATUS

The original shale fracture facility was built in 1963 to develop and test the process during four experimental injections. Since that time, an additional 3 experimental injections and 18 operational injections have been made and, although the facility has been improved several times, extensive modifications would be needed to satisfy the requirements for

continued use. Two considerations led to the decision to construct a new facility at a new site rather than modifying and retrofitting the old one:

1. The need to replace worn equipment, rebuild the solids handling equipment, and provide new instrumentation.
2. The limited thickness of the disposal formation remaining for future use. (Much of the usable disposal zone underlying the original facility was used for the initial experimental injections. These injections were spaced much farther apart than was subsequently found to be necessary.)

The new hydrofracture facility has been designed and built ~250 m (800 ft) south of the original facility. The disposal zone is about 60 m (200 ft) deeper at this location; otherwise, the geology of the two sites is similar. A site-proof test was made at the new site to verify its suitability for waste disposal by hydrofracture.<sup>5</sup>

An environmental impact statement, written to cover the operations of the facility, concludes that the overall impact would be beneficial.<sup>4</sup> The facility would remove large volumes of potentially hazardous radioactive wastes from the existing surface storage area and would fix these wastes in impermeable shale formations (well removed from the biosphere). All major incidents postulated are considered quite improbable, and the analysis of each case indicates that the ultimate release of radionuclides to the environment would be small.

The new facility will have improved shielding and containment so that wastes of higher specific activity can be handled. These wastes are expected to include currently generated intermediate-level wastes, resuspended sludges that have accumulated in waste storage tanks over the past 35 years, and possibly pilot-plant wastes with a specific activity of up to 8 Ci/L (30 Ci/gal). Although very little of this latter waste is expected, it was made the design-basis waste for the new facility. The operating pressures and flow rates for the new facility are similar to those of the original facility. The dry-solids handling equipment, which has been a source of chronic difficulty in the original facility, has been improved so that the flow of solids to the mixer is smooth and controlled. The process instrumentation has been improved by the incorporation of a weigh-belt feeder to measure the flow of solids more precisely. Improved mix ratio indicators have been installed

to determine and display the ratio of the weight of solids and the volume of liquid going to the mixer, which should help maintain the rather narrow limits required for good process control.

Construction of the new facility has been completed, a preoperating check of all equipment has been made, and the necessary approvals are being obtained. Injection of the first batch of waste is scheduled for June 1982.

The first major operational use of the new hydrofracture facility will be for the disposal of sludge that has precipitated and accumulated in a series of waste storage tanks for nearly 40 years. The approximately 400,000 gal of sludge that is contained in these tanks will be slurried with a water-bentonite suspension, mixed with an appropriate dry mix to form a grout, and injected. About 12 to 15 injections will be required over a period of a little over 2 years.



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## CONTROLLED WASTE OIL BIODEGRADATION AT EXISTING DRYING BEDS

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KEY WORDS: Radioactive, Waste, Oil, Disposal, Biodegradation, Landfarming

ABSTRACT

A feasibility study at the Portsmouth Uranium Enrichment Facility to determine if sludge drying beds at a sewage treatment plant could be used as controlled waste oil biodegradation plots has been completed. A greenhouse-like enclosure would be constructed over three 9.1 meter by 21.3 meter beds to allow for year-round use, and any waste oil runoff would be collected by existing leachate piping. It has been determined that this proposed facility could dispose of existing radioactive waste oil generation (7,200 liters/year) from the Gaseous Diffusion Plant (GDP); however, it would be inadequate to handle radioactive waste oil from the new Gas Centrifuge Enrichment Plant (GCEP) as well. The study reviewed nuclear criticality constraints, biodegradation technology, and the capital cost for an enclosed biodegradation facility.

INTRODUCTION

Past studies have shown that microorganisms occurring in soils will attack petroleum hydrocarbons added to the soil. This process has been used successfully as one method of waste oil disposal at the Portsmouth Gaseous Diffusion Plant for more than seven years. This paper examines a way to improve this disposal technique by enclosing and using existing sludge drying beds. The purpose of such a facility would be to dispose of radionuclide contaminated waste oils from the Gaseous Diffusion Plant (GDP) and the new Gas Centrifuge Enrichment Plant (GCEP). Such a disposal alternative has recently

gained additional importance because most of Portsmouth radioactive waste oils cannot be handled by the planned FY-1983 Compliance with Toxic Substances Control Act Line Item Project Incinerator due to nuclear criticality constraints. The enclosed beds would permit continuous (year-round) waste oil biodegradation, and oil runoff would drain to an existing sump. The existing anaerobic digester sludge drying beds located at the X-615 Sewage Treatment Plant would be used. Use of this facility for sewage treatment will be abandoned around August 1982, when sewage treatment operations will be transferred to a new GDP/GCEP plant. Radioactive waste oil disposal at the sludge beds could present several advantages over alternative disposal methods: no significant additional pollutants would be emitted by the process; disposal would be onsite, thus avoiding expensive transportation costs; administrative controls would assure nuclear criticality safety; and the biodegradation plot could be operated at low cost on a year-round basis.

## DISCUSSION

### Waste Characterization

Radioactive waste oils are generated at various facilities at the GDP; in addition, estimates have been made of the quantities of radioactive waste oil that will be generated at GCEP facilities. A flow diagram of the source and fractional quantities of radionuclide contaminated waste oils from Portsmouth GDP/GCEP facilities is shown in Figure 1. The GCEP quantity estimate is based on the assumption that eight process buildings will be constructed.

Extensive sampling and analysis of GDP waste oils has been conducted to determine the total uranium concentration and the assay of the uranium present in the oil. Knowledge of the U-235 assay is important to the development of a critically safe disposal facility.

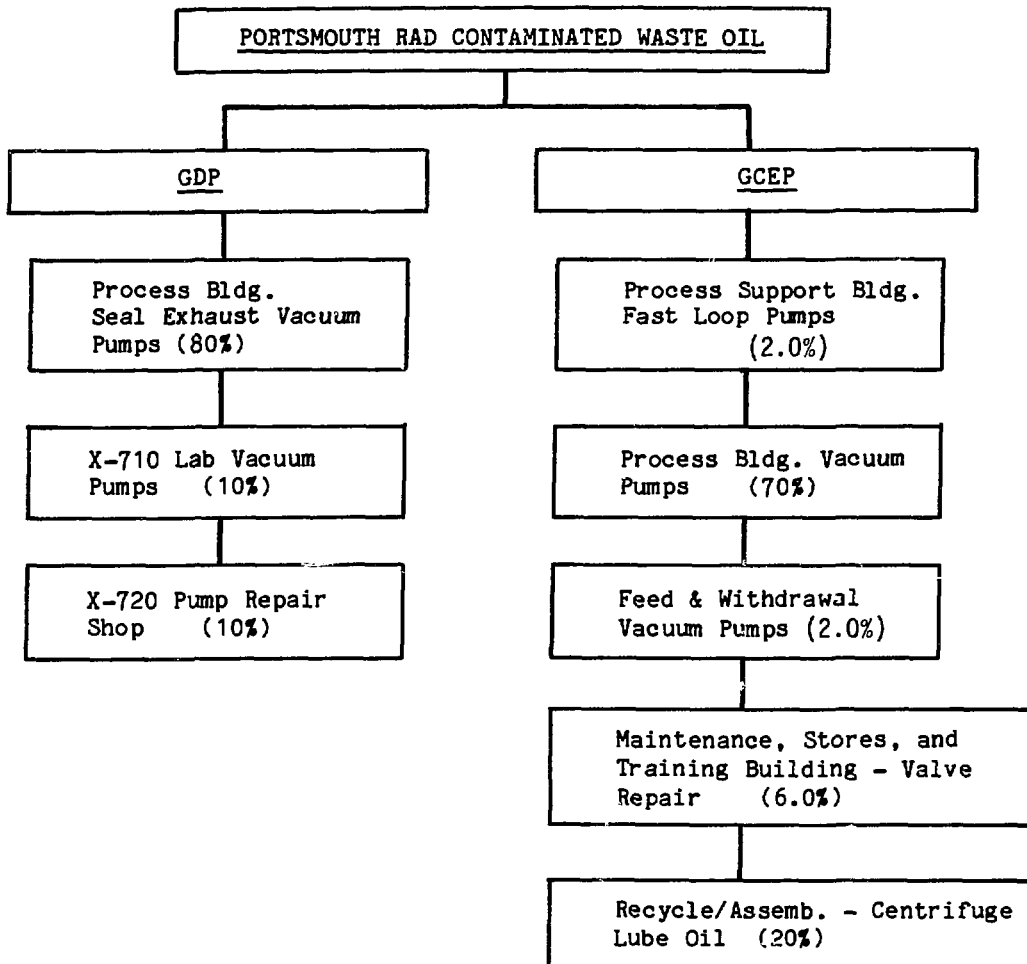


Figure 1 Portsmouth GDP/GCEP Radioactive Waste Oil Sources  
(Fractional volume from each plant is given in parentheses)

A summary of Portsmouth GDP/GCEP radionuclide contaminated waste oil characteristics is presented in Table 1.

Table 1 Waste Oil Characteristics

| <u>Plant</u>                   | <u>Annual<br/>Volume<br/>(l/yr)</u> | <u>Uranium<br/>Concentration<br/>Range<br/>(mg/l)</u> | <u>Average<br/>Uranium<br/>Concentration<br/>(mg/l)</u> | <u>Average<br/>Percent<br/>U-235</u> |
|--------------------------------|-------------------------------------|-------------------------------------------------------|---------------------------------------------------------|--------------------------------------|
| Gaseous Diffusion Plant        |                                     |                                                       |                                                         |                                      |
| drum oil (low assay)           | 4,700                               | 250-10,700                                            | 3,000                                                   | 1.0                                  |
| polybottle oil (high<br>assay) | 14,300                              | 97-43,900                                             | 12,000                                                  | 15.0                                 |
| GDP COMBINED TOTAL             | 19,000                              | -                                                     | 9,750                                                   | 11.5                                 |
| Gas Centrifuge                 |                                     |                                                       |                                                         |                                      |
| Enrichment Plant               | 57,000                              | -                                                     | 10,000                                                  | 1.0                                  |
| Portsmouth Site TOTAL          | 76,000                              |                                                       |                                                         |                                      |

The GDP waste oil generation rate estimate is based on plant operation at full power level (2,260 Mw); the GDP is currently operating at 785 Mw. Presently, the GDP radioactive waste oil generation rate (based on CY-1980 and CY-1981 data) is only 7,200 liters/year due to low power operation. The GDP waste stream has been split into two separate streams due to current nuclear criticality safety practices: 208-liter drums of oil; and 12.7 cm "critically safe" polybottles of oil. Estimates have also been included for GCEP oils. The maximum possible U-235 assay for GCEP oils is 2.85 percent; the average assay is estimated to be 1.0 percent.

#### Current Disposal Practices

Presently, the Portsmouth Gaseous Diffusion Plant either reclaims waste oils by fuller's earth filtration or applies them on open field biodegradation plots. Because radioactively contaminated waste oils cannot be reclaimed by filtration, they are disposed of on the plots. Portsmouth currently uses eight three-meter-wide plots

with an area totaling 1,750 square meters. Soil samples are collected and analyzed every six months to determine fertilizer needs. Oil is evenly sprayed on the plots during the summer months; records concerning the application of oil are maintained. The plots are routinely cultivated to aerate the soil and to promote aerobic decomposition.

#### Proposed Facility Site

An optimum waste oil biodegradation facility would allow for continuous, year-round microbial activity, and would be designed so that the runoff from the plots could be collected and reapplied. One method of developing such a facility would be to use the sludge drying beds at the X-615 Sewage Treatment Plant. Use of the beds would be possible since X-615 will be decommissioned around August 1982. In addition, use would be made of the existing leachate collection system for the beds. The only major modification would be the construction of a heated greenhouse-like enclosure over the beds.

The X-615 is a secondary treatment plant that uses a high-rate trickling filter and post chlorination. A profile of the sewage flow through the plant is shown in Figure 2. The untreated sewage first enters the screening chamber, where large particles of floating or suspended matter are shredded or screened out. Effluent from the screening chamber flows into a primary clarifier, where most of the suspended solids are reduced by sedimentation. The liquid effluent from the primary basin passes to a high-rate trickling filter, where organic matter remaining in the effluent is oxidized. The waste then flows to the secondary clarifier for final sedimentation; secondary clarifier effluent is chlorinated before being discharged to the Scioto River. Sludge from the two clarifiers is placed into a digester where it is decomposed by anaerobic bacterial action at controlled temperature and pH.

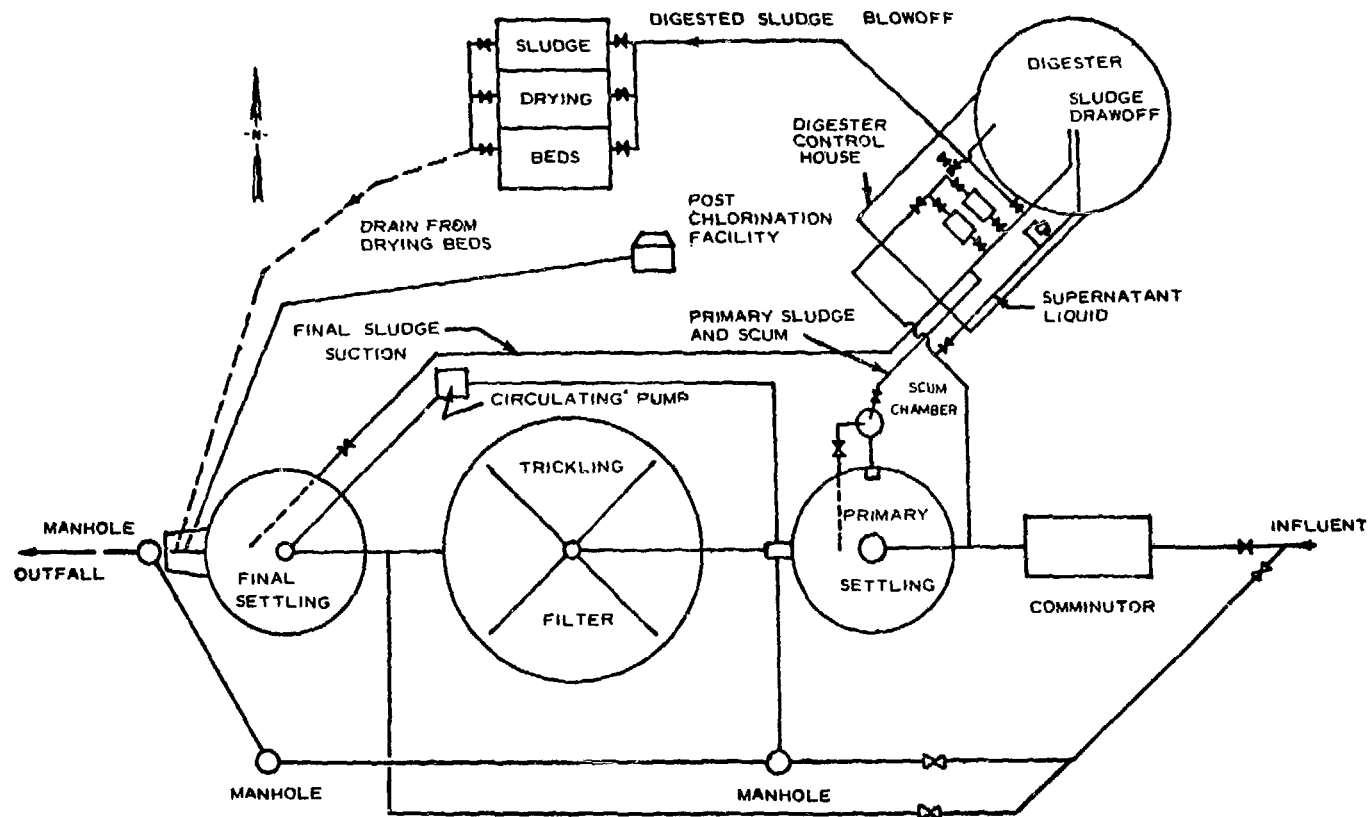


Figure 2 Schematic of the X-615 Sewage Treatment Plant



Once the sludge is digested, it is pumped to one of three 9.1 meter by 21.3 meter sludge drying beds. Sludge is pumped into the beds through a 15.2 cm cast iron pipe. The sludge is dewatered through a 25.4 cm thick bed of sand; runoff is collected by a series of 20.3 cm vitrified tile underdrains. All runoff drains to the outlet box of the secondary clarifier by way of a 20.3 cm vitrified clay pipe. The sludge is retained in the beds by 30 cm high wood planks. The total surface area of the three beds is 585 square meters.<sup>1</sup>

#### Criticality Constraints

Since Portsmouth waste oil contains quantities of enriched uranium, nuclear criticality safety considerations must be taken into account in the design of any disposal facility. The plant has established a comprehensive nuclear safety system to minimize the possibility of a self-supporting nuclear chain reaction. Critically safe masses and geometries have been developed by multiplying the experimental minimum critical mass or geometry by a safety factor. As a result, "individually always-safe" parameters have been calculated. The parameters are applicable to any U-235 assay and are listed in Table 2.

Table 2 "Individually Always-Safe" Parameters

| <u>Parameter</u>                     | <u>Quantity</u> | <u>Approximate Safety Factor</u> |
|--------------------------------------|-----------------|----------------------------------|
| Diameter of infinitely long cylinder | 12.7 cm         | 1.05                             |
| Thickness of infinite area slab      | 3.18 cm         | 1.3                              |
| Volume                               | 4.8 l           | 1.3                              |
| Concentration of U-235               | 5.0 g/l         | 2.3                              |
| Mass of U-235                        | 350 g           | 2.4                              |

These "individually always-safe" parameters must be adhered to since oils with U-235 assays ranging up to 97 percent may be applied on the plot. Deviations from these parameters may be made if extensive administrative controls are used (e.g., waste oil source segregation, U-235 assay determination, disposal of specific waste batches after approvals and disposal constraints are obtained from the nuclear safety group).

The proposed facility's bed (15.2 cm soil layer for oil biodegradation on top of the 25.4 cm sand layer for leachate collection) exceeds the 3.18 cm safe slab parameter. Consequently, administrative controls must be used to assure nuclear criticality safety. The following system is proposed: waste oils from the X-326 Process Building, X-710 Laboratory, and the X-720 Pump Shop would be applied after sampling and the necessary approvals; waste oils from the X-330 Process Building, X-333 Process Building, and GCEP could be applied directly on the plot.

No administrative controls would be required for X-330, X-333, and GCEP oils because the U-235 assay never exceeds five percent and the maximum total uranium concentration found in GDP oil has been 43,900 mg/l. Accordingly, the U-235 concentration in these oils would not exceed 2.2 g/l, which is well below the 5.0 grams U-235 per liter critically safe concentration. Oils originating from areas requiring administrative controls would be sampled and analyzed. Based on the sampling results, the oil would either be applied to the plot directly (if the U-235 concentration is less than 5.0 grams per liter) or applied after special approvals from nuclear safety personnel (if the U-235 concentration exceeds 5.0 grams per liter). Approvals for spreading oil exceeding the safe concentration would be based on the U-235 level in the oil and soil; constraints on the rate, volume, and area of application would be required.<sup>2</sup>

## Biodegradation Technology

A natural function of microorganisms abundant in soil is to decompose nitrogenous and carbonaceous materials into microbial cellular matter. Side products of gases and partially reacted organics are formed. When oil or hydrocarbons are the only source of carbon, oil degrading microorganisms survive and become the predominant species. Experimental tests have indicated that oil wastes can be biologically decomposed when the top 15.2 cm of the soil is cultivated periodically. Cultivation is necessary to promote aerobic conditions for maximum microbial response.

Waste oil decomposition rates of 16.0 to 24.0 kg waste oil/m<sup>3</sup> of soil per month have been reported. These rates were determined during open field, warm weather degradation experiments, with fertilizers being added to enrich the soil with nitrogen and phosphates. The 24.0 kg waste oil/m<sup>3</sup> of soil per month decomposition rate was calculated as a result of tests conducted at the Y-12 facility from May to September, 1973. This decomposition rate was used to evaluate the proposed enclosed biodegradation facility.<sup>3, 4</sup>

Past studies have shown that open field biodegradation sites are susceptible to the elements. The optimum temperature for the incubation of most hydrocarbon-oxidizing organisms has been reported to be 30°C.<sup>5</sup> Biodegradation rates have been reported to be consistently lower during winter months and periods of high precipitation. Temperature appears to have no affect on microbial count and distribution; however, microbial activity drops significantly at lower temperatures. Test plots have demonstrated that surface runoff from open field sites is an environmental problem; one series of tests reported oil and grease runoff concentrations of 30 to 100 mg/l.<sup>3</sup>

COST

The capital cost, in FY-1982 dollars, to enclose the X-615 sludge drying beds has been estimated. This cost includes providing a 22.9 meter by 29.0 meter truss frame greenhouse with clear plateglass (Figure 3). The facility would be heated and modifications would be made to the existing leachate collection piping. A breakdown of the cost estimate is shown in Table 3.

Table 3 Cost of Modifying X-615 (FY-1982 Dollars)

|                           | TOTAL<br>MATERIAL | TOTAL<br>LABOR  | TOTALS        |
|---------------------------|-------------------|-----------------|---------------|
| 1. Greenhouse             | 123,700           | 99,500          | 223,200       |
| 2. Glass                  | 50,300            | 15,200          | 65,500        |
| 3. Heating Equipment      | 46,900            | 30,500          | 77,400        |
| 4. Demolition             | -                 | 2,300           | 2,300         |
| 5. Earthwork & Foundation | -                 | 9,700           | 9,700         |
|                           |                   | -----           |               |
|                           |                   | Total           | 378,100       |
|                           |                   | Engineering     | 30,000        |
|                           |                   | 20% Contingency | <u>81,600</u> |
|                           |                   | FINAL TOTAL     | 490,000       |

RESULTS

Based on past waste oil biodegradation studies, and on an evaluation of the X-615 sludge drying beds, it is feasible to biodegrade radionuclide contaminated waste oils at Portsmouth on a year round basis. Figure 4 shows how the underground leachate collection piping would be modified at the existing facility. The 15.2 cm cast iron sludge conveyance piping to the beds would be abandoned, and the 20.3 cm vitrified clay collection piping would discharge to an existing manhole. This manhole would be converted to

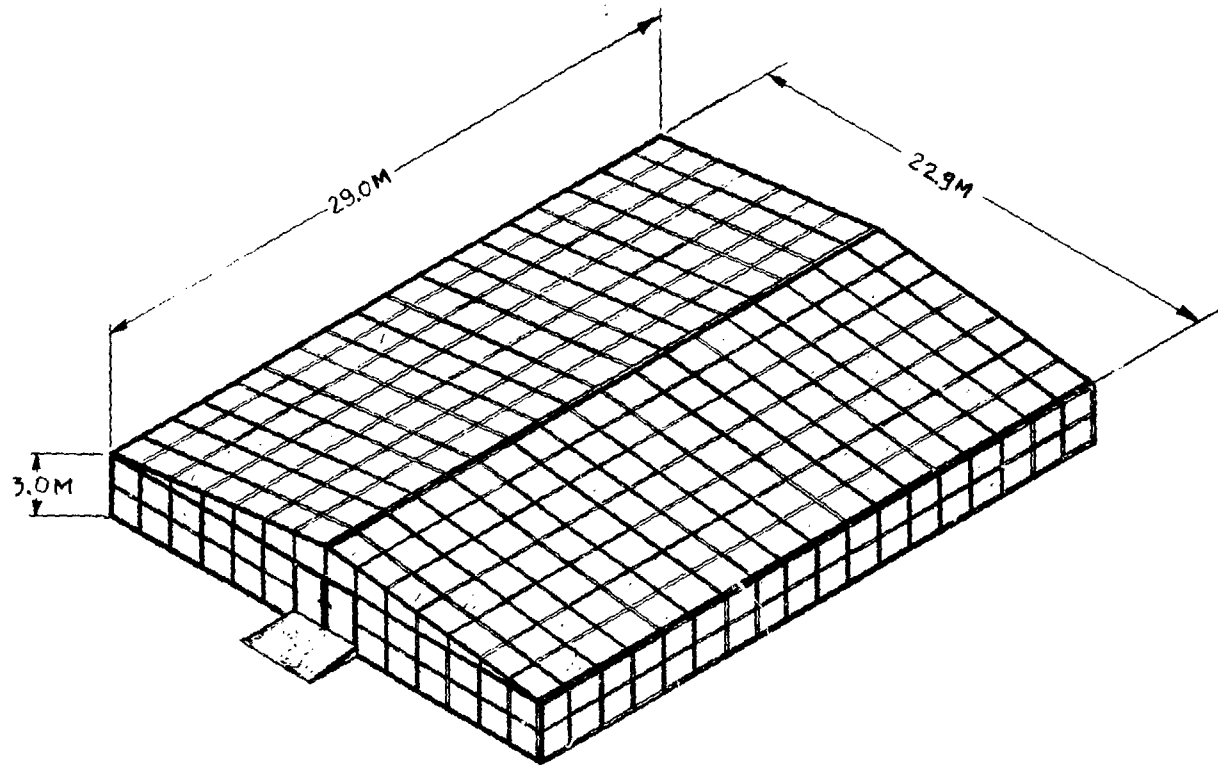


Figure 3 Proposed Biodegradation Facility

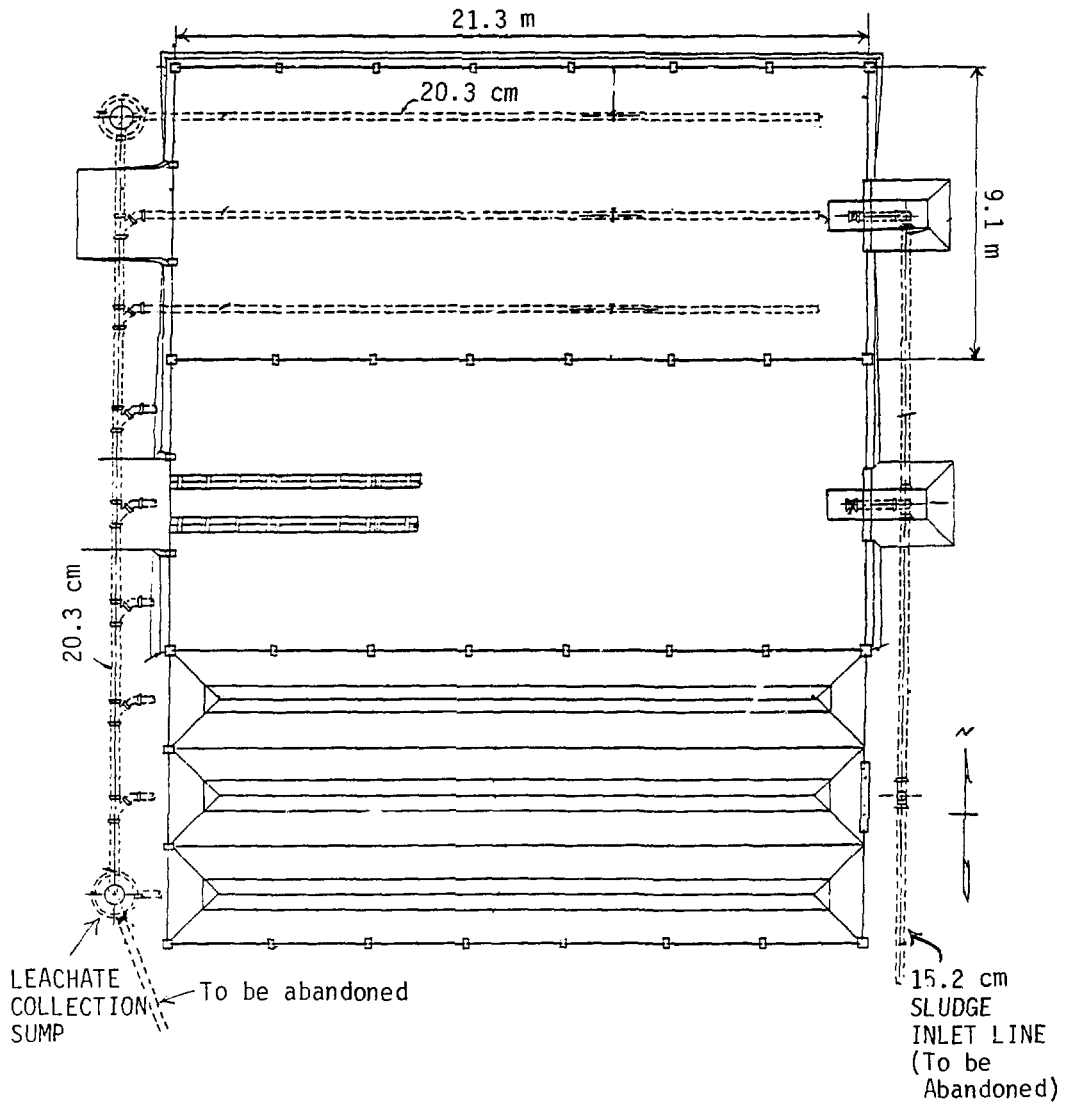


**Figure 4 Modifications of the Underground Leachate Collection Piping at Existing X-615 Sewage Treatment Plant**

a critically safe sump and the remaining discharge piping to the outlet of the secondary clarifier would be abandoned. The total degradation bed (21.3 m long x 27.4 m wide x 0.15 m deep) would have a volume of  $87.54 \text{ m}^3$ . Accordingly a total of 28,800 liters per year could be disposed of if a rate of  $24.0 \text{ kg waste oil/m}^3$  of soil per month is assumed.

### CONCLUSIONS

As previously stated, it is feasible to modify an existing Portsmouth waste treatment facility for biodegradation of radionuclide contaminated waste oils. There are a number of distinct advantages in controlled biodegradation. However, many of these could be outweighed by certain disadvantages and currently unidentifiable factors (Table 4).

Table 4 Advantages and Disadvantages/Unknowns

| <u>Advantages</u>                                | <u>Disadvantages/Unknowns</u>                                       |
|--------------------------------------------------|---------------------------------------------------------------------|
| Could handle current waste oil generation rates. | Could not handle estimated GCEP generation rates.                   |
| No significant pollutant streams.                | Soil disposal (burial) is complex and costly.                       |
| Low operating costs.                             | High capital cost.                                                  |
| Use of existing resource (sludge drying beds).   | Soil changeout rate due to uranium/heavy metals buildup is unknown. |

Table 4 shows that the conversion of the X-615 sludge drying beds is not a comprehensive solution to expected generation rates of radionuclide contaminated waste oils. However, it has the potential of being part of an overall radionuclide contaminated waste oil disposal system for the Portsmouth uranium enrichment complex.

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TR-022482-WTB



*Session 7: COST BENEFIT ANALYSIS*  
*Chairperson: J. F. Wing*

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## COST/BENEFIT ANALYSIS - ENVIRONMENTAL PROTECTION PROJECTS

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## Abstract

A review of cost/benefit analysis techniques and determinations of applications to environmental protection projects will be given. Incorporated in this discussion will be techniques for risk assessments which include the risk of not doing a project versus doing a project.

In the cost benefit approach, capital and operating cost will be included on the cost side. Cost savings, reduction in environmental impact, recovery of valuable constituents, public perception, and corrections of noncompliances will be on the benefit side.

Flow diagrams of the various steps in this type of analysis will be presented.

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

EVALUATION OF ALTERNATIVES FOR TREATMENT OF PGDP  
STEAM PLANT FLY ASH

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operated by  
UNION CARBIDE CORPORATION

for the  
U.S. DEPARTMENT OF ENERGY  
Under Contract No. W-7406-eng-26

Key Words: Fly Ash, Uranium, Material Balance, Treatment  
Options

ABSTRACT

The PGDP steam plant has two coal fired boilers. Ash from the boilers is vacuum fed into primary and secondary cyclones. The steam used in creating the vacuum for transfer of the fly ash is currently used in an air washer to scrub out residual fly ash particles entrained in the air. Potential problems created by the heavy solids loading of the fly ash slurry discharge necessitate the treatment of that solution or treatment of the fly ash particles exhausted from the secondary cyclone prior to the air washer. A material balance of the fly ash was developed and as a logical outgrowth of that study, a uranium in coal and fly ash material balance was completed. The definition of these problems, their impact, and an evaluation of viable alternatives will be presented.

### INTRODUCTION

Fly ash treatment studies were implemented to ascertain if the solids loading of the C-600 Steam Plant fly ash discharge could be reduced to meet the NPDES guideline of 30 ppm suspended solids (daily average) if required. The fly ash is withdrawn from six points for each of the two coal fired boilers at the PGDP. Three withdrawal points are at the electrostatic precipitators serving that boiler with the remaining three points being the bottom ash hopper and the rear pass hoppers of each boiler. The ash from these withdrawal points is vacuum fed into the primary and secondary cyclones which allow the ash to fall into the silo and air from the vacuum is exhausted. The steam used in creating the vacuum for transfer of the fly ash is used in the air washer to scrub out the residual fly ash particles entrained in the air.

The fly ash discharge presently flows from the air washer to the C-600 sump where it is pumped to the diversion ditch and from there to the C-616 full flow lagoon. Two other sources of full flow lagoon influent are from the C-616 clarifier effluent, an NPDES monitoring point, and the sludge lagoon overflow. The full flow lagoon effluent is discharged to the Big Bayou Creek. Analyses of suspended solids indicate that an average of 801 lb/day of solids are sent to the full flow lagoon from the diversion ditch. The average slurry solution discharge is 994 lb/day of solids with 193 lb/day being deposited in the diversion ditch. The overflow from the clarifier feeds in 22 lb/day of solids and the sludge lagoon overflow contributes a negligible

amount 5 lb/day. The effluent discharge is 34 lb/day retaining a total of 789 lb/day of solids in the full flow lagoon. If a solids reduction program were implemented, it would lower the frequency of diversion ditch dredging, reduce solids accumulation in the C-616 Full Flow Lagoon, and provide a longer service life for the new clarifier provided in the 1980 LIP Control of Water Pollution.

As a logical out growth of work performed on fly ash slurry treatment for the 1981 LIP Environmental Protection and Safety Modifications, a determination of a uranium in coal material balance was made. Equally important was the need to establish the amount of uranium in the particulate emissions from the C-600 stacks in anticipation of closer accountability of environmental standards for airborne emissions.

The treatment of the C-600 fly ash discharge has been examined and evaluated by comparison of three options: (1) chemical treatment of the liquid discharge subsequent to the existing air washer, (2) treatment of entrained particles in the exit gas prior to the air washer, and (3) addition of a settling basin for the air washer discharge requiring no chemical treatment. These three methods are described in this report, and the conclusion denotes the comparison of the operations.

## EXPERIMENTAL

### I. Fly Ash Slurry Treatment Options

#### 1. Chemical Treatment of the Fly Ash Discharge

Vendors were contacted regarding equipment designed for liquid solid separation and compatible with the parameters of the C-600 air washer discharge. Physical separation by particle size, centrifugal separation, and clarifier and multimedia filtration were considered but were deemed less effective than a chemical method of treatment with a settling system. The Lamella Gravity Settler™ was ascertained to be the most effective and cost competitive system evaluated.

In order to determine the most applicable chemical treatment to enhance the settling of the fly ash discharge, vendors of many different polymers were contacted and samples obtained. Flocculation studies of 30 polymers (300 tests) were conducted and evaluated to determine the type and dosage rate to provide optimum removal of suspended solids (ss).

To gain the maximum efficiency of the polymers, a determined dosage of 210 ppm lime was added to each sample to act as a coagulant aid prior to the polymer addition. Each polymer sample was tested at concentrations of 1, 5, 10, 15, 20, and 30 ppm. The solutions were stirred for one minute at 100 rpm, two minutes at 45 rpm, followed by a five minute settling period. The turbidities of the solutions were read and used to

interpolate the ss which were the determining factors in the evaluation, since there are presently no NPDES guidelines for turbidity limits.

After retesting the most effective of the polymers, the performance of American Cyanamid's Magnifloc 834A was determined to be not only the most beneficial in ss removal at a low-dosage rate (1.0 ppm) but also the most economical.

Additional investigation of the Lamella Settler revealed two potentially significant problems: (1) a large volume of sludge (889 ft<sup>3</sup> of 20% solids by weight)\* would be produced weekly creating disposal difficulties, and (2) the variability of coal's ionic characteristics could frequently cause poor or ineffective operation of the polymer feed used in the removal of suspended solids. The large volume of sludge obtained (889 ft<sup>3</sup>/week) would require a dewatering step prior to deposition of the sludge at the landfill. It would also necessitate the installation of a tank to contain the sludge preceding the dewatering step. Several processes for dewatering are available. Among these are filter presses, rotary drum vacuum

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\*The average slurry solids is 178 ft<sup>3</sup> per week, dry weight. The maximum Lamella Settler sludge production is 20% solids by weight; therefore, the total sludge volume per week would be 889 ft<sup>3</sup>.

filtration systems, centrifuges and belt filters. To alleviate these potential problems, a treatment scheme of air filtration prior to the air washer equipment was investigated.

## 2. Gaseous Treatment of Entrained Fly Ash Particles

Vendor literature was obtained pertaining to fabric type bag house filters for particulate removal of fly ash. This method of dry solids collection appears to be highly efficient and economical. The bag house would be placed upstream of the air washer vacuum jet. Particulates from the secondary separator would enter the bag filters removing practically all (99.9%) of the fly ash particles. The cleansed air would pass through the existing air washer while the solids collected in the bag house would discharge into the ash silo for normal disposal.

Bag house filter processes do not require the addition of chemicals and could provide 99.9% efficiency even at sub-micron (0.5 micron) particle sizes. Fly ash from C-600 ranges from 3 to 4 microns in particle size. The 9,282 ft<sup>3</sup>/year of dry solids produced from the present slurry discharge would require no additional cost for handling, other than occasional bag replacement, since the bag house filters would ideally empty directly into the ash silo, thereby eliminating sludge disposal problems.



The temperature range of the ash conveying gas dictates the type of filter fabric to be used for optimum filtering efficiency. Testing of the gas temperature in the primary separator at C-600 during the actual transfer of the fly ash to the scrubber system ascertained the maximum temperature of the exit gas to be 45°C (113°F) which is well below the recommended operating temperatures (170°F to 550°F) for filter fabrics.

### 3. Settling Basin Addition .

The usage of a pair of small settling basins would provide a solids reduction; however, without lime and polymer addition, the retention time would be 32 hours. This retention time is without any addition of other slurry solutions during the test period. The air washer slurry solution is normally discharged twice a shift, thereby significantly increasing the retention time required. The settling basin could receive coal pile runoff if placed adjacent to the ash silo where the slurry discharge piping is located. Periodic dredging of the basin and proper disposal of the sludge will be required if the settling basin addition is chosen as the treatment method.

## EXPERIMENTAL

### II. Uranium in Coal Material Balance for the Steam Plant

In order to implement a complete uranium material balance program, all sources for uranium discharges or emissions at

C-600 initially had to be identified, followed by development of procedures for sampling and analysis. At the completion of testing, the uranium total of the discharges would be compared to the total uranium input from the coal. Each of these steps is discussed in greater detail below.

#### 1. Identification of Uranium Discharges or Emissions

Ashes from the C-600 coal boilers are vacuum fed in a common line to the primary and secondary cyclone separators located atop the ash silo where the bulk of the ash is removed from the conveying air, falling into the ash silo. The uncollected ash particles pass through an induced draft air washer which condenses steam and washes the conveying air discharge of the steam jet exhauster, removing residual fly ash particles. This ash collection system provides two sampling points - the ash silo and the air washer slurry discharge. In addition, previous data<sup>1</sup> certified results of tests regarding particulate emissions from the C-600 stacks.

#### 2. Sampling Procedures

In addition to the two previously mentioned ash sampling points (ash silo and slurry discharge), a weekly sample of coal was analyzed to determine the total uranium input for the material balance. This sample was obtained from the C-600 pulverizer prior to being fed into the boilers.

Ash is normally removed from the silo two to three times weekly. Garage personnel weighed the ash in each truckload four

to six times per week for 12 weeks in order to give more accurate data for calculations of ash removed. (See Appendix for data listing.) A grab sample was obtained weekly upon deposition of the ash at the disposal site.

The air washer discharge containing the residual fly ash particles was sampled weekly upstream of the C-600 sump at a manhole located near the C-602 coal pile. The slurry is discharged two times per shift and the sample was collected during the discharge time so that no other discharges from the C-600 area were combined to affect the slurry.

A particulate matter emission test was conducted on the C-600 stacks by Burns and McDonnell Engineering Company. Testing procedures and results are recorded in detail in the Precipitation Performance Test Report May 1979. The average volume of the ash emitted per  $10^6$  BTUs generated was obtained from the report (0.068 lb ash/ $10^6$  BTUs) to determine the stack emissions of fly ash and uranium.

### 3. Analysis of Samples

Each of the three weekly samples (ash, air washer slurry, and coal) was sent to the Wet Chemistry Lab for uranium analysis. The coal and ash sample results were recorded on a ppm uranium, dry basis. In addition, the coal was tested for percent air dried moisture and the ash for percent oven dried moisture. The slurry discharges were analyzed for uranium in

the liquid and solid fraction plus grams of solids per liter, dry basis.

#### 4. Evaluation and Comparison of Data

##### a. Air Washer Slurry Discharge

The air washer discharges six times per day with an average flow of 56,700 gpw. The solid's loading ranged from 1057 ppm to 4491 ppm. Laboratory analyses indicated a range from 9 ppm to 12 ppm uranium, dry solids, which when calculated using the weekly grams of solids per liter and average flow rate of discharge per week resulted in totals of 3.0 g to 126.5 g uranium per week. (See Appendix for data listing.)

##### b. Fly Ash

The weight of the fly ash ranged from 109,830 lb to 247,478 lb per week. The laboratory analyses of 9 ppm to 16 ppm uranium (dry basis) were used with the percent oven dried moisture and total lb ash per week to calculate the total grams uranium per week which varied from 370.6 g to 945.5 g. (See Appendix for data listing.)

##### c. Coal

The total input of uranium from the coal was calculated weekly using the uranium analysis of the coal, which varied from 0.58 ppm to 1.60 ppm, the percent of air dried moisture, and the weekly coal usage. The weekly coal usage

reports were supplied by the Power, Utilities and Chemical Operations Division. The calculation of the total coal used includes an assumption of 83% coal plant efficiency. No actual coal weighing facilities are in use at C-600. The total uranium input varied from 381.6 g to 1385.0 g weekly. (See Appendix for data listing.)

d. Stack Emissions

The Precipitation Performance Test Report of May 1979 established an average emission of particulates from the stacks (units 2 and 3) to be 0.068 lb ash/ $10^6$  BTUs. The weekly Coal Usage Report supplied by Power, Utilities and Chemical Operations personnel reported the BTUs per pound of coal which when used in calculations with the above figure and the weekly coal usage resulted in a determination of the total grams uranium emitted from the stacks weekly. This total varies from 4.4 g to 10.8 g. (See Appendix for data listing.)

## CONCLUSIONS

### I. Fly Ash Slurry Treatment Options

From data generated, it has been established that 9,282 ft<sup>3</sup> per year of solids (primarily fly ash) are discharged to the North/South Diversion Ditch and ultimately to the C-616 Full Flow Lagoon from the C-600 air washer discharge. This paper discloses the evaluation of three methods of fly ash particulate removal: (1) A liquid treatment scheme which would involve the use of a Lamella Gravity Settler and require chemical treatment of the slurry with lime and polymer for optimum solid's settling; (2) A dry treatment scheme of air filtration which would require the installation of a bag house prior to the air washer. The bag house option provides significant advantages in that it would eliminate not only the heavy solid's loading to the diversion ditch and the full flow lagoon, but also any potential sludge problems associated with liquid treatment of the slurry discharge; (3) The settling basin option showed similar solid's dredging requirements as now practiced in the diversion ditch. In addition, extensive solid's settling time and scouring of the basin are possible problems. The three options are compared in Table I.

### II. Uranium in Coal Material Balance for the Steam Plant

Analysis and evaluation of all slurry samples for uranium content revealed that the liquid portion of the discharge had a

TABLE 1

## Comparison of Alternatives

| <u>Liquid Treatment</u>                                                    | <u>Bag House</u>         | <u>Settling basin</u>                                  |
|----------------------------------------------------------------------------|--------------------------|--------------------------------------------------------|
| 1. Lime and polymer addition requiring operational controls                | 1. Bags must be replaced | 1. Large land area required                            |
| 2. Sludge disposal required                                                |                          | 2. Dredging required for solids disposal               |
| 3. Dewatering necessary prior to landfilling                               |                          | 3. Settling time is extended without chemical addition |
| 4. Variability of coal's ionic characteristics affects system's efficiency |                          | 4. High influent flow may scour settling basin         |

less than detectable amount of uranium while the solids accounted for 0.1 lb uranium per week. Further evaluation of data established that 93% of the total output of uranium from the C-600 Steam Plant can be assigned to the fly ash, 6% to the slurry, and 1% to the stack emissions. Corresponding to these figures, 1.42 lb uranium per week is attributable to the ash, 0.10 lb uranium per week for the slurry and 0.01 lb uranium per week to the stack emissions. This data is shown in Table 2 which also includes the volume of solid waste produced from each source and the cumulative effect of continued discharge to the full flow lagoon.



TABLE 2

Uranium Material Balance, C-600  
Experiment Began 9-14-80 (Week 1), Continued through 1-4-81 (Week 17)

| Average                             | Output  |        |         | Input  |
|-------------------------------------|---------|--------|---------|--------|
|                                     | Fly Ash | Slurry | Stack   | Coal   |
| Lb Uranium week                     | 1.42    | 0.10   | 0.10    | 1.27   |
| % of total output for each emission | 93      | 6      | 1       | 100    |
| *Volume - ft <sup>3</sup> /week     | 4,313   | 178    | 32.1    |        |
| Volume - ft <sup>3</sup> /year      | 229,479 | 9,282  | 1,669.2 |        |
| Cumulative Effect                   |         |        |         |        |
| Uranium discharge lb/year, 1981     | 73.8    | 5.2    | 0.52    | 56.04  |
| Uranium discharge lb/year, 1982     | 147.7   | 10.4   | 1.04    | 132.08 |
| Uranium discharge lb/year, 1983     | 221.5   | 15.6   | 1.56    | 198.12 |

\*Total lb fly ash/week (average) = 169,648. Density of ash (average as received) = 10.1 g/cu in.

# APPENDIX

## Material Balance Data Sheet for C-600 Steam Plant

| Week    | Date     | Sample Number | Coal Feed (Dry Basis) | PPM Uranium Fly Ash (Dry Basis) | Air Washer Slurry (Solids) | Volume of Coal (t) | Volume of Fly Ash (lbs) | Volume of Air Washer Slurry (gpw ave.) |
|---------|----------|---------------|-----------------------|---------------------------------|----------------------------|--------------------|-------------------------|----------------------------------------|
| Week 1  | 9-14-80  | 1             | 0.71                  | 9                               | 21                         | 656                | --                      | 56,700                                 |
| Week 2  | 9-21-80  | 2             | 0.89                  | 11                              | 21                         | 653                | 170,920                 | 56,700                                 |
| Week 3  | 9-28-80  | 3             | 0.87                  | 14                              | 19                         | 677                | 171,520                 | 56,700                                 |
| Week 4  | 10-05-80 | 4             | 0.90                  | 16                              | 12                         | 730                | 166,250                 | 56,700                                 |
| Week 5  | 10-12-80 | 5             | 0.73                  | 9                               | 14                         | 722                | 170,910                 | 56,700                                 |
| Week 6  | 10-19-80 | 6             | 0.58                  | 14                              | 14                         | 738                | 176,820                 | 56,700                                 |
| Week 7  | 10-26-80 | 7             | 0.70                  | 15                              | 11                         | 794                | 179,580                 | 56,700                                 |
| Week 8  | 11-02-80 | 8             | 0.79                  | 9                               | 14                         | 764                | 160,620                 | 56,700                                 |
| Week 9  | 11-09-80 | 9             | 0.86                  | 11                              | 11                         | 686                | 168,840                 | 56,700                                 |
| Week 10 | 11-16-80 | 10            | 1.10                  | 11                              | 16                         | 629                | 151,230                 | 56,700                                 |
| Week 11 | 11-23-80 | 11            | 1.00                  | 10                              | 12                         | 637                | 109,830                 | 56,700                                 |
| Week 12 | 11-30-80 | 12            | 0.76                  | 11                              | 9                          | 623                | 179,230                 | 56,700                                 |
| Week 13 | 12-07-80 | 13            | 0.90                  | 10                              | 10                         | 545                | 158,380                 | 56,700                                 |
| Week 14 | 12-14-80 | 14            | 0.80                  | 9                               | 15                         | 664                | *151,916                | 56,700                                 |
| Week 15 | 12-21-80 | 15            | 0.94                  | 10                              | 19                         | 973                | *161,317                | 56,700                                 |
| Week 16 | 12-28-80 | 16            | 1.50                  | 11                              | 14                         | 702                | *247,478                | 56,700                                 |
| Week 17 | 01-04-81 | 17            | 1.60                  | 14                              | 15                         | 1,012              | *189,524                | 56,700                                 |
| Average |          |               | 0.92                  | 11.4                            | 14.5                       | 717.9              | 169,698                 |                                        |

\*Values calculated from previous data line equation.

# APPENDIX

## Material Balance Data Sheet for C-600 Steam Plant

| Week    | Amount of U in<br>Input Coal<br>(g) | Amount of U in<br>Fly Ash Disposal<br>(g) | Amount of U in<br>Air Washer<br>Disposal (g) | Amount of U in<br>Outlet Via the<br>Stack (g) | Total<br>Emission<br>(g) |
|---------|-------------------------------------|-------------------------------------------|----------------------------------------------|-----------------------------------------------|--------------------------|
| Week 1  | 414.8                               | --                                        | 82.4                                         | 4.7                                           | --                       |
| Week 2  | 500.7                               | 616.5 (92%)                               | 44.7 (6%)                                    | 5.9 (1%)                                      | 667.1                    |
| Week 3  | 511.5                               | 768.8 (97%)                               | 12.8 (2%)                                    | 7.4 (1%)                                      | 789.0                    |
| Week 4  | 567.4                               | 841.9 (96%)                               | 28.8 (3%)                                    | 9.1 (1%)                                      | 879.8                    |
| Week 5  | 467.0                               | 489.0 (86%)                               | 72.5 (13%)                                   | 5.1 (1%)                                      | 366.6                    |
| Week 6  | 381.6                               | 774.2 (94%)                               | 42.8 (5%)                                    | 8.1 (1%)                                      | 825.1                    |
| Week 7  | 471.1                               | 860.1 (96%)                               | 28.9 (3%)                                    | 9.5 (1%)                                      | 898.5                    |
| Week 8  | 526.2                               | 470.2 (91%)                               | 43.3 (8%)                                    | 5.7 (1%)                                      | 519.2                    |
| Week 9  | 514.3                               | 616.4 (95%)                               | 28.7 (4%)                                    | 6.2 (1%)                                      | 651.3                    |
| Week 10 | 597.9                               | 532.2 (94%)                               | 31.2 (5%)                                    | 5.5 (1%)                                      | 568.9                    |
| Week 11 | 534.8                               | 370.6 (90%)                               | 38.6 (9%)                                    | 5.0 (1%)                                      | 414.2                    |
| Week 12 | 339.4                               | 671.5 (90%)                               | 68.9 (9%)                                    | 5.4 (1%)                                      | 745.8                    |
| Week 13 | 408.4                               | 531.4 (92%)                               | 42.7 (7%)                                    | 4.4 (1%)                                      | 578.5                    |
| Week 14 | 450.0                               | 464.9 (95%)                               | 20.6 (4%)                                    | 4.4 (1%)                                      | 489.9                    |
| Week 15 | 789.0                               | 522.9 (80%)                               | 126.5 (19%)                                  | 7.0 (1%)                                      | 656.4                    |
| Week 16 | 909.3                               | 945.5 (95%)                               | 37.8 (4%)                                    | 5.5 (1%)                                      | 988.8                    |
| Week 17 | 1,385.0                             | 826.3 (98%)                               | 3.0 (1%)                                     | 10.8 (1%)                                     | 840.1                    |
| Average | 577.6                               | 643.9 (93%)                               | 44.4 (6%)                                    | 6.4 (1%)                                      | 692.45                   |

## REFERENCES

1. Private communication with Burns & McDonnell Engineering Company, Kansas City, Missouri, 1979.

## ACKNOWLEDGMENTS

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## AN OVERVIEW OF BIOASSAYS FOR MUTAGENS, CARCINOGENS AND TERATOGENS

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Over 75 years ago, in 1906, Congress enacted the first of a series of laws designed to guarantee the safety of food and cosmetic products. In response to this legislation the Federal Drug Administration (FDA) was established and is responsible for implementation of these laws. Almost 50 years ago, in 1938, another law was enacted to strengthen the first and required premarketing clearance of drugs. Twenty years later, in 1958, the Food Additives Amendment was added to the Food, Drug and Cosmetic Act. This amendment places safety liability on the producers and requires toxicological testing prior to marketing. More recently, the Toxic Substance Control Act was promulgated and empowers the Environmental Protection Agency (EPA) to regulate all potentially hazardous chemical substances to which man and the environment may become exposed either through manufacture, distribution, use or disposal. The EPA is, in addition, required to set standards for test protocols designed to provide data relevant to health and environmental protection.

With the large volume of chemicals reaching the market annually and with the mandate for health and environmental protection, there has been an increasing demand for the assessment of their risk as potential health hazards. In many ways biologists were unprepared to cope with the questions of biological testing and risk assessment, the aim of which is to regulate production, consumption and/or environmental exposure. Initially, there was not enough information available to recommend or even suggest minimal exposure levels or potential health hazards. As a result, under the pressure to provide data for regulation and protection, better and more informative ways to test and evaluate health hazards in a fast and economical way were sought. Basically, the biological scientist was faced with the task of developing bioassays

that would respond appropriately to a variety of chemical compounds or complex mixtures - respond in such a way as to permit interpretations that would provide meaningful data for human risk assessment. A number of bioassay models have been developed or proposed but the difficulty of determining the adequacy of these systems for human risk assessment remains. In terms of their predictive value, validity, and relevance to man, most in fact are inadequate.

Approach to Biological Testing: Because of the large number of chemicals and mixtures to be tested and because of the time and cost involved in mammalian testing procedures, the Tier System approach as proposed by Bridges<sup>1</sup> and Flann<sup>2</sup> has been generally accepted as the best way to confront the problem of biological testing.

Basically the Tier System approach consists of three levels of testing that are increasingly complex, lengthy and costly. Each tier consists of a battery of several tests since no single assay can possibly cover all mechanisms by which, for example, genetic mutational damage can be incurred. Tier I consists of a battery whose function it is to serve as an initial screen to identify potential hazards. The predominant test organisms are microbes. Tier II tests serve to confirm, using higher organisms, the genotoxic effects detected in Tier I. Tier I and II tests are basically qualitative and are designed to answer the question, "Is a chemical a mutagen or a carcinogen, yes or no?"<sup>3</sup>

Tier III tests are more quantitative whole animal mammalian tests which attempt to understand and ascertain risk to humans. The data provided by the tier test battery makes possible a progression of studies beginning with the identification of potential hazards at Tier I, confirmation in Tier II and, in Tier III, assessment of potential human risks based on studies using sub-human mammalian species (usually rats or mice). It must be noted, however, that the latter is at best an assessment of potential risk to humans for, without exception, it is virtually impossible at the present time to extrapolate these data to reflect actual human risk. Some reasons for this will be discussed later.

Biological Basis or Mechanisms of Bioassays: One may ask why it is important or even desirable to understand the biological mechanisms involved in a specific assay. The simple answer is that by understanding the biological mechanism through which the assays respond to give a detectable result, reasonable predictions and interpretations can be made about whether or not the same response could be expected in man.

Thus, the Tier I and II assays are basically genotoxicity tests. The assays are especially useful because they can demonstrate genetic effects such as mutations (DNA damage), chromosomal aberrations, mitotic poisons, unscheduled DNA synthesis and DNA repair. These assays are important because many focus on DNA, the molecule that contains the genetic code for specifying cellular and organismic functions. This code is passed from generation to generation and is also used continuously by all living cells to regulate structure and function. If DNA is damaged the code is also damaged and such damage is referred to as a mutation. Mutations in germ cells (oocytes and sperm) can be inherited and are thus detrimental to the next and possibly all future generations. Damage to DNA in somatic cells - all cells other than germ cells - can lead to a wide range of dysfunctions possibly including transformation into malignant (cancer) cells or, if the somatic cells are those of an embryo, the DNA damage is thought to be capable of causing abnormal embryonic development or teratogenesis.

The DNA molecules are contained in the chromosomes. Certain types of chemicals called clastogens cause the chromosomes to break or be otherwise damaged. As a result, portions of the genetic material are lost. Alternatively broken ends of chromosome can interact or reconnect with other broken pieces. If such rearrangements occur within or between chromosomes, muddled, defective or missing genetic messages may result. Defects which involve chromosomal breaks can frequently be detected by microscopic examination of cells or, if they occur in germ cells, they can be detected by death of the embryo or genetic defects present in the offspring.

Damage to chromosomes can be detected microscopically following staining procedures which allow differentiation between paired chromosomes. This damage can occur in various ways. For example,

Figure 1 demonstrates how interchanges between two chromosomes can occur resulting in the first case in the formation of dicentric chromosomes (chromosomes with two centromeres or anchoring points for the attachment of spindle fibers during mitosis) and chromosome fragments. The second example in Figure 1 shows the mechanism of translocation. This involves the actual exchange of parts between two separate chromosomes. Figure 2 is an array of normal chromosomes from a cell. The shape of each chromosome and the number present is specific for each species. Figure 3 is an array from a similar cell treated with a mutagen. A dicentric (C) and a chromosome fragment (F) are indicated. Under special conditions of staining exchanges between sister chromatids (i.e., the two arms of a single, replicated chromosome) can be dramatically demonstrated and forms the basis of a test for chromosomal damage referred to as sister chromatid exchange or SCE. Figure 4 is a control cell (Chinese hamster ovary cell, CHO) showing the two chromatids, one stained darkly the other lighter. Figure 5 shows a similar cell treated with a chemical mutagen and the exchanges between the chromatids. Normally each half of the chromatid would be uniformly stained (see Figure 4). Following SCE each half stains alternately light and dark and shows exchanges between the two.

Other inheritable effects are produced by toxicants called mitotic poisons that interfere with cell division. These compounds do not damage chromosomes per se, but rather damage or interfere with the mechanisms that insure the proper distribution of chromosomes during cell divisions. Improper distribution of chromosomes to daughter cells has severe genetic ramifications since daughters will have too many or too few chromosomes, i.e., will demonstrate changes in ploidy or chromosome number (Figures 6 and 7). The detection of ploidy as well as the detection of breaks and recombinations of chromosomes relies on the use of higher biological systems i.e., cells with observable chromosomes.

Other methods detect what is called unscheduled DNA synthesis. These tests usually use mammalian cells either in vitro or in vivo and take advantage of the fact that when DNA is damaged enzymatic processes in the cell may remove the damaged portion and replace it by synthesis of new DNA<sup>4</sup>. This frequently occurs at stages of the cell cycle when normally



# INTERCHANGES

## PRE-REPLICATION

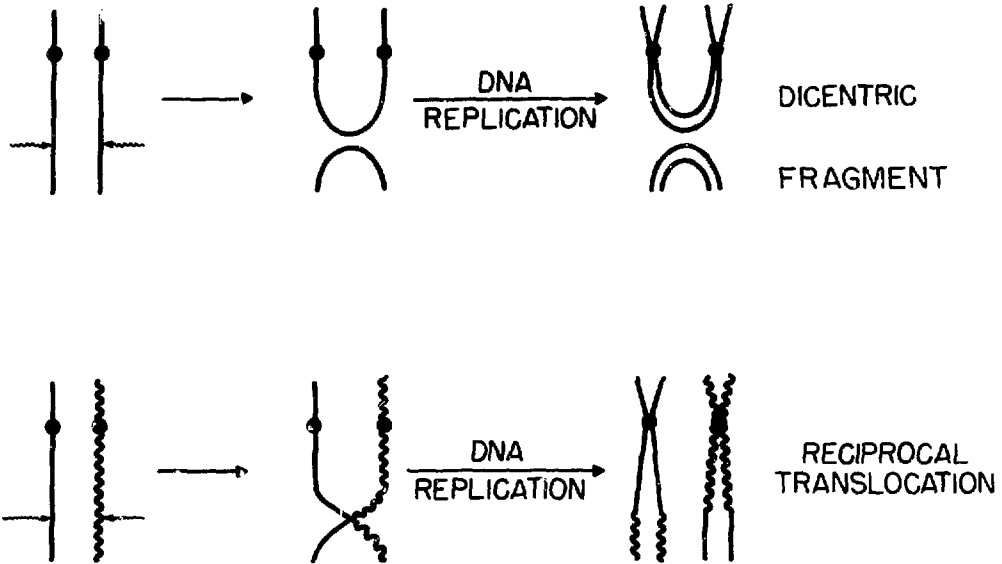
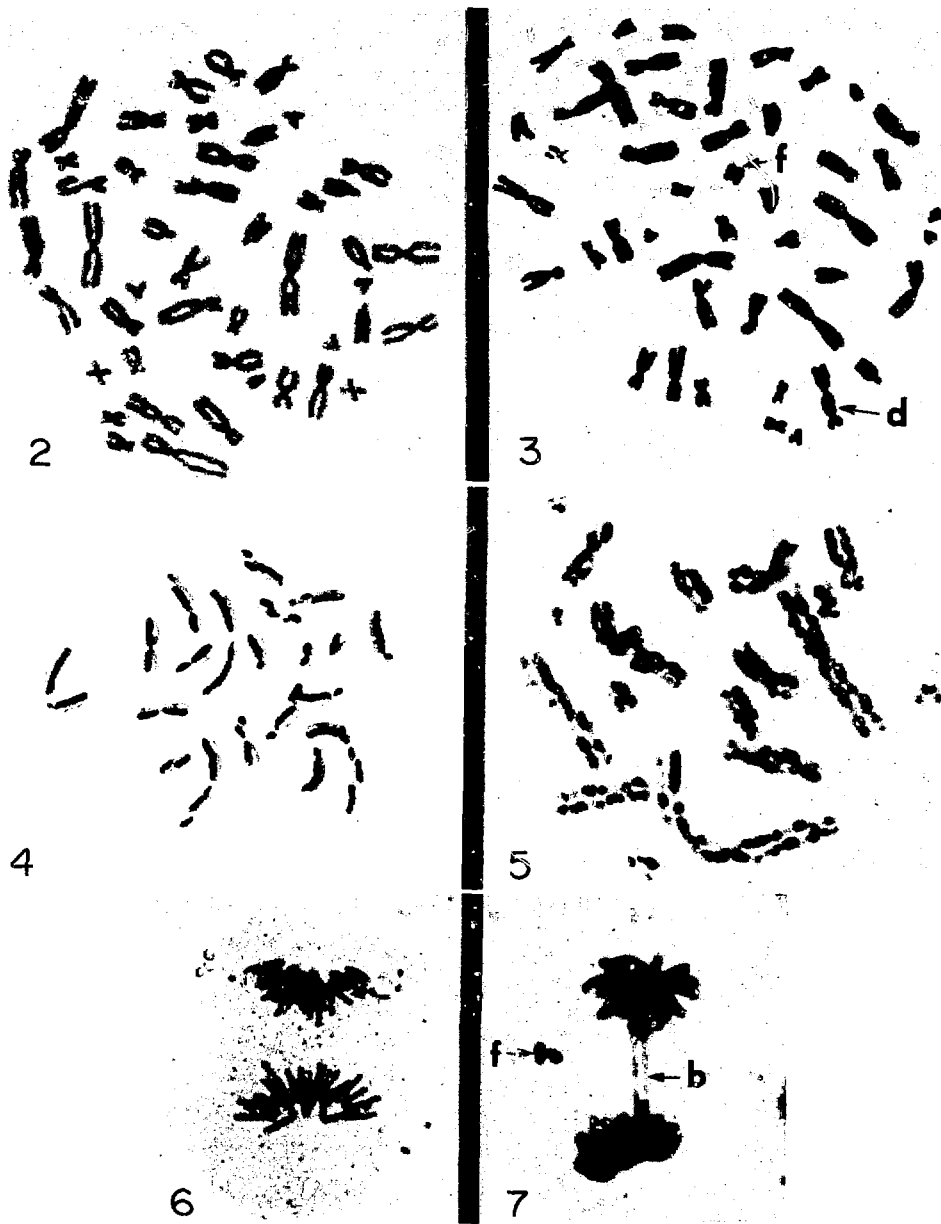


FIGURE 1. Diagrammatic representation of the formation of two kinds of chromosomal aberrations. In the first example the formation of a dicentric chromosome and a chromosome fragment is shown. In the second example the mechanisms of translocation of chromosomal parts is shown. The arrows at the left indicate damage by mutagens. (Courtesy of Dr. J. Preston, Biology Division, ORNL.)

FIGURES 2-7 from Kimball and Munro<sup>6</sup>.

Fig. 2: Chromosomes from a normal human leucocyte reveals a wide array of sizes and shapes. Fig. 3: Human leucocyte chromosomes showing aberrations; d, a dicentric and f, fragment. Fig. 4: Chromosome preparation of Chinese hamster ovary (CHO) cells stained to show sister chromatids. Fig. 5: Chromosomes from a CHO cells treated with a



mutagen. The staining procedure shows exchanges between chromatids, i.e., sister chromatid exchanges or SCEs. Fig. 6: Normal cell division (mitosis) with chromosomes separating to opposite poles (anaphase) of the mitotic spindle. Fig. 7: Abnormal separation of chromosomes during mitosis lead to changes in chromosome number (ploidy) in daughter cells; f, chromosome fragment; b, chromosome bridge.

no DNA synthesis occurs, i.e., at unscheduled times. Unscheduled DNA synthesis can be detected by autoradiographic (radioactive tracer) studies. Finally, there are also repair-deficient and repair-proficient strains of bacterial cells that can be used to detect mutations in the enzymatic mechanisms used to repair damaged DNA.

The comments above reflect some of the genetic mechanisms or events which result from exposure to mutagens (chemicals that cause mutations). The following comments will briefly review the most commonly used bioassay models.

Bioassay Models for Mutagens: Probably the most popular bioassay used to detect mutations is the Ames<sup>5</sup> or Salmonella test. Basically, this test uses mutant strains of the bacterium, Salmonella typhimurium. For example, some require the amino acid histidine for growth because they have lost the ability to synthesize it. The assay detects reverse mutations, that is, the reversion of a histidine-requiring mutation to one where growth can occur without the amino acid. Or, put another way, it detects reversion to a condition where the ability to synthesize histidine is re-acquired. Procedurally, one simply treats histidine-requiring bacteria with the suspected mutagen and then places them in an agar plate which does not contain histidine. Only those cells that mutate (revert) to a condition where they can synthesize their own histidine will grow and form colonies. The colonies can be counted for purposes of quantitation. Other assays using other bacteria such as E. coli are also available<sup>5</sup>.

Higher organisms can also be used to detect mutations. One commonly used is the fruit fly, *Drosophila*. There are a variety of tests in which the male, female or larvae can be treated with mutagen and various kinds of mutations (eye color, wing shape, bristle structure, etc.) can be detected in the offspring or adults. These organisms are useful because defects in germ cells can be detected by breeding experiments and damage to chromosome structure can be detected microscopically.

Tests such as those above have the advantage of being rapid and simple assays and are generally placed in Tier I or II. There are many more such tests but time and space do not permit their inclusion here.

For a more comprehensive treatment of the many tests available the reader is referred to references 6 and 7. A problem with all such tests is that not all genotoxic chemicals (those which damage genetic information) give positive results so some tests are negative even with known mutagens. Such negative results are called false negative and ideally would appear only infrequently. Some false negatives would be expected, however, in these qualitative screening assays.

Tier III bioassays usually involve whole animal mammalian studies and are designed to detect mutagenic events in both somatic and germ cells populations. By the time a chemical reaches Tier III testing, it would normally have been through Tiers I and II and have demonstrated positive results in those assays. Thus only the most potentially hazardous chemicals experience further Tier III testing.

The most frequently used whole animal test designed to detect somatic cell damage is the mouse spot test<sup>8</sup>. The assay is relatively rapid (about 5 weeks) and detects both gene mutations and various kinds of chromosomal damage. The protocol calls for application of the toxicant to embryos in utero that are genetically heterozygous for several specific coat colors. The embryos are allowed to continue development, be born, and develop fur. The fur is then examined, usually about 12 days after birth, for colored patches or spots. Different colored spots are diagnostic for clones of mutant pigment producing cells. A major drawback of this test is that, since the mutations detected are in somatic cells as opposed to germ cells, further genetic analysis by breeding tests is not possible.

Other whole animal tests are designed to detect mutational damage in the germ cells. These tests are important for two reasons: (1) germ cells, especially spermatogenic cells, are especially useful for detecting mutations because of their high division rates and (2) mutations to germ cells are usually inherited so potential risk to future generations can be evaluated. The specific locus test is probably the most reliable whole animal method for detecting mutations that are heritable<sup>9</sup>. This test uses nonmutant, wild-type mice which are exposed to the suspect mutagen. These are mated to a stock of mice which contain many recessive genes in their genetic makeup. Mutant offspring display identifi-

able and characteristic markers ranging from altered eye or hair color, hair structure, ear length or abnormal appendages. Other markers may include histo-incompatibility (i.e., an immunological characteristic in which skin-grafts between first generation offspring are rejected) or other biochemical markers. Advantages of this test include: (1) ease of identifying visible mutants, (2) mutants can be detected in the first generation, (3) mutant animals can be bred for further genetic analysis and (4) the test is fast and not labor-intensive.

There is a variety of other mammalian tests available for the detection of various mutagenic events. These are reviewed and described in some detail by Russell and Matter<sup>7</sup>. One must again emphasize that positive results in any of these tests simply show what chemicals may be potential mutagens in humans, not which ones actually are.

Bioassay Models for Carcinogens: The emphasis on mutagenesis in the preceding paragraphs comes from the fact that in some cases mutagenic events may precede carcinogenic ones. The correlation between these two events, however, is far from perfect<sup>6,10</sup>. Furthermore, what is known about the effects of mutagens and carcinogens in humans comes for the most part from epidemiological data and is not directly the result of bioassays. Chemicals have most often been shown to be mutagenic or carcinogenic in bioassays only after they were either demonstrated to be or suspected of being carcinogenic in humans. In validation studies of known carcinogens using the Ames test positive mutagenicity results range from 72-91% and false negatives from 9-28%. In studies using non-carcinogens 6-26% test positive for mutagenicity and 81-94% test negative<sup>10</sup>.

These data from validation studies of mutagenicity vs carcinogenicity present generally unsatisfactory levels of false negatives for carcinogens and false positives for noncarcinogens. The Salmonella test is therefore considered inappropriate for estimating carcinogenic activity or potential. It is felt that it is generally reliable as a screen for mutagens but not for carcinogens and these results suggest that there is more than one mechanism involved in both mutagenesis and carcinogenesis

and that some tests can detect some of them but none can detect them all.

With this background on the potential and in many cases tenuous relationship between mutagenesis and carcinogenesis we will turn the discussion to some bioassays available for carcinogens. A battery of reliable short-term in vivo or in vitro screens for carcinogenesis is available although many remain to be validated<sup>7</sup>. However, since it is possible to draw some correlations between mutations and carcinogenesis, some of the bioassays already described for mutagens are included in Tier I or II of the screening battery for carcinogens. The primary in vitro screen for carcinogenesis relies on the phenomenon of cell transformation and uses mammalian cells in culture. The endpoint is a change or transformation in the shape of cells following their exposure to carcinogens. Although cell transformation tests are not used for making regulatory decisions they are used to support those decisions.

Most cell transformation assays use fibroblast-like cell lines. The endpoint is morphologically transformed cells that will often produce tumors when injected into a suitable host. Cell types frequently used include hamster embryo cells (HEC), Syrian hamster embryo cells (SHE), or Chinese hamster ovary cells (CHO)<sup>11,12</sup> or human fibroblasts<sup>13</sup>. Following exposure to carcinogens, the morphology of some cells is altered. The morphological change is characterized by a loss of density-dependent growth so that cells pile up in colonies in random crisscross fashion (Figure 8). Transformation occurs only after treatment with carcinogen and is generally dose dependent. Typically, the assays require 1-5 weeks to complete. Assays using HEC cells show a high positive correlation between in vitro transformation and in vivo carcinogenic potential<sup>11</sup>. Human, guinea pig and rat cells can also be used in these assays but the hamster system appears to be the most expedient.

The most meaningful assays for carcinogenesis are the Tier III chronic, longer term, expensive, whole animal studies which have very involved protocols. These assays are used as the basis for setting standards by regulatory agencies. In these chronic assays the carcinogenic effects may be (1) increased incidence of malignant tumors,



FIGURE 8. A colony of transformed cells forms after treatment with a carcinogen. The cells of the colony have lost their density dependent growth and pile atop one another in random criss-cross fashion. Normal, non-transformed cells are also present. (Courtesy of Dr. J. Selkirk, Biology Division, ORNL).

(2) occurrence of rare or unsuspected tumor types or (3) the appearance of tumors earlier than expected following exposure. These bioassays usually require an initial 6-8 week dose range-finding study to determine the maximum tolerated dose (MTD). The National Cancer Institute recommends lifetime feeding studies using both sexes from two species and two dose levels - the MTD and one-half MDT (plus essential control groups) - a total of about fifty animals plus controls.

The epidermal or skin painting tests are popular for certain types of compounds, especially, but not limited to, those for which skin contact is apt to be a common route of exposure. Skin painting assays may take from 2-3 months or up to two years depending upon the potency of the carcinogen and the latency of appearance of tumors. In all of these

assays there is usually an inverse relationship between the time of appearance of tumors and the intensity of the dose. Smaller doses require longer times for tumor induction than larger doses. Thus high doses are frequently used to shorten the assay time and to reduce costs. Skin painting tests involve repeated application of the test material to a shaved area, usually the back, of mice. A positive result is the formation of a tumor similar to that shown in Figure 9.

Chronic inhalation studies are also used to detect potential carcinogens. Inhalation tests are usually expensive because they require large groups of animals and special inhalation chambers. Exposure is usually 6 hours per day, 5 days a week for the lifetime of the animal. At the termination of the experiment essentially all tissues of the test and control animals are examined for tumor pathology. Most human lung carcinogens have proven positive in rodent inhalation tests. It is whole animal tests such as these that have been used to assess risk and formulate regulations for carcinogen control and exposure.



FIGURE 9. A mouse treated by the skin painting technique. A large tumor has developed on the shaved area of the back to which carcinogen was applied. (Courtesy of Dr. J. M. Holland, Biology Division, ORNL).



Bioassay Models for Teratogens: Teratogenesis, or abnormal embryonic development is another area receiving increasing concern in recent years. Actually, teratology is but a small segment of a broader area that encompasses all aspects of reproductive capacity including inability to conceive (whether because of impairments in male or female), spontaneous abortions, premature birth, low birth weight, prenatal mortality and prenatal behavioral abnormalities. There is little doubt that environmental factors contribute to all of these facets of reproduction. Unlike the number of assays available for mutagen and carcinogen detection, there are relatively fewer available for the detection of teratogens. Validated, short-term tests are conspicuously missing although there are a number of submammalian screening assays under development<sup>14</sup>. Several of these screening assays involve the in vitro culture of mammalian embryos or, alternatively, certain organ primordia (usually limb-bud) which are removed and explanted to culture. As the embryo or explant grows anatomical deficiencies or defects can be detected. Such procedures are fairly standard and relatively simple but they do require some technical skill. However, less time and cost are involved than in whole animal studies. Aside from these embryo or explant cultures, which remain to be validated, there are essentially no other screens available.

Many of the requirements of a teratogenesis screen are similar to those of mutagenesis and carcinogenesis tests but several additional ones might be added. For example, the assay would ideally be developmentally relevant. That is, in the strictest sense, the assay should actually be a developing embryonic system capable of demonstrating developmental toxicity in the form of growth retardation, malformations and embryotoxicity. Of course dose-response relationships, easily detected endpoints, and test versatility are also important. Clearly no screening test exists, or will probably ever exist, that has all of the desired attributes. One assay, among several others, which holds some promise in terms of potential validation as a screen is one we have under development<sup>15</sup>. The assay, referred to as FETAX (Frog Embryo Teratogenesis Assay: Xenopus) uses amphibian (Xenopus laevis) embryos as the test organisms. By taking the approach of using an easily obtained

developing embryo system such as the amphibian, we confront immediately the problem of developmental relevance. The development of the amphibian embryo is similar (though certainly not identical) to that of higher vertebrates. Methodologically, the assay is simple, rapid, has a variety of easily detected endpoints (Figure 10) and shows quantitative dose-response relationships. We have examined about 25 known mammalian teratogens in this model. Some, like ethylene oxide, ethylene thiourea, dimethylbenz[a]anthracene and retinoic acid, may be classified as severe mammalian teratogens while others like aspirin, saccharin and ethanol may be thought of as weak teratogens. The severe teratogens cause dramatic developmental effects in FETAX and those which are weak teratogens cause milder defects. It is also interesting that in general the types of defects that occur in mammals are also seen in amphibians. Using a Teratogenic Index number generated from embryo lethality data and numbers of abnormal embryos produced, we are able to rank each teratogen in terms of its potency. So far this ranking follows the same ranking the teratogens would receive based on their potency in mammals. Thus, we are encouraged that the FETAX model may fulfill many of the requirements of a potential screen and that it appears to be a valid bioassay for detecting mutagens. Hopefully, it can be applied in much the same way as the Ames test for mutagens.

I do not wish to imply that these are the only tests available for teratogen screening. There are many others which use biological systems ranging from cell culture, planaria and hydra to chick and in vivo mammalian embryos. All measure as endpoints facets of cellular activities which are important to development (cell movements, cell sorting, cellular differentiation, cell death, etc.). Some proposed screening assays use mammals but simplify the test protocols and endpoint analyses<sup>16</sup>. Such adjustments in test procedures and data collection are beneficial for screening assays and do reduce cost, time and personnel requirements. Nevertheless, whole animal mammalian techniques remain comparatively expensive as screens.

The following Tier III tests are for general reproductive ability (these include observations on abnormal development), they are the so-called Reproductive Capacity test<sup>17</sup> and the Three Generation test<sup>17</sup>.

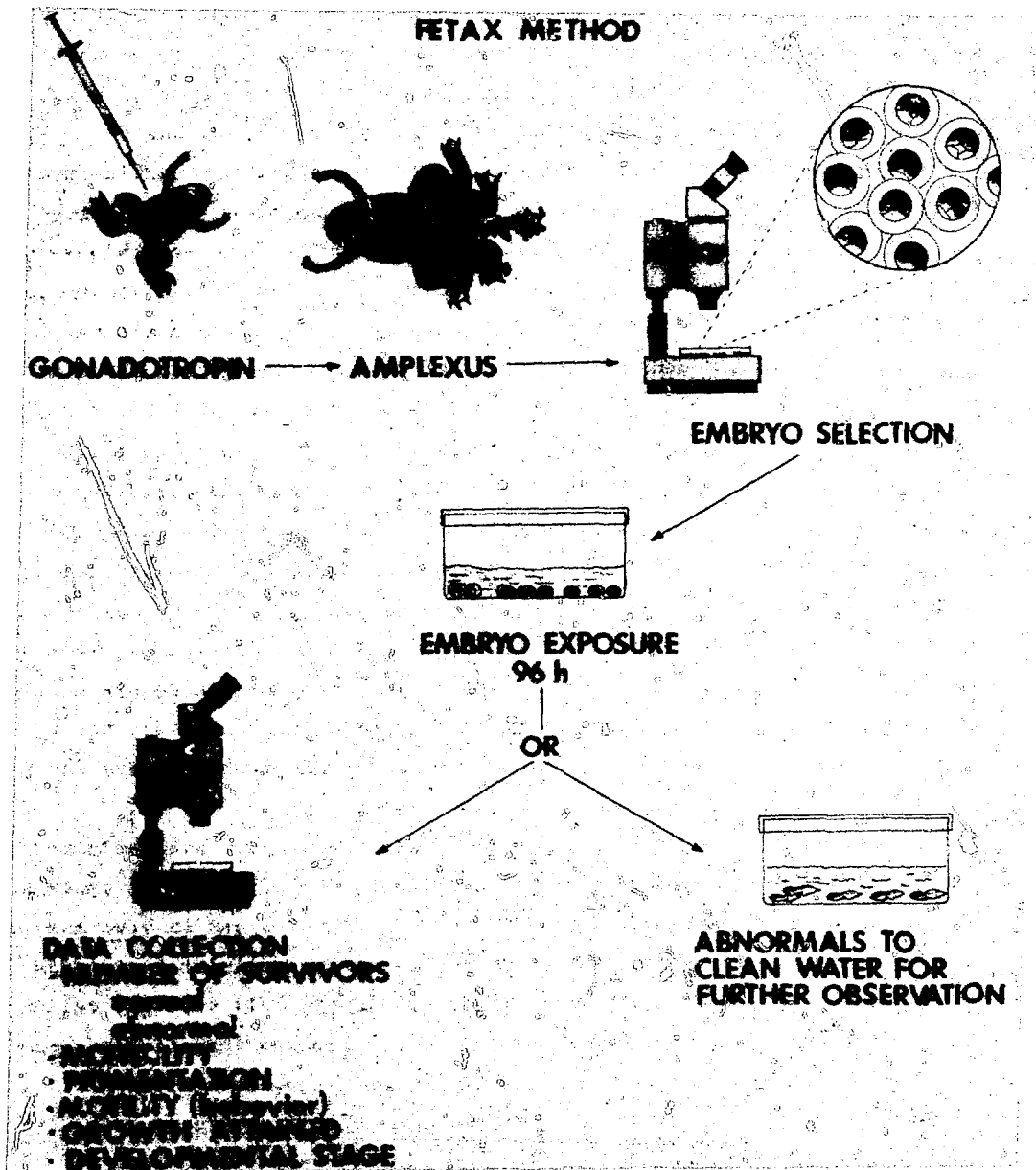


**FIGURE 10.** Diagrammatic representation of the FETAX methodology. Adults are given gonadotropin to induce breeding. Embryos in early stages of development are exposed for 96 hours to suspect teratogens. Endpoints include determination of embryo lethality, anatomical malformations, motility and pigmentation.

Both tests are lengthy and expensive. The protocol for the reproductive capacity test has been adopted by the FDA and is the more extensive of the two because endpoints other than anatomical defects are detected. The test basically involves a three-phased approach. Phase I consists of treating males for 60 days and females for 14 days prior to mating. Teratogen treatment of the pregnant female continues through gestation and weaning when the offspring are examined for defects. In Phase II pregnant females from two species (usually rabbit in addition to rat) are treated only during the most critical periods of fetal organogenesis — days 6-15 for the rat and days 6-18 for the rabbit. Fetuses are removed by cesarean section one day before birth and examined for malformation and general toxic effects. In Phase III pregnant females are treated during the last one-third of gestation through weaning. This phase tests for effects on later stages of fetal development including early postnatal development.

The protocol for the three-generation test is even more extensive and complicated. Test animals, usually rats, are continuously exposed through three generations to the toxicant added to their diet. The purpose of this assay is to test for cumulative effects through three generations. Each generation is examined for abnormalities and ability to reproduce normal litters. Special attention is given to effects that are consistent or that progressively increase through each generation.

Extrapolation of Test Data: Finally, we come to problems with current assays and why it is not possible to extrapolate data directly to humans. There are really many reasons why current assays are inadequate but I will touch on only two outstanding ones. First, humans are not rats or mice or guinea pigs or hamsters. Biologically, we are not simply a trillion or so cells thrown into a culture dish. Metabolically, physiologically, biochemically, all animal species including man, are different from each other. For example, the way humans metabolize or breakdown a molecule is not necessarily the way rats or mice or hamsters do it. This is an important point and one purposely not covered in the foregoing remarks so it could be emphasized here. The phenomenon is called metabolic activation. It involves the metabolic

processes by which an organism metabolizes any given chemical. It is important because a given compound may not be a carcinogen or mutagen or teratogen until it is metabolized, then one or more of its metabolic products may be a hazard. Since metabolism differs from species to species, toxic products may be formed during metabolism in rats but not in humans. Or, more importantly, in humans and not in rats. There are many examples of this but a striking one deals with the tranquilizer, thalidomide. Initial tests with this drug were negative when rodents were used in the assay system. As a result, the drug was approved for human use with catastrophic results. Thalidomide (or its metabolites) is not teratogenic in rodents but it certainly is in primates. Another example of a compound that requires metabolic activation or metabolism before being active is cyclophosphamide, an anti-cancer drug whose metabolic products are both teratogenic and carcinogenic. Alternatively, there are examples where the parent compound is active but its metabolites are innocuous. For example, diphenylhydantoin, an anti-seizure drug used in treating epilepsy, is a human teratogen, but its metabolic products appear not to be. Animals also contain enzymes that may metabolically deactivate or detoxify. These, like those which activate, vary from species to species. So the ability of a hamster or rabbit to deactivate does not necessarily mean that humans possess the same capability. Furthermore, the presence of activating or detoxifying enzymes varies with age, sex or general health of the animal or fetus. Unless these and other factors are known in addition to how they correspond to humans the differences in metabolism between various animal species and humans makes it impossible to ascertain the effects of a chemical based on its effects in other species. An additional complication for evaluating teratogens is the problem of placental permeability (or transfer) of a teratogen or its metabolites. Placentas vary both structurally and physiologically between species so it is difficult to know how the human placenta compares to rodent or other mammalian placentas in these aspects.

For the sake of completeness, however, I must mention that it is possible to artificially activate some of the bioassays discussed above. The procedure is relatively straightforward. One simply makes a labora-

tory preparation of liver, the organ which contains most of the metabolizing enzymes, and adds this preparation, called the S9 fraction, to, for example, the Salmonella or cell culture media<sup>18</sup>. Thus, metabolic activation in vitro is accomplished in a way resembling that which occurs in vivo. This procedure has increased the validity of many of the Tier I and II bioassays but still uses sub-human enzyme systems.

A second major reason why extrapolations are not possible is related to the multitude of factors which impinge upon an individual and which can potentially modify his or her response. Or, stated another way, the variation of response among individuals within a population is so great that accurate extrapolations to the generalized all-purpose human prove unacceptably inaccurate. Many factors such as age, sex, exercise, disease, occupational exposures, diet, physiological functions, stress and others can alter genetically controlled events<sup>19</sup>. The problem is that, unlike laboratory animals which are highly inbred to eliminate variations, human populations are heterogeneous with respect to both environmental and genetic factors. At present, it is impossible to account for all of these variations when attempting to apply animal test data to human populations. A partial list of other factors clouding the human risk assessment issue include: Dose response relationships - are they the same for humans and subhumans?; the effects of differences in mode or route of exposure, in the potential for exposure or in length of exposure. An area not mentioned at all deals with promoters and initiators in carcinogenesis<sup>7</sup>. This subject deals with one's susceptibility to cancer based on previous exposure experience. For teratogens, gestational stage of the embryo at time of exposure is important as well as metabolic activation<sup>20</sup>. Humans appear to be more sensitive to many teratogens than the many sensitive sub-primate species. The simple question becomes of paramount importance: "If we are going to extrapolate bioassays to humans, what is the best bioassay data from which to extrapolate?"

It is a generally held view that the best we can glean from any of the bioassays is some indication about which of the chemicals pose the most potent and severe potential human risk. With that knowledge steps

can be taken to limit exposure, which in the long run may be the safest, least expensive and easiest route.

Future Innovations: What about new developments, is there any hope that we can resolve some of this dilemma of risk assessment for humans? I think the answer is yes, because new approaches and developments are being brought to bear on the problem<sup>7,14,21</sup>. Some are new techniques that use human cells or body fluids. One important area deals with determining effects on human tissues (as opposed to rat, mouse or bacteria) and the other deals with the possibility of the early detection of human exposure.

The first, that of detecting effects on human cells, is really an extension of bioassays using other mammalian cells. The problem has been that until recently the successful culture of adult human cells was not possible. However, with new culturing techniques it is now possible to maintain human liver cells in culture for several weeks. Although the cells do not divide, they remain alive and healthy. Thus, the potential exists for the activation (or deactivation) of molecules by truly human enzyme systems instead of S9 fractions from rat liver. Species differences therefore do not impinge on interpretations of these studies using human cells.

Techniques for the use of human blood serum in cell or embryo cultures are also being developed. The serum from exposed individuals will contain the metabolites of toxicants. Serum with these metabolites can then be applied directly to the test system. Similar techniques are also being developed for the use of metabolites which occur in the urine. The use of body fluids in bioassays, while not necessarily protecting those already exposed, will certainly extend our knowledge about overall human risks. A teratogenesis assay is under development in which rat embryos are cultured in human serum for 48 hours<sup>22</sup>. Serum from epileptic subjects taking anti-convulsant drugs has been used with positive results. Abnormal development of the embryo constitutes a positive result. Abnormalities in the developing rat embryo have also been detected with serum from people who smoke and from those suffering from

poor dietary and nutritional conditions. The hope is to develop the assay to identify teratogens that would be otherwise undetected.

Assays using human somatic cells, especially the lymphocyte, are also being developed<sup>22</sup>. The lymphocytes can be cultured and exposed to toxicants and the endpoints are the detection of chromosomal abnormalities microscopically, and mutations through examination of DNA repair enzymes. This assay can be used to determine potential risk as well as to monitor effects on populations that are known to have, or suspected of having, received exposure to toxicants.

Other assays, involving abnormalities in the shape of sperm cells are being developed<sup>23</sup>. One especially exciting development involves the fusion of sperm cells with fibroblast cells. Following fusion the cell begins to divide and as it does its chromosomes become visible. Thus the possibility exists for the detection of chromosomal damage in human germ cells.

With the increasing sophistication of biochemical techniques, it is possible to detect abnormalities in the proteins synthesized by cells. For example, hemoglobin, a major blood protein, is synthesized according to instructions from the genetic DNA code. Thus variations in the structure of hemoglobin, such as abnormal sequences of amino acids, infer the existence of a mutation in the DNA code of cells producing hemoglobin.

A developing area that is attractive for predicting potential hazard is that of structure-activity relationships. The concept is to develop data bases that correlate the physiochemical characteristics of chemicals and their activity as mutagens, carcinogens or teratogens. The hope is to be able to predict, on the basis of molecular structure and physical properties, which chemicals might be hazardous.

Finally, in the area of teratology, a relatively new field of behavioral teratology is rapidly developing. This area is dedicated to the examination of subtle developmental defects that affect behavioral traits. Usually detectable gross malformations are absent but defects in the nervous system can be ascertained on the basis of behavioral phenomena such as abnormal swimming ability, righting reflexes, etc. The area holds much promise for detecting developmental damage that



would not be apparent from standard bioassays and would lead eventually to prevention of behavioral defects attributable to exposure to toxicants.

All of these approaches are useful but none have yet been adequately validated for extrapolation directly to humans. Tests for mutagens and carcinogens are closer to validation than are tests from teratogens. The important task of demonstrating a positive and high correlation between the endpoints of these assays and the actual human response to exposure remains. Also needed is support for basic research into the biological mechanisms of toxicant action in order to be able to interpret and predict human outcomes and develop better assays. In the meantime we will need to rely, as in the past, on a series of non-human test systems, recognizing their inadequacies while at the same time developing new ways to identify and measure potential hazards to man.

NOTE: No attempt has been made to make extensive literature citations. The information presented has been gleaned from many sources. For purposes of a general overview of biotesting and risk assessment, references 6, 7, 14 and 21 are recommended. From these the reader will be led to additional and more specific information.

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VALIDATION OF ANNUAL AVERAGE AIR CONCENTRATION  
PREDICTIONS FROM THE AIRDOS-EPA COMPUTER CODE\*

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## ABSTRACT

The AIRDOS-EPA computer code is used by the Industrial Safety and Applied Health Physics Division of Oak Ridge National Laboratory (ORNL) to assess the annual doses to the general public resulting from releases of radionuclides to the atmosphere by ORNL facilities. This code uses a modified Gaussian plume equation to estimate air concentrations resulting from the release of a maximum of 36 radionuclides. Radionuclide concentrations in food products are estimated from the output of the atmospheric transport model using the terrestrial transport model described in U.S. Nuclear Regulatory Commission Regulatory Guide 1.109. Doses to man at each distance and direction specified are estimated for up to eleven organs and five exposure modes. To properly use any environmental transport model, some estimate of the model's predictive accuracy must be obtained. Because of a lack of sufficient data for the ORNL site, one year of weekly average  $^{85}\text{Kr}$  concentrations observed at 13 stations located 30 to 150 km distant from an assumed-continuous point source at the Savannah River Plant, Aiken, South Carolina, have been used in a validation study of the atmospheric transport portion of AIRDOS-EPA. The predicted annual average concentration at each station exceeded the observed value in every case. The overprediction factor ranged from 1.4 to 3.4 with an average value of 2.4. Pearson's correlation between pairs of logarithms of observed and predicted values was  $r = 0.93$ . Based on a one-tailed student's t-test, we can be 98% confident that for this site under similar meteorological, release, and monitoring conditions no annual average air concentrations will be observed at the sampling stations in excess of those predicted by the code. As the averaging time of the prediction decreases, however, the uncertainty in the prediction increases.

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## INTRODUCTION

The AIRDOS-EPA computer code (Moore, et al., 1979) has been developed at Oak Ridge National Laboratory (ORNL) to be used by the U.S. Environmental Protection Agency as part of a methodology to evaluate health risks to man from atmospheric radionuclide releases. It is the latest documented version in the AIRDOS series of assessment codes (Moore, 1975; 1977). This series has been developed primarily to assess routine radionuclide releases, although it has been used for assessing accidental releases (Miller et al., 1980). The AIRDOS-EPA code provides estimates of individual and population doses to man resulting from atmospheric releases of radionuclides from point and area sources. AIRDOS has been used in the preparation of numerous environmental impact analyses and statements written at ORNL (USERDA, 1975a, 1975b; USERDA, 1977). One or more of the AIRDOS codes have been implemented at a number of other installations in the United States, and AIRDOS-EPA has recently been adopted by the Industrial Safety and Applied Health Physics Division at ORNL to assess the annual doses to the general public resulting from releases of radionuclides to the atmosphere by ORNL facilities.

To properly use any environmental transport model, some estimate of the model's predictive accuracy must be obtained. The best way to determine the accuracy of calculational procedures such as AIRDOS-EPA is to compare predictions from the procedure with field measurements taken under release conditions similar to those assumed by the model, a process commonly referred to as model validation. We know of no single existing data set that can be used to validate all aspects of the AIRDOS-EPA methodology. Therefore, various portions of the code must be validated independently of one another.

The atmosphere transport portion of the AIRDOS methodology has previously been used in a verification study for SO<sub>2</sub> air concentrations near the Kingston, Tennessee, steam electric generating plant near the ORNL site (Miller and Moore, 1977). However, a data set has recently been made available by the Savannah River Plant (SRP) at

Aiken, South Carolina, that makes it possible to perform a validation study of the atmospheric transport portion of codes such as AIRDOS-EPA out to a distance of 144 km (Pendergast et al., 1979; Telegadas et al., 1980). The purpose of this paper is to discuss the AIRDOS-EPA code and to present the results of a validation study using the SRP data base.

### AIRDOS-EPA

The AIRDOS-EPA computer code is a methodology, designed for use on IBM-360 computers, that starting from atmospheric releases of radionuclides, estimates radionuclide concentrations in air; rates of deposition on ground surfaces; ground-surface concentrations; intake rates via inhalation of air and ingestion of meat, milk, and fresh vegetables; and radiation doses to man. A modified Gaussian plume equation (Gifford, 1968) is used to estimate dispersion of the released radionuclides. The equation for the  $22.5^\circ$  sector-averaged ground-level concentration in air is given by

$$\chi = \frac{Q}{0.16\pi \times \sigma_z \bar{u}} \exp \left[ -1/2 \left( \frac{H}{\sigma_z} \right)^2 \right], \quad (1)$$

where

$\chi$  = concentration in air at x meters downwind ( $\text{Bq/m}^3$ ),

$Q$  = uniform emission rate from stack ( $\text{Bq/s}$ ),

$\bar{u}$  = mean wind speed ( $\text{m/s}$ ),

$\sigma_z$  = vertical dispersion coefficient (m), and

$H$  = effective stack height (m).

Values  $Q$  and  $\bar{u}$  are input parameters for AIRDOS-EPA. Values of  $H$  may be input or calculated within AIRDOS-EPA from other input variables.

The values of  $\sigma_z$  contained in AIRDOS-EPA are those recommended by Briggs (Gifford, 1976). While the Briggs dispersion parameters, as well as others, are generally based on data for downwind distances less than or equal to 10 km, they are routinely extrapolated to much greater distances.

Equation (1) assumes that there is no upper limit to vertical dispersion. In the atmosphere, however, such a limit or "lid" often affects the dispersion of a plume, eventually resulting in a uniform radionuclide concentration between the ground and the lid. When this occurs, Eq. (1) becomes:

$$x = \frac{Q}{0.40 \times L \bar{u}} , \quad (2)$$

where  $L$  = height of the lid (m). An average value of  $L$  for the time period being considered is part of the input for AIRDOS-EPA.

As many as 36 radionuclides released from one to six stacks or area sources can be handled in a single computer run. Meteorological data for the area surrounding a nuclear facility may be supplied as input to the code, which then estimates air and ground concentrations and intake rates by man for each radionuclide at various distances and directions from the release point or the center of an area source. Radionuclide concentrations in meat, milk, and fresh produce consumed by man are estimated by coupling the output of the atmospheric transport models with the terrestrial food-chain models found in U.S. Nuclear Regulatory Commission Regulatory Guide 1.109 (U.S. NRC, 1977). From these values, doses to man at each distance and direction specified are estimated for total body, red marrow, lungs, endosteal cells, stomach wall, lower large intestine wall, thyroid, liver, kidneys, testes, and ovaries through each of five exposure modes. These modes are (1) immersion in air containing radionuclides, (2) exposure to ground surfaces contaminated by deposited radionuclides, (3) immersion in contaminated water, (4) inhalation of radionuclides in air, and (5) ingestion of food produced in the area. The dose



calculations are made with the use of dose conversion factors supplied as input data for each radionuclide, exposure mode, and reference organ or tissue.

At the option of the user, the area surrounding the source may be subdivided either with a circular or a square grid. For the circular option, as many as 20 distances may be specified for each of 16 compass directions. Each distance represents the midpoint of a sector. The square option employs a 20 by 20 grid with the source at the center. The grid size is specified by the user.

The code may be run to estimate either the highest annual individual dose in the area or the annual population dose. For either of these options, tables are provided as output which summarize doses in several ways--by nuclide, exposure mode, and organ. Also, for either option selected, ground concentrations of radionuclides and intake rates by man are tabulated for each specified environmental location. In addition, working level exposures may be calculated and tabulated for inhalation of  $^{222}\text{Rn}$  and its short-lived progeny.

#### THE SRP DATA BASE

The SRP is a major production facility owned by the U.S. Department of Energy. Located on a 770-km<sup>2</sup> site south of Aiken, South Carolina, SRP is surrounded by gently rolling terrain. The site itself is covered with forests of mixed hardwoods and pines; the surrounding area is equally divided between mixed forests and cleared farm land (Pendergast et al., 1979).

The SRP facilities include two fuel reprocessing plants located near the center of the site. Fission product  $^{85}\text{Kr}$  is released as a nonbuoyant plume at a height of 62 m during dissolution of irradiated fuel. Since  $^{85}\text{Kr}$  is an inert gas with a long radioactive half-life (10.76/y), it can serve as a tracer of atmospheric dispersion processes without the complicating effects of wet deposition, dry deposition, and chemical transformations.

Beginning in March 1975 and continuing through September 1977, weekly  $^{85}\text{Kr}$  air concentrations were measured at 13 stations surrounding SRP. These stations are shown in Fig. 1 (Telegadas et al., 1980). Cryogenic air samplers were used to collect the  $^{85}\text{Kr}$  for laboratory processing and counting. The sampling stations ranged in distance from 28 to 144 km from the source of  $^{85}\text{Kr}$ .

Concurrent to the  $^{85}\text{Kr}$  sampling program, meteorological data were gathered from eight instrumented towers on or near the SRP site, also shown in Fig. 1. One of the towers used was the WJBF television tower, located approximately 21 km from the  $^{85}\text{Kr}$  source. A second of these towers is located over 200 km from the release point and is not included in Fig. 1. Stability wind-rose statistics (consisting of stability values for each of 16 compass sections) for the period March 1975 through August 1976 have been compiled from 15-minute-averaged data taken from the 62 m height on this tower (Pendergast et al., 1979). Also, average monthly mixing depths (equivalent numerically to lid height) for this same period of time have been calculated based on acoustic sounder data gathered at the SRP site (Pendergast et al., 1979).

## METHODOLOGY

Separate AIRDOS-EPA simulations of  $^{85}\text{Kr}$  transport were performed for each study period of the year September 1975 through August 1976 from the SRP data base (Pendergast et al., 1979). These calculations of ground-level  $^{85}\text{Kr}$  concentrations were performed using Eqs. (1) and (2).

Study periods of interest were twelve months, four seasons, and one annual value. Model parameters were chosen appropriate to release conditions at the SRP. Arithmetic average air temperature, lid height, and release rate values were computed from the SRP data base

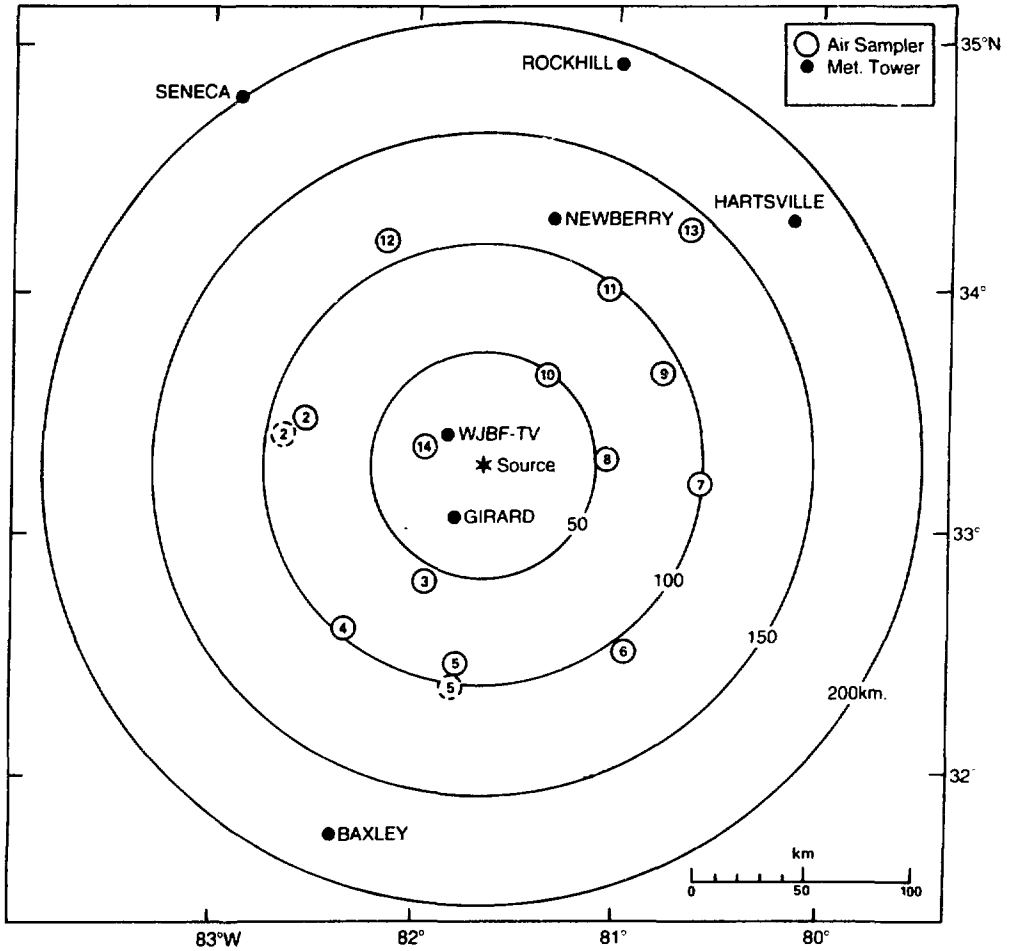


Figure 1. Krypton-85 cryogenic air sampling stations, meteorological towers and surface weather stations within 200 km of the SRP source. From Telegadas, et al., 1980.

for each period. The source term was assumed to be a steady atmospheric release from a single point source (stack). Values of simulated ground-level  $^{85}\text{Kr}$  concentrations were computed for each of 13 locations corresponding to the monitoring stations specified in the SRP data base.

Observed SRP data weekly concentration values were examined for each of the 13 monitoring stations to ascertain if they could be considered to have either a normal or a lognormal frequency distribution. The number of values available for each station ranged from 37 to 53. Depending on the sample size, either the Shapiro-Wilk W test (for 50 or fewer values) or the Kolmogorov-Smirnov one-sample D test (for greater than 50 values) was applied to compute the level for acceptance or rejection of the null hypothesis. The Statistical Analysis System (SAS)\* was used to perform this portion of the analysis.

From the results of this investigation, observed weekly concentration values appeared to be distributed more nearly lognormally than normally; thus, values appropriate for longer study periods were generated by computing the "log means" of the appropriate weekly values. For example, annual values were obtained by taking the anti-logarithm of the mean of the logarithms of the included weekly values. Seasonal observed values were computed in an analogous manner.

Comparison of observed and predicted  $^{85}\text{Kr}$  concentration values for each study period was performed. A background concentration of  $0.52 \text{ Bq/m}^3$  ( $14 \text{ pCi/m}^3$ ) provided by SRP (Pendergast et al., 1979) was subtracted from the measured concentrations at each station to derive the "observed" values used in these comparisons. The tendency of AIRDOS-EPA to either overpredict or underpredict was evaluated by examining the values of the ratio of predicted to observed air concentration. Also, Pearson's correlation was computed for the 13 station value pairs of log-predicted and log-observed concentrations.

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\*Proprietary software distributed by SAS Institute, Inc., of Raleigh, North Carolina.

## RESULTS

Table 1 shows a station-by-station comparison of the observed and predicted annual average  $^{85}\text{Kr}$  air concentrations. A summary of the frequency of occurrence of the predicted to observed ratio is included in Table 2. A plot of log-predicted vs log-observed ground-level concentrations is given in Fig. 2. These results show that the annual predicted ground-level  $^{85}\text{Kr}$  concentration exceeded the observed value for each of the 13 stations. The predicted-to-observed concentration ratio was less than 2 in five of the 13 cases. The mean logarithm of this ratio was 0.82, which corresponds to an overprediction factor of 2.27. The logarithms of predicted and observed values were well correlated ( $r = 0.93$ ).

If it is assumed that the predicted-to-observed air concentration ratios shown in Table 1 are lognormally distributed, these results may be used to estimate the confidence limits associated with a predicted air concentration. The value of the ratio ( $X_A$ ) associated with a particular percentile  $A$  is given by (Shaeffer, 1980):

$$X_A = \exp (\mu + Z\sigma) \quad (3)$$

where

$\mu$  = the mean of the logarithms of the ratios,

$\sigma$  = the standard deviation of the logarithms of the ratios, and

$Z$  = a factor corresponding to the  $A$ th percentile of a standard normal distribution.

It follows from Eq. (3) that

$$Z = \frac{\ln X_A - \mu}{\sigma} \quad (4)$$

Table 1. Comparisons of observed and predicted annual average air concentrations of  $^{85}\text{Kr}$  at the Savannah River Plant, September 1975 through August 1976.

| Monitoring station | Distance from source, km | $^{85}\text{Kr}$ concentration, $\text{Bq/m}^3$ ( $\text{pCi/m}^3$ ) |                       |                      |                       | Predicted |
|--------------------|--------------------------|----------------------------------------------------------------------|-----------------------|----------------------|-----------------------|-----------|
|                    |                          | Observed                                                             |                       | Predicted            |                       | Observed  |
| 2                  | 94                       | $3.2 \times 10^{-1}$                                                 | (8.6)                 | 1.1                  | ( $3.0 \times 10^1$ ) | 3.4       |
| 3                  | 60                       | $4.5 \times 10^{-1}$                                                 | ( $1.2 \times 10^1$ ) | 1.4                  | ( $3.8 \times 10^1$ ) | 3.1       |
| 4                  | 99                       | $5.6 \times 10^{-1}$                                                 | ( $1.5 \times 10^1$ ) | 1.4                  | ( $3.8 \times 10^1$ ) | 2.5       |
| 5                  | 98                       | $2.0 \times 10^{-1}$                                                 | (5.4)                 | $6.3 \times 10^{-1}$ | ( $1.7 \times 10^1$ ) | 3.2       |
| 6                  | 109                      | $3.7 \times 10^{-1}$                                                 | ( $1.0 \times 10^1$ ) | 1.4                  | ( $3.8 \times 10^1$ ) | 3.7       |
| 7                  | 100                      | $7.8 \times 10^{-1}$                                                 | ( $2.1 \times 10^1$ ) | 1.5                  | ( $4.1 \times 10^1$ ) | 1.9       |
| 8                  | 57                       | 1.9                                                                  | ( $5.1 \times 10^1$ ) | 2.8                  | ( $7.6 \times 10^1$ ) | 1.5       |
| 9                  | 93                       | 1.2                                                                  | ( $3.2 \times 10^1$ ) | 1.7                  | ( $4.6 \times 10^1$ ) | 1.4       |
| 10                 | 50                       | 2.7                                                                  | ( $7.3 \times 10^1$ ) | 3.7                  | ( $1.0 \times 10^2$ ) | 1.4       |
| 11                 | 98                       | $9.1 \times 10^{-1}$                                                 | ( $2.5 \times 10^1$ ) | 1.7                  | ( $4.6 \times 10^1$ ) | 1.8       |
| 12                 | 112                      | $3.7 \times 10^{-1}$                                                 | ( $1.0 \times 10^1$ ) | 1.4                  | ( $3.8 \times 10^1$ ) | 3.7       |
| 13                 | 144                      | $5.1 \times 10^{-1}$                                                 | ( $1.4 \times 10^1$ ) | 1.4                  | ( $3.8 \times 10^1$ ) | 2.7       |
| 14                 | 28                       | 1.4                                                                  | ( $3.8 \times 10^1$ ) | 4.1                  | ( $1.1 \times 10^2$ ) | 2.9       |

Table 2. Summary of observed vs. predicted annual, quarterly, and monthly air concentrations of  $^{85}\text{Kr}$  at the Savannah River Plant, September 1975 through August 1976.

| Time Period                     | Frequency of ratio |         |       | (Predicted concentration)<br>(Observed concentration) |      |     | Correlation<br>coefficient <sup>a</sup> |
|---------------------------------|--------------------|---------|-------|-------------------------------------------------------|------|-----|-----------------------------------------|
|                                 | ≤ 0.1              | 0.0-0.5 | 0.5-1 | 1-2                                                   | 2-10 | ≥10 |                                         |
| <u>Annual</u>                   |                    |         |       |                                                       |      |     |                                         |
| Sept. 1975-Aug. 1976            | 0                  | 0       | 0     | 5                                                     | 8    | 0   | 0.93                                    |
| <u>Quarterly</u>                |                    |         |       |                                                       |      |     |                                         |
| Fall (Sept.-Nov. 1975)          | 0                  | 0       | 1     | 6                                                     | 6    | 0   | 0.85                                    |
| Winter<br>(Dec. 1975-Feb. 1976) | 0                  | 0       | 0     | 11                                                    | 2    | 0   | 0.88                                    |
| Spring (Mar.-May 1975)          | 0                  | 0       | 1     | 4                                                     | 8    | 0   | 0.79                                    |
| Summer (June-Aug. 1976)         | 0                  | 0       | 0     | 2                                                     | 9    | 2   | 0.84                                    |
| <u>Monthly</u>                  |                    |         |       |                                                       |      |     |                                         |
| Sept. 1975                      | 0                  | 0       | 2     | 4                                                     | 7    | 0   | 0.57                                    |
| Oct. 1975                       | 0                  | 0       | 0     | 0                                                     | 12   | 1   | 0.84                                    |
| Nov. 1975                       | 0                  | 0       | 1     | 2                                                     | 6    | 2   | 0.61                                    |
| Dec. 1975                       | 0                  | 0       | 0     | 1                                                     | 9    | 2   | 0.57                                    |
| Jan. 1976                       | 0                  | 0       | 0     | 4                                                     | 8    | 0   | 0.68                                    |
| Feb. 1976                       | 0                  | 0       | 0     | 2                                                     | 10   | 1   | 0.82                                    |
| Mar. 1976                       | 0                  | 0       | 1     | 2                                                     | 8    | 2   | 0.63                                    |
| Apr. 1976                       | 0                  | 0       | 0     | 2                                                     | 10   | 1   | 0.79                                    |
| May 1976                        | 0                  | 0       | 0     | 2                                                     | 8    | 3   | 0.70                                    |
| June 1976                       | 0                  | 0       | 0     | 0                                                     | 8    | 5   | 0.89                                    |
| July 1976                       | 0                  | 0       | 0     | 0                                                     | 6    | 7   | 0.70                                    |
| Aug. 1976                       | 0                  | 0       | 0     | 1                                                     | 6    | 6   | 0.51                                    |

<sup>a</sup>A value of 1.0 indicates a perfect correlation.

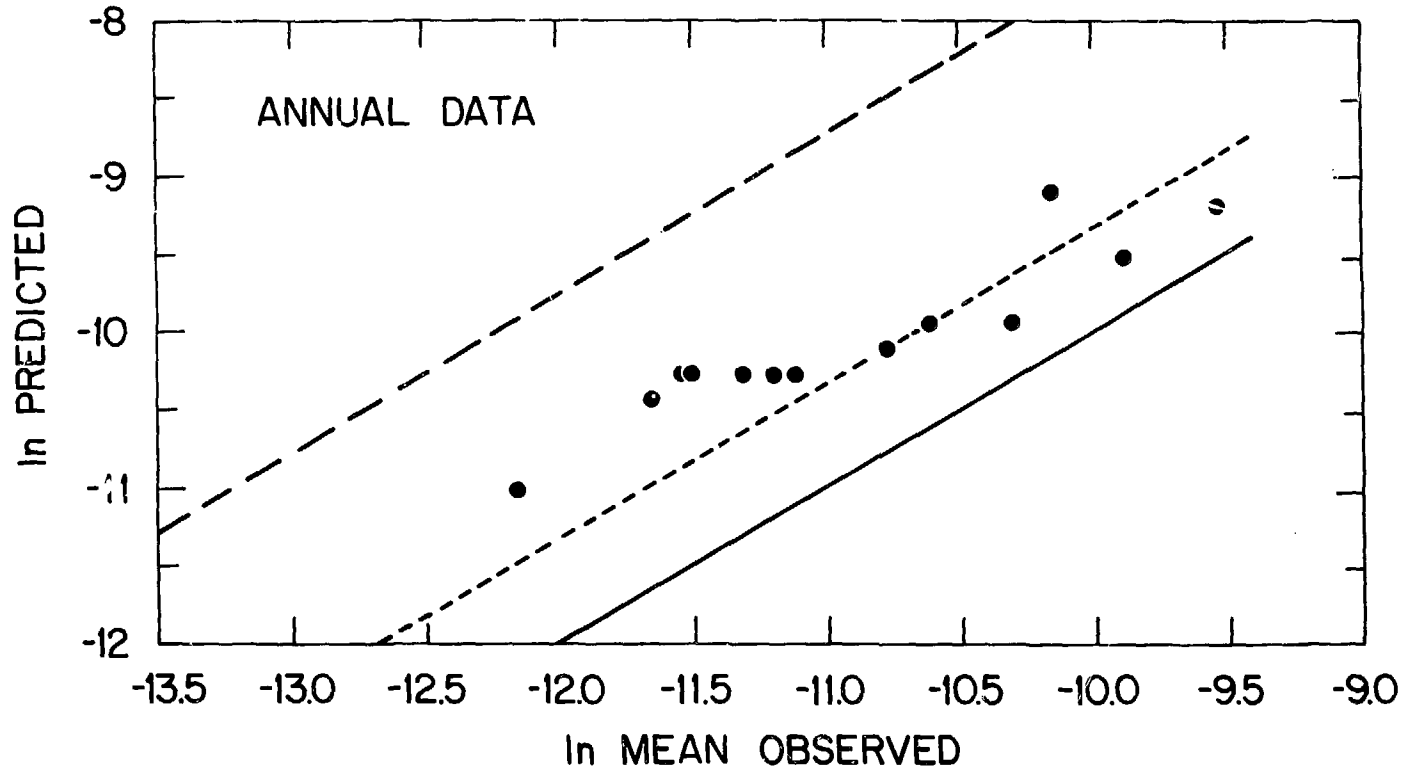


Fig. 2. Comparison of log-predicted and log-observed annual Krypton-85 ground-level concentrations at SRP monitoring stations. Values are plotted in units of  $\text{pCi}/\text{m}^3$ . The solid line implies prediction = observation; dashed line, prediction = 2 x observation; and broken line, prediction = 10 x observation.



For the ratios in Table 1,  $\mu = 0.88$  and  $\sigma = 0.37$ . If we chose  $X_A = 1$ , Eq. (4) yields  $\{Z\} = 2.38$ . For a one-tailed student's  $t$  distribution this corresponds to  $A = 98$  (Bailey, 1971). This 98th percentile result indicates that under the conditions considered in this annual average comparison we can be 98 percent confident that any value of air concentration we predict will be greater than or equal to any air concentration measured at the stations considered.

A summary of the frequency of occurrence of various predicted-to-observed ratios for the ground-level  $^{85}\text{Kr}$  seasonal average concentrations is also given in Table 2. Predicted concentrations exceed observed values in all but two cases. Spring values exhibited the lowest seasonal correlation ( $r = 0.79$ ), and only five predicted values were within a factor of 2 of the observed values. Summer values, although better correlated ( $r = 0.84$ ), were overpredicted by greater than a factor of 2 for all but one station. Fall values ( $r = 0.85$ ) and winter values ( $r = 0.88$ ) were the best correlated seasonal values and exhibited smaller overprediction factors. Six of the fall and 11 of the winter predicted values differed from the observed concentrations by less than a factor of 2.

Table 2 also includes a summary of the frequency of the ratio of predicted to observed air concentration for each of the twelve monthly averages considered in this study. The monthly results tend to show more scatter than do either the seasonal or the annual comparisons. The values of the correlation coefficient are generally lower, and there is a larger frequency of occurrence of values of the ratio greater than two and greater than ten. For example, the correlation coefficient for June ( $r = 0.89$ ) is relatively high, but all of the predictions overpredict by a factor of 2 or higher and 5 of the predicted values are overpredictions by a factor of 10 or higher. The monthly ratios also show two more ratios with values less than one, than do the other periods considered.

## DISCUSSION

The comparisons presented here assume that  $^{85}\text{Kr}$  is emitted by SRP in a continuous manner when, in fact, it is emitted intermittently. Because of the relatively long averaging times considered in this study, this assumption should not be critical to the conclusions of the study. These results also assume no significant problems with the cryogenic  $^{85}\text{Kr}$  sampling system or with the meteorological data acquisition system.

A more critical problem is the selection of a value for the limit to vertical mixing, or lid height. Simulated ground-level air-concentration values at mesoscale distances are quite dependent on this parameter. For distances at which Eq. (2) is used, computed concentration is an inverse function of lid height. Further, the effective limit to vertical mixing may be much higher than the classical lid height. For example, convective activity may serve to remove material from the lower layers of the troposphere. The presence of such activity may help explain some of the large over-prediction associated with the results for the spring and summer quarters (Garrett, 1980).

These results show the importance of considering averaging times when discussing the accuracy of Gaussian plume model air concentration predictions. The monthly comparisons were generally less accurate than the quarterly comparisons which were, in turn, generally less accurate than the annual average comparison. This decrease in accuracy with decrease in averaging time has been demonstrated previously for the Gaussian model (Little and Miller, 1978; Draxler, 1980). This trend has been attributed to the less uniform distribution of wind direction within a sector for the shorter averaging times (Draxler, 1980).

Strictly speaking, the results of this study are only applicable to the SRP site. The ORNL site, for example, has a very complex topography when compared to the relatively flat SRP terrain. AIRDOS-EPA has been compared to near-in air concentrations adjacent to the ORNL

site (Miller and Moore, 1977), and the results for this annual average comparison are very similar to those found here for the longer range SRP data. While the agreement between these two studies is encouraging, it may only be fortuitous. One should exercise great care when applying any Gaussian plume model out to 150 km in terrain as complex as that around ORNL. Only extensive validation studies carried out in such terrain can determine the true accuracy of such calculations.

No attempt has been made to judge the "acceptability" of the accuracy of results presented here. For example, are the annual average predictions too conservative, not conservative enough, or acceptable as presented? Only the user of these predictions should make this judgement. In the case of AIRDOS-EPA, the air concentration calculation portion of the code is only one part of total radiological assessment methodology. Validation studies are not available for all of the other portions of the assessment process. However, limited precision analyses indicate that in some situations the uncertainty associated with terrestrial food chain transport, dosimetry, etc., may be larger than the uncertainty associated with the atmospheric transport calculations (Schwarz and Hoffman, 1979).

## CONCLUSIONS

Comparisons have been made between observed ground-level  $^{85}\text{Kr}$  air concentrations out to 150 km downwind of a source and predicted air concentrations using a portion of the AIRDOS-EPA computer code. These predictions were made using the  $22.5^\circ$  sector-averaged form of a modified straight-line Gaussian plume atmospheric dispersion model. Comparisons were made for annual, seasonal, and monthly time periods.

There was a general tendency for the model to overpredict the observed air concentrations for the time periods considered. For the annual average case the overprediction was approximately a factor of two in value. The general accuracy of the results tended to decrease as the averaging time being considered decreased.

The results of model validation studies such as this one should be considered whenever AIRDOS-EPA or similar computer codes are applied to radiological assessment problems. The acceptability of the model accuracy indicated by such studies must be determined by the model user on the basis of the use to which the model is being applied.

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A Computerized Methodology for Evaluating the  
Long-Range Radiological Impact of Shallow-Land Burial\*

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ABSTRACT

We have implemented a computerized methodology to calculate the risk to local and intermediate-range (up to 80 km distant) populations resulting from water- and air-borne transport of radionuclides present in low-level wastes buried in shallow trenches such as those used at Oak Ridge. Our computer code, PRESTO (Prediction of Radiation Effects from Shallow Trench Operations), was developed under United States Environmental Protection Agency funding to evaluate possible health effects resulting from shallow burial operations. Sources of contamination include radionuclide releases from the trenches and from areas contaminated with operational spillage. The model is intended to predict radionuclide transport and the ensuing exposure and health impact to at-risk populations for a 1000-year period following cessation of burial ground operations. Several classes of submodels are used in PRESTO to represent "scheduled event," "unit system response," and risk evaluation processes. Examples of scheduled events are trench cap failure, stabilization of insoluble surface contaminant, the onset of farming or reclamation practices, and human intrusion. Unit system response submodels simulate processes such as infiltration of rainwater into the trench and erosion of soil overburden from the trench cover. System response submodels generate parameters used repeatedly in the 1000-year simulation loop.

Percolation of rainwater through the trench cap varies as weathering, surface erosion, and trench cap failure modify the immediate environment. Trench contents are assumed homogeneous for the extant version of the code, but algorithms may be incorporated to simulate canister failure or leaching from consolidated wastes. Radionuclide concentration in trench seepage is influenced by radionuclide solubility and seepage hydrology. Radionuclides are transported from the site principally by windblown dust, ground water, or surface water. The airborne source term is estimated using a time-dependent suspension factor and exposures are calculated using the Gaussian plume atmospheric transport formulation as implemented by Fields and Miller. Exposures from contaminated groundwater are computed assuming Darcy flow in the trench-to-aquifer region and constant velocity horizontal flow for

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the saturated aquifer domain. The combined effects of dispersion and radioactive decay in the groundwater pathway are accounted for by applying a correction term computed analytically from the integrated shape functions for dispersive and non-dispersive impulse releases in a manner similar to that described by Hung (in press). Radionuclides move at "retarded" velocities that are computed using a partitioning coefficient approach, and it appears that the transit time for the groundwater pathway is very long compared to the half-lives of most radionuclides found in low-level wastes. Exposures which result from groundwater transport include those resulting from irrigation (yielding exposures through food contaminated surface water). Exposures via the atmospheric pathway result from ingestion of contaminated food and inhalation.

The DARTAB computer code is used to combine radionuclide exposure rate values with health risk factors. The DARTAB methodology is described in reports by Dunning, Leggett and Yalcintas (1980) and Begovich et al. (1981).

## INTRODUCTION

The U. S. Environmental Protection Agency (EPA) is developing an environmental standard for the disposal of low-level radioactive waste (LLW). This standard is to be issued during 1982. The PRESTO code (Prediction of Radiation Effects from Shallow Trench Operations) is designed to allow the EPA to assess the impacts of shallow land burial under numerous situations in support of the standard development activities. The model is intended to predict radionuclide transport and the ensuing exposure and health impact to a local stable population for a 1000-year period following closure of the burial grounds.

The major portion of the PRESTO model development project is the development and implementation of an appropriate transport methodology and combination of these methodologies with a methodology for the calculation of ensuing risk. A second subtask consists of the identification and consideration of at-risk populations. Finally, we will apply the complete model to estimate the 1000-year impact of three major existing low-level waste shallow-land burial sites.



## TRANSPORT METHODOLOGY

Radionuclides are transported from the site principally by windblown dust, ground water, or surface water. Figure 1 summarizes the major pathways of aqueous transport accounted for in the PRESTO code. Transport processes shown in this figure are modeled with resolution of one year. Radionuclide output from the trench is strongly dependent on net infiltration input from the surface as computed by a modified version of Morton's evapotranspiration model (Morton 1976, 1978). As discussed in the introduction, infiltration is a function of cap status (a time-varying user input term) and surface modification by farming and/or intrusion.

Percolation of rainwater through the trench cap varies as weathering, surface erosion, and trench cap failure modify the immediate environment. Trench contents are presently assumed to be homogeneous but algorithms are being considered to simulate canister failure or leaching from consolidated wastes. Radionuclide concentration in trench seepage is influenced by radionuclide solubility and seepage hydrology. Exposures from contaminated groundwater are computed assuming Darcy flow in the trench-to-aquifer region and constant velocity non-dispersive horizontal flow for the saturated aquifer domain.

The combined effects of dispersion and radioactive decay in the aquifer are accounted for by applying a correction term computed analytically from the integrated shape functions for dispersive and non-dispersive impulse releases in a manner similar to that described by Hung (in press). Radionuclides move at "retarded" velocities relative to water that are computed using a partitioning coefficient approach, and it appears that the transit

time through the groundwater pathway is very long compared to the half-lives of the most commonly buried radionuclides. Exposures which result from radionuclide transport involving groundwater include those resulting from irrigation (yielding exposures through food contamination pathways) and direct ingestion of well water or contaminated surface water.

Atmospheric transport pathways are presented in Figure 2. Mobilization of dust is simulated by applying either a time-dependent resuspension factor (Anspaugh et al., 1975) or a resuspension rate (Healy, 1980) computation. Atmospheric transport is modeled using a Gaussian plume atmospheric transport formulation (Gifford, 1968) as modeled by Fields and Miller (1980).

The DARTAB computer code is used to combine radionuclide exposure rates with health risk factors. The DARTAB methodology is a life-table approach based on the RADRISK model described in reports by Dunning, Leggett and Yalcintas (1980) and Begovich et al. (1981).

#### MODEL ASSUMPTIONS

Transport-related computations are simplified by several model assumptions. First, daughter products of decay are not calculated because, for the most part, the inventory of commercial low-level waste burial grounds includes few radionuclides that are part of long chains. Chemical reactions are not modeled in detail, but are parameterized using factors such as the chemical exchange coefficient,  $K_d$ . Waste material in the trench is considered to be effectively homogeneous in terms of radionuclide distribution and type of material; i.e., no canister containment will be modeled. Groundwater transport is one-dimensional through a "tube" from

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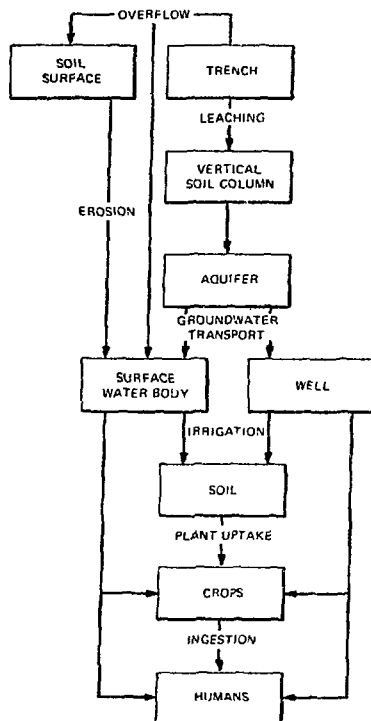


Fig. 1. Major pathways of water transport in PRESTO.

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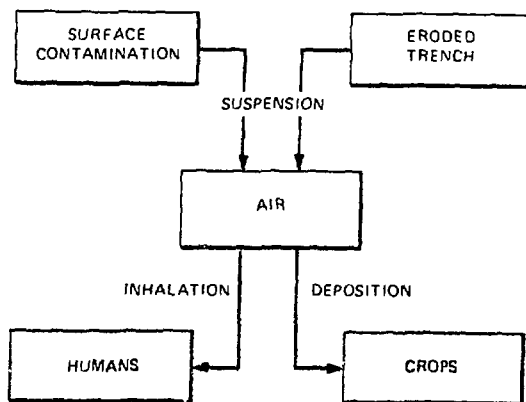


Fig. 2. Pathways of air transport considered in PRESTO.

the point of radionuclide input below the trench directly to a surface water body or well. A correction factor (Hung, in press) is calculated and applied to account for the combined effects of radioactive decay and dispersion in the groundwater pathway.

### PROGRAM STRUCTURE

The PRESTO code is structured in a modular form to permit simple upgrading or replacement of given submodels without rewriting the entire code. The code is written for an IBM 360 computer system to be operated in batch mode. The MAIN program accepts initialization and input data from an input subroutine and calls the process subprograms as needed. The subprogram structure is illustrated in Figure 3, which schematizes information flow within the model. All major subroutine blocks are called from the MAIN program. During a model run, the MAIN program may access the following submodels:

EVAP0. This unit response submodel is an adaptation of Morton's model (Morton, 1976, 1978), and calculates evapotranspiration as a function of continental location, time of year, precipitation, temperature, barometric pressure, and cloudiness. The output is combined with runoff and precipitation values to yield an annual average infiltration rate into the trench. The status of the trench cap modifies the rate and amount of infiltration. We assume that the breached portion of the cap supports no evapotranspiration; all precipitation falling on the breached region of the trench becomes available for leaching. Infiltration rates are also fed into the soluble surface component subroutine, SURSOL.

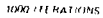


Fig. 3. Information flow between submodels in the PRESTO code.

ERORF. This unit response subroutine calculates the rate of erosion of soil from the trench cap and surrounding surfaces. Erosion by rainfall is calculated using an adaptation of the universal soil loss equation as described by the U. S. Department of Agriculture (USDA, 1961) and parameterized by McElroy et al. (1976). ERORF feeds information to the cap status algorithm that changes the relative rates of infiltration and evapotranspiration. ERORF also provides the amount of eroded soil into the INSOL subroutine.

AIRTR. This group of subroutines calculates the unit response of the Gaussian Plume model (Gifford, 1968). AIRTR is an adaptation of the interactive code DWNWND (Fields and Miller, 1980) and accepts both user input data and the suspended mass load to calculate a  $\chi/Q$  value for each impacted population.

SUSPEN. This submodel calculates the rate of suspension of soil from the ground surface as a time-dependent factor. The model equation as parameterized by Anspaugh et al. (1975) was used for this code. For the farming scenario, SUSPEN calculates mass loading of the atmosphere from mechanical tillage of the soil using a resuspension rate parameter.

TRENCH. This subroutine maintains a trench water budget and feeds the water content of the stored material into the LEACH code. As mentioned above, the water budget of the trench is affected by both cap status and precipitation or infiltration.

LEACH. The leaching subroutine accepts information about the annual water budget from TRENCH and the radionuclide inventory from the source input to calculate the rate of dissolution of materials within the trench. Depending on the conditions of loss from the trench, either downward leaching or trench overflow, the information is passed to either the VERT

or SURF codes. LEACH is formulated to contend with homogenized trench contents, but may ultimately be upgraded to consider canistered waste.

VERT. The VERT subroutine accepts user information about soil characteristics and depth of aquifer as well as the radionuclide concentrations and hydrologic data calculated by the LEACH code. Output from VERT is the annual amount of each nuclide added to the aquifer, the total water added to the aquifer from the vertical column, and the transit time of vertical radionuclide movement.

AQUIF. The AQUIF subroutine accepts user input about groundwater velocity, distribution coefficient (retardation coefficient), porosity, etc. Input from VERT includes the annual trench contribution to the aquifer water balance and the annual amount of water and radionuclide concentration to appropriate wells and groundwater-fed surface water used for irrigation or drinking.

SURF. User input to the SURF subroutine includes the annual rate of stream flow and location of the stream. Information flow into SURF from the other codes includes annual water input and radionuclide concentration from LEACH, SURSOL, and INSOL. SURF output is annual water budget and radionuclide concentration for that portion of irrigation water taken from surface sources.

SURSOL. The soluble component of operational spillage is transported to surface water bodies in SURSOL. Surface contamination (operational spillage) is assumed never to reach the aquifer. Input includes the radionuclide contamination of the soil surface and the rate of infiltration into the active soil exchange region (from EVAPO).

INSOL. The insoluble component of operational spillage may be transported to the surface water via INSOL. The annual rate of soil erosion is input to INSOL by ERORF along with the radionuclide concentrations of the surface soil.

AIRCON. This subroutine combines the unit response  $\lambda/Q$ , generated by AIRTR for each pertinent location, with radionuclides suspended in the air from the surface soil by SUSPEN to calculate the downwind radionuclide concentrations in air. AIRCON will output these data for use as deposition terms into the foodchain (FOODCH) and human inhalation (HUMEX) submodels.

IRRIG. Foods may be irrigated with contaminated water from either surface or groundwater sources. Input to IRRIG consists of the necessary user inputs and either the integrated or time-averaged radionuclide concentration in the water used for irrigation. IRRIG, which in function is similar to FOODCH, calculates the integrated or time-averaged radionuclide concentration from both deposition and root uptake in foodcrops, milk, and meat for human consumption.

FOODCH. Foods may be contaminated by atmospheric deposition and root uptake. FOODCH accepts user input and radionuclide concentration in air calculated by AIRCON to calculate nuclide concentrations in crops, meat, and milk for use by HUMEX. The equations used are basically those of the *USNRC Regulatory Guide 1.109* (USNRC, 1977).

HUMEX. The human exposure subroutine accepts user input and time-integrated or averaged data from AIRCON, FOODCH, IRRIG, and AQUIF. AIRCON will provide radionuclide concentrations in air for inhalation calculations. FOODCH and IRRIG will furnish radionuclide concentrations in foodstuffs for ingestion calculations.



DARTAB. This large routine accepts output from HUMEX and, using the RADRISK methodology, calculates and outputs risk and dose estimates according to numerous user-specific options for table format. RADRISK (Dunning et al., 1981) is a life-table approach to calculating the human health risk to a cohort of  $10^5$  people from a constant input of 1 pCi/y (0.037 Bq/y) for a lifetime (70.7 y). RADRISK is called by DARTAB, not by the MAIN program. DARTAB (Begovich et al., 1981) categorizes data and provides numerous tabular output options.

#### IDENTIFICATION OF AT-RISK POPULATIONS

PRESTO is intended to compute doses and risks over a 1000-year assessment period following closure of a shallow-land radioactive waste burial ground. The code is designed to permit flexibility in specifying the population of interest. At-risk populations may be presumed to reside at the following locations: (1) the geographic centroids of present off-site population centers; (2) the site boundary; or (3) within the extant boundary of the burial site itself. For example, populations of type (1) may have the number of individuals of currently local population centers. The population age distribution is that determined for the United States in the 1970 census. These individuals ingest off-site food and water and breathe off-site air. An example of the type (2) population is the farmer who is assumed to inhale suspended soil at the site. The type (3) population may represent an individual who actually lives on the reclaimed site. This maximally exposed individual, termed an intruder, may be assumed to ingest trench well water and incur an additional exposure

from residency in an excavated trench. The model is, therefore, designed to afford the user considerable flexibility in determining health effects on at-risk populations.

### CONCLUSIONS

The PRESTO model has been formulated to permit assessment of extant and proposed shallow-land radioactive disposal sites for the 1000-year period following site closure. The program is modular and is sufficiently versatile to allow consideration of representative populations and exposure scenarios.

Data are being compiled for application of the model to existing burial sites at Barnwell, South Carolina; Beatty, Nevada; and West Valley, New York.

Coding of the PRESTO model is approximately 80% complete; the code and a user's manual for the model will be released later in 1981.

### ACKNOWLEDGEMENTS

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