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1987 OAK RIDGE MODEL CONFERENCE

PROCEEDINGS

**Waste Management
Volume I
Part 3**

sponsored by

**The Department of Energy/Oak Ridge Operations
Research and Waste Management Division
and
Martin Marietta Energy Systems, Inc.**

Prepared by
ANALYSAS CORPORATION

Printed by
MARTIN MARIETTA ENERGY SYSTEMS, INC.
for the
U.S. DEPARTMENT OF ENERGY
under Contract No. DE-AC05-84OR21400

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**WASTE MANAGEMENT
SESSIONS
PART 3**

Overview of DOE's Transuranic Waste Program

Presented by:

M. H. McFadden, DOE/ALO

**OVERVIEW OF DOE'S
TRANSURANIC WASTE PROGRAM**

M. H. McFadden, U.S. Department of Energy
J. A. Detamore, Rockwell International Corp.

ABSTRACT

The United States Department of Energy has assigned to Albuquerque Operations the Defense Transuranic Waste Program responsibility for long-range planning and management of defense transuranic (TRU) waste. The Transuranic Waste Lead Organization (TLO) has divided the Program into seven elements which support its primary goal of ending interim storage and achieving permanent disposal. These are: waste generation site activities, storage site activities, burial site activities, technology development, transportation, institutional activities, and permanent disposal. This paper will briefly discuss these seven elements and how they are integrated to provide for successful achievement of the primary goal.

BACKGROUND

The defense TRU waste management program and its associated long-range planning activities are described in The Defense Waste Management Plan and The Long Range Master Plan for Defense Transuranic Waste Management (References 1-2). Since 1970, defense TRU waste has been retrievably stored at six Department of Energy (DOE) sites, pending selection and development of permanent disposal methods. There are, at present, approximately 90,000 cubic meters of retrievably stored contact-handled TRU waste at DOE sites, and new contact-handled waste is being generated at the rate of about 4,100 cubic meters per year. Additionally, there are approximately 1,400 cubic meters of remote-handled TRU waste in storage, with a projected generation rate of about 25 cubic meters per year through 1996.

Buried TRU waste is waste that was disposed along with low-level waste in shallow land fills prior to the implementation of retrievable waste storage in the early 1970's. Currently, estimates on the volumes of waste show

that there are about 192,000 cubic meters of TRU solid waste. Associated with this waste is contaminated soil resulting from breached containers. It is estimated that around 220,000-320,000 cubic meters of contaminated TRU soil exist.

In January, 1981, the DOE Assistant Secretary for Defense Programs issued a Record of Decision for the Waste Isolation Pilot Plant (WIPP), stating that DOE would proceed with the WIPP on a phased basis, starting with site and design validation, then construction of permanent facilities for research and demonstration. In July, 1983, DOE announced its decision to proceed with construction of the full WIPP. In June, 1983, President Reagan submitted to Congress The Defense Waste Management Plan, Reference 1, describing reference plans for the permanent disposal of high-level and transuranic wastes from defense programs.

The Long-Range Master Plan for Defense Transuranic Waste Program, Reference 2, expands on these reference plans for the TRU waste program, by providing a framework for detailed planning at each of the storage and generating sites. Schedules have been identified for design, construction, storage, retrieval, processing, and shipping activities over the period from the present to 2015, with particular emphasis on activities in the 1980s and early 1990s. Development of the Long-Range Master Plan has provided a vehicle for identification of program needs and for documenting a unified long-range strategy for all sites. This will be a "living" document, updated frequently to reflect progress and evolving site plans, all within a reference framework.

TRU PROGRAM GOAL

It is the goal of the DTWP to end interim storage and achieve permanent disposal of TRU waste. To accomplish this goal, as much TRU waste as possible will be certified to meet the WIPP Waste Acceptance Criteria (WAC). The certified waste will then be disposed of at WIPP. The small quantity of waste which is not practical to certify will be disposed of via an alternate disposal method.

Some waste will require processing to be certifiable. Hanford, the Idaho National Engineering Laboratory (INEL), the Savannah River Plant (SRP), and the Los Alamos National

Laboratory (LANL), are all going to build CH waste processing facilities. The Oak Ridge National Laboratory (ORNL) will develop a minimal CH waste repackaging capability. ORNL will have the only RH waste processing facility. No new facilities are currently planned for the Nevada Test Site (NTS), the Rocky Flats Plant (RFP), and the other small generators (Argonne National Laboratory-East, Lawrence Livermore National Laboratory, Mound, and Bettis).

SEVEN ELEMENTS

The TLO has divided the TRU Program into seven elements which support its primary goal. These are: waste generation site activities, storage site activities, burial site activities, technology development, transportation, institutional activities, and permanent disposal.

Waste Generation and Storage Site Activities

It is DOE policy that newly-generated waste be examined, sorted, processed if necessary, certified, and sent to WIPP for disposal. Currently, more than 90% of all newly-generated CH waste is being generated in certifiable form. When WIPP opens in October 1988, newly-generated waste will be given priority for emplacement.

A mobile non-destructive assay/examination (NDA/NDE) unit has been developed to provide for certification at small-site generators that are not building facilities. Larger sites will have permanent facilities.

Hanford is certifying on-site newly-generated CH waste in the Transuranic Storage and Assay Facility (TRUSAF). Processing of those wastes that require it will occur in the Waste Receiving and Processing (WRAP) facility. WRAP is scheduled to go operational in 1999, it will shred and grout CH TRU waste that requires processing for certification.

INEL has built the Stored Waste Examination Pilot Plant (SWEPP) to certify newly-generated and stored waste. Any CH waste which requires processing will be placed in storage until the Process Experimental Pilot Plant (PREPP) begins hot operations in FY 98. PREPP will shred, incinerate, and solidify waste so that it meets the WIPP WAC.

The ORNL is examining and certifying CH waste in the Waste Examination and Assay Facility (WEAF). Any CH waste requiring more extensive processing will be sent to the RH Waste Handling Pilot Plant (WHPP). The WHPP will be the only RH processing facility in the system. It will process all of ORNL's RH waste and will also receive and process RH waste from other sites. WHPP will be operational in 1996.

SRP is in the process of certifying CH waste in the Waste Certification Facility (WCF). The second phase of this project will include transportation loading capabilities. Waste requiring processing will be stored and processed in the Transuranic Waste Facility (TWF), which will begin operation in 1995. SRP has no RH waste.

LANL will use several small facilities to retrieve, process, and certify their waste. These facilities include the Waste Preparation Facility to clean and integrity check retrieved waste; the NDA/NDE facility to certify waste; the Waste Processing Facility to open, sort, shred, and grout wastes which require that type of processing; the Size Reduction Facility to handle oversized packages; the Treatment Development Facility to incinerate combustibles; and the TRU Transportation Facility to load transportation containers.

RFP is the single largest producer of CH TRU waste. Approximately 2300 cubic meters per year is projected to be produced over the next ten years. Currently, 95% of its newly-generated waste is certifiable. The remaining 5% is expected to be certifiable in 1987.

Burial Site Activities

Prior to 1970, there was no TRU waste classification, and radioactive waste contaminated with TRU elements was disposed of as low-level waste (LLW). This waste is referred to "buried solid waste, and contaminated soil". Contaminated soil falls into two categories: soil contaminated by being exposed to solid waste disposal, and soil contaminated through liquid waste injection in soil as a disposal method. Currently, there is estimated to be about 220,000-320,000 cubic meters of TRU contaminated buried waste. The TLO has prepared a Comprehensive Implementation Plan for DOE Defense TRU-Contaminated Buried Waste (CIP) which outlines the TLO's Plan for buried TRU waste. This Plan includes inventories, schedules, cost

estimates, and alternatives.

Each DOE Operations Office is responsible for developing and implementing plans for long-term management of its radioactive and hazardous waste sites. In doing this, Operations Offices must deal with unique technical, environmental, and institutional requirements existing at each site, while ensuring that all applicable federal and state laws and regulations and DOE Orders are complied with.

Each site is evaluating three broad alternatives to manage its buried waste and contaminated soil: 1) enhanced monitoring/no remedial action, 2) enhanced confinement through in situ stabilization, and 3) waste exhumation and disposal. The final action taken at any site could be any combination of these alternatives.

Technology Development

The TLO is currently funding technology development activities associated with the reduction of waste arisings and environmental compliance.

For several years, the TLO has funded activities designed to reduce the amount of waste generated during normal operations at the sites. To date, this work has many successes. First, a new composite coating system has been developed for casting molds used in the production of nuclear weapons components which is estimated to save several million dollars. Also, it was discovered that there was no need to immobilize HEPA filters at the RFP in order to certify for emplacement at WIPP. This should save several millions of dollars. Also, a pre-filter system was developed for HEPA filter systems which should save about 400K/year.

Currently, an exciting technology from Japan is being analyzed at RFP which utilizes microwaves to volume reduce process sludges. Also, work is being performed investigating the feasibility of assaying waste at the generation point to separate LLW from TRU, and also work is being done looking at processes in order to find equipment and/or material replacements which are more durable or have smaller volumes.

The TLO is also funding activities which are looking into developing covers for buried waste pits, developing

grouts for immobilizing waste in a trench, assaying waste in place, vitrifying waste in place, and using fiber optics to detect migration of waste. All of these technologies are being developed to facilitate the compliance of DOE sites with applicable regulations.

Transportation

The TLO is developing transportation packages for both CH waste and RH waste. The CH TRU waste transporter is presently in the final stages of development. This TRANSURANIC PACKAGE TRANSPORTER is called TRUPACT and is being specifically designed to transport CH TRU waste from interim waste storage and generating facilities to WIPP for final emplacement. TRUPACT-II design is currently in progress. TRUPACT-II will be submitted for certification by the Nuclear Regulatory Commission (NRC) and will be a Type B package with double containment and no filtered pressure relief system.

TRUPACT-II is a right circular cylinder with dimensions that will allow for transportation of three TRUPACTs and a total payload of 20,000 pounds per truck shipment. This drum package will be able to accommodate approximately 90% of the TRU contact-handled waste in the system. A box TRUPACT is being investigated which will accommodate the remaining 10% of the waste. The final transportation fleet is projected to consist of 16 TRUPACTs.

RH waste will be transported to WIPP in Type B packages which are currently being designed and tested specifically for RH canisters. Completion of testing, preparation of a Safety Analysis Report for Packaging (SARP), Certification by the NRC, and fabrication of two casks is scheduled for May 1989 to support the RH demonstration period at WIPP.

In addition to the canister cask, a drum cask will be evaluated. Shipping in drums is more cost-effective because waste handling at production sites is decreased and because more waste can be shipped in each shipment. The use of the drum cask does not alleviate the need for the canister cask. This is because some wastes may have dose rates that are too high to be used in the drum cask and some wastes have geometries that do not allow them to be put into 55-gallon drums.

Also, the DOE is developing a satellite tracking system

which will be capable of tracking all TRU waste shipments in the U. S. It will also be able to pre-notify states of shipments and identify whether an emergency exists. This is all part of a system to be called TRUSYSTEM which will perform logistics analyses and provide real time data base reports.

Transportation dispatching and control will be performed at the WIPP site with the assistance of the TRUSYSTEM computer network. A carrier will be contracted to provide tractors and driving teams which will meet predetermined requirements. The DOE will provide the transporter package and the trailer. Predetermined routes will be followed and the two driver teams will drive around the clock in order to minimize transportation time. The central dispatching center will determine where these driving teams will proceed to next, the routes they should use, and road conditions along the way. The TRUSYSTEM will be able to track their progress at all times and notify the appropriate persons if any problem should arise.

Institutional Activities

The TLO is currently contacting all states that TRU waste is expected to be transported through. Plans are that each state will be met with to discuss routing, emergency response, pre-notification, etc. To date, all of the states in the western U.S. have been met with individually. The southeastern states have been met with as a group. Individual state follow-up meetings are scheduled to be complete by the Spring of 1988. Other meetings as needed will continue through 1988.

The DOE has entered into an Agreement for Consultation and Cooperation with the State of New Mexico which outlines the roles played by all the players in achieving the WIPP mission.

Permanent Disposal

The WIPP consists of surface and subsurface facilities, including a waste handling and transfer building, ancillary buildings, and shafts leading to an underground salt formation with a mined area of about 100 acres for TRU wastes plus an additional 20 acres for high-level waste experiments. The WIPP is designed for underground emplacement of approximately 180,000 cubic meters of CH TRU

and 7,000 cubic meters of RH TRU.

The full design capability of the WIPP will not be utilized until sufficient operating and scientific data have been accumulated, beginning in 10/88 and lasting for a period of up to five years, to ensure the safe long-term disposal of radioactive waste in salt. The TLO is doing an alternative analysis to determine what course of action should be taken if it is determined that the WIPP does not meet long-term storage requirements.

At the end of the WIPP operation, the high-level radioactive waste experiments will be removed and a decommissioning program will be carried out for the safe permanent disposition of both surface and underground facilities.

PROGRAM INTEGRATION

The TLO provides technical planning and guidance for the development of advanced TRU waste management capabilities. Its responsibilities include assuring the TRU waste program requirements and needs for equipment/facility design, engineering, and construction; and operations are integrated to allow transition from interim storage to final disposition. Tasks include program requirements identification; long-range planning document preparation; task guidance development; task monitoring; and task progress information gathering and reporting to DOE; interfacing with other agencies, activities, and DOE lead programs; integrating public involvement with program efforts; and preparation of reports for DOE detailing program status.

All of the above mentioned activities and more comprise the TRU Waste Management Program. It is a program that is dynamic and very close to emplacing waste in a deep geologic repository... the WIPP.

REFERENCES

1. "The Defense Waste Management Plan," DOE/DP-0015, June 1983.
2. "Long-Range Master Plan for Defense Transuranic Waste Management," DOE-JIO-023, July 1987.

**DOE's Plan for Buried Transuranic –
Contaminated Waste**

Presented by:

**Julie D'Ambrosia,
Automated Sciences Group, Inc.**

Abstract

DOE'S PLAN FOR BURIED TRANSURANIC (TRU) CONTAMINATED WASTE

John Mathur

U.S. Department of Energy, Germantown, MD 20545

Julie D'Ambrosia and John Sease

Automated Sciences Group, Inc., Oak Ridge, TN 37830

Prior to 1970, TRU-contaminated waste was buried as low-level radioactive waste. In the Defense Waste Management Plan issued in 1983, the plan for this buried TRU-contaminated waste was to monitor the buried waste, take remedial actions, and to periodically evaluate the safety of the waste. In March 1986, the General Accounting Office (GAO) recommended that the Department of Energy (DOE) provide specific plans and cost estimates related to buried TRU-contaminated waste. This plan is in direct response to the GAO request.

Buried TRU-contaminated waste and TRU-contaminated soil are located in numerous inactive disposal units at five DOE sites. The total volume of this material is estimated to be about 300,000 to 500,000 m³.

The DOE plan for TRU-contaminated buried waste and TRU-contaminated soil is to characterize the disposal units; assess the potential impacts from the waste on workers, the surrounding population, and the environment; evaluate the need for remedial actions; assess the remedial action alternatives; and implement and verify the remedial actions as appropriate.

Cost estimates for remedial actions for the buried TRU-contaminated waste are highly uncertain, but they range from several hundred million to the order of \$10 billion.

DOE'S PLAN FOR BURIED TRANSURANIC-CONTAMINATED WASTE

John Mathur

U.S. Department of Energy

Germantown, MD 20545

Julie D'Ambrosia and John Sease

Automated Sciences Group, Inc.

Oak Ridge, TN 37830

INTRODUCTION

The Defense Waste Management Plan or DWMP (DOE/DP-0015) was issued in 1985 by the U.S. Department of Energy (DOE). The Plan provided a workable approach for permanent disposal of high-level and transuranic (TRU) waste from defense activities. As shown in the DWMP, the objectives for TRU waste management are to: (1) minimize addition to the backlog of already stored waste by establishing procedures and facilities to dispose of the newly generated waste routinely, safely, and effectively; (2) begin certification and disposal of stored TRU waste by funding processing facilities and pursuing the Waste Isolation Pilot Plant as a geologic repository; and (3) monitor the buried waste and contaminated soil, take remedial actions as necessary, and periodically reevaluate the safety of the waste.

In March 1986, after a review of the entire Department of Energy TRU Waste Management Program, the General Accounting Office recommended that DOE provide more specific plans and cost estimates for managing the buried TRU-contaminated waste, TRU-contaminated soil, and difficult-to-certify TRU waste. DOE's response to these recommendations is contained in the Defense Waste Management Plan for Buried Transuranic-Contaminated Waste, Transuranic-Contaminated Soil, and Difficult-to-Certify Transuranic Waste (DOE/DP-0044). The Plan was transmitted to the Congress in July 1987. This paper summarizes the information contained in the Plan regarding management of buried TRU-contaminated waste and TRU-contaminated soil. Additional details

on these waste types and DOE's plans for managing the difficult-to-certify TRU waste can be obtained from the Plan.

WASTE SITES

Buried TRU-contaminated waste and TRU-contaminated soil are located in numerous inactive disposal units at five DOE sites: Idaho National Engineering Laboratory (INEL) near Idaho Falls, Idaho; Oak Ridge National Laboratory (ORNL) at Oak Ridge, Tennessee; the Savannah River Plant (SRP) near Aiken, South Carolina; the Hanford Reservation (HANF) near Richland, Washington; and Los Alamos National Laboratory (LANL) at Los Alamos, New Mexico. The total volume of buried TRU-contaminated waste is about 140,000 m³ and contains about 125,00 Ci of alpha radioactivity (Table 1). TRU-contaminated soil comprises about 180,000-300,000 m³ and is estimated to contain at least 21,000 Ci of alpha radioactivity (Table 2).

Each of these DOE sites began operation at different times, has produced distinctly different waste streams, is located in different and discrete hydrogeologic settings, has different environmental issues which require resolution, and is within the jurisdiction of different state or regional offices of regulatory agencies. For these reasons, environmental monitoring activities, proposed remedial action evaluations or plans, and schedules are all managed on a site-by-site basis, with overview and guidance provided by DOE Headquarters.

REMEDIAL ACTION PLANNING

DOE is committed to meeting all applicable statutes, regulations, and orders. DOE's goal is to manage this and all waste programs in a manner that will appropriately protect the environment and the public, including all those who work at the DOE installations. Consistent with DOE orders, regulations, and statutes, each DOE site is conducting a program to ensure that relevant data are evaluated prior to the selection of a management alternative for the buried TRU-contaminated waste and TRU-contaminated soil. These programs are designed to meet the

TABLE 1
ESTIMATED VOLUME AND TRU
RADIOACTIVITY CONTENT OF BURIED WASTE^a

| Storage Site | Volume (m ³) | Alpha Radioactivity (Ci) |
|-------------------|--------------------------|--------------------------|
| | Buried Waste | |
| HANF | 70,000 | 33,000 |
| INEL | 57,100 | 73,300 |
| LANL ^b | 14,000 | 9,200 |
| ORNL | 6,200 | < 300 |
| SRP | <u>4,500</u> | <u>9,800</u> |
| Total | 151,800 | 125,600 |

- a) Consistent with data as of December 1986, to be reported in the next annual revision of the "Integrated Data Base: Spent Fuel and Radioactive Waste Inventories, Projections, and Characteristics", DOE/RW-0006, Rev. 2 (September 1986). (All numbers are rounded to the nearest hundred.)
- b) Includes 3 m³ of waste buried at Sandia National Laboratories, Albuquerque, New Mexico.

TABLE 2
 ESTIMATED VOLUME AND TRU RADIOACTIVITY
 CONTENT OF CONTAMINATED SOIL

| | Associated with Solid Waste | Associated with Liquid Waste | Alpha Radio- activity (Ci) |
|-------|-----------------------------------|------------------------------------|----------------------------------|
| HANF | 40,000 | 32,000 | 18,000 ^a |
| INEL | 56,600-156,000 | 0 | b |
| LANL | 1,000 | 100 | b |
| ORNL | 12,000-60,000 | ≤1,000 | b |
| SRP | <u><38,000</u> | <u>0</u> | <u>3,600</u> |
| Total | 147,600-295,000 | ≤33,100 | 21,600 |

a) Associated with liquid discharges.

b) Reported as unknown or less than 10.

requirements of the Resource Conservation and Recovery Act (RCRA); the Comprehensive Environmental Response, Compensation, and Liability Act/Superfund Amendments and Reauthorization Act (CERCLA/SARA); the National Environmental Policy Act (NEPA); and any other laws and applicable regulations; and to protect the surrounding population and environment over the short and long terms (Table 3).

Until 1980, methods used for radioactive waste disposal were assumed to safely isolate the hazardous components of the waste; monitoring for radionuclide migration was assumed to provide information on hazardous constituent movement. When DOE Order 5480.14 was issued to implement CERCLA, sites began planning activities for determining hazardous waste components in the buried waste as well as appropriate remedial actions for these components. Each site has developed a schedule for meeting the requirements of CERCLA, its amendment (SARA, passed in 1986), or RCRA, depending on the guidance that site has received from its regulatory agencies. However, regardless of the specific regulation or order being followed at a given site, the end results for all sites will be the same.

In short, DOE's plan for buried TRU-contaminated waste and TRU-contaminated soil is to characterize the disposal units; assess the potential impacts from the waste on workers, the surrounding population, and the environment; evaluate the need for remedial actions; assess the remedial action alternatives; and implement and verify remedial actions as appropriate. This is the same approach DOE will use to manage all other waste disposal units containing hazardous constituents. All assessments and remedial actions will be conducted in accordance with applicable environmental laws for inactive disposal units.

PLANNING ALTERNATIVES

For costing purposes, three generic planning alternatives are considered for buried TRU-contaminated waste and TRU-contaminated soil.

TABLE 3
COMPARISON OF CERCLA, RCRA, AND
DOE ORDER 5480.14 RESPONSE PROCESSES

| CERCLA | RCRA | DOE ORDER 5480.14 |
|--|-------------------------------------|--|
| Site discovery/notification | | |
| Preliminary assessment and site inspection | Facility assessment | Phase I -Instal- lation Assessment |
| Scoring priorities for remedial action hazard ranking system | | |
| Remedial investigation | Facility investi- gation | Phase II - Confirmation/ Qualification |
| Feasibility study | Corrective measures study | Phase III - Engineering Assessment |
| Remedial action design and construction ^a | Corrective measures ^a | Phase IV - Remedial Action Phase V - Compliance and Verification |

^a Under RCRA and CERCLA, maintenance, monitoring, and verification (equivalent to Phase V of DOE Order 5480.14) are considered as part of the remedial actions and corrective measures.

1. Leave the waste in place with continued monitoring and surveillance until closure is achieved.
2. Leave the waste in place but improve the confinement and continue monitoring and surveillance until closure is achieved.
3. Exhume, process, certify, and dispose of the TRU waste in a repository; segregate the low-level waste for disposal.

Alternative three assumes that a certain fraction of the exhumed waste would not be contaminated to 100 nCi/g of TRU radionuclides. This would not be TRU waste, would not require repository disposal, and therefore would be disposed of as mixed or radioactive waste, as appropriate.

These planning alternatives represent the broad spectrum of options that may be considered during assessment of alternatives for a specific disposal unit. The alternatives are not intended to represent actual selected options nor to imply preselection of any particular planning alternative for any specific disposal unit. The alternative selection process for all disposal units will be performed by DOE in accordance with applicable statutes, regulations, and orders.

Since all decisions for buried TRU-contaminated waste and TRU-contaminated soil will be disposal-unit-specific, it is possible that the evaluation and selection process may lead to implementation of different alternatives for different disposal units on a single DOE site.

COSTS AND SCHEDULE

Cost estimates for remedial actions for the buried TRU-contaminated waste and TRU-contaminated soil are highly uncertain because the characterization of the disposal units has not yet been completed. Site-specific (rough order-of-magnitude) cost estimates have been prepared (Table 4).

Since these cost estimates are site-specific, there are differences among the elements considered in each estimate. The

TABLE 4

ESTIMATED COSTS FOR BURIED WASTE
AND CONTAMINATED SOIL DISPOSITION (\$M)^a

| Activity | Planning Alter- native 1 | Planning Alter- native 2 | Planning Alter- native 3 |
|---|--------------------------------|--------------------------------|--------------------------------|
| Site-specific ^b | 200-500 | 600-2000 | 4000-7000 |
| LLW disposal | 0 | 0 | 70-700 |
| Geologic repository ^c | | | |
| Transportation | 0 | 0 | 150 |
| Construction | 0 | 0 | 420 |
| Operation | 0 | 0 | 1600 |
| Decontamination and decommissioning ^d | 0 | 0 | 10 |
| Total alternative costs | 200-500 | 600-2000 | 6000-10,000 |

- a) All costs in constant 1987 dollars; totals are rounded to 1 significant figure.
- b) These costs are based on site-specific estimates. There are differences among the elements considered in the site-specific estimates. The individual estimates are discussed in "Comprehensive Implementation Plan for DOE Defense Buried TRU-Contaminated Waste". These estimates are not budget quality; they will be refined as additional data are developed and uncertainties are resolved.
- c) Cost based on WIPP costs.
- d) Assumed to be \$10M for above-surface facilities.

estimates are not budget quality, and will be refined as the characterization activity proceeds and additional data are developed to resolve the uncertainties.

The schedule for implementing remedial actions at the various sites cannot be determined at this time. Remedial action planning that is being conducted at each site has not progressed to a stage where an implementation schedule can be developed. This schedule will be developed after the disposal units have been characterized.

CONCLUSION

The Department of Energy is committed to meeting all applicable statutes, regulations, and orders in managing its waste. In addition, the environment, public, and workers will also be protected. Site-specific disposal until characterization is underway, and remedial action planning for the disposal units will begin as soon as sufficient data are available. Cost estimates for meeting all applicable statutes, regulations, and orders are highly uncertain, but appear to range from several hundred million to some ten billion dollars.

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Tracking and Monitoring Transuranic Waste Shipments for the Waste Isolation Pilot Plant

Presented by:

**William C. Lattin,
Westinghouse Electric Corporation**

TRACKING AND MONITORING TRANSURANIC WASTE SHIPMENTS
FOR THE
WASTE ISOLATION PILOT PLANT

William C. Lattin
Westinghouse Electric Corporation
for the
U.S. Department of Energy
Joint Integration Office
Albuquerque, New Mexico

ABSTRACT

Beginning in October, 1988, the Department of Energy (DOE) will begin shipping contact-handled transuranic (CH-TRU) waste from the various DOE-owned facilities to the Waste Isolation Pilot Plant (WIPP) near Carlsbad, New Mexico. Shipment of the waste will be made in specially-designed containers, called TRUPACTs, and vehicle movement and status will be monitored by the Department of Energy's Transcom satellite system. That signal will be available for use by the States along the shipping routes, as well as provide a feed to the Central Coordination Center (CCC) in Carlsbad, NM. The Center will employ its own computer software (Phoenix) to refine the Transcom signal to more accurately locate, monitor, and communicate with these vehicles to ensure safe and efficient movement of wastes.

INTRODUCTION

Transportation of CH-TRU wastes from the various DOE-owned sites to the Waste Isolation Pilot Plant is scheduled to begin in October 1988 and will continue through 2013. This will involve a fleet of Transuranic Package Transporters (TRUPACTs) carrying waste from ten DOE sites and passing through at least twenty states. Remote-handled transuranic (RH-TRU) waste will be transported to WIPP in RH casks, which are currently being designed and tested specifically for RH canisters. Shipment of RH waste will begin in May 1989 to support a five-year demonstration program.

A state-of-the-art satellite tracking system will be used to track and to monitor all transuranic waste shipments in the United States. Using two satellites in geosynchronous orbit and individual transceivers in each vehicle, the relative position of each vehicle can be monitored. The tracking system will also allow communications from the vehicle to the Central Coordination Center in Carlsbad, New Mexico.

There are several reasons for monitoring individual waste shipments.

1. Safety. Real-time positioning and communication with each vehicle allows DOE to become aware of a non-routine event much sooner than it would with a "call-in" system. Notification would result through either a system-initiated signal or an improper response to a routine query. Such early notification would allow DOE to initiate emergency response activities, such as notification of state police, emergency response units and DOE assistance teams, thereby minimizing the impact on personnel, property, and the environment in general.
2. Prenotification. The system determines and notifies the CCC and the affected state whenever a shipment is close to entering a specific state's jurisdiction.
3. Route Verification. The system determines the speed at which the vehicle is moving, and whether the truck is on its assigned route. Based upon the longitude and latitude signals received from the truck, the map data base is automatically updated.
4. Efficiency. Early notification of any problems allows empty TRUPACTs to be diverted to other facilities, if necessary. The system also aids in scheduling maintenance activities at WIPP by providing accurate estimates of arrival times, allowing WIPP to schedule personnel, equipment and activities accordingly.

DOE's TRANSPORTATION COMMUNICATIONS SYSTEM (TRANSCOM)

The Department of Energy has established a system, (TRANSCOM), to track the location and monitor the status of designated DOE shipments, and to respond in the event of emergencies. TRANSCOM uses the GEOSTAR satellite system to provide the communications link between the vehicle and a central ground station. A computer on the ground at GEOSTAR Central transmits general interrogation signals through the geostationary satellite relays many times per second. The signals are received by a transceiver on the truck. Information, such as vehicle identification and status is then transmitted from the vehicle to two satellites in stationary orbit. The system measures the location of the transceiver by comparing the time of interrogation and the time at which the response is received.

The signal from the GEOSTAR system is fed to the TRANSCOM software. Using the USGS map data base as a reference and the longitude and latitude information from GEOSTAR, the location of the transceiver is determined. That information is displayed at TRANSCOM Headquarters, and is available to the states using a modem and a toll-free telephone line. The TRANSCOM signal is also fed to the Central Coordination Center at Carlsbad, New Mexico. There, the signal is processed by the software in the TRUPACT Monitoring and Dispatching System (TMADS) for use by WIPP personnel.

TRUPACT Monitoring and Dispatching System (TMADS)

While the TRANSCOM generated information is adequate for the needs of DOE Headquarters and the various state governments, both of whom are concerned with the location and progress of the shipments, the Central Coordination Center has the responsibility to ensure safe and orderly delivery of the waste to WIPP. The TRUPACT Monitoring and Dispatching System enables the TCC to fulfill that responsibility.

The software portion of this system, PHOENIX, includes the following state-of-the-art features:

1. Automatic Alarm Conditions. An alarm, or abnormal condition, signal is generated if the software determines that improper progress is being made, if the vehicle strays from its assigned route, if an improper response is made to a valid query, or if signalled by the driver.
2. Prenotification. The software determines and notifies the CCC and the affected state whenever a shipment is close to entering the state's jurisdiction within a given time frame.
3. Map Correction. Based on longitude and latitude signals, the maps in the data base are updated automatically using statistical methods. If the vehicle deviates from defined routes, the system will create and save the new route using the signals received.
4. Truck Location. The location of all shipments being monitored is displayed on a system map. Using the last four signals received, the general progress of the shipment is shown. The icons are color-coded to display the status of each shipment.
5. System Map. Coordinatized maps based on aeronautical charts are stored in the system's database. The entire country can be displayed, or it is possible to zoom in to individual streets within cities.

These features are possible because of the manner in which the map data is recognized by the software. The actual route coordinates have been entered into the database and according to the length of the segment, a tolerance band is established. The longitude/latitude signal from TRANSCOM is compared to those coordinates. If the signal falls outside the tolerance band, an alarm condition is detected. If the same set of coordinates is received two times in succession, and the vehicle is not scheduled for a stop, the software senses improper progress and generates an alarm. System operators are notified via audio and visual signals; therefore, they do not have to spend a majority of their time monitoring the screens and are free to perform other duties.

Historical Database. All information collected by the system is stored in a historical database. This information is be used to review the TRUPACT transportation record and forms the basis for periodic reports and responses to public inquiries concerning the transport system. In the event of a non-routine event or accident, the event can be reconstructed using tracking system data.

SUMMARY

In October 1988, the Department of Energy will begin monitoring and tracking transuranic waste shipments to the Waste Isolation Pilot Plant in Carlsbad, New Mexico. Because of a unique combination of capabilities, the location and status of every shipment will be known at all times. In the event of an emergency, Federal, state, and local emergency teams can be quickly notified to provide rapid response. Orderly dispatching and maintenance activities will allow optimum utilization of shipping containers. In this manner, the general welfare of the environment and the public is assured.

**Feasibility Study for an RH-TRU Waste
Sludge Facility at ORNL**

Presented by:

F. M. Saleh, Southern University

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**In Situ Grouting of Buried Transuranic Waste
with Polyacrylamide**

Presented by:

B. P. Spalding, ORNL

IN SITU GROUTING OF BURIED TRANSURANIC WASTE
WITH POLYACRYLAMIDE

B. P. Spalding and S. Y. Lee

Environmental Sciences Division
Oak Ridge National Laboratory¹

ABSTRACT

This task is a demonstration and evaluation of the in situ hydrologic stabilization of buried transuranic waste at a humid site via grout injection. Two small trenches, containing buried transuranic waste, were filled with 34,000 liters of polyacrylamide grout. Initial field results have indicated that voids within the trenches were totally filled by the grout and that the intratrench hydraulic conductivity was reduced to below field-measurable values. The grout was also completely contained within the two trenches as no grout constituents were observed in the 12 perimeter groundwater monitoring wells.

Polyacrylamide grout was selected for field demonstration over polyacrylate grout because of its superior performance in laboratory degradation studies. Also supporting the selection of polyacrylamide was the difficulty of controlling the set time of the acrylate polymerization process in the presence of potassium ferricyanide. Based on preliminary degradation monitoring, polyacrylamide was estimated to have a microbiological half-life of 115 years in the test soil. However, this calculated value is likely to be conservatively low because microbial degradation of the grout set accelerator (triethanolamine) or residual monomer may be contributing most to the measured microbial respiration. Additional work, using ¹⁴C-labeled acrylate and acrylamide grouts, is being carried out to more accurately estimate the grouts' microbiological half-life.

¹Operated by Martin Marietta Energy Systems, Inc., the U.S. Department of Energy under contract DE-AC05-84OR21400.

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INTRODUCTION

The objective of this task is to provide the field-scale development and demonstration of in situ grouting of buried transuranic waste for its hydrologic stabilization in humid regions. It will provide documentation of the degree of stabilization achieved from which the applicability of the technique to other environmental situations can be assessed. This information will enable grouting to be compared with other long-term management options in a detailed plan for remedial actions for buried transuranic waste.

Grouting is the process of forcing a fluid into the void space of a soil, rock, or waste formation which, after grout set, results in a cohesive mass which is considerably less permeable to water. The very heterogeneous and permeable mixture of waste and backfill in burial trenches of transuranic solid waste would make it an ideal candidate for grouting. If the permeability of the waste-backfill can be reduced significantly, then leaching of contamination from buried waste can be reduced. In addition, by the filling of trench voids, grouting could also alleviate the longer term problem of trench subsidence.

Many types of grout are commercially available (Herndon and Lenahan 1976) but grout selection needs to be designed for the particular operation under consideration. For grouting waste disposal trenches, an ideal grout for the hydrologic isolation of the buried waste would have the following properties: a low pre-set viscosity, preferably similar to that of water; none, few, or extremely small suspended solids; a controllable set time from minutes to days; an inherently low permeability after set; durability to resist the physicochemical and microbial stresses in its applied environment; low toxic hazard; and low cost. Actual grout formulations, of course, will represent some compromise among these properties.

Recently, a demonstration of grouting of low-level radioactive solid waste was completed at ORNL (Spalding et al. 1985). Seven grout formulations were tested in the laboratory for their ability to penetrate and to reduce the hydraulic conductivities of soils used as backfills for shallow land burial trenches. Three soluble grout formulations (sodium silicate, polyacrylamide, and resorcinol-formaldehyde) were able to both penetrate soil and sand columns and reduce the hydraulic conductivities from initial values of about 10^{-4} m/sec to less than 10^{-9} m/sec. Three particulate-containing grouts (lime-fly ash, fly ash-cement-bentonite, and bentonite slurry) could not penetrate columns; such formulations, therefore, would be difficult to distribute within a trench for assured hydrologic isolation. Field demonstrations with both sodium silicate and polyacrylamide showed that these grouts could be distributed throughout 1:10-scale burial trenches and that waste-backfill hydraulic conductivity could be reduced several orders of magnitude. Field grouting with polyacrylamide reduced the mean

hydraulic conductivity of nine intra-trench monitoring wells from 10^{-4} to $<10^{-9}$ m/sec.

The above tests were performed on 'pilot-scale' trenches whose dimensions, waste characteristics, void space, and hydrologic regime were either controlled or well defined. Although this demonstration provided much information concerning the technique of in situ grouting, it was somewhat unrealistic in the sense that the knowledge about both the site and the waste was so detailed. In a real disposal trench, dimensions and location are usually uncertain, waste characteristics are, at best, poorly defined, and the hydrologic regime, both of the trench and its host soil formation, poorly understood beforehand. Application and evaluation of grouting to a more realistic situation, as described herein, will require considerably more pre- and post-grouting characterization to establish effectiveness.

The physicochemical and microbiological stability of the polyacrylamide and polyacrylate grouts is also a key attribute in predicting the long-term performance of grouted waste. The quantification of rates of degradation of these grout polymers has not previously been measured. The manufacturers and distributors of these grouts offer much testimony for the permanence of these grouts, based on their extensive field experience, but no direct measurements of grout degradation rates have been published to date. The degradation rates of these organic polymer grouts can be measured from the rates of carbon dioxide evolution from amended soils as microorganisms metabolize the grout as a carbon and energy source. Under the environmental conditions of the test, microbiological half-lives can then be estimated from these rates of carbon dioxide evolution and predictions made for the durability of the grouts in soil. Additionally, by the use of ^{14}C -labeled monomers, the expected low rates of degradation can be measured more accurately by utilizing high radioactivity grouts. The actual carbon dioxide from polymer degradation can thereby be distinguished from the comparatively high background contributions of indigenous soil respiration and the microbial degradation of grout catalysts and tracers. Measurements of these degradation rates requires long-term (i.e., >1 year) monitoring of the grouts' carbon dioxide evolution so that first-order kinetics can be verified and cometabolic contributions from the degradation of monomers, oligomers, and catalysts, remaining after polymerization ceases, can be eliminated.

METHODS, MATERIALS, AND RESULTS

I. Laboratory Investigations

Soil for all laboratory tests was collected from recent disposal trench excavations in Solid Waste Storage Area (SWSA) 6. The soil used in this experiment was obtained from the C horizon (1 to 2 m from surface) of a Typic Dystrochrept; loamy-skeletal,

mixed, thermic (Berks variant series) soil profile, developed on residuum of Maryville Limestone (Conasauga Group), located in Solid Waste Storage Area 6 of the Oak Ridge Reservation. Detailed characterization of the soil sample (<2 mm size fraction) showed a clay loam texture (28% sand, 35% silt, and 37% clay), low organic matter content (0.17% carbon), moderate cation exchange capacity (11 meq/100 g), and acidic pH (5.4). Vermiculite and illite were the major clay minerals. Soil was allowed to air dry and sieved to <2 mm.

Magnesium acrylate grout (AC-400) and acrylamide grout (Q Seal) were purchased from Cues, Inc., Orlando, Florida. Also procured were ammonium persulfate and triethanolamine, the catalyst and accelerator, respectively, for both grouts. The source of materials is presented for identification purposes only and does not represent an endorsement or recommendation for their use. Potassium ferricyanide, technical grade, was obtained from MCB, Inc., and the Sequestrene 138Fe (Iron, Sodium salt of ethylenediamine -o-dihydroxyphenylacetic acid) was manufactured by Ciba-Geigy, Inc.

A. Microbial Degradation Studies

1. Grouts Labeled With ^{14}C

The polyacrylate grout components were prepared in two flasks: the first contained 50 μl of ^{14}C -tagged acrylic acid (98% by wt., 9.43 μCi total activity), supplied by Pathfinder Laboratories, Inc., to which was added 125 mL of AC-400 acrylic grout (40% solids by wt.), 4.5 mL triethanolamine (99% by wt.), and 68 mg potassium ferricyanide, and water to 250 mL. The second flask contained 250 mL of 0.1 M ammonium persulfate.

In the case of the polyacrylamide grout, a ^{14}C -acrylamide solution was first prepared by transferring 10 mg of dry acrylamide-UL- ^{14}C (94.2 μCi total activity), supplied by Pathfinder Laboratories, Inc., to a tared bottle and dissolving it in 10 mL distilled deionized water. From this solution, 1 mL (9.42 μCi) was transferred to a flask which also contained 100 g of Q Seal acrylamide grout (92% by wt.), 92 mg potassium ferricyanide, 8.2 mL triethanolamine (99% by wt.), and 128.7 mL distilled water to a total volume of 250 mL. A second flask contained 250 mL of 0.1 M ammonium persulfate.

For each experiment, six successive 40 mL aliquots of grout were prepared by mixing equal volumes (20 mL) from the two flasks. The polyacrylate grout contained 10% solids while the polyacrylamide grout contained 20% solids. The ^{14}C -tagged polyacrylate grout was added to six 450 mL jars containing 50 g each of air-dried soil which had been sieved to <2 mm grain size. The same was done with the ^{14}C -polyacrylamide. The ^{14}C activity added to each soil jar was calculated to be 0.620 μCi in the case of polyacrylate, and 0.626 μCi in the case of polyacrylamide, based on scintillation counting of 1 mL aliquots of the unpolymerized ^{14}C -acrylate and -acrylamide solutions.

After the grouts had set thoroughly, the soil and grout mixtures in three of the jars (designated 4, 5, and 6) in each experiment were macerated using a spatula. Jars 1, 2, and 3 in each experiment were left undisturbed. An open scintillation vial containing 1 mL of 1.0 M NaOH was placed in each jar; the jars were then sealed and stored in an incubator at 25°C. The scintillation vials were replaced at 3 to 5 day intervals initially, later at weekly intervals. The absorbed $^{14}\text{CO}_2$ in the vials was determined by adding 1 mL distilled water and 18 mL ACS scintillation cocktail to each vial, mixing, then measuring radioactivity with a Packard TriCarb Model 3255 liquid scintillation spectrometer.

In the course of the ^{14}C -polyacrylate experiment, it was observed that as the carbonate contents of some of the vials increased, precipitation of Na_2CO_3 began to occur upon addition of the scintillation cocktail. To prevent this, two methods for dilution were used. Initially, a 0.5 mL aliquot of 1.0 M NaOH solution was transferred from a "problem" vial to a new vial and diluted with 1.5 mL distilled water before addition of scintillation cocktail. When this became insufficient, an alternate method was used: 2 mL of 1.0 M NaOH were added to the vials before CO_2 collection, then 0.5 mL were transferred after collection, and diluted as before. This prevented precipitation and made for a four-fold dilution of the ^{14}C -bearing NaOH solution. Later, when activity levels in the ^{14}C -polyacrylate jars declined sufficiently, dilutions were reduced to twofold by transfer of 1 mL of NaOH from the sampling vial, with addition of 1 mL of distilled water. After Day 417, it was possible to eliminate the dilutions altogether and return to the original sampling procedure.

A first-order rate law for grout degradation was calculated by plotting concentration (radioactivity) versus time:

$$C = C_0 e^{-kt} , \quad (\text{Equation 1})$$

where C_0 = initial radioactivity of carbon-14, C = remaining activity, t = time (days), and k = reaction rate constant. The half-life (T) of the reaction was calculated using the equation:

$$T = 0.6931/k. \quad (\text{Equation 2})$$

Thus, the calculation of half-life of the grout is independent of its initial quantity.

Several factors could affect the degradation of added grout materials. The degradation rate of a given substrate will depend upon its composition and the physicochemical conditions in the surrounding environment. Temperature, O_2 supply, moisture, pH, available nutrients, and the C:N ratio of indigenous soil organic matter are the main environmental influences. In these laboratory experiments, incubation temperature was 25°C, under moist but unsaturated conditions, and aerobic conditions were maintained by periodic opening of the jars during sampling.

Degradation of ^{14}C -polyacrylate: When the results from scintillation counting of the CO_2 collection vials exposed to the polyacrylate-grouted soil were plotted in terms of evolved ^{14}C activity versus time, the three undisturbed soil and grout replicates (1, 2, and 3) showed an initially high activity, followed by a gradual decline. Replicates 1 and 2 appear to have "bottomed out" by approximately Day 40, but replicate 3 underwent a sharp increase in evolved ^{14}C activity, beginning around Day 30, peaking near Day 48, and declining gradually thereafter. Near Day 60, replicate 2 began a similar pattern, peaking near Day 75 at half again the activity of replicate 3. About that date, replicate 1 also increased sharply, and peaked around Day 90 at well over twice the maximum level of replicate 3. In each case, the increase in ^{14}C activity measured in the scintillation vials coincided with visual observation of fungal mycelia growth in the undisturbed soils.

The three macerated soil/grout replicates (4, 5, and 6) displayed a similar pattern, but at a later time. All had a sharp but relatively low ^{14}C peak within the first week after grouting, followed by a rapid decline and gradual leveling-off of activity. This was succeeded in each case by a period of rapid degradation accompanied by the appearance of fungal mycelia, beginning with replicate 6 on Day 150, then replicate 4 around Day 210, and replicate 5 after Day 250. Activities released from the macerated grout forms during these periods of rapid fungal growth, though occurring later, were nearly twice as great (0.063 μCi average, as compared with 0.034 μCi for the undisturbed grouts) (Table 1).

To calculate the grout degradation rates, the data were plotted as concentration versus time, i.e. $\ln(C_0/C)$ versus t , assuming the degradation processes to be first order reactions, at least over the selected ranges (Figure 1). The slopes of these curves represent different degradation rate constants, from which grout half-lives can be calculated. "Steady degradation" rate constants (k_1 - k_7) were determined for the polyacrylate grout replicates (Table 2).

Although "steady degradation" constituted an average of 59.3% of the time-period measured, it generated an average of only 22.5% of the total ^{14}C activity released from the polyacrylate grouts. The remaining 77.5% of the ^{14}C given off as CO_2 during the monitoring period was released during short bursts of rapid degradation by soil microorganisms. However, there has been no repetition of this sort of activity since approximately Day 355, and it appears that the rate constants (k_2 - k_7) from the later portion of the plot reflect long-term grout behavior. Monitoring of these samples will continue, at least, up to 800 days.

Degradation of ^{14}C -polyacrylamide: Data for the first 117 days of the ^{14}C -polyacrylamide experiment have been plotted as $\ln(C_0/C)$ versus t (Figure 2). Two phases of grout degradation based on ^{14}C -activity have appeared so far: an initial,

Table 1
Loss of ^{14}C Activity from Polyacrylate Grout by Degradation Stages

| Undisturbed | | | | Macerated | | | |
|-------------|---------|----------------|--------|-----------|---------|----------------|--------|
| Replicate | Days | μCi | % loss | Replicate | Days | μCi | % loss |
| 1 | 0-74 | 0.0078 | 1.26 | 4 | 0-208 | 0.0097 | 1.56 |
| | 74-161 | 0.0361 | 5.82 | | 208-355 | 0.0569 | 9.18 |
| | 161-445 | 0.0072 | 1.16 | | 355-445 | 0.0018 | 0.29 |
| | Total | 0.0512 | 8.26 | | Total | 0.0684 | 11.03 |
| 2 | 0-60 | 0.0075 | 1.21 | 5 | 0-249 | 0.0110 | 1.77 |
| | 60-147 | 0.0394 | 6.35 | | 249-355 | 0.0687 | 11.08 |
| | 147-445 | 0.0074 | 1.19 | | 355-445 | 0.0015 | 0.24 |
| | Total | 0.0543 | 8.76 | | Total | 0.0812 | 13.10 |
| 3 | 0-28 | 0.0051 | 0.82 | 6 | 0-147 | 0.0089 | 1.43 |
| | 28-161 | 0.0263 | 4.24 | | 147-347 | 0.0632 | 10.20 |
| | 161-445 | 0.0068 | 1.10 | | 347-445 | 0.0019 | 0.31 |
| | Total | 0.0382 | 6.16 | | Total | 0.0740 | 11.93 |

Table 2
Degradation Rate Constants and Half-Lives of Polyacrylate Grout in Soil

| Rate Constant day^{-1} | Half-life (years) | Remark |
|------------------------------------|----------------------|------------------------|
| k_1 3.5×10^{-5} | T_1 54 | 1st steady degradation |
| k_2 3.4×10^{-5} | T_2 55 | 2nd steady degradation |
| k_3 3.8×10^{-5} | T_3 50 | 2nd steady degradation |
| k_4 4.1×10^{-5} | T_4 47 | 2nd steady degradation |
| k_5 3.4×10^{-5} | T_5 55 | 2nd steady degradation |
| k_6 3.5×10^{-5} | T_6 55 | 2nd steady degradation |
| k_7 3.2×10^{-5} | T_7 60 | 2nd steady degradation |

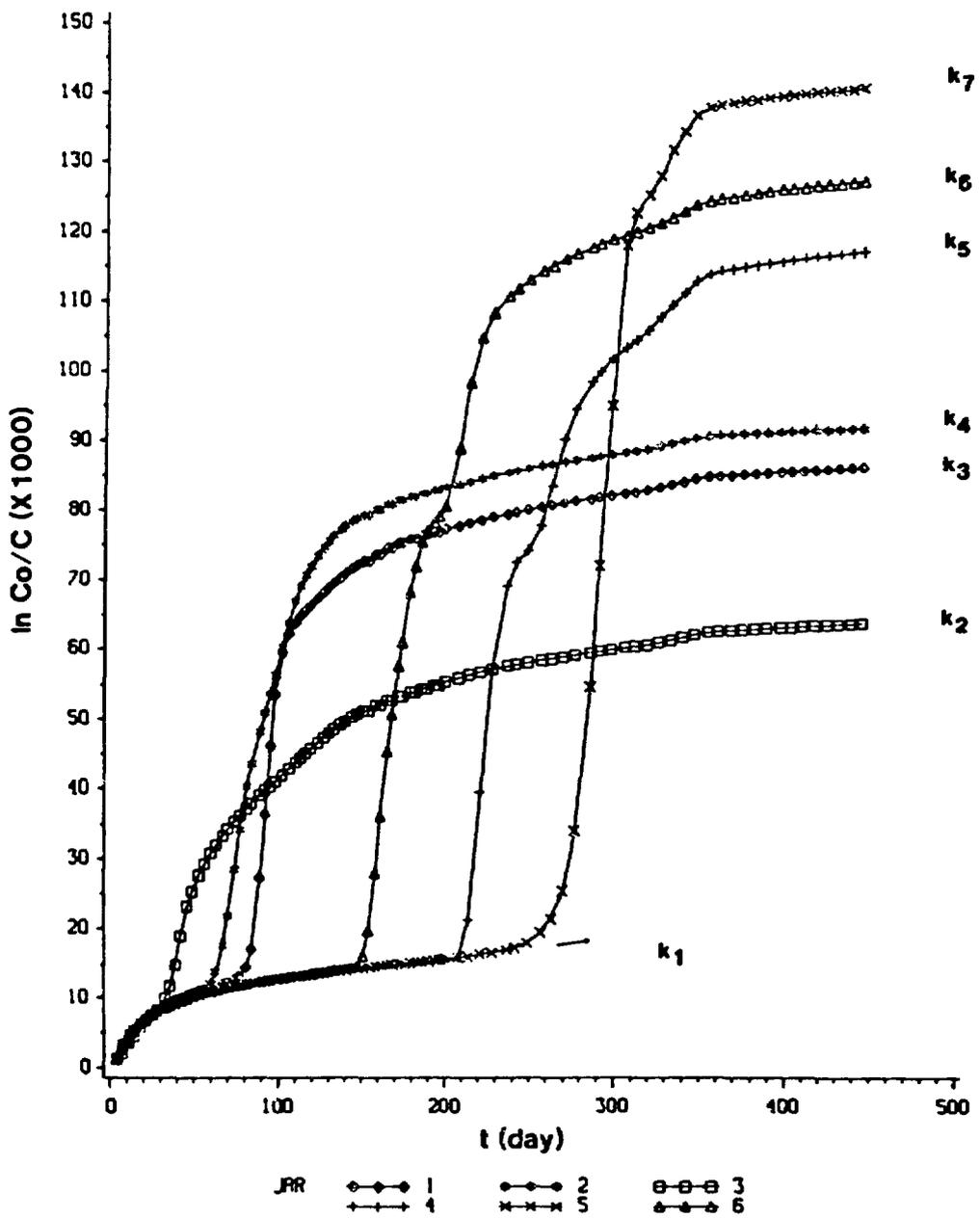


Figure 1. Degradation of ^{14}C -polyacrylate grout in soil, plotted according Equation 1 (k represents rate constant shown in Table 2).

relatively rapid phase (k_8) lasting approximately 20 days, and a slower, "steady degradation" phase observed from Day 21 onward. During the initial rapid phase, average ^{14}C loss among the replicates was 0.048% of the total activity applied for each jar (Table 3). The percent activity losses between day 21 and 117 were 0.048% for undisturbed and 0.064% for macerated replicates. A feature of the "steady degradation" phase has been the divergence of values for the undisturbed (k_8) versus macerated (k_{10}) grout replicates, much as recorded in the ^{14}C -polyacrylate experiment. The consistently higher rate of ^{14}C -release from the macerated replicates appears to indicate that a larger surface area facilitates microbial activity and/or diffusion of unreacted monomer (Table 4).

Based on the results to date, polyacrylate grout had an average decomposition rate constant of 3.6×10^{-5} per day and an average half-life of 54 years. On the other hand, polyacrylamide grout had an average decomposition rate constant of 5.5×10^{-6} per day and an average half-life 362 years. The polyacrylamide grout appears to have a half-life approximately 6.7 times that of the polyacrylate grout under "steady degradation" conditions in this test soil. It remains to be seen whether the polyacrylamide will be more or less resistant to fungal degradation in the long term.

2. Unlabeled Grout Specimens

Grout formulations, identical to the above but with 10% solids and without ^{14}C label, were employed for gross degradation studies. To 50 g of air-dried soil was added 40 mL of grout (20 mL of either the Mg acrylate or acrylamide grout solution plus 20 mL of 2% ammonium persulfate) with gentle swirling to mix with the soil. After allowing 3 hours for the grout to set, a disruptive treatment was applied to a subset of triplicate samples of both grouts. Maceration was achieved by slicing the grouted soil in the bottom of the 1-L wide-mouth screw-cap bottle into <0.5 cm blocks with a large spatula. The acrylamide grout appeared to have set firmly but the Mg acrylate grout had not completely set as evidenced by a lack of firmness experienced when slicing the grouted soil samples. All treatments were prepared in triplicate building an experimental matrix of two grouts x with/without maceration. Blanks with unamended soil, wetted with 30 mL of water, were also run concurrently. After 232 days of incubation, all specimens were inoculated with 50 mg of fresh forest soil suspended in 0.5 mL of water. This treatment was designed to stimulate degradation by providing microbial inocula.

The evolution of carbon dioxide from the soil samples was determined by adsorption into NaOH (Spalding 1977). Into a 30-mL capacity wide-mouth glass vial, 10 mL of 0.1 N NaOH was pipetted. The uncapped vial was placed into a 1-L wide-mouth bottle on top of a small aluminum weighing pan to absorb carbon dioxide which

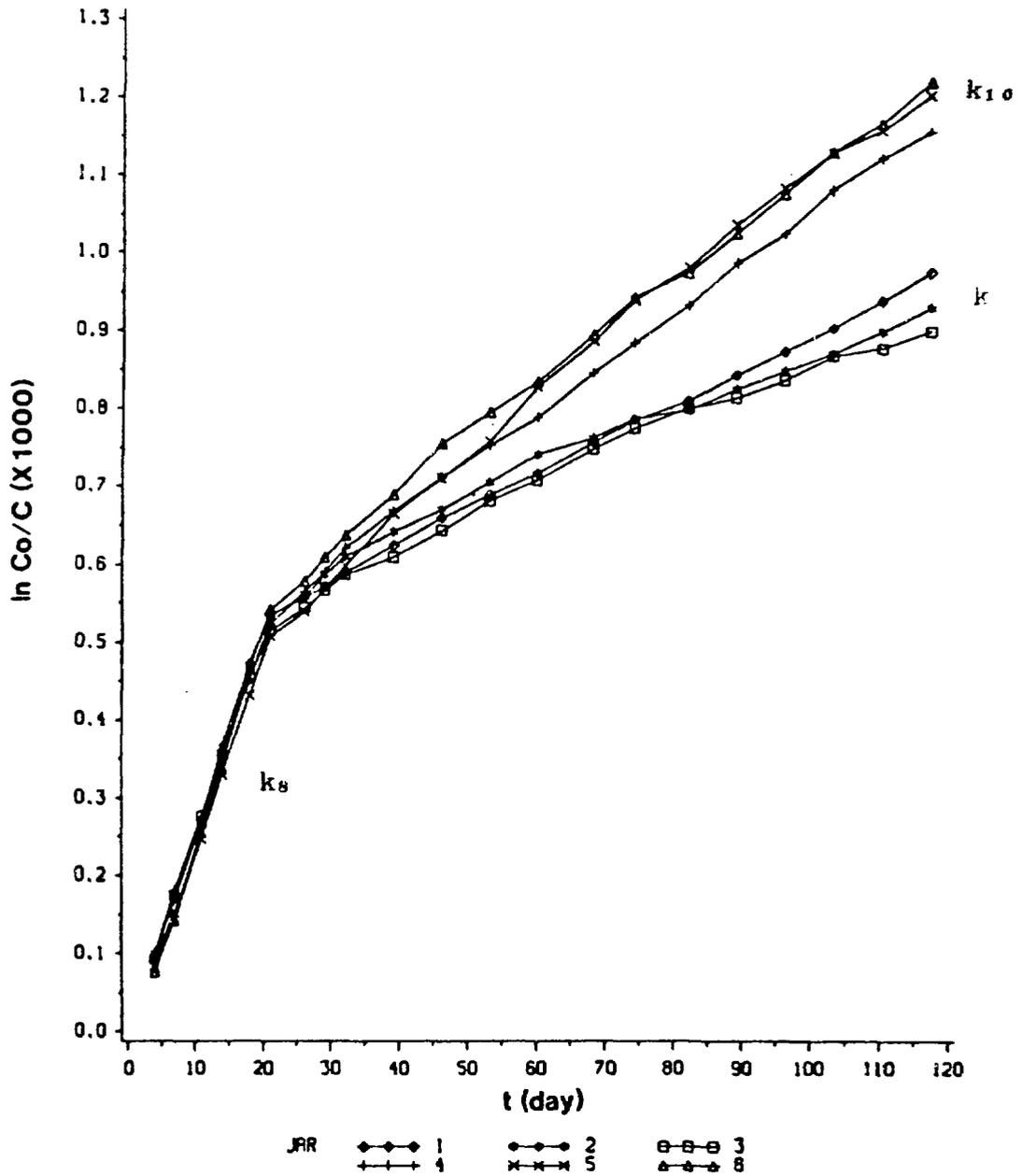


Figure 2. Degradation of ^{14}C -polyacrylamide grout in soil, plotted according to Equation 1 (k represents rate constant shown in Table 4).

Table 3
Loss of ^{14}C Activity from Polyacrylamide Grout in Soil

| Replicate | Treatment | Days | ^{14}C loss, μCi | % loss |
|-----------|-------------|--------|--------------------------------------|--------|
| 1 to 3 | Undisturbed | 0-21 | 0.0003 | 0.048 |
| | | 21-117 | 0.0003 | 0.048 |
| | | Total | 0.0006 | 0.096 |
| 4 to 6 | Macerated | 0-21 | 0.0003 | 0.048 |
| | | 21-117 | 0.0004 | 0.064 |
| | | Total | 0.0007 | 0.112 |

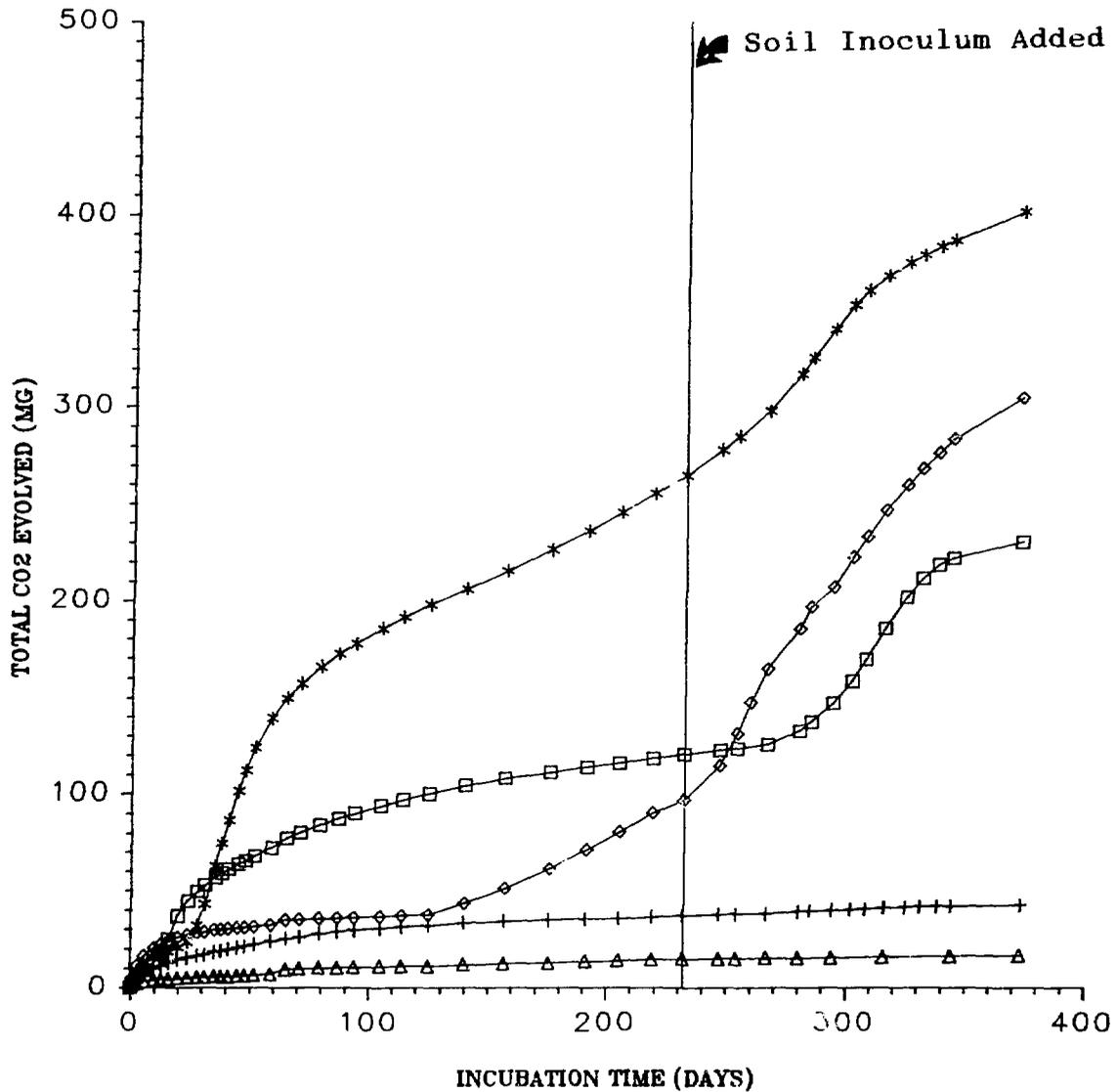
Table 4
Degradation Rate Constants and Half-Lives of Polyacrylamide Grout in Soil

| Rate Constant day^{-1} | Half-life (years) | Remark |
|------------------------------------|----------------------|---------------------|
| k_8 2.6×10^{-5} | T_8 73 | Initial degradation |
| k_9 4.3×10^{-6} | T_9 441 | Steady degradation |
| k_{10} 6.7×10^{-6} | T_{10} 283 | Steady degradation |

evolved from the soil and grout specimen. At intervals ranging from 2 to 20 days, the vials were replaced with others containing fresh NaOH solution. After addition of 2 mL of 1 M barium chloride to the vial, residual alkalinity was determined by titration with 0.8 M HCl to the phenolphthalein endpoint using a digital titrator (Hach Chemical Company). Three drops of a 0.5% phenolphthalein in isopropanol solution were used. The amount of CO₂ evolved was calculated from the difference between vials containing NaOH not exposed to soil (blanks) and that in the sample.

The average cumulative CO₂ evolution from the polymerized grout specimens is depicted in Figure 3. The undisrupted Mg acrylate grouted soil experienced considerably more degradation than the undisrupted acrylamide grouted soil. Notably, the total amounts of evolved CO₂ totaled to only 5.6 and 2.8% of the carbon added to the soil in the acrylate and acrylamide grouts, respectively. The two macerated polymerized treatments evolved considerably less CO₂ than their corresponding undisrupted treatments. An unambiguous explanation for this difference between undisrupted and macerated treatments cannot be ascertained from the monitoring information accumulated to date. The maceration of soil specimens may have increased the amount of oxygen accessible during the final stages of grout polymerization. The acrylate specimens, in particular, were not completely set when they were sliced up about 3 hours after adding the grout to the soil. In contrast, in the ¹⁴C-labeled degradation studies, maceration of grouted soil took place 24-48 hr after grout addition to the soil. Because air is a retardant to the polymerization process (Avanti 1985), sample disruption could have increased the amount of unreacted monomer compared with the undisrupted specimens. Notably, both the acrylate and acrylamide macerated specimens manifested an odor of acrylic acid indicating the presence of unreacted monomer. Acrylamide has been observed to hydrolyze enzymatically in soil at reasonably fast rates (Frankenberger and Tabatabai 1982) so that such a mechanism could well be a source of volatile acrylic acid from the acrylamide amended soils. If this hypothesis is correct, then once the inhibitory concentration of acrylic acid is reduced in these specimens, cumulative amounts of evolved CO₂ should eventually exceed those in the undisrupted grouted specimens. The beginning of such an upturn in the macerated acrylate treatment may be starting in the latter measurements of the twelve month observation period (Figure 3). Continued monitoring should provide the required evidence to support or refute this hypothesis.

These rates of CO₂ evolution can be used to calculate tentative first-order biological degradation rates for the grout polymers. Knowing the rate of CO₂ evolved in the last period of observation, i.e., the slopes of the lines in Figure 3, and the amount of grout carbon remaining, a first-order rate constant, k , in units of fraction per day, and microbiological half-life, T , can be calculated using equations 1 and 2, respectively. The



TREATMENT *-*-* POLYACRYLATE/U ◇-◇-◇ POLYACRYLATE/M
 □-□-□ POLYACRYLAMIDE/U +-+-+ POLYACRYLAMIDE/M
 ▲-▲-▲ SOIL CONTROL

Figure 3. Degradation of polyacrylamide and polyacrylate grouts in soil in undisturbed (U) and macerated (M) conditions.

half-lives for the undisrupted grouts calculate to 25 and 52 years for the acrylate and acrylamide grouts, respectively. These biological half-lives are based on first-order rate constants of 0.0000769 and $0.0000366 \text{ day}^{-1}$, respectively. The corresponding half-lives for the macerated acrylate and acrylamide grout were 52 and 655 years, respectively. The initial amounts of grout present for the acrylate and acrylamide treatments were equivalent to 7130 and 8166 mg of CO_2 , respectively. These totals include the carbon present as triethanolamine and potassium ferricyanide although the later ingredient makes only a minor contribution (0.04% of the total carbon). The triethanolamine, however, makes a much more significant contribution to the total carbon in the grouts (9.9 and 8.6%, respectively, for the acrylate and acrylamide). The triethanolamine would not be covalently bonded into the polymer in either grout and, hence, would remain free as a substrate for microbial growth. The determination of the precise fraction of the observed CO_2 evolution to ascribe to the metabolism of triethanolamine or to any unreacted monomer cannot be discerned from the present monitoring data. Use of the ^{14}C -labeled monomers to prepare the soil grout is the only definitive method to determine the actual contribution from grout degradation. The average final rate of CO_2 evolution from the macerated acrylamide grouted soil was 0.024 mg/day which was just slightly greater than the rate observed for unamended soil (0.014 mg/day). Thus, the advantage of using ^{14}C -labeled grouts would be high in order to separate contributions to respiration due to grout degradation and those due to indigenous soil sources.

The addition of microbial inocula at day 232 of the grout incubation had a pronounced effect on the rates of CO_2 evolution from the undisturbed polyacrylamide and macerated polyacrylate grouts. However, after the induced microbial proliferation, rates of CO_2 evolution declined to values similar to those before inoculation. No significant additional carbon sources were added in the inocula as evidenced by the lack of response of the unamended soil controls during the post inoculation period. The induced degradation by the soil inocula probably resulted from metabolism of unreacted monomer or the triethanolamine in the grout specimens. Similar stressing of the ^{14}C -labeled grout specimens will be attempted after stable degradation rates have been attained.

B. Degree of Polymerization

The Mg acrylate solution was prepared by diluting 293 mL of AC-400 (40% solids) to 500 mL with water after addition of 96 mg of potassium ferricyanide. Two batches were prepared, with and without the addition of 8.9 mL of triethanolamine. The acrylamide solution was prepared by dissolving 100 g of Q-1 (dry powder) up to 500 mL of water after addition of 96 mg of potassium ferricyanide. Two batches were also prepared with and without the addition of 8.9 mL of triethanolamine. The catalyst

solution for both grouts was prepared by dissolving 10 g of ammonium persulfate up to 500 mL of water. The soil samples were grouted by adding a premixed 40 mL volume of grout (20 mL of grout solution plus 20 mL of catalyst solution) to 50 g of air-dried soil contained in a 250-mL plastic centrifuge bottle. After swirling the contents to mix the grout and soil, the mixture was allowed to polymerize for 24 hours without disturbance. The grouted specimens were then diced into <1 cm blocks with a steel spatula and 150 mL of water added and the tubes shaken for several minutes. The tubes were then centrifuged for 25 min at 350 relative centrifugal force and 40 mL aliquots of the supernatant were decanted and filtered through 0.45 μ m membranes. Samples of the various grout solutions were also prepared without soil as well as soil blanks without grout amendments. All treatments were run in triplicate. The filtrates from the acrylate grout amendments were analyzed for water hardness (i.e., for soluble magnesium) with EDTA (APHA 1980) using 5 mL aliquots (Table 5). Attempts to interpret the titratable alkalinity (to pH 2) of the filtrates, as a measure of residual acrylate, were ambiguous due to interference by the triethanolamine. The acrylamide filtrates were analyzed for their saponification equivalent as a measure of soluble acrylamide. Aliquots of 10 mL were heated to dryness over a 15 min period after addition of 5 mL of 1 N NaOH. The residue was then redissolved in 25 mL of distilled water and titrated with 0.1 N HCl to the phenolphthalein endpoint. Additional 10 mL aliquots with 5 mL of NaOH, which had not been heated, were also titrated with the HCl. Both acrylamide and methylenebisacrylamide standards were saponified by this procedure and found to hydrolyze to >96% of their theoretical values. The polymerization of acrylamide was found to be near complete both in the presence and absence of soil (Table 6). Attempts to assay acrylamide colorimetrically using ninhydrin, 3,5-dinitrosalicylic acid, and p-dimethylaminobenzaldehyde showed acrylamide to be nonreactive to these reagents.

Both procedures for determining the degree of polymerization are subject to potential interferences which make the assays of >95% polymerization uncertain. The assay of hardness (Mg) as an indicator of the concentration of acrylate present ignores soil cation exchange effects. It also assumes a 1:1 equivalent ratio between magnesium and acrylate in the original grout formulation. The saponification equivalent, used for the acrylamide assay, does not account for possible removals of saponifiable species from soil by the acrylamide or possible transamidification reactions with the triethanolamine present.

For determining the degree of polymerization of the two grout formulations, using 14 C-labeled monomers, a scaled-down assay procedure was employed. Into a 50-mL screw-cap centrifuge tube, was weighed 2 g of soil to which 2 mL of freshly-prepared 14 C-labeled grout solution and 2 mL of 2% ammonium persulfate catalyst solution were added. The acrylate grout solution contained 60 mL of AC-400 liquid grout, 0.189 mCi of 14 C-acrylic

Table 5
Polymerization of Magnesium Acrylate Grout
in the Presence and Absence of Soil

| Treatment | Calculated Mg Concentration (Normality) | %Mg Recovery | % Polymerization |
|------------------------|---|-----------------|---------------------|
| Soil+Grout+ AP+ TEA | .025 | 4.6 | 95.4 |
| Soil+Grout+ TEA | .491 | 90.1 | - |
| Grout+AP+TEA | .013 | 2.4 | 97.6 |
| Grout+TEA | .540 | 99.0 | - |
| Grout+AP | .547 | 100.0 | - |
| Grout only | .542 | 99.0 | - |
| Soil only | .0008 | <0.2 | - |

Grout = AC-400 (Ques Inc.), AP = Ammonium Persulfate,
TEA = Triethanolamine.

Table 6
Polymerization of Acrylamide Grout Formulation
in the Presence and Absence of Soil

| Treatment | Acrylamide Recovery % | % Degree of Polymerization |
|-----------------------|--------------------------|-------------------------------|
| Grout+Soil+ TEA+AP | 7.8 | 92.2 |
| Grout+Soil+AP | 92.4 | - |
| Grout+TEA+AP | 5.8 | 94.2 |
| Grout+TEA | 99.6 | - |
| Grout+AP | 89.6 | - |
| Grout alone | 100.0 | - |
| Soil alone | 0.8 | - |

Grout = Q Seal (Cues Inc.), AP = Ammonium Persulfate,
and TEA = Triethanolamine.

acid in 1 mL of water, 19 mg of $K_3Fe(CN)_6$, and 1.8 mL of triethanolamine, diluted to 100 mL. The acrylamide grout solution contained 20 g of acrylamide grout (Q Seal), 19 mg of $K_3Fe(CN)_6$, 1.8 mL of triethanolamine, and 0.085 mCi of ^{14}C -acrylamide in 9 mL of water, diluted to a total of 100 mL. The contents of the centrifuge tube were mixed with a vortex mixer and allowed to stand overnight. Controls without soil were also run to check for any inhibition of polymerization by the soil. Soil controls, without ammonium persulfate catalyst (substituting 2 mL of water) were also analyzed. Finally, controls without either soil or catalyst solutions were run to determine exact amounts of soluble activity in the unpolymerized grout solutions. After the overnight period for grout set, 25 mL of water were added to each tube and the contents shaken lengthwise at 100 oscillations per minute for periods of 1, 3, and 13 days. After shaking, the tubes were centrifuged at 1,500 relative centrifugal force for 10 min and a 2 mL aliquot transferred to a scintillation vial with 18 mL of Aquasol liquid scintillation cocktail. All samples were then counted for 10 min with a Packard liquid scintillation counter employing a preset ^{14}C window. Degree of polymerization was calculated from the difference in counts between the controls without soil or catalyst solution and the various samples. The results are presented in Table 7.

Table 7
Polymerization of Acrylamide and Acrylate Grouts
in the Presence and Absence of Soil

| <u>Grout</u> | <u>Soil</u> | <u>Catalyst</u> | <u>% Polymerization After</u> | | |
|--------------|-------------|-----------------|-------------------------------|---------------|----------------|
| | | | <u>1 Day</u> | <u>3 Days</u> | <u>13 Days</u> |
| Acrylamide | Yes | Yes | 97.4 | 96.7 | 95.4 |
| Acrylamide | Yes | No | 14.5 | 7.2 | 10.5 |
| Acrylamide | No | Yes | 96.9 | 95.9 | 93.9 |
| Acrylate | Yes | Yes | 89.9 | 87.4 | 87.0 |
| Acrylate | Yes | No | 0.8 | 0.0 | 0.0 |
| Acrylate | No | Yes | 91.3 | 89.5 | 85.0 |

Soil does not appear to interfere with the polymerization of either grout formulation because the degree of polymerization was equivalent whether or not soil was present. Acrylamide appeared to be more completely polymerized than the acrylate grout, i.e., 95 versus 87% after 13 days, respectively. The magnitude of both grouts' polymerization appeared to be similar to that observed by the chemical assays (Tables 5 and 6) adding confidence to the

interpretations of those assays. The slight decrease in the calculated degree of polymerization of both grouts between 1 and 13 days probably results from the slow diffusion of unreacted monomer from the interior of the grout specimens. Additional work with similarly-sized grout specimens, containing unincorporated radioisotopes, indicates that 3 to 5 days are required for concentrations within the grout to reach equilibrium with the leaching solution via diffusive mechanisms. Thus, the 13-day leaching results should be interpreted as the most accurate estimate of the degree of polymerization.

C. Effects on Soil Hydraulic Conductivity

Columns of soil (at 50 g oven-dried equivalent) were prepared using the SWSA 6 soil moistened to 17.9% water content by a procedure described previously (Spalding et al. 1985). The columns were purged with carbon dioxide to eliminate trapped air prior to permeation with 250 mL of water. Using a constant head water delivery apparatus, the time required to collect two successive 100 mL volumes from the soil columns was measured and used to calculate the saturated hydraulic conductivity of each of eight soil columns (Klute 1965). The hydraulic conductivity averaged $2.2 \pm 0.3 \times 10^{-2}$ cm/sec. The columns were then grouted by allowing 150 mL (ca. 2 column volumes) of freshly prepared grout (a 1:1 mixture of grout and catalyst solutions as described previously) to percolate through the column until the grout solution was level with the top of the soil surface. The column flow was then interrupted for 24 hours to allow the grout to set. Measurements of postgrouting hydraulic conductivities were attempted the next day after replacing the protective sand and glass wool layers above and below the soil plug. However, no water conduction could be observed in any column over a week long period indicating that both grout formulations had sealed the soil columns. Four replicate columns of each of the two grouts were tested.

The Mg acrylate grout was observed to partially polymerize after about 30 min in the presence of triethanolamine and potassium ferricyanide even without the addition of the ammonium persulfate catalyst. Thus, solutions for the hydraulic conductivity and microbial degradation experiments had to be prepared immediately prior to use. This tendency of the Mg acrylate to spontaneously polymerize was a critical attribute which led to the selection of the acrylamide for the field demonstration. Solutions of acrylamide, containing both triethanolamine and potassium ferricyanide, have been stable for periods of several months and their polymerization could be controlled identically to freshly prepared solutions.

II. Field Investigations

A. Site Selection and Characterization

Solid Waste Storage Area (SWSA) 4 at ORNL was selected as a candidate disposal area to locate burial trenches of transuranic waste. Although there are no records of surveyed trench locations or waste characteristics for SWSA 4, which was operated between 1951 and 1959, a crude area map which includes types of trenches (Figure 4) is available (Huff et al. 1982; Davis and Schoun 1986). The indicated trench orientations seem to be correct as evidenced by the orientation of subsidence depressions on the present SWSA 4 land surface. According to a description of solid waste handling and disposal methods prepared during the operation of SWSA 4 (Browder 1959), 'alpha' contaminated waste was segregated from beta-gamma waste for disposal: "The alpha contaminated wastes are buried in holes approximately 15 by 15 feet deep. The waste materials are placed in the hole and covered by about a foot of earth. Approximately 8 inches of concrete are poured over the earth in the hole. The concrete is followed by an additional two or more feet of earth to fill the hole to the surface level. The use of concrete is a precaution to prevent anyone from inadvertently digging into the long-lived plutonium-contaminated alpha wastes at some future date. Beta-gamma wastes are buried in long trenches and covered with three or more feet of earth." Thus, the areas in Figure 4, which indicate that they contain trenches covered with concrete, were considered likely to contain buried transuranic waste.

Surface 'outcrops' of concrete were visible in the area on the eastern side of SWSA 4 and several were located near the eventual study area. The use of the shallow concrete caps over these older alpha burial trenches was deemed a facile means to precisely locate a trench for the grouting demonstration. Between June 16 and 20, 1986, probing for the location of shallow subsurface concrete was attempted using a trailer-mounted drill rig (Giddings Drill Co.) fitted with an 18-inch long section of 3-inch diam auger. Several 50-m transects of the area were laid out and augering was attempted every 2 m to a maximum depth of 50 cm. A refusal of auger penetration was tentatively interpreted as evidence of concrete when several adjoining points on a transect exhibited this refusal. Auger refusal was also noted for abundant limestone cobble presumably from old access roads or fill materials in the area. Notably, only two small areas of concrete were identified in the whole eastern region of SWSA 4 which Figure 4 indicated would contain trenches which were all covered with concrete. Thus, it appears that the use of concrete caps in SWSA 4 was nowhere near as extensive or routine as published records would seem to indicate. However, a probable concrete-capped trench, of an appropriate size for the grouting demonstration, was located by this probing method in the area indicated in Figure 4. On July 10, 1986, the earthen cover over the concrete cap was scraped off using a front-end loader. This

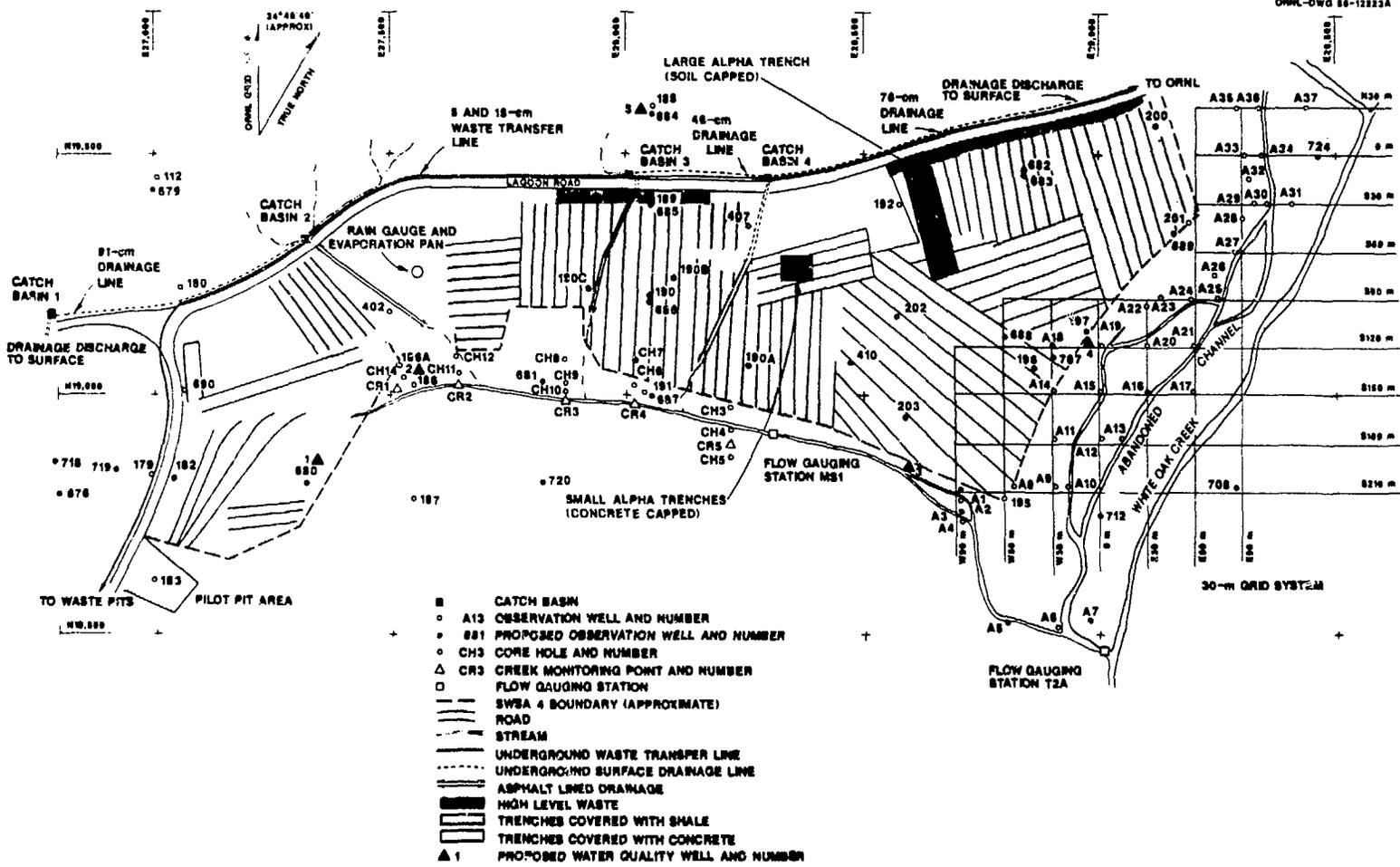


Figure 4. Map of Solid Waste Storage Area 4, ORNL, showing the study area selected for the buried transuranic waste grouting demonstration.

uncovering revealed that the concrete cap was actually two smaller roughly rectangular caps. The caps were neither level nor smooth indicating that the concrete had been dumped rather than formed and worked. Each cap was approximately 3.5 x 6 m and subsequent drilling revealed that its thickness varied between 10 and 30 cm with an estimated area-weighted average thickness of 15 cm. The exact cap locations, within the DOE administrative grid, are depicted in Figure 5. For discussion and identification purposes, these two trenches have been designated as the east and west trench.

Beginning July 24, 1986, several 17-cm diam holes were drilled through the concrete caps using a carbide-tipped 'Bulldog' bit (Mobil Drill Co.) with 6-inch diam hollow stem auger and a trailer-mounted drill rig (Mobil Drill Co., Model B-24). Continuous wetting of the bit facilitated drilling and about 30 min per hole were required to penetrate the cap. Augering was continued into the backfill below the concrete until the first evidence was encountered that waste constituents were being brought to the surface. Cuttings were continuously monitored for beta-gamma and alpha activity by ORNL health physicists. Seven holes were placed in the west trench and six were placed in the east trench. In an effort to minimize the amounts of contaminated auger cuttings from the trenches, an attempt was made to insert well casings by either pushing manually or driving with a safety drop hammer. However, only two stainless-steel, 2-inch diam well screens with pointed ends were available at the time. These were used to prepare wells 1 and 2 in the east and west trench, respectively (Figure 5). Attempts to insert various types of plastic well screens and casings were not successful. To make boreholes for these well casings, a 'cuttingless' auger method was devised by using a 3-foot section of 4-inch diam auger with either a fishtail or drag bit coupled to drill rod extension above. Thus, without the continuity of augers no cuttings were brought to the surface but the borehole was opened by allowing the auger to push trench materials (waste and backfill) laterally into the comparatively large voids within the trench. This procedure worked quite well in the east trench where mostly soft waste materials (i.e., wood, plastic, and cloth) were encountered. In the west trench, much more metallic waste was encountered and resulted in the loss of two bits and auger sections due to breakage within the trench. Only one well casing could be fitted into the seven holes in the concrete cap of the west trench. However, the remaining uncased holes were still useful for visual inspection of the waste and, later, for pouring grout into the trench. Well 4 (Figure 5) was placed along the eastern wall of the west trench and behaved hydrologically as though it were probably within the trench. The characteristics of all wells constructed in the area are given in Table 8.

A group of twelve monitoring wells were placed around the two trenches between August 4 and September 14, 1986. All well holes were augered to a nominal depth of 6.5 meters using 6-inch

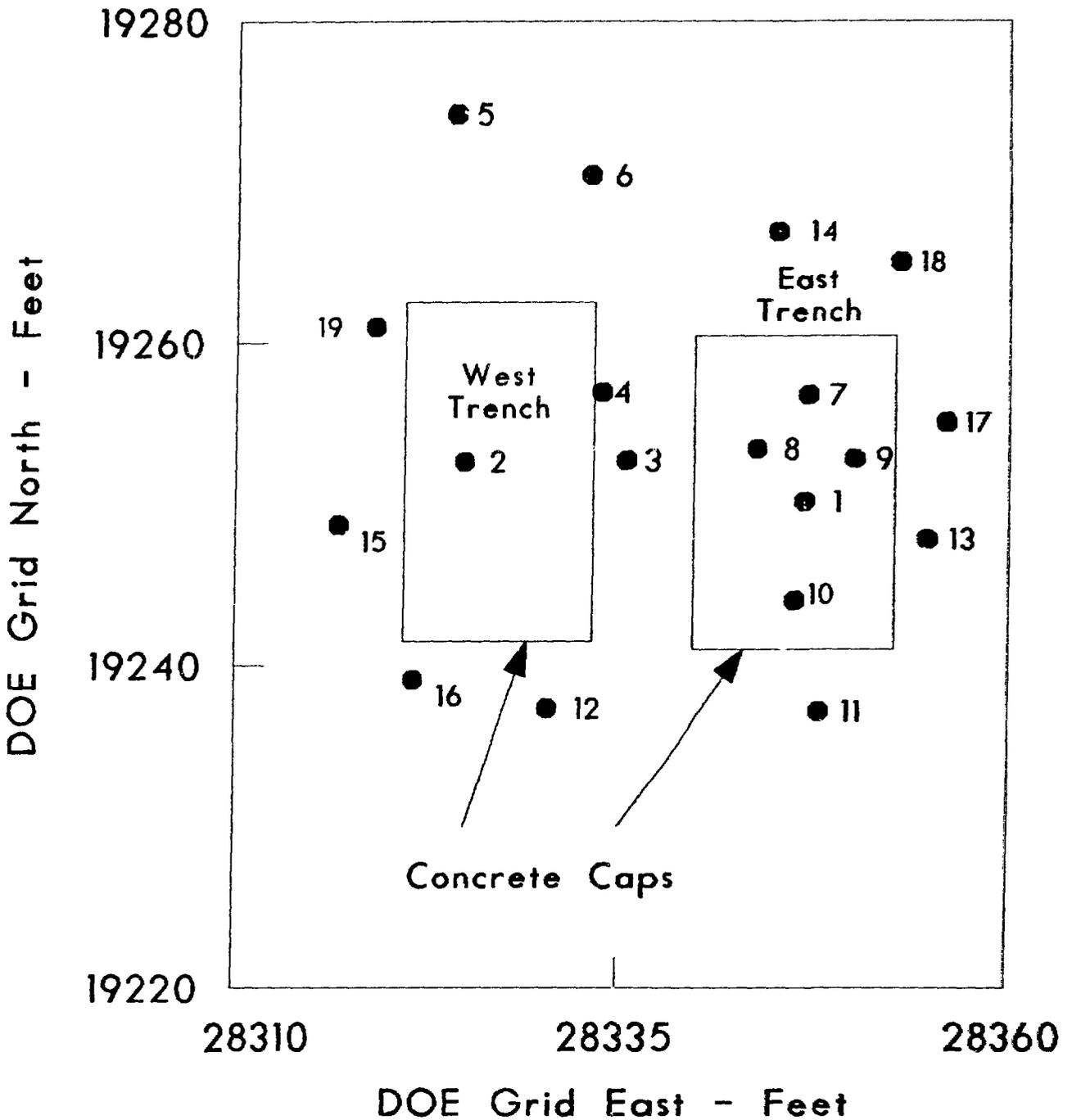


Figure 5. Plan view of trench caps and monitoring well locations in the study area for the buried transuranic waste grouting demonstration in Solid Waste Storage Area 4, ORNL.

Table 8
Monitoring Well Locations and Characteristics
at the Buried Transuranic Waste Immobilization Site
in Solid Waste Storage Area 4.

| Well | Grid Coordinates | | Elevation of | | | | |
|------|------------------|-------|------------------|----------------|---------------|-------------|------------------|
| | East | North | Top of Casing | Ground Surface | Casing Length | Inside diam | Length of screen |
| | (--- feet ---) | | (m above NGVD) | | (m) | (cm) | (m) |
| 1 | 28347 | 19250 | 245.47 | 244.85 | 4.31 | 5.1 | 1.52 |
| 2 | 28325 | 19253 | 245.23 | 244.25 | 4.31 | 5.1 | 1.52 |
| 3 | 28335 | 19253 | 245.35 | 244.10 | 4.26 | 10.2 | 1.52 |
| 4 | 28334 | 19257 | 245.55 | 244.19 | 4.33 | 7.6 | 1.52 |
| 5 | 28322 | 19271 | 245.33 | 244.74 | 6.53 | 7.6 | 1.52 |
| 6 | 28331 | 19269 | 245.23 | 244.88 | 6.18 | 7.6 | 1.52 |
| 7 | 28347 | 19257 | 245.17 | 244.81 | 3.31 | 3.4 | 3.04 |
| 8 | 28344 | 19253 | 245.22 | 244.86 | 2.26 | 3.4 | 1.99 |
| 9 | 28350 | 19253 | 245.13 | 244.82 | 3.45 | 3.4 | 3.04 |
| 10 | 28346 | 19244 | 245.05 | 244.78 | 3.31 | 3.4 | 3.04 |
| 11 | 28348 | 19237 | 245.19 | 244.82 | 6.53 | 7.6 | 1.52 |
| 12 | 28331 | 19237 | 244.76 | 244.63 | 6.18 | 7.6 | 1.52 |
| 13 | 28355 | 19248 | 245.89 | 245.03 | 6.18 | 7.6 | 1.52 |
| 14 | 28344 | 19267 | 245.92 | 245.16 | 5.97 | 7.6 | 1.52 |
| 15 | 28317 | 19248 | 244.80 | 244.30 | 5.97 | 7.6 | 1.52 |
| 16 | 28322 | 19238 | 244.72 | 244.43 | 5.06 | 7.6 | 1.52 |
| 17 | 28356 | 19255 | 245.90 | 245.12 | 6.53 | 7.6 | 1.52 |
| 18 | 28353 | 19265 | 245.51 | 245.20 | 6.11 | 7.6 | 1.52 |
| 19 | 28319 | 19261 | 244.79 | 244.43 | 6.10 | 7.6 | 1.52 |

Grid coordinates were calculated using well 407 as a reference as given in Webster et al. 1981.

NGVD = National Geodetic Vertical Datum.

Wells 1 and 2 were made of stainless steel. All others were PVC.

diam continuous flight auger and a carbide-tipped drag bit. However, well 3, because of its location, was much shallower than the other wells. All wells were cased with 3-inch diam, threaded, flush-joint PVC casing (Timco Manufacturing Co.). The bottom 5-foot section was slotted (0.020 inch) well screen with a threaded PVC plug on the end. The annulus around the well screen was filled with 45 kg of coarse sand. The remaining annulus above the screened section was filled with the soil which had been augered from the hole. Monitoring of the auger cuttings indicated that the soil depths ranged between 4 and 5 m when harder rock, usually limestone, was encountered. This limestone was encountered in most locations but was usually only about 20-50 cm thick and under lain by a red and/or gray shale. The augering confirmed the extent of trench borders inside the perimeter of monitoring wells because all holes encountered only undisturbed residuum including well 3 in the narrow band of undisturbed formation between the east and west trenches.

Another transuranic waste disposal trench, without a concrete cap, was identified immediately to the west of the west trench during monitoring well construction. The initial attempt to auger a hole on the western side augered up two small metallic waste fragments at a depth of 1.5 m below the land surface. These metallic pieces, each estimated at about 100 g, exhibited low beta-gamma activity but saturated available alpha survey equipment (i.e., $>2 \times 10^6$ cpm). Later alpha spectroscopy of several paper smears of the auger identified the active nuclides as ^{239}Pu , ^{240}Pu . The drill bit was successfully decontaminated but one section of auger could not be decontaminated. This auger section and the contaminated metallic pieces were placed into an extra borehole which was later filled with grout. This incident confirmed that this area of SWSA 4 does contain buried transuranic waste in small trenches consistent with the records (Figure 4). Occasionally, cuttings, which adhered to the auger after boring the holes in the east and west trenches, exhibited very low-level beta-gamma and alpha activity although no waste as radioactive as the metallic pieces described above were encountered in these trenches. Samples of contaminated backfill, when encountered in the placement of intratrench wells, were stored for later analysis.

B. Trench Void Space Determination

When the monitoring of water levels within each trench was initiated on August 14, 1986, both the west and east trench were more than half full of water. Because the East Tennessee region had experienced in the previous two years one of the worst droughts in the historical record with the rainfall in 1986 less than half the annual average, the water levels within these trenches were likely near the lowest point achievable through natural drainage. In the original experimental design, it was anticipated that the demonstration trench(es) would be dry initially and trench void space could be measured by a technique

which filled the trenches with water (Spalding 1986). The water would then be allowed to seep away from the trench prior to filling with grout. However, the presence of so much standing water within both trenches required that the water be removed prior to filling with grout. Trench void space could still be determined, however, by measuring the volume of water which could be pumped from the trenches. However, before emptying the trenches, additional water was added to each at different intervals to measure trench void space above their ambient water levels (Table 9). Water was pumped from White Oak Creek at a point approximately 350 m to the east of the study site. The delivery hose contained a water meter by which volumes placed in each trench were measured. Both trenches were filled within a relatively short interval (<8 hours) even at the modest pumping rate of about 6 gal/min. After filling, subsequent seepage was quite slow as evidenced by the very slow decline in the intratrench water levels over the next several days.

The water removed from each trench was initially pumped into three 1,500-gallon storage tanks at the site to measure its volume. Subsequently, this water was transferred into two trenches, just to the east of monitoring well 192 (Figure 4), through several existing subsidence craters which provided access to these trenches. The water was pumped from the trenches by attaching a 2-inch diam intake hose of a self-priming gasoline-powered centrifugal pump to the top of the casings of either well 1 or 2 for removal from the east or west trench, respectively. Once the water level had been drawn down to an elevation below the screened interval as evidenced by air in the discharge line, each well was pumped further by placing a 1.5-inch diam intake hose to the bottom of the well casing. All but a few cm of water could be removed from the west trench by this method. In the east trench, however, water levels could only be drawn down to within about 80 cm of the bottom of the casing which was assumed to be resting on the trench floor. At this point, the pump would only remove small amounts of water mixed with large volumes of air. Thus, well 1 may have penetrated about a meter deeper than the actual trench floor and, hence, could retain the observed 80 cm of standing water due to rapid recharge from residual water on the trench bottom. The other wells in the east trench were considerably shallower than well 1 and for most of the time after water removal, these elevations were at or near the well bottom. Water levels within all intratrench wells receded uniformly when the trenches were pumped indicative of the large voids (hydrologic connection) between them. Once water had been removed from both trenches, water levels remained fairly steady for several days in spite of the steep hydraulic gradient to the surrounding water table indicating a very slow recharge from the surrounding water table.

The water removed from both trenches contained only low levels of dissolved and/or suspended radioactivity. Samples of the interstitial water were obtained from the intratrench monitoring wells between August 6 and 12, 1986. Five mL aliquots

Table 9
Summary of Fluid Additions and Removals from the
East and West Transuranic Waste Burial Trenches
in Solid Waste Storage Area 4

| | Trench | |
|-----------------------------------|----------|----------|
| | East | West |
| Water Pumped In | 9,369 L | 4,369 L |
| Water Pumped Out | 15,143 L | 15,437 L |
| Grout Added | 14,763 L | 16,277 L |
| Percent of Trench Voids Filled | 97.5% | 105% |
| Estimated Trench Dimensions: | | |
| Length | 4.49 m | 6.40 m |
| Width | 3.96 m | 3.66 m |
| Depth | 3.63 m | 3.26 m |
| Volume | 78,849 L | 76,351 L |
| Percent Void Space In Trench | 19% | 21% |

Table 10
Chemical and Radioactive Quality Characteristics of
Water Removed from the East and West Trenches
in Solid Waste Storage Area 4

| Characteristic | Units | Trench | | | | |
|--------------------------------------|-----------------------|--------|---------|---------|--------|---------|
| | | East | | | West | |
| | | 8/6/86 | 8/11/86 | 8/12/86 | 8/6/86 | 8/11/86 |
| Gross Alpha | Bq/L | nd | nd | nd | nd | nd |
| Gross Beta/ Gamma | Bq/L | 280 | 280 | 280 | nd | nd |
| pH | -log[H ⁺] | 6.5 | 6.5 | 6.3 | 6.3 | 6.4 |
| Electrical Conductivity | dS/m | 400 | 440 | 580 | 1120 | 1420 |
| Dissolved and Suspended Solids | mg/L | 300 | 320 | 520 | 1580 | 2240 |

nd = none detected above the detection limit of 10 Bq/L for both
gross alpha and gross beta/gamma.

were dried on tared 2-inch diam stainless steel planchets. After drying, the weight of deposited solids was determined by reweighing. The planchets were then counted repeatedly for one min intervals using an end-window Geiger-Muller tube for beta-gamma detection and an end-window alpha scintillation probe for gross alpha detection. Certified standards of ^{90}Sr (^{90}Y) and ^{241}Am were employed for the determination of beta-gamma and alpha counting efficiencies, respectively. Both radiation detectors were connected to a ratemeter (Ludlum Measurements Inc., Model 2001) with a one min preset counting interval. Electrical conductivity and pH were measured by procedures described elsewhere (Spalding 1984). Results of these water analyses are presented in Table 10. It should be noted that the samples from each trench initially appeared clear and uncolored and exhibited a strong anaerobic 'sulfide' odor. Within an hour of sample collection, a reddish iron hydroxide floc appeared indicative of ambient reducing conditions within each trench. The iron hydroxide precipitate was redissolved by acid addition prior to radioactivity determination to avoid any radionuclide scavenging from solution. Both the pH and electrical conductivity were determined before acid addition. In addition, samples from well 2 (west trench) contained an oily layer floating on top of the aqueous phase. A sample of this oil was collected from the interim storage tank used to measure the volume of water removed from the trench. The amount of oil removed from the trench was estimated to be no more than 10 gallons but was not transferred to the eastern trenches with the bulk of the water removed from the trench. It was incorporated in later batches of grout and returned to the study area trenches. It is most likely that this oil is residual machining oil as evidenced by the frequent encounter of metallic shavings during the augering of well holes in the west trench. A sample of this oil has been submitted for analysis of its composition.

The fractional trench void space was also calculated from the volume of water pumped from each trench and the trench overall dimensions (Table 9). The east and west trenches were estimated to contain 19 and 21% water accessible void space, respectively. These estimates of the volumes of trench void space are probably quite accurate; however, the expression as a fraction or percentage of the total trench volume may be considerably greater than presented in Table 9. The length and width of the trenches were estimated from the dimensions of the concrete cap and could be too large if the cap extends beyond the actual trench walls. Conversely, several borings near the trench cap indicate that the trench cap is at least no smaller than the actual trench. Likewise, the estimated trench depth, as discussed above, may be overestimated due to the extension of well casing below the true trench floor. Thus, the actual fractional trench void space may be greater than indicated above, perhaps up to the 30% recently measured in an older low-level waste trench in SWSA 6 (Spalding 1986).

The monitoring wells outside the trench exhibited a much

slower hydrologic connection to the two trenches. Before water was pumped into or out of either trench, the water levels within both trenches were perched above the water table elevation in the region. The perimeter monitoring wells did respond to several precipitation events during the period of observation and also responded slowly to fluid additions and removals from the trenches. The hydraulic gradient at the site appeared to be toward the south which is also the topographic gradient.

C. Grouting Operations

Field grout application consisted of mixing the grout and catalyst solutions as they were fed into a trench under a gravity head. Solutions of grout and catalyst were made up in 1,500 gallon seamless, polypropylene tanks. Each tank was fitted with a 2-inch diam three-way ball valve at its lower access port (Figure 6). One side of the valve was used for delivery of solution to the trench while the other side was used to recirculate solution to the tank's top access port when grout components were being dissolved in the tank.

A 10% acrylamide grout formulation was selected for the field operations. Into the first tank was placed approximately 1,200 gallons of water which was pumped from White Oak Creek. Fifty bags, at 50 pounds each, of AV-100 (Avanti International Inc.) were then emptied into the tank (Figure 7) followed by 30 L of AV-101 (triethanolamine blended with ethylene glycol, Avanti International Inc.), 1.14 kg of potassium ferricyanide, and 2.27 kg of Fe-EDDHA (Sequestrene 138Fe, Ciba-Geigy Inc.). The tank volume was then made up to 1,500 gallons with water. Into the second tank, was pumped 1,500 gallons of water into which was added 57 kg of ammonium persulfate (AV-102, Avanti International Inc.). Using two gasoline-powered centrifugal pumps, the solutions were recirculated through each tank until all solids were dissolved. Usually, complete dissolution required no more than 30 min. Three tanks were used in a rotation which allowed a second batch of grout to be prepared while the initial batch was being delivered to a trench (Figure 8). It generally required two people working about four hours to prepare a 3,000 gallon batch of grout and an additional four hours to deliver the grout to a trench under gravity head. Grout was delivered by mixing the outflow of two one-inch diam hoses at the delivery point of a trench. The final formulation contained 10% acrylamide grout (actually, 9.5% acrylamide plus 0.5% methylenebisacrylamide), 0.3% triethanolamine, 0.01% potassium ferricyanide, 0.5% ammonium persulfate, and 0.02% Fe-EDDHA. In the laboratory, samples of the trench water were used to prepare test batches of grout to determine what, if any, effect trench water constituents might have on grout set times. No inhibitions of grout set times were observed which indicated that there were no components in the indigenous trench water which could inhibit grout set. In these test batches, grout set times were actually decreased from 45 to 33 min by the trench water. Additions of

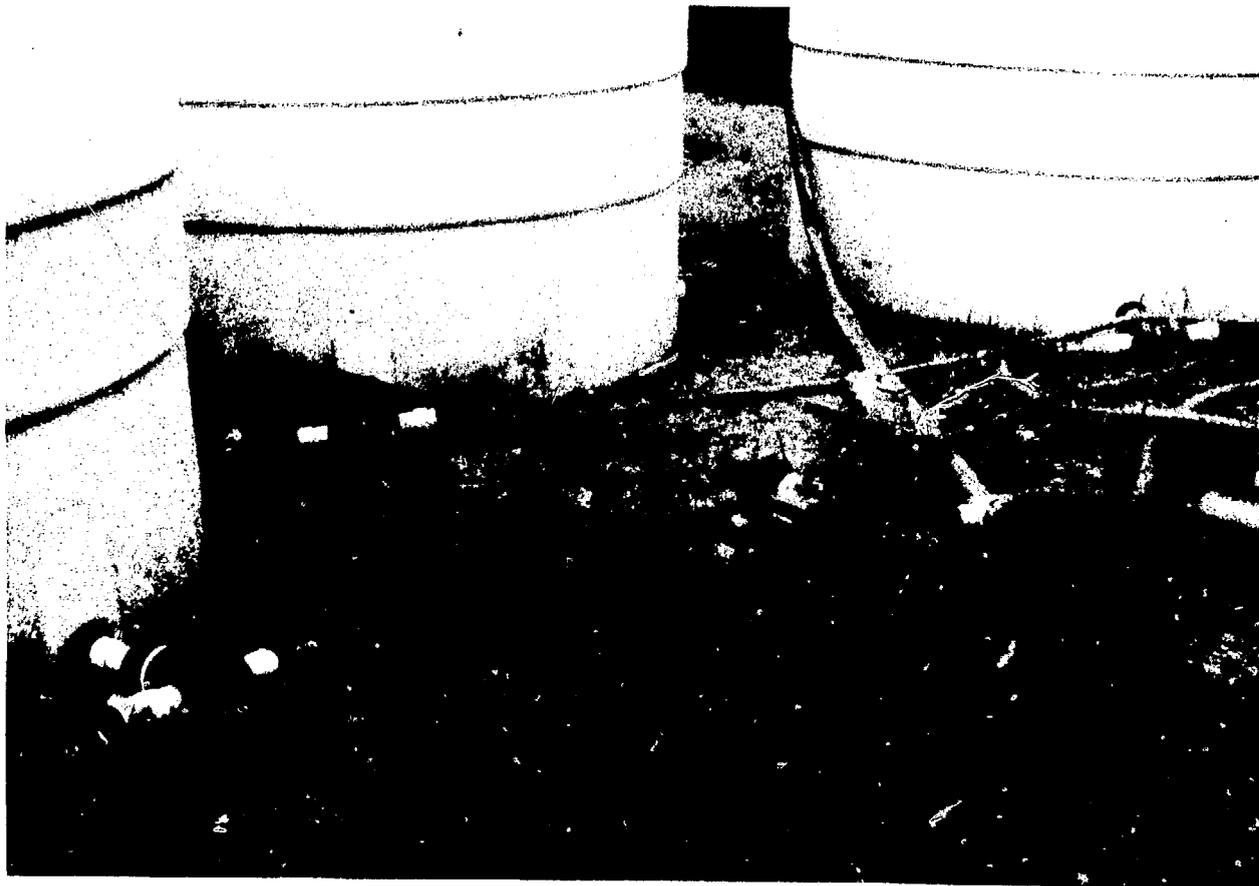


Figure 6. The arrangement of valves for recirculation and delivery of acrylic grout from the 1,500 gallon capacity polypropylene storage/mixing tanks.



Figure 7. Procedure for adding acrylamide grout in 50 pound bags to the 1,500 gallon capacity mixing tank.

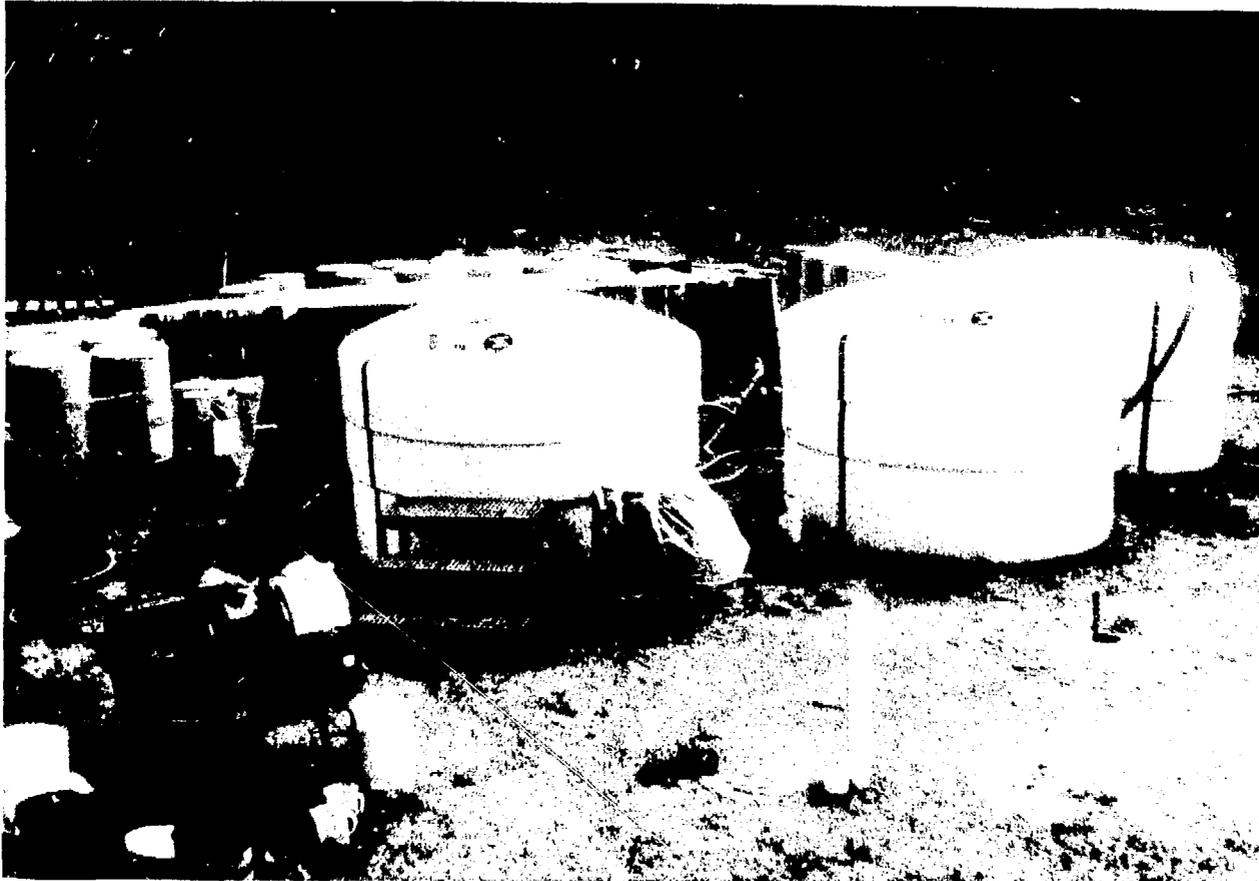


Figure 8. The field arrangement of the three 1,500 gallon capacity tanks for mixing and storing grout solutions in SWSA 4 in August 1986.

Fe-EDDHA up to the 0.02% concentration had no effect on grout set times. In the field, a 1:1 test aliquot of each batch was prepared for measurement of set time before adding that batch to a trench. Grout set times varied from 26 min to about 90 min for the various field batches prepared.

Grout was found to flow without restriction into both trenches. In the west trench, grout was introduced through one of the central boreholes in the concrete cap which could not be used for well casing insertion. In the east trench, the open annulus of well 7 was used for more than 95% of the grout addition while in the final stages of trench filling the annulus of well 10 was used. A total of about three batches was required to completely fill both trenches. Grout was placed into the west trench on August 27 and 28, 1986, while the east trench received grout on August 29 and September 2, 1986. Grout elevations were observed to rise quite uniformly into the open annuli of all well casings and into the open boreholes in the west trench. The total volumes placed in each trench are presented in Table 9. The volume of grout placed into the east and west trench amounted to 97 and 105% of their measured water accessible void space, respectively.

D. Grouting Evaluation

Although grout appeared to be uniformly distributed within the annuli outside well casings and in open boreholes within trenches, it was not as uniformly distributed inside well casings. Because each trench was grouted in at least two batches, the first batch apparently sealed the depth interval which contained the slotted portion of the well casing so that no further change in grout elevation within the casing was possible. A small amount of water was often trapped within the casing above the set grout. The grout is actually slightly more dense (specific gravity = 1.05 g/cm³) than water so that, if it did not mix completely with residual water within the trench, this water could float over the grout. Solidified grout was noted in all intratrench wells (Table 11). Several wells, which initially accepted water as fast as it could be delivered to the casing, became plugged after grouting (Table 11). These wells remained nonconductive to water when periodically observed over the following year.

Eleven weeks after grouting the trenches, sampling of the grout in the trenches was attempted to determine the vertical distribution of grout. Both split-spoon and thin-walled (Shelby tube) samplers were driven into the trenches through either the access holes in the concrete cap of the west trench or through the annular space around wells 7, 9, and 10. However, in no case was any significant amount of material retained within either sampler even when a plastic core-retaining spring was employed in the split-spoon sampler. Apparently, the grout fractured and deformed around rather than entered into the various sampling devices. When rotary coring tools were employed, the grout

Table 11
Grout Thickness and Hydraulic Conductivity of
Intratrench Monitoring Wells on September 22, 1986,
Three Weeks After Trench Grouting

| Well | Grout Thickness (m) | Hydraulic Conductivity |
|------|-----------------------------|---------------------------|
| 1 | 1.80 | None |
| 2 | 3.32 | None |
| 4 | 0.40 | Very slow |
| 7 | 2.21 | * |
| 8 | 1.01 | * |
| 9 | 2.80 | None |
| 10 | 2.60 | None |

* Wells 7 and 8 had leaks in their casings near the ground surface above the level of grout and could not be measured.
All other wells at the site did not contain any set grout.

behaved in the same way, i.e., deforming around rather than entering into the core barrel. Thus, traditional soil and rock sampling devices cannot be used to sample polyacrylamide grouted trenches.

An alternate approach was used to obtain 'core' material from these trenches. Because wells 7 and 9 appeared to be filled with grout (Table 11) and because these wells were slotted (screen open to the trench) for over 90% of their length (Table 8), it was presumed that their contained grout would be representative of the grout formed at various depths in the trench. Both well casings were pulled from the trench by lifting with the hydraulic drive head of the Mobile Drill rig. The removed casings were cut into 23 cm long pieces in the field, returned to the laboratory, and frozen to facilitate removal of the grout from the PVC casing. Using a ramrod, the frozen grout was extruded from the casing into plastic bags, and weighed. Samples from all sections appeared to contain solidified grout. Each sample was dried to constant weight at 100°C to determine moisture content. To determine organic matter content, i.e., the percentage of polyacrylamide grout, samples were ashed for 48 hr at 550°C and reweighed.

The results of this analysis for the sections of casing 'core' from well 7 are presented in Figure 9. A very similar pattern was also observed in the sections from well 9. The organic matter content (i.e., grout) was well above the target 10% for most of the core. The top three segments contained significant amounts of soil as evidenced by the high ash content

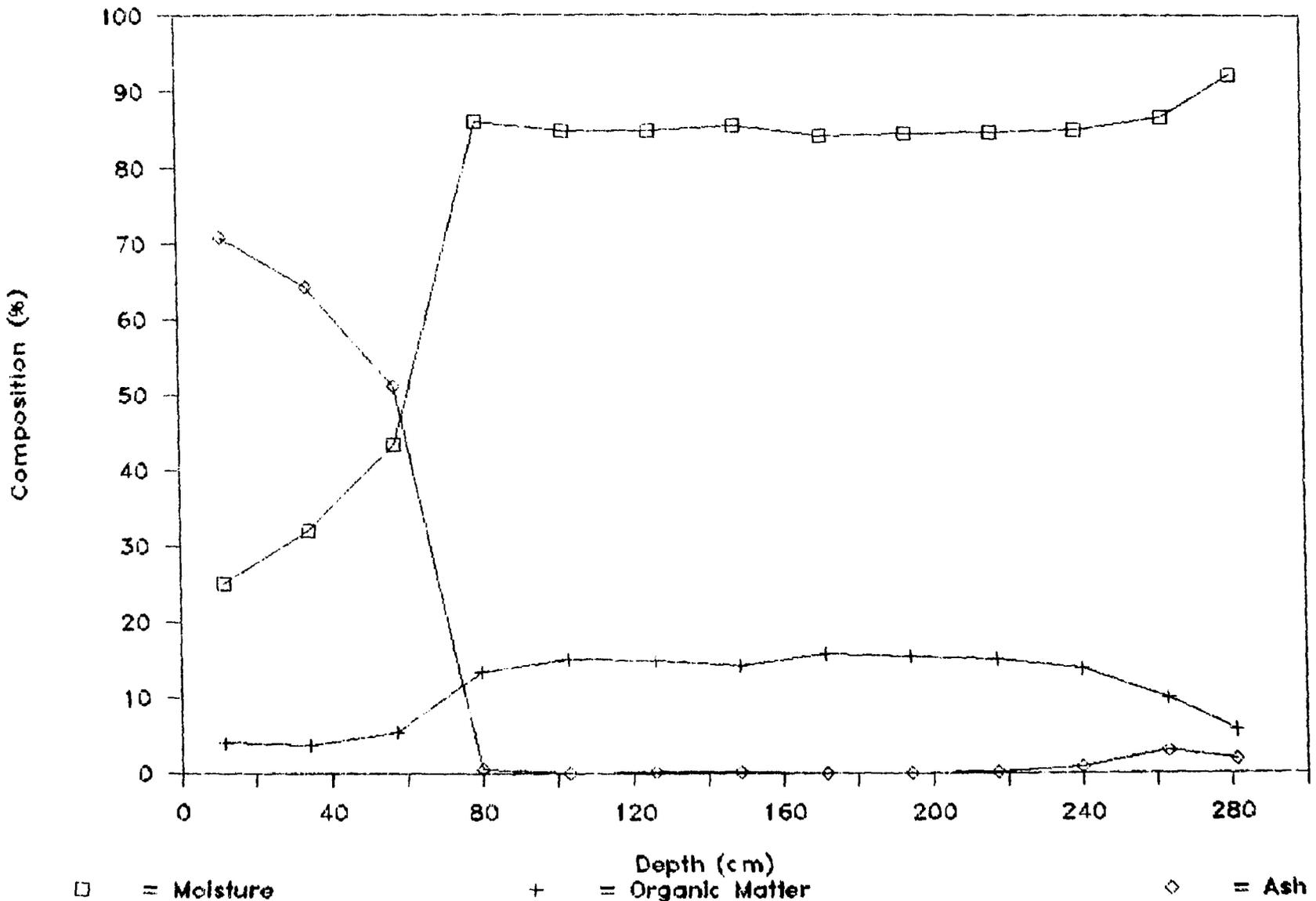


Figure 9. Characteristics of a grout core taken from Well 7 of east trench, Solid Waste Storage Area 4, November 19, 1986.

of these sections. On an ash-free basis, the grout content of these sections is also well above the 10% target level. Laboratory specimens of grout, analyzed by this procedure, were found to be essentially ashless (<.003%, fresh weight basis) whereas the test soil, described previously, contained 94.8% ash. Samples of the residual ash from all segments of well 7 and 9 were analyzed for ^{137}Cs and ^{60}Co but no activity was detected. These 'core' results confirm that the polyacrylamide grout was both present and solidified throughout the depth of the east trench.

The sampling of the monitoring wells around the two trenches was performed twice after grouting (Table 12). Water samples were filtered through 0.45 micron disposable filter units. Five mL aliquots were dried down on planchets and counted for gross alpha and beta activities as described previously. Samples were also analyzed for pH, electrical conductivity, hardness, alkalinity, and total dissolved solids (APHA 1980). Notably, no gross alpha or beta activity was observed in any sample above the routine detection limit of 10 Bq/L. The general chemical characteristics appeared to be typical of a groundwater in equilibria with excess carbonate. The dissolved solids contents of these samples are low enough to preclude the presence of significant amounts of grout components outside the trenches. The grout formulation pumped into these trenches had a dissolved solids content of 120 g/L. Recent samples from these wells are undergoing analysis for traces of all grout constituents (acrylamide, methylenebisacrylamide, acrylic acid, triethanolamine, and ethyleneglycol) via a recently developed direct injection liquid chromatographic separation. In addition, groundwater samples are also undergoing analyses for a variety of elements as part of water quality screening for this area.

The cost of grouting materials ran about \$1.83 per gallon. Figuring labor at \$40 per hour, would put grout preparation costs at about \$0.25 per gallon. This is based on two people working 8 hours to prepare and deliver a 3,000 gallon batch of grout. Equipment costs for this demonstration ran about \$5,000 for three tanks, three pumps, and miscellaneous hoses and pipe fittings. Actual site preparation and well placement costs are more difficult to estimate. Recent experience with direct insertion of well screens into burial trenches without concrete caps indicates that about 50% of the time wells can be driven to the bottom of a burial trench. Thus, well placement into trenches for grout injection can be quite facile and inexpensive.

DISCUSSION OF FUTURE AND CONTINUING WORK

Several characteristics of these grouted trenches need to be monitored for several years to enable long-term performance on in situ grouting to be assessed. First, the temporal persistence of the apparent high degree of hydrologic isolation needs to be documented. Periodic monitoring of the hydraulic conductivity of intratrench access wells will be used to assess this attribute.

Table 12
Chemical and Radiochemical Characteristics
of Waters from Monitoring Wells
Surrounding Polyacrylamide Grouted Trenches

| Well | pH | Electrical Conductivity (dS/m) | Hardness (mg CaCO ₃ /L) | Alkalinity | Dissolved Solids (mg/L) |
|------------------------------|-----|--------------------------------------|---|------------|-------------------------------|
| ----- Sampled 10/29/86 ----- | | | | | |
| 3 | 6.3 | 600 | 212 | 170 | 1600 |
| 5 | 7.9 | 280 | 162 | 148 | 200 |
| 6 | 7.9 | 312 | 204 | 153 | 240 |
| 11 | 7.9 | 580 | 298 | 310 | 420 |
| 12 | 7.9 | 670 | 344 | 359 | 440 |
| 13 | 7.0 | 505 | 246 | 257 | 360 |
| 14 | 7.7 | 470 | 268 | 257 | 360 |
| 15 | 7.2 | 1700 | 330 | 412 | 2020 |
| 16 | 6.6 | 620 | 274 | 176 | 540 |
| 17 | 8.1 | 645 | 344 | 323 | 400 |
| 18 | 8.2 | 430 | 234 | 211 | 300 |
| 19 | 8.0 | 820 | 356 | 196 | 840 |

| | | | | | |
|------------------------------|-----|------|-----|-----|------|
| ----- Sampled 08/04/87 ----- | | | | | |
| 5 | 6.8 | 315 | 146 | 159 | 1980 |
| 6 | 6.6 | 325 | 168 | 152 | 1660 |
| 11 | 6.1 | 790 | 298 | 310 | 760 |
| 12 | 6.3 | 660 | 290 | 260 | 640 |
| 13 | 6.1 | 660 | 318 | 274 | 1520 |
| 14 | 6.6 | 500 | 232 | 214 | 1300 |
| 15 | 7.1 | 1650 | 228 | 431 | 1540 |
| 16 | 6.1 | 660 | 240 | 124 | 160 |
| 17 | 6.6 | 650 | 258 | 210 | 260 |
| 18 | 7.0 | 440 | 200 | 168 | 460 |
| 19 | 6.4 | 1150 | 440 | 248 | 3200 |

Neither gross alpha nor gross beta activity was detected above the detection limit of 10 Bq/L for both gross alpha and gross beta.

Additional wells will be installed in the trenches to aid in this determination. Monitoring wells around the trench will need to be assayed for grout constituents in periodic samples to determine if any unpolymerized grout components have migrated from the trench. The durability of grout will also continue to be monitored in the laboratory degradation experiments. Additional ^{14}C -labeled grouts will be prepared to accurately assess long-term stability of the polyacrylamide. If the concerns over actual field grout performance and long-term stability can be answered by this work, then in situ immobilization of buried transuranic waste with polyacrylamide may become an appropriate and feasible remedial action.

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**Waste Examination Assay Facility Operations
TRU Waste Certification**

Presented by:

F. J. Schultz, ORNL

79/80

WASTE EXAMINATION ASSAY FACILITY OPERATIONS

TRU WASTE CERTIFICATION

F. J. Schultz
B. A. Caylor
D. E. Coffey
L. B. Phoenix

Operations Division

ABSTRACT

The ORNL Waste Examination Assay Facility (WEAF) was established in a cooperative program with the Los Alamos National Laboratory (LANL) in April, 1982 to nondestructively assay (NDA) transuranic (TRU) waste generated at ORNL. The present facility charter encompasses the NDA and nondestructive examination (NDE) of both TRU and low-level wastes (LLW).

Presently, the WEAFF's NDA/NDE equipment includes a Neutron Assay System (NAS), a Segmented Gamma Scanner (SGS), a drum-sized Real-Time Radiography (RTR) system, and a Neutron Slab Detector (NSD). The first three instruments are computer interfaced.

To date approximately 2300 TRU waste drums have been assayed with the NAS and SGS. Approximately 2500 TRU and LLW drums have been examined with the RTR unit. Computer data bases have been developed to collate the large amount of data generated during the assays and examinations.

Additional NDA and NDE instruments will be added to the WEAFF in the near future; a crate-sized RTR unit and an external gamma and neutron dose rate scanner. The WEAFF is being expanded (1600 sq. ft.) to accommodate the new instruments additional office space, and drum storage.

WASTE EXAMINATION ASSAY FACILITY OPERATIONS

TRU WASTE CERTIFICATION*

F. J. Schultz
B. A. Caylor
D. E. Coffey
L. B. Phoenix

Operations Division
Oak Ridge National Laboratory

To be presented at
Oak Ridge Model Conference '87
Oak Ridge, Tennessee
October 13-16, 1987

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*Research sponsored by the Defense Waste and Transportation Management Office, U.S. Department of Energy, under contract DE-AC05-84OR21400 with the Martin Marietta Energy Systems, Inc.

WASTE EXAMINATION ASSAY FACILITY OPERATIONS, TRU WASTE CERTIFICATION -
F. J. Schultz, B. A. Caylor, D. E. Coffey, L. B. Phoenix, Martin Marietta
Energy Systems, Oak Ridge National Laboratory, Oak Ridge, Tennessee

ABSTRACT

The ORNL Waste Examination Assay Facility (WEAF) was established as a cooperative program with the Los Alamos National Laboratory (LANL) in April, 1982 to nondestructively assay (NDA) transuranic (TRU) waste generated at ORNL. The present facility charter encompasses the NDA and nondestructive examination (NDE) of both TRU and low-level wastes (LLW).

Presently, the WEAF's NDA/NDE equipment includes a Neutron Assay System (NAS), a Segmented Gamma Scanner (SGS), a drum-sized Real-Time Radiography (RTR) system, and a Neutron Slab Detector (NSD). The first three instruments are computer interfaced.

Approximately 2300 TRU waste drums have been assayed with the NAS and the SGS. Another 3000 TRU and LLW drums have been examined with the RTR unit. Computer data bases have been developed to collate the large amount of data generated during the assays and examinations.

Additional NDA and NDE instruments will be added to the WEAF in the near future: a crate-sized RTR unit and an external gamma and neutron dose rate scanner. The WEAF is being expanded by an additional 1600 sq. ft. to accommodate the new instruments, additional office space, and drum storage.

1. INTRODUCTION

The Oak Ridge National Laboratory (ORNL) Waste Examination Assay Facility (WEAF) was established as a cooperative program with the Los Alamos National Laboratory (LANL) in April, 1982 to nondestructively assay (NDA) contact-handled transuranic (CH-TRU)* waste generated at ORNL. The WEAF is a 50 ft. by 100 ft. converted general storage building located in Solid Waste Storage Area 5 (approximately one-half mile south of the main ORNL complex), adjacent to the CH-TRU waste retrievable storage bunkers and the remote-handled transuranic (RH-TRU) waste storage area. Present WEAF personnel include one supervisor and three technicians.

*Transuranic waste as defined by DOE Order 5820.2 (ref. 1) is radioactive waste, without regard to source or form, that at the end of institutional control periods is contaminated with alpha-emitting transuranium radionuclides (any radionuclide having an atomic number greater than 92) with half-lives greater than 20 years and concentrations greater than 100 nCi/g. CH-TRU waste is defined as that waste whose measured container surface dose rate is less than 200 mrem/h.

ORNL was chosen by DOE as the site to field test a new NDA instrument developed by LANL (ref. 2). The unique waste characteristics and a willingness to test and demonstrate the instrument led to the selection of ORNL. The NAS, which was developed by LANL researchers John T. Caldwell and Walter E. Kunz (ref. 3, 4, 5), assays bulk solid waste to determine the TRU content. The lower limit of detection of the instrument allows the examiner to ascertain the fissile content (e.g., ^{239}Pu and ^{235}U) and the spontaneous fission component (e.g., ^{240}Pu and ^{252}Cf) of the waste at the 10 nCi/g level, which was the old definition of TRU waste. The NDA of these waste drums and, also, the NDE is required by the Waste Isolation Pilot Plant Waste Acceptance Criteria (WIPP-WAC) for those drums being shipped to the WIPP (ref. 6).

The original charter of the TRU Waste Drum Assay Facility (the name of WEAFF from 1982 to 1985) called for the NDA of CH-TRU waste packaged in 55- and 30-gallon mild and stainless steel drums. The NDA instruments which were first available to accomplish this task included a SGS, a NSD, and the LANL-developed NAS. Descriptions of these systems, as well as proposed systems, are found in the Systems Descriptions section of this report.

2. SYSTEMS DESCRIPTIONS

Present Systems:

Neutron Assay System:

The NAS is a $4\text{-}\pi$ neutron detection system using shielded (cadmium-wrapped) and bare ^3He detectors embedded in the assay chamber walls. The system is capable of both active and passive scans. The active scan uses a deuterium-tritium pulsed neutron generator which emits 14-MeV neutrons and is pulsed 2000 times per assay. The neutrons are thermalized by the surrounding graphite chamber walls. These thermal neutrons are then captured by any fissile nuclides (e.g., ^{235}U and ^{239}Pu) contained in the waste drum. The resulting fission neutrons are detected by the cadmium-wrapped ^3He detectors. The passive scan detects any spontaneous fission and (alpha,n) neutrons. The combined assay yields the total TRU content of the waste drum.

Segmented Gamma Scanner:

The SGS is a passive gamma-ray detection system using a high-purity germanium detector. Gamma rays which are emitted during radionuclide decay and are contained in sufficient quantities in the waste drum are detected and the energies compared by the system software to a nuclide library. A printout listing the possible radionuclides emitting the detected gamma-rays is produced. The system is being upgraded to perform quantitative measurements. The upgrade is expected to be completed in October 1987. The system has been in operation since April 1982.

Real-Time Radiography:

The RTR unit is used to detect nonconformance items (e.g., lead, liquids, etc.), as defined by ORNL and the Waste Isolation Pilot Plant Waste Acceptance Criteria Certification Committee (WIPP-WACCC), contained in LLW and CH-TRU waste drums. A 320 kV (max) constant potential X-ray tube head generates the X-rays used in the examinations. A rare-earth phosphor screen converts the X-ray energy to light energy, which, in turn, is viewed on a TV screen. The drum is rotated and scanned vertically, while the X-ray generator and image system remain stationary. The system has been in operation since November 1985.

Neutron Slab Detector (NSD):

The NSD is used as a screening station to segregate "hot" ($> 1.0 \text{ E}04 \text{ n/s}$) from "cold" ($< 1.0 \text{ E}04 \text{ n/s}$) drums. The "hot" drums are sent through the WEAFF systems first to reduce the background encountered during assay of the "cold" drums. The drums are also weighed at this station. This system has been operational since January 1983.

Proposed Systems:Crate RTR Unit:

The crate RTR unit will nondestructively examine crate-size containers (up to 10 ft. long x 6 ft. wide x 7 ft. high) in the same manner as previously outlined in the drum RTR unit description. The system will use a 420 KV (max) constant potential X-ray tube head and will also be capable of examining drums. A vendor has been selected, and the system is scheduled to be delivered to ORNL by January 1988.

External Gamma and Neutron Dose Rate Scanner:

The gamma and neutron external dose rate scanner will automatically scan each waste package, including both drums and crates, for total external dose rate (neutron and gamma ray). Each hot spot detected by the NaI crystal detectors will be recorded by an IBM-AT computer and located relative to a starting position on the waste container surface. This measurement will negate the need for the WEAFF technicians or Health Physicists to perform these measurements manually. The installation of this system will reduce the radiation dose received by the WEAFF technicians and thus follow the ALARA principle. The waste package will also be weighed at this station (replacing the weigh station described above). Funding in the amount of \$110K has been approved for this system. Specifications have been developed and are being reviewed prior to initiating the bidding cycle.

3. PAST CERTIFICATION ACTIVITIES

A DOE-HQ controlled milestone (OR85.10), which required the assay of all newly-generated (NG) and stored inventory CH-TRU waste drums, was accomplished on schedule (September 1985). The number of waste drums assayed by the NAS and SGS systems totaled 2151. Of this total, 1489 drums (69% of drum population) were categorized TRU, while 118 drums (6% of drum population) were categorized LLW. The remaining 544 drums (25% of drum population) were not categorized. The criteria used to establish each drum's category (i.e., TRU, LLW, or unknown) are presented in Table 1.

Table 1. CH-TRU Waste Drum Categorization Criteria

| Waste Type | Criteria |
|------------|--|
| LLW* | 1. NAS assay scan |
| | a. active: less than 67 mg ^{239}Pu equivalent and, |
| | b. passive: less than 20 neutrons per second (n/s) |
| | 2. SGS scan |
| | a. Did not detect presence of ^{241}Am or ^{237}Np daughters |
| TRU | 1. NAS assay scan |
| | a. active: greater than 67 mg ^{239}Pu equivalent or, |
| | b. passive: greater than 1.0 E05 n/s |
| Unknown | 1. NAS assay scan |
| | a. active: less than 67 mg ^{239}Pu equivalent and, |
| | b. passive: greater than 20 n/s and less than 1.0 E05 n/s |
| | 2. SGS scan |
| | a. Detects presence of ^{241}Am or ^{237}Np daughters] |

*For a drum to be categorized low-level waste (LLW) both criteria (1 and 2) must be satisfied.

4. PRESENT CERTIFICATION ACTIVITIES

The present charter of the WEAFF calls for the continuation of the NDA of CH-TRU waste drums using the NAS and SGS systems. Additional certification activities now include the NDE of both CH-TRU and LLW drums using the RTR system (see Systems Descriptions section). The waste acceptance criteria used in the examination of LLW are very similar to those used in the examination of CH-TRU waste drums.

The waste acceptance criteria of interest which are noted by the WEAFF examination technicians during RTR inspections of waste drums are (1) no free liquids, (2) no compressed gas cylinders, (3) note presence of lead, and (4) note presence of high-efficiency particulate air filters (HEPA filters). Waste drums (both CH-TRU and LLW) are rejected, a nonconformance report filed, and returned for repackaging if the presence of free liquids and/or unpunctured compressed gas cylinders are confirmed by RTR inspection. Drums are either returned to the waste generator or stored to await construction of a repackaging facility depending on the generation date of the drum. LLW drums are rejected if the presence of lead is confirmed by the RTR inspection. CH-TRU waste drums are tagged "HOLD" if the presence of HEPA filter(s) is detected by RTR inspection.

A DOE-HQ milestone, OR087.01, which requires the completion of the NDE (using RTR unit) of the stored inventory of CH-TRU waste drums, is due to be completed by second quarter fiscal year 1988. To date (September 1987), 1826 CH-TRU waste drums have been examined at the WEAFF using the RTR unit and 984 drums (54%) have passed the inspection, while 736 drums (40%) have been rejected. One hundred and six drums have been tagged "HOLD" due to the suspected presence of HEPA filter(s). The rejection rate of the NG CH-TRU waste drums has declined steadily since the inception of the program. The rejection rate since March 1987 through the present is 11%.

As of September 1987, 1198 LLW drums have been examined at the WEAFF using the RTR unit. Of this number, 942 drums (79%) have passed the inspection, and 256 drums have failed (21%). The rejection rate time history for LLW drums parallels the rate for the CH-TRU waste drums.

A variety of computer data bases have been developed by WEAFF personnel to collate and analyze the large volume of data acquired during the NDA and NDE waste drum certification activities. The data bases use commercially available software.

5. FUTURE CERTIFICATION ACTIVITIES

Future certification activities at the WEAFF will include the NDE of CH-TRU and low-level wastes packaged in boxes using the crate-sized RTR unit. This activity is scheduled to begin in the second quarter of fiscal year 1988.

The waste acceptance criteria, which had been established for the waste drums, will be applied to the acceptance or rejection of waste boxes. The NDA and NDE of NG CH-TRU and low-level waste drums and boxes will continue.

The WEAFF is scheduled to be expanded by an additional 1600 sq. ft. The expansion is required to accommodate the new instruments expected (see Proposed Systems in Systems Descriptions section) to be installed, additional office space, and waste drum and box storage areas.

CH-TRU waste drums are scheduled to be shipped from ORNL to WIPP beginning in the first quarter fiscal year 1989 (DOE-HQ controlled milestone, OR087.02). To prepare for these shipments, WEAFF future certification activities will focus on the preparation of the WIPP waste drum data packages and completion of the NDA and NDE of all CH-TRU waste drums and boxes. These data packages must accompany each shipment to the WIPP.

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**Membrane-Based Systems for Speciation and
Removal of Metals from Wastewater**

Presented by:

**James A. Cox,
Miami University, Oxford, Ohio**

MEMBRANE-BASED SYSTEMS FOR SPECIATION AND REMOVAL OF METALS FROM WASTE-WATER, James A. Cox, Atul Bhatnagar, and Samar Al-Shakshir, Department of Chemistry, Miami University, Oxford, OH 45056.

The separation of a sample (feed solution) from a receiver (stripping solution) by a membrane comprises a simple method for removal of selected species from the sample. To have a sufficient transport rate, the process must be driven against the concentration gradient of the test species. Two methods for accomplishing uphill transport of metal ions, Donnan dialysis across ion exchange membrane and proton-coupled transport across ligand-containing liquid membranes, will be described and compared. In addition, a method which uses only ion-pairing to cause uphill transport of arsenic across a nonpolar liquid membrane will be described.

Data will be shown to demonstrate that Donnan dialysis and proton-coupled transport have similar transport rates under ideal conditions. The latter may be less useful when a set of metals is to be removed by immobilization of a general complexing agent in the liquid membrane. The former has a limited ability to separate a selected metal and also is not suitable for high ionic strengths samples. Among the systems to be described is the transport of Zn(II) from a mixture of metals by Donnan dialysis and by coupled transport across a dithizone-containing liquid membrane. In the latter case, the presence of other metals in the sample lowered the transport rate.

The methods differ in their responses when the test metals are complexed in the sample. Because of the presence of a strong complexing in the liquid membrane, this process extracts metals from virtually all samples, whereas Donnan dialysis can be used to selectively remove free plus labile-complexed metal ions. The test samples include Cu(II) complexes of humic acid, glycine, and ethylenediamine and the Ni(II)-phenanthroline complex that is very inert.

MEMBRANE-BASED SYSTEMS FOR SPECIATION AND REMOVAL
OF METALS FROM WASTEWATER

James A. Cox and Atul Bhatnagar
Department of Chemistry
Miami University
Oxford, OH 45056

Samar Al-Shakshir
An-Najah University
Nablus, Israel

The separation of an aqueous sample (feed solution) from a receiver (stripping solution) by a membrane can result in removal of components from a sample. For a practical system, the species to be removed must transport against their concentration gradients (uphill transport) across the membrane (Figure 1). Our program has been focused on using chemical methods to "pump" selected ions out of aqueous samples (Figure 2).

The most studied method for chemically-causing uphill transport is Donnan dialysis [1-4]. Here, an ionic strength gradient across an ion-exchange membrane provides the driving force. Ideally, only counterions (ions of charge-sign opposite to those of the fixed exchange sites on the membrane) are transported across the membrane. Thus, the electrostatic imbalance in the chamber of higher ionic strength (i.e. the receiver) that would result from passive diffusion of these counterions can only be compensated by entry of counterions from the sample into the receiver. This exchange will continue until Donnan equilibrium is reached (Figure 3). If the ionic strength of the receiver is much higher than that of the sample, virtually all of the counterions that were originally present in the sample will be replaced by counterions from the receiver. A sample calculation is included in Figure 3.

Donnan dialysis can be used as an enrichment technique for trace chemical analysis as well as a means of water treatment. In order to be a practical preconcentration technique, the enrichment factor (EF), which is defined as the concentration of the analyte in the receiver after dialysis divided by its initial concentration in the sample, must be high, independent of the initial concentration of the analyte in the sample, and independent of the sample matrix over a wide range of conditions. The overall transport rate and its independence of the sample matrix determine whether Donnan dialysis (or, in fact, any membrane method) is a practical method for water treatment. The EF cannot be independent of sample matrix if the system is allowed to go to Donnan equilibrium (Figure 4); therefore, the enrichment factor is determined after a prescribed dialysis time (i.e., the resulting fixed-time kinetic mode is

used for quantitation). The EF so obtained satisfies the above conditions when the composition of the receiver is properly selected [1-4].

Uphill transport across liquid membranes has recently received attention as a means for removal of metal ions from water (see references 5-8) and as an analytical preconcentration technique [9,10]. Most commonly, the supported liquid membrane (a polypropylene microporous membrane that is soaked with kerosene, for example) is impregnated with a complexing agent for the metal of interest. If the complexing agent is the conjugate base (acid) of a weak acid (base), transport of the metal from a relatively basic (acidic) sample into a relatively acidic (basic) receiver is driven by coupled transport of hydrogen ion. This scheme is illustrated in Figure 5.

Any coupled transport mechanism or any procedure by which the diffusion gradient of the test species into the receiver is maintained by a chemical method (Figure 2) will result in net uphill transport. An example of the latter is ion-pair extraction. Here, a neutral complex in an aqueous sample can partition into the less-polar organic membrane, diffuse to the receiver/membrane interphase and dissociate into the receiver solution, which does not contain a high concentration of the ion-pairing reagent. The flux can continue until the build-up of the ion-pairing reagent in the receiver slows the dissociation reaction. Figure 6 shows a scheme that we have used to preconcentrate As(III) from water samples. The need to have a high concentration of an ion-pairing agent in the sample limits the applicability of this approach to water treatment.

In this paper, the coupled transport modes will be illustrated, and their relative merits for application to removal of metal ions from samples will be compared. Special concerns will be the effect of complexing agents and of mixtures of metal ions in the samples on transport rates as these are problems that are encountered in wastewater treatment.

Figures 7 and 8 illustrate the cells used for stirred-solution, sheet-membrane and for flowed-solution, tubular-membrane experiments, respectively. The latter are far more efficient because for a defined receiver volume the surface area of the tubular membrane is much higher than that of the sheet-membrane cell (about 20-times higher in our cells). As a result, with a sample flowed a 2.2 L min^{-1} , a receiver of 5 mL of 0.2 M MgSO_4 , 0.5 mM $\text{Al}_2(\text{SO}_4)_3$ at pH 5, and 10 m of Nafion 811 tubing as the cation-exchange membrane, the transport rates of Cd(II) and Cu(II) were 17-times higher than with the Figure 7 set-up and a 11.3 cm^2 cell. After 15 minutes during which the sample was recirculated, 13% of Cd(II) and Cu(II) was removed from a 2000 mL sample. This fraction was unchanged as the sample concentration was varied from 10^{-6} to 10^{-9} M; higher concentrations were not investigated in that series of experiments, but generally we have found that the range can be extended to at least 10^{-4} M.

Coupled transport that is driven by a hydrogen-ion gradient across a liquid membrane that contains a complexing agent (mobile carrier) yields

about the same rate of metal ion removal as Donnan dialysis. For example, a pair of experiments was performed with the apparatus shown in Figure 7. In one, the membrane was Celgard 2400, 0.025 mm thickness, which contained an equal-volume mixture of carbon tetrachloride and kerosene that was saturated with diphenylthiocarbazon (dithizone); 0.1 M HCl (5 mL) was the receiver. In the other experiment, an R-1010 cation-exchange membrane (RAI Research Corp.), 0.035 mm thickness, was used with 0.2 M MgSO_4 , 0.5 mM $\text{Al}_2(\text{SO}_4)_3$ at pH 5 as the receiver. The test ion was Zn(II). In the former experiment the sample was a pH 4.7 acetate buffer (0.1 M) that contained 10 mM thiosulfate (which increases the transport rate of Zn(II) by displacing water from otherwise-unoccupied coordination sites in the complex); in the latter, water was the sample matrix. Five trials were performed for each experiment. The pH-driven experiment yielded a flux of $1.11 \pm 0.04 \mu\text{mol Zn/h}$ and the latter, $0.78 \pm 0.04 \mu\text{mol Zn/h}$, from a 1.52×10^{-5} M sample (200 mL). In each case the flux is nearly proportional to the initial concentration of the Zn(II) in the sample over the range 10^{-4} M to 10^{-7} M when the dialyses are performed for 60 minutes.

Tubular microporous supports for liquid membranes are available. Studies by others indicate that the merits of the tubular geometry relative to sheets which we demonstrated for Donnan dialysis are observed with liquid membranes as well.

When a complexing agent is present in the sample, it can be hypothesized that the rate of Donnan dialysis will decrease because of the lower equilibrium concentration of the free metal ion; the hypothesis assumes that the complex does not completely dissociate on the time scale of contact of an incremental volume of the sample with the membrane when the solution is flowed or stirred (a few msec). With the complex-impregnated liquid membrane, a lesser effect is predicted as long as the formation constant of the complex between the metal and the immobilized ligand is greater than that between the metal ion and the complexing agent in the aqueous solution.

The data in Tables 1-3 support this prediction. With Cu(II) as the analyte, the effect of concentration of various complexing agents in the sample is less with proton-driven transport across a LIX-64N containing membrane than with Donnan dialysis into a 0.2 M MgSO_4 , 0.5 mM $\text{Al}_2(\text{SO}_4)_3$ receiver at pH 5. The selective complexing agent for Cu(II), LIX-64N, is a commercial (Henkel Corp.) mixture of substituted oximes of the general structure shown in Figure 9.

In general, the above result that the liquid membrane method is relatively advantageous is not observed. We have identified three problems. Perhaps most important is that the transport rate of a given metal can markedly change when other cations are present in the sample. For example, the transport rate of 1×10^{-5} M Cu(II) from a pH 2.5 sample across a 10% LIX-64N/90% kerosene membrane into 0.1 M HCl decreases by 70% when 1.1×10^{-4} M Fe(III) is also present [9]. With a pH 4.7 sample the decrease is only 20%. The probable cause of the decrease is the formation

of a charged complex between Fe(III) and a component of the membrane; no transport of Fe(III) was observed, so a neutral complex was probably not formed.

The above results suggest that the use of the liquid membrane method where a general complexing agent is immobilized may fail to remove metals from mixed samples, which is a desired application in water treatment. This was tested with a membrane comprising an equal-volume mixture of carbon tetrachloride and kerosene as the matrix and dithizone as the immobilized complexing agent. The primary test species was Zn(II), and the interferent was Cu(II). In a pH 4.7 sample (0.1 M acetate buffer), both Zn(II) and Cu(II) form neutral dithizonates. For the previously-discussed reason, the sample also included 0.01 M thiosulfate.

When Cu(II) was not present, 80% of the Zn(II) was removed in 4 hours from a 200 mL sample with an initial Zn(II) concentration of 10 μ M. This efficiency is high when it is considered that the cell was of the design in Figure 7 with a 11.3 cm² membrane. When the sample also included 1.0×10^{-4} M Cu(II), the removal decreased to only 9% in 4 hours. Our earlier work [1,4] demonstrated that with either a Mg(II), Al(III) mixture or an EDTA solution as the receiver, mixtures of metals can be Donnan-dialyzed at the same rate as single-component samples.

The above experiments suggest a second problem with the liquid membrane method. Metals that form coordinately unsaturated complexes will have otherwise-unoccupied sites filled by water. The resulting hydrophilic system will only slowly partition into the membrane phase unless a complexing agent is also added to the feed solution. For example, the transport rate of Zn(II) is decreased by 92% if thiosulfate is not added to the 10 μ M Zn(II) solution at pH 4.7.

The third problem is readily predicted. In order to overcome the effect of complexation in the sample on transport across the liquid membrane, the ligand therein must form the stronger complex with the metal of interest. Considering the other constraints on the system (in order to have rapid transport, the latter complex must be neutral and coordinatively saturated) the choices for mobile carriers are limited.

As an example, Table 4 summarizes the effect of pH on the Donnan dialysis of Ni(II) from triethylenetetramine (trien)-containing solutions. The Ni(trien)₂²⁺ complex is known to have a high formation constant and is quite inert. Unless the pH of the solution is in a range where trien is protonated rather than complexed with Ni(II), i.e. a pH below 4, the transport rate is markedly decreased by the complexation.

We have not yet found a liquid membrane system that overcomes this problem. Neither dithizone nor dimethylglyoxime in the membrane promoted Ni(II) transport. With 8-hydroxyquinoline, the membrane was destroyed when contacted to a Ni(II) solution; this may have been the result of precipitate formation in or on the membrane.

Donnan dialysis can be used to transport metals from samples that contain complexing agents as long as the complexation in the sample is either very-or-moderately labile or is slowly labile and pH dependent. Of importance is that it does not require adjustment of the pH of the sample. Instead, the fact that the receiver pH controls the acidity at the sample/membrane interphase is used.

Table 5 shows the rate of Donnan dialysis from humate-containing solutions into 0.2 M MgSO_4 , 0.5 mM $\text{Al}_2(\text{SO}_4)_3$ receivers at pH's 4.7 and 1.0. Into the former, the rate is dependent upon the humic acid concentration, which is consistent with the data in Tables 1-3. However, with the pH 1.0 receiver, the addition of 10 mg of humic acid/L only decreased the transport rate by about 20%.

These results suggest that at present Donnan dialysis is superior to mobile carrier dialysis for the general removal of metals from wastewater unless: 1) a separation of one metal from a mixture is the objective or 2) the ionic strength of the sample is too high (greater than about 0.05 to 0.10) to yield rapid transport.

Two facets of the previous discussion indicate that Donnan dialysis can be used for a degree of speciation of complexes. The metal that dialyzes into a ca. neutral receiver is indicative of the free ion plus the metal that is bound in a "labile" complex (i.e., a complex that can dissociate on the earlier-mentioned time scale of contact between an incremental volume of sample and the membrane). An independent determination of the total quantity of metal allows calculation of the "free-plus-labile complexed" metal fraction. With an acidic receiver, metal from even "slowly labile" complexes is dialyzed. By difference, the "inert-complex" fraction is determined. We have described this scheme [11] and compared it to results obtained by a column and bulk ion-exchange approach [12] for systems that involved neutral complexes.

When the sample contains charged-complexes, ion-exchange chromatography cannot be used for speciation because the metal is retained on the column even when the complex in the sample is inert. Thus, it would be incorrectly assigned as in the "free-plus-labile complexed" metal fraction [12]. With Donnan dialysis, an inert, charged complex is not dialyzed because of its size.

The above points are illustrated in Table 6. With Donnan dialysis the results follow the known order of the kinetics of dissociation, but the ion-exchange column retains the metal in all cases.

Although the data in Table 6 demonstrate the utility of Donnan dialysis as a means of speciation of metals, they also show a limitation in terms of removal of metals from water samples. If the metal is bound in an inert complex, it will remain in the feed solution. These complexes cannot be dissociated by simply acidifying the receiver solution (and therefore the sample/membrane interphase). Of course, mobile carrier dialysis can also be predicted to fail in this case.

ACKNOWLEDGEMENT

This work was performed in part at Southern Illinois University where it was supported by the EPA and NSF through grants to JAC.

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TABLE 1. Removal of Cu(II) from Ethylenediamine (en)-Containing Samples by Donnan Dialysis and Mobile Carrier Dialysis

| conc. en, μM | % Cu removed by: | |
|-------------------------|------------------------------|--------------------------------------|
| | Donnan Dialysis ^a | Mobile Carrier Dialysis ^b |
| 0 | 1.8 %/cm ² -h | 1.2 %/cm ² -h |
| 40 | 1.8 %/cm ² -h | 1.2 %/cm ² -h |
| 100 | 1.8 %/cm ² -h | 1.2 %/cm ² -h |

Sample volume, 100 mL; initial conc. of Cu, 10 μM ; cell-type, sheet membranes with a magnetic stirrer.

^a cation-exchange membrane; 5 mL Mg(II), Al(III) receiver.

^b LIX-64N, kerosene membrane; 5 mL 0.1 M HCl receiver.

TABLE 2. Removal of Cu(II) from Glycine (gly)-Containing Samples by Donnan Dialysis and Mobile Carrier Dialysis

| conc. gly, mM | pH | % Cu removed by: | |
|---------------|----|--------------------------|---------------------------|
| | | DD, %/cm ² -h | MCD, %/cm ² -h |
| 0 | 3 | 2.1 | 1.2 |
| 1 | 3 | 2.1 | 1.2 |
| 0 | 5 | 2.1 | 1.1 |
| 1 | 5 | 1.7 | 0.9 |
| 0 | 7 | 2.1 | 1.2 |
| 1 | 7 | 1.0 | 1.2 |

Conditions the same as in Table 1.

TABLE 3. Removal of Cu(II) from Humate-Containing Samples by Donnan Dialysis and Mobile Carrier Dialysis

| humic acid, mg/L | Removal of Cu by: | |
|------------------|-------------------------|--------------------------|
| | DD %/cm ² -h | MCD %/cm ² -h |
| 0 | 2.2 | 1.2 |
| 1 | 1.8 | 1.1 |
| 3 | 1.5 | 1.1 |
| 5 | 1.1 | 1.1 |
| 7 | 1.0 | 1.2 |
| 10 | 0.8 | 1.2 |

Conditions the same as Table 1.

TABLE 4. Donnan Dialysis of Ni(II) from Trien-Containing Solutions.

| Ni(II), μ M | Sample | | removal of Ni(II), %/cm ² -h |
|-----------------|-----------|-----|--|
| | trien, mM | pH | |
| 50 | 0.0 | 6.0 | 2.6 |
| 50 | 0.2 | 5.5 | 1.5 |
| 50 | 0.2 | 6.9 | 1.1 |
| 50 | 0.2 | 9.6 | 0.5 |
| 50 | 0.2 | 3.5 | 2.4 |
| 50 | 0.2 | 4.0 | 2.4 |

100 mL sample; Figure 7 cell; 5 ml Mg(II), Al(III) receiver at pH 5.

TABLE 5. Effect of the pH of the Receiver on the Donnan Dialysis of Cu(II) from Humate-Containing Samples

| humic acid, mg/L | Removal of Cu in %/cm-h | |
|------------------|-------------------------|-----------------|
| | pH 4.7 receiver | pH 1.0 receiver |
| 0 | 2.2 | 2.7 |
| 1 | 1.8 | 2.5 |
| 3 | 1.5 | 2.5 |
| 5 | 1.1 | 2.4 |
| 7 | 1.0 | 2.3 |
| 10 | 0.8 | 2.2 |

Figure 7 cell design.

TABLE 6. Speciation of Charged Complexes by Donnan Dialysis.

| Sample | EF | % nonlabile by: | |
|--|---------------|-----------------|---------------------|
| | | Donnan dialysis | ion-exchange column |
| 10 μM Fe(II) | 4.3 ± 0.2 | | |
| 10 μM Fe(II), 40 μM phen | 0.2 ± 0.0 | 95 ^a | 0.0 |
| 50 μM Ni(II) | 5.3 ± 0.3 | | |
| 50 μM Ni(II), 0.2 mM trien, pH 8 | 1.6 ± 0.1 | 70 | 0.0 |
| 50 μM Ni(II) | 5.3 ± 0.3 | | |
| 50 μM Ni(II), 0.2 mM en | 5.0 ± 0.3 | 0.1 | 0.0 |

phen, orthophenanthroline; trien, triethylenetetramine; en, ethylenediamine.

$$^a \text{ 95\%} = \left(1 - \frac{0.2}{4.3}\right)100$$

$$\begin{array}{l} t = 0 \\ \\ t = t_D \end{array} \quad \begin{array}{l} C_{A,S} = C_{A,S}^* \\ C_{A,R} = 0 \\ C_{A,R} > C_{A,S}^* \end{array}$$

S = sample sol'n

M = membrane

R = receiver sol'n

A = analyte

D = dialysis time

Figure 1. Definition of Uphill Transport.

Instrumental

- a. Constant current electro dialysis
- b. Constant potential electro dialysis

Chemical

- a. Sustained passive diffusion
 - i. redox of transported species in receiver
 - ii. complexation of transported species in receiver
 - iii. ion-pair dissociation at the membrane/receiver interphase
- b. Coupled transport
 - i. ion-strength driving force (Donnan dialysis)
 - ii. pH gradient driving force

Figure 2. Modes of Uphill Transport . .

CATION EXCHANGE MEMBRANE

| | | |
|---------------------------|--|----------------------|
| SAMPLE (200 mL) | | RECEIVER (5 mL) |
| 1×10^{-5} M NaCl | | 1.0 M KNO_3 |
| | | |
| | | |

At Donnan Equilibrium:

$$\frac{[\text{Na}^+]_R}{[\text{Na}^+]_S} = \frac{[\text{K}^+]_R}{[\text{K}^+]_S} = \frac{(\text{total initial positive charge})_R}{(\text{total initial positive charge})_S}$$

$$\frac{[\text{Na}^+]_R}{[\text{Na}^+]_S} = 1 \times 10^4 \quad \text{or} \quad [\text{Na}^+]_R = 3.98 \times 10^{-4}$$

Enrichment factor = 39.8

(99.5% removed)

Figure 3. General Model for Donnan Dialysis.

- A. It takes too long to reach equilibrium.
- B. The position of equilibrium depends on ionic strength of the sample.
- C. The transport rate is directly proportional to initial concentration so linear calibration curves can be constructed via the kinetic method.

Figure 4. Factors favoring Fixed-Time Kinetic Applications of Donnan Dialysis.

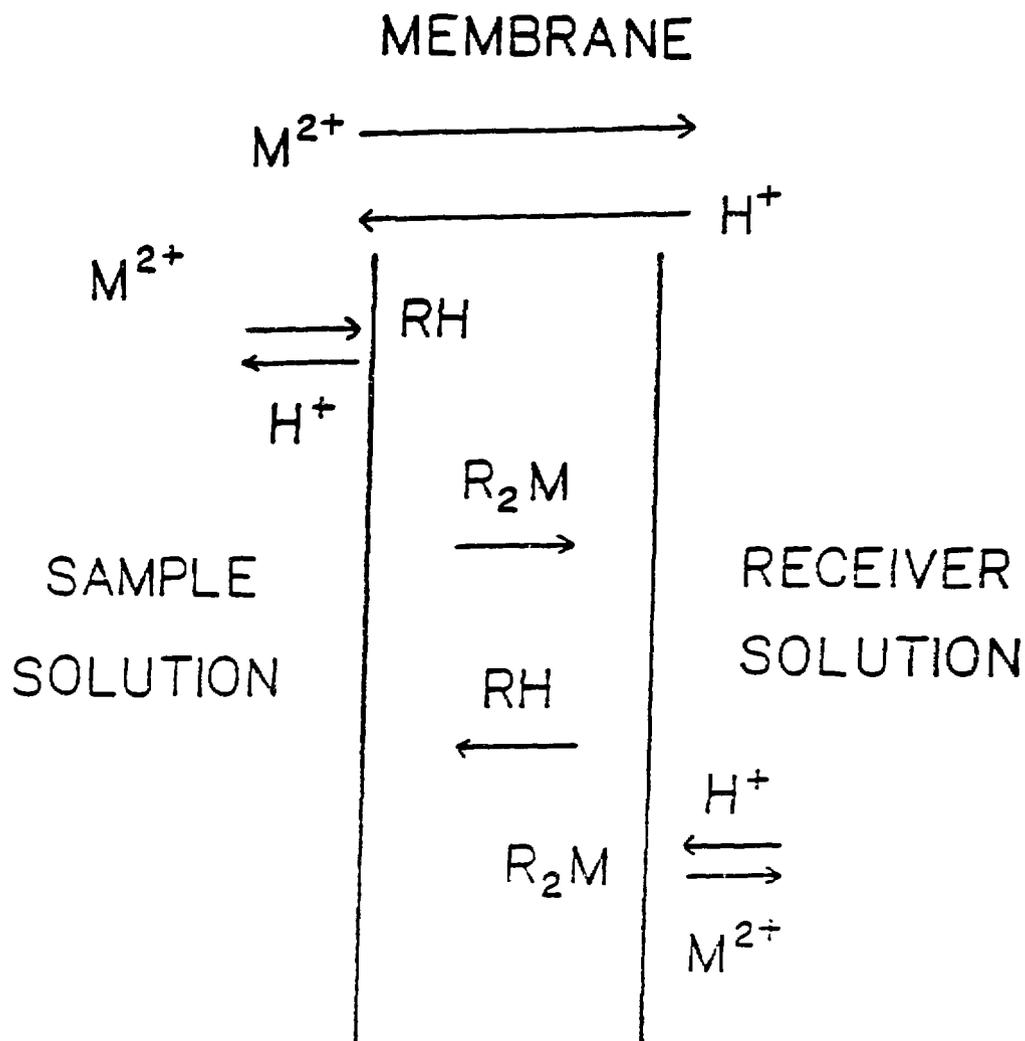


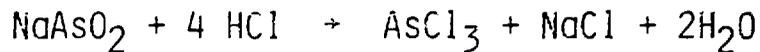
Figure 5. Hydrogen-Ion Driven Coupled Transport (Mobile Carrier Dialysis).

Sample: As(III) in 9 M HCl

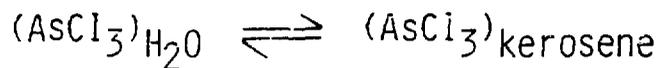
Membrane: kerosene

Receiver: water

Sample:



Membrane/Sample Interface:



Receiver/Membrane Interface:

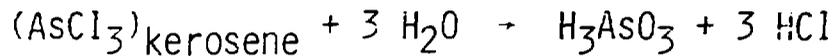
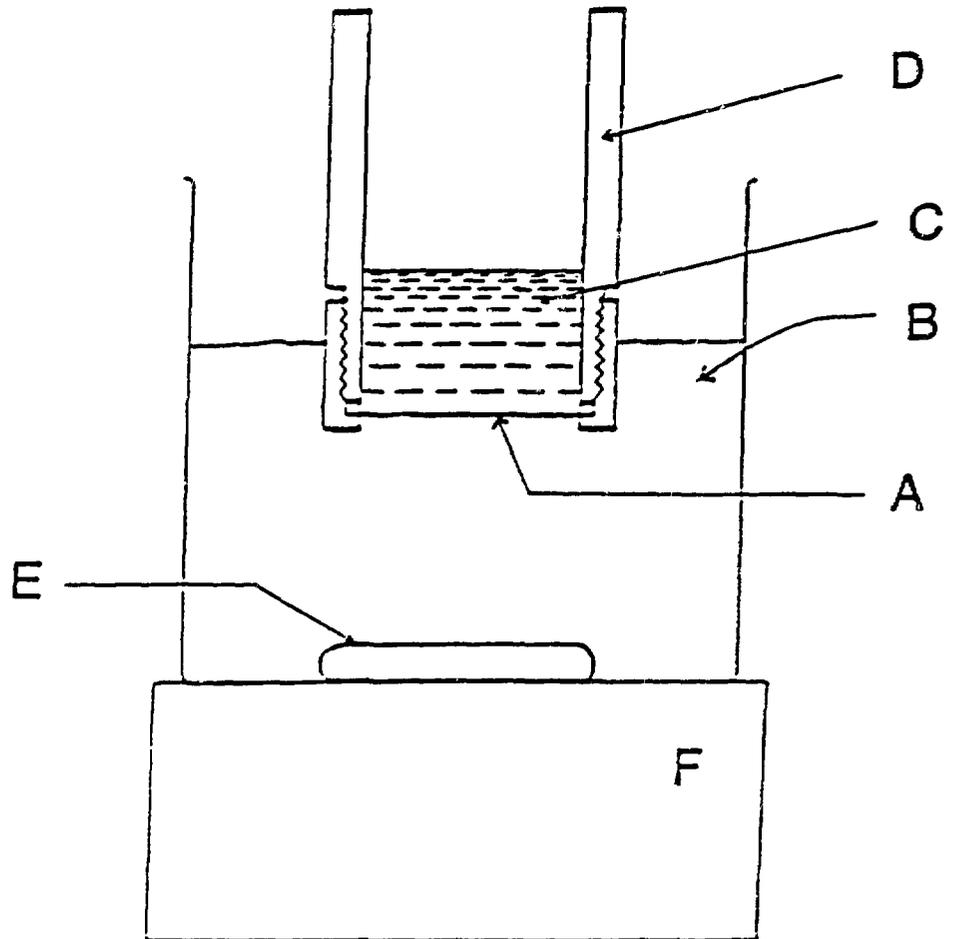
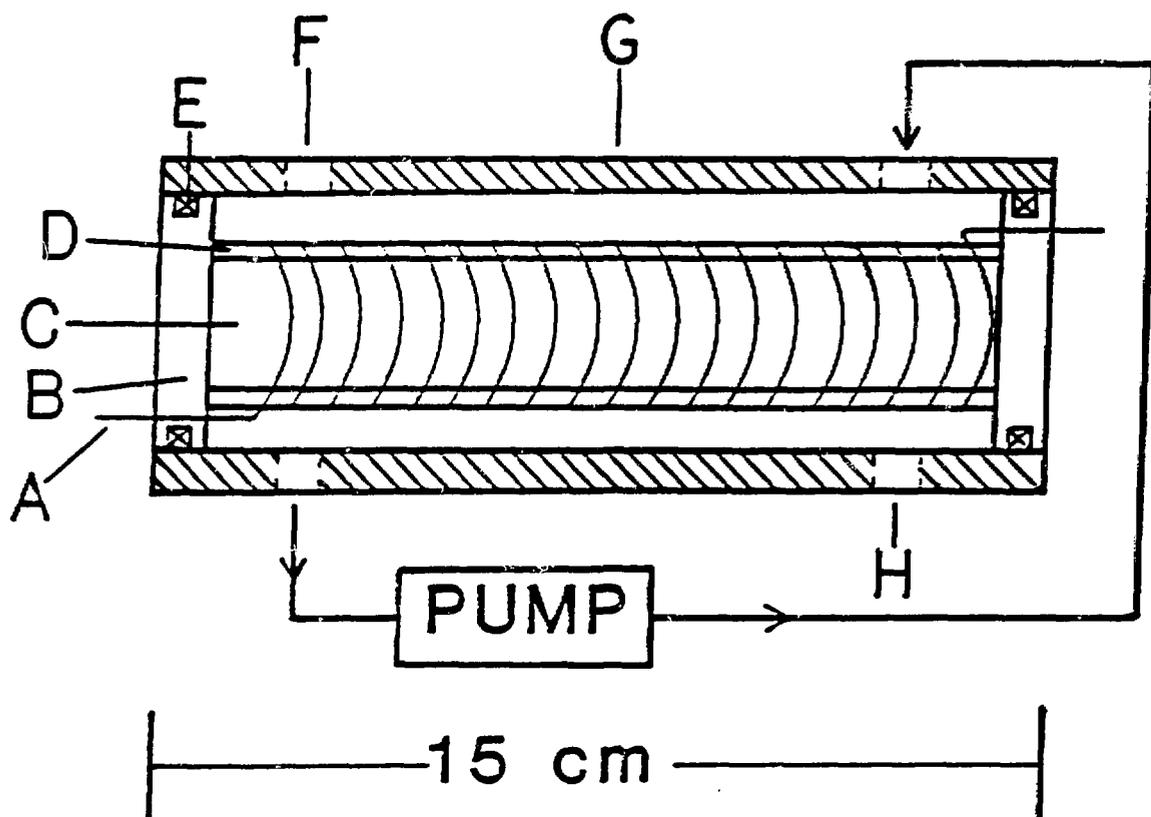


Figure 6. Uphill Transport by Ion-Pair Dissociation.



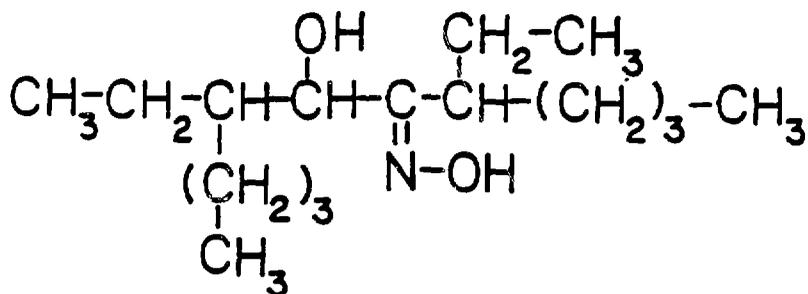
- A CATION-EXCHANGE MEMBRANE
- B 200-500 mL SAMPLE
- C 5 mL RECEIVER
- D PLEXIGLAS TUBE WITH RETAINER RING
- E, F MAGNETIC STIRRER

Figure 7. Stirred-Solution Donnan Dialysis Cell.

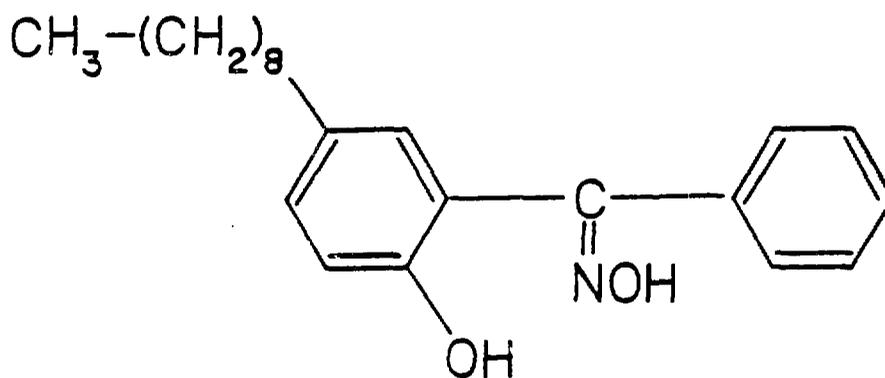


- A. Nafion 811 tubing
- B. End of inner spool
- C. 2-cm diameter rod
- D. 3-mm diameter rod
- E. O-ring
- F. Threaded sample outlet port
- G. Cell jacket
- H. Threaded sample inlet port

Figure 8. Flow Donnan Dialysis Cell.



LIX 63



LIX 65 N

Figure 9. Structure of LIX-64N, a Mixture of LIX-65N and LIX-63.

111/113

REPRODUCTION
DISALLOWED

**Treatment of Chemical Waste and Contaminated Soils
Containing Halogenated Compounds and Various Metals
with a Potassium-Polyethylene Glycol Reagent**

Presented by:

Thomas O. Tiernan, Wright State University

TREATMENT OF CHEMICAL WASTE AND CONTAMINATED SOILS CONTAINING HALOGENATED COMPOUNDS AND VARIOUS METALS WITH A POTASSIUM-POLYETHYLENE GLYCOL REAGENT-Thomas O. Tiernan, Daniel J. Wagel, Garrett F. VanNess, John H. Garrett, Joseph G. Solch, Leslie Harden, Wright State University, Department of Chemistry, Dayton, Ohio 45435; Charles Rogers, U.S. Environmental Protection Agency, Hazardous Waste Engineering Research Laboratory, Cincinnati, Ohio 45268

1. OBJECTIVES OF THE STUDY

1. DETERMINE THE EFFICACY OF THE KPEG REAGENT FOR DESTROYING TETRACHLORINATED AND HIGHER CHLORINATED PCDD AND PCDF CONTAINED IN A PENTACHLOROPHENOL (PCP) - OIL WOOD TREATMENT WASTE AND SOIL CONTAMINATED WITH THIS WASTE BY LABORATORY TESTS
2. OPTIMIZE REACTION CONDITIONS IN THE LAB TESTS TO MAXIMIZE THE EFFICIENCY OF THE DESTRUCTION AND OBTAIN DATA USEFUL FOR ENGINEERING SCALE-UP OF THE LABORATORY-SCALE PROCESS
3. EVALUATE THE KPEG PROCESS IN FIELD TESTS ON HAZARDCUS WASTES AT SEVERAL U.S. SITES
4. DEVELOP NEW PROTOTYPE REACTOR FOR FUTURE FIELD TREATMENT APPLICATIONS

2. KPEG REAGENT

THE KPEG REAGENT IS FORMED BY MIXING A POLYETHYLENE GLYCOL (PEG), TYPICALLY AVERAGE MOLECULAR WEIGHT OF 400, WITH SOLID KOH (SUFFICIENT TO SATURATE THE SOLUTION) AND HEATING THE MIXTURE TO 90-100°C FOR ABOUT ONE HOUR. APPROXIMATELY TWO MOLES OF KOH ARE ADDED FOR EACH MOLE OF PEG. A METAL ALKOXIDE IS PRODUCED WHICH REACTS WITH CHLORINE ATOMS ON A CHLORINATED MOLECULE, YIELDING POTASSIUM CHLORIDE AND POSSIBLY AN ETHER.

3. PROCEDURES UTILIZED IN LABORATORY ASSESSMENT OF KPEG PROCESS

THE FOLLOWING PROCEDURES WERE CARRIED OUT IN A GLOVE BOX VENTED THROUGH CHARCOAL FILTERS:

1. FOR LIQUID WASTES (PCP/OIL), PLACE A WEIGHED QUANTITY OF SAMPLE, TYPICALLY, 20-1000 G, INTO A GLASS REACTION VESSEL, ADD SOLID KOH, HEAT THE MIXTURE TO A TEMPERATURE IN THE RANGE 85-105°C WHILE STIRRING CONSTANTLY FOR A PERIOD RANGING FROM 30 MINUTES TO 20 HOURS.
2. FOR PCP/OIL-CONTAMINATED SOILS, PLACE 50 G OF SOIL INTO A GLASS REACTION VESSEL, ADD 20 G OF DMSO (OR OTHER SOLVENT), TO FORM AN EASILY MIXED SLURRY, AND 2 G OF SOLID KOH. RAISE THE SLURRY TEMPERATURE SLOWLY TO 95°C, WHILE STIRRING CONSTANTLY, AND MAINTAIN THIS TEMPERATURE FOR 30 MINUTES.
3. REMOVE THE REACTION VESSEL FROM THE HEAT SOURCE, AND ALLOW IT TO COOL TO ROOM TEMPERATURE. REMOVE A 0.1-2 G ALIQUOT OF THE REACTION MIXTURE FOR ANALYSIS.
4. ADD 20-600 G OF THE HOT (ABOUT 70°C) KPEG TO THE REACTION VESSEL CONTAINING THE LIQUID WASTE. ADD 11 G OF THE HOT KPEG REAGENT TO THE SOIL SLURRY.
5. MAINTAIN THE REACTION VESSEL AT A TEMPERATURE IN THE RANGE 70°-105°C WHILE STIRRING CONTINUOUSLY AND PERIODICALLY WITHDRAW 0.2-2 G ALIQUOTS OF THE REACTION MIXTURE FOR ANALYSIS AT INTERVALS OF 0.25, 0.50, 0.75, 1.0, 1.5, 2.0, 2.5, 3.0, 4.0 AND 8.0 HOURS AFTER THE KPEG IS ADDED.
6. FOLLOWING REMOVAL OF EACH ALIQUOT, ADD A SUFFICIENT QUANTITY OF 50% H₂SO₄ TO MAKE THE SOLUTION ACIDIC (pH-2), QUENCHING THE KPEG REACTION.

4. GENERALIZED PROCEDURE UTILIZED IN QUANTITATING TETRA - OCTA PCDD/PCDF AND OTHER CHLORINATED CONSTITUENTS IN KPEG-TREATED WASTES AND SOILS

1. ADD STABLE ISOTOPICALLY LABELLED INTERNAL STANDARDS ($^{13}\text{C}_{12}$ -LABELLED TETRA-, PENTA-, HEXA-, HEPTA- AND OCTA-CD AND CDF) TO THE ALIQUOT OF THE TREATED SAMPLE IN A GLASS BOTTLE.
2. EXTRACT THE SAMPLE USING HEXANE AND PARTITION THE RESULTING EXTRACT AGAINST WATER, AQUEOUS BASE, WATER, CONCENTRATED SULFURIC ACID AND WATER.
3. DRY ORGANIC LAYER OVER Na_2SO_4
4. CONCENTRATE ORGANIC LAYER AND SUBJECT THE CONCENTRATE TO A SEQUENCE OF ELUTION CHROMATOGRAPHIC CLEAN-UP STEPS INCLUDING AN ACID/BASE SILICA COLUMN. A WOELM BASIC ALUMINA COLUMN AND A PX-21/CELITE 545 COLUMN.
5. QUANTITATE THE PCDD/PCDF AND OTHER CHLORINATED COMPOUNDS OF INTEREST PRESENT IN THE SAMPLE EXTRACT USING COMPUTER CONTROLLED HRGC-MS (SELECTED ION MONITORING IS EMPLOYED, MONITORING AT LEAST TWO ION-MASSSES FOR EACH CHLORINATED COMPOUND TO BE DETERMINED). a 60 M DB-5 CAPILLARY GC COLUMN IS UTILIZED.

5. SOURCE AND TYPE OF HAZARDOUS WASTES TREATED IN THE PRESENT STUDY

- A. PENTACHLOROPHENOL (PCP)-PETROLEUM OIL WASTE WAS FROM A WOOD-TREATMENT PROCESS CONTAINED IN A 9000-GALLON TANK LOCATED AT MONTANA POLE CO., BUTTE, MONTANA. PCP-OIL CONTAMINATED SOILS WERE FROM THIS SAME SITE. THE WASTE CONTAINED 3% PCP AND CDD/CDF RANGING FROM 442 PPB (TETRA-) TO 83,923 PPB (OCTA-). OWING TO THE PRESENCE OF THESE TOXIC COMPOUNDS, THE WASTE COULD NOT BE TRANSPORTED OFF SITE.
- B. A MIXTURE OF SOLVENTS, OIL AND WATER, CONTAINING 2,3,7,8-TCDD, AMOUNTING TO 7,550 GALLONS, WAS FROM A FORMER HAZARDOUS WASTE PROCESSING FACILITY LOCATED AT WESTERN PROCESSING CO., KENT, WASHINGTON. THIS WASTE, ORIGINALLY CONTAINED IN 55-GALLON DRUMS, HAD BEEN RECEIVED FROM A PESTICIDE MANUFACTURER, AND NO PERMITTED INCINERATOR WOULD ACCEPT IT FOR BURNING. THIS HETEROGENEOUS MIXTURE WAS TRANSFERRED TO A 12,000-GALLON HOLDING TANK AT THE SITE, AND CONTAINED ABOUT 42% OILS, 10-50% SOLIDS, 28% WATER, 6% PHOSPHATE ESTERS, AN UNDEFINED QUANTITY OF PESTICIDES, AND 120 PPB OF 2,3,7,8-TCDD.

6. RESULTS OF LABORATORY TESTS ON PCP/OIL WASTE FROM MONTANA POLE SITE

| CDD/CDF | RAW OIL | FOLLOWING KPEG TREATMENT AT 70°C FOR 15 MINUTES | FOLLOWING KPEG TREATMENT AT 100°C FOR 15 MINUTES | AVERAGE MDC (PPB) |
|---|------------|---|--|----------------------|
| Concentration in Parts-Per-Billion (PPB) ^a | | | | |
| TCDD (2378) | 28.2 | ND | ND | 0.65 |
| TCDD (total) | 422 | ND | ND | 0.37 |
| PeCDD (total) | 822 | ND | ND | 0.71 |
| HxCDD (total) | 2982 | ND | ND | 2.13 |
| HpCDD (total) | 20671 | 11.2 | 2.25 | -- |
| OCDD | 83923 | 6.50 | 4.40 | -- |
| TCDF (2378) | 23.1 | 12.1 | ND | 0.23 |
| TCDF (total) | 147 | 33.3 | ND | 0.35 |
| PeCDF (total) | 504 | ND | ND | 0.36 |
| HxCDF (total) | 3918 | 4.91 | ND | 0.76 |
| HpCDF (total) | 5404 | 5.84 | ND | 1.06 |
| OCDF | 6230 | ND | ND | 2.62 |

a. "ND" INDICATES "NONE DETECTED" IN EXCESS OF THE MINIMUM DETECTABLE CONCENTRATION (MDC) INDICATED.

7. CONCENTRATIONS OF CDD AND CDF IN SOIL CONTAMINATED WITH PCP-OIL WASTE
PRIOR TO AND FOLLOWING TREATMENT WITH KOH ONLY, OR WITH KOH/KPEG AT 100°C

| Description | Concentrations Found (Nanograms Per Gram or Parts-Per-Billion) | | | | | | | Total CDD/CDF |
|---|---|--------------------|--------------------|----------------------|----------------------|--------------------|--------------------|------------------|
| | 2,3,7,8- Tetra-CDD/Tetra-CDF | Total TCDD/TCDF | Total PCDD/PCDF | Total HxCDD/HxCDF | Total HpCDD/HpCDF | Total OCDD/OCDF | Total CDD/CDF | |
| Untreated PCP Contaminated Soil | ND (5.65) | ND (3.83) | 8.22/ND (5.17) | ND/17.9 (6.45) | 544/686 | 5020/1072 | 19266/1237 | 24838/3013 |
| Treated Soil KOH Only, 80°C, 1 hr. | 4.40 | 10.9 | 60.6/29.8 | 2350/8.46 | 3632/5.51 | 227/ND (2.49) | 113/ND (3.78) | 6382/43.8 |
| Treated Soil KOH/KPEG, 100°C, 15 min. | ND (0.745) | 0.673 | ND/18.0 (0.745) | 27.1/ND (0.729) | 63.4/ND | 13.6/ND | 20.5/ND | 125/18.0 |
| Treated Soil KOH/KPEG, 100°C, 30 min. | ND (0.561) | ND (0.450) | ND/ND (0.543) | ND/ND (1.34) | 9.21/ND (0.589) | 11.5/ND (0.377) | 21.1/ND (2.37) | 41.8/ND |
| Treated Soil KOH/KPEG, 100°C, 45 min. | ND (0.787) | ND (0.509) | ND/ND (0.787) | ND/ND (1.53) | 1.07/ND (0.977) | 8.20/ND (0.345) | 14.5/ND (1.41) | 33.4/ND |
| Treated Soil KOH/KPEG, 100°C, 1 hr. | ND (0.163) | ND (0.216) | ND/ND (0.163) | ND/ND (0.393) | 1.40/ND (0.340) | 6.86/ND (0.199) | 16.8/ND (1.44) | 25.0/ND |
| Treated Soil KOH/KPEG, 100°C, 1.5 hr. | ND (0.825) | ND (0.497) | ND/ND (0.825) | ND/ND (2.51) | 10.4/ND (1.46) | 5.78/ND (0.374) | 12.5/ND (0.514) | 28.7/ND |
| Treated Soil KOH/KPEG 100°C, 2 hr. | ND (1.02) | ND (0.610) | ND/ND (1.02) | ND/ND (1.97) | 9.06/ND (0.907) | 5.77/ND (0.307) | 12.1/ND (0.639) | 28.7/ND |

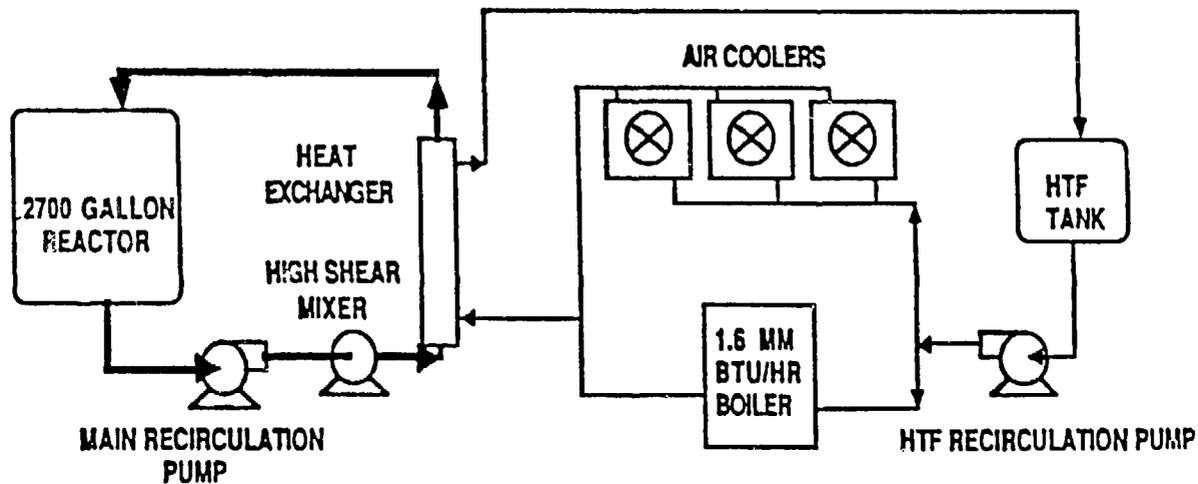
8. RESULTS OF LABORATORY TESTS OF KPEG REAGENT ON KENT, WASHINGTON WASTES

| TIME (HOURS) FOLLOWING KPEG TREATMENT ^a | CONCENTRATION OF 2,3,7,8-TCDD (PPB) IN SAMPLE |
|---|--|
| 0 ^b | 120 ^b |
| 5.5 | 5.5 |
| 6.5 | 2.5 |
| 12 | ND (0.3) |

a. A 250-G ALIQUOT OF THE WASTE WAS TREATED WITH 25 G KOH, FOLLOWED BY 75 G KPEG AND 25 G DIMETHYL SULFOXIDE AT A TEMPERATURE OF 115°C.

b. REFERS TO THE ORIGINAL WASTE, PRIOR TO TREATMENT.

9. SCHEMATIC DIAGRAM OF REACTOR, MOUNTED ON 45-FOOT TRUCK TRAILER,
USED IN FIELD TESTS OF KPEG PROCESS



10. CONCENTRATIONS OF CDD AND CDF (PPB) IN MONTANA POLE WASTE
AFTER KPEG TREATMENT AT BUTTE, MONTANA FIELD SITE^a

| CDD/CDF | Batch #1 | Batch #2 | Batch #3 | Batch #4 | Batch #5 | Reagent Sludge | Average MDC |
|--|-------------|-------------|-------------|-------------|-------------|-------------------|----------------|
| <u>Concentration (Parts-Per-Billion)^b</u> | | | | | | | |
| TCDD | ND | ND | ND | ND | ND | ND | 0.64 |
| PeCDD | ND | ND | ND | ND | ND | ND | 0.64 |
| HxCDD | ND | ND | ND | ND | ND | ND | 0.57 |
| HpCDD | ND | ND | ND | ND | ND | ND | 0.33 |
| OCDD | ND | ND | ND | ND | ND | ND | 0.84 |
| TCDF | ND | ND | ND | ND | ND | ND | 0.64 |
| PeCDF | ND | ND | ND | ND | ND | ND | 0.69 |
| HxCDF | ND | ND | ND | ND | ND | ND | 0.98 |
| HpCDF | ND | ND | ND | ND | ND | ND | 0.81 |
| OCDF | ND | ND | ND | ND | ND | ND | 0.66 |

a. EACH BATCH, CONSISTING OF 1400 TO 2000 GALLONS OF WASTE OIL, WAS TREATED WITH 600 GALLONS OF KPEG FOR 1.5 HOURS AT A TEMPERATURE OF 150°C.

b. "ND" INDICATES "NONE DETECTED" IN EXCESS OF THE MINIMUM DETECTABLE CONCENTRATION (MDC) CITED.

11. FINAL RESULTS OF FIELD TESTS OF KPEG TREATMENT OF WESTERN PROCESSING CO. WASTES
AT KENT WASHINGTON SITE

| Run # | Description of Waste | Concentration of 2,3,7,8-TCDD (PPB) Following KPEG Treatment ^b |
|-------|--------------------------------|--|
| 1 | Oil from bulk tank | ND(0.3) |
| 2 | Oil from bulk tank | ND(0.3) |
| 3 | Oil from bulk tank | 7.1 |
| 4 | Oil from bulk tank | ND(0.3) |
| 5 | Oil from bulk tank | 7.7 |
| 6 | Oil and rinsate from bulk tank | ND(0.3) |
| 3B | Retreatment of Run 3 | 2.6 |
| 3C | Retreatment of Run 3B | ND(0.3) |
| 5B | Retreatment of Run 5 | ND(0.3) |

- a. EACH TEST RUN INVOLVED TREATING APPROXIMATELY 1300 GALLONS OF WASTE LIQUID WITH ABOUT 500 GALLONS OF KPEG REAGENT FOR 12 HOURS AT A TEMPERATURE OF 115°C.
- b. "ND" INDICATES "NONE DETECTED" IN EXCESS OF THE MINIMUM DETECTABLE CONCENTRATION (MDC) CITED.

12. RESULTS OF MUTAGENICITY TESTS (MODIFIED AMES TEST) ON KPEG BYPRODUCTS

(EXPRESSED AS THE RATIO OF COLONY COUNTS OF THE TEST MATERIAL
TO COLONY COUNTS OF THE CONTROL

| <u>MATERIAL</u> | <u>STRAIN TA98</u> | | <u>STRAIN TA100</u> | |
|-----------------|--------------------|--------------|---------------------|--------------|
| | <u>S9</u> | <u>No S9</u> | <u>S9</u> | <u>No S9</u> |
| TCDD/KPEG | 1.3 | 1.2 | 1.0 | 1.1 |
| KPEG | 1.1 | 0.7 | 1.1 | 1.0 |
| DSMO | 1.2 | 0.7 | 1.0 | 1.0 |
| ANTHRAMINE | 41.6 | - | 6.1 | - |
| 2-NITROFLUORENE | - | 14.9 | - | - |

13. RESULTS OF TOXICITY TESTS OF RESIDUAL PRODUCTS FROM KPEG TREATMENT OF 2,3,7,8-TCDD

A. AQUATIC TOXICITY

CARP (15 FISH) WERE EXPOSED TO A WATER CONCENTRATION OF 250 PPQ OF KPEG/TCDD PRODUCTS FOR 30 DAYS. CONDITIONS IN A CONTROL AQUARIUM WERE IDENTICAL EXCEPT THAT KPEG REAGENT ALONE WAS INJECTED INTO THE WATER TO PRODUCE A CONCENTRATION EQUIVALENT TO THE REAGENT CONCENTRATION IN THE KPEG/TCDD REACTANT EXPOSURE AQUARIUM. AT THE END OF THE EXPOSURE PERIOD, NO FISH DIED IN EITHER AQUARIUM AND NONE SHOWED SIGNS OF TCDD TOXICITY. CARP EXHIBIT MORTALITY TO 2,3,7,8-TCDD AT WATER CONCENTRATIONS AS LOW AS 60 PPQ.

B. MAMMALIAN TOXICITY

TOXICITY STUDIES WERE CONDUCTED ON MALE GUINEA PIGS (36 ANIMALS) IN WHICH 0.5, 1, 2 AND 100 TIMES THE LD-50 AMOUNT OF KPEG/TCDD PRODUCTS WERE ADMINISTERED ORALLY. (THE LD-50 FOR 2,3,7,8-TCDD IN THE GUINEA PIG IS 0.6 $\mu\text{G}/\text{KG}$.) SIMILAR STUDIES WERE CONDUCTED USING A PURE KPEG REAGENT ALONE. AFTER 50 DAYS (THIS TIME PERIOD WAS CHOSEN BECAUSE TCDD SOMETIMES SHOWS DELAYED TOXICITY THAT MAY NOT APPEAR FOR SEVERAL WEEKS AFTER ADMINISTRATION), NO ANIMALS HAD DIED. IN ADDITION, WEIGHT GAIN AND LIVER WEIGHT WERE NORMAL. THE CONCENTRATIONS OF VARIOUS LIVER ENZYMES AND OTHER COMPONENTS IN THE BLOOD WERE MEASURED, AS WERE THE LEVELS OF CHOLESTEROL, TRIGLYCERIDES, ALBUMIN, AND TOTAL BILIRUBIN. ELEVATED LEVELS OF THESE ENZYMES AND OTHER COMPONENTS WOULD INDICATE LIVER DAMAGE, WHICH IS ONE OF THE TOXIC EFFECTS OF TCDD. NO INCREASES IN THESE ENZYMES AND COMPONENTS IN THE BLOOD WERE OBSERVED.

14. CONCLUSIONS

- A. THE KPEG REAGENT EFFECTIVELY DECHLORINATES PCDD/PCDF CONTAINED IN PENTACHLOROPHENOL - OIL WASTE AND IN SOILS CONTAMINATED WITH THIS WASTE. UNDER OPTIMUM CONDITIONS, COMPLETE DECHLORINATION OF TETRA- THROUGH OCTA- ISOMERS OCCURS. DESTRUCTION EFFICIENCIES ACHIEVED FOR THESE COMPOUNDS WERE $\geq 99.9\%$ IN THE WASTE SAMPLE.
- B. THE KPEG REAGENT EFFECTIVELY DECHLORINATES 2,3,7,8-TCDD CONTAINED IN A HETEROGENEOUS WASTE PESTICIDE MIXTURE YIELDING A DESTRUCTION EFFICIENCY $\geq 99\%$ UNDER OPTIMUM CONDITIONS.
- C. THE KPEG REAGENT IS EFFECTIVE WHEN A REACTION TEMPERATURE OF 70°C IS EMPLOYED, AND HIGHER TEMPERATURES (100°C) ENHANCE THE EFFICIENCY OF THE DESTRUCTION REACTION ONLY SLIGHTLY. AT THESE TEMPERATURES REACTION TIMES OF 15 MINUTES TO 1 HOUR ARE ADEQUATE FOR SOME WASTES. FOR SOME WASTES CONTAINING RELATIVELY LARGE QUANTITIES OF WATER OR OTHER REACTIVE COMPONENTS, LONGER REACTION TIMES (12 HOURS OR MORE) MAY BE REQUIRED.
- D. BIOASSAYS OF THE RESIDUES OF THE KPEG TREATMENT TESTS EVALUATED IN THIS STUDY INDICATE THAT THESE DO NOT BIOACCUMULATE OR BIOCONCENTRATE, DO NOT CAUSE MUTAGENICITY, AND ARE NOT TOXIC TO AQUATIC ORGANISMS OR MAMMALS.
- E. THIS PROCESS CAN BE SUCCESSFULLY IMPLEMENTED AT FIELD SITES BY USING A PORTABLE REACTOR, AND SEVERAL THOUSAND GALLONS OF APPROPRIATE WASTE CAN BE PROCESSED IN A FEW DAYS TIME.
- F. THE COST OF KPEG TREATMENT OF LIQUID WASTES AT FIELD SITES EVALUATED TO DATE IS APPROXIMATELY \$24.00 PER GALLON, ESTIMATED TO BE 10% OR LESS OF THE COST OF INCINERATING SUCH WASTE (EVEN THROUGH THIS IS OFTEN IMPRACTICAL).

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**Purification and Recovery of Waste Acids
by Continuous Ion Exchange**

Presented by:

Irwin R. Higgins, CSA, Inc.

PURIFICATION AND RECOVERY OF WASTE ACIDS BY CONTINUOUS ION EXCHANGE - Mark S. Denton and Irwin R. Higgins, CSA, Inc., Oak Ridge, TN 37830

ABSTRACT

Two very different ion exchange methods are to be discussed for the purification and reuse of acid. One is based on recycle of phosphoric acid. The other is called Acid Retardation, and applies to the highly ionized acids (e.g., HCl, H₂SO₄, and HNO₃).

Phosphoric acid is commonly used for metal treatment. Decorative aluminum gets its "bright" finish by being dipped in H₃PO₄. Phosphoric acid is used to clean other metals, steel, and stainless steel, to remove scale, or radioactivity. Activated carbon is made by leaching out the ash components of wood, Ca, Mg, K, and Na, using H₃PO₄. Phosphoric acid is not only expensive, but also enhances algae growth when dumped to the environment.

Continuous Countercurrent Ion Exchange (CCIX) equipment, is paramount in maintaining H₃PO₄ strength and being able to tolerate the very low distribution coefficient of metal ions for cation resin. A successful production plant will be presented which has included mobile equipment and a Model 3624 Folded CCIX unit that extracts 95% to 99% of the metals from 35% H₃PO₄ at about 60 gpm.

In strong ionized acids or salt plus acids (i.e., 2M to 5M of chloride, sulfate, or nitrate), there is selective and strong sorption of the H-ion. Water (of dilution) is, therefore, the only eluting agent necessary for the acid. This is called "Acid Retardation" and is useful for salt-acid separations. Specific areas of application are, anodizing wastes, cation regenerant wastes, lead battery waste, electrowinning cell blow-down waste, and more generally almost any industrial waste that is a mixture of acid and salts. Again, continuous countercurrent flow is vital for practicability, to keep solutions strong.

INTRODUCTION

The CSA-CCIX system historically started at ORNL in 1951 and was first reported in ORNL-1310⁽¹⁾. There has been continual development and application since that time. This CCIX system is adaptable to a wide variety of applications that push the limits of throughput rate, solution density, and extremes of flow ratios of solution-to-resin. In particular, it has been used worldwide in water and waste water treatment, fertilizers, hydrometallurgy, and general chemical processing. The purpose of this paper is to point out these unique

features and describe how the system works as it is applied to acid purification and recovery.

Two examples were chosen that illustrate these features. In keeping with the goals of the first Oak Ridge Model Conference, the applications discussed herein have been demonstrated on a bench-scale followed by a pilot-scale, and finally two production units are in operation. The older model vertical loop has been in operation for over ten years, while the Folded-Loop CCIX has been operational for about 1 1/2 years.

The first application involves the purification and recovery of phosphoric acid used in the production of activated carbon. In this case, the trace metal contaminants that must be removed come from the trees themselves which are charred. The capital payback here is not only from the reuse of the rather costly acid, but also the savings in land filling, neutralization and related environmental concerns.

The other example application, called "Acid Retardation", demands operation in a very dense solution where the feed-to-resin flow ratio is sometimes as low as 0.2⁽²⁾. Acid Retardation is an example of an ion exchange system that must be run in a continuous countercurrent flow system to be practical. The efficiency increases with solution strength. The higher the acid concentration the lower the solution-to-resin flow ratio. Because of special features of the CSA-CCIX system, these flow ratios are tolerated or handled. An attractive feature inherent with Acid Retardation is that water is the only consumed reagent. Several examples will be given of acid-salt separations. Unlike the phosphoric acid application, here the bulk acid is being removed from the trace contaminants rather than removing the trace metals from the bulk acid.

CSA CONTINUOUS COUNTERCURRENT ION EXCHANGE (CCIX) FEATURES AND HOW IT WORKS

Continuous Countercurrent Ion Exchange (CCIX) is an advanced technology for ion exchange. This technology involves some forty-four U.S. and worldwide patents. The systems consist of a packed bed of resin contained in a closed loop made up of reacting sections. The resin moves in one direction while the liquid moves in another direction (Countercurrent). The ion exchange resin is continuously reacted and regenerated, thus minimizing the amount of resin required for a given amount of liquid to process.

This technology is a great improvement over fixed-bed systems which do not efficiently react the resin, have high regenerant cost, fluctuating effluent quality, large batch waste disposal, and high water consumption. CCIX offers large economic savings, is adaptable to a wide range of waste streams, and has high capacity. For these reasons, CCIX has gained in favor as a practical and valuable process for industrial, municipal, utility, and research applications.

Advantageous Features of the CSA CCIX Unit.

Over the years, there have been several different types of continuous ion exchange equipment. Based on similar features, these may be divided into a few groups. Most of these have come and gone over the last thirty years. The CSA CCIX system claims to be unique and have all the following attractive features. In comparing this CCIX system with other ion exchange systems, the following points may be used for guidelines.

Maximum liquid production rate per unit size equipment. The reason for this is that the resin is retained in the sections with no danger of fluidization. All solutions enter and exit the unit via well screen which will not allow resin to pass. Other than ion exchange kinetics, the only limitation on production rate is pumping pressure drop. This variable is controlled by choosing resin bed depth and resin particle size. In addition, pressure drops in this moving bed are generally lower than in conventional fixed-beds because the top filtration layer is continually broken up when it reaches the backwash section.

Resin is retained as a packed bed. This means that resin beads are adjacent, or as close as they can be together. This also keeps the bed from fluidizing. Each resin bead retains its position relative to all other beads. This allows minimum engineering stage height (H_{tu}), or the maximum amount of ion exchange work per unit size equipment. The contrast in equipment size is very striking in comparison to fluidized-bed type continuous units.

Processing and maintenance of strong solutions. The CCIX system excels in this area because the full ion exchange cycle is carried out in a single loop. Just as much importance is assigned to water rinse and water displacement areas as loading and stripping sections. Dilution and tailing streams are avoided. This emphasis on the handling of water is increasingly important when processing strong solutions where one solution volume exhausts the ion exchange capacity utilization in less than one volume of resin.

In order to squeeze these solution concentrations to a maximum, it is important to maintain sharp interfaces between reacting solutions. This is readily achieved by obeying solution density rules. Almost always, low density liquids are allowed to float on top of high density ones. It should also be noted that solutions may be processed that would normally float the resin if the packed bed of resin was not confined.

A resin pumping system that is accurately controlled and highly variable in rate. By contrast, many other systems depend on the free fall of resin through processing liquid by the force of gravity. This is an enormous limiting factor on production rate or the density of solutions to be processed. In the CCIX system, the resin rate is accurately controlled over a wide range of very fast and very slow rates. It is not uncommon to have solution-to-resin flow ratios of 100

to 1000. It is just as common for the flow ratio to be 0.5. No mechanical or operating burden is imposed by going through this tremendous variation. This feature is of great significance and explains why this particular device is applicable to such a wide variety of problems.

Handling of slurries. One of the distinctive advantages of ion exchange over solvent extraction or reverse osmosis is that unfiltered or unclarified solutions may be processed. Other types of continuous units with fluidized beds have claimed to be better slurry handlers. A standard packed bed of resin is, in fact, like a sand bed filter. However, the packed bed in the CCIX unit does not act as a filter because its filtration tendency is continually broken up. The backwash section continually flushes out foreign matter and resin fines.

It is important that there be a pre-screening unit operation to remove a few types of larger particles, flakes, or fibers which may be present. Finely divided particles which are characterized as being filtered with difficulty, pass through the packed ion exchange bed with ease.

The only special added feature of a slurry handling contactor is to avoid stagnant pockets and provide extra flush out capability.

A prime target for slurry handling CCIX operation is the slimes from phosphate fertilizer operation. The slime particles are very small and the volume of this waste is enormous. From one-third to one-half of the known phosphate and uranium values are contained in these slimes.

How the CSA System Works

Operation. Continuous Countercurrent Ion Exchange consists of a packed bed of resin contained in a closed loop made up of reacting sections which are separated by valves built into the loop (any type of valve which will shear the resin bed such as ball valves, plugcock valves, or butterfly valves). The resin is moved around the loop in one direction while the solutions brought into the loop through screens (referred to as distributors and having a mesh opening of smaller size than the resin beads) flow countercurrent to the flow of the resin for a predetermined length of time. During this time, the ion exchange reaction takes place and the waste and product solutions are removed from the column through another set of screens called collectors.

Figure 1 shows the general configuration of the system. Any number of reaction sections can be built into the loop depending on the flowsheet requirements. These normally include a loading section, a regeneration section, a regenerant-rinse section, and a water elimination section.

In this system, the counterflow of resin and solution is accomplished by alternately, (1) pulsing an incremental amount of resin while the solution flows are stopped, and then (2) locking the resin in

the respective sections while the solution flows are resumed countercurrent to the previous flow of resin.

Step-wise the contactor cycles as follows:

1. During the solution pumping period, which may last for 2 to 10 minutes, Valves B, C, and D are closed and A is open. These butterfly valves isolate the various ion exchange sections. The resin bed is stationary while the solutions are flowing through the sections.

2. Just before the resin movement period, which lasts for about 5 to 10 seconds, the valve between the upper and lower reservoirs, "A", closes and the other valves "B", "C", and "D" open. The solution flows are stopped. A hydraulic pulse is applied which slides the entire resin bed a few inches as if it were a piston.

3. When this pulsing phase is complete, the valves are again reversed and the resin locked in the reacting section to be contacted by the solutions. The valve between the upper and lower reservoirs, "A", is open to allow displaced resin to drop into the lower reservoir ready for another cycle.

From the point of view of maintaining interface positions and solution concentrations, the rinse and water elimination sections are most important to understand. During resin movement, the liquids move faster and farther than the resin -- usually two to three times. This movement of liquid by the resin is referred to as slippage.

Thus, the interfaces between the various solutions move around into other sections and it becomes necessary to return them to their original position. This is accomplished in the rinse sections where a countercurrent water rinse makes a void volume displacement of the solution. The rinsing operation is controlled by a conductivity instrument which stops the rinsing action when the interface crosses a probe built into the section.

Also, during the resin pulse, water and resin are moved into the loading and regeneration sections. To avoid mixing this water with the products, a conductivity probe senses the salt-water interface and allows this slippage volume to be separately eliminated before drawing off undiluted product. This is accomplished in the contactor by opening the valve in the elimination port, and keeping the product valve closed until the interface moves past the product port and is sensed by the conductivity probe. The valves are then reversed and strong product is again removed.

PHOSPHORIC ACID PURIFICATION AND RECOVERY BY CCIX

Phosphoric Acid has been a paramount cost factor for the preparation of activated carbon. Phos. Acid is mixed with wood chips which is subsequently charred in a furnace to form charcoal. This

charcoal is then washed and the mineral, or ash, components are washed out. The predominant metals are calcium (Ca), potassium (K), and sodium (Na), with Ca and K being the majority.

Not only is phos. acid an expensive once through chemical, but it is also a highly objectionable environmental pollutant. With the formation of the Environmental Protection Agency in the mid 1970's, attention was turned to this discharge to the environment. Westvaco Corporation of Covington, Virginia learned of the work we had done on the recycle of phos. acid from Bright Dip solutions (e.g., Aluminum Finishing Corp., Arco and Production Plating) and the partial purification of fertilizer 30% P_2O_5 using CCIX. The removal of aluminum from Bright Dip 35% phos. acid by CCIX has been going on since 1959. See Figure 2 for this flowsheet. In the mid-1960's, several contracts were underway with the major fertilizer companies to upgrade 30% P_2O_5 to avoid post precipitation.

In 1977, we began an R&D contract with Westvaco to remove Ca, Mg, K, and Na from 35% H_3PO_4 using a one-inch diameter pilot CCIX unit. Ca, Mg, and K were 95% extracted, while Na was 75-80% extracted on a standard, vertical CCIX unit (Figure 1). Ten percent (10%) hydrochloric acid (HCl) was selected as the regenerant of choice. Sulfuric acid (H_2SO_4) was used as the regenerant in our Bright Dip operations. This was acceptable for the extraction of Al, but the use of H_2SO_4 was contraindicated for Ca removal due to the formation of gypsum ($CaSO_4$) within the resin bed.

A Model 1818, 316-L stainless steel CCIX unit had been in operation for several years on Bright Dip treatment at Production Plating (now Production Anodizing) in Adel, Georgia when the Westvaco production unit was installed in 1978. The latter was nearly a direct copy of the Bright Dip unit, but with some Hastalloy-C sections and internals for handling HCl. This unit is still fully functional and is extracting 90-95% of the metal contaminants. The capital payback due to the resource recovery and environmental savings was quite rapid and has been recovered many times over.

In 1985, due to the need for an increased capacity and higher grades of activated carbon, pilot R&D began again to develop a higher throughput and more efficient CCIX unit. The Folded-Loop CCIX, developed over the years, was ideal for this very strong solution application. The flowsheet developed for this application is shown in Figure 3. It is shown here in conjunction with the Acid Retardation recovery of the HCl regenerant to be discussed later.

This Folded-Loop design allows one to maintain a maximum (i.e., non-dilution of) product as well as regenerant waste. The pilot Folded-Loop shown in Figure 4 was first demonstrated here in Oak Ridge prior to the fabrication of the first (to our knowledge) trailer-mounted Mobile Ion Exchange (MIX) System (Model 1212) shown schematically in Figure 5. This self-contained trailer system was delivered to the site and was used to process 6 gpm of phos. acid for one year. This allowed the

processing of the entire backlog of acid while the much larger, Model 3624 shown in Figure 6 was under fabrication.

The production Folded-Loop CCIX has been in full operation since Spring of 1986 at approximately 60 gpm of 35% H_3PO_4 . Although design guarantees were more similar to the vertical Model 1818, the new 3624 is achieving an unprecedented 99+% extraction of Ca, Mg, and K and 98% extraction of Na. This has been an excellent demonstration of the capabilities of the Folded-Loop design. Higher throughputs per unit size and much higher grades of carbon have been achievable.

ACID PURIFICATION AND RECOVERY BY ACID RETARDATION USING CCIX

The hardest things to describe are those that are extremely simple. This is a problem with "Acid Retardation". The actual mechanism is not really fully understood by the experts in the field (2).

Acid Retardation is a method for selectively extracting strongly dissociated acids from concentrated solutions (Typically 2N to 5N) using strong-base type anion exchange resins. There is no acid sorption from dilute solutions, therefore, by definition, water is the acid elution agent. This simplicity, with water being the only consumed chemical, is a paramount economic factor inherent to the Acid Retardation system.

For practicality, Continuous Countercurrent Ion Exchange (CCIX), is uniquely necessary. The stronger the acid, the greater the resin capacity utilization. The stronger the acid, the lower the ratio of solution-to-resin flow. Subsequently, the lower the solution-to-resin flow ratio, the greater the demand for the inherent efficiency of continuous countercurrent flow. With CCIX equipment, it is common to have a salt and acid product effluent each of no greater volume than the feed. Flow ratios of solution-to-resin typically range from 0.2/1 to 0.5/1. This is quite unthinkable in conventional fixed-bed equipment. The reason that there are not many references to Acid Retardation is because of impracticality with conventional equipment.

Another unique feature using CCIX equipment is the ability to reflux. This means that the sorbed acid may be eluted at increased strength up to the concentration of the salt plus acid concentration of the feed. A concentration of 0.4M HCl to 2.0M has been demonstrated in our laboratory (i.e., not only without dilution, but with a concentration factor of 5).

Acid Retardation is a general purpose treatment method with the most wide spread utilization expected for salt-acid industrial wastes. Not only is alkali saved for neutralization, but acid is recovered for reuse. Problems studied have been anodizing wastes, ion exchange regenerant wastes, metal treating baths, and purification and recovery of lead battery wastes. A comparison of the efficiency of Acid Retardation of the various acids will be given.

Since we have tied Acid Retardation to CCIX operation it will be described in this context. See Figure 7.

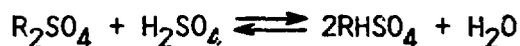
As already indicated, feed strengths are usually in the range of 2N to 5N although not tightly limited to this. Only highly ionized acids are considered, or common HCl, HNO₃, or H₂SO₄. The higher the acid strength, the higher the capacity utilization. See Figure 8. The ion exchange capacity of strong-base type resin is usually about 1.2 eq/l. Acid Retardation capacity is not limited to this. Hydrogen ions are crowded into the resin matrix not necessarily one per resin equivalent.

Although the mechanism of Acid Retardation is not proved for sure, it is thought to be a restructuring or denser packing of the H-ion within the resin particle. Basically, the exchanger distinguishes between H⁺ and metal cations rather than acids and salts. The degree of H-ion uptake is related to total anion strength with total exclusion of metal cation, except for those that form metal anion complexes.

In reference to the resin-solution counterflow system depicted in Figure 7, feed acid is sorbed and travels with the the resins and metal contaminants pass on through uninhibited. By utilizing continuous countercurrent flow, economical use is made of the water strip to the point that the acid may be eluted no more diluted than the feed. The degree of separation of acid and metals may be controlled by refluxing or scrubbing with product acid. These options exhibit as inverse proportionality. To increase the degree of metal exclusion, the acid production rate can be decreased.

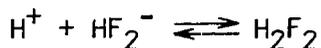
A most interesting and potentially useful aspect of Acid Retardation is that H-ion may be crowded into the resin bead relative to the total anion strength; not just the free acid strength. This means that acids may be concentrated as well as be separated, when bulk salts are present in the feed. For example, a solution 0.4N in HCl, in a total CaCl₂, KCl, HCl solution 3.6N, was concentrated to 2.0N HCl. An interesting way to express this is to say acid was increased 5 fold in strength when adding water. See Figure 9.

There is a striking difference in the water elution of a polyvalent acid like H₂SO₄ as compared to HCl or HNO₃. This is attributed to another and very different "acid sorption - water elution" system called Sul-bisul (Dow trade name) or "Site Sharing" (term coined by Fred Helfferich). For example, H₂SO₄ may be sorbed from dilute solution on sulfate form resin, R₂SO₄ to the bisulfate form R-HSO₄. The reaction is reversed by adding water.



This is a system useful in certain water demineralization processes, but the reconversion to R₂SO₄ is inefficient just using water. Acid capacity utilization increases with acid strength, but it is difficult to distinguish where Sul-bisul stops and Acid Retardation takes over.

This great difference in the acid elution efficiency for HCl and H₂SO₄ using CCIX is depicted in Figure 10. This is interpreted as a Sul-bisul effect acting independently from Acid Retardation. All polyacids as H₂SO₄, H₃PO₄, etc, act by Sul-bisul and Acid Retardation. Monovalent highly ionized acids, such as HCl and HNO₃, use Acid Retardation only. Poorly ionized HF reacts by the Sul-bisul mechanism, and probably ionizes as follows:



There is a special physical problem in loading acid from strong solution (low in salts) without avoiding dilution. The stronger the acid the higher the acid loading, but the lower the solution-to-resin flow ratio. Resin void volume in a packed column of uniform beads is 0.4. Whenever the F/R (Feed-to-Resin) flow ratio is less than 0.4, this means that there is not enough feed solution to occupy this void and displace its contained void volume of water. This causes dilution. By the definition of Acid Retardation, dilution causes less resin capacity utilization and increased acid loss. This effect is counteracted by recycling some of the highly conductive salt waste to displace this void volume water, or to avoid water intrusions. See Figure 7. Whenever there is trace acid with bulk salt, the F/R may be greater than 0.4 and this special recycle feature is not required.

Thus far, CSA has pilot demonstrated five systems; three with H₂SO₄ and two with HCl. The first was treatment of spent Al anodizing bath. The purpose was to recycle H₂SO₄ and reduce alkali consumption for neutralizing Al₂(SO₄)₃. About 90% of the acid was removed from the salt waste and about 90% of the Al from the acid product. One hundred percent separation could not be attained because of the Sul-bisul mechanism with H₂SO₄. Because of the inherent continuous countercurrent efficiency of the CCIX equipment used, neither the H₂SO₄ nor the Al₂(SO₄)₃ streams were diluted as compared to the feed.

Another sulfate system was with regenerant waste from a cation exchange treatment of Bright-Dip AlPO₄·H₃PO₄. Four normal H₂SO₄ is used as regenerant. The Al (plus Fe, Cr, Ni, Cu, etc.) is transferred from the H₃PO₄ to the H₂SO₄. This sulfate waste, undiluted from 4N, is sent through Acid Retardation. The H₂SO₄ is recovered with no dilution, with greater than 90% rejection of metals, and in suitable form for reuse as cation regenerant.

A third sulfate system was for recovery and recycle of lead storage battery acid. Specification for trace metals was very low; Fe, Sb, Ni, Mn, As, Zn, Cd, Cu, etc. Emphasis was placed on refluxing H₂SO₄ to scrub out metal contaminants. Production rate of product H₂SO₄ suffers somewhat to attain high degree rejection of metals because some is used for scrubbing, but one has the option to adjust this as needed.

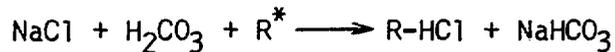
One HCl system was a metal treating waste primarily made up of HCl·AlCl₃. The objectives were to prepare an acid-free AlCl₃ and to recycle HCl. The AlCl₃ was practically neutral at about pH 3.

Another chloride waste was about 3N and from a cation exchange regeneration. The bulk salts were Ca, Mg, K, and Na with traces of Fe, As, Al, Mn, Cr, Pb, and Ni. Again, the HCl was recovered slightly concentrated with a 90% to 95% elimination of metals.

An area that seems especially attractive for Acid Retardation is treatment of spent electrowinning cell liquors, both chloride and sulfate. Build up of acid in an electrowinning bath reduces current efficiency. This accumulated acid may be continually extracted, and concentrated, by Acid Retardation.

Another interesting utilization of Acid Retardation is to make strong acids from weak acid. No other ion exchange system is known for doing this.

The following weak-base resin reactions is common:



However, the HCl on the resin cannot be removed as acid and must be neutralized.

The question here was, would the same reaction occur with strong-base resin by Acid Retardation? The acid could then be removed with water. In order to function, the Acid Retardation resin affinity for ionized H-ion had to be stronger than the coordinated bond of H-ion for the weak acid.

Nearly saturated NaCl, 4M, was mixed with a highly soluble weak organic acid, formic as 3M, which has an ionization of $K = 1.77 \times 10^{-4}$. The mixture was fed to a column of SBR and eluted with water.

As noted from Figure 11, chloride was taken up by the resin in the only form it could by Acid Retardation, as highly ionized HCl, with displacement of Na and formate.

A long range goal is production of ion exchange water treatment strong acids from lower cost sources or wastes of HCOOH, HAC, SO₂, and hopefully CO₂.

CONCLUSION

Since the early 1970's, steady progress has been made on the purification/recovery of phosphoric acid from a variety of industries such as bright dipping, activating carbon or nuclear decontamination. The flow sheet on Continuous Countercurrent Ion Exchange (CCIX) has been successfully demonstrated on bench-, pilot-, and production-scales, not to mention on the first trailer mounted, continuous Mobile Ion Exchange (MIX) system.

The second example was the adaptation of Acid Retardation to CCIX

where it is necessary to utilize very low solution-to-resin flow ratios in the range of 0.2/1 to 0.5/1. This must be done without dilution because, by definition, Acid Retardation only functions in strong solutions. These examples of high degree performance; (1) high liquid throughput rate, and (2) maintenance of strong solutions, are inherent features of continuous countercurrent flow. The particular device described herein, known as the CSA CCIX system, mechanically allows extremes in flow ratios to be achieved.

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1. I.R. Higgins, "A Countercurrent Solid-Liquid Contactor for Continuous Ion Exchange", USAEC ORNL - 1310 (1952).
2. Hatch, Merlin J., and Dillon, John A., "Acid Retardation", Ind and Eng Chem, Vol 2, No 4, Oct. 1963.

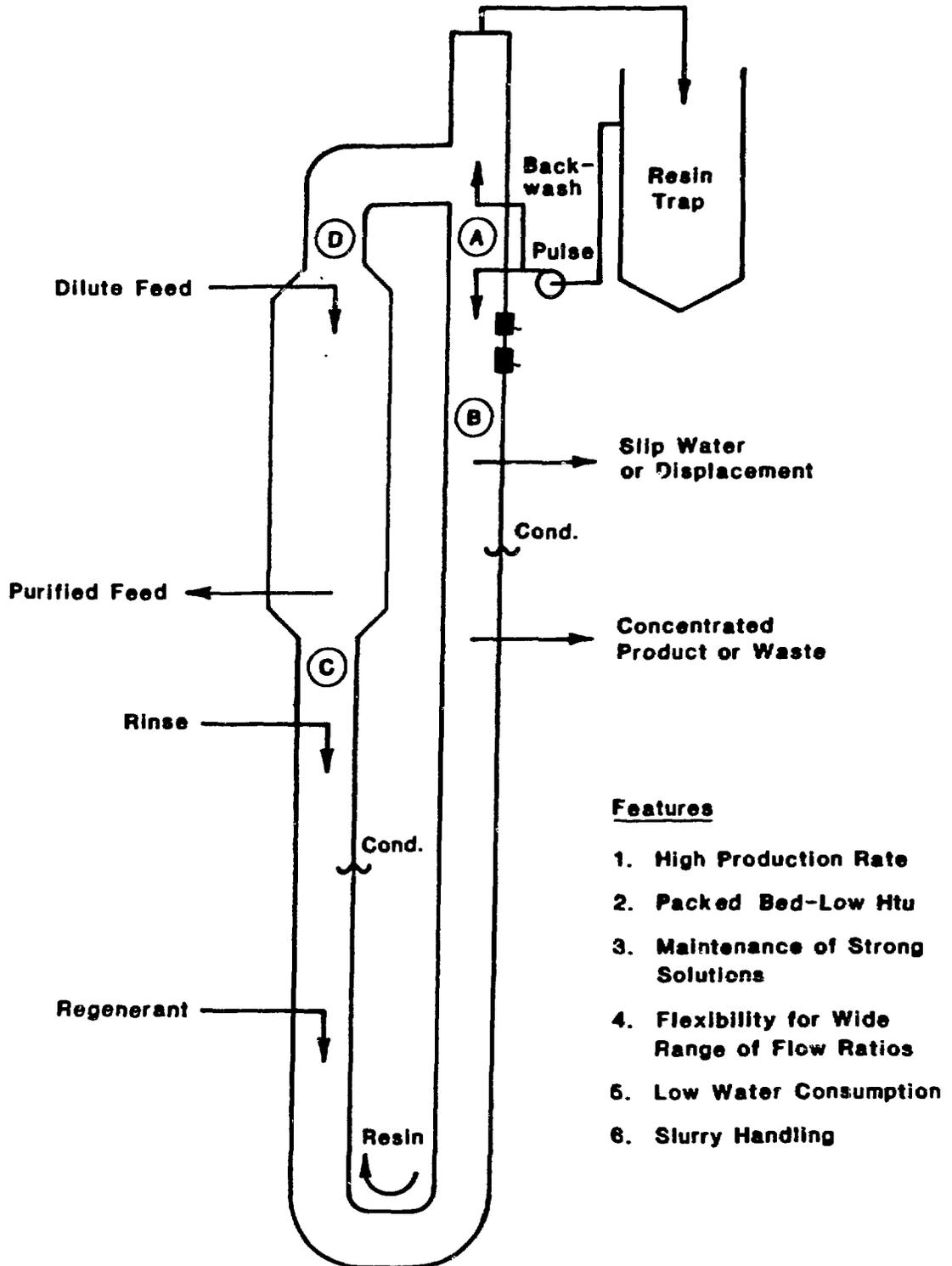


Figure 1: CSA CCIX Contactor - How it Works and Attractive Features

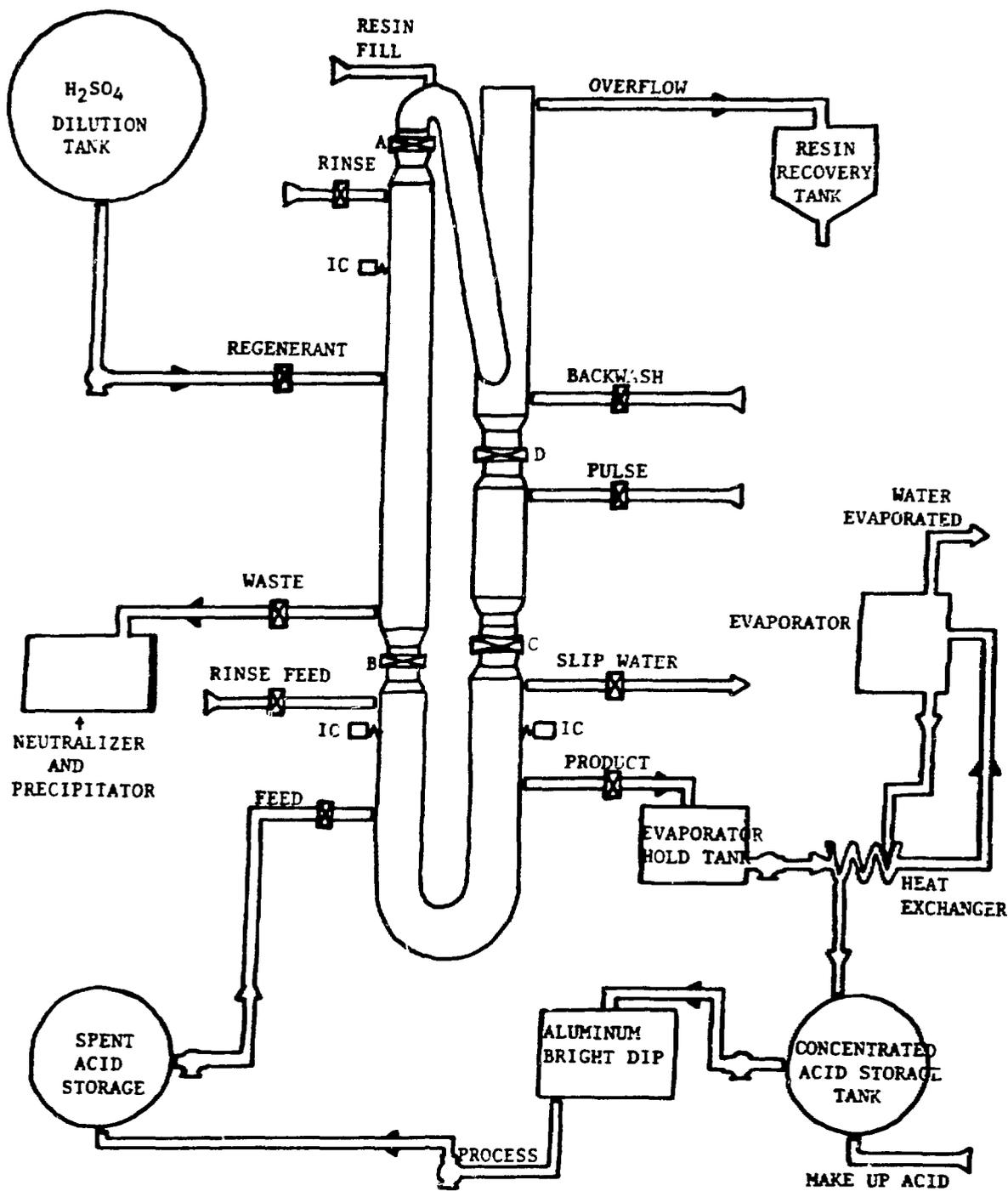


Figure 2: Phosphoric Acid Recovery and Recycle

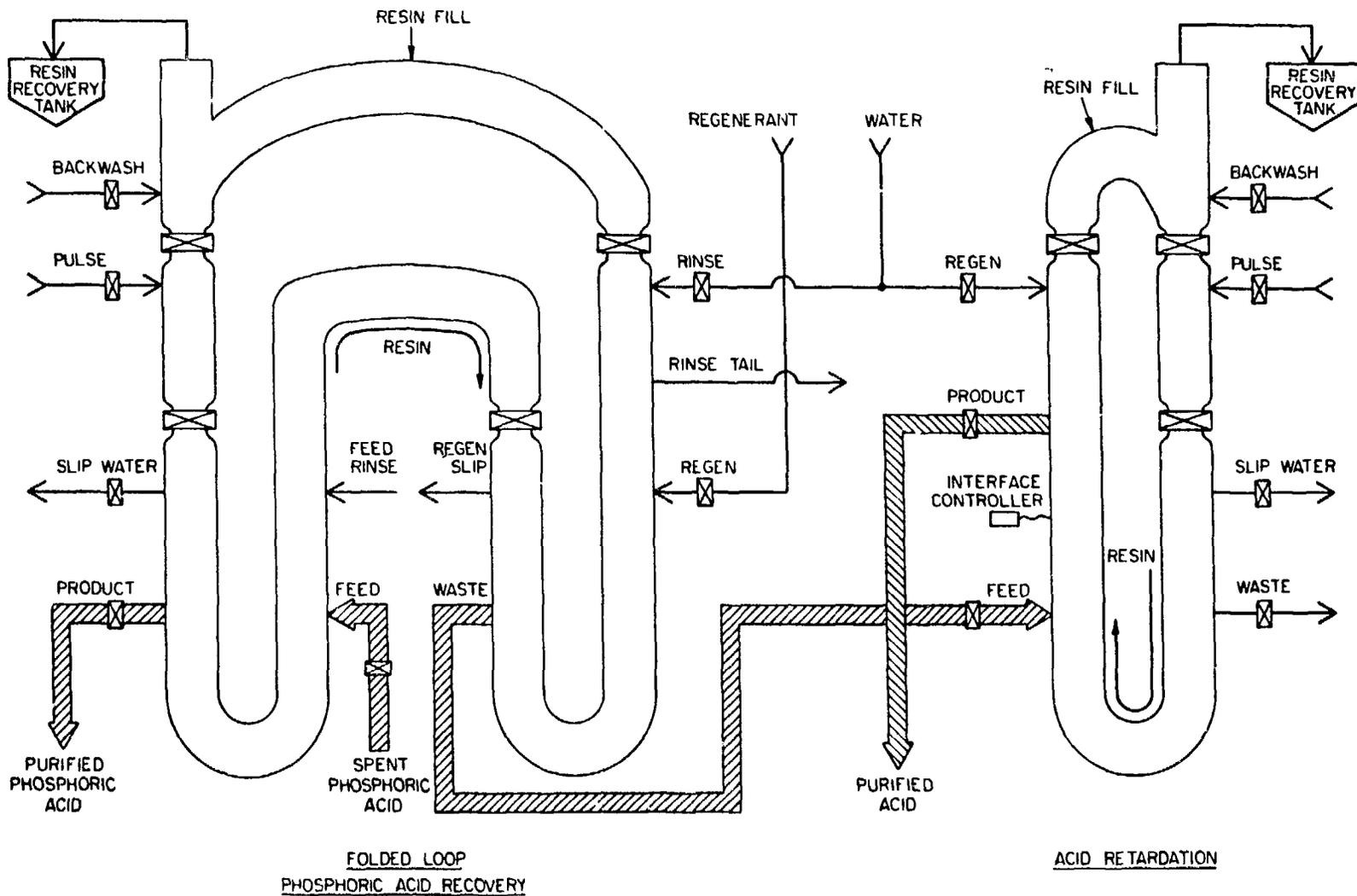


Figure 3: CSA Countercurrent Ion Exchange Acid Purification and Recovery System

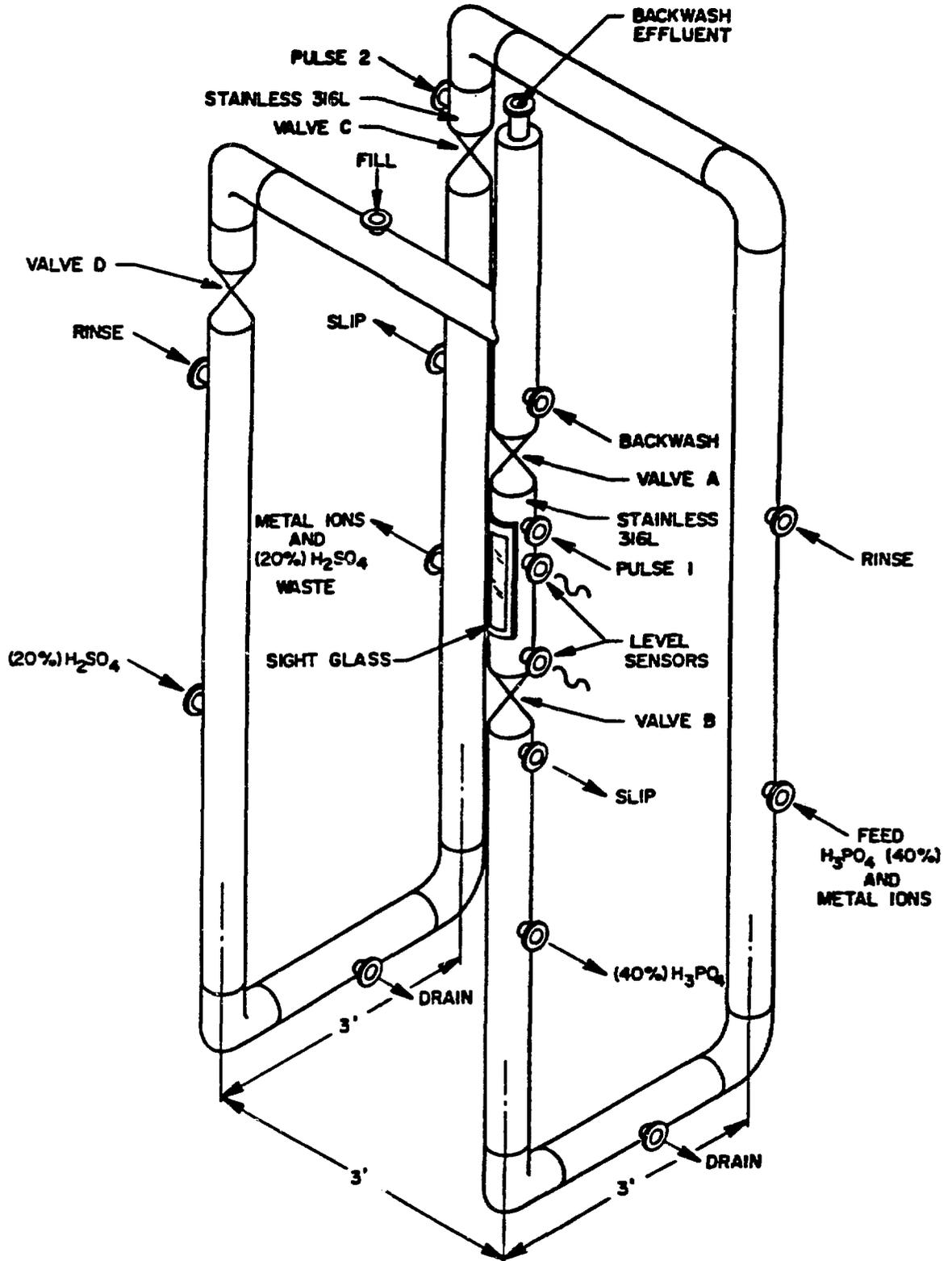
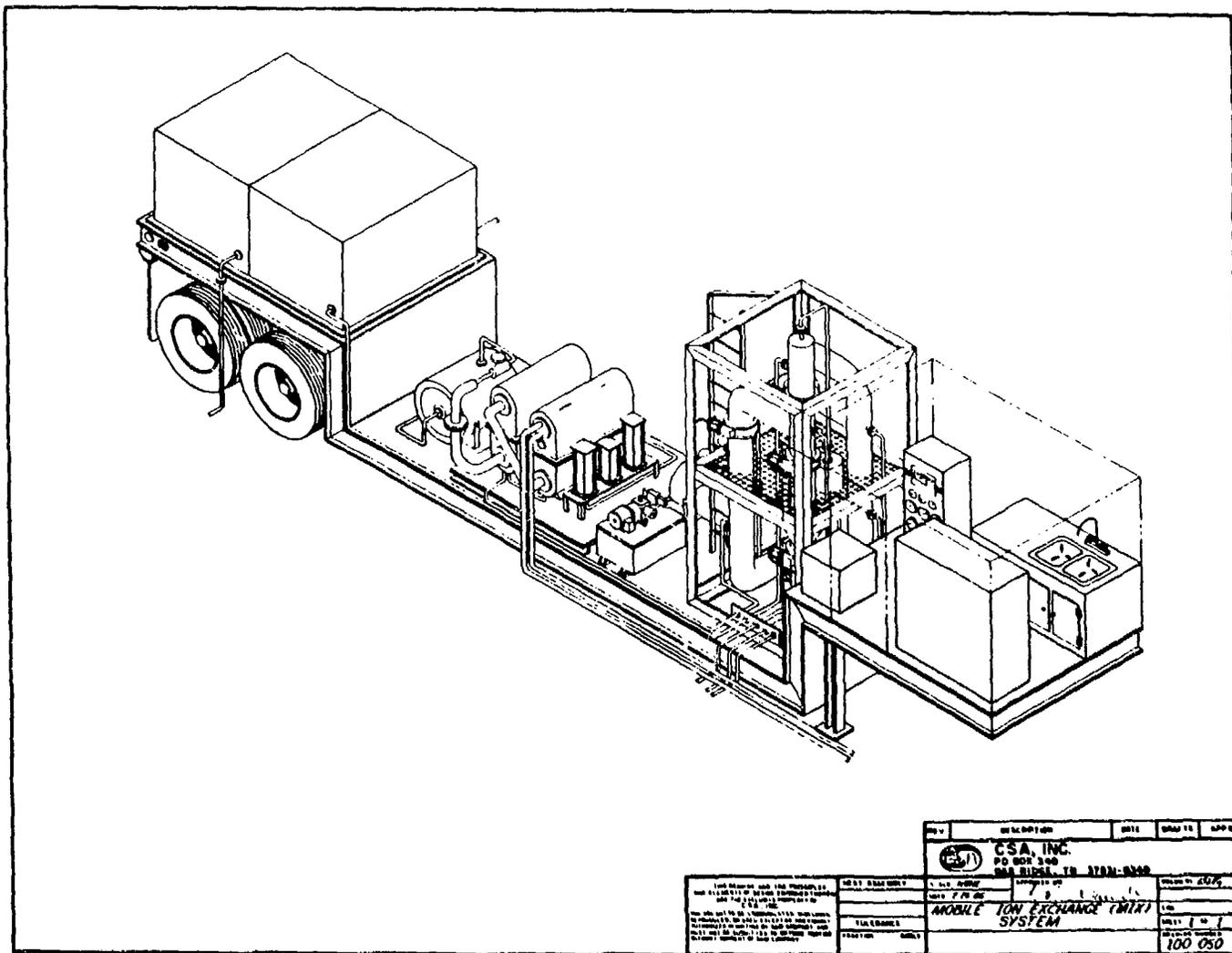


Figure 4: Folded Loop Design



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| CSA, INC. PO BOX 300 224 RIDGE LN ATOM-9340 | | <small>PROJECT NO.</small> 78 |
| <small>MOBILE ION EXCHANGE (MIX) SYSTEM</small> | | <small>DATE</small> 100 050 |

Figure 5: Mobile Ion Exchange (MIX) System

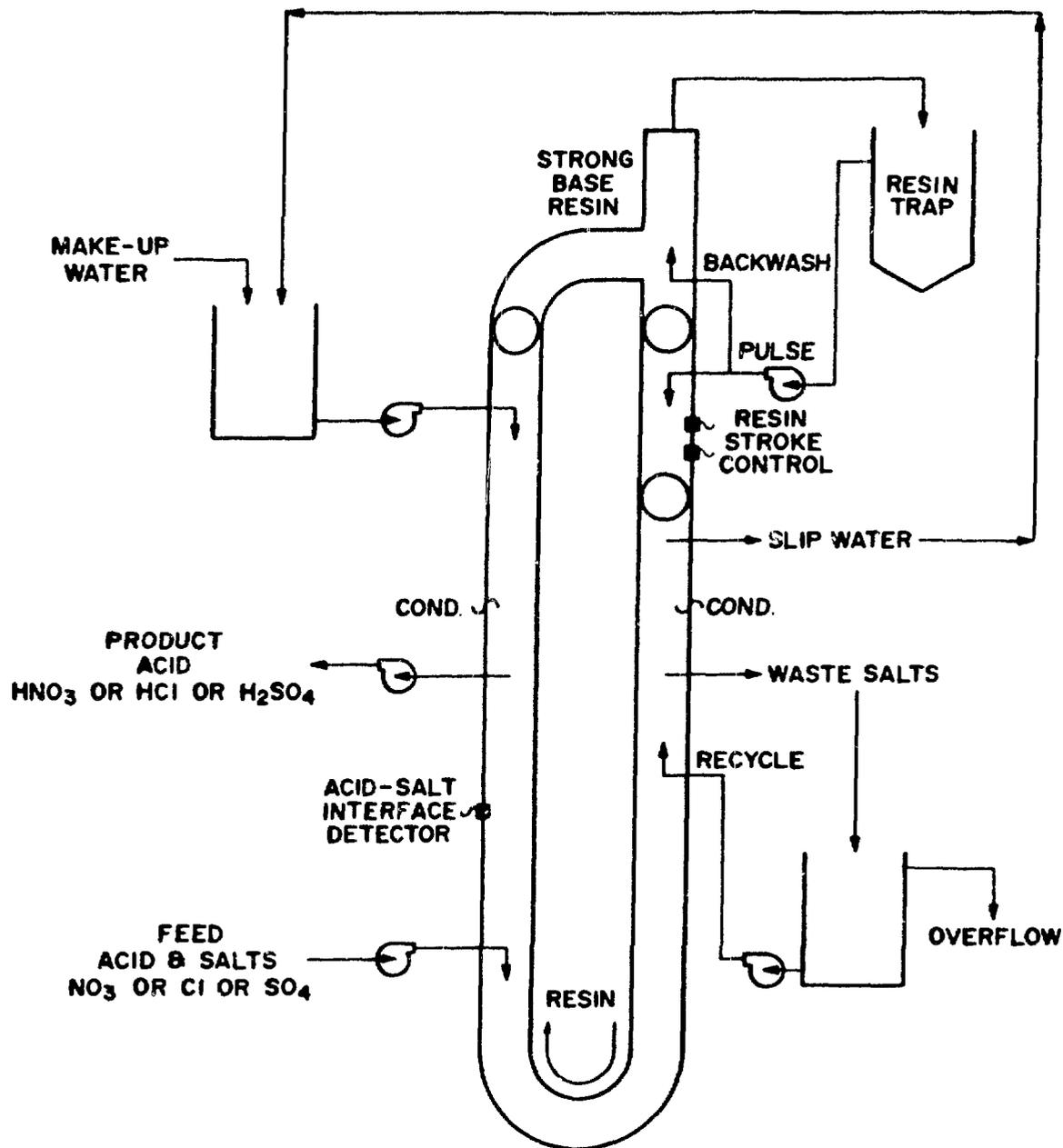


Figure 7: Acid Retardation by CCIX

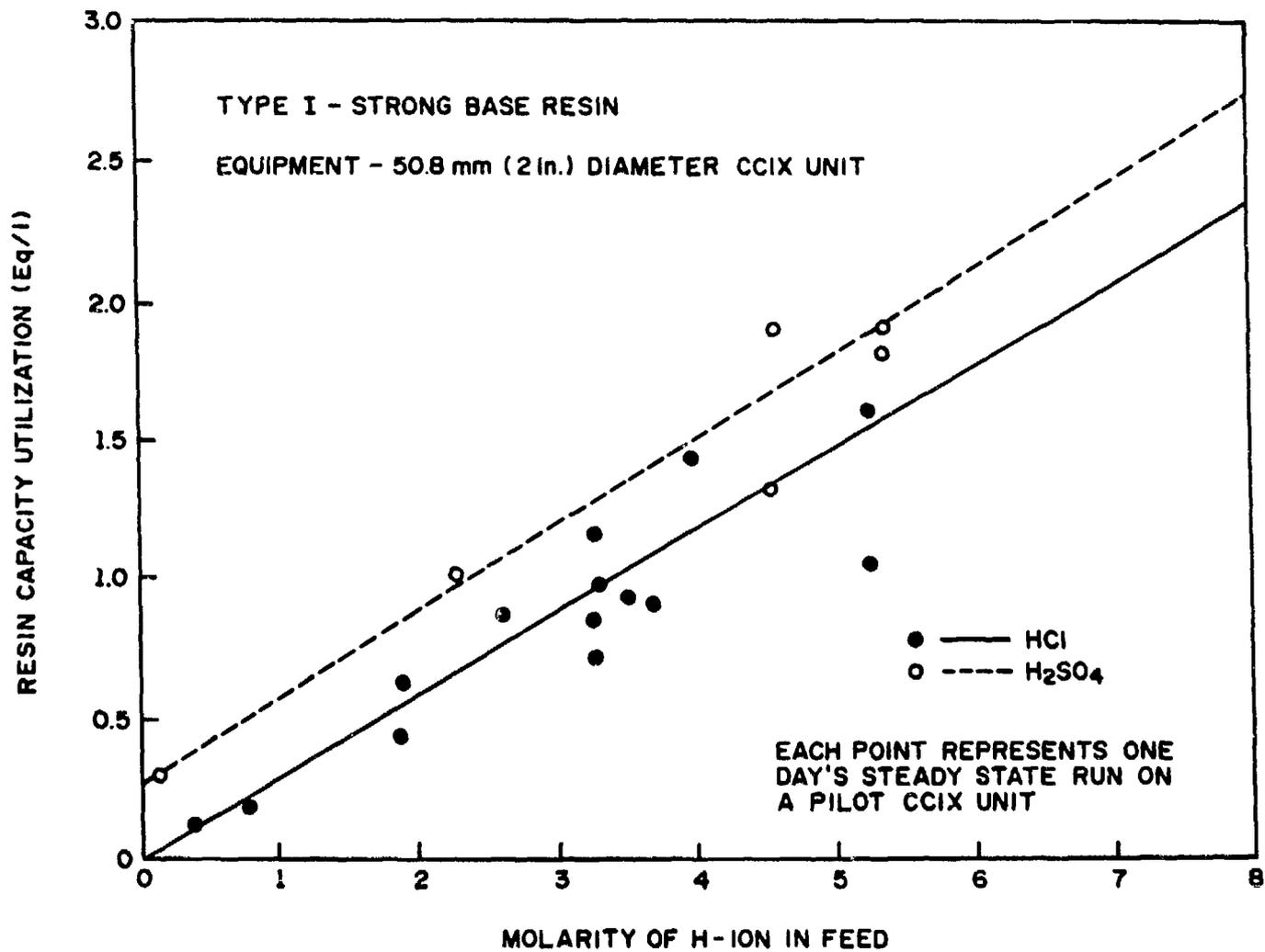


Figure 8: Acid Retardation - Capacity Utilization Versus Acid Feed Strength for HCl and H₂SO₄

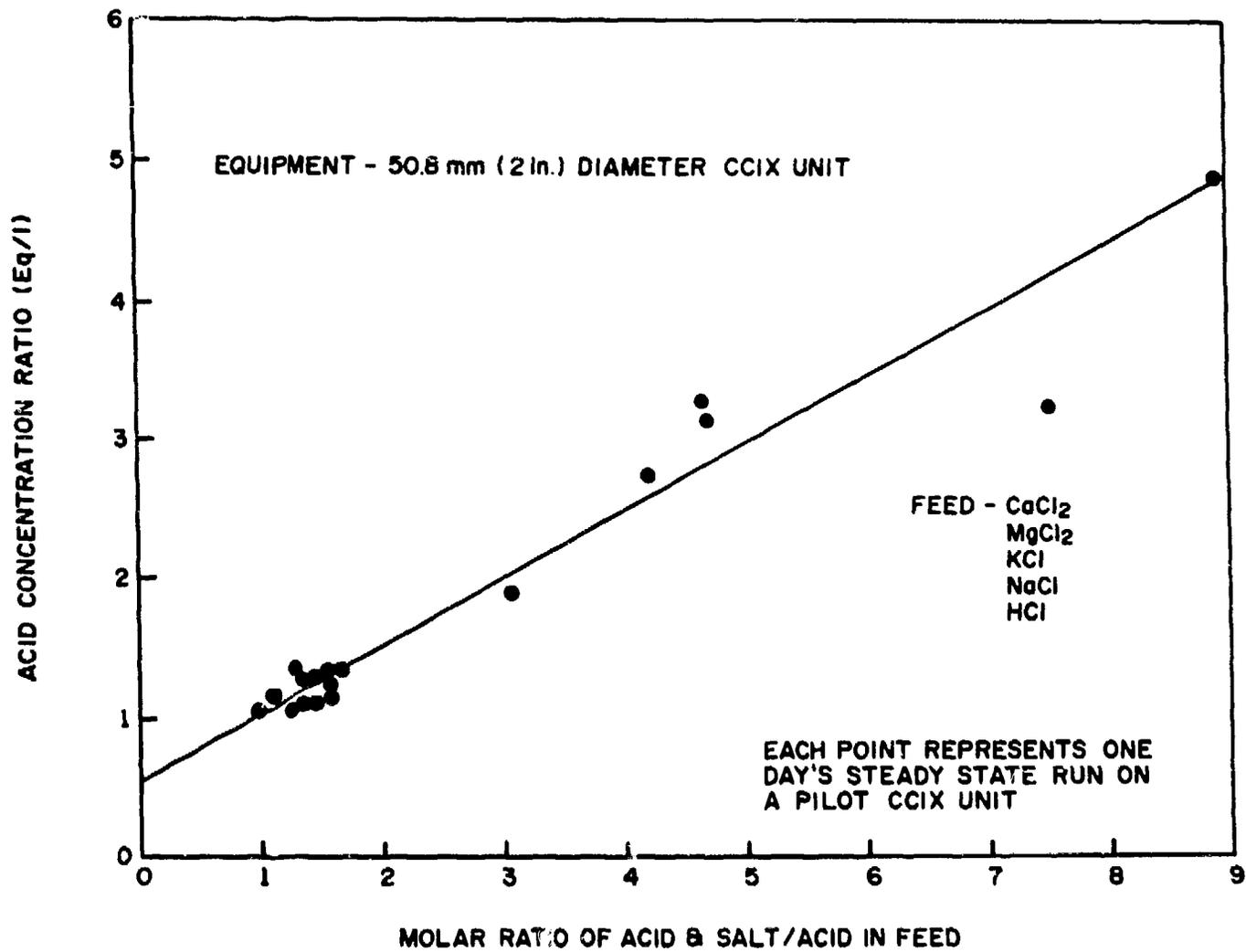


Figure 9: Acid Retardation Concentration of Acid Versus Salt Concentration in Feed Via CCIX Refluxing (Chloride System)

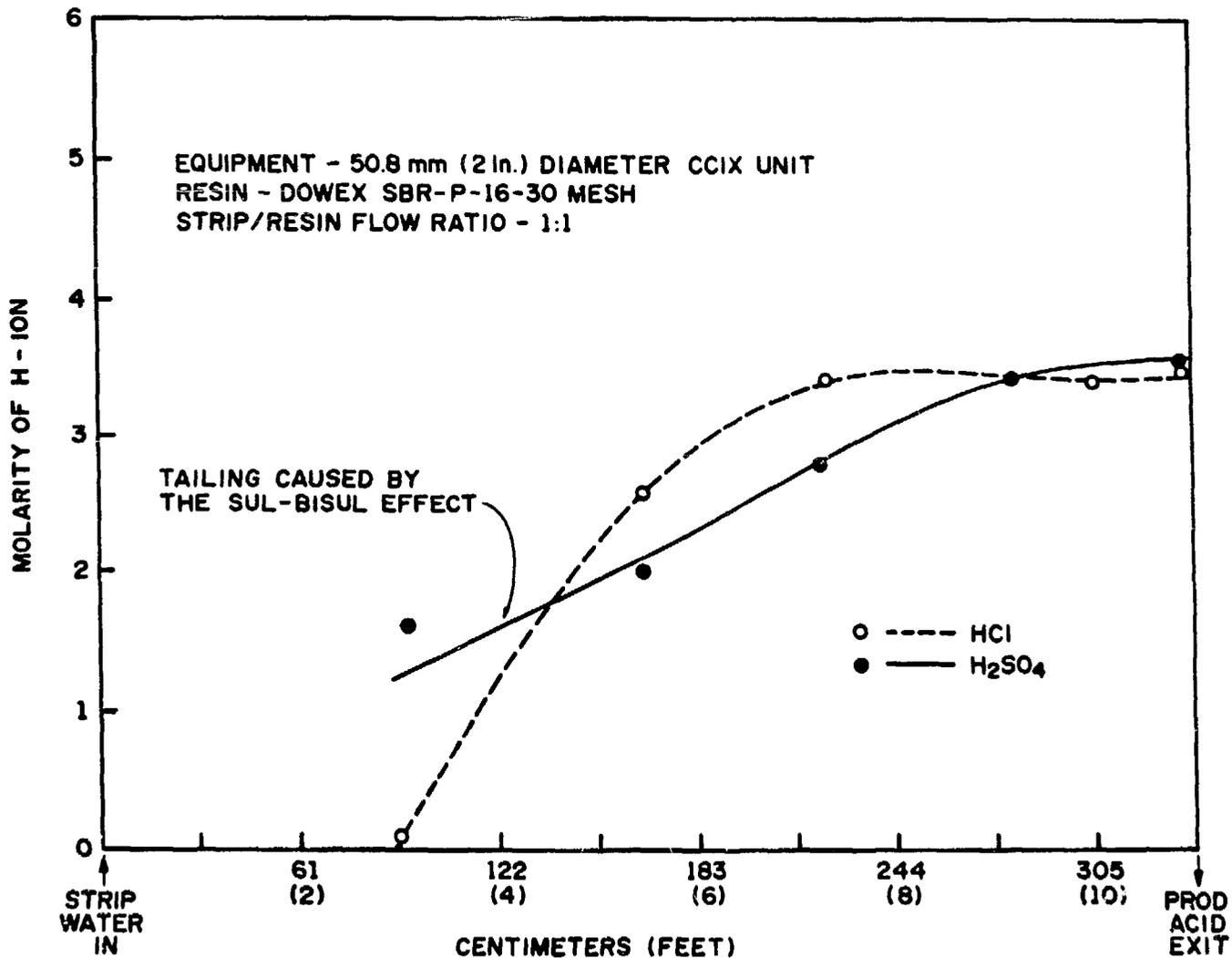


Figure 10: Comparison of Stripping Efficiency
 HCl Versus H₂SO₄

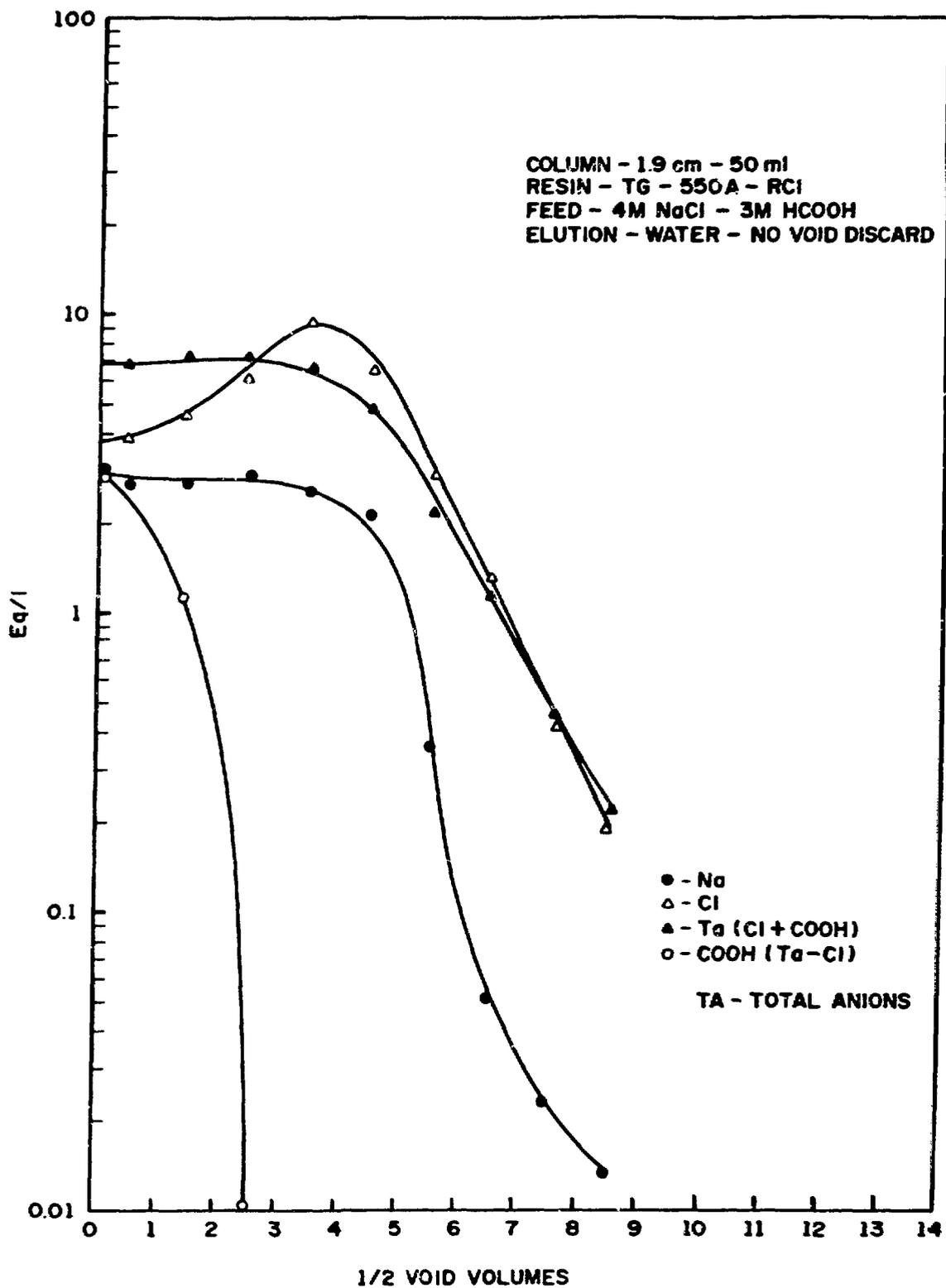


Figure 11: Production of Strong Acid from Weak Acid by Acid Retardation

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**Toxicity Reduction and Improvements in
Biodegradability of Industrial Wastes
Using Hydrogen Peroxide**

Presented by:

Alan R. Bowers, Vanderbilt University

TOXICITY REDUCTION AND IMPROVEMENTS IN BIODEGRADABILITY
OF INDUSTRIAL WASTEWATERS USING HYDROGEN PEROXIDE OXIDATION

by

A.R. Bowers, W.W. Eckenfelder, Jr., P. Gaddipati,
and R. M. Mosen

A procedure to evaluate the technical and economic feasibility of chemical oxidation for the pretreatment of toxic and hazardous organic compounds in industrial wastewaters has been developed. The proposed process involves the reaction of catalyzed hydrogen peroxide with refractory, toxic and/or inhibitory organics to produce intermediate oxidation products, i.e., organic carbon based compounds, rather than CO_2 , that are much more "biocompatible" than the original compounds. By coupling the oxidative pretreatment of toxic compounds with conventional biological treatment processes, and eliminating the need for complete chemical oxidation to CO_2 , chemical oxidation becomes more economically attractive.

Pure compounds, such as 2,4-dichlorophenol, and actual industrial wastewaters were evaluated. In general, the toxicity rating of the organic compounds was improved by at least an order of magnitude for those wastes which were reactive with hydrogen peroxide (from Microtox^R data).

The biodegradability, before and after reaction with hydrogen peroxide, was evaluated using "Fed-Batch" reactors and both unamended municipal sludge (Metro Nashville) and standard laboratory biomass. In several cases, the reacted wastes exhibited an increase in the biodegradability, even though the sludge was not specifically acclimated to the oxidation products.

TOXICITY REDUCTION AND IMPROVEMENTS IN BIODEGRADABILITY OF INDUSTRIAL WASTES USING HYDROGEN PEROXIDE - Alan R. Bowers, W. W. Eckenfelder, Jr., P. Gaddipati, Vanderbilt University, Nashville, TN; and R. M. Monsen, Interlox America, Inc., Deer Park, TX

Introduction

A procedure to evaluate the technical and economic feasibility of chemical oxidation, using catalyzed hydrogen peroxide, for the pretreatment of toxic and hazardous organic compounds in industrial wastewaters has been developed. The proposed process involves the reaction of catalyzed hydrogen peroxide with refractory, toxic, and/or inhibitory organics to produce intermediate oxidation products, i.e., organic carbon based compounds, rather than CO_2 , that are much more "biocompatible" than the original compounds. Coupling oxidative pretreatment of toxic compounds with conventional biological treatment processes, and eliminating the need for complete chemical oxidation to CO_2 , makes chemical oxidation more economically attractive.

When a refractory, toxic or inhibitory organic is reacted with a chemical oxidant, several types of degradation may occur (1):

1. Primary Degradation - a structural change in the parent compound; biodegradability may be improved;
 2. Acceptable Degradation - degradation to the extent that toxicity is reduced;
- or, 3. Ultimate Degradation - complete destruction to CO_2 , H_2O and other inorganics.

A primary or acceptable degradation may occur at relatively low consumptions of oxidants and be much more efficient than ultimate degradation. However, evaluating the effect of chemical oxidation on the acceptability of the by-products may be difficult, especially when specific compounds are not identified. Conventional parameters, such as Total Organic Carbon (TOC) and Chemical Oxygen Demand (COD), indicate the amount of ultimate conversion (TOC) and degree of oxidation (COD). In addition, the average oxidation state (OX) of organic carbon in the waste mixture may be expressed as (2):

$$\text{OX} = 4 (\text{TOC} - \text{COD})/\text{TOC} \quad (1)$$

In complex wastewaters ("biocompatible" and "nonbiocompatible organics"), there is no way to predict which components have been altered. Therefore, the relation between the extent of reaction and the biocompatibility of the wastewater is more difficult to quantify. Biochemical Oxygen Demand (BOD) is not a valid tool for measuring the original "non-biocompatible" components due to their toxic or refractory nature. Upon reaction with oxidants, these original species may be partially degraded, resulting in more "biocompatible" components. However, the BOD test requires an acclimated seed, and failure to exhibit a

significant increase in BOD after reaction does not rule out the success of the chemical oxidation process.

Toxicity of the wastewater may be evaluated before and after chemical oxidation by any of a variety of standard techniques. Typically, one would compare effluents based on the tests required by the discharge permit. However, tests based on Microtox^R and/or LD₅₀ (Daphnia Magna, misid shrimp, etc.) will reflect the effects of chemical oxidation on toxicity.

With these limitations in mind, a Fed-Batch Reactor scheme was developed to evaluate the biodegradability of components before and after reaction with hydrogen peroxide. In addition, a continuous sludge culture, acclimated to 2,4-dichlorophenol and a variety of other organic compounds, was used as a standard sludge throughout testing.

Materials and Methods

Hydrogen Peroxide Oxidation

The reaction of toxic and/or refractory organics was carried out in batch stirred reactors. The pH was maintained constant during the course of reaction by addition of NaOH or H₂SO₄ as required (pH ± 0.2). Free radical formation was catalyzed by ferrous sulfate (Fentons Reagent) addition, 10 to 100 mg/L as Fe⁺², added from a stock solution of FeSO₄, (1000 mg/L as Fe) which was stored under refrigerated conditions and replaced with fresh solution on a monthly basis.

Sample analysis during the reaction included Chemical Oxygen Demand (COD), Total Organic Carbon (TOC), total phenolics (measured by the 4-aminoantipyrine, 4AAP, colorimetric technique), and residual hydrogen peroxide (by potassium iodide-sodium thiosulfate titration procedure). To preserve the samples for tests other than residual H₂O₂, the peroxide was quickly destroyed by the addition of catalase (Fermcolase-1000, Finnsugar Biochemicals, Inc., Elk Grove Village, IL) and the absence of H₂O₂ was confirmed by H₂O₂ test strips (E.M. QUANT, EM Science, Inc., Cherry Hill, NJ).

All oxidation experiments were carried out at a pH of 3.5 as the optimum. This correlates well with data of previous researchers who reported pH 3.5 as corresponding to the maximum rate of free radical formation in the H₂O₂-Fe⁺² system (3).

Hydrogen peroxide was added in equal steps at one-hour intervals. Each step input was equivalent to a 1:1 molar ratio of H₂O₂ to equivalent DCP, and total cumulative dosage of H₂O₂ did not exceed a 4:1 ratio. It was found that less H₂O₂ was consumed to achieve the same results when a step input was used, as compared to a large initial dose.

A variety of organic compounds was evaluated. These included 2, 4-dichlorophenol (DCP), 4,6-dinitro-o-cresol (DNOC), and two industrial wastewaters. The original organics and the by-products were compared at three points of reaction:

Point A - the original compound(s) prior to oxidation

Point B - an intermediate time during oxidation (15 minutes)

Point C - after the reaction with H_2O_2 is essentially complete (4 hours)

At these times, the compound were tested for toxicity using Microtox^R, and rate of biodegradation, using unamended municipal sludge (Metro Nashville) and a laboratory sludge acclimated to a standard feed. Details of the Fed-Batch Reactor test procedure may be found elsewhere (4,5,6). Results were reported and compared based on the maximum specific substrate utilization rates (q_{max}).

Results and Discussion

The tests results are exhibited in Table 1 and Table 2 for the wastes tested.

Table 1. Toxicity of Various Organic Wastes Before and After Pretreatment with Hydrogen Peroxide

| Waste | Reaction Point | EC 50 ^a (%) |
|-------------------|----------------|---------------------------|
| I ^b | A | 1.05 |
| | B | 2.00 |
| | C | 83.10 |
| II ^b | A | 1.30 |
| | C | 15.20 |
| DCP ^c | A | 0.32 |
| | B | 0.27 |
| | C | 2.53 |
| DNOC ^d | A | 8.96 |
| | C | > 100 |

a: based on Microtox^R data

b: industrial wastes obtained from the chemical industry

c: initial concentration was 650 mg/L

d: initial concentration was 200 mg/L

Table 2. Biodegradability of Various Organic Wastes Before and After Pretreatment with Hydrogen Peroxide

| Waste | Reaction Point | q_{\max}^a | | q_{\max}^a | |
|-------|----------------|-------------------------------|--------------------------------|-------------------|-------------------|
| | | (mg TOC/g VSS-hr) | | (mg COD/g VSS-hr) | |
| | | <u>Municipal</u> ^b | <u>Acclimated</u> ^c | <u>Municipal</u> | <u>Acclimated</u> |
| I | A | 3.89 | 4.37 | 10.80 | 12.10 |
| | B | 5.10 | 5.37 | 11.76 | 11.88 |
| | C | 5.10 | 5.17 | 10.30 | 9.71 |
| II | A | 4.17 | 7.64 | 6.50 | 8.03 |
| | C | 6.28 | 7.60 | 9.86 | 9.02 |
| DCP | A | -0- | 1.44 | -0- | 4.42 |
| | B | 0.66 | 1.51 | -0- | 5.23 |
| | C | 3.47 | 1.65 | 7.58 | 6.00 |

a: from Fed-Batch Reactor data

b: Metro Nashville sludge

c: standard laboratory sludge acclimated to 2,4-dichlorophenol and a standard mixture of organics as described by Kincannon, et. al. (7)

The results indicate several positive effects of hydrogen peroxide oxidation. Principally, the toxicity of the organic compounds was greatly reduced and, in general, at least an order of magnitude improvement in toxicity was achieved by allowing the peroxide reaction to go to completion at low H_2O_2 dosages, i.e., an acceptable rather than an ultimate degradation. In addition, the peroxide oxidation did have a positive impact on the biodegradability of these compounds. For example, although DCP is biodegradable, the municipal sludge was not previously acclimated to DCP and, therefore, had no capacity for biological uptake ($q_{\max} = 0$). However, after pretreatment with hydrogen peroxide, the reaction by-products were biodegradable and the unacclimated municipal sludge exhibited significant uptake of these compounds ($q_{\max} = 3.47$ mg TOC/g VSS-hr) and, in fact, performed better than the "acclimated" sludge. This implies that a substantial fraction of the oxidation by-products are very similar to typical compounds encountered in municipal wastewaters. Much the same is seen for the two chemical wastewaters (I and II). The biological uptake of organics is significantly improved on a TOC basis (I: q_{\max} increased 1.3 x, and II: q_{\max} increased 1.5 x; both values for municipal sludge). Although the "acclimated" sludge showed little or no significant improvement, the by-products were generally as biodegradable as the original compounds.

The efficiency of pretreatment is based on the ability of hydrogen peroxide to produce an acceptable organic by-product without significant ultimate conversion of organic carbon to carbon dioxide. This may be expressed as follows:

$$f = \frac{H_2O_2}{HPD_L} \quad (2)$$

where: f = fraction of ultimate hydrogen peroxide demand

H_2O_2 = hydrogen peroxide consumed (mg/L)

and, $HPD_L = 2.13$ (initial COD)

The data for the wastes tested is shown in Table 3.

Table 3. Fraction of Ultimate Hydrogen Peroxide Demand and Fraction of TOC Converted to Carbon Dioxide for Various Organic Wastes

| | f^a | TOC converted ^a (%) |
|------|-------|-----------------------------------|
| DCP | 0.13 | 36.1 |
| DNOC | 0.56 | 30.2 |
| I | 0.26 | 12.1 |
| II | 0.34 | 22.4 |

a: all data at reaction Point C

The data indicates that a small portion of the organic carbon was converted to carbon dioxide (12.1 to 36.1%). However, the savings in peroxide usage were still substantial compared to ultimate oxidation ($f = 0.13$ to 0.56). In addition, the initial and final mean oxidation states of the organic carbon were compared (Figure 1).

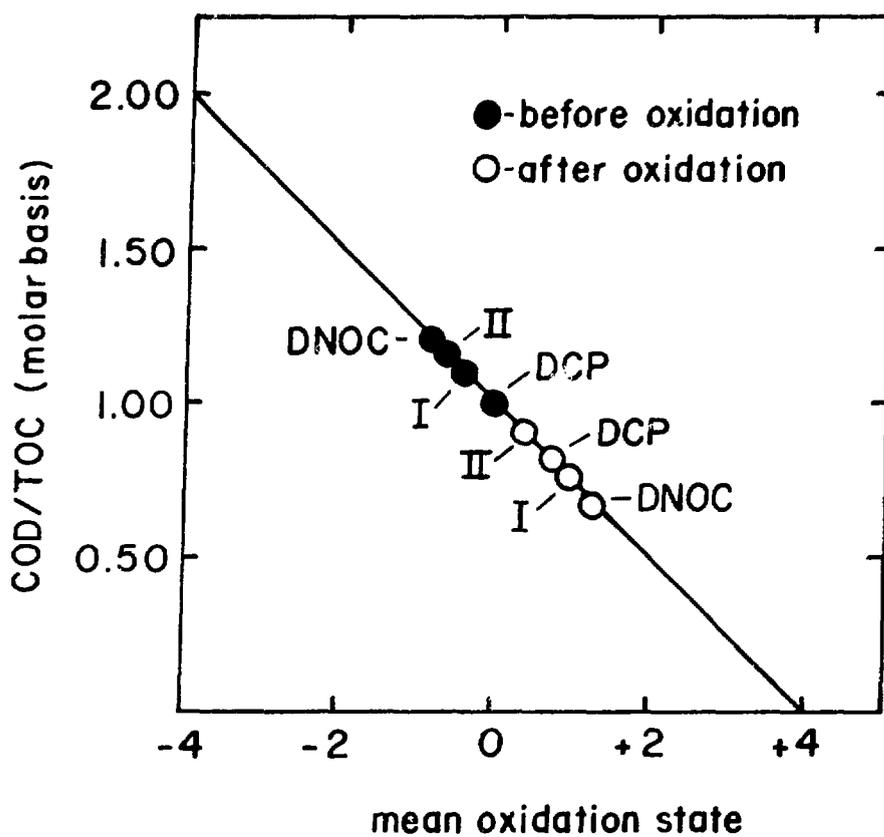


Figure 1. The COD/TOC ratio versus the mean oxidation state of carbon in the system. Note: a +4 oxidation state corresponds to inorganic carbon (CO_2) and a -4 oxidation state corresponds to methane.

The data shows conclusively that all of the hydrogen peroxide was not used for ultimate conversion of organic carbon, but rather the original compounds were drastically altered, leaving by-products in which the mean oxidation state of the carbon were more highly oxidized (positive instead of negative). DNOC exhibited the greatest change ($\Delta\text{OX} = +2.22$) and the smallest change was for DCP ($\Delta\text{OX} = +0.867$).

Conclusions

Many organic compounds are toxic, inhibitory or refractory to bacteria, preventing the effective use of biological waste treatment to degrade these wastes. Hydrogen peroxide may be used to treat these compounds by conversion to carbon dioxide, however this requires high peroxide dosages and may be prohibitively expensive. Peroxide may instead be applied at low dosages, resulting primarily in organic carbon by-products which are structurally different than their parent compounds. For those compounds tested, DCP, DNOC and two industrial wastewaters, the partial oxidation by hydrogen peroxide left by-products which were far less toxic and generally more biodegradable than the initial organics. This pretreatment process may be coupled with an in-house biological treatment system or, where permitted, as pretreatment prior to discharge into municipal sewers, since the by-products generated were fairly degradable without acclimation of a typical municipal sludge.

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**Application of Fixed Bed Trapping Technology
for Removal of Low Concentration UF_6
from Plant Gaseous Effluent Streams**

Presented by:

**R. G. Russell,
Paducah Gaseous Diffusion Plant**

ABSTRACT

Application of Fixed Bed Trapping Technology for Removal of Low Concentration UF_6 From Plant Gaseous Effluent Streams*, R. G. Russell, Paducah Gaseous Diffusion Plant, Paducah, Kentucky.

A major concern and responsibility of the uranium enrichment enterprise is the protection of the environment from uranium contamination. The best available technology is being used to successfully minimize cascade light gas vent stream uranium emissions at Paducah. Experimental work is being performed to apply and expand trapping technology to different sources of emissions with various gas composition, pressure, and superficial velocity constraints. The performance of two trapping media--sodium fluoride (NaF) and alumina (Al_2O_3), objectives, test method, and conclusions will be discussed. Approximately 50 experimental runs have been completed to date with the following major conclusions: velocity has an effect on uranium loading on alumina, but UF_6 concentration does not; the UF_6 outlet concentration prior to breakthrough has been measured to be as low as <1 ppb; higher trap loadings occur at lower pressure and superficial mass velocity; higher uranium loading occurs with Al_2O_3 until breakthrough, after which NaF experiences more loading; and Al_2O_3 is more efficient than NaF at higher velocities.

*Prepared by the Paducah Gaseous Diffusion Plant, Paducah, Kentucky 42002, operated by MARTIN MARIETTA ENERGY SYSTEMS, INCORPORATED, for the U.S. DEPARTMENT OF ENERGY, Under Contract No. DE-AC05-84OR21400.

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**APPLICATION OF FIXED BED TRAPPING TECHNOLOGY
FOR THE REMOVAL OF LOW CONCENTRATION UF₆ FROM
PLANT GASEOUS EFFLUENT STREAMS**

**R. G. RUSSELL
QUALITY & TECHNICAL SERVICES DIVISION
PADUCAH GASEOUS DIFFUSION PLANT
MARTIN MARIETTA ENERGY SYSTEMS, INC.**

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**OAK RIDGE MODEL CONFERENCE
OCTOBER 13-16, 1987**

Prepared by the
Paducah Gaseous Diffusion Plant
Paducah, Kentucky 42001
operated by
MARTIN MARIETTA ENERGY SYSTEMS, INCORPORATED
for the
U. S. DEPARTMENT OF ENERGY
Under Contract No. DE-AC05-84OR21400

RGR1

OBJECTIVES

- TO EXPAND TRAPPING TECHNOLOGY TO OTHER SOURCES OF EMISSIONS
- TO INVESTIGATE DIFFERENT GAS COMPOSITION, PRESSURE, AND SUPERFICIAL VELOCITY CONSTRAINTS

EXPERIMENTAL CONDITIONS

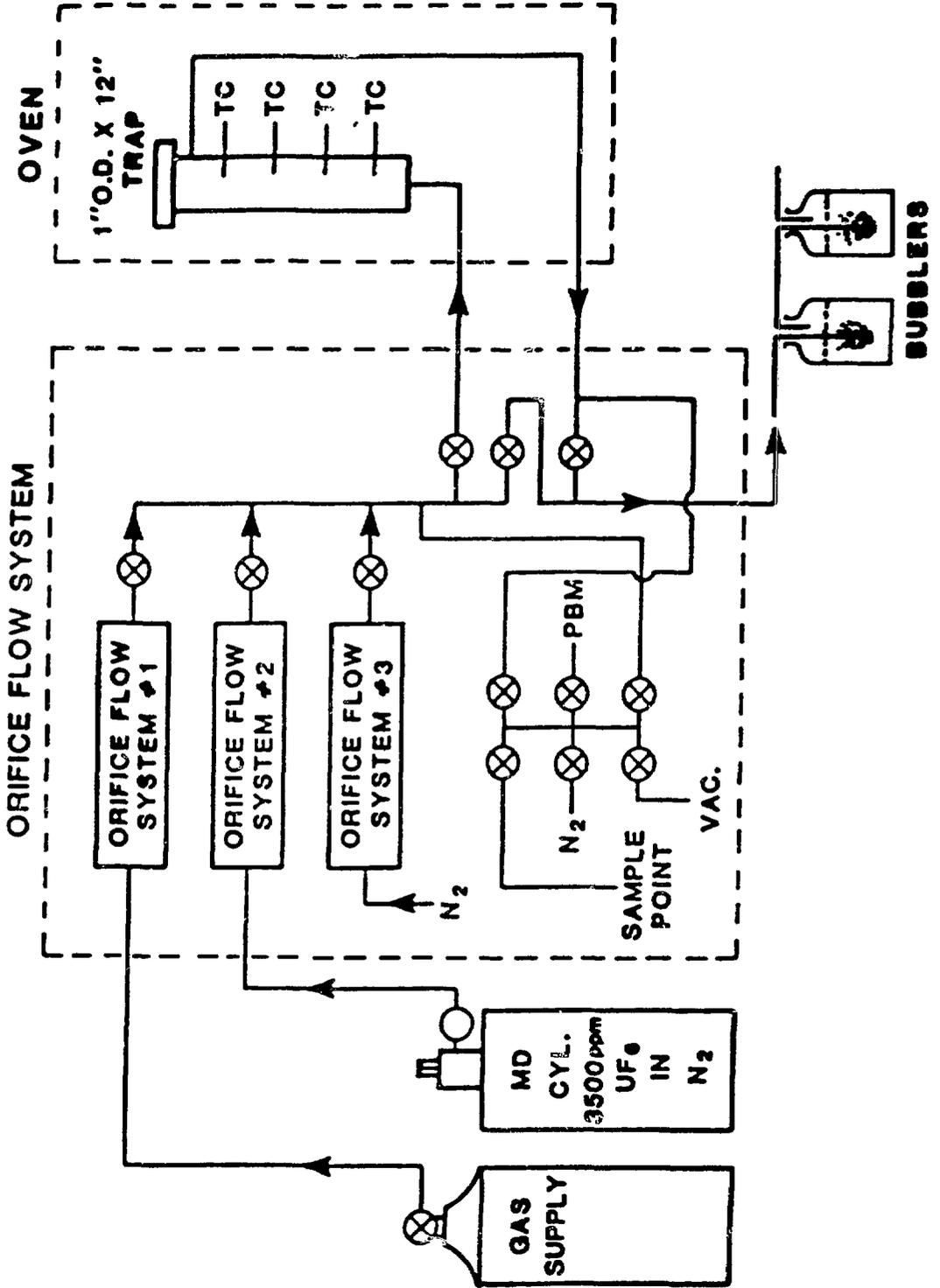
| | |
|-------------------------------------|-----------------|
| SUPERFICIAL VELOCITY | 0.1 - 3 ft/sec |
| UF ₆ INLET CONCENTRATION | 15 ppm - 4.5 % |
| SYSTEM PRESSURE | 900 - 200 mm Hg |

EXPERIMENTAL MATERIALS

| | <u>ALUMINA 201A</u> | <u>ALUMINA 202HF</u> | <u>SODIUM FLUORIDE</u> |
|-------------------------------------|--|--|--|
| MOLECULAR FORMULA | Al_2O_3 | Al_2O_3 | NaF |
| PELLET SIZE, INCHES | 0.127 | 0.124 | 0.124 X 0.135 |
| SURFACE AREA, M^2/g | 309 | 289 | 1.2 |
| DENSITY, g/cm^3 | 3.0 | 3.0 | 2.7 |
| TRAPPING MECHANISM | HYDRATION (UO_2F_2) | HYDRATION (UO_2F_2) | COMPLEXING (Na_2UF_8) |

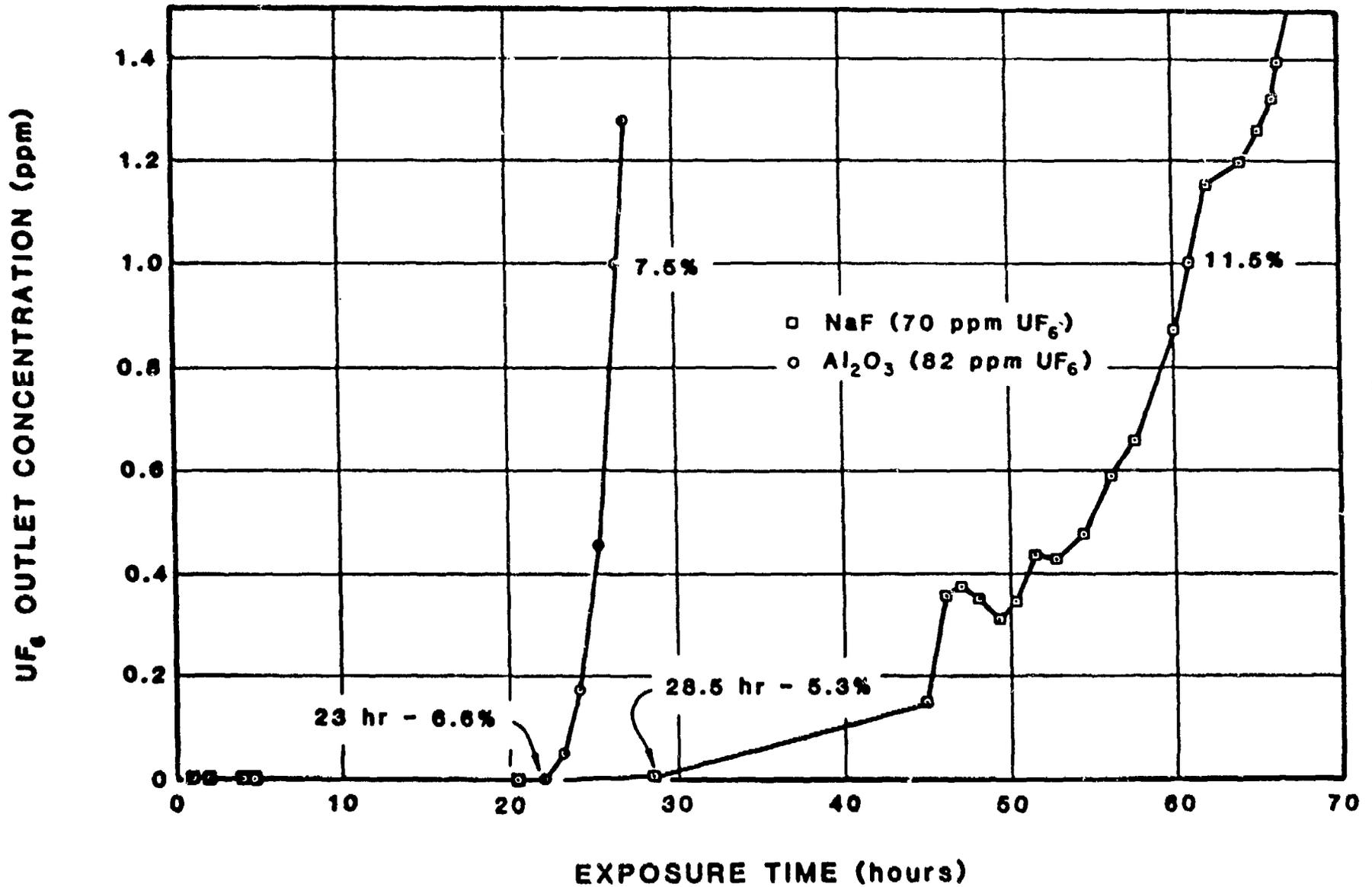
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TRAPPING SYSTEM



UF₆ OUTLET CONCENTRATION vs TIME

0.5 ft/sec - ATMOSPHERIC PRESSURE



VELOCITY EFFECTS

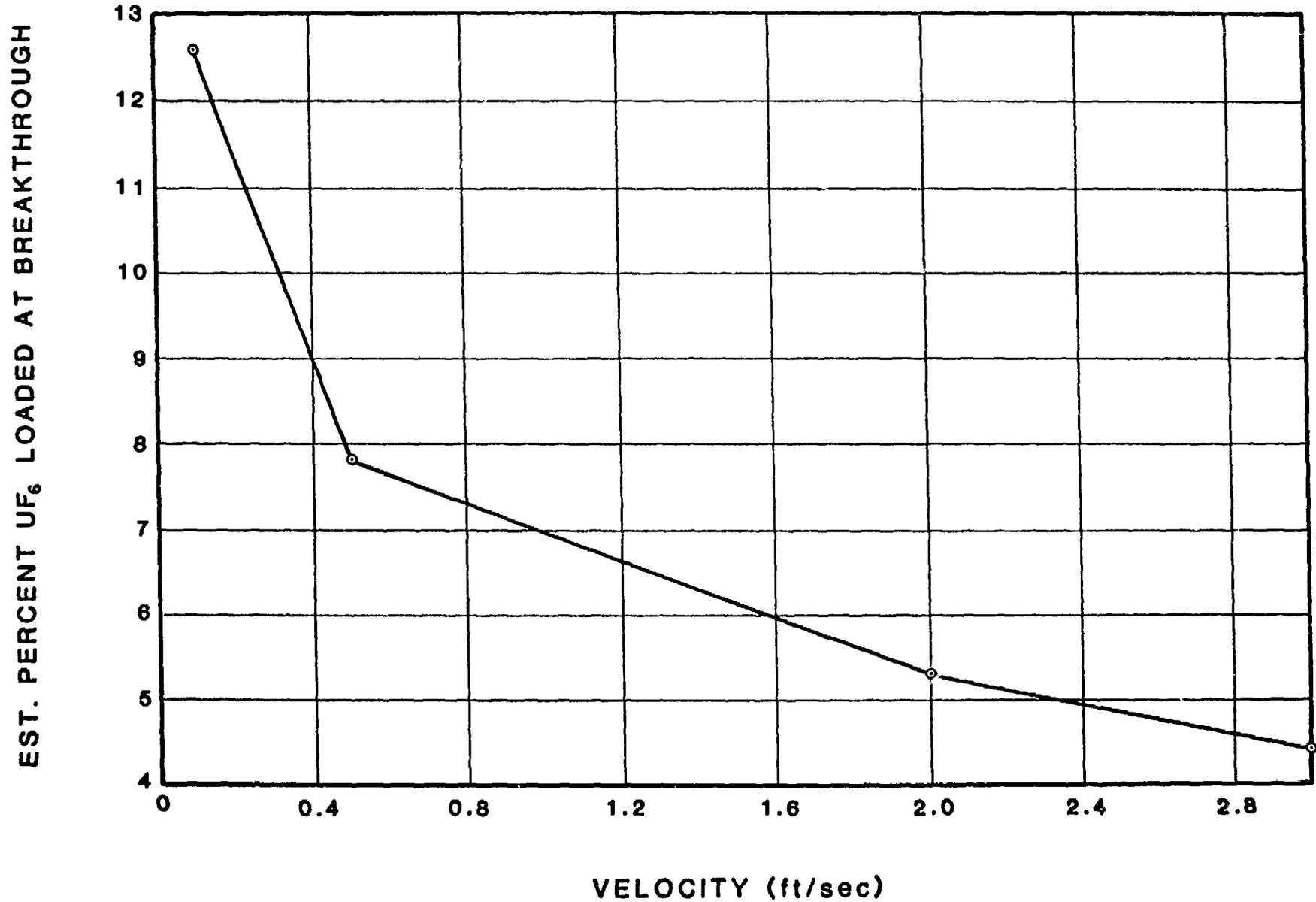
VELOCITY INFLUENCES URANIUM LOADING

| <u>MATERIAL</u> | <u>VELOCITY FT/SEC</u> | <u>INLET UF₆ CONC.</u> | <u>OUTLET UF₆ CONC.</u> | <u>BREAKTHROUGH TIME, MIN.</u> | <u>EST. % UF₆</u> | <u>RUN TIME, MIN.</u> | <u>BED ANALYSIS % UF₆</u> |
|-------------------------------------|----------------------------|---|--|--|----------------------------------|-------------------------------|--|
| A1 ₂ O ₃ -201 | 3.0 | 70 PPM | 0.2 PPM ^a | 198 | 4.4 | 240 | 5.5 |
| A1 ₂ O ₃ -201 | 2.0 | 88 PPM | 1-2 PPM ^b | 300 | 5.3 | 362 | 6.9 |
| A1 ₂ O ₃ -201 | 0.5 | 89 PPM | 1 PPM ^b | 1762 | 7.8 | 2276 | 7.7 |
| A1 ₂ O ₃ -201 | 0.1 | 4.5% | <20 PPM ^c | 24 | 12.6 | 48 | 17.9 |

- a. ANALYZED BY BUBBLERS
- b. ANALYZED BY GAS BULBS
- c. ANALYZED BY INFRARED

VELOCITY EFFECT ON UF₆ LOADING

Al₂O₃ RUNS CONDUCTED IN N₂/UF₆



CONCENTRATION EFFECTS

URANIUM INLET CONCENTRATION HAS LITTLE INFLUENCE ON PERCENT LOADING

| <u>MATERIAL</u> | <u>VELOCITY FT/SEC</u> | <u>INLET UF₆ CONC.</u> | <u>OUTLET UF₆ CONC.</u> | <u>BREAKTHROUGH TIME, MIN.</u> | <u>EST. % UF₆</u> | <u>RUN TIME, MIN.</u> | <u>BED ANALYSIS % UF₆</u> |
|-------------------------------------|----------------------------|---|--|--|----------------------------------|-------------------------------|--|
| Al ₂ O ₃ -201 | 0.5 | 14.7 PPM | <1 PPB ^a | 9488 | 7.1 | 9858 | 7.8 |
| Al ₂ O ₃ -201 | 0.5 | 89 PPM | 1 PPM ^b | 1782 | 7.8 | 2276 | 7.7 |
| Al ₂ O ₃ -201 | 0.5 | 4.5% | --- | 3 | 6.9 | 3 | 6.4 |

a. ANALYZED BY BUBBLERS

b. ANALYZED BY GAS BULBS

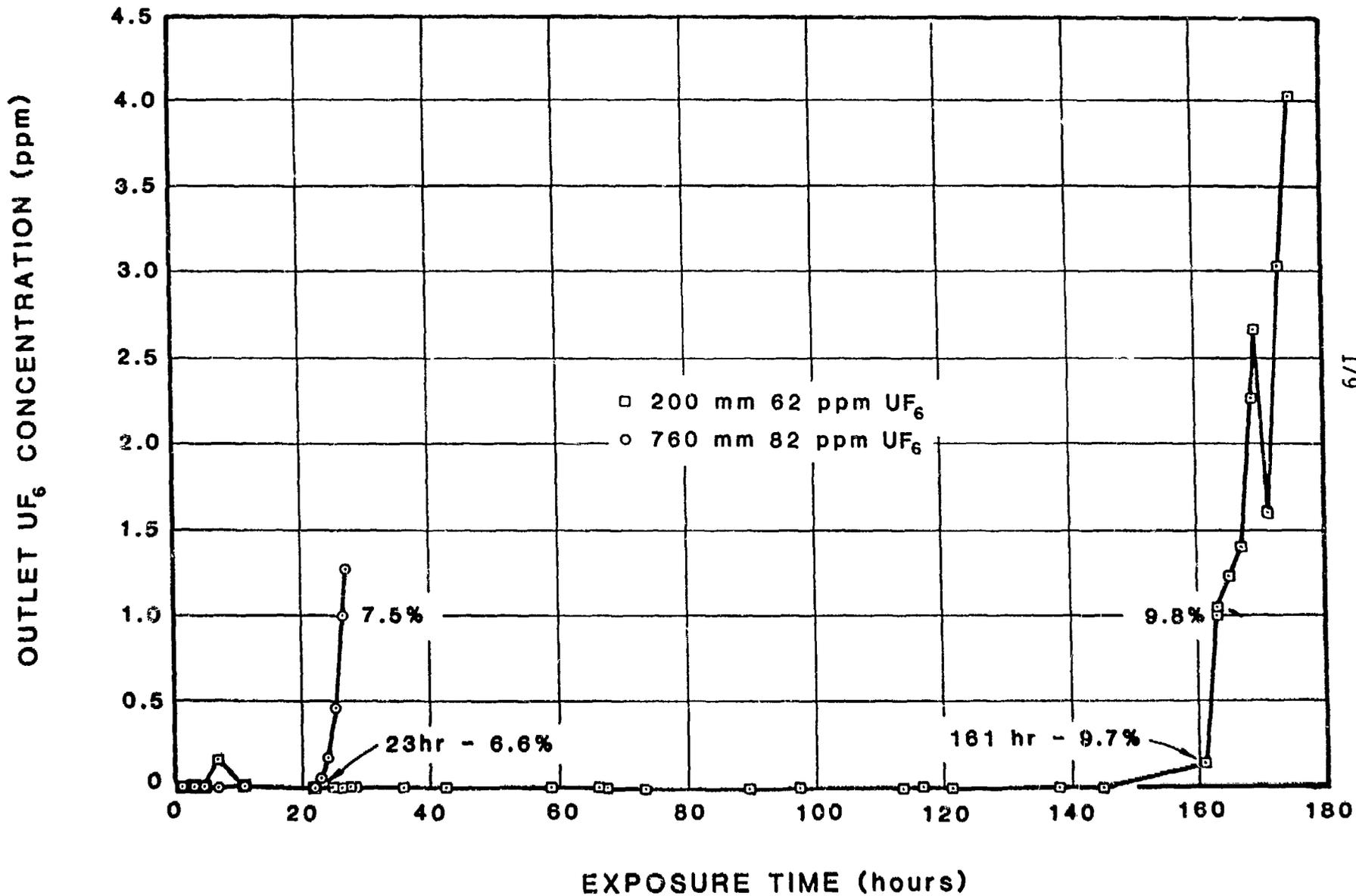
SYSTEM PRESSURE EFFECT
Al₂O₃ - NaF

| <u>MATERIAL</u> | <u>TRAP PRESSURE, MM</u> | <u>INLET UF₆, PPM</u> | <u>BREAKTHROUGH</u> | | <u>1 PPM UF₆ IN OUTLET</u> | |
|--------------------------------|----------------------------------|--|---------------------|-------------------------|---|-------------------------|
| | | | <u>TIME, MIN</u> | <u>% UF₆</u> | <u>TIME, MIN</u> | <u>% UF₆</u> |
| Al ₂ O ₃ | ~800 | 82 | 1388 | 8.8 (X3-7) | 1585 | 7.5 |
| Al ₂ O ₃ | ~200 | 82 | 8640 | 9.7 | 9780 | 9.8 |
| NaF | ~800 | 451 | 330 | 6.7 (X3-6) | 616 | 12.5 |
| NaF | ~200 | 307 | 4480 | 17.5 | 5970 | 23.4 |

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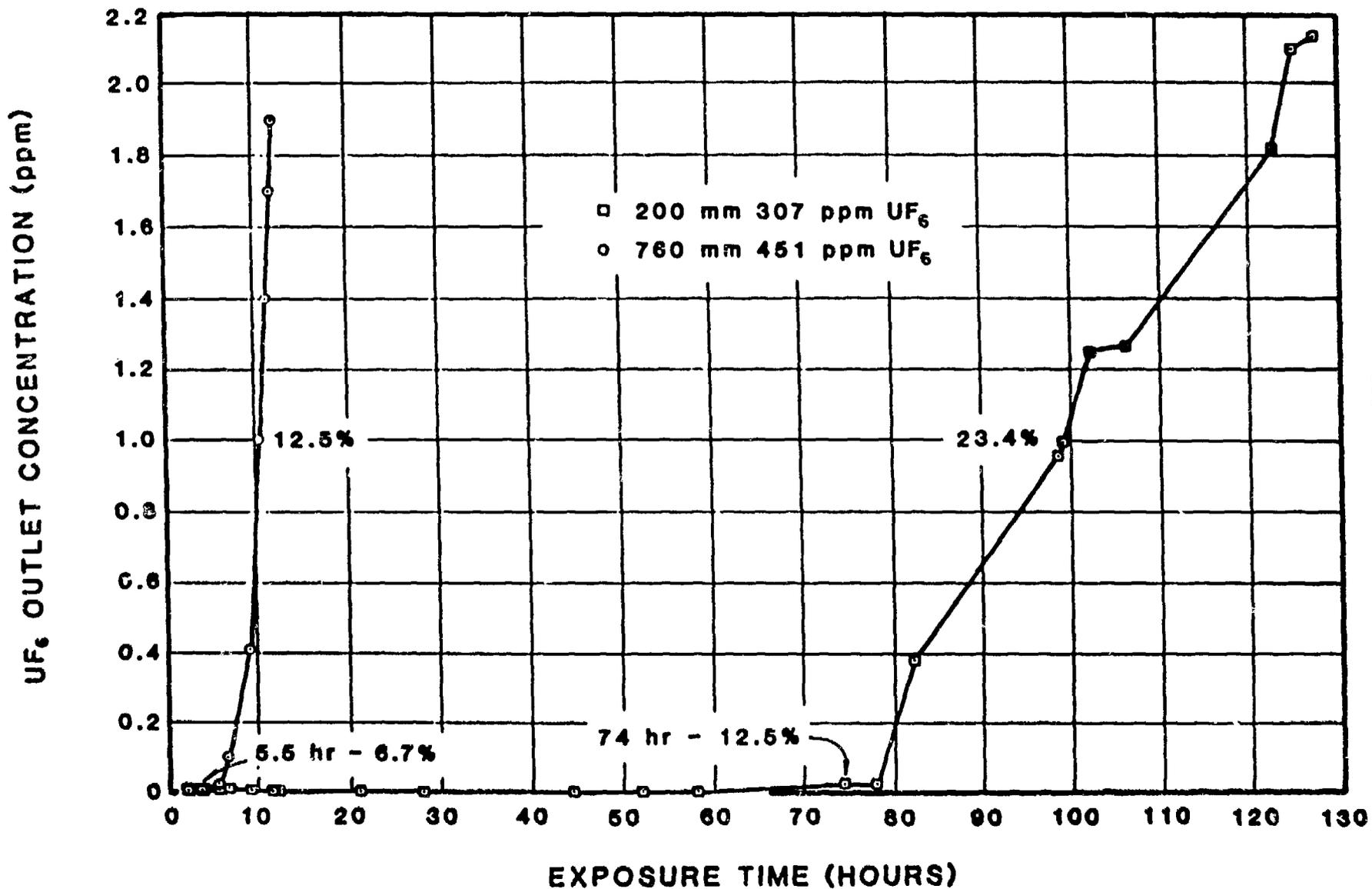
UF₆ OUTLET CONCENTRATION vs TIME

SYSTEM PRESSURE EFFECT Al₂O₃ 0.5 ft/sec



UF₆ OUTLET CONCENTRATION vs TIME

SYSTEM PRESSURE EFFECT NaF 0.5 ft/sec



SUPERFICIAL MASS VELOCITY EFFECT

| MATERIAL | VELOCITY, FT/SEC | INLET UF ₆ , PPM | FLOW, SCCM | PRESSURE, MM | SUPER MASS VEL. G/MIN/FT ² | LOADING % UF ₆ @BT |
|--------------------------------|---------------------|-----------------------------------|---------------|-----------------|---|----------------------------------|
| Al ₂ O ₃ | 0.5 | 82 | 3570 | 800 | 1005 | 6.6 |
| Al ₂ O ₃ | 0.8 | 82 | 1100 | 200 | 309 | 9.7 |
| NaF | 0.5 | 451 | 3500 | 800 | 984 | 6.7 |
| NaF | 0.5 | 307 | 1000 | 200 | 281 | 17.5 |

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HIGH VELOCITY EFFECT

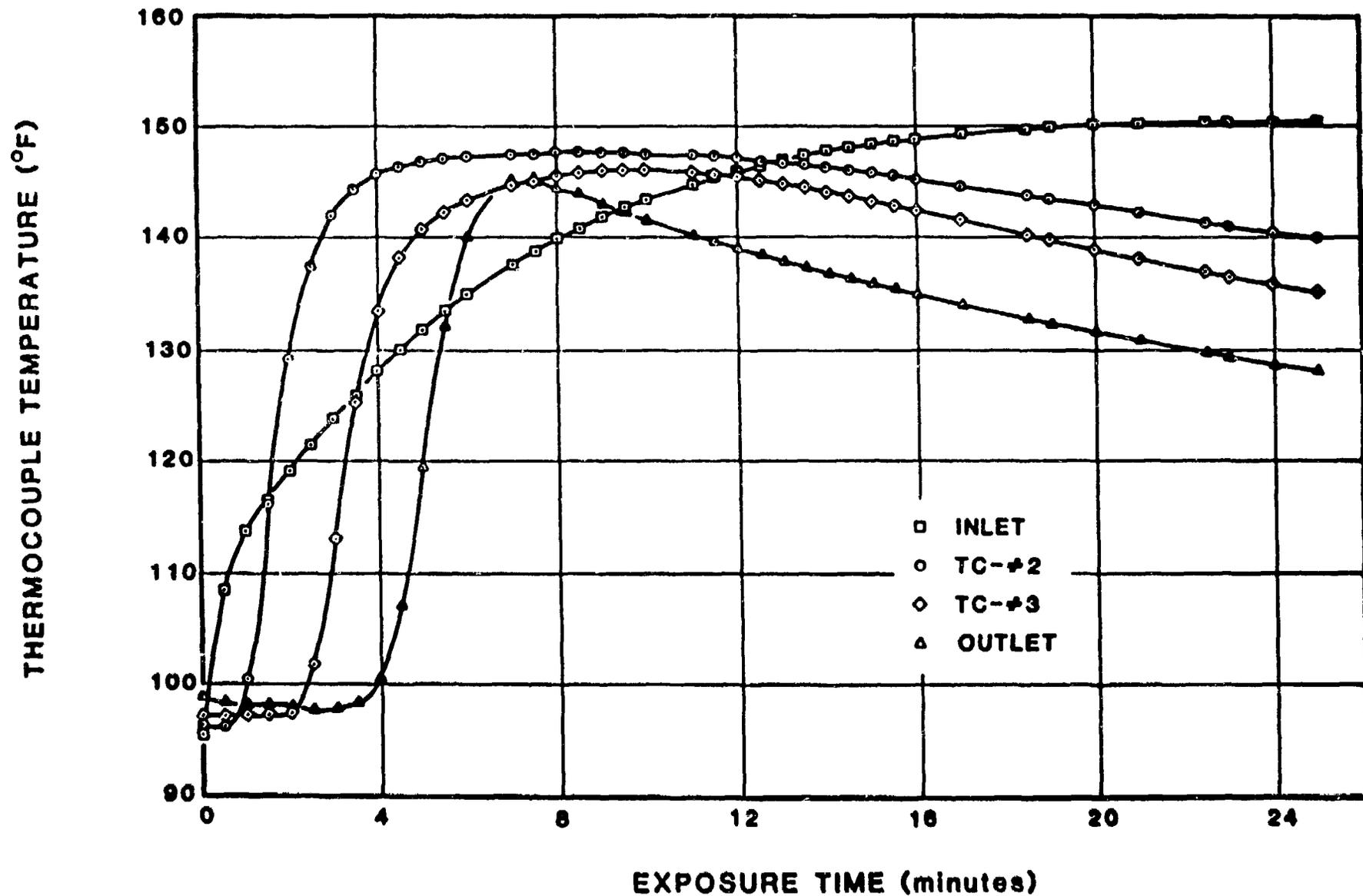
ALUMINA IS MORE EFFICIENT THAN NaF AT HIGHER VELOCITIES

| MATERIAL | VELOCITY FT/SEC | INLET UF ₆ CONC. | OUTLET UF ₆ CONC. | BREAKTHROUGH | | | RUN TIME, MIN. | BED ANALYSIS | | EST. FEED TOTAL, g |
|-------------------------------------|--------------------|-----------------------------------|------------------------------------|---------------|---------------------------|--------------------------|----------------------|-------------------|-------------------|-----------------------|
| | | | | TIME, MIN. | EST. % UF ₆ | EST g UF ₆ | | % UF ₆ | g UF ₆ | |
| Al ₂ O ₃ -201 | 2.0 | 14 PPM | <1 PPB | 1500 | 4.3 | 4.3 | 1860 | 5.4 | 5.4 | 5.3 |
| Al ₂ O ₃ -201 | 2.0 | 88 PPM | 1-2 PPM | 300 | 5.3 | 5.4 | 362 | 6.9 | 7.1 | 6.5 |
| Al ₂ O ₃ -201 | 3.0 | 70 PPM | 0.2 PPM | 198 | 4.4 | 4.2 | 240 | 5.5 | 5.5 | 5.1 |
| NaF | 2.0 | 356 PPM | 2.6 PPM | ~11 | ~0.7 | ~0.8 | 180 | 12.0 | 15.2 | 13.1 |
| NaF | 2.0 | 88 PPM | 335 PPB | ~25 | ~0.4 | ~0.5 | 240 | 4.0 | 5.0 | 4.3 |

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THERMOCOUPLE READINGS vs EXPOSURE TIME

ALUMINA - 4.3% UF_6 - 0.5 ft/sec



CONCLUSIONS

1. FOR THE TRAPPING OF UF_6 IN NITROGEN $NaF > Al_2O_3 > CaSO_4$
2. UF_6 INLET CONCENTRATION HAS LITTLE EFFECT ON LOADING OF ALUMINA
3. VELOCITY SHOWS AN EFFECT ON UF_6 LOADING ON ALUMINA - WITH HIGHER LOADING AT LOW VELOCITY
4. NO SIGNIFICANT DIFFERENCE IN UF_6 LOADING BETWEEN ALUMINA 201A AND 202HF
5. UF_6 OUTLET CONCENTRATIONS PRIOR TO BREAKTHROUGH MEASURED TO BE AS LOW AS <1 PPB
6. HIGHER URANIUM LOADING OCCURS WITH Al_2O_3 UNTIL BREAKTHROUGH (6.6% VS 5.3%), AFTER WHICH NaF EXPERIENCES MORE LOADING (7.5% VS 11.5% AT 1 PPM IN THE OUTLET)
7. HIGHER TRAP LOADINGS AT LOWER PRESSURES FOR BOTH NaF AND Al_2O_3
8. Al_2O_3 WAS MORE EFFICIENT THAN NaF AT HIGHER VELOCITIES

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Photocatalytic Oxidation of Toxic Organic Substances

Presented by:

C. P. Huang, University of Delaware

Photocatalytic Oxidation of Toxic Organic Substances

A. P. Davis, J. M. Tseng, and C. P. Huang
University of Delaware
Newark, DE 19716

ABSTRACT

An innovative physico-chemical method, photocatalytic oxidation, for the treatment of toxic organic compounds in waters and waste waters was studied. Absorption of light radiation corresponding to the bandgap energy of a semi-conductor results in the formation of electrons and holes in the solids. Electrostatic forces attract the positive holes, which are powerful oxidizing agents, to the surface where adsorbed organic contaminants can be oxidized to harmless products, e.g., H_2O , CO_2 , and other environmentally acceptable inorganic forms. Powdered TiO_2 and WO_3 are semi-conductors examined under UV light excitations. Visible light is used for oxidation using CdS and Fe_2O_3 . Organic compounds such as phenol, chlorophenol, dichlorophenol, and trichlorophenoethylene all can be oxidized under photocatalytic conditions. The formation of CO_2 is verified by the precipitation of $BaCO_3$ from a purge gas stream.

Phenol oxidation using CdS is first order with respect to light intensity and close to zero-order with respect to catalyst concentration as is expected for photocatalytic reactions. Efficient oxidation requires a high dissolved oxygen concentration. Solution pH plays an important role and the presence of dissolved metals inhibit the reaction.

A mechanism and kinetic model was exemplified by phenol oxidation.

PHOTOCATALYTIC OXIDATION OF TOXIC ORGANIC SUBSTANCES- A. P. Davis, J. M. Tseng, & C. P. Huang* Environmental Engineering Laboratory, Civil Engineering Department University of Delaware Newark, DE 19716

INTRODUCTION

Groundwater is an important water resource; much of the nation's domestic, agricultural and industrial water comes from groundwater sources. About a half of the population rely on subsurface water as their source of drinking water. However, groundwater systems are contaminated by a wide variety of hazardous substances, namely heavy metals and toxic organic chemicals. Most of these hazardous substances originate from poorly designed and managed landfills and waste disposal operations.

Several methods have been developed for groundwater detoxification; activated carbon adsorption, air stripping, photolysis, and chemical and biological oxidation are but a few of the most commonly mentioned. Each method has its inherent merits as well as limitations and none is definitely cost-effective. While the degree of groundwater pollution by hazardous and toxic substances has continued to rise, techniques with high efficiency and reliability for the removal of these harmful substances are not yet available.

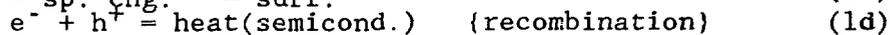
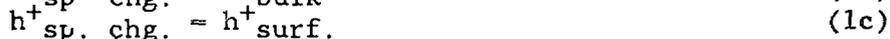
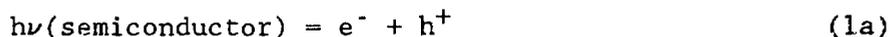
The oxidation of organic compounds, although thermodynamically favorable, is kinetically slow. Most organic chemicals contain numerous covalent bonds. Therefore the organic oxidation reaction has an activation energy higher than that of the inorganic oxidation(1). Strong oxidizing agents such as ozone have proven effective in organic oxidation. But this is an energy intensive and thus expensive process(2). The use of chlorination for organic oxidation always yields toxic chlorinated intermediates(3). It has been shown that oxidation is generally promising if these toxic intermediates can be avoided by adding sufficient oxidizer for total oxidation.

PROCESS DESCRIPTION

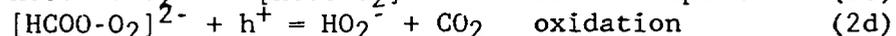
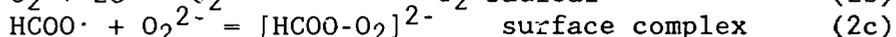
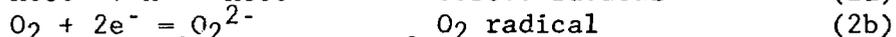
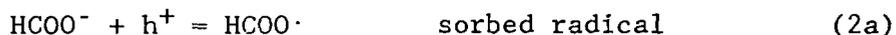
Photo-excitation in a semiconductor occurs as the absorption of bandgap irradiation that excites an electron into the conduction band. There is correspondingly, an electron vacancy, or hole left behind in the valence band (Figure 1). It has been found that these holes, very strong oxidizing agents, can chemically execute a variety of photocatalytic processes. The number of these electron/hole pairs is dependent on the intensity of the incident light. The electron is free to move throughout the crystal in the almost empty conduction band. Similarly, the hole can migrate by valence band electrons filling the hole, leaving behind another hole in the previous position.

The manner in which to efficiently utilize this radiant energy is to effectively separate these two charge carriers before recombination occurs. The electric field created at a semiconductor/electrolyte interface induces this separation. This series of events can be

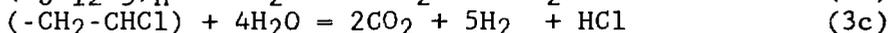
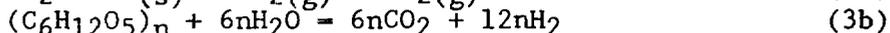
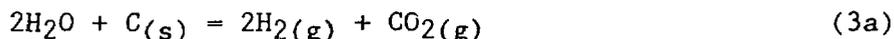
represented as(4):



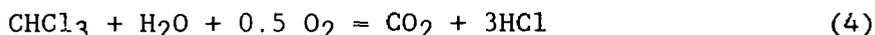
During the 1950's there was a series of work completed studying zinc oxide. It was found that illuminating aqueous solutions of ZnO produces hydrogen peroxide. Organic substances such as phenol, formate, oxalate, and toluene were found to increase the yield and rate of H₂O₂ formation. Oxalate and formate ions were oxidized to either carbon dioxide or bicarbonate(5-7). A mechanism for this process that includes an adsorbed surface complex was proposed(8).



Kawai and Sakata(9-11) demonstrated that H₂ gas could be photocatalytically produced by oxidizing many organic products, including carbohydrates, solid carbon, and polyvinyl chloride, instead of oxidizing H₂O to O₂ gas. The photocatalyst was titanium dioxide with a thin coating of platinum or ruthenium dioxide. The overall reactions being:



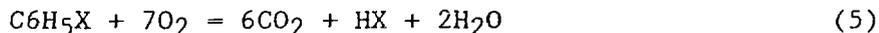
Later, some focus began to shift from the production of hydrogen to the the oxidation and destruction of toxic substances. Frank and Bard (12,13) established that cyanide as well as sulfite could be photocatalytically oxidized by TiO₂. Titanium dioxide is a semiconductor with a large bandgap, 3.4 eV. Therefore, ultraviolet light is needed to produce electron/hole pairs. The complete degradation of chloroform (CHCl₃) to carbon dioxide, water, and chloride ions was shown by Ollis and Pruden (14), again using TiO₂. A specific chloride electrode was used to monitor the increase in Cl⁻ concentration as the oxidation process proceeded. A stoichiometric decrease in chloroform according to



was detected using gas chromatography. Carbon dioxide was confirmed by precipitation of BaCO₃ in a CO₂ trap. Continued work by the same researchers examined the mineralization of trichloroethylene(15,16), dichloromethane, chloroform, carbon tetrachloride(17), trichloromethane (16), perchloroethylene, dichloroethane, and mono- and dichloroacetic

acid(18). Complete degradation of these reactants to inorganic products was observed. A simple kinetic model was proposed assuming that the reaction rate was proportional to the TiO₂ surface coverage by the organic compound. An overview of this work has been recently published (19). Formic(20) and oxalic(21) acid oxidation and the effect of different conditions, such as temperature, reactant and catalyst concentration, and oxygen flow, on the reaction process has been examined. Barbeni *et al.*(22) demonstrated the oxidation of 4-chlorophenol by TiO₂ under simulated and natural sunlight. The reaction is favored at high pH due to the suggested mechanism of hydroxyl radical formation. Additionally, the same workers established the photodegradation of chlorinated phenol, benzene, biphenyl, and dioxin on titanium dioxide(23). Other semiconductors were investigated as photocatalysts, but none was found superior to TiO₂.

Titanium dioxide is also an active photocatalyst in the degradation of a common surfactant, sodium dodecylbenzene sulfonate(24). Although surface tension is increased and CO₂ is formed, complete mineralization is slow. A recent paper(25) again establishes the ability of illuminated TiO₂ to oxidize toxic organic compounds. This time 21 different substances, including some aromatic hydrocarbons, were found to be degraded completely to CO₂. The general reaction presented was:



This entire work was completed using acidic conditions to facilitate the capture and measurement of carbon dioxide. The mechanism presented for oxidation on TiO₂ have all transpired via the initial formation of hydroxyl radicals and the presence of peroxide adsorbed on illuminated titanium dioxide surfaces has been confirmed(26).

Photocatalysis has also recently been demonstrated using iron oxide. α -Fe₂O₃ has been determined to oxidize chloride ions into chlorine gas via a chloride radical intermediate(27). This powerful oxidation is assisted by the accumulation of Cl⁻ ions near the positively charged oxide surface in acid media. Khader *et al.*(28,29) have shown the decomposition of water into H₂ and O₂ using a slightly reduced, heat treated, iron oxide photocatalyst.

In summary, it has been established that UV illuminated titanium dioxide can oxidize many different toxic organic compounds in aqueous solution. Chlorinated hydrocarbons as well as some simple and halogenated aromatics were mineralized completely to CO₂, H₂O, and HCl. In fact, it is now common to add a sacrificial electron donor, such as methanol or ethanol to increase the efficiency of photocatalytic reduction processes such as hydrogen production(30,31).

Cadmium sulfide is a n-type semiconductor with a bandgap corresponding to excitation by visible light. CdS, as is typical with heavy metal sulfides, is extremely insoluble (pK_{SO} = -28.3) and has been proven to have photocatalytic properties(32-34). TiO₂ with a band gap of 3.4 eV is

photosensitive to natural solar irradiation. This photocatalyst is also used in this study for the purpose of comparison. Phenol is a common petrochemical pollutant and has been found in toxic waste sites(35). Therefore, it was used as the major organic substance in this study.

METHODS AND MATERIALS

Batch Experiments with CdS

The cadmium sulfide is powdered, electronic grade and 99.999% pure (Aldrich Chem Co.). The phenol is "Baker Analyzed" grade (J. T. Baker Chem Co.). The reaction is conducted as a slurry in 2 liter, double-jacketed, airtight vessels to insure temperature control. Slurries of small semiconductor particles are efficient in the absorption of light. A 500 ml aqueous organic solution with an ionic strength of 0.05 M NaClO_4 is placed inside the vessel and adjusted to the desired pH value with NaOH or HClO_4 .

ELH lamps (300 Watt, GE) provide the photo-illumination. These lamps yield a spectrum that is similar to that of sunlight(36), allowing possible correlation with the use of solar energy as a treatment process. A radiometer (Yellow Springs Inst. Co.) was used to monitor the photointensity in the reactor. For most photocatalytic work, an intensity of 700 W/m^2 is used, equivalent to that of an average solar intensity in middle latitudes(37). The lamps are situated directly above the reaction vessels. Pyrex glass is implanted into the reactor lid to allow maximum visible light passage.

The solution is continuously bubbled with O_2 or N_2 throughout the entire reaction process. The purge gas is passed through a solution of Ba(OH)_2 and NaOH before entering and after exiting the reactors to capture CO_2 produced during the oxidation process. In all cases, 3 reactors are operated simultaneously and mixing is provided by a multi-magnetic stirrer.

Approximately 8 ml samples are withdrawn by a syringe and filtered using a $0.45 \mu\text{m}$ microfilter. The pH is recorded and adjusted if necessary. The residual organic concentration is measured using a Hitachi Perkin-Elmer UV- VIS spectrophotometer. The addition of Cd(II) salts to the organic solution does not affect the standard calibration. The dissolution of CdS is measured using a Perkin Elmer Model 5000 Zeeman Atomic Absorption Spectrophotometer (AA). The CO_2 captured is gravimetrically determined from the precipitated BaCO_3 .

Kinetic experiments were performed over 3 days, with the majority of samples being examined during the early stage of the reaction. At the completion of each experimental run, the solution is acidified and purged with N_2 gas to remove carbonate species. The BaCO_3 precipitate is filtered through a Whatman # 1 filter and dried overnight. The BaCO_3 present is determined by weight difference.

Batch Experiments with TiO₂

A commercial grade titanium dioxide, having a specific surface area of 6.78 m²/g determined by the BET method, was supplied by the DuPont Co (#R-107-CD). Samples were pretreated by rinsing with 1M HClO₄ and water several times until the conductivity dropped to less than 10 μmho/cm. Samples were centrifuged at 10000 rpm for 30 minutes, then the titanium dioxide was ground to a fine powder and dried overnight at 105 °C. The zeta potential of the titanium dioxide was measured using a Laser-zee meter (Pen-ken Inc.). The pH_{zpc} for TiO₂ is about 6.1 in a 0.05 M NaClO₄ solution. The light source used to illuminate TiO₂ samples was a 1500 Watt medium-pressure mercury vapor discharge lamp (American Ultraviolet Co.). The spectral irradiation for the UV lamp is 260 Watts/m² between 228 and 420 nm at 1 meter distance from the light source. The light intensity was recorded using a Radiometer (Model 65A, YSI-Kettering Co.). The band gap energy of TiO₂ (3.4 eV) is located in the ultraviolet range (362 nm).

All reactions for TiO₂ were performed in pyrex tubes with 15 ml of 10⁻³ M phenol solution and 0.15 g of TiO₂. Samples were shaken to insure complete mixing. The temperature of the sample was controlled and monitored immediately after sampling. Samples were filtered by using 0.45 μm microfilters. Dissolved Ti(VI) ions were monitored by AA (Perkin-Elmer, model Zeeman 5000).

RESULTS

The effect of phenol concentration

The effect of phenol concentration is presented in Figure 2. The percent removal is clearly a function of the amount of organic initially present. As the concentration decreases, the time for effective removal decreases. At an initial concentration of 10⁻⁴ M phenol, over 80% removal is accomplished after only 8 hours. This is promising for the removal of low concentrations of contaminants. The results shown in Figure 2 also demonstrate that without illumination and in the absence of any cadmium sulfide catalyst the amount of phenol remains unchanged. The removal of phenol by adsorption onto CdS surface is insignificant. Additionally, as shown in Table 1, a substantially greater amount of BaCO₃ was generated from the photo-catalytically operated sample in comparison to the other 2 trials.

It is assumed that the reaction rate is proportional to the coverage of the catalyst by the phenol, as was found for UV illuminated titanium dioxide (15,17,20,25,38), as well as oxygen. A dependence on light intensity and catalyst concentration is also expected. Assuming Langmuir type isotherms for both phenol and oxygen and first order dependence on illumination and catalyst concentration, the reaction rate is given by:

$$r = \frac{kK_1K_2C[O_2][h\nu][CdS]}{1 + K_1C + K_2[O_2]} \quad (6)$$

Table 1. Recovery of Carbon Dioxide (as BaCO₃) from the Photocatalytic Oxidation of Phenol.

| Conditions | BaCO ₃ (grams) |
|----------------|---------------------------|
| Photocatalytic | 0.229 |
| Darkness | 0.117 |
| No Catalyst | 0.086 |

where C is the phenol concentration, K₁ and K₂ are respectively, the adsorption constants for phenol and oxygen, and k is the reaction rate constant. For the special case of only a variable phenol concentration the equation becomes:

$$r = k\theta = \frac{kK_3C}{1 + K_4C} \quad (7)$$

where K₃ and K₄ are collections of terms which are constant here and to be discussed in more detail later. Rearranging this formula allows a linearization.

$$1/r = 1/kK_3 \cdot 1/C + K_4/kK_3 \quad (8)$$

A plot of this data is presented in Figure 3. A best fit line provides a value of 0.065 (hr⁻¹) for kK₃ and 3487 (mole/l)⁻¹ for K₄. In comparison, values for K₄ in the range of 10² - 10³ have been reported for photocatalytic oxidations of chlorinated hydrocarbons and oxalic acid over UV illuminated TiO₂(15,17,18,21).

Independently, an adsorption isotherm for phenol onto CdS was obtained by mixing varying phenol concentrations with 5 g/l CdS in test tubes. The tubes were completely wrapped in aluminum foil to keep out all light and shaken for at least 24 hours. The solution was filtered and the supernatant examined for the final phenol concentration. The amount adsorbed is taken as the difference between the initial and final phenol concentrations:

$$q = \frac{q_m K' C}{1 + K' C} \quad (9)$$

where q , q_m , and K' are adsorption density, monolayer coverage density, and the Langmuir adsorption constant respectively. A value of K' obtained from this data is 38 (mole/l)^{-1} . With the rate, $r = -dC/dt$ as in batch reactors, Equation 7 can be integrated, resulting in:

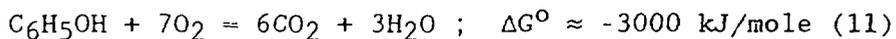
$$\ln (C_0/C) + K_4(C_0 - C) = kK_3t \quad (10)$$

Using a K_4 value of $3,487 \text{ (mole/l)}^{-1}$ as found previously, a linear plot of this equation is presented in Figure 4. The value of kK_3 found from this plot is 0.079, in good agreement with the value of 0.065 found using initial rates. This provides strong proof of the adsorption dependence of the oxidation rate. In fact, it has been noted that substances must be adsorbed onto the catalyst for the hole/electron charge transfer to take place and that this charge transfer is an extremely fast process(32,39).

The effect of O₂

It is clearly shown in Figure 5 that oxygen is essential for the oxidation of phenol. A similar requirement for oxygen has been demonstrated for the photocatalytic degradation of chloromethane(17) and acetic acid(40) by TiO₂. Correspondingly, the rate of CN⁻ oxidation using TiO₂ was an order of magnitude larger in the presence of O₂ over that of nitrogen bubbling(12). The oxygen uptake on a CdS photocatalyst doubled as the dissolved oxygen was increased from 22% to 83%(41).

These observations may result from a number of causes. As stated previously, the oxidation of organic substances is thermodynamically favored.



However, the difficulty in breaking the O=O double bond as well as the stability of the aromatic ring kinetically impede this reaction. The photocatalyst assists in overcoming these barriers in the oxidation process. The formation of O₂ from water is possible as proven by experimentation on water splitting and should account for the phenol oxidation under nitrogen. However, this reaction requires a high oxidation potential, and in the presence of organics, should be nominal, as evidenced by the very small reaction rate. Izumi *et al.*(42) attributed the increase in the photocatalytic activity of TiO₂ in the presence of O₂ to oxygen reduction. Oxygen reduction is thermodynamically advantageous and the ease of electron removal from the CdS increases the oxidation rate by creating unmatched holes. It has been noted that electrons are scavenged by oxygen in cadmium sulfide photocorrosion(43). In contrast, Duonghong *et al.*(32) found that the capture of holes during SCN⁻ oxidation is fast enough so that it is not affected by the reduction process. However, SCN⁻ oxidation is only a single charge transfer process as opposed to the multiple charge transfer of phenol oxidation. Therefore, the SCN⁻ reaction may be faster than organic oxidations, whose rate may not be independent of the reduction process.

Similarly, the presence of oxygen decreased the reduction of thionine to semi-thionine by competing for the interfacial electrons, $[E_{O_2/O}^0 - 0.78 \text{ V (SCE)}]$ (44). Indeed, O_2^- surface species have been detected on cadmium sulfide by electron spin resonance spectroscopy(45). It is assumed that oxygen must be adsorbed onto the CdS surface for the photocatalytic oxidation to transpire. This has been noted as a necessary step in oxygen reduction on TiO_2 (46,47). In this case a Langmuir type of rate is also proposed with the linearization given as:

$$1/r = 1/kK_5 \cdot 1/[O_2] + K_6/kK_5 \quad (12)$$

where as before, K_5 and K_6 are constant only during this experimentation. From the data it is found that $kK_5 = 3.81 \times 10^{-11} \text{ hr}^{-1}$ and $K_6 = 3.81 \times 10^{-7} (\text{moles/l})^{-1}$. Overall, a strong dependence of aqueous dissolved oxygen is required for the efficient oxidation as would be expected for a truly catalytic reaction.

The effect of pH

The ultimate phenol oxidation is optimum at neutral pH values for both the CdS and the TiO_2 systems with only slightly lower removal at pH < 5 (Figure 6a & b). Poor removal occurs at pH 11. However, evaluation of initial rate data show the reaction to be independent of solution pH, even at high pH. Phenol adsorption experiments onto CdS have shown this phenomenon to be pH independent (Figure 7). The eventual non-reaction at pH 11 must be due to an unreactive intermediate formation that blocks the active catalyst area. Results reported by Matthews(48) using TiO_2 to oxidize 4-chlorophenol demonstrated that the maximum carbon dioxide yield resulted at neutral pH values with lower rates occurring under high and low pH conditions. Similarly, four other compounds produced lower yields at pH values below 3, than for slightly higher pH solutions. The photocatalytic oxidation of the surfactant DES is also favored in neutral solutions(24). Ollis and Pruden(49) reported that protons inhibit chloroform degradation on illuminated TiO_2 , but gave no mechanistic reason for this occurrence. Kraeutler and Bard(40) found the rate of CO_2 formation from acetic acid/sodium acetate on undoped anatase to be a maximum at pH 3.6. although, again, no explanation for this phenomenon was offered. It seems reasonable to examine the pH dependence of adsorption of the reactant in these cases. Matsumura *et al.*(34) reported the rates of gas evolution on illuminated CdS to be highest at low pH for formic acid solutions and greatest at high pH for methanol solutions. Solutions of formaldehyde resulted in gas evolution rates that were essentially pH independent. Photocurrents, using CdS electrodes, followed similar pH trends. These results were explained by noting that the flat band potential of a CdS electrode becomes more negative at higher pH, attributed to hydroxylation of the CdS, producing a negative surface. Adsorption of H^+ and OH^- ions onto the CdS surface have been determined to change the Fermi level of CdS according to(50):

$$E_f = E_f(\text{pH} = 0) - 0.04\text{pH} \quad (13)$$

indicating higher (more oxidizing) energetics for lower pH values. Greater oxidation has not been found to be the case for phenol at low pH values. This hydroxylation also changes the surface charge of the catalyst, which affects the adsorption of the organic molecule. Results from phenol oxidations using ozone, chlorine dioxide, Fenton's Reagent, and ozone/UV combined suggest that the pH dependence of the reaction is controlled by the activity of the oxidant and not of the organic substance being oxidized(51-55). The optimum pH for phenol oxidation varied from below 4 to above 10 and even no effect, depending on the oxidizing agent.

The effect of catalyst concentration

The effect of varying the catalyst concentration is presented in Figure 8 (a & b). The oxidation rate is slightly elevated by an increase in semiconductor concentration. Initial rate data show only a slight dependence on the CdS concentration, approximately equal to $[CdS]^{0.16}$. This is in explicit contrast to common catalytic reactions in which the rate is always directly proportional to the concentration of catalyst. However, photocatalytic reaction rates are almost independent of catalyst concentration(56). This is due to the fact that for a site to be active, it must be activated by photons. This photon impingement is controlled by the macroscopic area of the reactor. Once complete absorption of the incoming light occurs, additions of more catalyst will not increase the reaction rate. Indeed, a saturation of catalytic activity for increasing concentrations of TiO_2 for photocatalytic detoxification has been noted (25) which agrees well with Figure 8b. Bideau and co-workers(20) examined photocatalysis rates of formic acid in small concentrations of titanium dioxide and found a limiting reaction rate (r_{lim}). By assuming a first order reaction on light, and absorption by the particles in an annular reactor, they derived:

$$\ln(1 - r/r_{lim}) = -2\epsilon lC \quad (14)$$

where ϵ = absorptivity, l is the path length and C is the catalyst concentration. Whereas typical catalytic reaction rates are given as per weight of catalyst, it seems that photocatalytic reaction rates need to be standardized as per unit area of reactor exposed to illumination.

The effect of illumination intensity

The light sensitivity of the photocatalytic reaction is clearly shown in Figure 9a. The rate and the extent of reaction are increased by each incremental increase in light intensity. This data clearly proves that this reaction is indeed photocatalytic. Using an extrapolation of initial rates, it is found that phenol oxidation is explained well as a first order reaction with respect to light intensity (Figure 9b). Many photocatalytic reactions using titania were found to be first order with respect to light(57). Correspondingly, it is known that photocurrent (electron rate) is directly proportional to the incident light intensity on solar cell surfaces(58). Gomes et al.(59) reported photocurrents on

ZnO to be proportional to light intensity. However, it has been noted that photocatalytic reactions are not directly proportional to light intensity, as photoelectrochemical reactions are (56). This is due to the fact that the flow of electrons and holes to the semiconductor surface must be equal, which results in a complex, but not exactly linear, relationship of rate and light intensity. Nonetheless, within the light intensity range examined here:

$$r = k' [h\nu] \quad (15)$$

with k' equal to parameters constant during this phase of experimentation.

The Effect of Temperature

Solution temperature has a strong effect on phenol photocatalytic oxidation as shown in Figure 10. Increases in temperature greatly increase the removal efficiency. The oxidation rate increases with increasing temperature as expected from kinetic theory. Almost complete removal is obtained after only 5 hours for TiO_2 (Figure 10a) and 48 hours for CdS (Figure 10b) at the highest temperature. A linear Arrhenius plot is obtained (Figure 11). The activation energy for this process is 19.4 kJ/mole for CdS and 19.9 kJ/mole for TiO_2 , respectively. It is interesting to note that the activation energy is almost the same regardless of the photocatalyst used (Figure 11). This is comparable to the value of 13 kJ/mole obtained for oxalic acid(41) and 16.7 kJ/mole for formic acid(21) photocatalytic oxidation over UV illuminated TiO_2 .

Overall Kinetic Expression for CdS photocatalyst

Values obtained from phenol and oxygen concentrations provide a method for independently determining the adsorption constant. From the phenol concentrations at various experimental parameters, one has:

$$\begin{aligned} kK_3 &= 0.0652 \text{ hr}^{-1} = kK_1K_2[\text{O}_2][h\nu][\text{CdS}]^{0.16} \\ K_4 &= 3487 (\text{moles/l})^{-1} = K_1/(1 + K_2[\text{O}_2]) \end{aligned}$$

Similarly from a variable oxygen concentration, one has:

$$\begin{aligned} kK_5 &= 3.81 \times 10^{-11} \text{ hr}^{-1} = kK_1K_2C[h\nu][\text{CdS}]^{0.16} \\ K_6 &= 3.81 \times 10^{-7} (\text{moles/l})^{-1} = K_2/(1+K_1C) \end{aligned}$$

By applying these values to the following experimental conditions:

$$\begin{aligned} C &= 10^{-3} \text{ moles/l} \\ [\text{O}_2] &= 5.25 \times 10^{-2} \text{ moles/l} \\ [h\nu] &= 700 \text{ W/m}^2 \\ [\text{CdS}] &= 5 \text{ g/l} \end{aligned}$$

it is found that $K_1 = 1.47 \times 10^4 (\text{moles/l})^{-1}$ and $K_2 = 5.94 \times 10^{-6}$

(moles/l)⁻¹. Using these values for the adsorption constants, separate rate constants for each case can be determined. From the variable phenol concentration data, it is found that $k = 6.4 \times 10^{-9} \text{ (W/m}^2 \cdot \text{hr)}^{-1} \text{ (moles/l) (g/l)}^{-0.16}$. The variable oxygen concentration data give $k = 7.6 \times 10^{-9} \text{ (W/m}^2 \cdot \text{hr)}^{-1} \text{ (moles/l) (g/l)}^{-0.16}$. Presenting k as per unit illuminated reactor area, i.e. 177 cm², $k = 4 \times 10^{-11} \text{ (W/m}^2 \cdot \text{hr)}^{-1} \text{ (moles/l) (g/l)}^{-0.16} \text{ (cm}^{-2})$.

Other Organics

Trichloroethylene (TCE): Figure 12 shows that, even though some of this substance is lost to the atmosphere due to its volatility, under illumination it is efficiently removed much greater than that under dark conditions. The most effective reaction took place at pH 7 where complete removal occurs after 24 hours of reaction time. The difference between the 2 pH values must be due to pH modification of the CdS surface since TCE does not deprotonate with pH; either due to adsorption or oxidation potential modifications.

Chlorinated Phenols: Figure 13 shows that 2-chlorophenol, 2,4-dichlorophenol, and 2,4,6-trichlorophenol are all oxidized photocatalytically. The removal coincides with the degree of chlorination. This removal may be due to the increase in adsorption of the chlorinated phenols over that of the non-chlorinated compound, which is apparent for 2,4-dichlorophenol (Figure 13), or the ease of oxidation of the halogenated compound. The increase in adsorption may be due to the decrease in pKa as the compound becomes more chlorinated, resulting in more anionic species present at pH 7 (Table 2). The CdS surface has a slight positive charge at this pH.

Table 2. Dissociation Constants of Chlorinated Phenols

| Compound | pKa |
|-----------------------|-----|
| Phenol | 9.9 |
| 2-Chlorophenol | 8.3 |
| 2,4-Dichlorophenol | 7.8 |
| 2,4,6-Trichlorophenol | 6.1 |

It is generally seen that oxidation rates of aliphatic compounds become smaller as the degree of chlorination is increased due to the replacement of the reduced hydride(61-63). However, the addition of electrophilic chloride to the phenolic base alters the electron density of the aromatic ring. The high electronegativity of chlorine weakens the electronic characteristics of the ring, making it more susceptible to oxidation

SUMMARY

It is clear that the potential for water detoxification by photocatalytic

oxidation is promising. The oxidation is first order with respect to light intensity, and shows Langmuir-Hinshelwood kinetics with respect to the phenol concentration. With increasing problems surfacing over the ultimate disposal of hazardous wastes and chemicals, it seems likely that eventually we must stop looking for a place to dump material, but develop methods that treat it, render it harmless and environmentally acceptable by returning it to the carbon cycle of the earth.

The major setback with cadmium sulfide is that it is relatively unstable under illuminated conditions and corrosion of the catalyst does occur. Large concentrations of cadmium, maximum at 10^{-3} M, have been detected in the final solution, which so far can not be prevented. Although it has been reported that reduced substances can stabilize CdS(49,64,65), it seems that the oxidation of phenol cannot completely compete with the lattice sulfide for the photo-produced holes. Optimizing the phenol oxidation also results in the largest dissolved cadmium. Work is underway to prevent the cadmium dissolution, such as using high pH conditions. Also possible are various unit processes such as separating the removal and oxidation steps, or a second treatment for cadmium precipitation. These reaction engineering problems also need to be solved before CdS photocatalysis is practical as a water detoxification process

An advantage of using TiO_2 as a catalyst is that it is a very stable component to be able to carry electrons without itself decomposing in a photoirradiation process. Although a small amount of titanium ions may exist in the environment due to the reaction, human health effects have not yet been found. There is no criteria for a permissible concentration of TiO_2 in water, but EPA has suggested a quantity of 83 $\mu\text{g/L}$ for health reasons. Another benefit of application of TiO_2 is that the unit price of TiO_2 is affordable to use as a catalyst in water and wastewater treatment plants. However the use of TiO_2 as a catalyst needs more detailed study to understand its nature in the environment.

ACKNOWLEDGMENT

The research on which this report is based was financed in part by the United States Department of the Interior as authorized by the Water Research and Development Act of 1978 (P.L. 95-467). Contents of this publication do not necessarily reflect the views and policies of the United States Department of the Interior, nor mention of trade names or commercial products constitute their endorsement by the U. S. Government.

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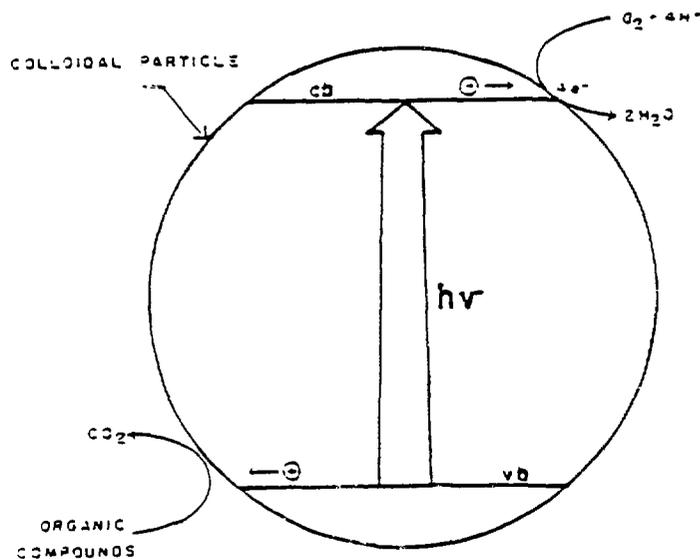


FIGURE 1. SCHEMATIC DIAGRAM OF THE GENERATION OF ELECTRONS AND POSITIVE HOLES IN A SEMICONDUCTOR.

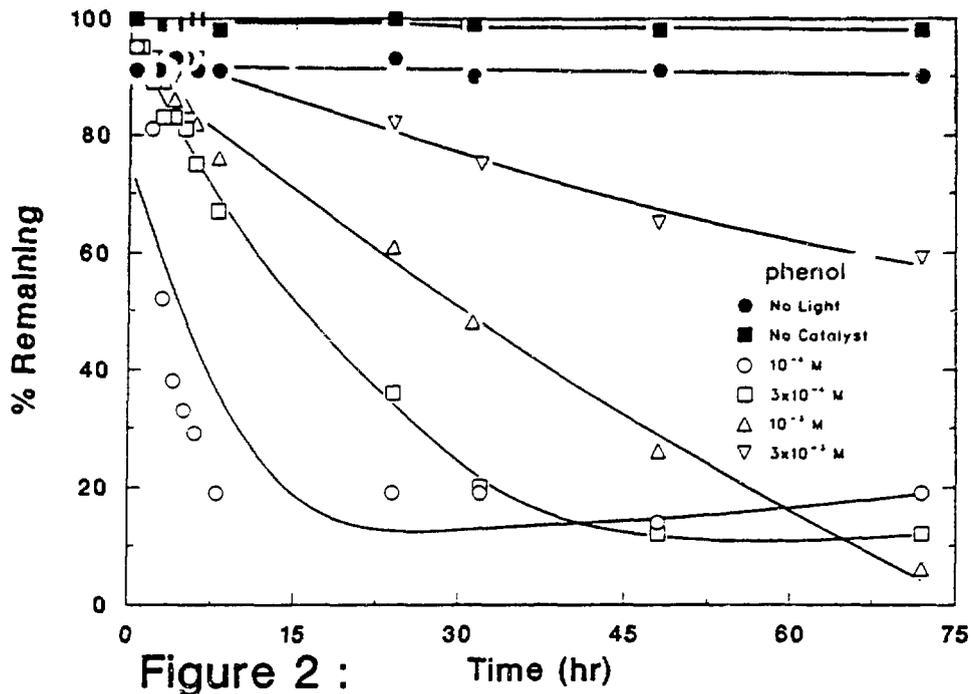


FIGURE 2. THE EFFECT OF PHENOL CONCENTRATION ON PHOTOOXIDATION

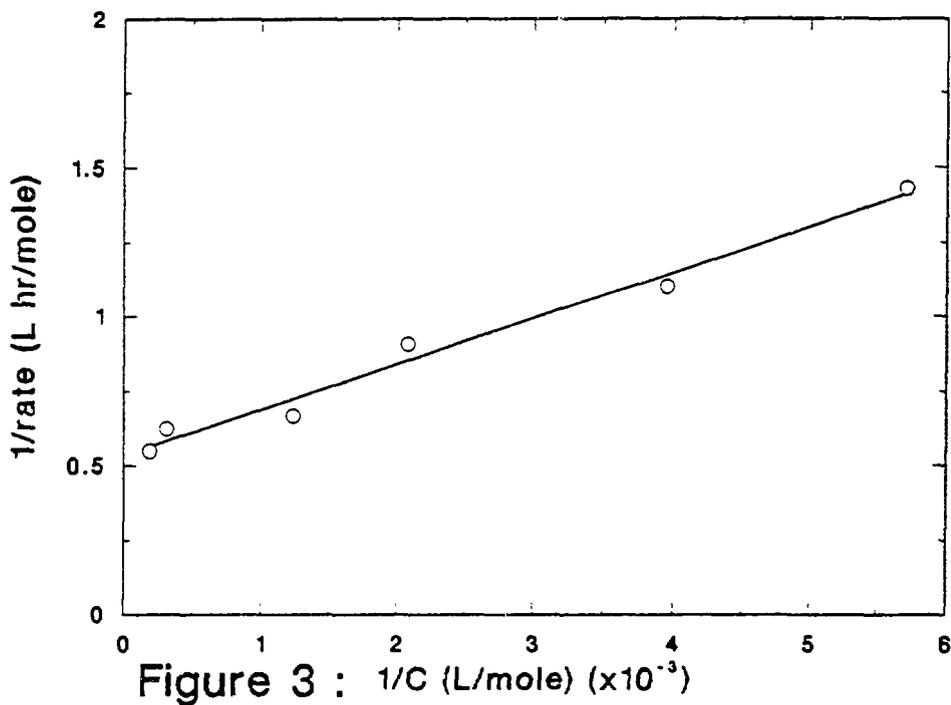


FIGURE 3. LINEARIZED KINETIC PLOT FOR CdS/PHENOL SYSTEM (EQ. 8)

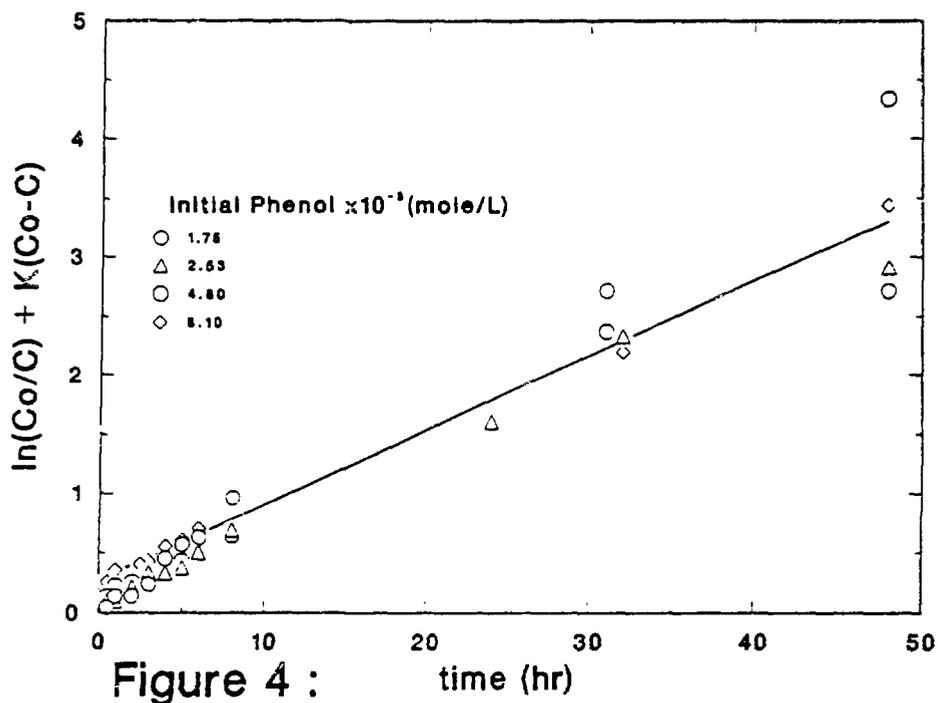


FIGURE 4. LINEARIZED KINETICS PLOT(EQ.10)

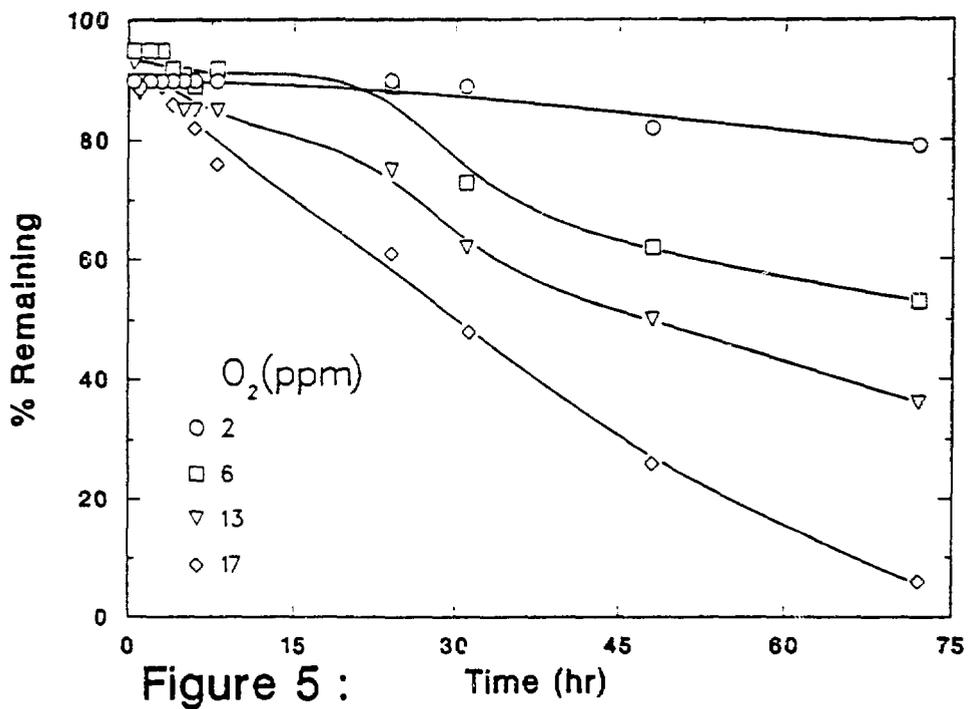


FIGURE 5. EFFECT OF OXYGEN CONCENTRATION; CdS/PHENOL SYSTEM

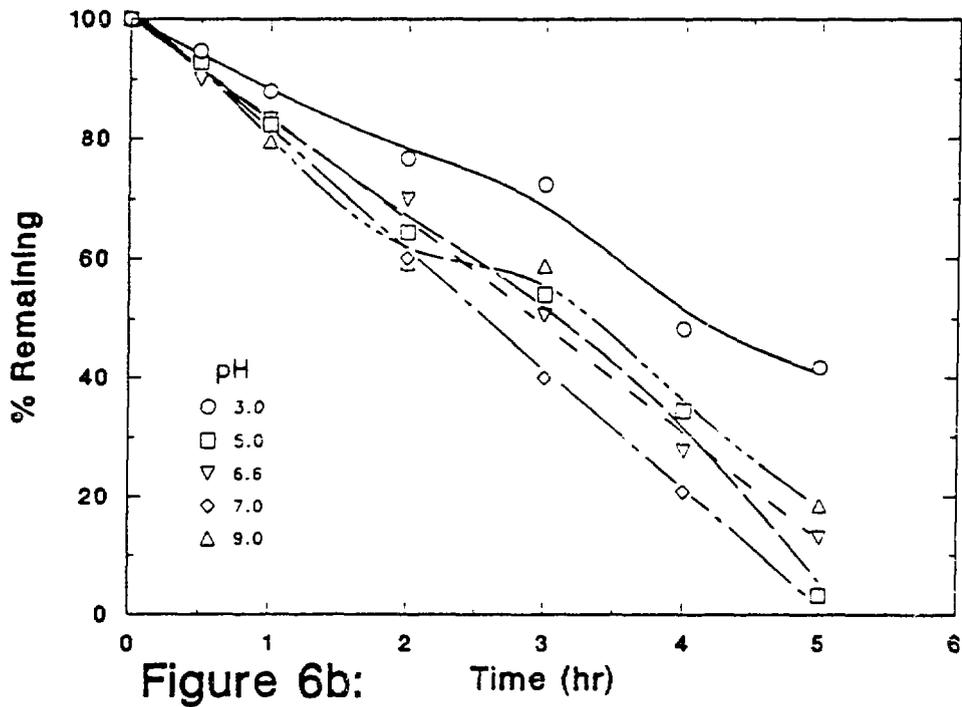
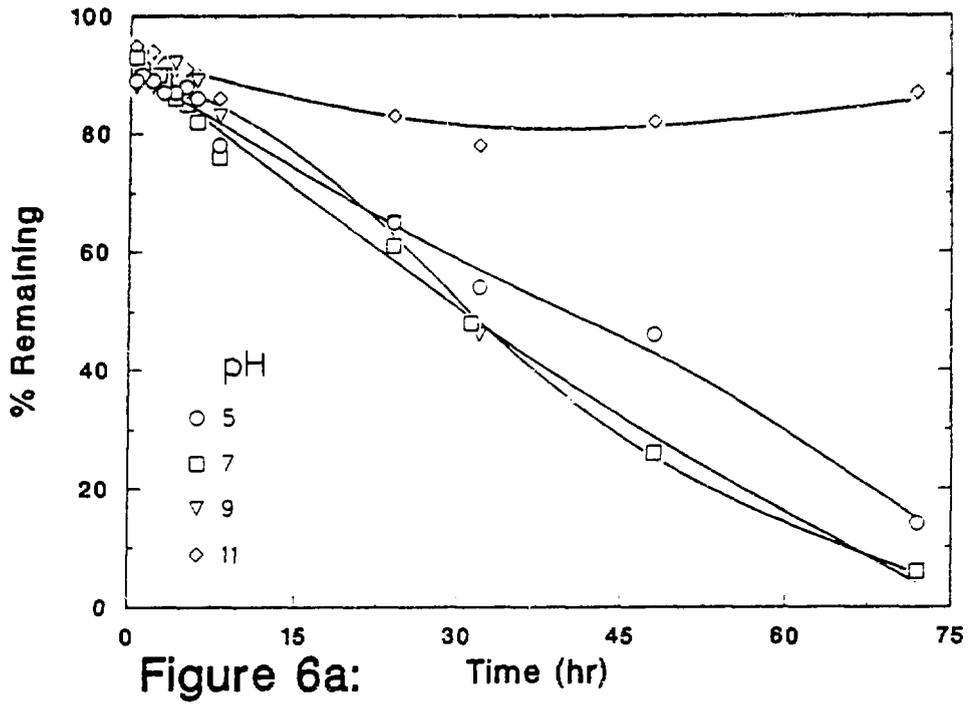


FIGURE 6. EFFECT OF PH. (A) CdS; (B) TiO₂

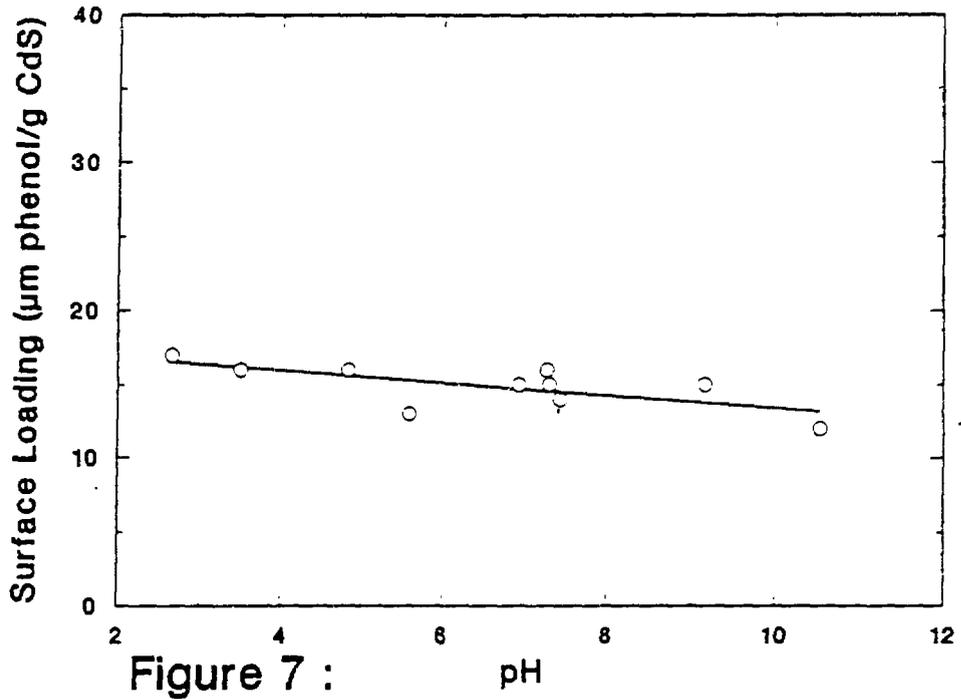


FIGURE 7. EFFECT OF PHENOL ADSORPTION ONTO CdS AS AFFECTED BY pH

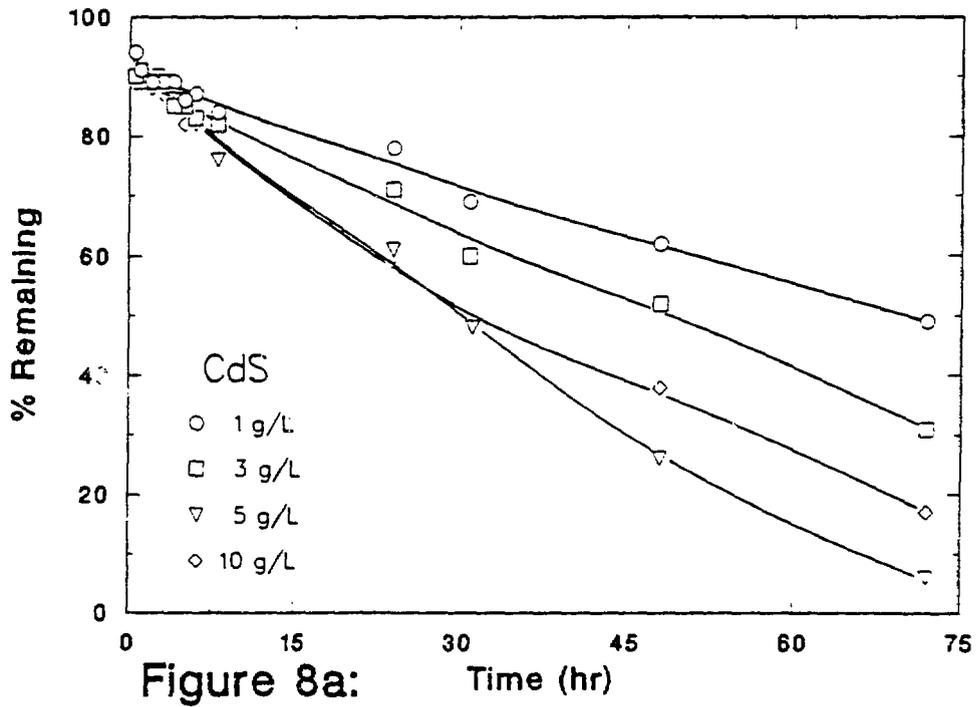


FIGURE 8. EFFECT OF PHOTOCATALYST CONCENTRATION. (A) CdS

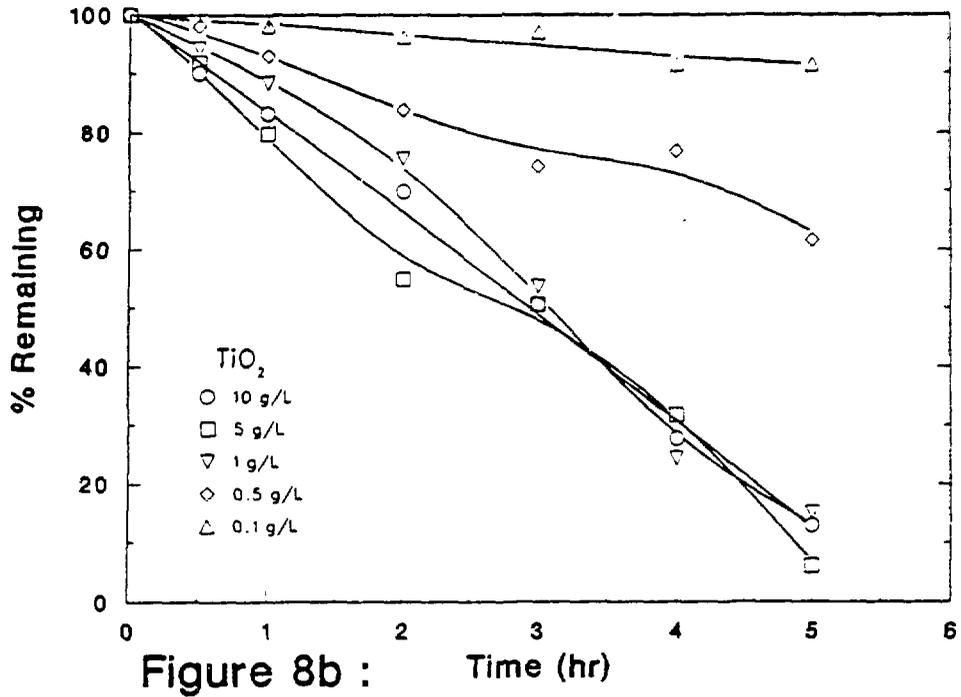


FIGURE 8. EFFECT OF PHOTOCATALYST CONCENTRATION. (B) TiO_2

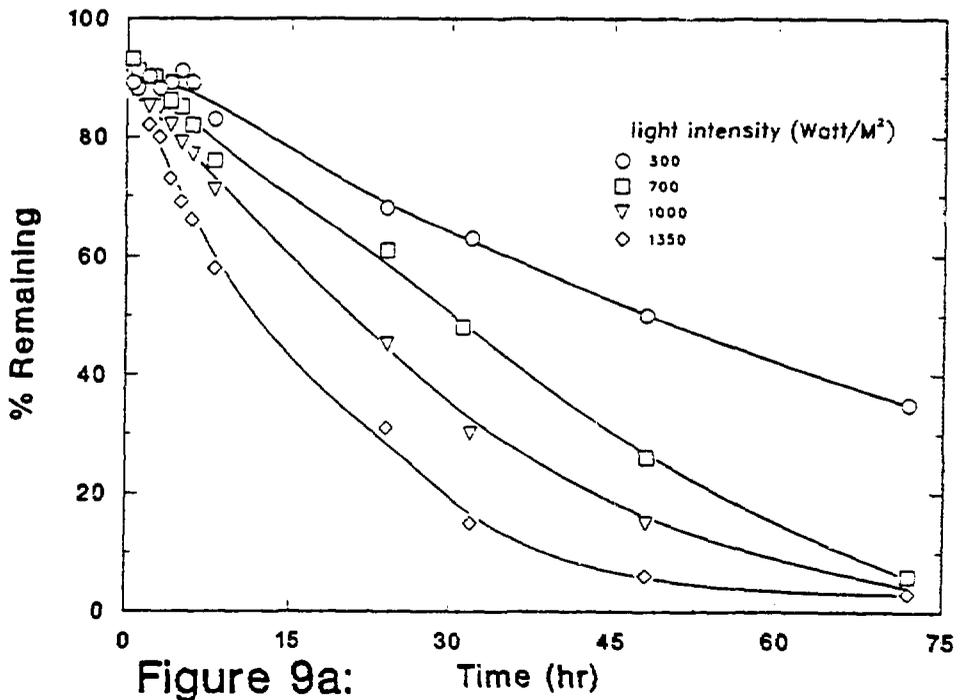


FIGURE 9. EFFECT OF LIGHT INTENSITY. (A) TIME CHANGE OF PHENOL CONCENTRATION

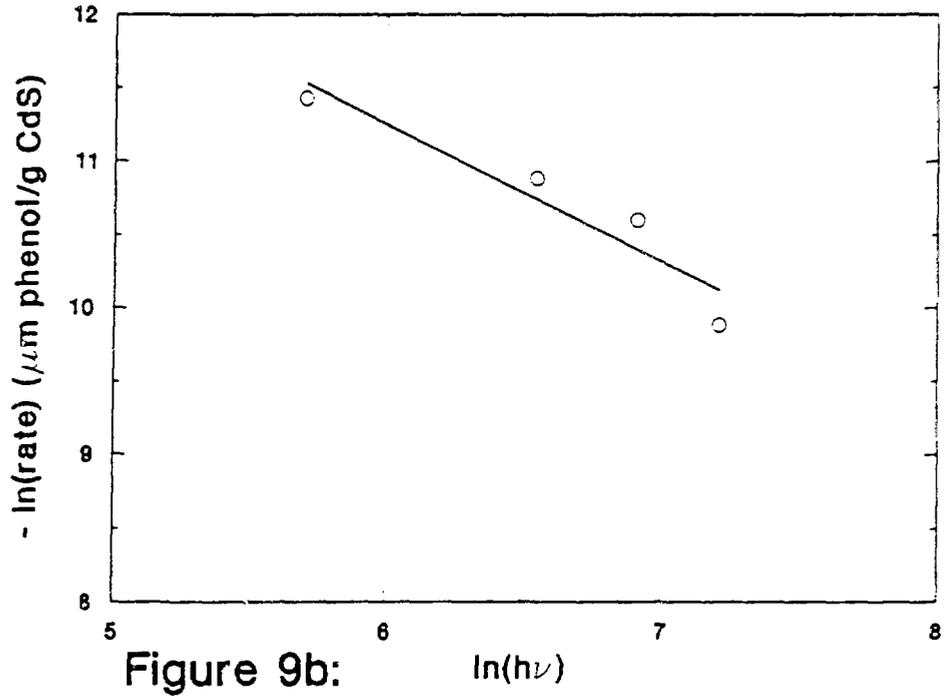


FIGURE 9. EFFECT OF LIGHT INTENSITY. (B) LINEARIZED PLOT

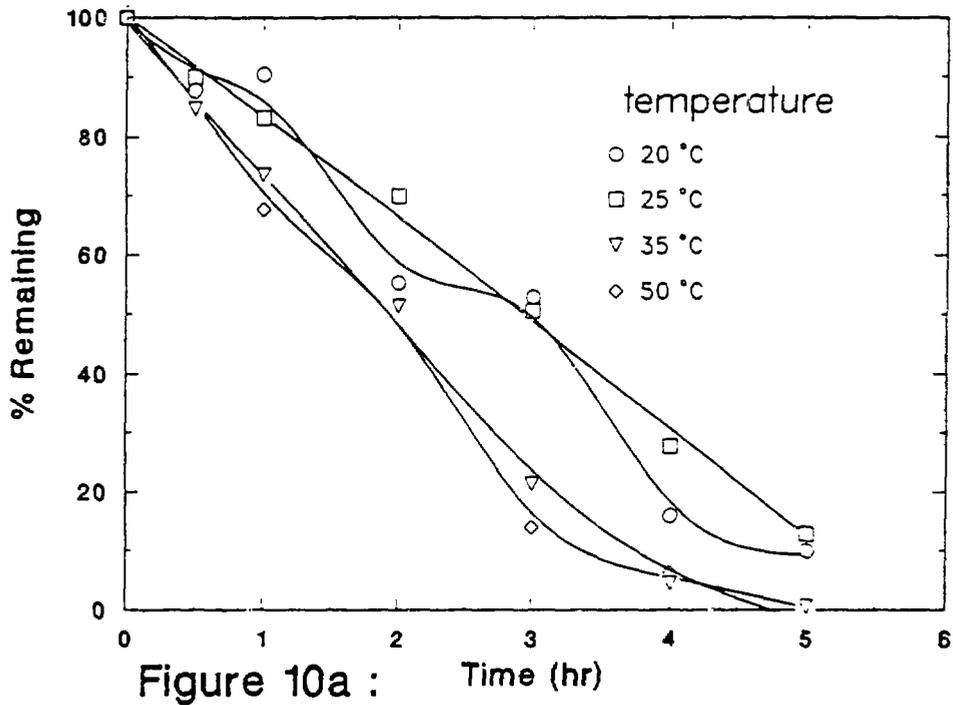


FIGURE 10. EFFECT OF TEMPERATURE. (A) TiO_2

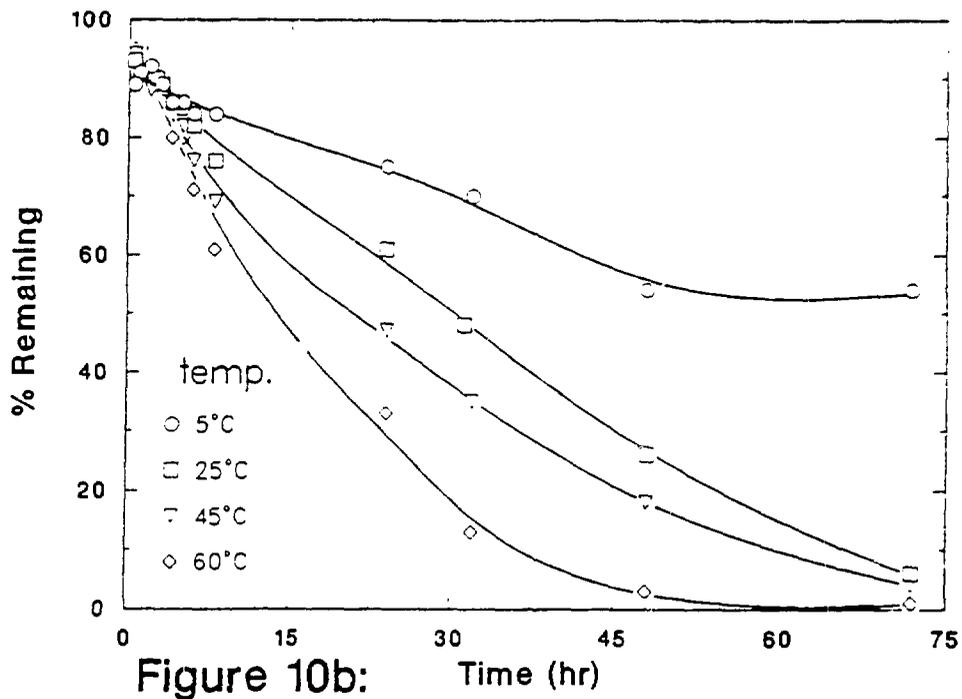


FIGURE 10. EFFECT OF TEMPERATURE. (B) CdS

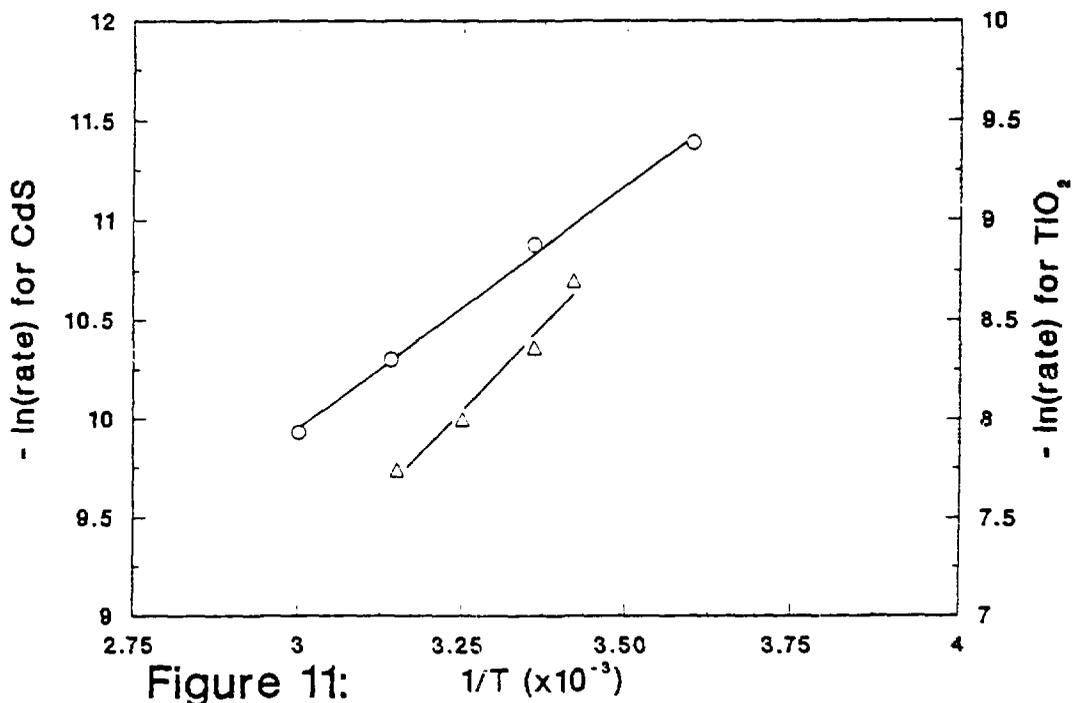


FIGURE 11. ARRHENIUS PLOT OF TEMPERATURE EFFECT

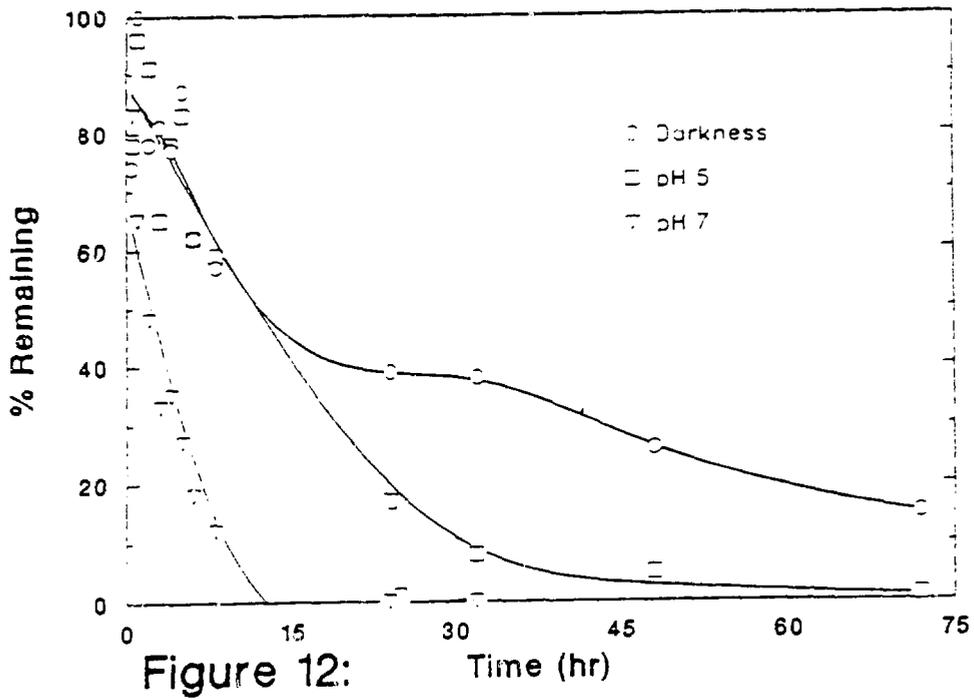


FIGURE 12. PHOTO-OXIDATION OF TCE BY CdS

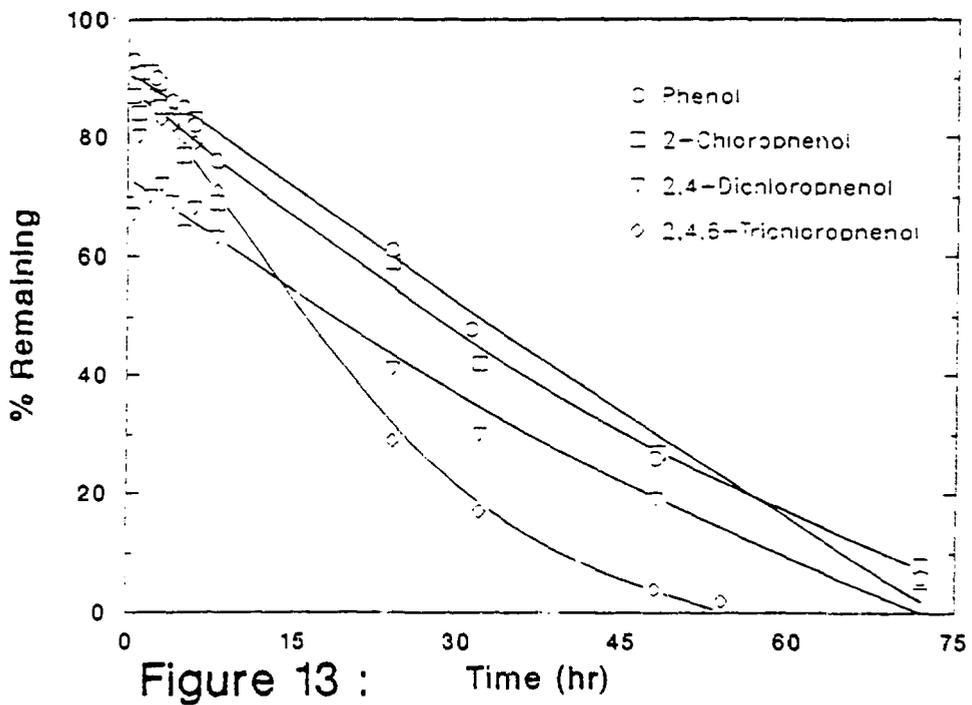


FIGURE 13. PHOTOXIDATION OF CHLORINATED PHENOLS BY CdS

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**The Waste Minimization Program at the
Feed Materials Production Center**

Presented by:

**M. E. Crotzer,
Westinghouse Materials Company of Ohio**

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THE WASTE MINIMIZATION PROGRAM AT
THE FEED MATERIALS PRODUCTION CENTER

J. E. Blasdel, M. E. Crotzer,
R. L. Gardner, T. R. Kato, C. N. Spradlin

Westinghouse Materials Company of Ohio

ABSTRACT

The Feed Materials Production Center (FMPC) is a Department of Energy (DOE) facility that produces high purity uranium (U) metal for the USA's defense program. During the course of its operation, the FMPC generates large quantities of waste contaminated with depleted U which must be disposed of as low level radioactive waste. The 1984 RCRA amendments and the draft revision of DOE Order 5820.2, Chapter III contain provisions obligating waste generators to have a waste minimization program. It is also generally recognized that waste minimization often reduces operating costs. The Westinghouse Materials Company of Ohio, in conjunction with the DOE, is therefore pursuing an aggressive waste minimization effort. Following a brief description of the FMPC production process and waste streams, this presentation will describe current programs which address contaminated wood and metals, process and non-process area trash, used metal drums, and major waste streams such as contaminated magnesium fluoride and nitrates. Waste minimization techniques described will include waste generation reduction, volume reduction, material substitution and waste recycle and recovery. The importance of training, incentives and awards will also be covered.

THE WASTE MINIMIZATION PROGRAM AT
THE FEED MATERIALS PRODUCTION CENTER

J. E. Blasdel, M. E. Crotzer,
R. L. Gardner, T. R. Kato, C. N. Spradlin

Westinghouse Materials Company of Ohio
Post Office Box 398704
Cincinnati, Ohio 45239

Operated for the U. S. Department of Energy by Westinghouse Materials Company of Ohio under contract No. DE-AC05-86OR021600.

For Presentation at the
Oak Ridge Model Conference
Oak Ridge, Tennessee
October 13-16, 1987

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J. E. Blasdel, M. E. Crotzer,
R. L. Gardner, T. R. Kato, C. N. Spradlin

Westinghouse Materials Company of Ohio
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ABSTRACT

A waste minimization program is being implemented at the Feed Materials Production Center to reduce the generation of uranium-contaminated wastes and to comply with existing and forthcoming regulations. Procedures and plans are described which deal with the following wastes: process and non-process trash, contaminated wood and metals, used metal drums, and major process wastes such as contaminated magnesium fluoride and neutralized raffinate. Waste minimization techniques used include segregation, source reduction, volume reduction, material substitution and waste/product recycle. The importance of training, communication, and incentives is also covered.

INTRODUCTION

The Feed Materials Production Center (FMPC) is a Department of Energy (DOE) facility that produces high purity metallic uranium (U) for the USA's defense program. It is operated for the DOE by The Westinghouse Materials Company of Ohio (WMCO). During the course of its operation, the FMPC generates large quantities of waste contaminated with depleted U (DU) which must be disposed of as low level radioactive waste (LLW). Currently, most of the waste generated directly from U processing is packaged and shipped to the Nevada Test Site (NTS) for disposal. Other contaminated wastes, such as used pallets, 55-gallon drums, and scrap metal, have been stored at the FMPC while packaging and disposal plans are being developed.

There are several reasons why waste minimization has become a priority objective at the FMPC. First, burial costs at the NTS are increasing, making waste disposal an expensive activity. Second, the backlogged waste inventory at the FMPC is taking up valuable storage space. This is apparent from Figure 2, which will be discussed later. Third, waste minimization is becoming incorporated in government regulations and corporate policy. For example, the 1984 RCRA amendments (Ref. 1) and the draft revision of DOE Order 5820.2, Chapter III, (Ref. 2) contain provisions obligating waste generators to have a waste minimization program. In response to these provisions, the Westinghouse Electric Corp. now requires all of its production facilities, both

commercial and government-owned, to implement written waste minimization programs. Another provision of DOE Order 5820.2, calls for minimizing the quantity of waste shipped offsite for disposal. This means that the FMPC cannot rely solely on increasing waste shipments to the NTS as a solution to its waste generation problems. Finally, notwithstanding the regulatory pressure, most waste generators, including WMCO, realize that waste minimization is in their own best interest since such programs often streamline operations and reduce operating costs.

For the above reasons, WMCO, in conjunction with the DOE, is pursuing an aggressive waste minimization effort. The purpose of this paper is to describe some of the programs developed to deal with FMPC's major wastes. The techniques employed include volume reduction, waste/product recycle, and material substitution. However, the ultimate goal in all cases is to eliminate the generation of the waste in the first place. As pointed out in a recent study on hazardous waste reduction, minimizing waste generation is the only effective means of avoiding future remediation and the associated costs of regulatory compliance (ref. 3).

The following two sections describe the FMPC's U production process and the wastes that are generated as a result. Specific waste reduction activities will then be presented.

The Uranium Production Process

As mentioned previously, the FMPC produces purified U metal for use at other DOE sites. A flow chart of the production process is shown in Figure 1.

Uranium production begins with recycled U-bearing residues, oxides, scrap metal, and other U compounds. This impure starting material is dissolved in nitric acid and the U is extracted into an organic liquid and then back-extracted into deionized water to yield a solution of uranyl nitrate. Evaporation and heating convert the nitrate solution to uranium trioxide (UO_3) powder. This compound is reduced to uranium dioxide (UO_2) with hydrogen and then converted to uranium tetrafluoride (UF_4) by reaction with anhydrous hydrogen fluoride. UF_4 can also be produced by reacting uranium hexafluoride (UF_6), received from other DOE sites, with hydrogen. Uranium metal is produced by reacting UF_4 and magnesium metal (Mg) in a refractory-lined reduction vessel. This primary U metal, called a derby, is then remelted to yield a purified U ingot which is extruded to form rods or tubes. Sections are then cut and machined to final dimensions. These machined cores are shipped to other DOE sites for canning and final assembly into reactor fuel or target elements.

Figure 2 is a recent aerial view of the FMPC. The upper two-thirds of the photograph show the production area. The buildings in which the U processing is performed are shown in the upper right quadrant of Figure 2. Other areas of the plant contain storage pads, warehouses, shops, utilities and other facilities that support production.

Prominent are the areas where backlogged waste is stored.

Waste Generation

All of the production steps described above produce LLW, as shown in Figure 1. Some of the waste, such as magnesium fluoride (MgF_2) or neutralized raffinate, is generated directly by the process. The largest process waste, MgF_2 , is produced during the reduction of UF_4 with magnesium. It is contaminated with DU and DUO_2 , and also contains some Mg and MgO . The second largest process waste is generated when MgF_2 containing enriched U is recycled to the refinery. The neutralized, filtered residual material left after most of the enriched U is extracted (leached) from the MgF_2 is called slag leach filter cake. Neutralized, filtered raffinate, the third largest waste stream, is generated following extraction of U from other refinery feed materials. The raffinate stream is also the largest source of nitrates which contribute to water pollution at the FMPC. Other process wastes contaminated with DU include dust collector residues, sump sludges, and process spills.

Many items become LLW as a result of coming into contact with DU. These include used metal drums, used wooden pallets, and trash, such as contaminated rags, paper, wood etc. Other wastes, such as construction rubble and scrap metal are generated from the large number of ongoing renovation projects at the FMPC.

As mentioned previously, process wastes, which are relatively easy to package, are being shipped to the NTS for disposal. There remains, however a large backlog of drummed residue that needs further processing before it can be sent to the NTS. Other wastes have been stored on-site while plans for their disposition are being formulated. The types of stored waste are identified in Figure 2. A close-up of the backlogged process waste, used wooden pallets, and baled trash is shown in Figure 3. Together, Figures 2 and 3 indicate the quantity of waste that must be dealt with. The strategy is to complete and implement plans for the disposal of the backlogged waste while reducing or eliminating the waste streams feeding this inventory.

MINIMIZING TRASH GENERATION

Trash generally consists of small pieces of paper, wood, rags, plastic, cafeteria waste etc. which is generated every day, regardless of the production level. In the past, trash was either incinerated or placed in an on-site storage area. In 1986, the storage area was closed and the incinerator was shut down. Trash was then accumulated in warehouses and on controlled run-off pads. A large fraction of this trash was contained in 55-gallon drums. A new compactor/baler was purchased. All FMPC trash was processed through this equipment and stored on-site in trailers while approval for its transport to and disposal at the NTS was being expedited.

This sudden increase of contaminated trash prompted a number of waste

minimization initiatives. A mobile high-force compactor (HFC) was leased to process the trash stored in 55-gallon drums. Over a 6-month period, the HFC crushed drums from 1/3 to 1/6 of the original volume, depending on the drum contents. The crushed drums were packaged in metal overpacks. Operation of the HFC and crushed drum packaging are shown in Figure 4.

Meanwhile, a new procedure was implemented to segregate clean trash from office areas. Trash in these areas is placed in clear plastic liners. Porters carry the filled liners to blue-colored dumpsters marked "Clean Waste Only". The dumpsters remain locked when not in use. When the dumpsters are full, technicians radiologically monitor the bags to verify that the trash is clean. The bags are then disposed of at a local sanitary landfill. Figure 5 shows bags of office trash being monitored before disposal. This segregation procedure is reducing the volume of trash considered contaminated by at least 25% and is saving up to \$3000 per week.

Approval was finally obtained to ship and dispose of the baled process area trash and the crushed, over-packed drums. As a result, the inventory of baled process trash shown in Figures 2 and 3 is rapidly being reduced. The block-shaped bales are packaged in strong nylon containers as shown in Figure 6. Another inventory of trash-- drummed glass, paint cans, and metal tubes-- will also be eliminated soon. This waste is being shipped to a contractor for processing and disposal.

The effort is now being focused on segregating contaminated process area trash. Approximately 30 dumpsters are distributed throughout the process area marked "Contaminated Trash Only". A training course will be conducted to instruct plant employees regarding what should and should not be placed in these dumpsters. Opportunities for eliminating waste in the first place are being pursued. For example, aerosol cans, which pose a disposal problem, are no longer used at the FMPC. Also, incoming parcels will be separated from their packaging material outside of the process area, thus eliminating one potential source of contaminated trash.

MINIMIZING USED METAL DRUMS

There has been a long history of using metal drums to carry U compounds and other materials between buildings at the FMPC. Drums are also used to store materials on-site and to contain the waste being shipped to the NTS. Drums used for on-site transport are subject to deformation after extensive use, while drums used for storage may suffer deterioration due to environmental factors or to the contents of the drum.

The useful life of a drum can be extended by reconditioning it. This consists of rounding the drum out, refurbishing corroded areas, and painting it. Drum reconditioning has been successfully used at the FMPC for several years. Once a drum can no longer be used, it is compacted in a baler and stored on-site for eventual disposal. Eventually, however, the baled drums became a significant waste inventory to deal

with, as shown in Figure 7. This example clearly illustrates the limitations of waste recycle and volume reduction as waste minimization techniques.

Arrangements are being made to have a contractor remove and dispose of the baled drums. Attention is now focused on preventing future occurrences of this situation. Although technologies such as pneumatic conveyance could be applied to some areas of the FMPC, there will probably always be a need for drums or similar containers. Several substitutes for metal drums are being evaluated. One example is shown in Figure 8. This square plastic container is not only more durable than a metal drum, but also makes better use of space. It is also easy to decontaminate.

ELIMINATING WOODEN PALLETS

Wooden pallets have been used for several years at the FMPC to carry drums from one plant area to another. Their availability makes them convenient to use. However, they are easily damaged and are difficult to decontaminate. The result is an accumulation of contaminated wood as shown in Figure 3.

Several substitutes for wooden pallets are currently being evaluated. Metal pallets are being used to a limited extent at the FMPC to evaluate their effectiveness relative to wooden pallets. Figure 9 shows two metal pallet designs alongside a wooden pallet. Although metal pallets are durable and relatively easy to decontaminate, they are heavy. Some plastic pallets have recently been fabricated and will be tested along with the metal pallets. Technologies such as overhead monorails could be used to carry material from one plant to another. However this would require a major capital project and a major change in operating procedures. Like the situation with metal drums, pallets are unlikely to be totally eliminated at the FMPC. It does appear, however, that wooden pallets will eventually be eliminated.

Arrangements have been made to have a contractor remove and dispose of the backlogged wooden pallets. The scrap pallet inventory shown in Figures 2 and 3 will soon be eliminated.

DEALING WITH SCRAP METAL

As a result of maintenance and renovation activities over the years, a large quantity of contaminated scrap metal had accumulated at the FMPC. This metal, along with assorted refuse, was stored on a controlled run-off pad, which was becoming filled to capacity as scrap from ongoing renovation projects was added to the inventory. The scrap piles were also becoming a potential source of airborne and groundwater contamination and a potential source of radiation exposure to FMPC employees working around a nearby decontamination building.

During 1986 and early 1987 approximately 4600 tons of scrap on the run-off pad were separated into potentially salvageable metal and refuse.

This project was undertaken to create space for additional scrap metal, to improve environmental conditions around the scrap metal storage area, and to prepare the metal for DOE's scrap reclamation program (discussed below). The potentially salvageable metal was separated into ferrous and nonferrous categories. Each category of scrap (ferrous, nonferrous, and refuse) was in turn separated into either a high or low contamination level category. The scrap with a high contamination level was either covered in plastic or containerized and moved away from the run-off pad. Figure 10 shows the scrap metal storage area following the scrap separation project. The boxes and drums in the foreground contain refuse, which includes nonmetals, mixed metals, highly-deteriorated metals and large quantities of asbestos.

The potentially salvageable metal will eventually feed DOE's contaminated scrap reclamation program. This Oak Ridge Operations (ORO) program will involve private subcontractors in the decontamination of potentially salvageable metal at all ORO sites. The scrap will then be returned to the private sector as clean scrap. The scrap reclamation program is therefore a large-scale recycle operation which will eliminate a large waste inventory at the FMPC.

In addition to the ferrous scrap, there are approximately 1250 tons of slightly contaminated copper scrap, mainly motor windings, stored at another location (See Figure 2). Segregation is not required for this scrap. It is ready for DOE's scrap reclamation program in its present condition.

Better control of scrap is now being exercised at the point of generation. Potentially salvageable metal is separated from refuse and is radiologically monitored to determine if it is contaminated. Contaminated metal is sent to the scrap storage area where it is placed in the appropriate category. Clean metal is sent to local scrap dealers or possibly used in other on-site projects.

MINIMIZING PROCESS WASTES

Eliminating process wastes is difficult because it usually involves changing the process itself which in turn involves capital expenditures, new procedures, training etc. There are, however, some technologies that might enable the FMPC to reduce the quantity of process waste it generates.

Slag Leach Filter Cake

For every unit of MgF_2 containing enriched U that is processed in the refinery, several units of slag leach filter cake are produced. This occurs because of the neutralization agent and filter aid added in the subsequent processing of the waste stream. Any process that can concentrate the enriched U in the MgF_2 will thus provide a significant reduction in the waste generated. Results of recent bench-scale experiments at the Oak Ridge National Laboratory (ORNL) have indicated that magnetic field gradients (MFG) can concentrate U in MgF_2 (Ref. 4).

The physical principle involves the different magnetic susceptibilities of materials. Many heavy metals, including U, have positive susceptibilities and are attracted to the strongest part of the MFG. Many elements and compounds of low molecular weight, including MgF_2 , are repelled to the weaker part of the MFG.

The principle of operation is illustrated in Figure 11. The mixture of materials passes down a tray that is inclined longitudinally and transversely. The MFG is applied across the width of the tray (transversely). Separation occurs when the force of the MFG overcomes the longitudinal force of gravity. A pilot plant demonstration at the FMPC is being considered.

Neutralized Raffinate

Following the extraction process, the acidic waste stream (raffinate) is neutralized with lime to precipitate the impurities and any U not extracted. The resulting slurry is then filtered through rotary filters coated with a filter aid. Excess lime and the filter aid increase the waste volume from 25% to 50% over what would otherwise be collected.

An alternate treatment is now being evaluated. If successful, it would simultaneously neutralize the waste and cause it to coalesce into larger particles which are more easily filtered. This treatment would eliminate or greatly decrease the use of lime and filter aid.

Magnesium Fluoride and nitrates

The reduction of UF_4 with Mg is currently the most effective way to make U metal. Likewise, the use of nitric acid is fundamental to the refining process. Therefore, nitrates and contaminated MgF_2 are waste streams that must be dealt with in the foreseeable future. Technologies are being appraised for their potential to minimize these wastes.

For example, these wastes could possibly be reduced, eliminated, or even converted to a recyclable material by processing them through a high-temperature device such as a plasma torch. A proof-of-principle test in which pure MgF_2 was hydrolyzed to produce magnesium oxide and hydrogen fluoride was recently conducted at the Westinghouse Plasma Center. The results are encouraging and confirm the analytical model used to predict reaction products in plasmas. The application of plasma technology to the nitrates in the raffinate stream is now under investigation.

Other U Residues

As noted above, the enriched U recovery process produces a larger volume of waste than the original feed volume due to waste treatment additives. By comparing the costs of recovering U from residues to the costs of producing U from UF_6 , a combination of U-235 enrichments and total U concentrations can be established below which recovery is not economic. A preliminary evaluation of slag residues indicates that this combination of U parameters, called the economic discard limits, can be

increased. Therefore, a certain fraction of the U residue inventory that is now classified as recoverable could be reclassified as nonrecoverable. These residues could then be shipped to the NTS for disposal. A more detailed economic evaluation of recoverable residues is planned.

The backlogged residues shown in Figures 2 and 3 are being processed on-site and will eventually be shipped to the NTS for disposal.

TRAINING, COMMUNICATION, AND INCENTIVES

Training, communication, and incentives are essential components of a successful waste minimization program. Accordingly, several initiatives are being implemented or planned at the FMPC to encourage waste minimization. A training program on waste reduction awareness is being developed and will soon be given to all WMCO employees. A newsletter, the "Waste Minimizer", has been established to communicate waste-related procedures, reminders, progress, etc. to FMPC employees.

A program will soon be started to solicit waste minimization suggestions from FMPC employees. The employee with the best suggestion each month, as judged by a preselected panel, will receive a gift certificate. This FMPC program builds on a DOE-ORO initiative to recognize outstanding achievement and raise contractor employee awareness in the area of waste minimization. The DOE recognition program has prompted a number of suggestions at the FMPC. One example that is easy to implement is the substitution of water reducible paint for xylene-based paint in the FMPC drum reconditioning facility. A more complex idea is the machining improvements for graphite molds to reduce the generation of scrap graphite.

A cost incentive program is planned for the FMPC that will make each process center financially responsible for the waste it generates. The procedures for this program will make use of the experience gained in a similar program established at the ORNL (Ref. 5).

CONCLUSION

The above description of FMPC's waste minimization program illustrates a number of points. First, a large effort has been put into FMPC's program. Although much remains to be done, considerable progress has been made. Second, the majority of the examples do not involve "high technology". Procedural changes and the use of alternate materials can have just as large an impact on waste management activities as hardware changes or new technologies. Finally, waste minimization is a process towards which all employees can contribute. Many ideas and solutions have come from those closest to the problem.

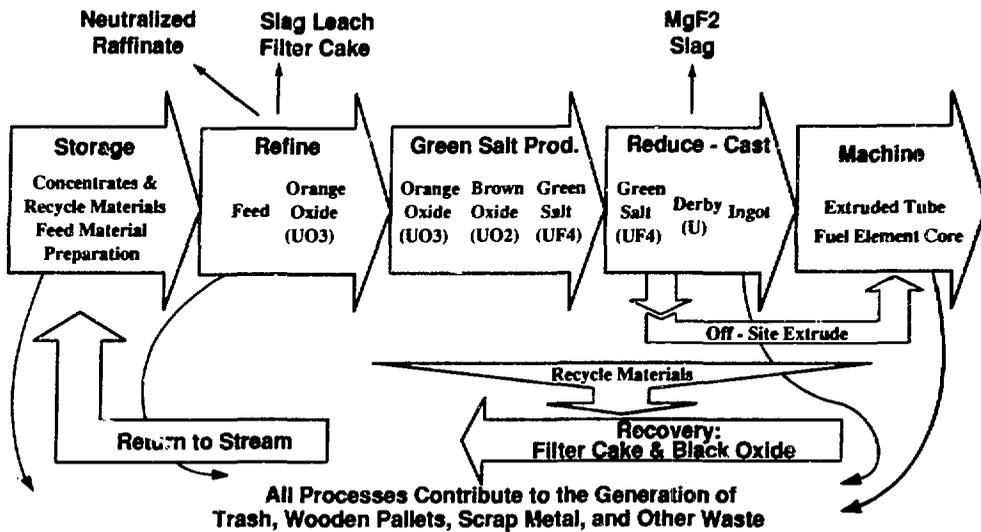


Figure 1 The FMPC Uranium Production Process Including Significant Wastes.



Figure 2 An Aerial View of the FMPC Production Area. Production Buildings Are Shown in the Upper Right. The FMPC Waste Inventory Includes: 1-Baled Trash in trailers. 2-Wooden Pallets. 3-Backlog Drummed

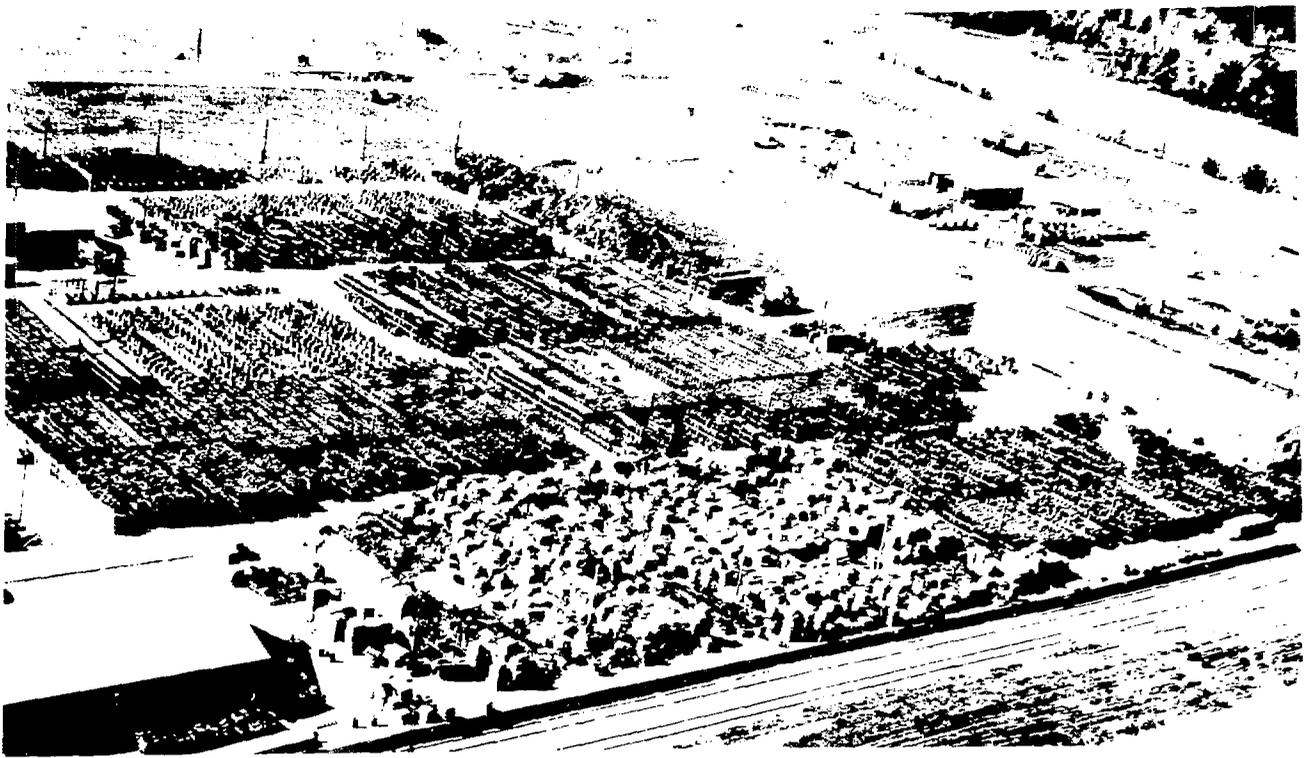


Figure 3 A Close-up view of the Trailers Containing Baled Trash (Upper Right), Wooden Pallets (Foreground), and Backlog Drummed Residues.

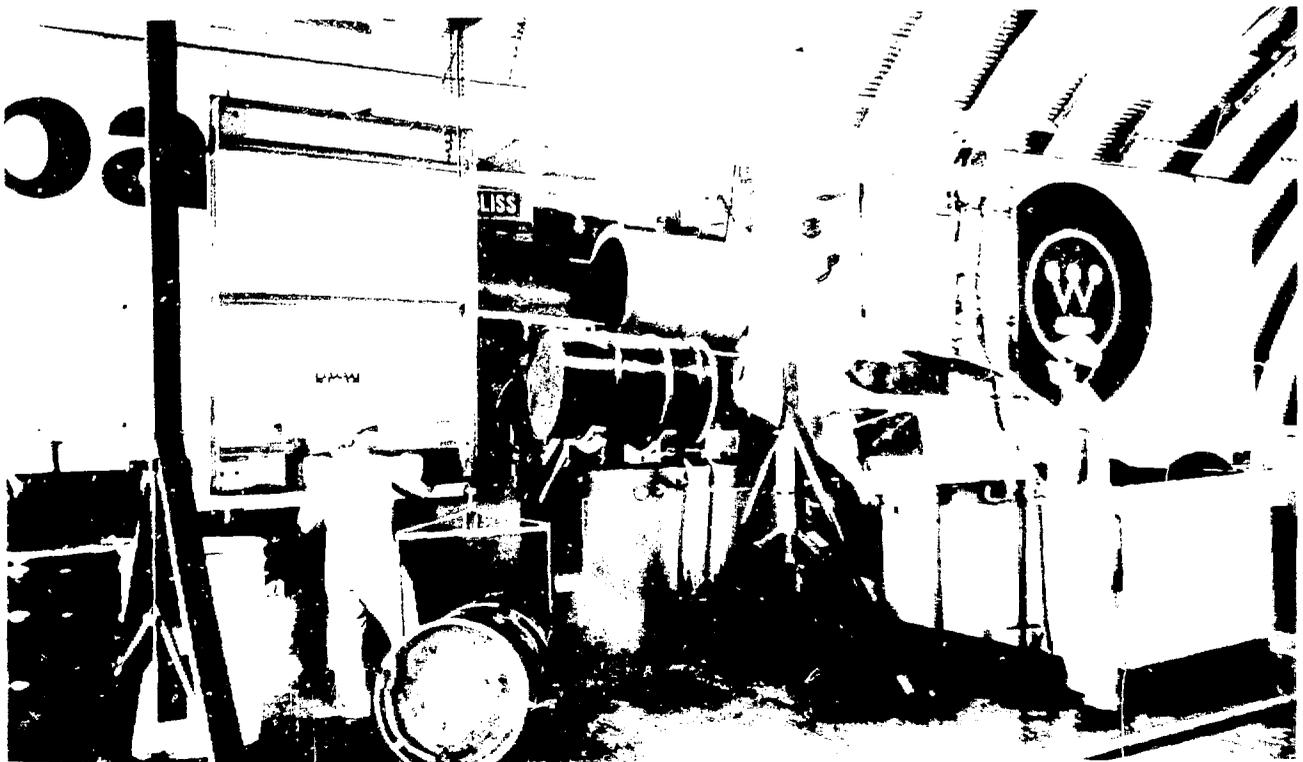


Figure 4 The Mobile High Force Compactor in Operation. The Crushed Drums Are Loaded into the Box at the Right.



Figure 5 Technicians Radiologically Monitoring Bags of Trash to Ensure there is No Radioactive Material.





Figure 7 Compacted, Baled 55-Gallon Drums.



Figure 8 55-Gallon Drums on a Wooden Pallet Next to a Larger, More Durable Plastic Alternative.

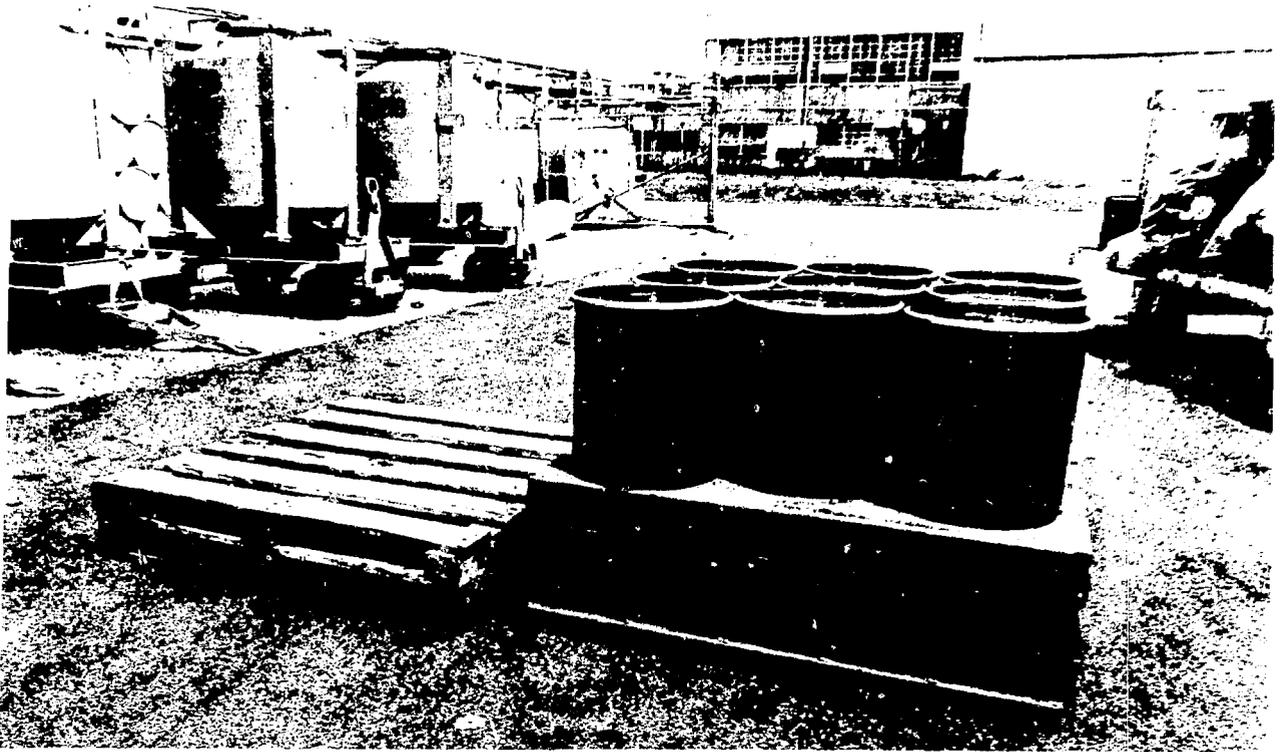


Figure 9 A Wooden Pallet Next to More Durable, More Easily Cleaned Metal Pallets. Two Metal Pallet Designs Are Shown.

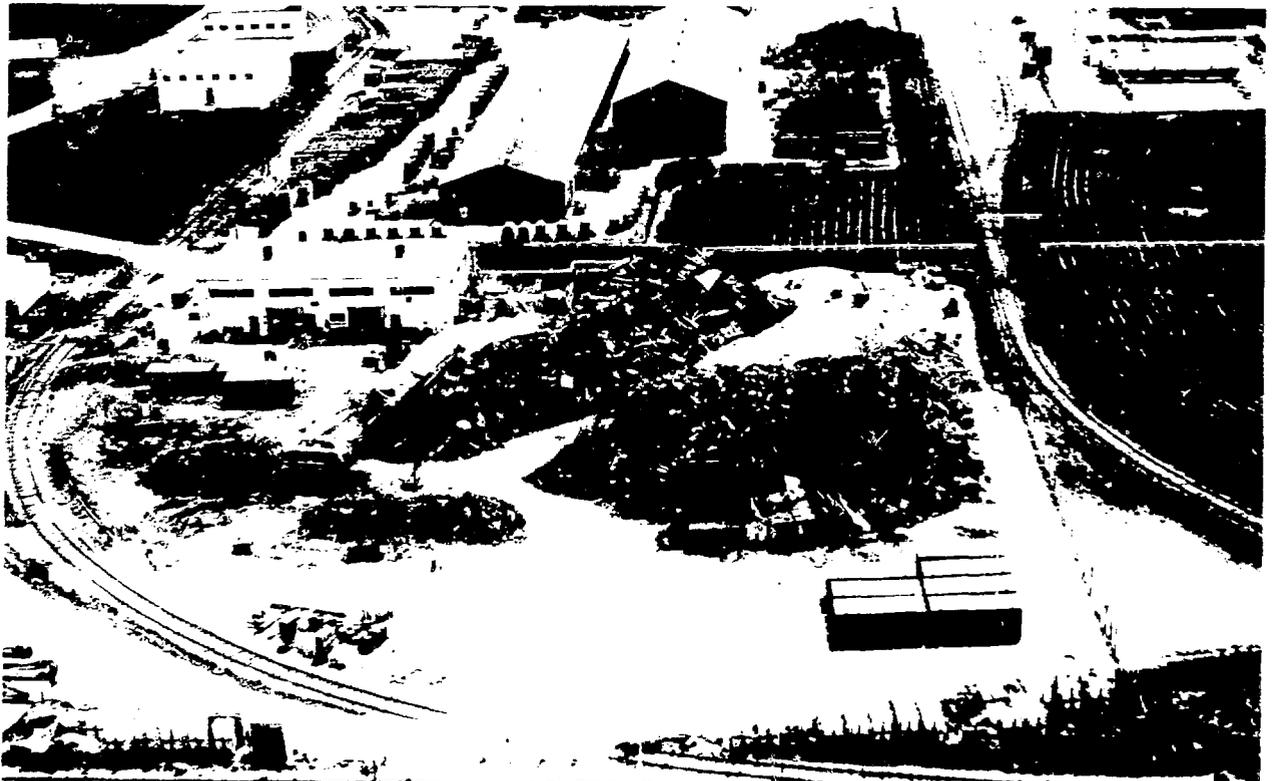


Figure 10 An Aerial View of the Scrap Metal Storage Area Following The Scrap Separation Project. The Six Piles of Separated Scrap are Shown on the Right. Highly Contaminated Metal is Covered with Plastic. The Boxes and Drums in the Foreground Contain Refuse.

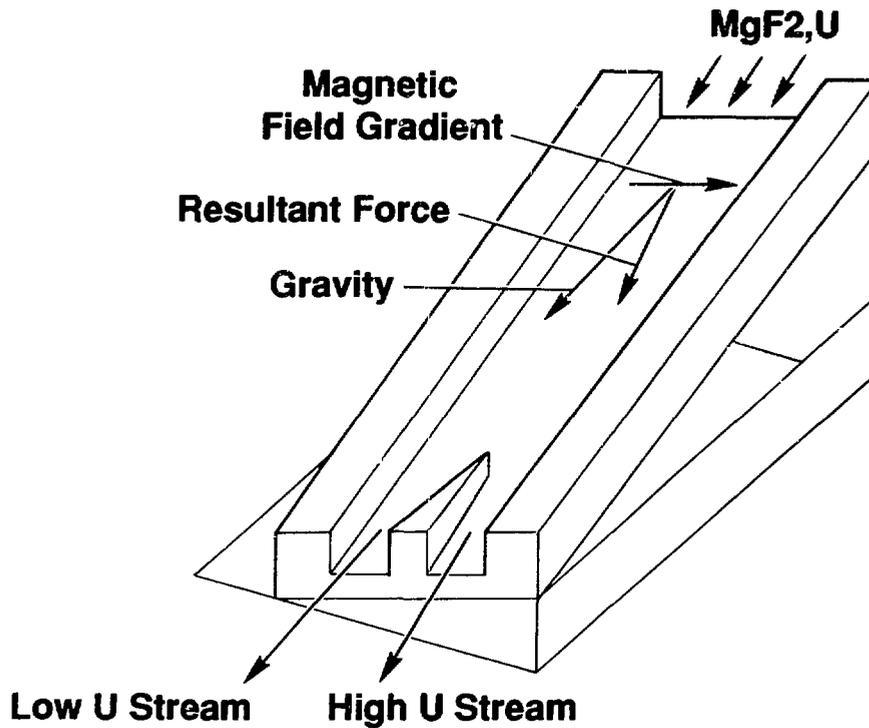


Figure 11 A Schematic Showing How a Magnetic Field Gradient Can Concentrate Uranium in Contaminated Magnesium Fluoride.

REFERENCES

1. The Resource Conservation and Recovery Act (RCRA), as amended in 1984, Section 3002(b).
2. J. A. Logan, et al, "Revision of DOE Order 5820.2 Chapter III-Management of Low-Level Waste", presented at the Ninth Annual DOE Low-Level Radioactive Waste Management Conference, August 25-27, 1987.
3. "Serious Reduction of Hazardous Waste", OTA-IT-317, GPO stock no. 052-003-01048-8, Office of Technology Assessment, Washington, D.C., 1986.
4. J. M. Hoegler, "Bench-Scale Magnetic Separation of DOE Wastes", DOE/HWP-34, Martin Marietta Energy Systems, Inc., July, 1987.
5. J. B. Berry and F. J. Homan, "Charging Generators for Waste Management Costs", presented at the Ninth Annual DOE Low-Level Radioactive Waste Management Conference, August 25-27, 1987.

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ORO Scrap Metal Decontamination Program

Presented by:

M. Jugan, DOE/ORO

ORO SCRAP METAL DECONTAMINATION PROGRAM

The Oak Ridge Operations Office (ORO) of the U.S. Department of Energy (DOE) has approximately 80,000 tons of contaminated scrap metal at the Oak Ridge Gaseous Diffusion Plant in Oak Ridge, Tennessee; Paducah Gaseous Diffusion Plant in Paducah, Kentucky; Portsmouth Gaseous Diffusion Plant in Piketon, Ohio; and the Feed Materials Production Center in Fernald, Ohio. After unsuccessful in-house attempts to eliminate/recycle the contaminated metal, DOE is allowing private enterprise the opportunity to participate in this program. DOE is making this opportunity available under a two-phase approach, which is being supported by two separate and corresponding Request for Proposals. Phase I, which is nearing completion, is a demonstration phase to establish a group of companies that the DOE will consider qualified to eliminate the scrap at one or more sites. In Phase I, the companies decontaminated 25-50 tons of scrap to demonstrate capabilities to DOE and to gain the knowledge required to plan/bid on elimination of the scrap at one or more sites. Phase I contracts were of the cost-plus-fixed-fee type. Phase I awards were made to the best qualified firms based on the evaluation criteria in the Request for Proposals (RFP). These firms were Babcock & Wilcox, Bechtel, and the Scientific Ecology Group, Inc. As noted in the Commerce Business Daily announcement and the RFP associated with Phase I, only the firms awarded contracts and successfully completing Phase I will be eligible to participate in Phase II.

Phase II, for which the Request for Proposals is currently being written, will request proposals for elimination of the total scrap at one or more of the above noted sites. Multiple awards for Phase II are also anticipated. Companies participating in Phase II will be required to take title to the contaminated scrap and decontaminate/process the scrap for beneficial reuse. Radioactive wastes and metal that cannot be successfully decontaminated/processed will be returned to DOE. It is anticipated that Phase II awards will be made based on low bid and contracts will be of the fixed-price type. It is also expected that costs to the Government will be off-set by the value that the firms receive from the decontaminated/processed metal.



ESTIMATED SCRAP METAL INVENTORY

DOE FACILITIES - OAK RIDGE OPERATIONS

(TONS)

| TYPE SCRAP | ORGDP ¹ | PADUCAH ² | PORTSMOUTH ² | FERNALD ² | Y-12 ² | TOTAL |
|--|--------------------|----------------------|-------------------------|----------------------|-------------------|-------|
| Steel | 15000 | 10500 | 13000 | 3000 | 2000 | 43500 |
| Aluminum | 1350 | 2150 | 420 | - | - | 3920 |
| Stainless Steel | 130 | - | - | - | - | 130 |
| Copper | 25 | - | 90 | 1250 | - | 1365 |
| Brass | 10 | - | 2 | - | - | 12 |
| Monel | 30 | - | - | - | - | 30 |
| Mixed Metal | 900 | 1000 | - | 2000 | 3000 | 6900 |
| ----- | | | | | | |
| Subtotal | 17445 | 13650 | 13512 | 6250 | 5000 | 55857 |
| ***** | | | | | | |
| Steel Tube Sheets ¹ | 2827 | 3000 | 7600 | - | - | 13427 |
| UF ₆ Cylinders ¹ | 225 | - | 247 | - | - | 472 |
| Nickel Ingots ¹ | - | 8515 | - | - | - | 8515 |
| Monel Ingots ¹ | - | 15 | - | - | - | 15 |
| Aluminum Ingots ¹ | - | 1618 | 1000 | - | - | 2618 |
| Crushed Steel Drums ² | - | 2000 | - | - | - | 2000 |
| ----- | | | | | | |
| Subtotal | 3052 | 15148 | 8847 | 0 | 0 | 27047 |
| ----- | | | | | | |
| Grand Total | 20497 | 28798 | 22359 | 6250 | 5000 | 82904 |
| ===== | | | | | | |

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(1) Figures Based on Actual Weights
 (2) Estimated - Yet to be Processed

westscrp
 10/9/85



ESTIMATED CONTAMINATION LEVELS

| | | |
|----------------------|---|------------|
| URANIUM (U & U-235)* | < | 500.00 PPM |
| TECHNETIUM (TC-99) | < | 10.00 PPM |
| NEPTUNIUM (NP-237) | < | 0.05 PPB |
| PLUTONIUM (Pu-239) | < | 0.05 PPB |

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* AVERAGE ENRICHMENT 1 - 1.5% U-235



PROCESSING OF SURFACE CONTAMINATED SCRAP METAL FOR REUSE

PROGRAM OBJECTIVE

- DEMONSTRATE THE FEASIBILITY OF METAL DECONTAMINATION BY COMMERCIAL FIRMS
- PERMIT RELEASE OF THE DECONTAMINATED METAL INTO THE COMMERCIAL STREAM
- CLEAN-UP AND CLOSE-OUT OF THE EXISTING DOE CONTAMINATED SCRAP METAL STORAGE YARDS



METHOD OF ACCOMPLISHMENT

TASK 1 – DEMONSTRATION OF ABILITY

- A SUFFICIENT QUANTITY OF SCRAP METAL WILL BE MADE AVAILABLE TO DEMONSTRATE PROCESS EFFECTIVENESS AND FEASIBILITY
- SPACE WILL BE MADE AVAILABLE AT THE OAK RIDGE FACILITY FOR A MOBILE UNIT SETUP IF IT IS NEEDED FOR THE INITIAL PROCESS DEMONSTRATION
- METAL MAY BE MOVED OFF-SITE FOR PROCESSING IF THE PARTICIPANT POSSESSES THE NECESSARY LICENSES (I.E., STATE AND FEDERAL)
- WASTE BYPRODUCTS WILL BE RETURNED TO DOE FOR FINAL DISPOSITION
- RESULTS FROM THIS TASK WILL DETERMINE PROGRAM FUTURE



METHOD OF ACCOMPLISHMENT

TASK II – TOTAL INVENTORY PROCESSING

- PARTICIPANTS WILL TAKE TITLE TO THE METAL TO BE PROCESSED
- RELEASE OF THE PROCESSED METALS WILL BE IN ACCORDANCE WITH THE PARTICIPANTS' OPERATING LICENSE
- OVERALL COST TO DOE IS EXPECTED TO BE OFFSET BY REVENUES FROM THE SALE OF CLEAN METALS VERSUS INITIAL PROCESSING COSTS
- WASTE BYPRODUCTS FROM THE PROCESSING OPERATIONS WILL BE RETURNED TO DOE FOR FINAL DISPOSITION



SCRAP METAL DECONTAMINATION PHASE I

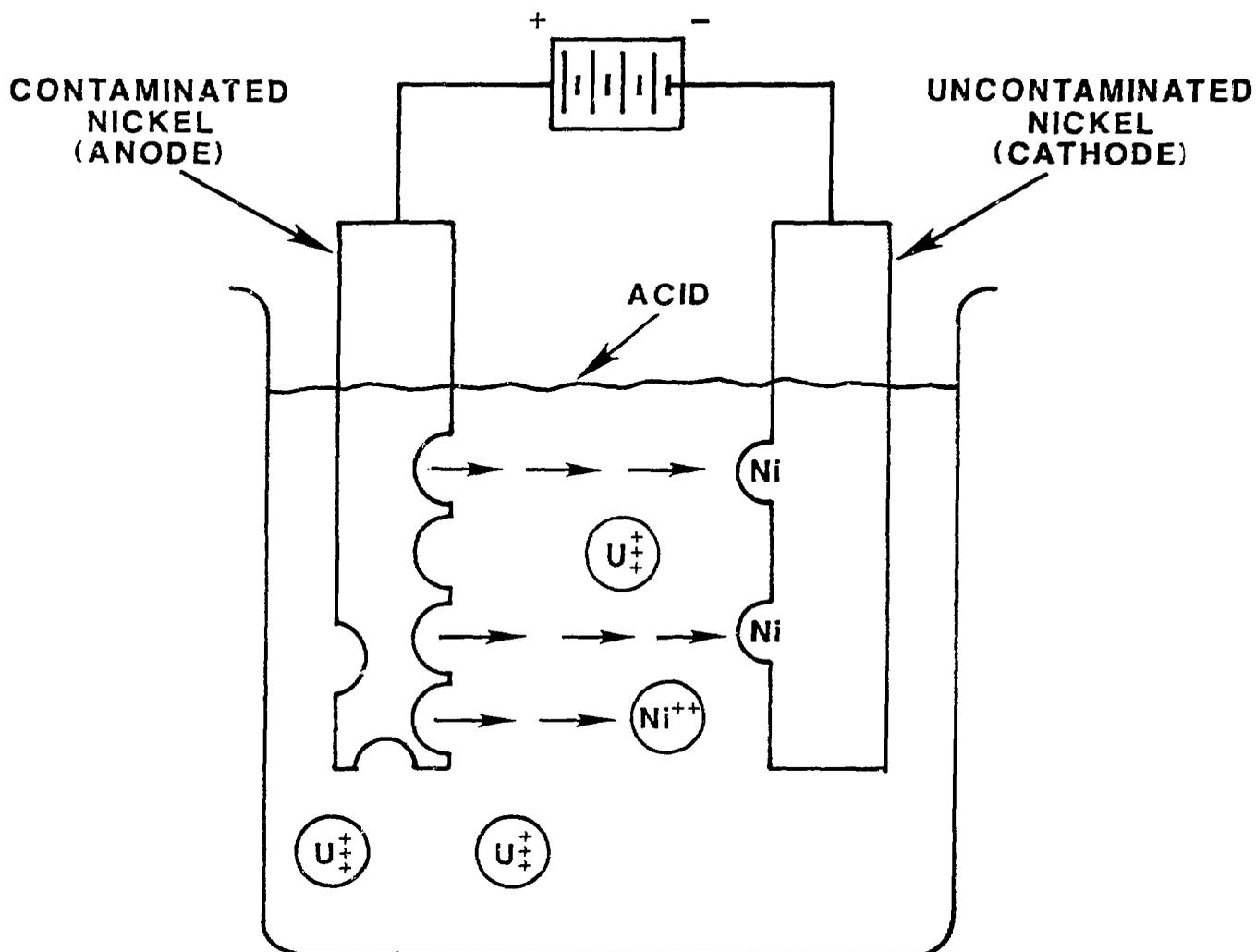
- BABCOCK & WILCOX
 - 25 TONS AT OAK RIDGE AND VIRGINIA

- BECHTEL NATIONAL, INC.
 - 50 TONS AT OAK RIDGE

- SCIENTIFIC ECOLOGY GROUP
 - 25 TONS AT OAK RIDGE AND PENNSYLVANIA



ELECTROREFINING





SCRAP METAL DECONTAMINATION PHASE I

- LIQUID ABRASIVE BLASTING
- HIGH PRESSURE WATER BLASTING
- DRY ABRASIVE BLASTING
- FREON SPRAY
- SPOT CUTTING, GRINDING, SCRUBBING
- ELECTRO-REFINING
- CHEMICAL REFINING
- MELT REFINING
- NUCLEAR USES



- CONVENTIONAL DECONTAMINATION WAS MORE DIFFICULT THAN ANTICIPATED, BUT NOT IMPOSSIBLE
- GREATER THAN 80% OF METAL CAN BE DECONTAMINATED BY CONVENTIONAL METHODS
- DECONTAMINATION OF Ni INGOTS RELATIVE TO URANIUM WAS VERY SUCCESSFUL
- DECONTAMINATION OF Ni INGOTS RELATIVE TO Tc-99 WAS UNCERTAIN
- DECONTAMINATION OF Cu INGOTS AND WIRE WAS VERY SUCCESSFUL



PROBLEMS

- CURRENTLY, INGOTS WITH ANY DETECTABLE CONTAMINATION CANNOT BE FREE-RELEASED
- CONVENTIONAL DECONTAMINATION IS EXPENSIVE
- PROGRAM CURRENTLY MUST BE SELF-SUPPORTING



SCRAP METAL SCHEDULE

PHASE I

B&W

BNI

SEG

| | | | | |
|--------------------------------------|----------|----------|----------|----------|
| ISSUE REQUEST FOR PROPOSALS | 2/18/86* | | | |
| RECEIVE PROPOSALS | 5/02/86* | | | |
| RECEIVE BEST & FINAL OFFERS | 7/03/86* | | | |
| SELECTION OF AWARDEES | 7/18/86* | | | |
| AWARD CONTRACTS | | 9/16/86* | 9/25/86* | 9/24/86* |
| METAL DECONTAMINATED (25-50 TONS) | | 4/13/87* | 5/20/87* | 2/22/87* |

PHASE II

| | |
|-----------------------------|----------|
| ISSUE REQUEST FOR PROPOSALS | 11/15/87 |
| RECEIVE PROPOSALS | 1/01/88 |
| SELECTION OF AWARDEE(S) | 9/15/88 |
| AWARD CONTRACT(S) | 12/15/88 |

* ACTUAL

249/1250

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**The Reduction of Hazardous Solvent Wastes
Through the Application of a
Mobile Solvent Recovery System**

Presented by:

Tim C. Keener, University of Cincinnati

ABSTRACTThe Reduction of Hazardous Solvent Wastes Through The
Application of a Mobile Solvent Recovery System

Tim C. Keener*

The recovery and re-use of commercial solvents has become a major operating concern for the small to medium user of these materials in light of current Federal regulations. Pending regulations severely limit these businesses in the manner in which they may treat, store or dispose of these materials in the near future. A novel mobile solvent recovery system for reclaiming usable solvents and thereby minimizing the amount of waste generation has been developed and tested at a number of industrial sites. The system has been designed to have the flexibility of reclaiming a wide variety of industrial solvents while still adhering to EPA's regulations governing the quantities of wastes which remain within the system as residue, and minimizing the amount of cross-solvent contamination. It employs a specially engineered vacuum distillation unit equipped with two unique cleaning systems for continuous cleaning of the side walls and dome head. The paper will discuss the current progress of this project including the design and construction of the system and its operation. Results will be given from a field test verification study conducted on various solvent containing wastes, generated from a number of industrial sources. The wastes tested have consisted of sludges with solvents such as toluene, trichloroethane, n-propyl acetate, MEK, xylene, acetone, methylene chloride and others. The results to date have been very promising and indicate that from 50-90% of the initial volume of these wastes may be reduced and that reusable solvent may be obtained, thereby providing an economic, as well as a waste management incentive for on-site reclamation.

* Civil & Environmental Engineering
M.L. #71, University of Cincinnati
Cincinnati, Ohio 45221

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MOBILE SOLVENT RECOVERY

BY

TIM C. KEENER

UNIVERSITY OF CINCINNATI

CINCINNATI, OHIO

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INDUSTRIAL ORGANIC

SOLVENTS

- WIDE VARIETY OF TYPES
- NECESSARY IN ALL MANUFACTURING
MANY SERVICE INDUSTRIES
- USED BY LARGE AND SMALL COMPANIES
- WHEN SPENT, PRESENT SERIOUS PROBLEMS
TO THE ENVIRONMENT AND THE
GENERATOR

ENVIRONMENTAL
PROBLEMS

- LARGE QUANTITIES
- WIDE-SPREAD GENERATION
- GROUNDWATER CONTAMINATION
POTENTIAL
- SPILLS, E.G., PUBLIC
HIGHWAYS

GENERATOR
PROBLEMS

- SOLVENTS NECESSARY FOR OPERATIONS
- REGULATIONS MORE AND MORE
RESTRICTIVE
- CURRENT OPTIONS EXPENSIVE AND
DIMINISHING

WASTE SOLVENT

OPTIONS

- LANDFILL DISPOSAL (X)
- INCINERATION
- OUTSIDE RECLAMATION
(DISTILLATION)
- IN-HOUSE RECLAMATION
(DISTILLATION)

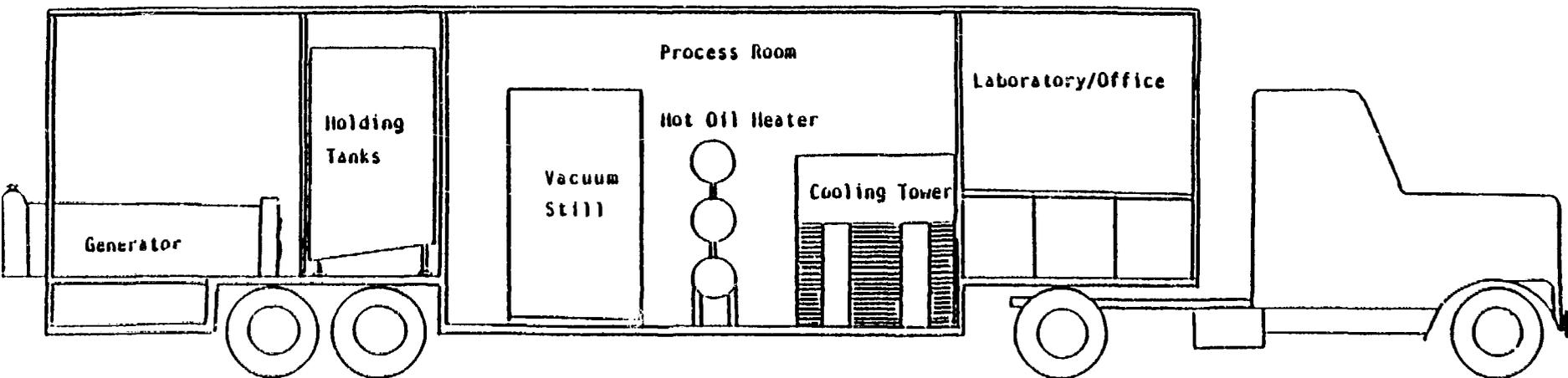
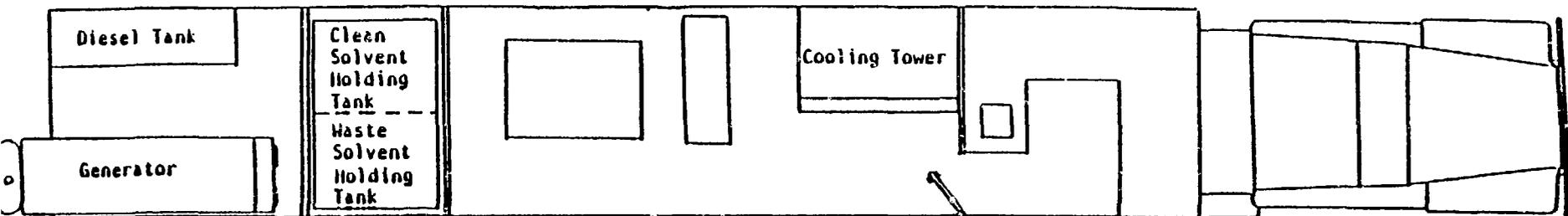
ANOTHER OPTION NEEDED

TO:

- SERVE SMALL/MEDIUM SIZE
GENERATORS
- REDUCE COSTS
- REDUCE ENVIRONMENTAL
RISK
- ELIMINATE CROSS-CONTAMINATION
POTENTIAL
- (MEET WASTE MINIMIZATION
REQUIREMENTS)

THE MSR OPTION

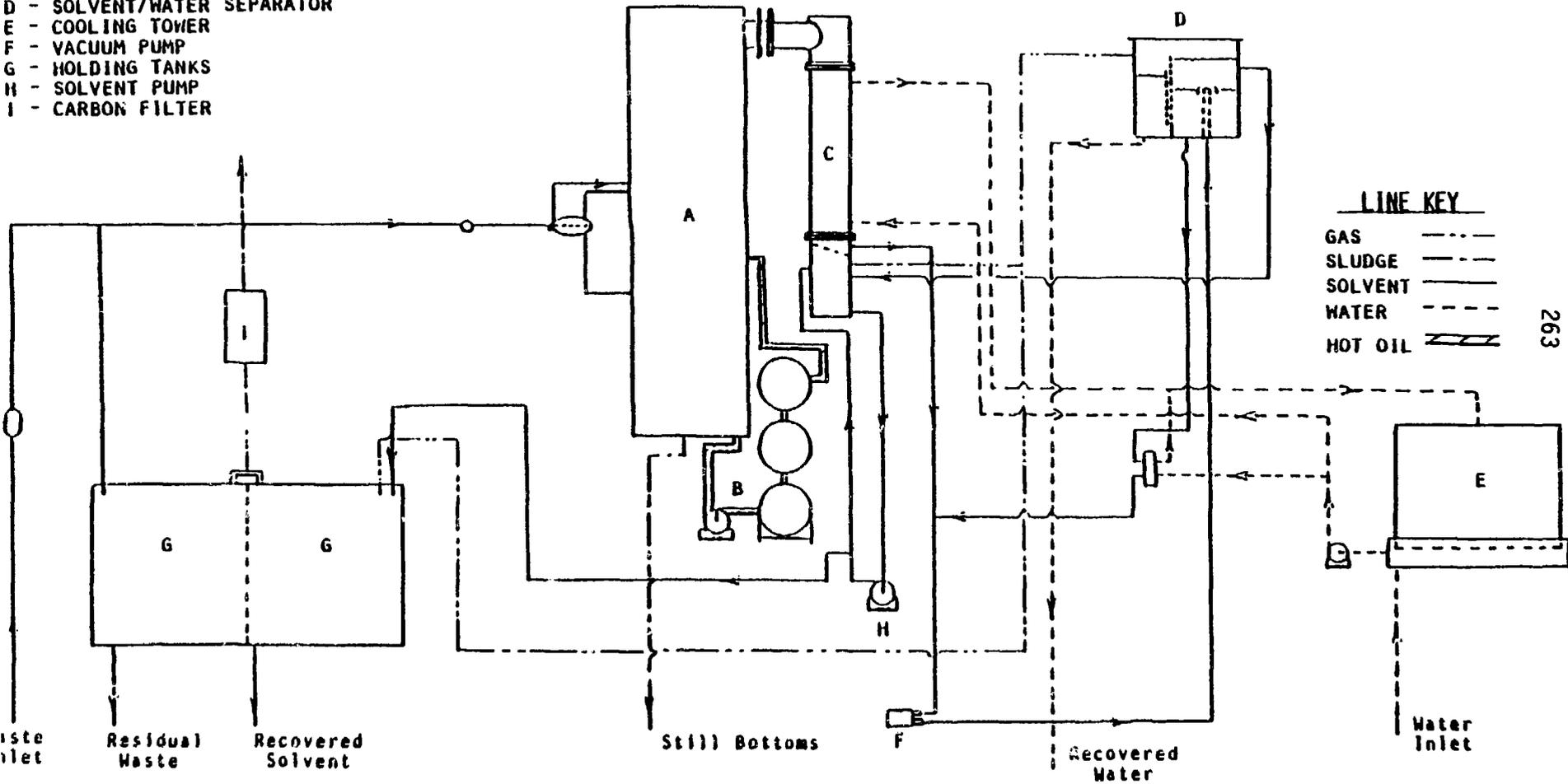
- A COMPLETE MOBILE SYSTEM
 - STAND ALONE Q/A OPERATION
 - CAN PROCESS VARIETY OF SOLVENTS/VOLUMES
 - HIGH YIELD → WASTE MINIMIZATION
 - LOW COST
- ADVANCED, SAFE AND RELIABLE TECHNOLOGY BROUGHT TO THE GENERATOR



Mobile Solvent Recovery Unit

EQUIPMENT KEY

- A - STILL
- B - HOT OIL UNIT W/PUMP
- C - CONDENSER
- D - SOLVENT/WATER SEPARATOR
- E - COOLING TOWER
- F - VACUUM PUMP
- G - HOLDING TANKS
- H - SOLVENT PUMP
- I - CARBON FILTER



LINE KEY

- GAS - - - - -
- SLUDGE - - - - -
- SOLVENT - - - - -
- WATER - - - - -
- HOT OIL - - - - -

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Schematic of the MSR

STATUS OF MSR

- PROTOTYPE
 - DESIGNED
 - CONSTRUCTED
 - DEMONSTRATED

- GENERATOR PROFILE SURVEY
OF CINCINNATI AREA
COMPLETED

RESULTS OF DEMONSTRATION TESTS

- TO DATE - FIVE DIFFERENT TEST SITES
- SOLVENTS RECLAIMED HAVE INCLUDED
 - 1, 1, 1, TRICHLOROETHANE
 - TOLUENE
 - N - PROPYL ACETATE
 - XYLENE
 - MEK
 - MIXTURES
- RATES HAVE BEEN UP TO 190 GALLONS PER HOUR
- YIELD HAS BEEN OVER 90%
- PRODUCT QUALITY HAS BEEN EXCELLENT

CONCLUSIONS

- MSR HAS BEEN DEMONSTRATED TO BE
A VIABLE WASTE MINIMIZATION
OPTION
- SYSTEM IS CAPABLE OF TREATING A
WIDE RANGE OF SOLVENT TYPES
AND VOLUMES
- SYSTEM IS SAFE AND AESTHETICALLY
ACCEPTABLE
- SYSTEM WILL HELP TO REDUCE THE
COST OF HAZARDOUS WASTE MANAGE-
MENT
- SYSTEM WILL REDUCE THE VOLUME OF
TRANSPORTED WASTES

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Recent Technology Developments for PCB Destruction and Oil Recycling

Presented by:

**John P. Woodyard,
International Technology Corporation**

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RECENT TECHNOLOGY DEVELOPMENTS
FOR
PCB DESTRUCTION AND OIL RECYCLING

John P. Woodyard, P.E.
James J. King
IT Corporation
Oak Ridge, Tennessee

Presented at the
DOE Oak Ridge Model Conference
Oak Ridge, Tennessee
October 16, 1987

RECENT TECHNOLOGY DEVELOPMENTS FOR
PCB DESTRUCTION AND OIL RECYCLINGJOHN P. WOODYARD
JAMES J. KING
IT CORPORATION
OAK RIDGE, TENNESSEEABSTRACT

This paper discusses the status of two newly commercialized processes for treating PCB, the KPEG process for PCB treatment, and a reagent process for treating PCB on surfaces and in concrete. The KPEG process has already been permitted for full-scale use in USEPA Region II and New York State and is currently scheduled for a national TSCA mobile treatment permit demonstration in October. The process has also been used commercially to treat PCB and dioxin contamination in waste oils as part of several major Superfund projects, illustrating that its versatility in handling waste contaminated with water, solids, and other contaminants are conducive to treatment by other available processes. The paper includes several case studies in which different waste materials have been treated successfully and identifies plans for second and third generation technology designs for commercial deployment. The reagent, developed in Europe specifically for treatment of chlorinated hydrocarbons, is applied in a heated liquid form and allowed either to penetrate porous surfaces or coat non-porous surfaces. The technique provides a significant advantage in many instances; for concrete it allows destruction of PCB in place without concrete removal, while on metal or other non-porous surfaces it can be used to reduce or eliminate the need for PCB disposal of decontamination residues. The technique has also been used successfully for treatment of dioxin and dibenzofurans and provides an initial response tool in PCB transformer fire incidents involving significant levels of these compounds.

KPEG PCB TREATMENT IN HYDROCARBONSBackground

In 1982, researchers under contract to the Niagara Mohawk Power Corporation (NMPC) developed a series of non-thermal processes for removal of PCB from transformer oil. These processes use low toxicity, low hazard reagents to react the PCB to a dechlorinated material which is not soluble in the original oil. The process does not use metallic sodium, thereby providing a safe and economical method for removal of PCBs, either in a mobile or stationary fashion.

In 1985, NMPC was granted a mobile PCB treatment permit by USEPA Region II and the NYDEC, using a full-scale demonstration treatment rig. To date, the full-scale unit has treated over 6,000 gallons of

transformer oil and 20,000 gallons of dioxin-contaminated waste oil under a variety of contracts.

Chemistry

The basic chemistry of the NMPC process was described in an earlier paper presented at the 1985 EPRI PCB Seminar (Ref. 1). To summarize, tests conducted for NMPC confirmed that PCBs mixed directly with a hydroxide/glycol reagent were rapidly dechlorinated to less than 2 ppm. However, hydroxide/glycol reagents used to dechlorinate 500 ppm PCB in transformer oil reacted very slowly (6 to 7 hours).

In an effort to improve the rate of extraction of contaminant from the oil phase into the reagent phase, a variety of co-solvents were tested, including sulfoxides, amines, alcohols, and ketones. The most promising results were obtained with sulfoxides such as dimethyl sulfoxide or sulfolane and amines such as ethylene diamine. The addition of sulfoxide to the hydroxide/alcohol mixture in laboratory testing caused a substantial increase in the overall rate of reaction.

The reagent for the oil treatment process consists of two components: a solid component (KOH) and a mixture of liquid reagent materials. The proportions of these reagent components are varied to meet the needs of a particular decontamination problem, primarily due to considerations of viscosity and reactivity.

The KOH is first loaded into the reactor in a flake or prill form. The PEG, DMSO, and FMH are then added, followed by the contaminated oil. The reagent is then drawn into the recirculation line and crushed by the mixer into a powdered form which flows easily. Nitrogen is drawn from the vapor space at the top of the reactor for the conveying process.

The mixture is slowly heated using an on-board boiler/heat transfer system. The oil/reagent mixture continues to heat until a pre-determined temperature is reached. The mixture is then allowed to recirculate through the heat exchanger until analysis of the oil indicates that the PCB content is less than 2 ppm PCB. The oil is then cooled by circulating it through coolers until the oil/reagent mixture reaches the desired temperature.

The reagent then settles over a period of several hours, providing a well-defined phase separation from the oil. The oil phase is then withdrawn and stored for any additional filtration or pretreatment for subsequent use. Several tests of the treated mineral oil product have shown the oil to be suitable for reuse as transformer oil, although certain other tests have shown that oil quality prior to treatment can impact its reusability.

The solvent phase can be recycled for up to nine batches of oil, depending on the degree of contamination and general condition of the incoming oil. The reaction time for each batch tends to lengthen as the number

of recycles increases, until the cycle time for the last batch becomes inconveniently long.

The waste reagent is a mixture of potassium chloride, unreacted reagent, and small quantities of dechlorinated biphenol. The mixture is currently being incinerated, as it represents only around 1 to 5 percent of the treated product. Testing is being conducted to determine the feasibility of solidification for landfill disposal or delisting as a hazardous waste.

Test Results

The KPEG technology has been used on several commercial projects involving PCB or dioxin decontamination in hydrocarbon fluids such as mineral oil and waste oil, all with success.

The most noteworthy early project using the technology was conducted for USEPA in Butte, Montana at the Montana Pole Superfund site. Approximately 9,000 gallons of dioxin-contaminated waste oil were processed over a period of approximately two weeks.

Subsequent treatability studies have been conducted for several other materials to determine the potential for the technology. Some examples of treatability results are shown in Table 1. Attempts to decontaminate oil at one Superfund site were moderately successful, reducing the level of PCB to below 10 ppm in waste oil. Because the phase separation was not as clean as in mineral oil and much of the reagent was lost to the oil phase, the speed and associated cost of treatment were relatively high compared to mineral oil. Similar tests conducted on gas line condensate have shown the process to be effective at reducing PCB concentration from 150 ppm to below 2 ppm with the first reagent pass. Again, reagent reutilization was not always feasible based on these test results.

Field demonstrations using the gas line condensate and selected waste oil products are planned for later in 1987 and early 1988. The laboratory test results have shown promise for treatment of virtually any hydrocarbon fluid contaminated with PCB of any aroclor type, although the cost of processing will vary significantly depending on the effectiveness of reagent recovery.

Permits

NMPC successfully demonstrated the KPEG technology on PCB for USEPA Region II and NYDEC in 1985, resulting in the granting of a permit to operate the system at several NMPC-owned sites in New York State. Upon licensing the technology, IT was subsequently granted operator status in New York State and is currently treating PCB-contaminated mineral oil under that permit.

IT has applied for permission to demonstrate the technology to USEPA and hopes to obtain a permit to operate on a mobile basis throughout all fifty states. The USEPA demonstration is scheduled to take place in October, attempting PCB decontamination for levels up to 5,000 ppm in mineral oil.

Plans for Development

Upon receipt of the initial USEPA mobile treatment permit for PCB, IT plans to construct several additional units specifically designed for different fluid treatment problems, including mineral oil and waste oil. Pending the results of the demonstration, IT hopes to offer this service commercially later this year.

In addition, several utilities and other private organizations have expressed interest in developing fixed facilities using the treatment technology, primarily for mineral oil. These projects are currently under study, particularly in locations that are remote from alternative means of disposal. The results of one or two studies should be announced shortly.

The unit as currently designed is capable of processing between 500,000 and 1,000,000 gallons per year of oil, depending on operating schedule. Modifications to the next generation of design will allow for faster processing, perhaps increasing the unit capacity by as much as 100 percent.

IN SITU PCB TREATMENT FOR SURFACES

Background

PCB spill and fire cleanup projects require expertise in a variety of decontamination technologies, given the similar variety of surfaces and materials that require decontamination, while improvements in technology have resulted in cost savings and efficiencies through the use of recyclable cleaning solvents and low volume cleaning techniques, decontamination of concrete continues to be one of the most difficult problems facing utilities and decontamination contractors. Traditional methods of washing or otherwise removing portions of concrete is well documented. These methods alone can account for the most significant portion of a decontamination project cost.

IT licensed a patented reagent process in 1986, designed to be used in a solid or liquid form to dechlorinate PCB. After reviewing and confirming some of the initial field results from the European use of the reagent, IT applied for a TSCA research permit in January, 1987 and received permission from USEPA to proceed with field-scale demonstration of the technology in May. IT has completed its first field trial of the reagent and has plans for several additional tests in the next six months. Field research will focus on a variety of surfaces, levels of

contamination, aroclor types, penetration effectiveness, and dibenzofuran destruction.

Chemistry

The IT reagent is based on phase transfer catalysis chemistry, in which one of the chemicals to be reacted is transferred from a phase in which it is relatively unreactive to one in which it can be reacted. In the IT reagent, the reactive chemicals in the formulation are an alkali metal alkoxide or peroxide and a polyglycol of varying molecular weight. The high molecular weight glycols are solid at room temperature, but liquid at the reaction temperature range of 60 to 90°C.

The liquid reagent is prepared by suspending the alkoxide in the liquid polyglycol (low molecular weight) at elevated temperature. The mixture is then heated and applied to the surface to be treated. The material remains in intimate contact with the contaminants for days or weeks until the reaction proceeds to completion. Experimental use of ultraviolet light has also been conducted to enhance the free radical formation association with the reaction.

Test Results

The liquid reagent has been applied to commercial surface decontamination in Europe on several projects involving PCB, dibenzofurans, and dioxins (Ref. 2). These field-scale demonstrations have shown the liquid reagent to be an effective destruction agent in as little as one week. Because of differences in spill cleanup standards and approaches, however, these projects do not provide sufficient information for ready technology transfer in this country.

In July 1987, IT conducted the first U.S. test of the reagent technology at a transformer fire site in Shreveport, Louisiana. Results of the Shreveport test will be available just before the presentation of this paper.

Permits

Because spilling PCB liquid constitutes illegal disposal as interpreted by USEPA, destruction of PCB in place constitutes an alternative to conventional disposal and must therefore be permitted. IT received a TSCA Research and Development permit from USEPA in May 1987, allowing for the demonstration of the technology at several active PCB decontamination project sites. The first such demonstration was conducted in Shreveport on an emergency basis, where the state and EPA region waived notification requirements in order to proceed expeditiously with the test during normal decontamination.

Attempts to permit the technology for commercial application will hinge on the results of the first several field demonstrations, all scheduled

this year. While the reagent is known to be effective for surface or shallow contamination, the optimum reagent recipe and application parameters are not sufficiently known to guarantee commercial success. Any degree of technical success in the initial field demonstrations could result in an application to EPA for a commercial permit, although such a permit would likely be limited to the only specific type of successful application associated with the demonstration. The USEPA permitting process clearly did not anticipate the advent of this type of technology; therefore, fairly stringent USEPA testing requirements, thorough permit review, and narrowly defined permit conditions would be required.

Plans for Development

The liquid reagent technology has several obvious applications in industrial PCB decontamination, including the following:

1. Treatment of contaminated non-porous surfaces, such as metal cabinets and machinery
2. Treatment of porous surfaces such as concrete and wood
3. Initial response treatment of furan/dioxin contamination following PCB fire incidents.

The technology has been proven effective in situations such as 1 and 3. Successful field confirmation of the European results will result in commercialization of a viable emergency response technology for PCB spills and fires, as well as a means of decontaminating industrial equipment which has been in contact with PCB during years of use. Successful use in decontaminating concrete and wood in particular would perhaps provide the most dramatic improvement in technology due to the primitive nature and high cost of currently available technologies.

Table 1. KPEG PCB Treatability Results for Selected Contaminated Hydrocarbons (Concentrations in ppm)

| Parameter | <u>Asphaltic Waste Oil</u> | | | | <u>Gas Line Condensate</u> | | | |
|-----------|----------------------------|---------|---------|---------|----------------------------|---------|---------|---------|
| | Initial Conc. | Batch 1 | Batch 2 | Reagent | Initial Conc. | Batch 1 | Batch 2 | Reagent |
| Aroclor | | | | | | | | |
| 1242 | | | | | 150 | <4 | 110 | 46 |
| 1248 | 136 | 9 | 40 | 16 | | | | |
| 1254 | 48 | <4 | <5 | <4 | <30 | <4 | <10 | 4 |
| 1260 | | | | | <30 | <4 | <10 | 4 |
| Total | 178 | 9 | 40 | 16 | 150 | <4 | 110 | 46 |

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2. Nobile, G. W. Tumiatti, and P. Tundo, May 1986. "In-Situ Decontamination and Chemical Degradation of PCDFs and PCDDs Coming from Thermal Oxidation of PCBs." Presented at the American Chemical Society Division of Environmental Chemistry Symposium, New York.

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**Processing of Stored Uranium Tetrafluoride
for Productive Use**

Presented by:

**Walter N. Whinnery III,
Paducah Gaseous Diffusion Plant**

PROCESSING OF STORED URANIUM TETRAFLUORIDE
FOR PRODUCTIVE USE*

W. N. Whinnery III
Paducah Gaseous Diffusion Plant
Paducah, Kentucky 42001

Chemical Operations
Operations Division

Waste uranium tetrafluoride (UF₄) was created from converting uranium hexafluoride (UF₆) to UF₄ for generation of hydrogen fluoride. This resulted in more tails cylinders being made available in the early days of the Paducah Gaseous Diffusion Plant. A need arose for the UF₄; however, a large portion of the material was stored outside in 55-gallon drums where the material became caked and very hard. Chemical Operations crushed, ground, and screened a large portion of the waste UF₄ from 1981 - 1987. Over 111,935,000 pounds of the material has been processed and put into productive use at Westinghouse Materials Company of Ohio or at Department of Defense facilities. This long-term effort saved the disposal cost of the material which is estimated at \$9,327,900. In addition, the work was for an outside contract which lowered the operating cost of the Chemical Operations Department by \$4,477,400. Disposal options for the material still present in the current inventory are outlined.

Prepared by the
Paducah Gaseous Diffusion Plant
Paducah, Kentucky 42001
operated by
MARTIN MARIETTA ENERGY SYSTEMS, INC.
for the
U. S. DEPARTMENT OF ENERGY
under Contract No. DE-AC05-84OR21400

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PROCESSING OF STORED URANIUM TETRAFLUORIDE FOR PRODUCTIVE USE -
Walter N. Whinnery, Martin Marietta Energy Systems, Inc., Paducah, Kentucky

Introduction

Uranium tetrafluoride (UF₄) was a by-product from a former operation involved in the generation of hydrogen fluoride. The UF₄ would have eventually been disposed of; however, a suitable disposal site was not available. Therefore, the material was placed in storage (55-gallon drums) as a temporary measure. A portion of the material was stored outside where it was exposed to moisture and became caked and solidified. Waste minimization was accomplished by finding a market and then recycling the uranium tetrafluoride; however, the material needed to be put into a reusable form by grinding and screening into a powder.

Background of material

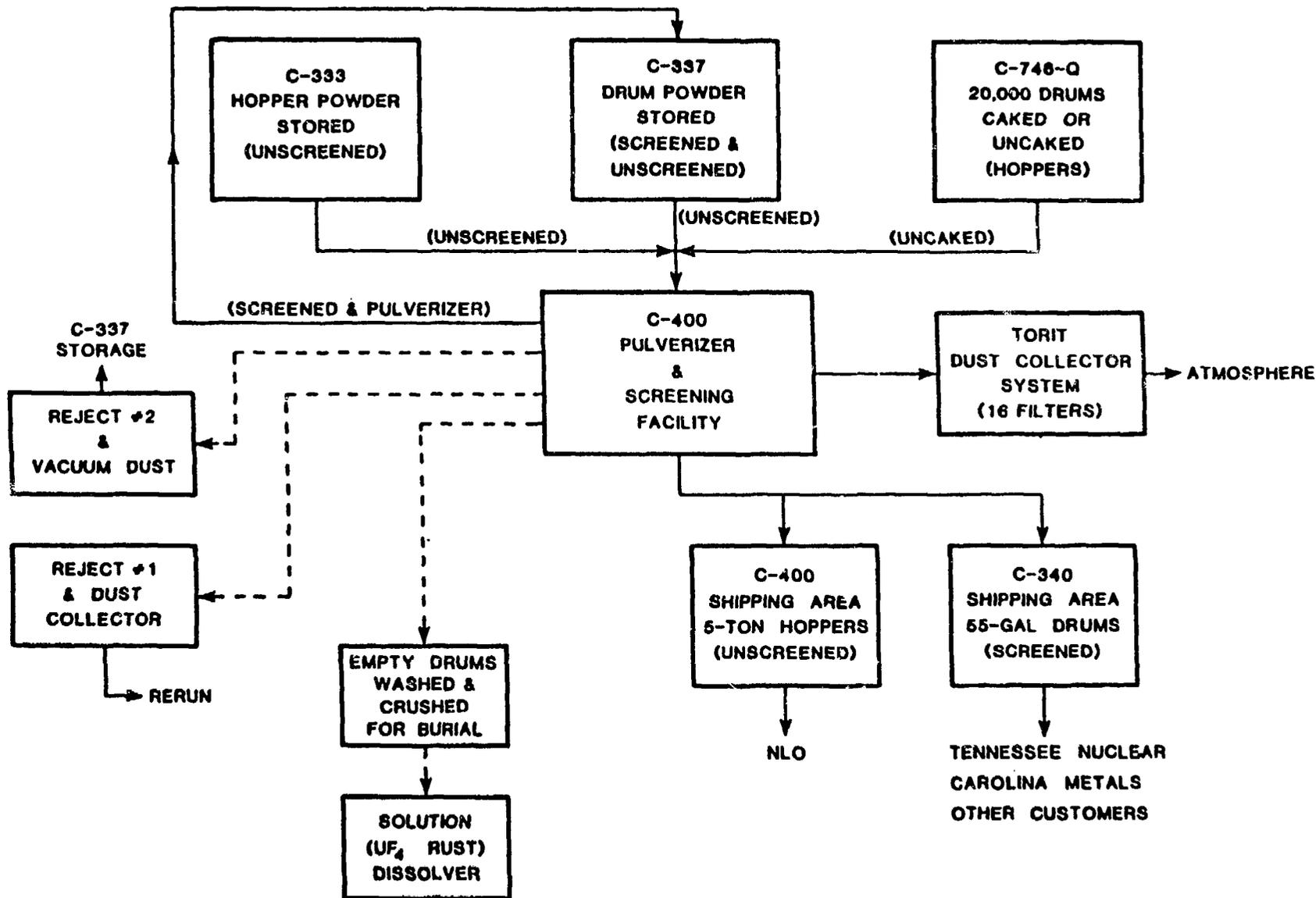
Two separate flow patterns are shown in the overall picture of the powder distribution in figure 1. One final designation for the UF₄ is to Westinghouse Materials Company Of Ohio (WMCO). This material is shipped in 5-ton hoppers and is not screened. The second designation for the UF₄ was to Department of Defense contractors. This material was shipped in 55-gallon drums and was screened.

Present day storage is concentrated in four buildings. All UF₄ processing is done in the Chemical Operations building. Over 111,935,000 pounds of UF₄ has been processed through September of 1987. This long-term effort saved the disposal cost of the material which is estimated at \$9,327,900. In addition, the work was for an outside contract which lowered the operating cost of the Chemical Operations Department by \$4,477,400.

Process of grinding and screening

A flow sheet of the process of grinding and screening the UF₄ in the Chemical Operations building is shown in Figure 2. The original finished product powder was stored in 55-gallon drums. Therefore, initially the drum of UF₄ is loaded onto a roller conveyor that leads to a drum dumper. The material goes into a hopper then through a rotary feeder to a selector valve. The selector valve can be set in either of two ways. The position used for the Department of Defense contractor work allows the UF₄ to go through a micro

THE PRESENT UF₄ FLOW CHART WILL GIVE AN OVERVIEW OF THE POWDER MOVEMENT



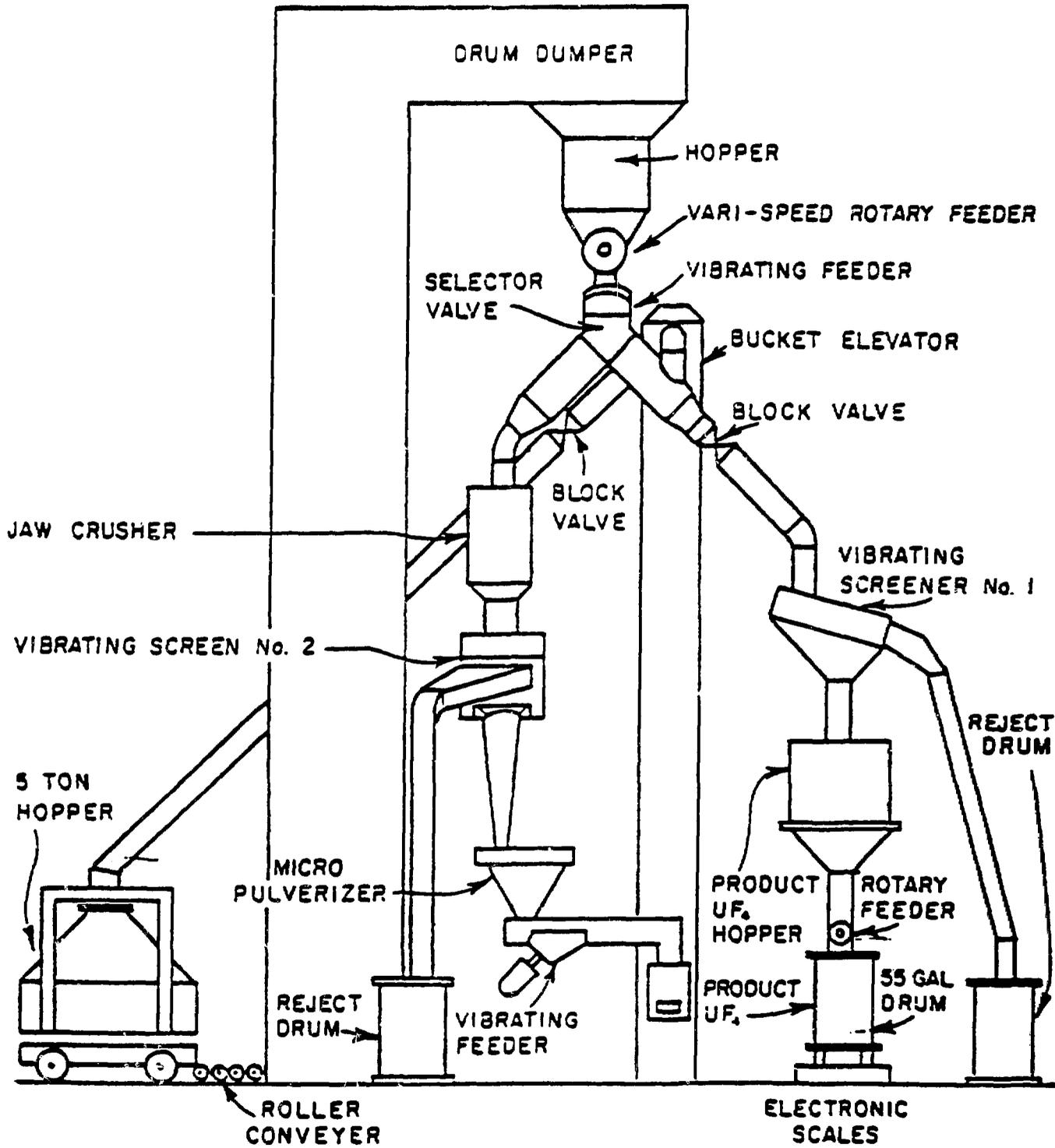


FIGURE 2

pulverizer and two screeners, finally being repackaged into new 17H drums. The selector valve set in the opposite direction is for UF4 that goes to WMCO. This material is repackaged into a 5-ton hopper shipping container. The only restriction on the material sent to WMCO is that the feed material be able to pass through the rotary feeder before being fed to the 5-ton hopper. All the drums that are emptied are washed free of any UF4 and crushed. The drums are taken to the contaminated scrap yard for disposal.

General requirements and training

The chemical operators that work at the pulverizer facility receive training on two standard operating procedures (SOP's); "Operation of Pulverizer Screener Facility and Associated Equipment" (CH-353), and "Inspection of Radioactive Shipment other than UF6" (CH-425). Pulverizer pre-job instructions, hopper inspection sheets, and a quality assurance assessment and plan are also reviewed.

5 ton hoppers

Special precautions are taken when filling the 5-ton hoppers. A dust preventer is put in place when filling the hoppers. The wing nuts on each hopper lid were changed to hex nuts to allow a torque to be applied to each of the hopper lid nuts. The original torque guidelines on the hopper was 90 ft-lbs.; however, the eyebolts begin to distort at over 50 lbs torque. The new guideline is set at 40 ft -lbs. Two numbered seals are used to provide tamper protection on each hopper. The weight of each full hopper and the tare weight are recorded in log books for uranium accountability.

Checks on hopper

The highest probability of contamination escaping the container is from the sealing surfaces, such as the lid and the bottom inspection plate. A straightness test of the lid with a metal straight edge, tests the lid for any warping that would prevent a good sealing surface. Any caked UF4 buildup on the lid will require the lid to have the surface blasted clean. Originally, a gasket of a much harder composition than called for on the drawing was being used. In addition, the drawing had the incorrect size of the gasket. The gasket has been changed to conform to the correct diameter and durometer reading. Checks on the hopper include inspecting for any signs of moisture on the inside of a hopper.

Shipments of material

Each incoming and outgoing hopper has a hopper inspection sheet to check prior to shipment. Eyebolts are checked to see if they are bent or stripped. Pins and nuts are inspected for cracks. Washers are inspected to determine if an improper washer is installed or a washer is missing. The bottom flange and pipe cap are checked for looseness. Hopper supports are inspected for cracks. Pressure testing of the hoppers is done on a five-year interval to ensure the integrity of the hopper container. This air test of the hoppers at 4.5 psig for leaks helps maintain only good hoppers for in-service use.

Surface wipe tests are required on every incoming hopper and for every hopper leaving the building. A test stand is in place to obtain wipe counts from bottom of the hopper. Radiation meter readings are recorded on the uranium accountability tally-outs of the hoppers. The hoppers are to be free of outside contamination before leaving the building and comply with DOT shipping regulations on contamination control. All full hopper truck shipments are escorted to the gate by Chemical Operations operators.

A hopper status board is kept up to date to record the number of full hoppers at Paducah, the number of hoppers at WMCO, and the number of empty hoppers to be filled. Empty hoppers that are received from WMCO are wipe-tested and meter readings recorded on the incoming hoppers.

Torit dust filter equipment

Any escaping air from the pulverizer operation is filtered through Torit dust filter equipment. A sixteen cartridge filter system is used to collect any emissions from the process. A photohelic gauge and an opacity monitor have been installed. An audible and visual alarm are connected to the opacity monitor. A daily dust control check sheet is used to monitor the condition of the filter system.

Air filter system operation

The Torit dust collector operates with a blowback on the filter in the filter system, when the pressure differential across the filters is 2" or greater. Initially, the blowback was operated continuously but testing of the emissions proved that the filters operate better without the blowback until the preset pressure differential across the filter

system is reached. An air pulse forces the dust off of the filters on the blowback every 10 seconds. Originally the blowback was set to pulse every 3 seconds which also contributed to the high filter change-out rate in the beginning of the filter's operation. Additional changes in filter system suggested by the manufacturer were to reduce the velocity through the filters and to shut off the dust collection system when it is not in operation.

UF4 pulverizer filter changeout

Improvements in the UF4 pulverizer filter changeout have been made to reduce any air emissions due to the maintenance on the unit. A platform was fabricated for the filter change operation to aid in installation and removal of the filters. Plastic bags are placed over the used filters as they are removed to minimize any UF4 from becoming airborne. Personnel protection improvements such as better shoe covers, a portable vacuum cleaner to vacuum off clothing, and use of the full face respirator instead of a half face respirator inside the filter housing has reduced personnel exposure. A 50 ft. perimeter around the pulverizer filter changeout operation, plus respirator protection requirements to enter the area, provide protection against any incidental exposure. All building doors are closed when changing filters to minimize draft in and out of the building. Industrial Hygiene obtains high volume air samples and personnel air samples during a pulverizer filter change out.

Monitoring on the stack

The exhaust of the pulverizer is routinely monitored for uranium emissions. The limit of uranium emissions is 4.54 gram/hr. or 0.24 lb./day. The material processed in the pulverizer is 0.2% U235 assay material. Natural occurring uranium is 0.7% U235 assay. Sample data is returned to Chemical Operations and Environmental Control to monitor the emissions. Monthly and yearly environmental reports are issued on the operation of the pulverizer facility.

Drum washer

The drum washer is used to clean out the UF4 drum after it has dumped the contents. The drum is inverted and placed on a rotating grated platform. Spray nozzles then inject a sodium carbonate solution into the drum to decontaminate and remove any residual UF4 that remained in the drum. A pH of 7 is maintained in the drum washer solution to prevent corrosion of the metal in the washing unit. Once the drum washer solution becomes concentrated it is transferred to another tank and sent to the uranium precipitation operations in our building. The low assay of the drum washer solution makes recovery of the uranium

economically unfeasible. The drum washer sludge is stored in a long-term above-ground storage area.

Iron contamination

Due to the early storage conditions on many of the 55-gallon drums, the drums deteriorated and rust formed on and inside the drums. Iron is considered a contaminate in the UF4 feed stream. Magnetic separation was suggested to remove the iron; however, the majority of the iron is in the non-magnetic form. Special cautions are taken to ensure the least amount of iron gets into the product, such as, vacuuming the rust off of the lids and any that had fallen off the walls on the interior of the drum. Caked material was created when water hydrated to the UF4 making an extremely hard material. The caked drums normally have a layer of UF4 built up on the sides where the rusting has occurred. When dumped from the drum dumper the UF4 will still adhere to the drum walls creating a partially dumped drum.

PGDP depleted UF4 stockpile estimated usage table

An inventory of UF4 in the plant is maintained by Uranium Accountability. The stockpile is being depleted such that the caked material will be the only grade of material left in the plant. Analysis of the caked UF4 shows an iron content above the guidelines unless a method can be perfected that would auger or bore out the center core. The iron contamination concentrates around the drum with the interior core relatively free of iron. A high moisture content in the UF4 is considered a contaminate in the UF4 feedstream. It is very difficult to dry UF4 without oxidation of the material. Without drying the UF4 would be of questionable use in metal derby production.

Possible options

UF4 is exempt from standard excess property disposal procedures which allows the material to be disposed of on the commercial market. The purchasers are required to have a current license to possess and process the material. A sale of one million pounds of caked material to Carolina Metals and a one million pounds sale of caked material to Aerojet has provided an option to the disposal of the caked material. Other methods of grinding the powder and separating the iron contamination have been explored but were ruled out due to the technical problems involved in the separation of the non-magnetic iron.

Prepared by the Paducah Gaseous Diffusion Plant Paducah, Kentucky 42001
Operated by MARTIN MARIETTA ENERGY SYSTEMS, INC., for the U. S. Department
of Energy under Contract No. DE-AC05-84OR21400

291/293

PERIODIC TABLE
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Recovery of Zinc, Iron, and Sulfur from Galvanizer Wastes

Presented by:

**Joe R. Trimm,
Tennessee Valley Authority**

RECOVERY OF ZINC, IRON, AND SULFUR FROM GALVANIZER WASTES - Joe R. Trimm, Louis A. Stumpe, Tina M. Tomaszewski, Tennessee Valley Authority, Muscle Shoals, Alabama

At TVA's National Fertilizer Development Center in Muscle Shoals, Alabama, researchers are engaged in essentially all areas of fertilizer research. Included in this research is the recovery of plant nutrients from material which would normally be considered waste, particularly toxic or hazardous wastes.

Agronomists generally classify fertilizers according to three categories: the primary nutrients - nitrogen, phosphorus, and potassium; the secondary nutrients - calcium, magnesium, and sulfur; and the micronutrients - zinc, boron, cobalt, iron, manganese, copper, sodium, and molybdenum. Whereas the need for primary nutrients has been known for decades, the acute need for micronutrients has become apparent only in recent years. Land, in many cases, that has been farmed for relatively long periods of time and fertilized with proper amounts of the primary nutrients has become deficient in some of the secondary and micronutrients. In order to restore optimum yields, the level of these nutrients must be brought to acceptable levels. For example, rice grown in the State of Arkansas requires approximately three pounds of zinc per acre per year. Researchers at NFDC are currently exploring the possibility of recovering some of these nutrients from material currently being discarded as hazardous or toxic wastes.

Waste acids and sludges, particularly from the galvanizing industry, have historically been discarded because of the high cost of recovering individual elements for reuse or sale. However, with the onset of regulations by the EPA in recent years, disposal costs have risen drastically.

The yearly production of waste sulfuric acid and impure crystals of iron and zinc sulfate from the galvanizing industry totals over 100,000 tons. These waste materials result from the cleaning of metals prior to galvanizing. Both acid and crystals contain substantial quantities of zinc, iron, and sulfur, all of which are potentially valuable plant nutrients depending upon their extraction as nontoxic and nonhazardous products. Because of its greater quantity and higher cost, the zinc is the most valuable of the elements in these wastes.

In order to successfully market the zinc from these wastes as fertilizer additives, the zinc needs to be a solution of zinc sulfate or crystals of zinc or zinc-ammonium sulfate.

Researchers at TVA's National Fertilizer Development Center have developed two processes for the recovery of zinc, iron, and sulfur from these waste materials.

In the first process or process A, the galvanizer acid or a solution prepared from the crystals of iron and zinc sulfate is ammoniated to a pH of about 10 with anhydrous or aqueous ammonia. The rate of

ammoniation appears unimportant; however, the pH of about 10 is critical. During the ammoniation, the sulfuric acid is neutralized, most of the iron is precipitated as ferrous hydroxide and the zinc is precipitated as zinc hydroxide at near neutral pH values but redissolves as the pH is raised to 10 due to the formation of the tetra-amine zinc complex in the highly ammoniacal solution. Figure I illustrates this solubility. During the neutralization and ammoniation of the acid, the temperature of the slurry rises to about 80°C due to the heat of neutralization of the sulfuric acid while the temperature of the crystals solution will rise only a few degrees. In both cases the temperature is maintained at about 80°C to aid in the redissolution of the zinc. Attempts at separating the solids from a liquid product at this point were unsuccessful due to the gelatinous nature of the ammoniated slurry. A separation is easily accomplished, however, following a partial oxidation of the iron.

This oxidation can be brought about in a number of ways. Air sparging is the simplest. Oxygen can be used as a sparging gas or as a surface oxidant. With air, oxidation is accomplished in about 8 hours whereas the same oxidation can be accomplished in less than one hour using oxygen in the simple equipment shown here. As you can see, the oxidation rate is dependent upon the pH of the slurry showing again that a pH of 10 is critical. (Figure II) A closed system with surface oxidation has other advantages also. One advantage is that the absence of ammonia containing off-gas eliminates the need for a scrubber system. Also, since there is no loss of ammonia from the

system, the pH remains constant. Once the oxidation of the iron has reached about 70% it is discontinued and the slurry is allowed to stir for an additional 1-2 hours to allow for the formation of the magnetite to go to completion. The advantages of the formation of the magnetite instead of other oxides or hydroxides of iron are apparent in the separation step. Both centrifugation and filtration rates are greater for magnetite than for iron oxide, but the greatest advantage is the fact that 80-90% settling can be accomplished in about 10 minutes with the aid of a magnet. This is due to the magnetic properties of the magnetite.

Once a separation of solid and liquid have been made the products are in a marketable form. The liquid products contain from 2-5% zinc, 4-8% nitrogen, and 5-10% sulfur with essentially no iron, thus making it a readily marketable fertilizer or fertilizer additive with a value of over \$100 per ton.

The solid portion of the separation when dried contains 30-50% iron, 1-4% zinc, 2-5% sulfur, and 6-10% nitrogen, but represents only about 5% of the weight of the original waste material. If no toxic metals are contained in the solid product, it can also be marketed as a fertilizer additive with a value of over \$100 per ton. If the solid product contains toxic metals, it can be marketed to reclamation plants for further processing.

The second process, or process B, involves the selective decomposition of iron sulfate without the decomposition of the zinc sulfate. This process is better suited for the treatment of galvanizer crystals, but can be used for the acid also. In this process, the crystals are heated stepwise beginning at 80°C where all the free water is expelled in addition to some of the hydrated water.

If heating is increased to 615°C a number of changes occur. Excess sulfuric acid is evaporated, the zinc sulfate is dehydrated to the anhydrous salt and the iron sulfate is oxidized and decomposed to iron oxide and SO₂. The expelled SO₂ is absorbed in water to yield sulfuric acid which can be returned to the system. As much as 70% of the sulfuric acid is returned to the system. This is important because of the rising cost of sulfuric acid together with predictions of shortages as early as the late 1990s. The solid material from the heaters is a mixture of iron oxide and anhydrous zinc sulfate. Once the pyrolysis is complete the solid mixture is cooled and mixed with water. The water hydrates and dissolves the zinc sulfate, but not the iron oxide. Upon separation of the solid and liquid portions, usually by centrifugation, two readily marketable materials are obtained.

The liquid product is a solution of zinc sulfate with a concentration of up to 10% zinc or a 70% solution of zinc sulfate heptahydrate. The concentration of the zinc is dependent upon the amount of water used for the extraction. A 10% solution of zinc as zinc sulfate is the most desirable product for sale, particularly as a fertilizer additive. Since the product is a simple aqueous solution of zinc

sulfate, other options are available. The water can be evaporated to yield a product of dry zinc sulfate or the zinc may be electrolyzed from the solution to give zinc metal as a product.

The solid consists primarily of red iron oxide with only a small quantity of zinc sulfate. With continued processing the iron oxide can be purified to a relatively high level for sale to markets such as the paint industry. The solid product, however, amounts to only about 3% of the weight of the original acid and about 15% of the weight of the crystals, making further processing questionable.

Since both processes start with materials which are classed as toxic or hazardous, or both, then the condition of the product is naturally of concern. The pH of all products is now in a range which is safe by EPA guidelines.

In order to determine the fate of toxic metals listed in the EPA toxic extraction test, samples of waste acid and crystals were spiked with the toxic metals to a level of 100 ppm or above. The acid was subjected to cleanup by process A and the crystals to process B. It is clear from the table that cadmium is the only metal with concentration in the liquid product from either process. The presence of cadmium in a liquid product is of no concern because it is easily removed by passing the product over a bed of zinc. Greater than 99% of other metals in the EPA toxic list series is either evolved during the process or is deposited in the solid product in both processes. However, when the EPA extraction test for metal toxicity was applied

to the products, the amount of the metal extracted was very low, indicating that the material would not be considered either hazardous or toxic by EPA standards for toxic wastes. This means that the material could be disposed of as a byproduct instead of a costly or hazardous waste.

Treating waste galvanizer acid or crystals with one of the described processes can result in a net savings of over \$500 per ton of material. Wastes which were costing as much as \$300 per ton for disposal in addition to analytical costs can be processed to yield products valued at \$100 or more per ton. The equipment and labor required for processing the waste materials would be no greater than that required for the neutralization and dewatering done currently prior to disposal.

Toxic Metals (ppm)

| <u>Metal</u> | <u>Process A</u> | | <u>Process B</u> | |
|--------------|------------------|------------------------------|------------------|------------------------------|
| | <u>Liquid</u> | <u>EPA ext. of solid</u> | <u>Liquid</u> | <u>EPA ext. of solid</u> |
| As | 1 | <1 | <1 | <1 |
| Cd | 84 | 4 | 138 | 1 |
| Cr | <1 | <1 | <1 | <1 |
| Pb | <1 | <1 | 2 | 2 |
| Se | 2 | <1 | 3 | <1 |
| Ag | <1 | <1 | <1 | 2 |
| Hg | <1 | <1 | <1 | <1 |

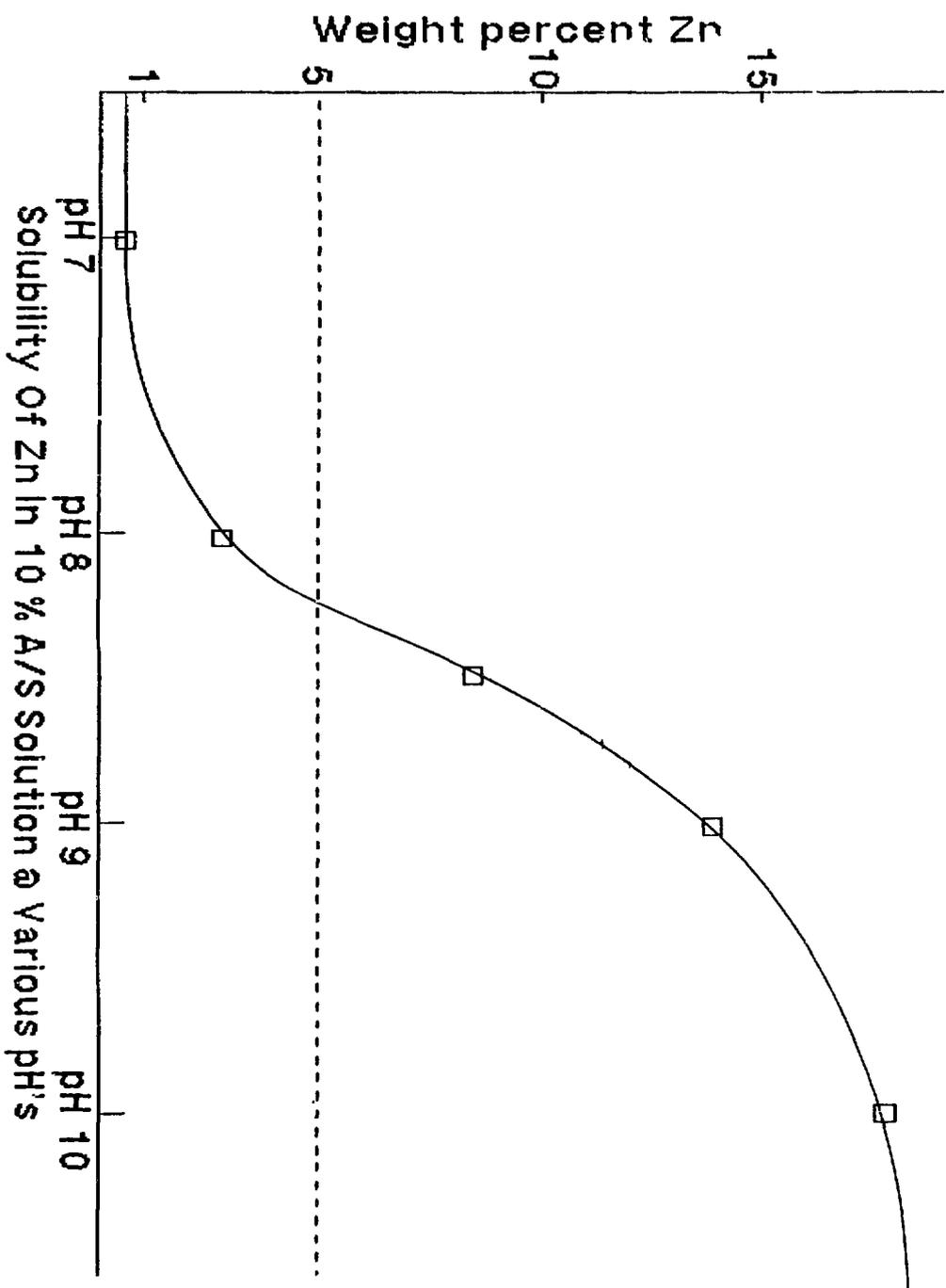


FIGURE 1

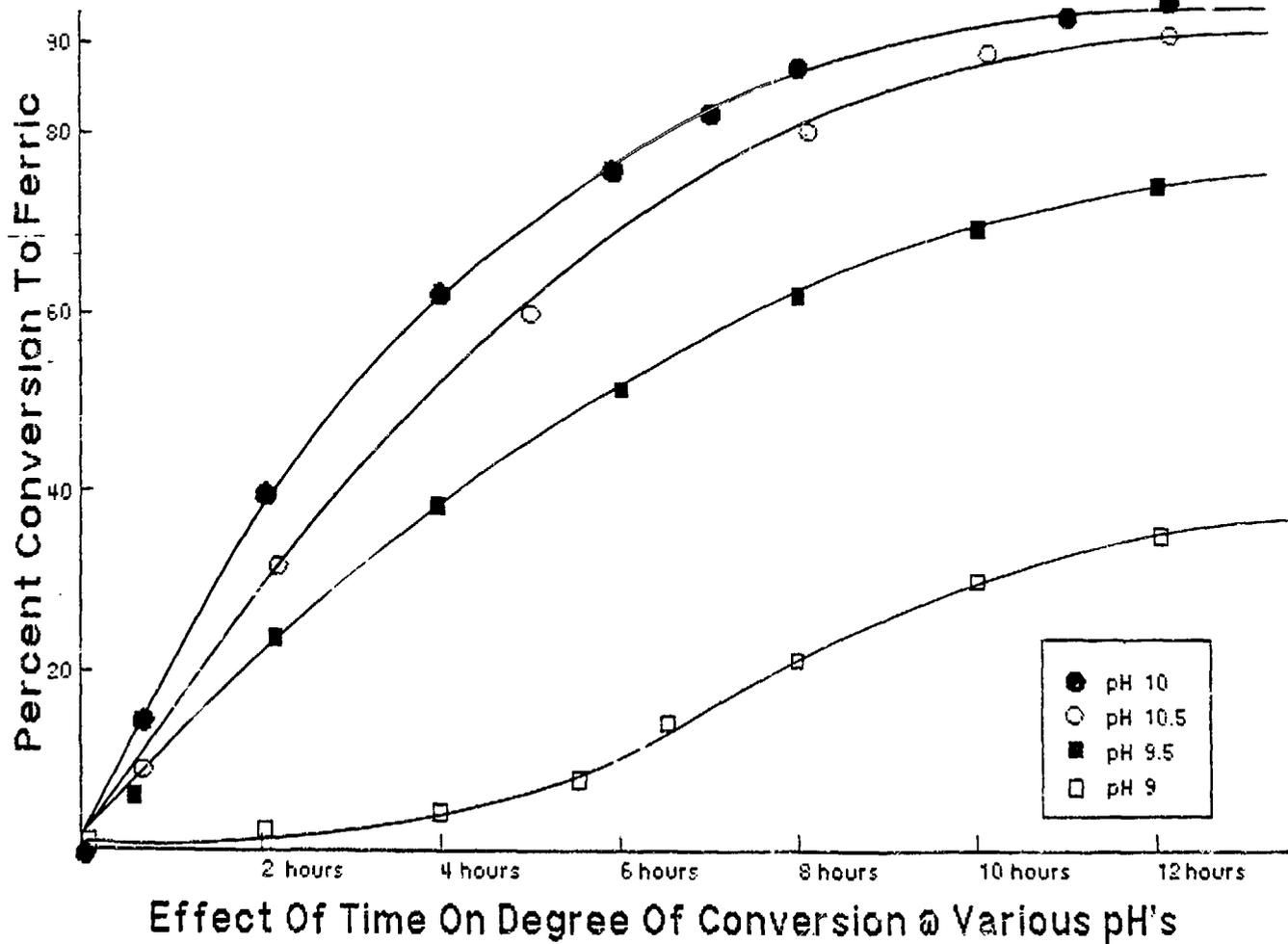


FIGURE II

301 | 3003

303 | 324

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**Evaluation of Proposed Shallow-Land Burial Sites
Using PRESTO-II Methodology and Code**

Presented by:

D. E. Fields, ORNL

EVALUATION OF PROPOSED SHALLOW-LAND BURIAL SITES

USING THE PRESTO-II METHODOLOGY AND CODE⁺

D. E. Fields, I. Uslu*, and M. G. Yalcintas

Health and Safety Research Division
Oak Ridge National Laboratory
Oak Ridge, Tennessee 37831

*Turkish Atomic Energy Authority

ABSTRACT

PRESTO-II (Prediction of Radiation Effects from Shallow Trench Operations) is a computer code designed to evaluate possible doses and risks (health effects) from shallow-land burial sites. The model is intended to serve as a non-site-specific screening model for assessing radionuclide transport, ensuing exposure, and health impacts to a static local population for a 1000-year period following the end of disposal operations. Human exposure scenarios include normal releases (including leaching and operational spillage), human intrusion, and limited site farming or reclamation. Pathways and processes of transport from the trench to an individual or population include ground-water transport, overland flow, erosion, surface water dilution, suspension, atmospheric transport and deposition, inhalation, external exposure, and ingestion of contaminated beef, milk, crops, and water. The proposed waste disposal area in Koteyli, Balikesir, Turkey, has been evaluated using the PRESTO-II methodology. The results have been compared to those obtained for the Barnwell, South Carolina, site. Dose estimates for both sites are below regulatory limits, for the release and exposure scenarios considered. The doses for the sites are comparable, with slightly higher estimates obtained for the Turkish site.

INTRODUCTION

The Turkish Government is in the process of planning two nuclear reactors in Turkey. Studies have begun to develop for improved control of low level wastes (LLW) in Turkey before establishments of these reactors. In this study, PRESTO-II (Prediction of Radiation Exposures from Shallow Trench Operations) computer code (1) is used to assess the risk associated with the shallow land disposal of low level radioactive waste (LLW) in various sites in Turkey. PRESTO-II is a computer code designed for the evaluation of possible health effects from shallow-land and, waste disposal trenches.

⁺Research sponsored by Office of Health and Environmental Research, U.S. Department of Energy, under contract DE-AC05-84OR21400 with the Martin Marietta Systems, Inc.

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A preliminary simulation using the PRESTO-II computer code has been run for the site in Koteyli-Balikesir, Turkey (2). This example simulation was performed using the same radionuclide data set believed representative of the LLW disposal facility in Barnwell, South Carolina. Site environmental variables were selected to typify credible worst case exposure scenarios. Radionuclide inventories are primarily based on estimated waste composition rather than measured values.

THE PRESTO-II METHODOLOGY

PRESTO-II (Prediction of Radiation Effects from Shallow Trench Operations) is a computer code (1) designed for the evaluation of possible doses and risks (health effects) from shallow-land and, waste-disposal trenches. The model is intended to serve as a non-site-specific screening model for assessing radionuclide transport, ensuing exposure, and health impacts to a static local population for a 1000-year period following the end of disposal operations. Human exposure scenarios include normal releases (including leaching and operational spillage), human intrusion, and limited site farming or reclamation. Pathways and processes of transit from the trench to an individual or population include ground-water transport, overland flow, erosion, surface water dilution, suspension, atmospheric transport, deposition, inhalation, external exposure, and ingestion of contaminated beef, milk, crops, and water.

The PRESTO-II methodology and code have been well-documented. A code listing and example input for each of three example sites have been published (3). Also included in this report is a sample run, and using the 1981 version of the RADRISK data set (4). The code has also been made available through the Radiation Shielding and Information Center (RSIC) in Oak Ridge. One component of the PRESTO-II code is the DARTAB model, which has been separately documented (5). Still another component is the RADRISK data set (6). The DARTAB code is also available from RSIC.

The PRESTO-II code tracks radionuclide transport through surface and subsurface pathways and human exposures through external exposure, inhalation, and ingestion, with a resolution of 1 year (some processes are simulated with higher temporal resolution, and the results applied within portions of the code having a 1 year resolution). The methodology is mechanistic and physical transport processes are modeled separately and in detail. Valid results require adequate knowledge of site variables. Source terms are initial radionuclide distributions in the atmosphere, streams, land surfaces, and in subsurface trenches. Human exposure scenarios include migration of radioactivity from the trench in hydrologic and atmospheric environmental pathways to food and drinking water. At-risk individuals and populations include those ingesting contaminated on-site or off-site food and water, breathing contaminated off-site or on-site air, undergoing

external exposure to ground surface contamination, or living in an on-site basement.

Water, principally from precipitation, is often a primary transport medium for radioactivity from LLW stored in shallow trenches. Precipitation or irrigation water falling on the waste disposal site may either infiltrate the soil or trench cap, run off the surface, or evaporate, and radionuclides may be transported from a LLW disposal trench by groundwater or by precipitation runoff. Runoff also causes erosion of the soil surface and erode the trench cap. Water percolating downward through the trench to the subtrench soil zone may ultimately enter an aquifer. Radionuclides that finally reach the aquifer will generally be transported more slowly than the characteristic flow velocity of water in the aquifer because the radionuclides interact with the solid materials in the aquifer. Some of the radionuclides which enter the aquifer may eventually reach irrigation or drinking wells or surface streams. Contaminated water from the trench may overflow onto the surface soil. Once overflow has occurred, radionuclides may be transported by runoff water to nearby streams and become available for human consumption via irrigation or drinking. Humans may also be exposed to radionuclides transported from LLW sites by atmospheric processes.

Atmospheric transport processes are included in the PRESTO-II methodology. Radionuclides left on the soil surface by trench overflow, by spillage during disposal operations, or by complete removal of the trench cap may be suspended in the atmosphere and transported downwind where they may be inhaled or deposited on vegetation and soil. In the case of deposition, the radioactivity may produce external exposure to humans or may enter into the food chain and result in radioactivity in crops, meat, and milk. For atmospheric transport calculations, the total population is assumed to reside within the same 22.5-degree sector. User-specified parameters give the fraction of the year that the wind blows into that sector. A user option allows the results of the atmospheric dispersion calculation in the code to be replaced by an externally calculated dispersion coefficient which considers several population centers.

Processes considered in calculating individual or population exposure include: groundwater transport, precipitation runoff, trench water overflow and seepage, chemical exchange, trench cap erosion, stream dilution, and resuspension and atmospheric dispersion of contaminated soil followed by inhalation or oral and external exposure subsequent to deposition on crops and land.

The termination of LLW disposal operations (as associated with final trench closure) is the starting time for the total assessment period considered by the code. The user specifies the total length of the assessment period, from 1 to 1000 years. The health effects for a user-specified length of time within this assessment period are calculated. The averaging time for health effects can be as short as any single year of the assessment period or as long as the entire assessment period. The maximum concentration of each radionuclide and the year of this maximum for each of the four major exposure pathways for each nuclide is calculated. The initiation time and period for mechanical suspension of the surface soil by farming is specified by the user. The user can also specify the time at which the trench cap begins to fail and the temporal profile of this failure, which results in exposure of the trench contents. The primary code time step is fixed at one year, while the printout interval is user-specified.

The resident intruder scenario assumes that an intruder digs into the disposal trench while building a residence. The individual will receive external exposure to the buried radionuclides due to time spent in the basement of the residence, which is assumed to have walls made of trench material. The user-specified length of residency, time in the assessment period when the residence is first occupied, and the composition of the initial trench inventory will all contribute to the dose from external exposure.

Farming the site after loss of institutional control is treated as a separate intrusion scenario. By farming the site a farmer will be affected by most of the hydrologic and atmospheric transport processes described above. In contrast to an off-site population, however, a larger portion of the farmer's food may consist of crops grown in the contaminated zone near the trench. The water used by the farmer for irrigation, drinking, and livestock may be taken from directly beneath the trench or from a nearby stream and thus contain a much higher concentration of radioactivity than water used by the off-site population. The farming process may also mechanically suspend contaminated soil in the atmosphere. Such mechanical suspension may impact both the farmer and a downwind population.

Annual-average concentrations of each radionuclide in environmental media (such as well water or the atmosphere) over the assessment period are used to calculate radionuclide concentrations in foodstuffs. Foodstuff information and human ingestion and breathing rates are utilized to calculate the annual average radionuclide intake per individual in the population by ingestion and inhalation. These intake data are used by the exposure and risk submodels to estimate dose rate and health risk. Each member of the population is assumed to eat the same quantities of food (vegetables, beef, and milk). These foods are assumed produced on the same fields and spray irrigated with contaminated water. Contaminated water is assumed drunk by

beef and dairy cattle. The code user may independently specify the fractions of water taken from wells or streams and used for human consumption, for irrigation, or for livestock consumption. The health risk estimation methodology assumes that each member of the population is a member of a cohort that is exposed to constant, annual-averaged radionuclide concentration levels. The PRESTC-II model is most appropriately used as a screening model, and site specific codes should be considered in cases where PRESTO-II numerical results fall close to reference values used for decision making.

The code contains algorithms to track both radionuclide amounts and radionuclide concentrations in well water. This approach permits the code to correctly conserve radionuclide mass. Radionuclides are first withdrawn from the well for human ingestion in an amount appropriate to the number of exposed persons specified, and remaining radionuclides may be withdrawn to be used for irrigating crops and watering livestock. A second reason to account for both amount and concentration of radionuclides at the well is to insure that the amount withdrawn at the well (based on the calculated concentration at the well) does not exceed the amount available. As a result of this calculation, the dose and risk calculated for a single individual may exceed the dose and risk calculated for individual members of a large population taking water from a well.

PRESTO-II, like any complex computer code, may be misapplied. Misapplication may consist of trying to apply the code to examine a site where one or more modeling assumptions are invalid, or of choosing values of input parameters that do not accurately reflect variables such as radionuclide inventory, site meteorology, surface and subsurface hydrology and geology, and future population demographics. One serious misapplication of the PRESTO-II methodology would be use of carelessly chosen k_d values to determine hydrologic transport. Element-specific values of k_d vary widely as sites, chemical forms, and other waste components are changed.

Some release and transport scenarios, such as those necessary to consider major meteorological changes, mining of the trench contents, in-situ combustion of trench wastes, and intrusion and radionuclide transport by burrowing animals or plant roots, are not considered in the PRESTO-II model and code. The user must make significant changes to the code and the input data in order to consider those scenarios. If such mechanisms are added to a version of the PRESTO-II model, the authors of this report would appreciate being informed, and will consider adding these capabilities to their version of the code for future distribution.

RESULTS AND DISCUSSION

Table 1 summarizes the simulation results of the dose and health effects for Barnwell site and Koteyli site associated with the radionuclide data set believed representative of the LLW disposal facility in Barnwell, South Carolina. These simulation results must be generally regarded as estimates based on the assumptions about waste stream composition, disposal methodology, and site geography. The simulation results presented in Table 1 indicate that relative human radiological impacts for these sites according to the relative gross radioactivity of the streams. Lower consequences are predicted for the Barnwell, South Carolina site, relative to the Koteyli, Turkey site but this conclusion results largely from the assumption that the Koteyli, Turkey site may eventually be used for farm land. If the Koteyli, Turkey site were not irrigated, predicted consequences for this site would be considerably lessened.

Table 1. Summary of population doses and health effects for Barnwell Site and Koteyli site associated with the radionuclide data set believed representative of the LLW disposal facility in Barnwell, South Carolina

| | Koteyli | Barnwell |
|----------------------------|-----------------------|-----------------------|
| Lifetime fatal cancer risk | 1.68×10^{-4} | 0.56×10^{-5} |
| Health Effects (Deaths/y) | 2.04×10^{-2} | 5.53×10^{-4} |

The sum of all radiological impacts from exposure of the local population of 7033 persons to contaminants in all low-level waste disposal area near Barnwell is 5.53×10^{-4} deaths/y. By comparison, the current annual death rate from cancer for a representative population of 7033 is 13 persons (7). the waste disposal-associated death rate is less than the background cancer death rate by a factor of 4.2×10^{-5} .

CONCLUSION

Preliminary simulations have been performed of release and transport of radionuclides from a proposed low-level radioactive waste disposal site in Turkey. We expect that the results of such simulations will be useful in providing estimates of the consequences of alternative disposal sites and practices.

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**Disposal Barriers That Release Contaminants
Only by Molecular Diffusion**

Presented by:

David E. Daniel, University of Texas

DISPOSAL BARRIERS THAT RELEASE CONTAMINANTS ONLY BY MOLECULAR DIFFUSION - David E. Daniel, the University of Texas, Department of Civil Engineering, Austin, Texas; Charles D. Shackelford, the University of Texas, Department of Civil Engineering, Austin, Texas

ABSTRACT

Engineered barriers that retard the release of contaminants from land disposal facilities have traditionally been designed solely on the permeability of the material. However, even barriers with a permeability of zero will not stop the release of contaminants because flow will still occur from molecular diffusion of contaminants across the barrier. Many engineers and scientists have ignored the release of contaminants via molecular diffusion either out of lack of knowledge of this transport process or in the belief that rates of release would be insignificant. However, with increasing concern over the effects of groundwater contamination and improved techniques for detecting minute concentrations of pollutants in groundwater, there is heightened realization that all transport processes, including molecular diffusion, must be considered.

A barrier which allows escape of pollutants only by molecular diffusion is the best that can be built. There are several ways to make a barrier essentially a diffusion barrier, including the use of extremely low-permeability materials and inward hydraulic gradients. The analysis of release rates associated with diffusion is relatively straightforward because the diffusion coefficient is known fairly accurately for many materials. The uncertainty in the diffusion coefficient is much less than the typical uncertainty in permeability. Thus, not only are barriers that release contaminants only by molecular diffusion the best engineered barriers possible, but their performance is also more predictable than barriers designed solely upon permeability.

TYPES OF BARRIERS

Up until about a decade ago, uncontrolled dumping of waste in landfills and lagoons was not uncommon. In recent years, engineers and scientists have tried to minimize groundwater contamination near waste disposal sites by installing engineered barriers around and beneath the waste. The barriers have usually involved liners or cutoff walls (Fig. 1). Most liners are constructed of earth, plastic, rubber, asphalt, or concrete. Cutoff walls may be formed by grouting or driving steel sheet piling, but more commonly the walls are formed by excavating a trench and backfilling it with low-permeability materials such as soil or a soil-cement mix (e.g., slurry walls).

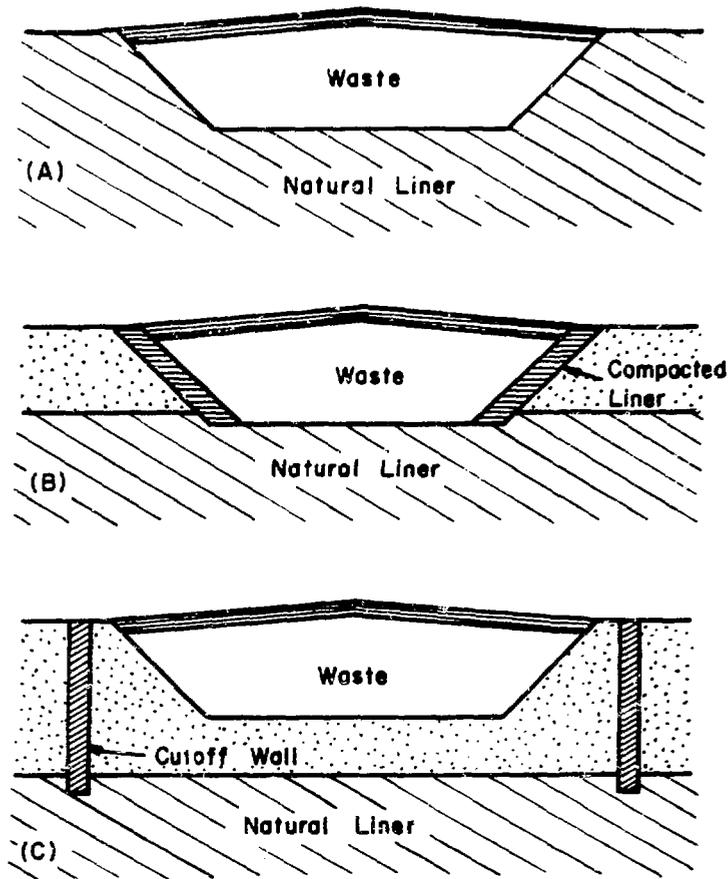


Fig. 1. Examples of engineered barriers

With such barriers, the design has almost always been based on the permeability, or hydraulic conductivity, of the barrier material. However, the permeability of barrier materials is very difficult to predict or determine accurately. As a result, predictions about the probable performance of engineered barriers are fraught with considerable uncertainty.

MOLECULAR DIFFUSION

Diffusion is a process in which solutes in a solution flow in response to a gradient in concentration. The solution itself need not flow for diffusive transport to occur. An example of solute transported purely by molecular diffusion is given in Fig. 2. In this case, there is no advective flow because the hydraulic gradient is zero. However, since there is a gradient in solute concentration, there will be solute transport via molecular diffusion.

The process of diffusion is usually assumed to occur in accord with Fick's first and second laws. For free solutions (i.e., no porous matrix), Fick's first law states that one-dimensional diffusion occurs as follows:

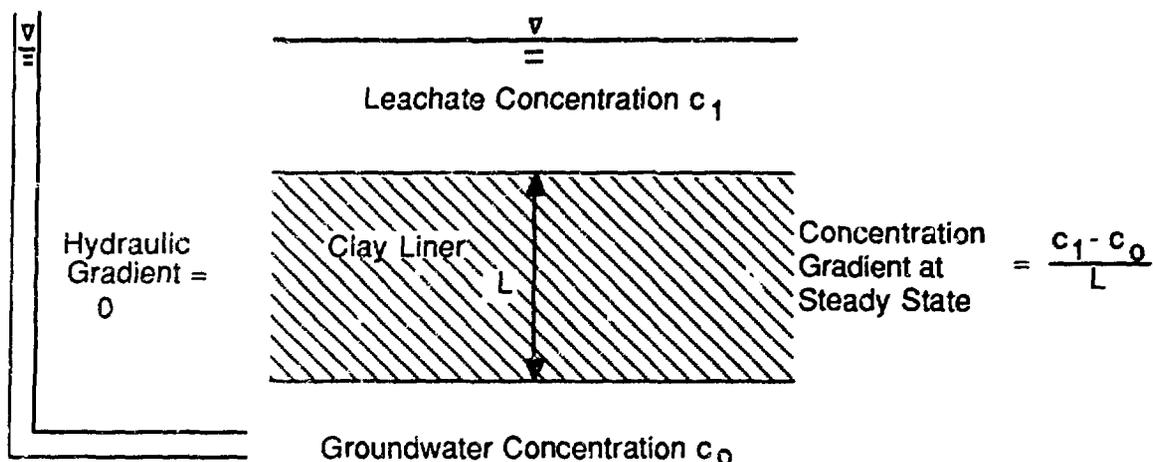


Fig. 2. Example of a clay liner system in which molecular diffusion is the transport mechanism

$$J_d = -D_o \frac{\partial c}{\partial x} \quad (1)$$

where J_d is the diffusional mass flux (mass transported per unit area perpendicular to the direction of transport, per unit time, or $M L^{-2} T^{-1}$), D_o is the free-solution diffusion coefficient ($L^2 T^{-1}$), c is the concentration of a solute ($M L^{-3}$), and x is the direction in which the diffusion is occurring (L).

The driving force for diffusion of individual ions or molecules is the gradient in chemical potential. Also, the limiting velocity of a particle may be defined as the product of the absolute mobility of the particle and its driving force. When these relations are combined with the definition of mass flux, the following expression results:

$$J_d = \frac{uRT}{N} \frac{\partial c}{\partial x} \quad (2)$$

The expression for the free-solution diffusion coefficient at infinite dilution is:

$$D_o = \frac{uRT}{N} \quad (3)$$

where R is the Universal Gas Constant ($8.134 J mol^{-1} K^{-1}$), T is the absolute temperature (K), N is Avogadro's number ($6.022 \times 10^{23} mol^{-1}$) and u is the

absolute mobility of a particle ($LT^{-1}F^{-1}$). This expression is known as the Nernst-Einstein equation (Jost, 1960). By combining Eq. 3 with expressions relating the absolute mobility to the limiting ionic equivalent conductivity (Robinson and Stokes, 1965) and to the viscous resistance of the solvent molecules, i.e., Stokes' Law (Bird et al., 1960), two additional expressions for D_o result:

$$D_o = \frac{RT\lambda^\circ}{F^2|z|} \quad (4)$$

and

$$D_o = \frac{RT}{6\pi N\eta r} \quad (5)$$

where F is the Faraday (96,490 Coulombs), $|z|$ is the absolute value of the ionic valence, λ° is the limiting ionic equivalent conductivity [$LT \text{ equiv}^{-1}$], η is the absolute viscosity of the solution [FTL^{-2}], and r is the molecular or hydrated ionic radius [L]. Equations 4 and 5 are the well-known Nernst and Einstein-Stokes equations, respectively. Although the above equations apply only to ideal conditions, i.e., infinite dilution and the assumptions inherent therein, they do provide an indication of some of the factors affecting D_o .

The usefulness of Eq. 4 is that limiting values of D_o (known as self-diffusion coefficients) can be calculated provided the associated λ° values are known. These calculations have been made for a number of ions using λ° values from Appendix 6.2 of Robinson and Stokes (1965) and the results are indicated in Table 1. A similar table has been provided by Quigley et al. (1987).

The values for D_o reported in Table 1 should be considered to be the maximum values attainable under ideal conditions (i.e., microscopic scale, infinite dilution, etc.). Under non-ideal conditions (e.g., macroscopic scale, concentrated solutions), a number of effects, negligible for ideal conditions, become important. A good example of one of these effects is given by Robinson and Stokes (1965). When two oppositely charged ions are diffusing in solution, a microscopic charge separation or electrical potential gradient is set up between the ions due to their different mobilities. The effect of this charge separation is to speed up the slower moving ion and to slow down the faster moving ion. Since, on a macroscopic scale, electroneutrality must be satisfied, the resultant speeds of both ions must be equal. This electrical potential effect is responsible, in part, for the differences between the simple electrolyte diffusion values, shown in Table 2, and their respective

TABLE 1. CALCULATED SELF-DIFFUSION COEFFICIENTS FOR REPRESENTATIVE IONS AT INFINITE DILUTION IN WATER AT 25°C.

| Anions | $D_0 \times 10^{10} \text{ m}^2/\text{s}$ | Cations | $D_0 \times 10^{10} \text{ m}^2/\text{s}$ |
|-------------------------------|---|------------------|---|
| OH ⁻ | 52.76 | H ⁺ | 93.07 |
| F ⁻ | 14.74 | Li ⁺ | 10.27 |
| Cl ⁻ | 20.31 | Na ⁺ | 13.33 |
| Br ⁻ | 20.79 | K ⁺ | 19.56 |
| I ⁻ | 20.43 | Rb ⁺ | 20.70 |
| HCO ₃ ⁻ | 11.84 | Cs ⁺ | 20.54 |
| Acetate | 10.88 | Be ²⁺ | 5.98 |
| SO ₄ ²⁻ | 10.64 | Mg ²⁺ | 7.05 |
| CO ₃ ²⁻ | 9.22 | Ca ²⁺ | 7.92 |
| | | Sr ²⁺ | 7.90 |
| | | Ba ²⁺ | 8.46 |
| | | Pb ²⁺ | 9.245 |
| | | Cu ²⁺ | 7.13 |
| | | Zn ²⁺ | 7.02 |

*Note: D_0 values calculated from the Nernst equation.

TABLE 2. REPRESENTATIVE VALUES OF FREE-SOLUTION DIFFUSION COEFFICIENTS (CRC HANDBOOK OF CHEMISTRY AND PHYSICS, 66th EDITION, 1985-86)

| Solute | Concentration | $D_0 \times 10^9, \text{ m}^2/\text{s}$ |
|-------------------|---------------|---|
| HCl | 0.1 M | 3.1 |
| LiCl | 0.1 M | 1.3 |
| NaCl | 0.1 M | 1.5 |
| CaCl ₂ | 0.1 M | 1.1 |
| Glucose | 0.4% | 0.7 |
| Citric Acid | 0.1 M | 0.7 |

component self-diffusion coefficients given in Table 1. Other effects responsible for the difference in D_0 values under non-ideal conditions include solute-solute and solute-solvent interactions.

Solutes will not diffuse as quickly in soil as they will in free solutions. For soil, Eq. 1 becomes

$$J_d = -(\tau D_0) \theta \frac{\partial c}{\partial x} \quad (6)$$

or

$$J_d = -D^* \theta \frac{\partial c}{\partial x} \quad (7)$$

where τ is a tortuosity factor (dimensionless), θ is the volumetric moisture content of the soil (dimensionless), and D^* is the effective diffusion coefficient (L^2T^{-1}). It should be noted that some researchers include θ in the tortuosity factor. The volumetric moisture content is equal to the product of the porosity, n , and the degree of saturation, S_r .

In general, the tortuosity factor is considered to account for the increased distance of flow and the more tortuous pathways experienced by solutes diffusing through soil. It is expressed as

$$\tau = \left(\frac{x_\theta}{x} \right)^2 \quad (8)$$

where x (L) is the straight-line distance between two points defining the flow path, and x_θ (L) is the actual, effective distance of flow through the soil between the same two points. Since $x_\theta > x$, $\tau > 1$. Typical values of τ reported in the literature are provided in Table 3. Many of the values of τ in Table 3 are based on results of diffusion tests performed with unsaturated soils.

In reality, there may be other effects associated with the tortuosity factor. For example, Olsen et al. (1965) considered two other effects, the variation in the viscosity of the solvent within the pore space, represented by the factor, α , and the negative adsorption (i.e., exclusion) of ions, represented by the factor, γ . They combined all these effects (including the volumetric moisture content) into one factor and termed it the "transmission factor," or

TABLE 3. REPRESENTATIVE TORTUOSITY FACTORS TAKEN FROM THE LITERATURE.

| τ Values | Soil | Tracer | Reference |
|---------------|--|------------------|-------------------------------|
| 0.08-0.12 | 50% Sand/Bentonite | ^{36}Cl | Gillam & Sharma (1985) |
| 0.04-0.49 | 0,10,25,50,75% Bentonite/Sand | ^{36}Cl | Johnston et al. (1984) |
| 0.01-0.22 | " | ^3H | " |
| 0.59-0.84 | 0,5,10,15,25,50,100% Bentonite/Sand | ^{36}Cl | Gillham et al. (1984) |
| 0.33-0.70 | " | ^3H | " |
| 0.20-0.33 | Silty Clay Loam, Clay (1982) | Br | Barracough & Tinker |
| 0.08-0.31 | Silty Clay Loam, Sandy Loam | Br | Barracough & Tinker (1981) |
| 0.033-0.539 | 6 Natural Soils | ^{65}Zn | Warncke & Barber (1972a) |
| 0.01-0.58 | 5 Natural Soils | ^{36}Cl | Warncke & Barber (1972b) |
| 0.0032-0.023 | Loam | ^{86}Rb | Patil et al. (1963) |
| 0.027-0.31* | Loam, Silty Clay Loam, Clay | Cl | Porter et al. (1960) |
| 0.04-0.45 | 75 μ & 200 μ Glass Beads | ^{86}Rb | Klute & Letey (1958) |

*Transmission Factors

$$\tau = \alpha\gamma \left(\frac{x}{x_e} \right)^2 \theta \quad (9)$$

While these and other effects may be present in many situations, it is neither possible nor feasible in most cases to separate them. In short, the tortuosity factors reported in the literature may account for more than just the pore geometry of the porous matrix.

Fick's first law describes steady-state flux of solutes. For unsteady (transient) transport, Fick's second law applies:

$$\frac{\partial c}{\partial t} = D \cdot \frac{\partial^2 c}{\partial x^2} \quad (10)$$

Equation 10 is integrated for appropriate initial and boundary conditions to obtain a description of the solute concentration changes with respect to time and space. Complex error functions facilitate the integration.

An example of the application of Fick's second law is as follows. A 1-m thick clay liner retains leachate containing a particular solute at a concentration of 10,000 mg/L. The underlying ground water is completely free of this solute. The effective diffusion coefficient is 2×10^{-10} m²/s. The resulting distribution of solute in and at the bottom of the liner as a function of time solely due to diffusional transport is illustrated in Fig. 3. The solute distribution was determined from the following solution to Eq. 10 (Crank, 1975) which assumes the leachate concentration is constant with time:

$$\frac{c}{c_0} = \operatorname{erfc} \left(\frac{x}{2 \sqrt{D t}} \right) \quad (11)$$

where erfc is the complementary error function. The concentrations of solute reaching the base of the liner at 10, 20, 40, and 80 years are approximately 50, 460, 1600, and 3200 mg/L, respectively. Since, in some cases, these concentrations exceed allowable values, it is apparent that diffusion of chemicals through fine-grained materials can be an important transport mechanism even over relatively short (20 - 30 years) periods.

ADVECTIVE TRANSPORT

Advective transport of contaminants through porous materials is generally assumed to occur in accordance with Darcy's law in which

$$v = ki = -k \frac{\partial h}{\partial x} \quad (12)$$

where v is the Darcian velocity (L/T), k is the hydraulic conductivity (L/T), i is the dimensionless hydraulic gradient, h is the total hydraulic head (L), and x is the distance along the path of flow (L). The advective flux, J_a , is given by:

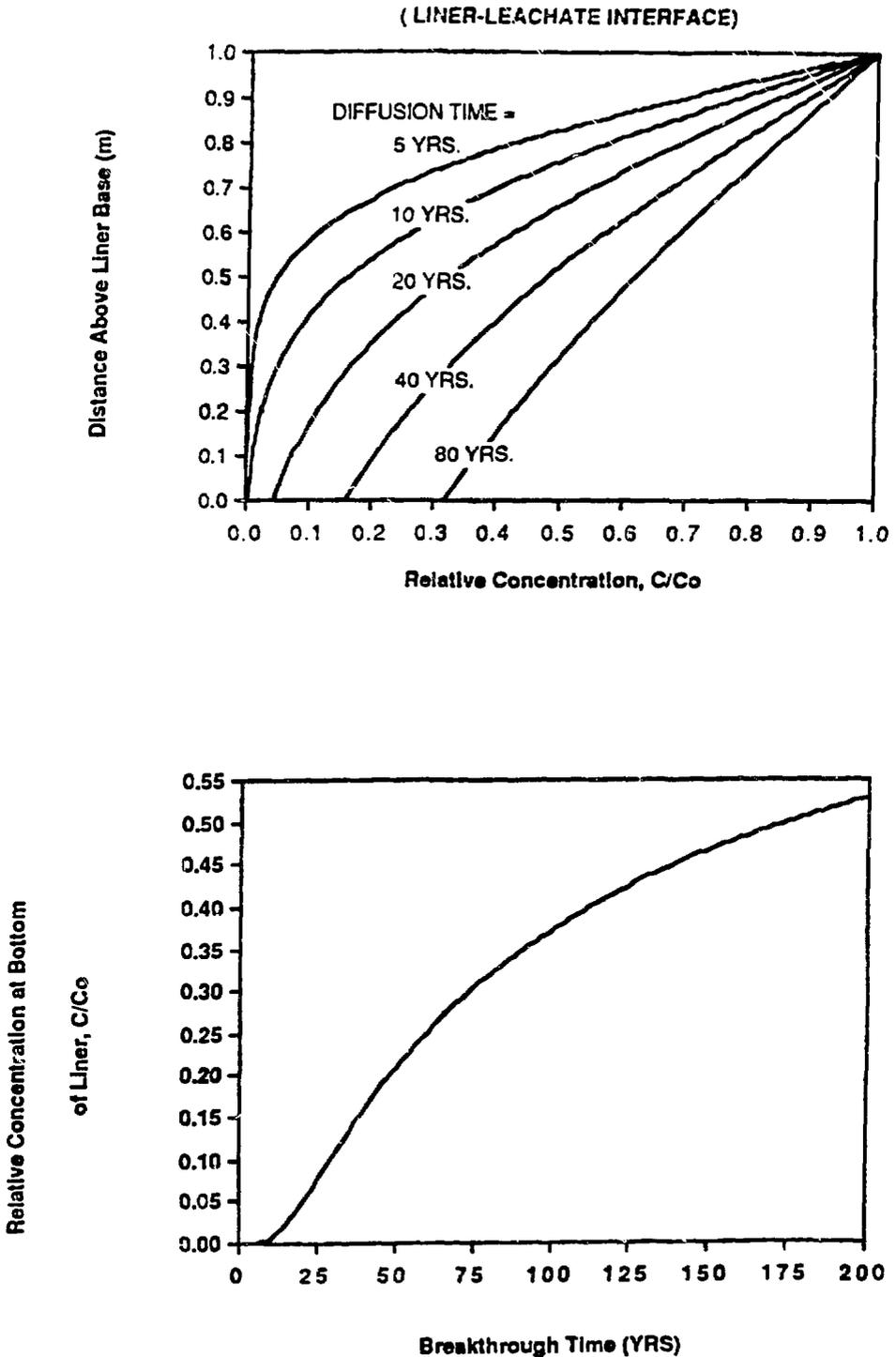


Fig. 3. Concentration profiles for 1-m thick clay liner and $D^* = 2 \times 10^{-10} \text{ m}^2/\text{s}$

$$J_a = v c = n_e v_s c \quad (13)$$

where v_s is the seepage velocity, or average linear velocity along the path of flow, and n_e is the effective porosity, i.e., the volume of pore fluid that is effective in conducting flow divided by the total volume. A comparison of Eqs. 12 and 13 reveals that the seepage velocity is given by:

$$v_s = \frac{v}{n_e} = \frac{ki}{n_e} = -\frac{k}{n_e} \frac{\partial h}{\partial x} \quad (14)$$

Considerable controversy exists over typical values of n_e for relatively impermeable soils. Some have suggested that n_e is more-or-less equal to the total porosity of the soil, n , whereas others suggest that $n_e < n$ because most of the flow occurs through macropores, cracks, fractures, or other features. In clays, dead-end pores, exceedingly small pores, and soil-water sorbed onto the surfaces of clay particles may occupy a significant percentage of the total pore space but contribute very little to flow.

Even more controversy exists over the hydraulic conductivity of relatively impermeable soils. Daniel (1984), Day and Daniel (1985), and Daniel (1987) report data showing how difficult it is to predict the hydraulic conductivity of clayey soils. Other investigators have observed similar problems. As a result, it is very difficult to make accurate predictions of seepage velocities caused by advective flow.

ATTENUATION OF CONTAMINANTS

Contaminants (solutes) may migrate slower than the transporting solution (solvent) for a variety of reasons. Some of the causes of contaminant attenuation in soil include ion exchange, precipitation, biological reactions, and radioactive decay.

Suppose a solution contains two solutes, A and B. Solute A is conservative, viz., is not attenuated by soil; solute B is attenuated. A column test in which there is negligible diffusive flow (just advective flow) is performed and effluent analyses yield the results shown in Fig. 4. We define the "retardation coefficient", R , as follows:

$$R = \frac{Q_B}{Q_A} \quad (15)$$

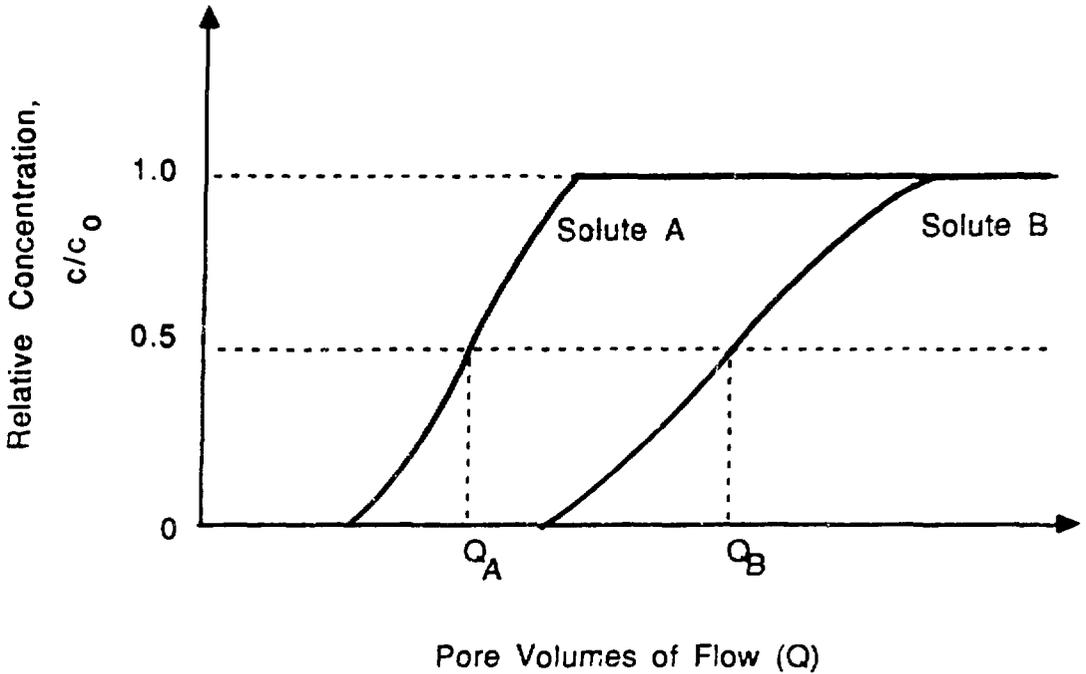


Fig. 4. Breakthrough curves for retarded (B) and unretarded (A) solutes

where Q_A and Q_B are the pore volumes of flow for solutes A and B, respectively, at a relative concentration, c/c_0 , of 0.5. Since $Q_B > Q_A$, $R > 1.0$ for a retarded solute.

The retardation coefficient may also be calculated independently by the following relationship:

$$R = 1 + \frac{\rho_d}{\theta} K_p \quad (16)$$

where ρ_d is the dry bulk density of the soil (ML^{-3}) and K_p is the partition coefficient (L^3M^{-1}). The partition coefficient relates mass of solute sorbed per mass of soil, q , to the concentration of solute in solution, c , at equilibrium. Batch adsorption tests are often used to determine the relationship between q and c over an appropriate range of concentrations. When the q vs. c relationship is constant (i.e., linear isotherm), the partition coefficient is given a specific name, i.e., the distribution coefficient, K_d . Unfortunately, K_p is often dependent upon the equilibrium concentration of the solution (Fig. 5). Nonetheless, it is usually convenient to assume a linear relationship for the purpose of calculating retardation coefficients, as indicated in Fig. 5. The

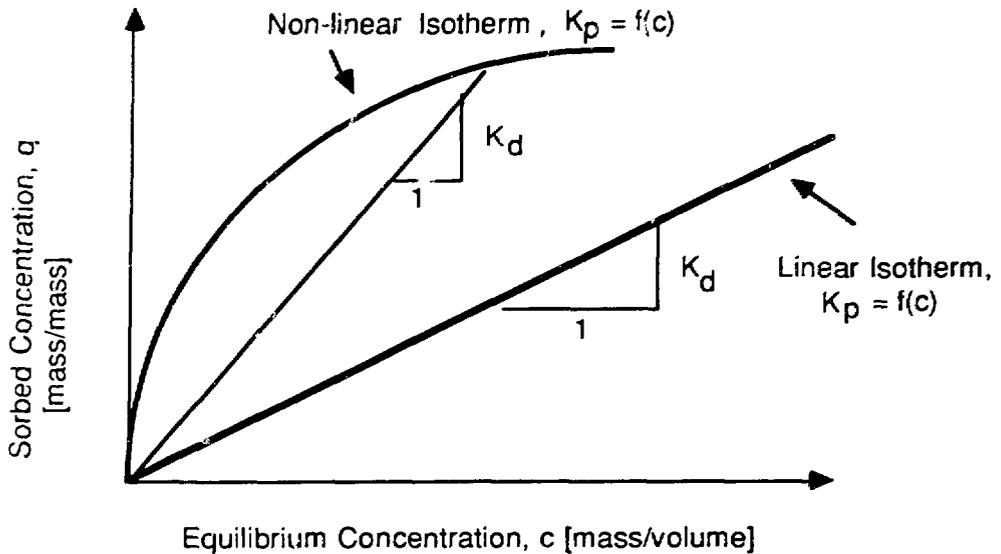


Fig. 5. Typical adsorption relationships for reactive solutes

procedures for performing batch isotherm tests and the factors affecting those procedures are discussed extensively in U.S. EPA (1985).

The sorption of hydrophobic organic pollutants also can be described adequately by Eq. 16 provided the distribution coefficient is defined as follows:

$$K_d = f_{oc} \cdot K_{oc} \quad (17)$$

where f_{oc} is the fraction of organic-carbon in the soil (dimensionless) and K_{oc} is the organic carbon partition coefficient (Karickhoff et al., 1979). The organic-carbon partition coefficient has been empirically correlated with a number of parameters, especially the octanol-water partition coefficient, K_{ow} . These empirical correlations are covered in detail by Griffin and Roy (1984).

EXAMPLE: COMPARISON OF CLAYS AND GEOMEMBRANES

Clay and geomembrane liners are both used to line landfills and lagoons. They have their advantages and disadvantages. Geomembranes have lower hydraulic conductivity and can be constructed to more exacting standards than earthen liners. However, geomembranes are very thin, can be torn or punctured, do not tend to self-heal, and have ill-defined longevity. Earthen liners are much thicker, may undergo some self-healing if damaged, can

attenuate many contaminants, and should test for millennia. On the negative side, clay liners are much more permeable than geomembranes, require a local source of soil, occupy more volume than geomembranes, and are more difficult to construct to precise standards. However, because geomembranes have much lower hydraulic conductivity than clay, geomembranes are considered by many to be superior to clay. But are they really better when we also consider diffusion?

An interesting question is how the performance of geomembrane liners compares to clay liners. Some calculations may help to answer this question. For example, consider two liners, a geomembrane and a compacted-clay liner, each with the following properties:

| <u>Property</u> | <u>Geomembrane</u> | <u>Clay</u> |
|--|-----------------------|-----------------------|
| porosity | 0.10 | 0.50 |
| hydraulic conductivity, k (m/s) | 1.0×10^{-14} | 1.0×10^{-9} |
| diffusion coefficient, D^* (m^2/s) | 3.0×10^{-14} | 2.0×10^{-10} |
| thickness (m) | .00152 (60 mils) | 0.91436 (3 feet) |
| hydraulic gradient, i | 100 | 1.16 |

These values are assumed, and some discussion of their magnitudes is warranted. The hydraulic conductivity and thickness of the clay are the maximum and minimum values, respectively, currently being allowed by the U.S. EPA for double-liner systems. The clay porosity is a representative, average value, and the diffusion coefficient for the clay is representative of values currently being measured at the University of Texas. The thickness of the geomembrane is typical of current U.S. practice. The diffusion coefficient for the geomembrane is about the same as a value reported by Lord and Koerner (1984) based on water adsorption tests. This diffusion coefficient for the geomembrane is from two to four orders of magnitude less than other reported values which were measured using radioactive tracers (Hughes and Monteleone, 1987; Lord and Koerner, 1984). Also, the hydraulic conductivity for the geomembrane is thought to be conservative. Finally, the hydraulic gradient in each case represents 0.152 m (0.5 ft) of ponded leachate assuming atmospheric pressure at the base of the liner and no suction within the liner.

If the values stated above are utilized in conjunction with the well-known Ogata (1970) solution to the differential equation describing solute transport, breakthrough curves may be calculated and compared. This calculation has been performed and the results are presented in Fig. 6. Note that the breakthrough time (at $c/c_0 = 0.5$) for the geomembrane is exceedingly fast, about 1.7 years, especially when compared with the breakthrough of 11.5 years for the clay liner. This difference results even though the geomembrane has a hydraulic conductivity which is 5 orders of magnitude less than the clay

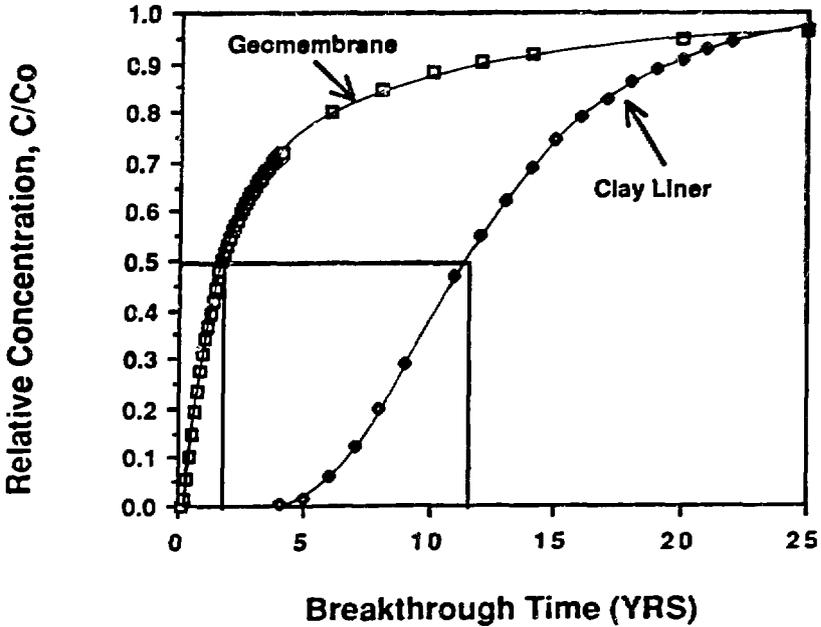


Fig. 6. Solute breakthrough curves for geomembranes and clay liners

and an effective diffusion coefficient which is about 4 orders of magnitude less. The reason for this difference is the relative thickness of the two liners and rapid diffusional transport across a very short distance through the geomembrane.

BARRIERS DESIGNED AS DIFFUSION BARRIERS

The total flux, J , of contaminants breaching a barrier is the sum of the advective and diffusional fluxes given by Eqs. 13 and 7, respectively, or:

$$J = J_a + J_d = vc - D \theta \frac{\partial c}{\partial x} \quad (18)$$

A barrier will release contaminants almost exclusively via molecular diffusion if the advective flux is much less than the diffusional flux. The desirability of designing a barrier to release contaminants only by diffusion should now be clear; the question is how to effect such a design.

One way to make a diffusion barrier is to utilize materials having exceedingly low hydraulic conductivity. Geomembranes, asphaltic materials, and clay

soils may meet such requirements. Our experience indicates that for hydraulic gradients on the order of 1, materials with hydraulic conductivities less than roughly 1×10^{-8} cm/s release contaminants primarily by molecular diffusion. Thus, it is desirable to design barriers to have this magnitude of hydraulic conductivity. For barriers that release contaminants only by molecular diffusion, the hydraulic conductivity has no bearing on the rate of release. Accordingly, it is a waste of time and money to try to achieve a lower hydraulic conductivity once the conductivity is low enough so that release of contaminants is primarily via diffusion.

The advective component of flow may also be minimized by reducing the hydraulic gradient. For cutoff walls, this may be accomplished by pumping ground water and producing a gradient toward the source of groundwater contamination. For landfills, leachate removal will minimize the gradient. For lagoons, an intermediate barrier underlain by a drainage system may be needed.

One factor that many designers fail to recognize is the importance of the thickness of the barrier. Thick barriers reduce the concentration gradient and increase the time required for contaminants to diffuse through the barrier. This was illustrated in the earlier example where a geomembrane was compared to a clay liner.

CONCLUSIONS

Engineered barriers can slow the movement of pollutants out of land disposal facilities in several ways. If the advective velocity is low, release will be primarily by molecular diffusion. Attenuation processes also work to slow the transport of many contaminants. Barriers that cause pollutants to be released almost entirely by molecular diffusion represent the best barriers achievable. Use of thick barrier materials will maximize the breakthrough time of contaminants that diffuse through the barrier. Thin barriers with exceedingly low permeabilities will not necessarily outperform thicker, more permeable liners. In fact, if diffusion is the dominant mechanism of release, the thicker, more permeable barrier may actually outperform the thinner barrier with lower permeability.

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Allowable Residual Contamination Levels of Radionuclides in Soil from Pathway Analysis

Presented by:

J. E. Nyquist, ORNL

Allowable Residual Contamination Levels of Radionuclides in Soil from Pathway Analysis

J. E. Nyquist and C. F. Baes III

The Remedial Action Program (RAP) at Oak Ridge National Laboratory will include well drilling, facility upgrades, and other waste management operations likely to involve soils contaminated with radionuclides. A preliminary protocol and generalized criteria for handling contaminated soils is needed to coordinate and plan RAP activities, but there exists only limited information on contaminate nature and distribution at ORNL RAP sites. Furthermore, projections of long-term decommissioning and closure options for these sites are preliminary.

We have adapted a pathway analysis model, DECOM (Till and Moore 1986), to quantify risks to human health from radionuclides in soil and used it to outline preliminary criteria for determining the fate of contaminated soil produced during RAP activities. We assumed that the site could be available for unrestricted use immediately upon decontamination. The pathways considered are consumption of food grown on the contaminated soil, including direct ingestion of soil from poorly washed vegetables, direct radiation from the ground surface, inhalation of resuspended radioactive soil, and drinking water from a well drilled through or near the contaminated soil.

We will discuss the assumptions and simplifications implicit in DECOM, the site-specific data required, and the results of initial calculations for the Oak Ridge Reservation.

ALLOWABLE RESIDUAL CONTAMINATION LEVELS OF RADIONUCLIDES IN SOIL FROM PATHWAY ANALYSIS

J. E. Nyquist, Health and Safety Research Division, C. F. Baes III, Environmental Sciences Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee*

STATEMENT OF THE PROBLEM

Remedial actions at Oak Ridge National Laboratory (ORNL) will include well drilling, facility upgrades, and other waste management operations involving soils contaminated with radionuclides. Planners and program managers in ORNL's Remedial Action Program (RAP) will need a way to determine what health risks remain after a proposed cleanup. How much soil will have to be removed? Will 50 or 100 years of institutional control eliminate most of the risk through radioactive decay? Which radionuclides pose the greatest risk and by what pathways might they reach man?

For most radionuclides released into the environment, current regulatory standards (in some instances no applicable standards exist) are based on the concept of limiting the dose from ionizing radiation to humans. Doses to potentially exposed individuals or populations are estimated using models that predict exposures to radionuclides via multiple pathways (e.g., external exposure, inhalation of radionuclides in air, and ingestion of radionuclides in food and water) and calculated doses from those exposures.

We need a method which incorporates models and approaches consistent with those taken by the regulatory agencies [e.g., the Environmental Protection Agency (EPA)] and with the current recommendations of the International Commission on Radiological Protection (ICRP) models. But to be useful, the models must also be flexible enough to encompass the diversity of situations and applications expected to be encountered in the ORNL RAP, without being too complicated for use by planners and program managers.

*Research sponsored by Division of Facility & Site Decommissioning Projects, U.S. Department of Energy, under contract DE-AC05-84OR21400 with Martin Marietta Energy Systems, Inc.

The submitted manuscript has been authored by a contractor of the U.S. Government under contract No. DE-AC05-84OR21400. Accordingly, the U.S. Government retains a nonexclusive, royalty-free license to publish or reproduce the published form of this contribution, or allow others to do so, for U.S. Government purposes.

GENERAL APPROACH

The uncertainty regarding radionuclide distributions among RAP sites and long-term decommissioning and closure options for these sites requires a flexible approach capable of handling different levels of contamination, dose limits, and closure scenarios. This requirement led to the identification of a commercially available pathway analysis model, DECOM (Till and Moore 1986), which had been used previously in support of remedial activities involving contaminated soil at the Savannah River Plant. The DECOM computer code, which estimates concentrations of radionuclides uniformly distributed in soil that correspond to an annual effective dose equivalent (EDE), is written in BASIC and runs on an IBM PC or compatible microcomputer.

We obtained the latest version of DECOM and modified it to make it more user friendly and applicable to the ORNL RAP. Some modifications involved changes in default parameters (Table 1) or changes in models based on approaches (or anticipated approaches) used by the EPA in regulating remedial actions for hazardous substances under the Comprehensive Environmental Response, Compensation, and Liability Act of 1980 (CERCLA or "Superfund"), as amended by the Superfund Amendments and Reauthorization Act of 1986 (SARA), or under the Resource Conservation and Recovery Act of 1976 (RCRA), as amended by the Hazardous and Solid Waste Amendments of 1984 (HSWA). In addition, we created a version of DECOM as a LOTUS spreadsheet, using the same models as the BASIC version of DECOM.

In the following sections we discuss the specific modeling approaches taken, the regulatory framework that guided our efforts, the strengths and limitations of each approach, and areas for improvement. We also demonstrate how the LOTUS version of DECOM can be applied to specific problems that may be encountered during ORNL RAP activities.

DECOM (BASIC)

In the BASIC version of DECOM, two modes are available to the user. In Mode 1, activities are calculated under the assumption that no data are available regarding the concentration of radionuclides as a function of depth. The user is prompted for the radionuclides to be considered, their relative fractions, pathways to be considered, the EDE standard, and various site-specific parameter values. At each point, the user is given the opportunity to change various default values and, before final calculations, to reconsider initial responses. DECOM then prints on the screen the uniform soil concentrations that would meet the standard and the percentage contributions from each pathway for each radionuclide considered. In Mode 2, the concentration of each radionuclide in soil is entered for depth increments of 15 cm. These values are

Table 1. Default Input Values for DECOM
(Consumption values are dry weights)

| | |
|---|--------------------------|
| Soil bulk density (food pathway) | 1.4 g/cm ³ |
| Ground bulk density (external exposure pathway) | 1.7 g/cm ³ |
| Thickness of contaminated layer | 100 cm |
| Area of contaminated region | ∞ |
| Depth of plowed layer | 15 cm |
| Vegetation consumption by milk cattle | 18 kg/d |
| Vegetation consumption by beef cattle | 8 kg/d |
| Soil consumption by cattle | 500 g/d |
| Consumption of produce | 100 kg/y |
| Consumption of leafy vegetables | 15 kg/y |
| Consumption of soil | 40 g/y |
| Consumption of milk | 100 L/y |
| Consumption of meat | 35 kg/y |
| Consumption of drinking water | 500 L/y |
| Atmospheric soil loading by suspension | .000016 g/m ³ |
| Breathing rate | 8000 m ³ /y |

used to calculate a total EDE from all 15-cm soil layers down to a maximum of 20 layers. If the calculated EDE exceeds the limit specified by the user, DECOM reports how many successive 15-cm layers of soil must be removed for the calculated dose to be less than the standard.

In all calculations, the DECOM methodology assumes that following remediation, land is released for unrestricted use at a user-specified time after cleanup, and possible pathways are: (1) external radiation from the radionuclides in soil, (2) inhalation of suspended soil, (3) ingestion of contaminated food, and (4) ingestion of contaminated drinking water (Figure 1). DECOM assumes that removal of radionuclides from contaminated soils occurs via radiological decay and leaching. The decay constants used in DECOM are based on radiological half-lives compiled by Kocher (1981). Leaching removal constants are calculated according to a model proposed by Baes and Sharp (1983) that is appropriate only for tilled agricultural surface soils. Because the model overestimates the leaching losses from untilled soils, the original version of DECOM was modified to turn off the leaching removal calculation. We suggest that a user of DECOM assume that remedial options will include provisions to significantly reduce or eliminate leaching of radionuclides from RAP sites (e.g., fixation, capping, etc.) and use the code

with leaching removal turned off. The following paragraphs briefly describe the pathway models incorporated into DECOM.

Direct Exposure Pathway

In the BASIC version of DECOM, the external exposure calculation assumes that an individual is standing on an infinite slab of soil uniformly contaminated with the user-specified mixture of radionuclides. There are no other pathways of external exposure (e.g., contaminated structures). The code employs a "look-up" table of precalculated values that, in effect, correct the estimated external dose rate at 1 m above a contaminated ground surface for attenuation of gamma radiation by soil. The values in the table are based on numerous runs of a computer code that estimates dose rates for a target 1 m aboveground from radionuclides in infinite slabs of soil at different depths (Kocher and Sjoreen 1985). The basic methodology is documented in the MLSOIL and DFSOIL computer codes (Sjoreen et al. 1984). DECOM allows the user to specify the bulk density of the ground containing the radionuclides and makes a correction from the bulk density of 1.4 g cm^{-3} assumed in MLSOIL and DFSOIL. The user may also specify the fraction of time the exposed person spends on-site (default of 1.0). The annual EDE is calculated by multiplying dose rate by an "external dose conversion factor," which is based on recommendations by the ICRP (1977), but modified to account for contributions from decay products (see below).

A very important consideration for potential users of the DECOM methodology is that DECOM cannot handle radionuclide decay chains explicitly, and as a consequence, the authors of the code attempted to incorporate the effects of daughters into the external exposure calculations. That is, a radionuclide that emits no gamma radiation may, nevertheless, have an external dose calculated for it by DECOM if the radionuclide has decay daughters which emit high energy gamma radiation. As a case in point, ^{234}U , which has a half-life of 244,500 years, decays by emission of alpha particles and very weak gamma radiation. However, DECOM attributes 99% of the dose from ^{234}U to external exposure. This paradox is explained by the fact that it is the gamma radiation from daughters down the decay chain from ^{234}U (not entered separately by the user) that account for the external exposure attributed to ^{234}U . Generally, DECOM assumes that all short-lived daughters of longer-lived parents are in secular equilibrium with the parent, and the authors of the code have used some judgment in modifying accepted external dose conversion factors (ICRP 1977) to reflect such contributions in DECOM. In situations where secular equilibrium should not be assumed (e.g., contamination from processed fuels) or where buildup of daughters through time may be important, the user is cautioned to make appropriate adjustments to the original source term or take

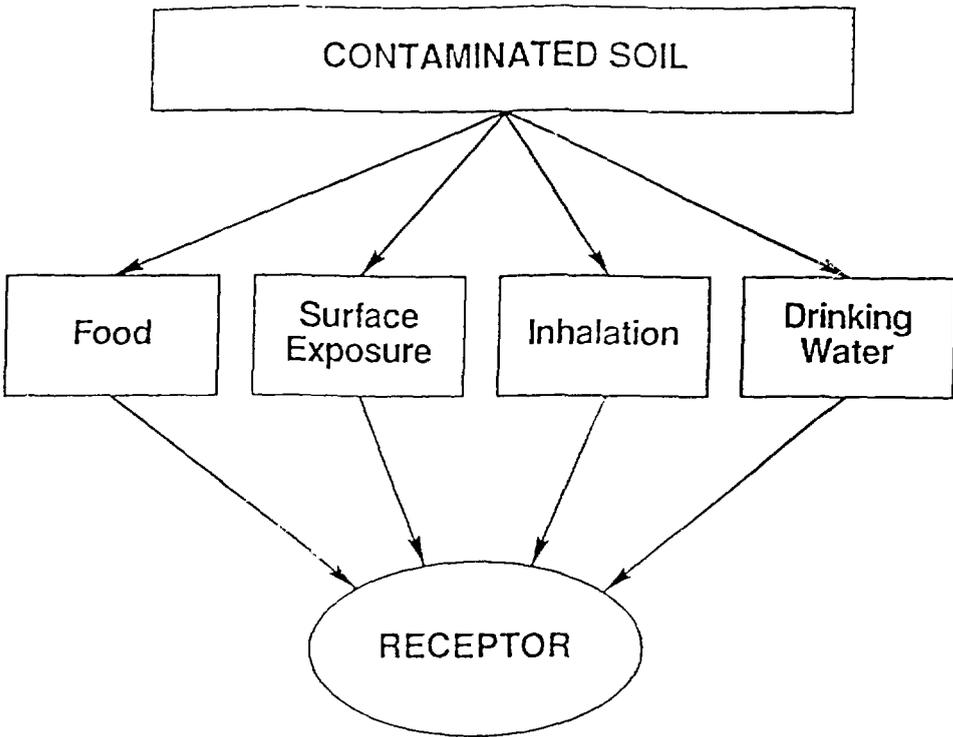


Figure 1. Pathways in DECOM

such considerations into account when interpreting DECOM's results.

Inhalation Pathway

The annual EDE (mrem) via the inhalation pathway is calculated by multiplying the following parameters: (1) the concentration of radionuclides in soil (pCi/g), (2) an atmospheric mass loading factor (g/m^3), (3) the inhalation rate (m^3/y), (4) the dose conversion factor for inhalation (mrem/pCi), and (5) the fraction of time spent on-site (unitless). That is, doses are assumed to occur by inhaling soil suspended into the atmosphere (specific activity is assumed to be the same for all particle sizes). The critical parameter in this calculation is the mass loading factor, which in turn depends on type of soil, vegetation cover, and average wind velocity. That is, mass loading would be expected to be greater in arid, windblown areas than in lush, wet areas. The default mass loading factor in DECOM is $1.6 \times 10^{-5} \text{ g}/\text{m}^3$ (Baes et al. 1984a). This value is the geometric mean of values (range 5×10^{-5} to $3 \times 10^{-4} \text{ g}/\text{m}^3$) for the 2.5 to 15 μm diameter particle fraction collected with high volume samplers by the EPA (Suggs et al. 1981).

Food Ingestion Pathway

The annual EDE (mrem) via ingestion is calculated for the following food categories: (1) leafy vegetables, (2) produce, (3) milk, and (4) beef. Milk and beef are assumed to be from cows and cattle grazing pastures and fed grains produced on-site. For leafy vegetables, produce, forage, and cattle feeds, the concentration of radionuclides in soil (pCi/g) is multiplied by a soil/plant concentration ratio (unitless) for either vegetative portions of plants (B_v) or reproductive portions of plants (B_r). This approach is basically the approach taken in the computer code TERRA (Baes et al. 1984b), and the concentration ratios used as default are based on a review and analysis of many studies of plant uptake of radionuclides and trace metals from soil (Baes et al. 1984a).

Concentrations of radionuclides in beef and milk are estimated via a modification of the approach adopted by the U.S. Nuclear Regulatory Commission (NRC 1977); i.e. cattle are also assumed to ingest soil while grazing pastures. The daily ingestion rate of radionuclides by milk cows and beef cattle (pCi/d) is calculated by multiplying the concentration of radionuclides in forage and feed (pCi/kg) by feed ingestion rates (kg/d) for milk cows and beef cattle and adding the product of the soil concentration of radionuclides (pCi/g) and a soil ingestion rate (g/d). The soil ingestion rate used in DECOM is based on a review of the subject by Zach and Mayoh (1984). The forage and feed ingestion rates used in DECOM are based on an analysis performed by Shor et al. (1982). The estimated daily ingestion rate of radionuclides by milk cows and beef cattle is then multiplied by either a milk-beef transfer factor (d/kg) that relates the

ingestion rate of a radionuclide to its equilibrium concentration in milk or beef (Ng 1982).

Once concentrations of radionuclides in the food items have been calculated (pCi/kg), the consumption rate of the food item (kg/y) is multiplied by the dose conversion factor for ingestion (mrem/pCi) and the fraction of the food item consumed that is grown on-site (unitless). Consumption rates for leafy vegetables, produce, milk, and beef used in DECOM are based on a review of the 1977-1978 U.S. Department of Agriculture nationwide food consumption survey (Nelson and Yang 1984).

Drinking Water Pathway

The basic calculation for estimating the annual EDE for the drinking water pathway in DECOM is to multiply: (1) the concentration of radionuclides in drinking water (pCi/L), (2) the consumption rate of drinking water (L/y), (3) the dose conversion factor for ingestion (mrem/pCi), and (4) the fraction of drinking water from on-site (unitless). The critical parameter in this calculation is the estimation of radionuclide concentration in drinking water. In all models that make such calculations, a soil-water distribution coefficient, K_d (mL/g), is used in the calculation. The default K_d values in DECOM are based on a review of measured K_d s for radionuclides and trace metals in agricultural soils (Baes and Sharp 1983). The review, however, indicated large uncertainties (several orders of magnitude) associated with K_d values owing to effects of soil type, organic matter content, chemical form of the radionuclide, soil pH, and other variables. Additionally, considerations of transport of radionuclides to aquifers and dilution effects make selection of a generic drinking water model extremely difficult.

The original BASIC version of DECOM contained a single drinking water pathway model based on a spill-dilution transport model (Codell and Duguid 1983). This model essentially moves a pulse of radionuclides in leachate from the contaminated soil to an aquifer and then dilutes the pulse in the total volume of the aquifer in order to calculate the concentration of radionuclides in drinking water. A second, and much more conservative model was added to the BASIC version of DECOM based on the approach that the EPA uses in regulating final closure of hazardous waste land disposal units under RCRA (EPA 1987). Although RCRA does not regulate radionuclides, the EPA continues to adopt strategies that make the various regulations dealing with hazardous substances consistent with each other. In other words, remedial action strategies adopted under CERCLA and SARA for radionuclides are very likely to be based on strategies for demonstrating cleanup of hazardous wastes under RCRA.

Under the RCRA closure strategy, demonstration of no harm to human health and the environment requires very conservative models if wastes and residues remain on site. When the closed unit is to be released for unrestricted use, the model that the EPA uses for demonstration of no harm assumes that exposure occurs within the unit boundary, takes no consideration for control measures (e.g., fencing or capping), and allows no consideration for attenuation during transport. Therefore, we added a second, highly conservative model that estimates the concentration of radionuclides in pore water by dividing the concentration of radionuclides in soil (pCi/g) by the soil-water distribution coefficient, K_d (mL/g). This pore water is assumed to be the drinking water consumed by the on-site inhabitant.

For most radionuclides, the drinking water pathway often makes only a small contribution to the total annual EDE to a person living on a decommissioned site. In situations where the drinking water pathway makes a significant contribution, the large uncertainties associated with estimating leachate concentrations, transport, and dilution in a generic model should be considered. If the second drinking water option is selected, the extremely conservative nature of the model should be taken into account. A user of DECOM might consider omitting the drinking water pathway and using a more sophisticated model.

DECOM (LOTUS)

The BASIC version of DECOM has several strengths: (1) it is interactive, (2) it runs on an IBM PC or compatible with as little as 64K memory, and (3) it has been tested with satisfactory results at the Savannah River Plant (Till and Moore 1986). Unfortunately, the original code is cumbersome to use because a separate run (beginning with the first screen and continuing through each option offered) is required each time a single parameter is changed. Additionally, DECOM back-calculates to an initial soil concentration rather than the reverse, calculating a dose from an observed soil concentration – a more useful application for the RAP. Typically, a user would know radionuclide concentrations in soils based on field and laboratory analysis and would be interested in the effectiveness of various remedial options in limiting the potential dose to persons who might inhabit the area after decommissioning the site.

To remedy these problems, we entered the DECOM models into a LOTUS spreadsheet. The spreadsheet version of DECOM has the advantages that: (1) calculations are made in the forward direction, with the user entering radionuclide concentrations and the program automatically recalculating the dose each time a parameter is changed, (2) the effect of varying a single parameter is easily tested, allowing the user to conduct a sensitivity analysis,

and (3) the graphics package built into LOTUS can be used to display results. We also added an option in the spreadsheet not available in DECOM BASIC. In the LOTUS version, the user may identify depths to the top and bottom of the contaminated layer of soil with the implicit assumption that soil above the top of contamination is a cap of clean soil. This option allows the user to examine the effects of cap thickness on external doses. We also included in the LOTUS version an option that allows direct ingestion of contaminated soil in the food ingestion pathway (poorly washed vegetables).

We are convinced that both the spreadsheet and BASIC versions of DECOM provide an easy-to-use dose assessment model. However, the user must keep in mind the limitations of the models incorporated into DECOM. Dose assessment models are limited by the data used, and many of the parameters built into the model are approximations, mathematical measures of central tendency of a distribution of measured values (often derived from different sources, each more or less representative of the parameter as defined by the model), or best guesses. The user is encouraged to examine the effect of varying parameter values on the results, and, of course, to replace default values with site-specific measurements.

EXAMPLE APPLICATIONS OF DECOM

The examples discussed in this section were designed to illustrate the ease and flexibility of DECOM. They are not intended to represent most probable exposure scenarios for the Oak Ridge Reservation (ORR).

The Jogger

Suppose that a jogging enthusiast jogs one half hour per day along the Oak Ridge Reservation's perimeter 365 days a year. What is annual effective dose equivalent that DECOM predicts? The food and drinking water pathways are turned off, and the total exposure time is about 180 h/y. We will assume that the jogger's breathing rate is doubled (8000 m³/y is the default) and that he kicks up a lot of dust (atmospheric mass loading is 1.0×10^{-4} g/m³).

Eighteen soil samples collected around the ORR perimeter (Williams et al. 1987) were analyzed by gamma spectroscopy (Table 2).

For this simple example DECOM calculates a total annual EDE of less than 1 mrem. This small dose from the soil is mainly by external radiation. We conclude that the jogger need not alter his route.

The Farmer

Now let us consider a slightly more complicated example. Assume that after 100 years of institutional control the Oak Ridge Reservation is released for unconditional use. Further assume that a homesteader settles at the present

Table 2. Jogger Scenario

| Radionuclide | Activity(pCi/g) | Annual EDE (mrem) |
|-------------------|-----------------|----------------------|
| ¹³⁷ Cs | 0.77 | 0.06 |
| ⁴⁰ K | 10.0 | 0.04 |
| ²³² Th | 1.9 | 0.8 |
| ²³⁸ U | 1.0 | 0.03 |

location of a storage pad near building 3503 (selected only because we have data for the soil there), and that there has been no remediation at this site. The farmer lives there year round, and this is where he grows all his crops, and raises all his livestock.

A gamma survey (Williams et al., 1987) found that most of the contamination at this site is concentrated in a few "hotspots". Sixty-nine soil samples were taken at the site and analyzed by gamma spectroscopy and neutron activation. The area-weighted average radionuclide activities in soil are presented in Table 3. Radionuclides present in negligible amounts have been omitted.

Table 3. Farmer Scenario

| Radionuclide | Activity (pCi/gm) | Annual EDE | |
|-------------------|----------------------|-----------------|-------------------|
| | | t=0 y (mrem) | t=100 y (mrem) |
| ⁶⁰ Co | 0.86 | 13 | 0.0 |
| ¹³⁴ Cs | 6.8 | 63 | 0.0 |
| ¹³⁷ Cs | 140 | 520 | 53 |
| ¹⁵² Eu | 1.7 | 12 | 0.1 |
| ⁴⁰ K | 16 | 47 | 47 |
| ⁹⁰ Sr | 5.1 | 27 | 2 |
| ²³² Th | 13 | 260 | 260 |
| ²³⁸ U | 13 | 14 | 14 |

DECOM's predictions (Figure 2) show that both at the present and in 100 years; the primary pathway is from external radiation. While ¹³⁷Cs is the most important contributor at present, it is relatively short lived, and in 100 years the daughters of ²³²Th predominate (this assumes secular equilibrium,

see earlier discussion). The naturally occurring ^{40}K and residual ^{137}Cs are of lesser importance but still contribute significantly to the annual EDE. Given these results, remediation is advised before the farmer is allowed to settle.

CONCLUSIONS

BASIC DECOM and LOTUS DECOM are potentially useful tools for the RAP planners and program managers. They are easy to use and run quickly on an IBM PC or compatible. By varying input values such as the radionuclide concentrations, thickness of cap layer, period of institutional control, etc., the user can explore a series of "what ifs" to gain an appreciation of the relative importance of the model parameters.

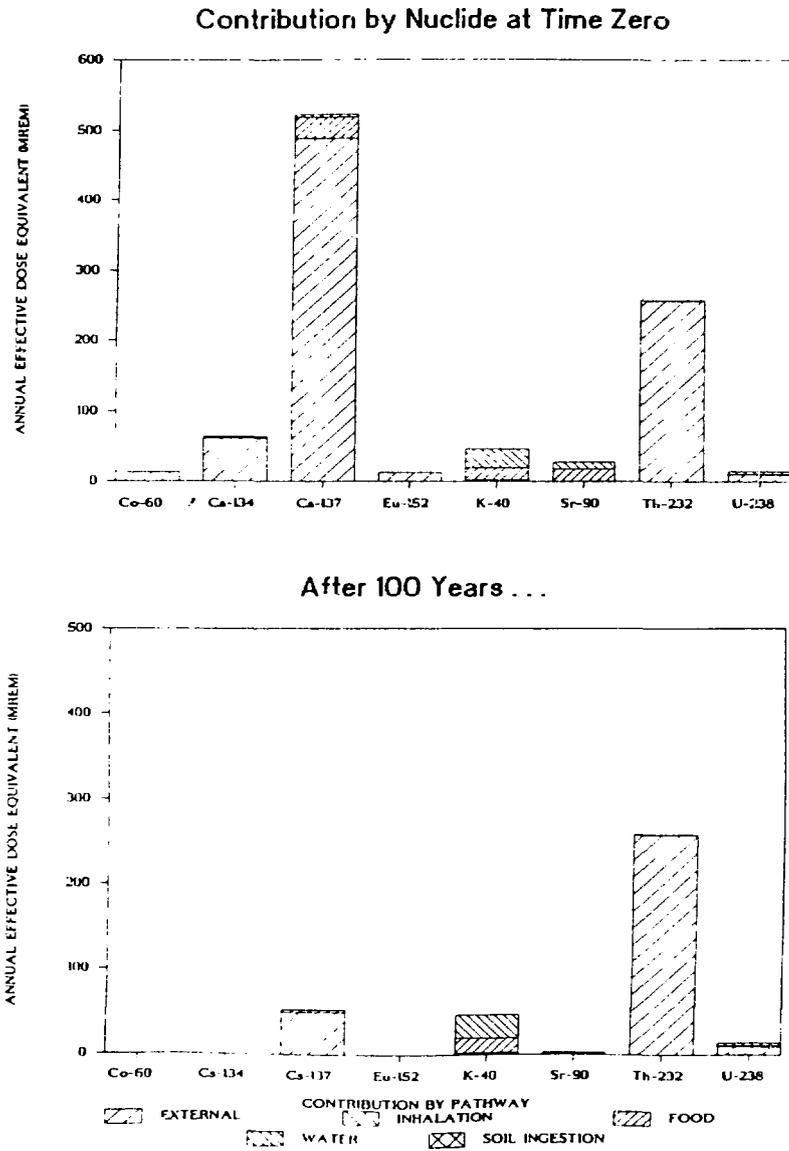


Figure 2. Contribution by radionuclide to the annual effective dose equivalent after 0 and 100 years (Farmer Scenario).

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Control of Water Infiltration Into Near Surface LLW Disposal Units

Presented by:

Edward O'Donnell, NRC

Control of Water Infiltration Into Near Surface LLW Disposal Units -
Edward O'Donnell, U.S. Nuclear Regulatory Commission, Washington, D.C.,
Robert K. Schulz, University of California, Berkeley CA., Robert W. Ridky,
University of Maryland, College Park, MD.

To control water infiltration through LLW disposal unit covers, a thesis is developed in this paper that solely run-off can be subject to unlimited manipulation. Necessary run-off can be surface or sub-surface.

A procedure named "hydroengineering management" is described which uses engineered features at the surface to ensure adequate run-off. Investigation on that procedure is underway with a pilot study at Maxey Flats, KY and a large scale demonstration at Beltsville, MD and results to date are encouraging.

Two types of sub-surface features that may be constructed to enhance run-off are described. One is the "restrictive layer" barrier, and the other is the "conductive layer" barrier.

The "restrictive layer" barrier is the well known compacted clay layer and depends on compaction of permeable porous materials to obtain low flow rates. Flow through a restrictive layer is described by Darcy's law (1856) Investigations on flow through such layers have gone on for over 100 years, so further progress in this area can be expected to be slow.

The "conductive layer" barrier is based on the capillary barrier concept and has little been investigated. No definitive full scale field experiments have been carried out in humid regions. It is in this relatively unplowed ground that the greatest advances might take place in the near future, is where new effort should be directed.

CONTROL OF WATER INFILTRATION INTO NEAR SURFACE LLW DISPOSAL UNITS

Edward O'Donnell
U.S. Nuclear Regulatory Commission
Washington, DC 20555

Robert K. Schulz
University of California
Berkeley, CA 94720

and

Robert W. Ridky
University of Maryland
College Park, MD 20742

ABSTRACT

The principal pathway for water entry into LLW disposal units in the humid eastern United States is through their covers. Most of that water is derived from precipitation. On a long term basis, precipitation has three possible fates: (1) some water will be returned to the atmosphere by evaporation and plant transpiration; (2) some water may run-off laterally; and (3) some may percolate below the root zone of the vegetation. Since deep percolation is undesirable in a waste isolation system, it is required that the sum of run-off plus evapotranspiration approach or equal precipitation. It should be noted that the run-off can be surface or sub-surface so long as the lateral transport occurs before the water can contact the waste.

If deep percolation is to be close to zero, then only two parameters are left for possible control, evapotranspiration and run-off. Evapotranspiration, however, has a very definite maximum. The energy available for evaporation is incident solar radiation and is not subject to control. Thus only run-off is subject to unlimited management.

Two types of sub-surface features that may be constructed to enhance run-off are: (1) the "resistive layer" barrier, and (2) the "conductive layer barrier". The "resistive layer" barrier is the well known compacted soil or compacted clay layer and depends on compaction of permeable porous material to obtain low flow rates. The "conductive layer" barrier is a special case of the capillary barrier. Use is made of the capillary barrier phenomenon not only to increase the moisture content above an interface but to divert water away from the waste. During such diversion the water is at all times at negative capillary potential or under tension in the "flow layer". The use of capillary barrier concept is perhaps most readily apparent upon consideration of the "outflow law" (Richards, 1950) which explains the existence of dry caves present in porous materials and also why gopher holes do not fill up during a rainstorm. This is because, that as long as the soil moisture has a path to follow so that water pressure remains negative (less than atmospheric) no water will enter the cavity. That is, outflow from a soil to a cavity or rock layer occurs if

the pressure in the soil water exceeds atmospheric. A conductive layer barrier has a theoretical efficiency approaching 100%. But on both a theoretical and practical basis, such a barrier can work only under relatively low water flows. On the other hand, the resistive layer barrier works most efficiently at higher precipitation rates. Based on these two considerations, a very effective barrier system might be constructed by placing a "resistive barrier" over a "conductive barrier". A note of caution: such a system must fail if appreciable subsidence takes place.

An alternate procedure, called "bioengineering management" utilizes engineered features at the surface (as opposed to the subsurface) to ensure adequate run-off. The engineered features are combined with stressed vegetation, that is vegetation in an overdraft condition, to control deep percolation. Investigation on that procedure in lysimeters designed to give full water budget data are encouraging.

INTRODUCTION

Water is referred to by chemists as the universal solvent. The entry of this "universal solvent" into all of the major low level radioactive waste disposal sites (1-8) located in the humid regions of the United States is a noteworthy occurrence. Water infiltrating to buried wastes, contacting the wastes, and then exiting the area can reasonably be expected to be the most important of radionuclide transport agents. Some radionuclides, such as tritium present as tritium oxide, and those in anionic form will essentially move with the flow of water; others present as multivalent cations will move much more slowly, but all will move to a greater or lesser degree. To date, tritium migration has been found in all six of the major LLW sites referred to above (9). The object of the present paper is to discuss pathways of water entry to waste placed in near surface, low level disposal units and to suggest likely fruitful areas of investigation.

WATER PATHWAYS TO THE WASTE

Essentially there are three directions from which water can approach emplaced waste. One direction is from above; generally the source being precipitation. Isolation of waste from precipitation water will be the principal topic in this presentation. A second direction of water movement to waste could originate from upward movement of water by a rising water table. A third direction could be lateral movement, also of free water, or groundwater. The best solution to problems two and three is very simple. Do not locate a LLW disposal unit where a groundwater table may be a problem. It is just not reasonable. If, in spite of these considerations such a siting should be made, the area must be artificially drained. An enormous drainage literature exists and procedures are well established. Drainage of agricultural lands has been carried out for

centuries. Extensive drainage is routinely done in all sorts of engineering projects such as road and airport construction. Since such an extensive body of knowledge and experience is in existence on the subject of land drainage, engineering procedures are well known and results are predictable.

In contrast to problems related to land drainage, which has received extensive investigation, means of reducing infiltration has received relatively little study. To the contrary, agricultural studies along these lines are directed to means of increasing infiltration, not decreasing it. In the agricultural case, water run off is generally to be reduced, thus increasing irrigation efficiency. Probably the relative lack of emphasis on studies relating to means of reducing infiltration has contributed to the lack of success in prevention of water entry into humid area LLW trenches. For this reason the discussion in this paper will concentrate on the infiltration-percolation pathway of water entry into near surface low level waste disposal units.

Before examining the water pathway problem, it is interesting to note that the lack of success in keeping buried waste isolated from water has led to the expenditure of considerable effort on improved packaging as a preventative effort. Concrete, especially, has received much attention along these lines (10-17). Questions of long term stability of concrete surrounded by acid soil, cost, etc. suggest that concrete may not be the best solution. Isolation using natural materials should not yet be given up on but should be investigated further, especially in the areas that have received relatively little attention.

Up to this time, LLW disposal unit covers have been constructed from soil materials. The covers have proved unsuccessful from the standpoint of exclusion of water from waste buried in humid regions. Quite to the contrary, the trench covers have been the principal pathway for water passage to the waste (5, 8, 18-24). To provide a basis for a discussion of what might be done to improve on this situation, we shall next review some of the principles describing water transport through porous media such as soils or clays.

SOIL WATER MOVEMENT

In 1856 Darcy (25) published an article describing flow of water in filter beds. From this came Darcy's law: The flow rate through a porous media is proportional to the head loss and inversely proportional to the length of the flow path. The equation resulting from this law may be written in many ways but we will write it here:

$$v = K \frac{P_1 - P_2}{s} \quad (1)$$

where v is the flow velocity, K is the hydraulic conductivity, and P_1 and P_2 are inlet and outlet pressures of the porous body of length s . It can be noted that this equation closely resembles the Pouseulle

equation describing flow of water through capillary tubes. Darcy's law is also quite analogous to Ohm's law which describes electrical current flow through a wire. Other analogies between water flow through porous media and electrical flows become apparent upon examination of later articles such as that of Buckingham (26).

By the 19th century it was already known that all soil water is not free to move under the influence of gravity. King (27) and Briggs (28) were cognizant of various states of water in soils. "Gravity water" was described as water in soil free to move under the influence of gravity. "Capillary water" was water held in capillary spaces under the influence of surface tension. "Hygroscopic water" was film water and not free to move under gravity or capillary forces. It is interesting to note that the "capillary water" concept can furnish an explanation for the capillary barrier concept for protecting wastes from percolating water. The displacement of capillary water under the influence of gravity was described by Briggs (28) in 1897.

When air is introduced into a porous media, the saturated media becomes an unsaturated media. Air replaces water and the cross section available for liquid flow is reduced and flow will be reduced accordingly. In 1907, Buckingham (26) incorporated this reduction of conductivity into a flow equation. Later Richards (29), and Childs and Collis George (30, 31) showed that Darcy's law basically also applied to the movement of soil moisture under unsaturated conditions and hence the following simple equation can be written:

$$v = k \frac{P_1 - P_2}{s} \quad (2)$$

where k is the capillary conductivity and $P_1 - P_2$ represents the difference of the combined gravitational and capillary forces in the soil.

It should be further noted that K in equation (1) will be fairly constant for a given soil, but k in equation (2) will vary with moisture content. Another difference to be noted in the use of equations (1) and (2) is that in unsaturated conditions, flow may take place in any direction and in the case of upward flow, the gravitational force must be subtracted from capillary force to obtain $P_1 - P_2$.

Darcy's law and the equations derived from it then form a foundation for describing protection that may be afforded to waste isolated by a compacted clay layer. Such a clay layer is, in essence, a resistance layer, i.e. a layer of material that offers resistance to water flow. The greater the resistance of the layer the better the performance in isolating waste from water flow.

A quite different concept is that of the capillary barrier. The capillary barrier concept depends on the observation that water will not flow into a cavity from an unsaturated porous media such as soil. In this concept a relatively low resistance to flow (or high hydraulic conductivity) is essential for the barrier to give good performance in isolating waste from water infiltration. In 1930 Zunker (32) discussed a field drainage case

where a layer of fine textured soil is underlain with coarse material. The transition zone from fine to coarse texture acts like a perched water table in the fine textured material. Zunker presented an explanation for the phenomena based on capillary forces. Richards and Joffe (33) reported in 1939 that zero pressure (or zero soil moisture tension) are the required boundary conditions for outflow from the bottom of a soil column. In 1950 Richards (34) published an article titled "Laws of Soil Moisture". Here he put forth his Outflow Law: Outflow of free water from soil occurs only if the pressure in the soil water exceeds atmospheric pressure. The outflow law applies to drains and explains why dry caves exist and why gopher holes do not fill up with water during a period of rainfall. As long as the soil moisture has a path to follow so that the water pressure remains negative (or less than atmospheric), no water will enter the cavity. This principle has obvious interesting implications for isolating wastes from percolating waters.

ISOLATION OF WASTE FROM PERCOLATING WATER

On a long term basis, precipitation falling onto an area has three possible fates. (1) Some water will be returned upward to the atmosphere by evaporation and plant transpiration (evapotranspiration). (2) Some water may run-off laterally. (3) The third possible fate of the water over a long term period is deep percolation. Since deep percolation is undesirable in a waste isolation system, it is required that the sum of run-off plus evapotranspiration approach or equal precipitation. It should be noted that the run-off can be surface or sub-surface so long as the lateral transport occurs before the water can contact the waste.

If deep percolation is to be close to zero, then only two parameters are left for possible control, evapotranspiration and run-off. Evapotranspiration, however, has a very definite maximum when considered over an extended area. The energy available for evaporation of water is incident solar radiation and is not subject to control. About 588 calories are required to evaporate each gram of water in the field, so we can see that evapotranspiration has a maximum. By definition, a humid area is one in which precipitation exceeds evapotranspiration. This leaves only one degree of freedom, that is, only run-off is subject to unlimited management. As stated earlier, that run-off may be surface or sub-surface so long as the lateral transport of water takes place so that the water does not reach the waste.

METHODS FOR CONTROLLING WATER MOVEMENTTHE RESISTIVE LAYER BARRIER

The major burial sites in the humid areas of the United States have, to date, consisted of trenches partly filled with wastes, then trench caps have been constructed using compacted soil materials. A trench cap constructed from compacted clay or soil could be termed a resistive layer since the function of the cap is to provide a low hydraulic conductivity or high resistance to water flow through the layer to the emplaced waste. Such a "resistive layer" or compacted clay layer can have a low hydraulic conductivity and afford a high degree of protection to waste. Water movement through such a layer can be described by adaptations of Darcy's law. However, as noted earlier in this paper, all of the major waste sites located in the humid U.S. have reported some water movement into trenches and the caps are the major pathway (5, 8, 18-24).

It should be noted that it is the nature of compacted porous material to allow some water passage. All such materials have a measurable hydraulic conductivity. In addition, trench caps tend to become more permeable to water with the passage of time. This can be ascribed to two occurrences.

(1) Subsidence:

Subsidence of waste which causes shear failure of the clay layer is a serious problem and is one that is not easily managed. Waste compaction will not solve the problem as organics will still decay with time, creating voids leading to subsidence. The subsidence problem can be managed by one of two ways. One is to prevent subsidence by construction of very expensive vaults or containers or by reduction of the waste to a compact inorganic material that would not undergo further volume reduction with the passage of time. The other way could be by simply managing the subsidence as it occurs. This second practice has been followed to date but with limited success in preventing water infiltration to buried wastes. As the cap subsides it is simply repaired.

(2) Plant root penetration:

The growth of plant roots results in increased hydraulic conductivity of disposal unit covers with passage of time. Roots increasingly penetrate clay or compacted soil layers and upon death and decay of the roots, channels or macropore paths are formed (18). Bio-barriers have been suggested to prevent such root penetration (35), but it is unlikely that the suggested rock or cobble barrier will prove effective in stopping root penetration over long periods of time in humid areas. Roots are perfectly able to penetrate gravel or rock for long distances if the rock is kept wet.

In summary, the restrictive layer barrier, with either continued maintenance or extraordinary initial measures can be expected to provide an effective but not perfect barrier to water passage. Lateral run-off of water caused by the restrictive layer barrier can be through a gravel drainage layer above the clay layer or may be at the ground surface.

THE CONDUCTIVE LAYER BARRIER

The conductive layer barrier is a special case of the capillary barrier. Use is made of the capillary barrier phenomenon not only to increase the moisture content above an interface but to divert water away from the waste. During such diversion the water is at all times at negative capillary potential or under tension. (Note: the energy status of water present in unsaturated porous media is alternatively referred to as capillary potential, hydraulic potential and more recently as matric potential. All of these terms are still in use and are defined differently, but the differences are not important to this discussion).

The use of the capillary barrier concept is perhaps most readily apparent upon consideration of the "outflow law" (34) described earlier in this paper. This law, along with the explanation based on capillary considerations by Zunker (32), readily explain the existence of dry caves present in porous materials and also why gopher holes do not fill up during a rainstorm. As was mentioned earlier, as long as the soil moisture has a path to follow so that the water pressure remains negative (less than atmospheric) no water will enter the cavity. That is, outflow from a soil only occurs if the pressure in the soil exceeds atmospheric. Perhaps the same principles can be applied to isolate waste from water where the waste is disposed of in a near surface facility. Such disposal could be either above or below grade.

Cartwright, et al. (9) described results from a field experience at Sheffield where the layering sequence resulted in a wick effect so that extra moisture is retained in the upper fine grained layer, thus making it more available for evapotranspiration. This is probably not the most important attribute of a capillary barrier system. In many cases the waste itself will serve as the cavity so that a capillary break (barrier) is established. It should be noted that merely increasing the water holding capacity of the soil above the waste will not, in itself, prevent water from infiltrating the waste. If this were the case, simply making the cover thicker would suffice. By definition, in a humid area precipitation exceeds evapotranspiration. As mentioned earlier, only by increasing run-off to the point that E.T. will use the rest of the water, will percolation be prevented.

In the special case of waste isolation, the capillary barrier needs only to provide sub-surface run-off to divert water from the waste. If the water is shunted around the waste to a porous unsaturated zone below the waste, our goal of waste isolation from percolating water will be achieved. (See Figure 1).

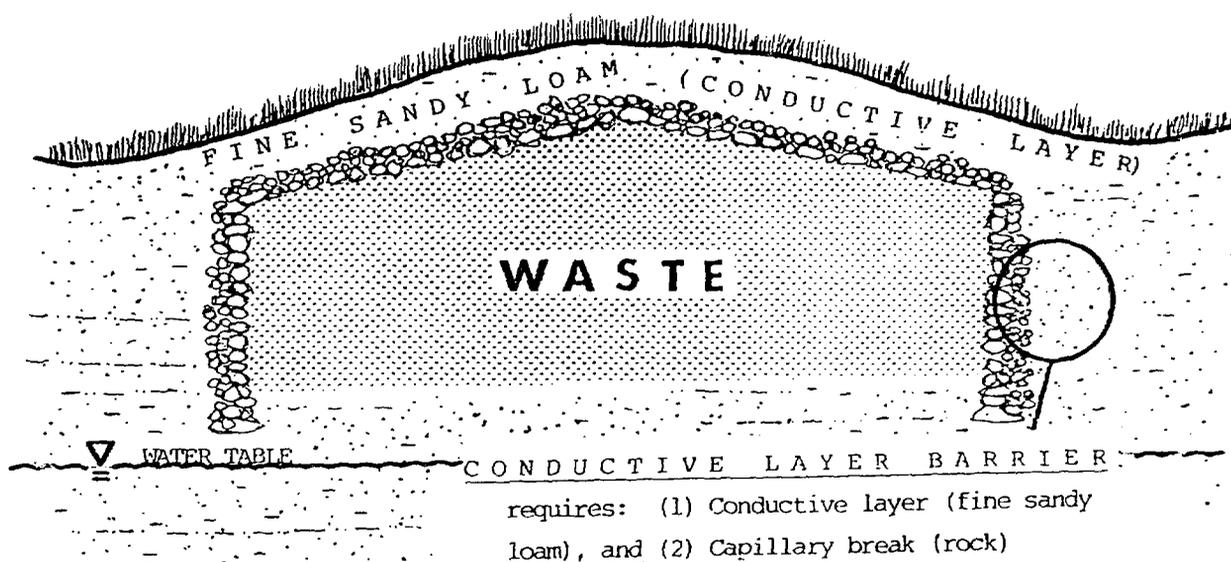


Figure 1 CONDUCTIVE LAYER BARRIER (simplest case)

For a well drained soil the soil itself will act as a conductor. As long as the soil is unsaturated water will not enter a drain (the rock layer). This system will work best when there are slow percolation rates. Water will be conducted around the rock layer to the water table or to drains (not shown) which should be located below the waste. If percolation rates are high, a resistive layer barrier should be added as shown in the following figure.

In addition to the work at Sheffield a number of investigators have suggested or tried to use the capillary barrier concept to protect waste from water infiltration (35-58). Simulations have perhaps worked best, followed with decreasing success with laboratory models, then field experiments. Some of the field experiments have met with little success (9); some showed some promise (38, 52, 58). The most successful field demonstration was reported by Rancon (55). However, in this most successful case, the trench cap was less than three meters wide, therefore this experiment does not yield conclusive proof that the concept will be useful to isolate waste of greater lateral dimensions. Probably the usefulness of the capillary barrier-conductive layer barrier concept has not yet been given a definitive trial.

In designing a conductive layer barrier system, one condition is paramount. The rock layer must be clean or free of fines so as to form the necessary "cavity", or the outflow law does not apply. The second condition is that the conductive layer above and around the "cavity" must be conductive. That is, that layer must have a reasonable hydraulic conductivity in the negative moisture potential range of -10 cm to -200 cm of water. Third, the water being transported in the capillary layer must have somewhere to go. Ideally, this will be into an unsaturated region below the waste. If the conductive layer terminates at a drain located at or above the elevation of the waste, the capillary potential of the water must rise to zero at that point (outflow law), and water may seep into the waste.

In the various reports on the capillary barrier referred to above, it has been stated that it is very important that the fine/coarse grained interface be very sharp. This is not necessarily so. A graded interface made of several particle size layers or other filter materials may be superior. It is absolutely essential that large amounts of fine materials do not penetrate long distances into the "cavity". A diffuse barrier of a few centimeters thickness has a penalty of only that of gravity. That is, a "pocket" of fine material extending 5 cm into the "cavity" will have a 5 cm water pressure disadvantage only. If water at the plane of the top of "pocket" has a capillary potential of -6 cm, no water will drip off of the bottom of the pocket. That water will still have a potential of -1 cm.

A conductive layer barrier has a theoretical efficiency approaching 100%. But on both a theoretical and practical basis, such a barrier can work well only under relatively low water flows. On the other hand, the resistive layer described earlier, works most efficiently (that is, diverts a higher percentage of infiltrating water) at higher precipitation rates. Based on these two considerations, it seems reasonable that a very effective barrier system might be constructed by placing a "resistive barrier" over a "conductive barrier". (See Figure 2 and 3). A note of caution: Such a system must fail if appreciable waste subsidence takes place.

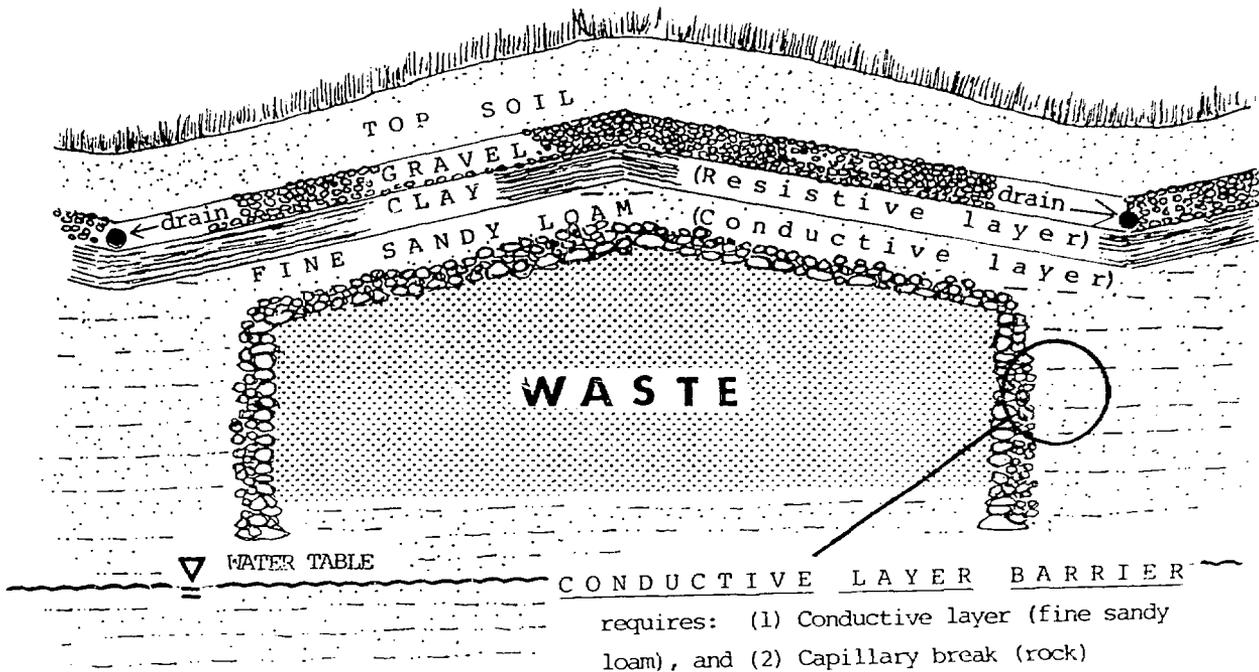
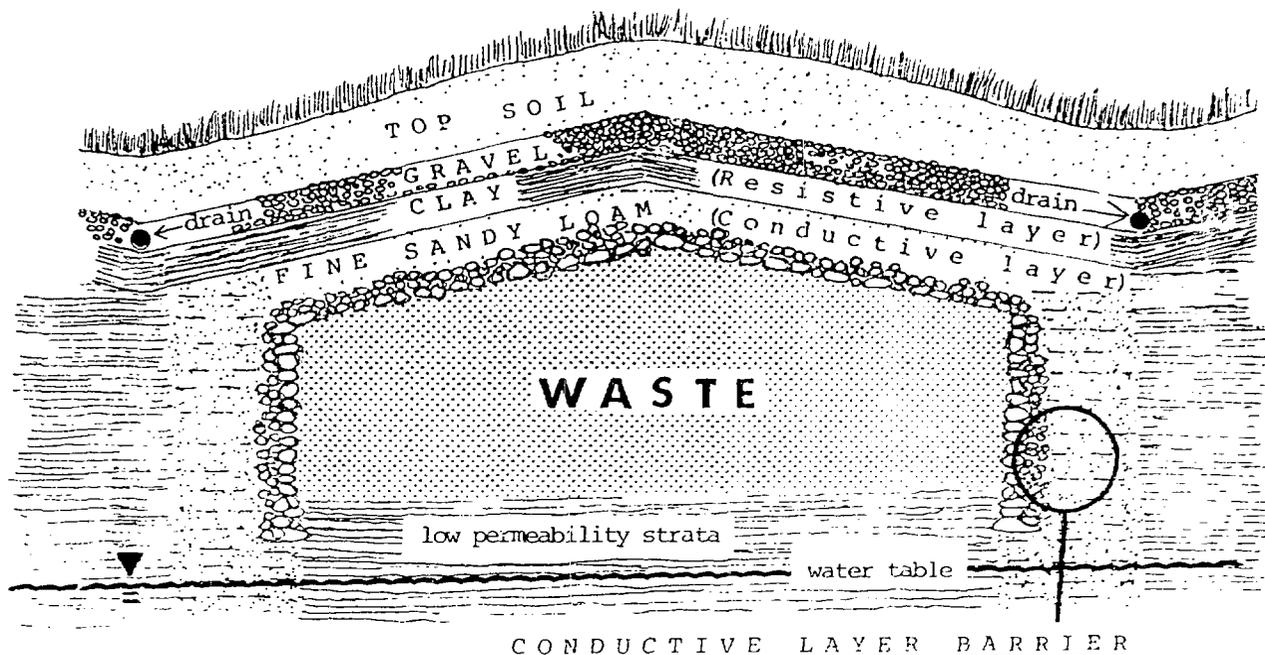


Figure 2. CONDUCTIVE LAYER BARRIER USED
IN CONJUNCTION WITH A RESISTIVE
LAYER BARRIER

The resistive layer barrier functions best with high percolation rates. Its purpose here is to reduce the amount of water that reaches the conductive layer barrier. As noted in Figure 1, the conductive layer barrier functions most efficiently with slow percolation rates. As long as the conductive layer remains unsaturated water will not enter the rock layer. Under unsaturated conditions water will be conducted around the rock layer to the water table or to drains (not shown) which should be located below the waste.



CONDUCTIVE LAYER BARRIER

requires: (1) Conducting layer (fine sandy loam), and (2) Capillary break (rock)

Figure 3. USE OF THE CONDUCTIVE LAYER BARRIER AT A SITE CONTAINING LOW PERMEABILITY STRATA

In the case shown above, the conductive layer barrier conducts water to the water table or to drains (not shown) that should be located below the waste. As long as the conductive layer remains unsaturated, water can not pass into the rock layer.

BIOENGINEERING MANAGEMENT

As noted several times in this paper, infiltration barriers such as capillary barriers or clay layer barriers (or a combination thereof) must fail if subjected to substantial shearing caused by waste subsidence. Re-establishment of a layered system after subsidence failure is a difficult undertaking and would be especially onerous if this remedial action had to be taken repeatedly.

In this section we will examine a procedure where the necessary run-off is provided by features installed at or above the soil surface rather than within the profile. The procedure has been described by Schulz et al., (59) and was designated bioengineering management. The principle advantage of the bioengineering management system is that subsidence can be easily managed by relatively simple, inexpensive maintenance of the above ground features rather than difficult reconstruction of below ground layers. It should be noted, that after a sufficient passage of time so that the organics have decayed out and the waste containers have completed failure, subsidence will cease and a layered system could be then installed which could last over geologic time periods.

In essence, the "bioengineering management" technique utilizes a combination of engineered enhanced run-off and stressed vegetation in an overdraft condition to control deep water percolation through disposal unit covers. To describe it further: if a waste burial site is selected so that incoming subsurface flow is negligible, then precipitation is the sole source of input water. In a simplified model, that water has three possible fates: (1) evapotranspiration, (2) run-off, and (3) deep percolation. Evapotranspiration has a definite limit governed by energy input. Ideally, deep percolation should be zero, leaving only the run-off component available for unlimited manipulation. Positive control of run-off becomes difficult with the use of compacted porous media trench caps as the sole barrier to water infiltration. The compacted material tends to become more permeable with the passage of time, due to fractures caused by waste subsidence and from the inexorable process of root growth followed by death and decay of the roots, thus creating water channels. Evapotranspiration is then not adequate to use all of the infiltrating water, and water percolates downward to the waste. As stated before, evapotranspiration has a theoretical maximum dictated by solar energy input to the system; only run-off remains available for nearly unlimited management. This run-off can be surface or sub-surface as long as it occurs before water reaches the waste.

Surface run-off can be managed to as high as 100 percent (perfect leak-proof roof, expensive and hard to guarantee). Alternately, run-off can be engineered rather inexpensively by using an impermeable ground cover over part of the surface to achieve high and controlled levels of run-off. Vegetation planted between areas of impermeable cover will extend over the cover to intercept incoming solar energy to evaporate water. Roots will extend under the cover in all directions to obtain water. Such a system can be visualized similarly to a supermarket parking lot where trees are planted in islands among an extensive paved area with the island having curbing around them. Utilizing this concept,

it should be possible, by combining engineered run-off with vegetation, to maintain the soil profile in a potential overdraft condition on a yearly basis.

Investigations of the Bioengineering management technique are underway in lysimeters at Maxey Flats (Figures 4-6) and large scale field plots (Figures 7, 8, 9) at Beltsville, MD (59). To date, results have been reported on the lysimeter experiments and are quite encouraging. (See Figure 10). Data acquisition has been initiated at Beltsville but not yet reported. The installations at both the Maxey Flats and Beltsville sites afford complete water balance accountability.

MAXEY FLATS

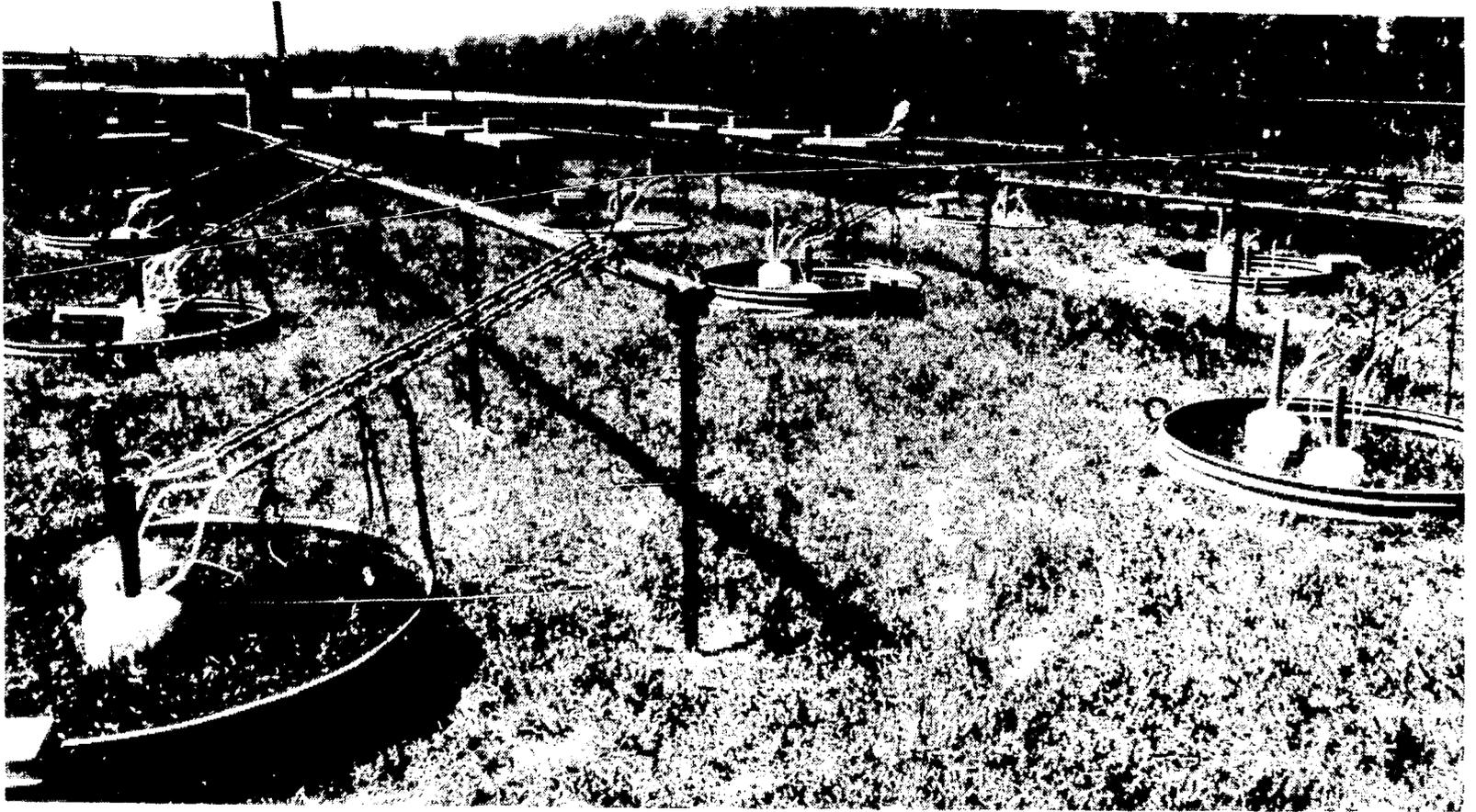


FIGURE 4 . Lysimeter installation, 1983. System gives complete accountability of all rain water falling on soil surface of each lysimeter. Amount of water striking soil surface is known from rainfall measurements. Over a sufficiently long time period, the water striking the surface has three fates: 1) surface run-off, measured by collection in surface run-off sump and pumping collection tank; 2) deep percolation to the water table, measured by maintaining constant water table level by pumping to storage tank; and 3) surface evaporation and plant transpiration. Surface evaporation and plant transpiration = rainfall - (surface run-off + deep percolation).

MAXEY FLATS

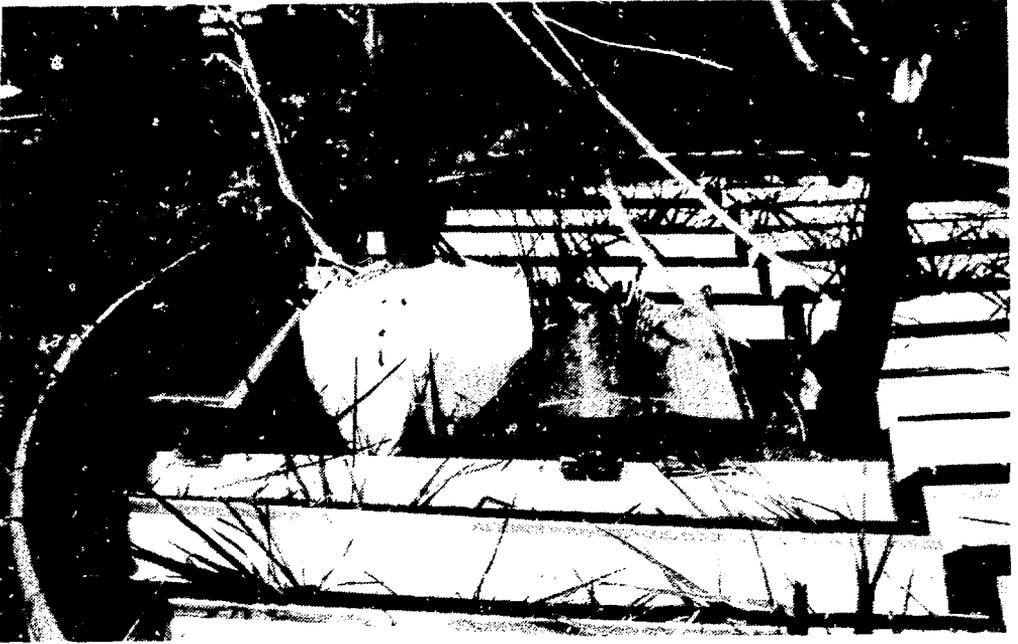


FIGURE 5. Lysimeter with engineered run-off system installed. Lysimeter has two surface run-off measurement capabilities. The soil surface run-off is collected in a sump and pumped out to a measuring tank. The engineered run-off is measured similarly. 1984.



FIGURE 6. Lysimeter with Kentucky fescue grass one year after addition of enhanced run-off system. Grass has grown up between gutters and provides substantial evapotranspiration. 1985.

BELTSVILLE, MARYLAND

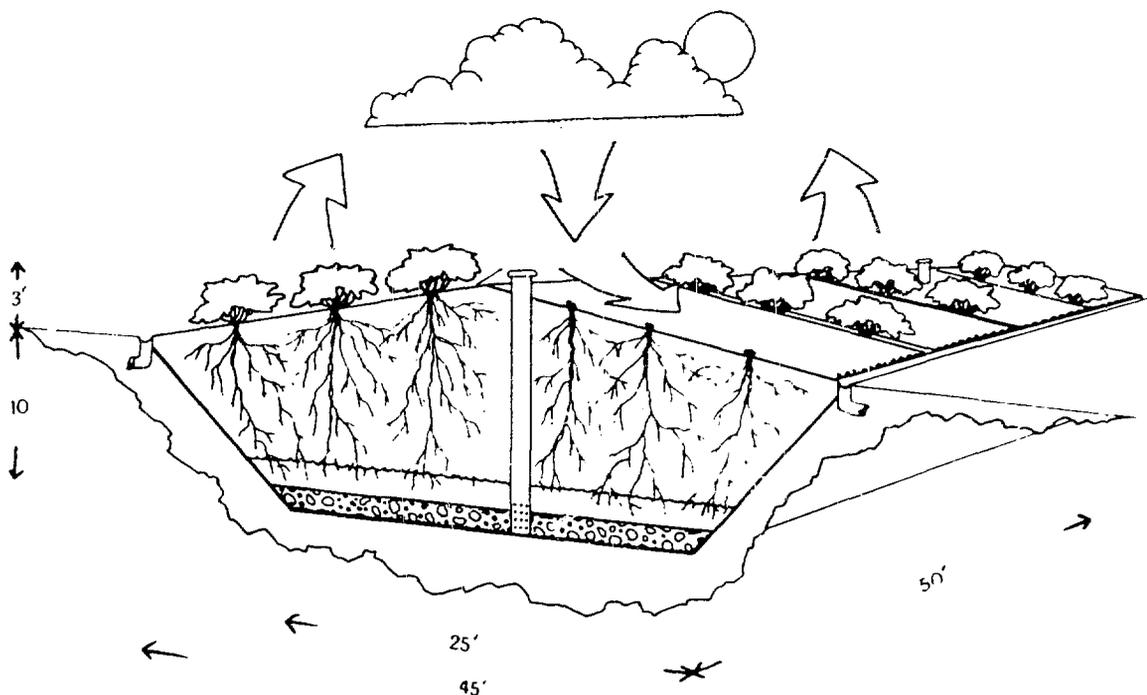


FIGURE 7. Large lysimeter for complete water balance measurements. Precipitation, surface run-off, percolation and evapotranspiration will be measured. Diagram shows positive run-off feature which, in this case, is provided with corrugated panels. Junipers are planted between panels and are grown to extend over panels to provide potential evapotranspiration greater than infiltration on an annual basis. The soil mass acts as a reservoir to sustain the plants in dry periods, and acts as a sponge during wet periods.

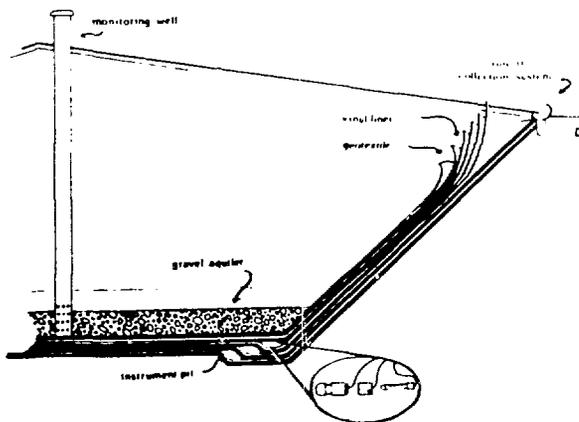


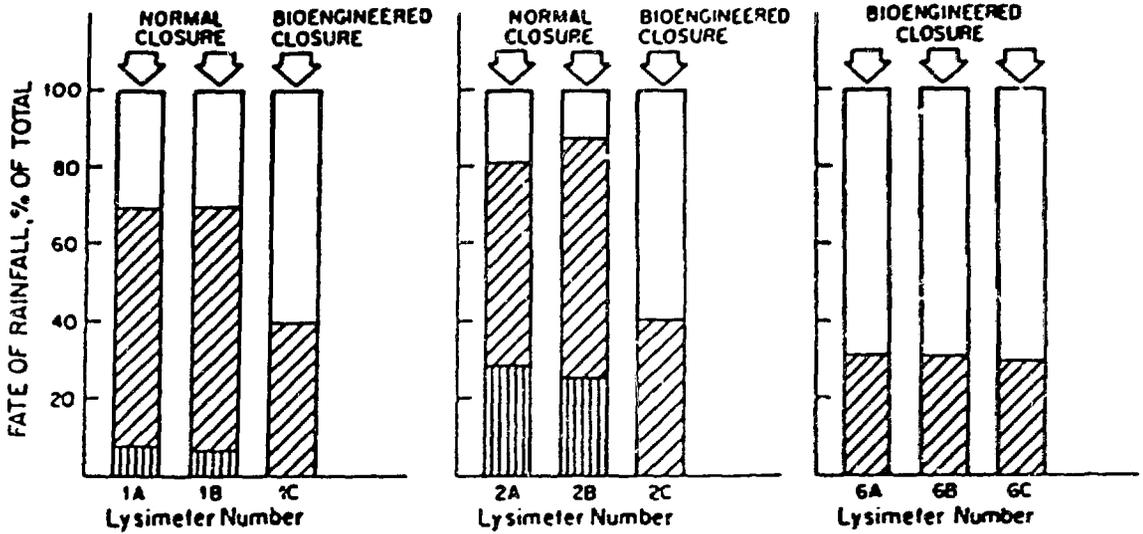
FIGURE 8. Detail of cell construction. There are 4 layers of 20 mil PVC liners and 5 layers of geotextile to serve as water barriers to isolate the cell. Three discrete barrier partitions are thus created. Leakage through any partition is monitored.



FIGURE 9. Large-scale bioengineering management lysimeters. Each cell (lysimeter or plot) is 14 m x 21 m with Pfitzer Juniper growing through the 4-inch gaps between panels. The light appearing panels are corrugated aluminum and the darker panels are corrugated green fiberglass panels. Two crowned lysimeters behind the bioengineered lysimeters are cropped to fescue grass for comparative purposes. Two lysimeters at the rear are reserved for future work.

RESULTS OF MAXEY FLATS LYSIMETER EXPERIMENTS

Seasonal 1984-85



Seasonal 1985-86

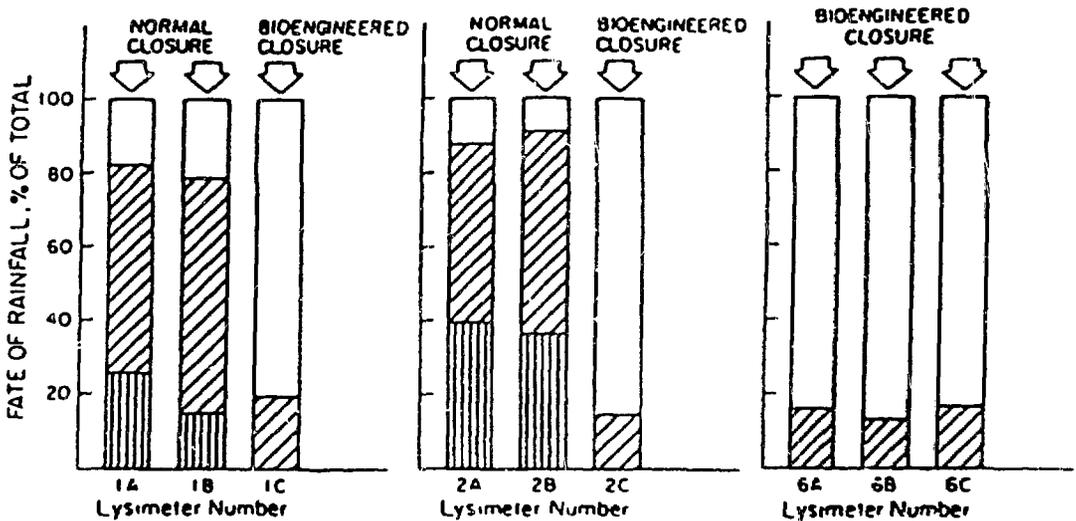


FIGURE 10. Fate of water entering the system. Evapotranspiration, total surface run-off, and deep percolation given as a percent of precipitation for the seasonal years 1984-1985 and 1985-1986. One of the essential requirements of a bioengineered closure system is that substantial evapotranspiration be maintained after the installation of an engineered run-off system; that requirement was readily met. (Ref. 59)

PRESENT OUTLOOK AND RECOMMENDATIONS

The thesis has been developed in this paper that solely run-off can be subject to unlimited manipulation. Necessary run-off can be surface or sub-surface.

A procedure named "bioengineering management" has been described which used engineered features at the surface to ensure adequate water run-off. Investigation on that procedure is underway, and results to date are encouraging.

Two types of sub-surface features that may be constructed to enhance run-off are described. One is the "resistive layer" barrier, and the other is the "conductive layer" barrier.

The "resistive layer" barrier is the well known compacted clay layer and depends on compaction of permeable porous materials to obtain low flow rates. Flow through a resistive layer is described by Darcy's law (1856). Investigations on flow through such layers have gone on for over 100 years, so further progress in this area can be expected to be slow.

The "conductive layer" barrier is based on the capillary barrier concept and has but little been investigated. No definitive full scale field experiments have been carried out in the humid regions. It is in this relatively unplowed ground that the greatest advances might take place in the near future, and is where new effort should be directed.

PLANS FOR FUTURE WORK

EXPERIMENTAL OUTLINE FOR FY 88

In the preceding discussion of fundamental concepts which might prove useful for control of water in infiltration and percolation three broad types of waste covers are:

- (1) Resistive layer barrier (clay layer barrier)
- (2) Conductive layer barrier (capillary barrier)
- (3) Bioengineering management (surface barrier)

Evaluation of (3), the bioengineering management procedure, is underway in lysimeters at Maxey Flats and two large scale field plots at Beltsville, MD. To date, results have been reported on the lysimeter experiments and are quite encouraging (59). Data acquisition has been initiated at Beltsville but not yet reported. The installations at both the Maxey Flats and Beltsville sites afford complete water balance accountability.

The conductive layer barrier (2), is based on the capillary barrier concept. The term "conductive layer barrier" was introduced to point out that in this concept, downward percolating water is transported or diverted laterally within the conductive soil layer. On the other hand, with the clay barrier concept, water "piles up" above the clay layer and is transported laterally above the clay layer. That transport often occurs in a gravel layer provided above the clay layer or may take place as surface run off. It was pointed out in the report that under certain conditions a conductive layer barrier could have a theoretical efficiency approaching 100%, but on both a theoretical and practical basis such a barrier can be effective only under relatively low water flows. Conversely, the resistive layer barrier works most efficiently (that is, diverts a higher percentage of infiltrating water) at higher precipitation rates. Based on these two considerations it seems reasonable that a very effective barrier system might be constructed by placing a "resistive barrier" over a "conductive barrier". We propose to carry out such a study in one of the Beltsville plots as depicted in figure 11.

Complete water balance measurements are to be made by quantitative water measurements at each point depicted by an arrow in figure 11. Surface run off will be measured. Lateral water transport in the drain conductive layer barrier is composed of a fine sandy loam soil underlain by a rock layer. (Graded materials will be present to provide soil/rock separation). The diversion flow through the conductive soil layer will be measured. Any water percolating downward through all the layers and infiltrating the "waste" will be caught in the pan or liner depicted by the heavy lines in figure 11. The amount of such water infiltration will be recorded.

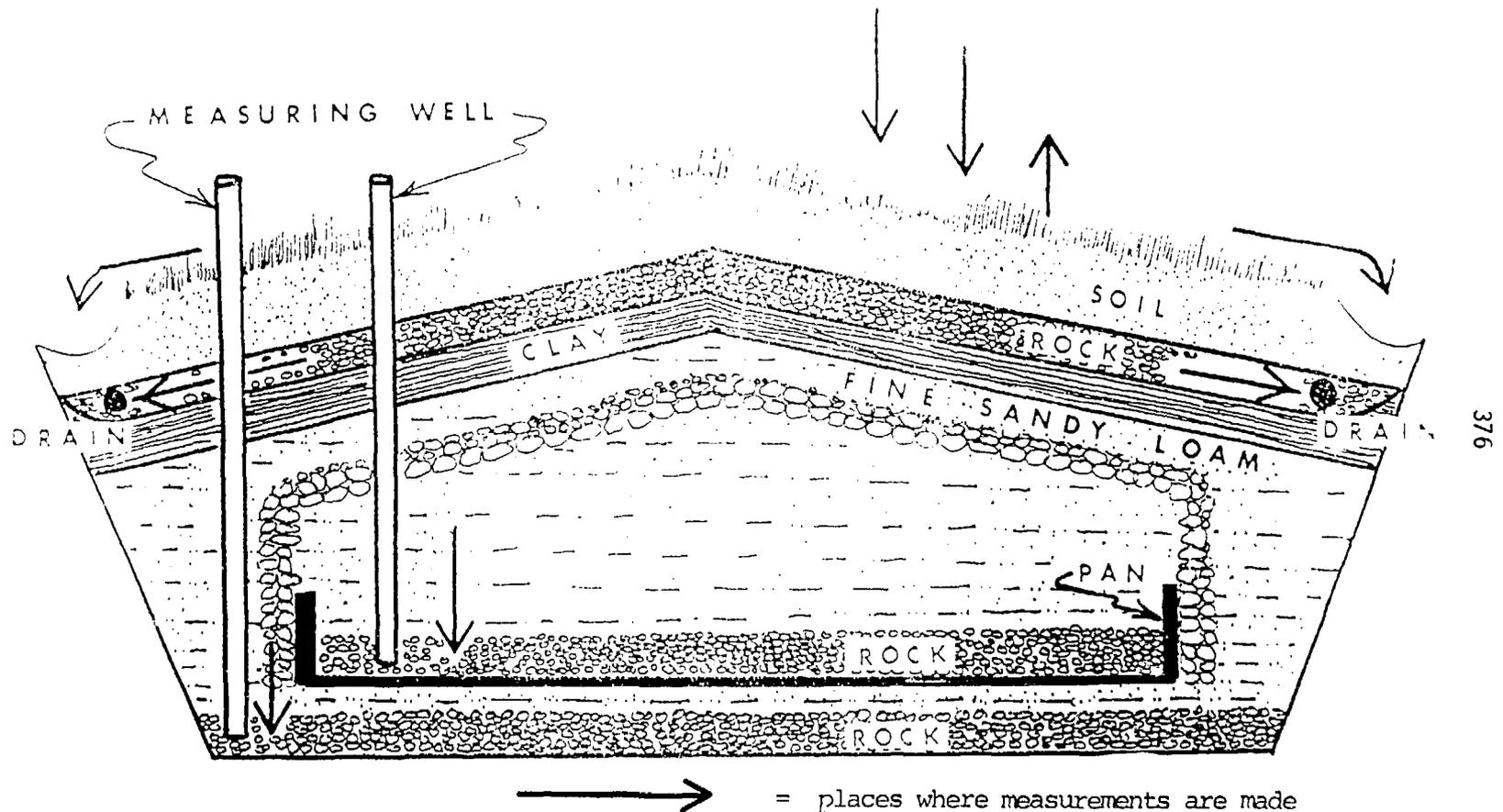
At this point it should be noted that one of the problems associated with experiments of the type depicted in figure 11 (also 12 and 13) is that the measurement devices themselves may tend to compromise the results. Of special concern here is that the standpipes penetrating various layers may disrupt the integrity of the layers. In the experiment collars or "fins" will be installed on the pipes so as to coincide with the layers to help alleviate this problem. Soil moisture status will be measured using instrumentation including the neutron probe and tensiometers but will be done in a fashion to minimize experimental anomalies caused by the instrumentation. It will be necessary to strike a careful balance reflecting the natural desire for extensive instrumentation with the need to prevent experimental anomalies caused by the presence of that instrumentation.

Figure 11 is depiction of the second plot (lysimeter) we propose to set up during FY 88. Figure 12 is quite similar to figure 11 except that the conductive layer barrier is absent, therefore this is solely a study of the resistive layer barrier (compacted clay layer). The usefulness of this plot is two-fold. 1) It serves as a reference for the plot depicted in figure 11 thus giving additional information on the effectiveness of a capillary barrier sued in conjunction with a compacted clay layer. 2) At this time, the simple clay barrier seems to be the most likely choice of SLB operators. Operation of a plot dependent on the clay barrier concept should give verification and/or show problems associated with that design.

The plot depicted in figure 13 essentially is a study of the UMRAP design. It is a variation on the resistive layer barrier (1). It differs from the design depicted in figure 12 in that a rip rap erosion protection layer replaces the topsoil and vegetation shown in figure 12. A very negative aspect of this design is the virtual elimination of evapotranspiration. The rip rap (or boulders) will serve as a one way valve, allowing water to readily infiltrate the surface of the cap but will also act as a mulch, seriously retarding evapotranspiration. The effectiveness of the clay layer as a water barrier will consequently be sorely tested. On the positive side the rip rap will immediately prevent erosion whereas it takes time to establish an erosion resistant vegetative cover. Also, in the absence of vegetation, the clay layer will tend to remain quite wet and a wet compacted clay layer is a very effective barrier to gas transport. This is particularly important when one is concerned with radon migration upward from buried uranium mill tailings. Also, since vegetation will be absent, roots will not penetrate the clay layers and cause an increase in hydraulic conductivity of that layer.

If we proceed with set up of three plots at Beltsville according to this outline, the status of the work at Beltsville will be as summarized in Table 1.

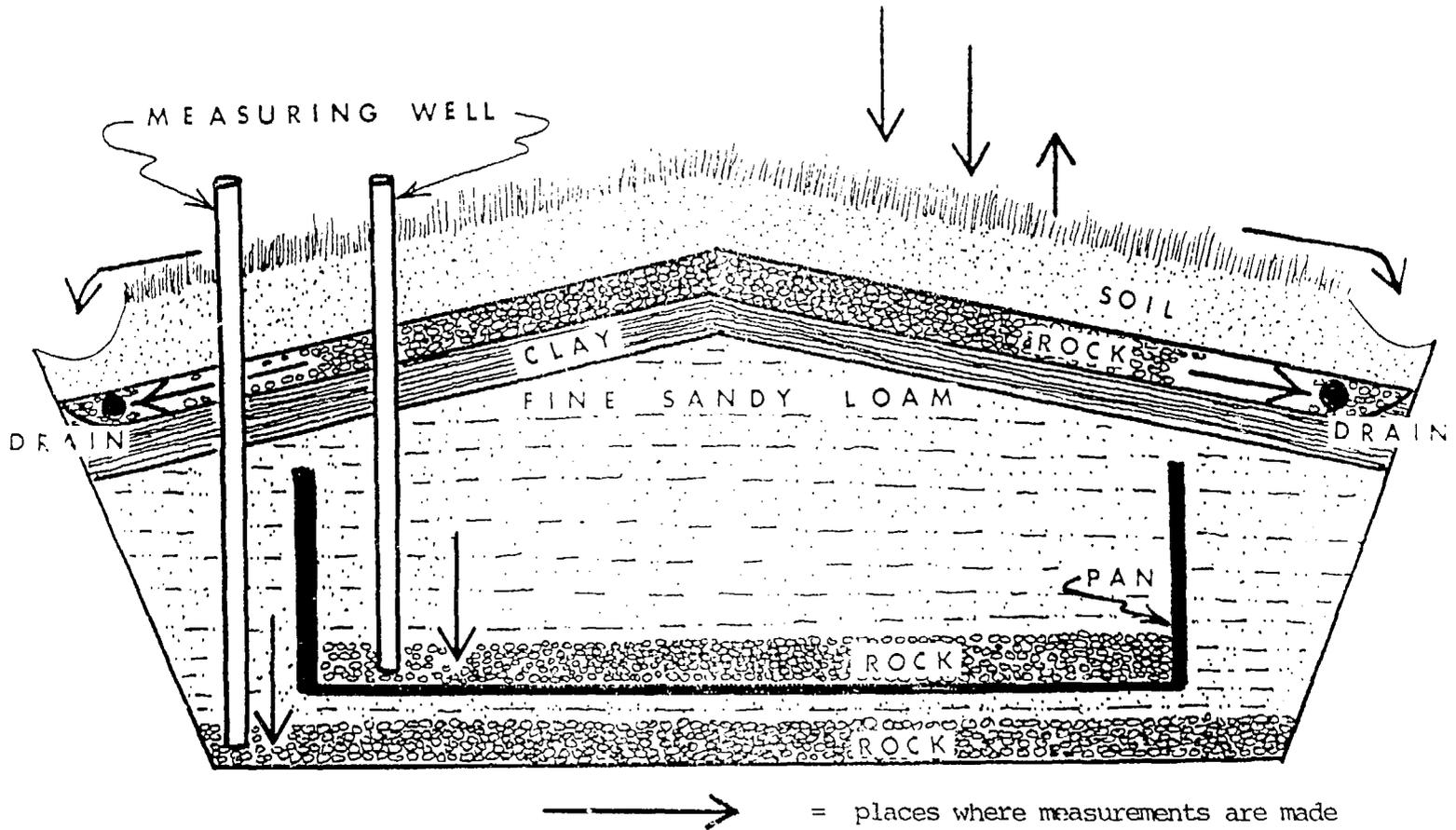
CONCEPTUAL DESIGN



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Figure 11. Conceptual design for test of the Resistive Layer Barrier (clay barrier) + Conductive Layer Barrier (capillary barrier) planned for construction in the large lysimeters at Beltsville, Maryland (Figures 8, 9, 10).

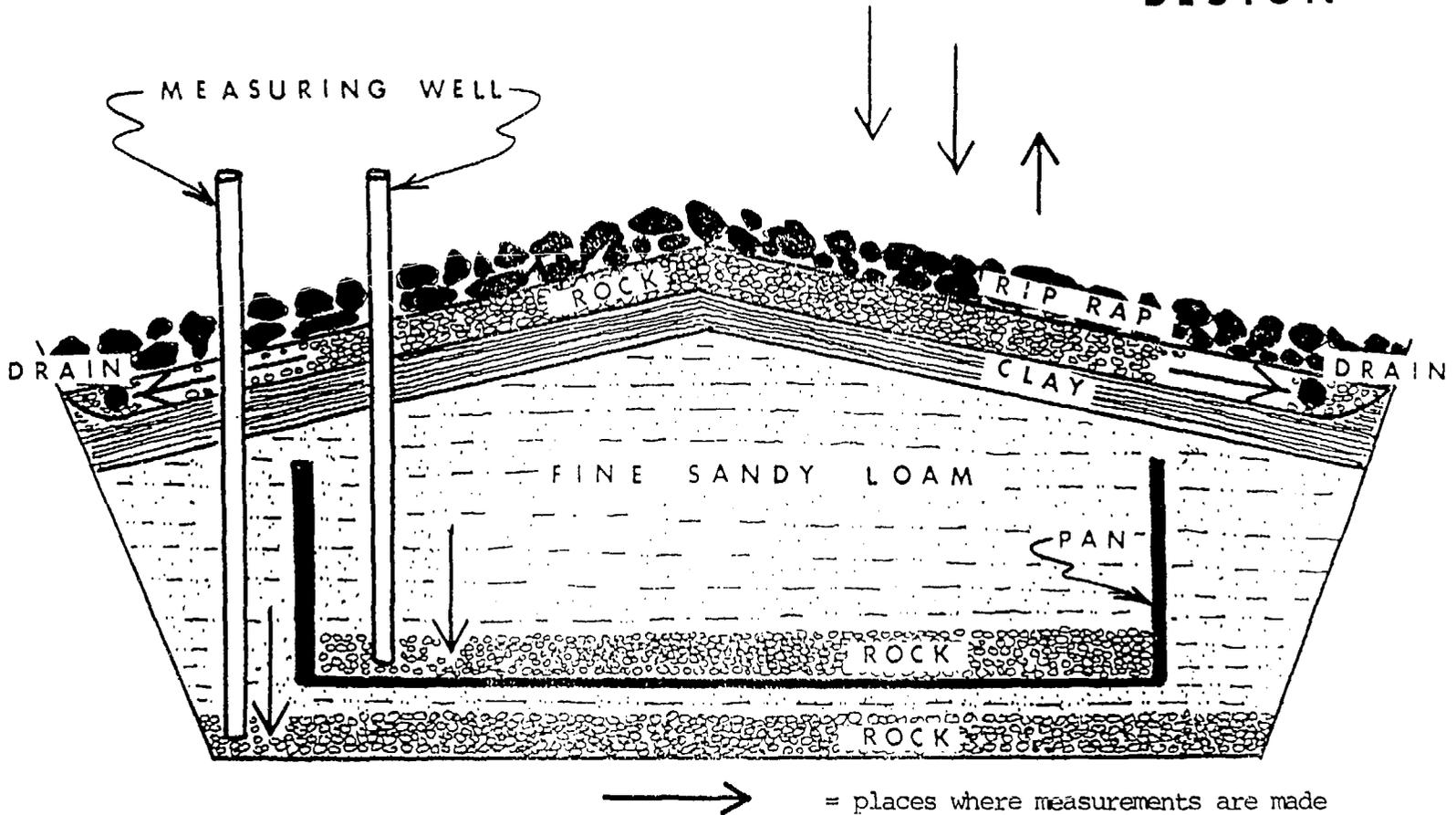
CONCEPTUAL DESIGN



377

Figure 12. Conceptual design for test of the Resistive Layer Barrier (clay barrier) planned for construction in the large lysimeters at Beltsville, Maryland (Figures 8, 9, 10)

CONCEPTUAL DESIGN



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Figure 13. Conceptual design for test of Resistive Layer Barrier (clay barrier) with erosion protection cover (rip rap) planned for construction in the large lysimeters at Beltsville, Maryland (Figures 8, 9, 10).

TABLE 1

Proposed Status of Work at Beltsville, MD, FY 88

| Plot number | LLW Cover (Import feature) | Status |
|-------------|------------------------------------|-------------------|
| 1 | Bioengineering | Underway |
| 2 | Bioengineering | Underway |
| 3 | Backfill (comparison purpose only) | Underway |
| 4 | Compacted clay layer | Constructed FY 88 |
| 5 | Clay layer & capillary barrier | Constructed FY 88 |
| 6 | Clay layer & surface rip rap | Constructed FY 88 |

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**Greater Confinement Disposal of Radioactive Waste
at the Nevada Test Site**

**Dr. Lynn L. Ebling,
Reynolds Electric and Engineering Co., Inc.**

Computer Modeling of Greater Confinement Disposal
of
Radioactive Waste at the Nevada Test Site

by Lynn L. Ebeling, Ph.D., P.E.
Reynolds Electrical & Engineering

ABSTRACT

A 1.1 megaCuri and 3.5 kilowatt waste source has been buried 30 meters down an auger hole in a tuffaceous alluvium for over three years. Temperature and moisture have been monitored in the surrounding soil during this time and two gaseous tracer migration studies conducted to determine flow parameters. Temperatures exceeding 300°C have been recorded and the moisture range has increased from 10-12% to 2-14%. The tracer migration data is being analyzed. A two-dimensional transient multi-phase and E.P.A. accepted model, WAFE, is being used to simulate this data and make long term performance projections. Many problems associated with precession, array boundaries and local subroutines have been encountered in converting the model which was developed on the Los Alamos National Laboratory's CRAY based computer system to run on a DEC/VAX 750. Documentation, which is still in rough draft, has also made the valid modification of the code or organization of an input data file difficult.

**GREATER CONFINEMENT DISPOSAL
of
RADIOACTIVE WASTE
at the
NEVADA TEST SITE**

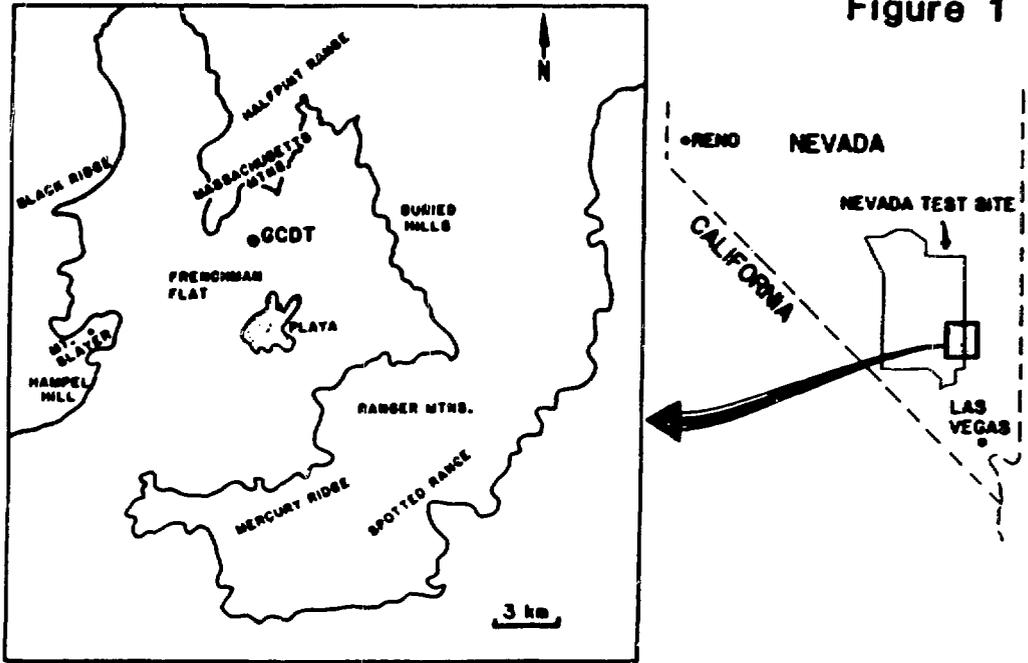


OCTOBER 1987

Lynn L. Ebeling, Ph.D., P.E.

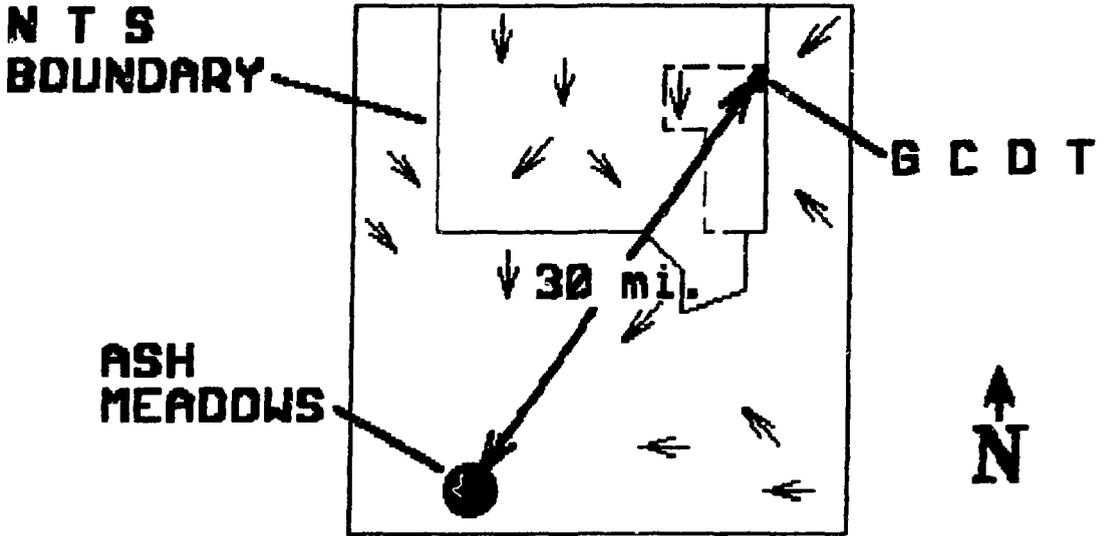
REYNOLDS ELECTRICAL & ENGINEERING CO., INC.

Figure 1

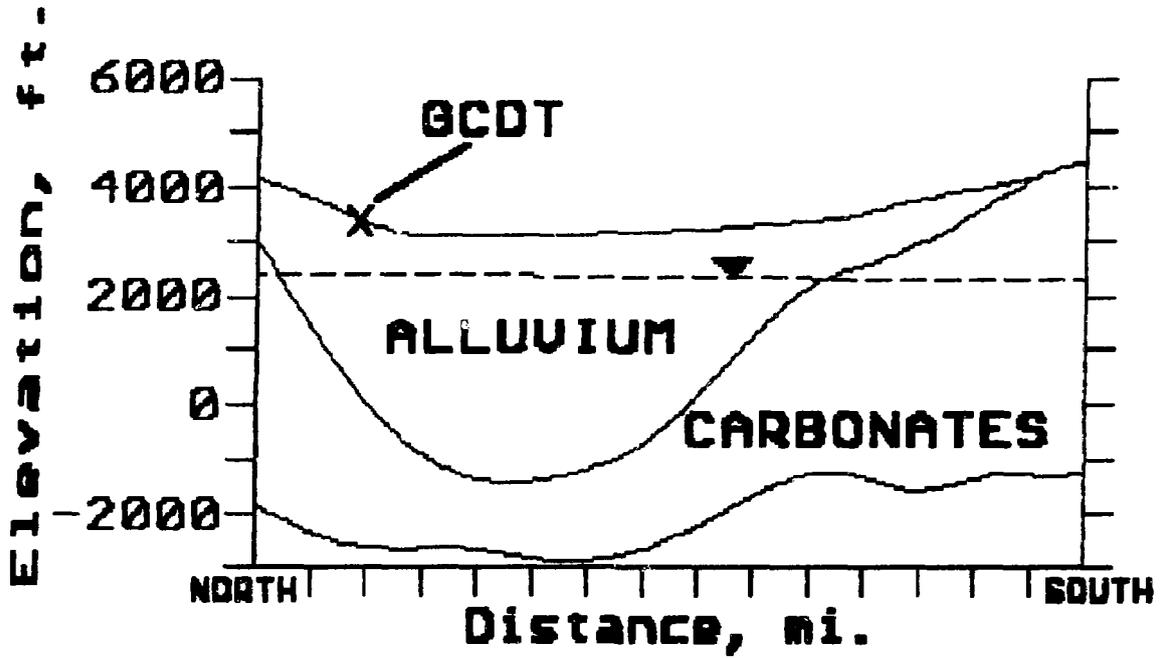


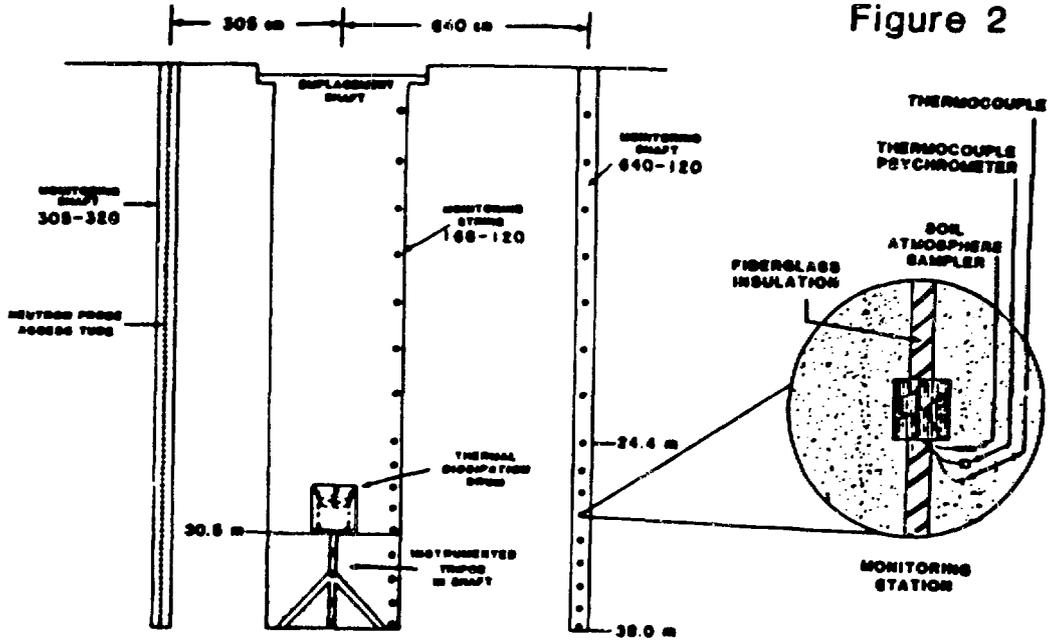
General location map

REGIONAL FLOW



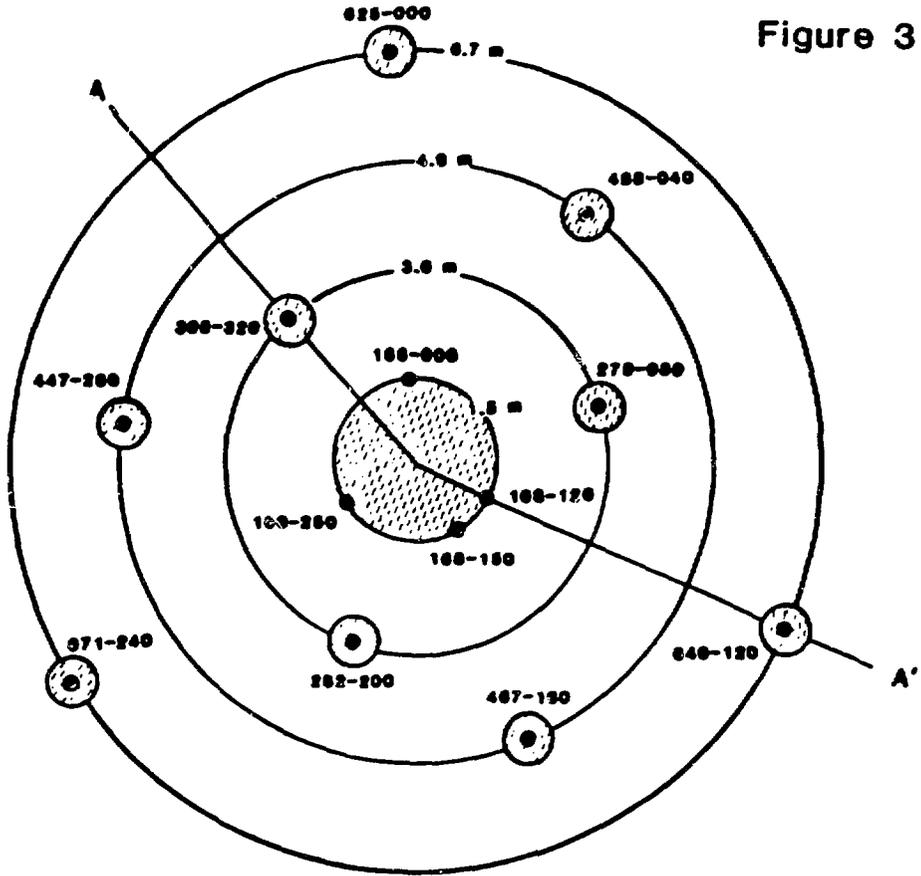
HYDROGEOLOGY





Monitoring layout design

Figure 3

**LEGEND**

- 8-cm-diameter steel access tube for neutron scatter probe
- In situ instrument strings with soil atmosphere samplers, thermocouples, and thermocouple psychrometers
- Quaternary alluvium
- ▨ Shifted quaternary alluvial backfill

NOTE: Location descriptors; point 278-000 is at a radius of 278 cm, and an azimuth of 80°

Instrument line distribution

G C D T Waste

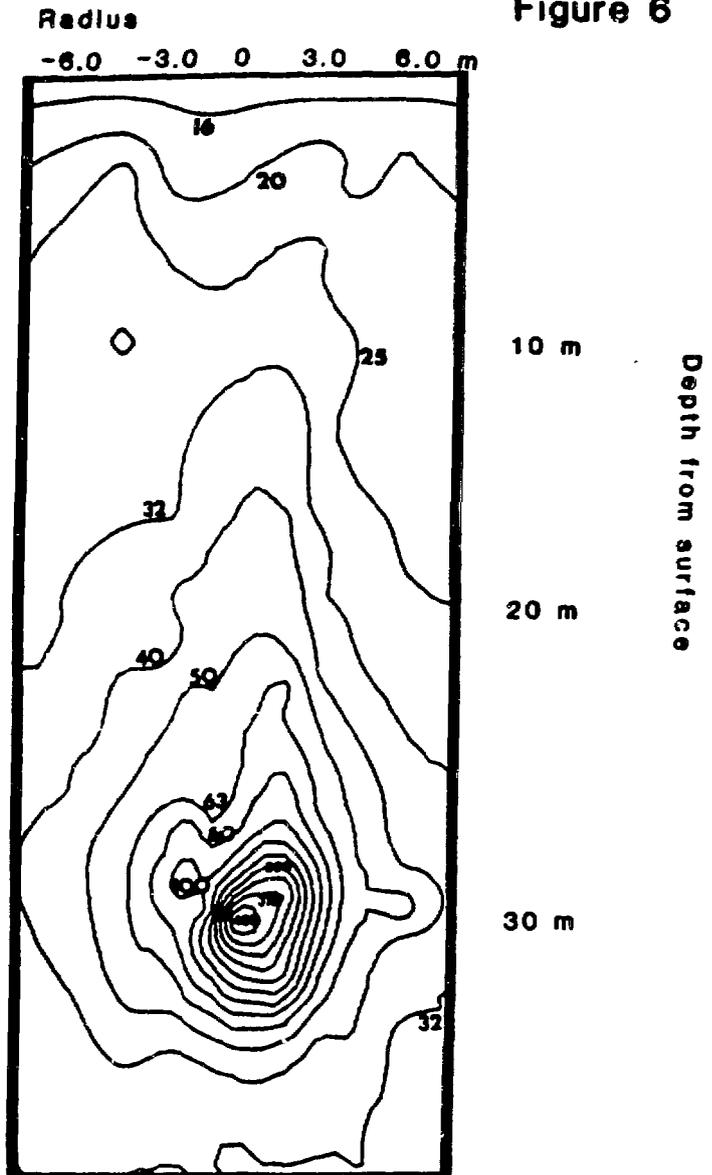
22 Cubic Meters

1,100,000 Curies

3,200 Watts

3 Years

Figure 6

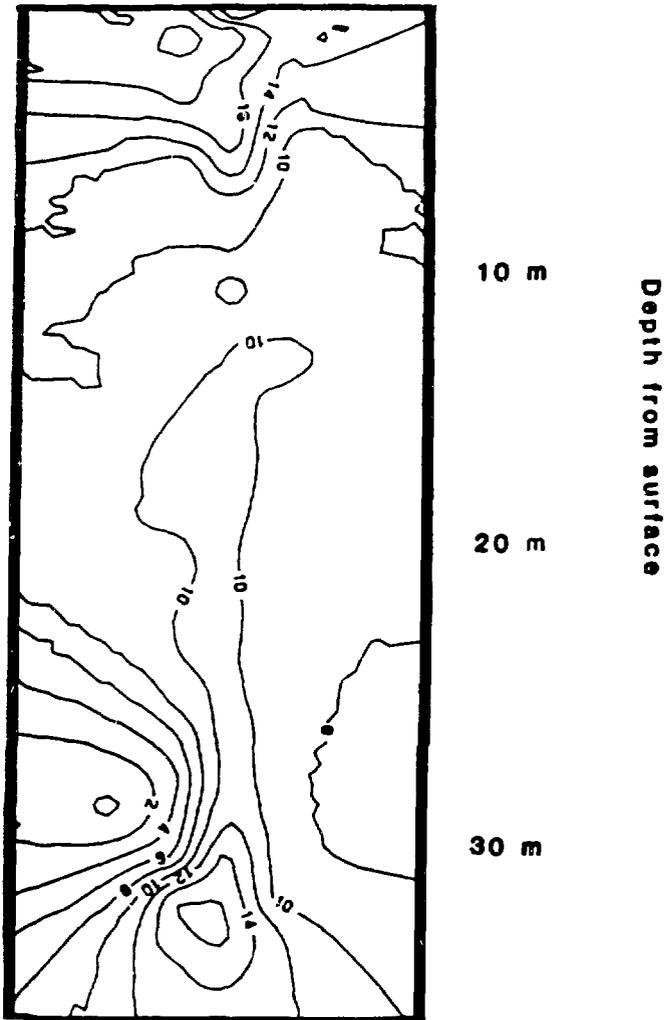


Isothermal map for March 20, 1986
(2 years after waste emplacement)

Radius

0 3.0 6.0 m

Figure 8



**Moisture distribution for July 1986
(2 1/4 years after waste emplacement)**

W A F E

Water Air Fire Earth

Mass and Heat Migration in Porous Media

Multi-Phase/Component flow

Radioactive Decay

Non-Homogeneous, Anisotropic

Transient, Two-Dimensional

Implicit Finite-Difference

E P A Accepted

W A F E Input

Media & Fluid Properties

Relative Permeability

Density

Thermal Conductivity

Porosity

Molecular Weight

Sorption

Matric Potential

Diffusivity

Half-Life

Specific Heat

Tortuosity

W A F E Input

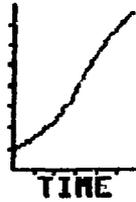
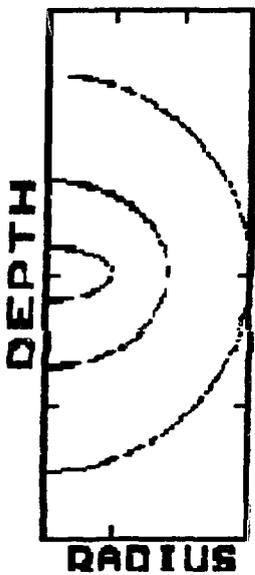
Histories

Boundary Conditions

Geometry

Source/Sinks

WAFE Output

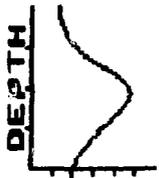


Temperature



Saturation

Concentration



Pressure

Velocity

W A F E Difficulties

Documentation

Code

Cray-→VAX 750

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Low-Level Waste Disposal Techniques and Experience in France

Presented by:

Cheryl A. Hutchison, NUMATEC

LOW-LEVEL WASTE DISPOSAL TECHNIQUES AND EXPERIENCE IN FRANCE

Cheryl A. Hutchison, NUMATEC
Bertrand de Wavrechin, SGN
Yves Marque, ANDRA

ABSTRACT

The "Centre de Stockage de la Manche" (CSM) is the first near-surface disposal facility for short-lived, low- and medium-level radioactive waste in France.

It began operations in 1969, at which time French safety regulations stipulated that shallow land burial was acceptable for very low-level unstabilized waste and low-level stabilized waste so long as the trenches had adequate drainage and a waterproof disposal cap. Waste with higher activity levels and uncontainerized solid waste had to be grouted inside concrete boxes in the trenches. This situation changed in 1979 with the issuance of regulatory guidelines by SCSIN, the French nuclear safety authority, which eliminated shallow land burial as a disposal option while establishing maximum values for alpha and beta/gamma activity levels acceptable for disposal, as well as an activity level threshold above which waste immobilization was mandatory. That same year, ANDRA, the French waste management agency, was created and the CSM was turned over to its control.

In 1985, the general technical requirements were updated to include design guidelines for new disposal structures at the CSM, whose components include "tumuli" (stacks of stabilized waste packages), "monoliths" (monolithic blocks created by grouting unstabilized or irradiating packages inside concrete boxes), concrete pads and separate rainwater and leachate collection systems. The updated requirements also introduced the notion of a waste acceptance procedure to be implemented by ANDRA. These requirements, along with the need for quality assurance of the waste from cradle to grave, led to the establishment of an integrated waste management system. These management principles, now being applied to the CSM, will be utilized at the second French disposal facility currently under construction and scheduled to start up in 1991.

This paper will provide background on the regulatory framework applicable to low-level waste management in France, and will describe the siting, design and operation of the CSM as well as the integrated waste management system of which it is a part.

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Oak Ridge Greater Confinement Disposal Demonstrations

Presented by:

R. W. Morrow, ORNL

OAK RIDGE GREATER CONFINEMENT DISPOSAL DEMONSTRATIONS -

S. D. Van Hoesen, Martin Marietta Energy Systems, Inc., Engineering Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee;
R. B. Clapp, Martin Marietta Energy Systems, Inc., Environmental Sciences Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee*

I. Introduction

A number of Low-Level Waste (LLW) disposal demonstrations are being conducted by the Low-Level Waste Disposal Development and Demonstration Program (LLWDDD) for the Department of Energy (DOE). This paper will focus on Greater Confinement Disposal (GCD) demonstrations being conducted in association with the disposal of a high activity low-level waste (LLW) stream to be produced by Oak Ridge National Laboratory (ORNL).

The waste stream in question will result from the cement solidification of decanted liquids from the Melton Valley Storage Tanks (MVST). The solid waste will be produced beginning in mid summer 1988. It is anticipated to have significant concentrations of Cs-137 and Sr-90, with smaller amounts of other radionuclides and <100 nCi/gm of TRU. The solid waste forms are expected to have surface dose rates in the 1-2 r/hr range. The solid waste will also contain several chemical species (nitrates, chlorides, heavy metals, etc.), at concentrations which are below those of concern from a Resource Conservation and Recovery Act (RCRA) viewpoint, but which may present enhanced corrosion potential for the disposal units.

The development of the GCD units is a joint effort among several groups. ORNL Waste Operations is responsible for the placement of the waste in the GCD units. LLWDDD will provide technical support for this effort, including conduct of an extended monitoring program to evaluate the effectiveness of the disposal units. Martin Marietta Energy Systems Engineering Division is responsible for managing project design and construction. An architect-engineer (A-E), Lee Wan and Associates has prepared the Title I and II design. Several fixed price subcontractors will be used to manufacture/construct the disposal units.

II. Disposal Unit Criteria

The GCD units are expected to provide capacity for up to 80 6-ft diameter by 6-ft high concrete waste forms cast in steel containers, each weighing 10-15 tons. The first solidified waste is expected to be produced in June 1988. While the waste forms are expected to meet all DOE and Nuclear Regulatory Commission (NRC) stability criteria, the disposal unit design will include provisions for protecting the disposal units from the potentially corrosive materials contained in the waste.

* Based on work performed at Oak Ridge National Laboratory, operated for the U. S. Department of Energy under contract DE-AC05-84OR21400 with the Martin Marietta Energy Systems, Inc.

The disposal units are required to provide multiple barriers to prevent release of radionuclides to the environment. The disposal unit design life is to be 100-300 years, with a goal of "zero" release to the environment during this control period. The disposal units and associated operation will include provisions for keeping worker exposures as-low-as-reasonably-achievable (ALARA) (the surface dose rate of the waste after emplacement should be <200 mr/hr). The location and design will provide for at least a 2-ft buffer between the disposal unit and the highest recorded groundwater elevation. Disposal unit design will provide protection from natural events such as flood (above 500 yr flood plain), wind, and earthquake (0.12g acceleration). Design, construction, and operations are to be conducted to NQA-1 standards.

III. Disposal Unit Designs

Considering the foregoing criteria, and experience gained over the last year, it was determined that two disposal technologies - an above-grade concrete tumulus and below-grade concrete silos will be engineered to provide greater confinement disposal. These disposal configurations are described later. Recognizing the nature of the solidified liquids, it was determined that corrosion and radiation resistant inner shells and liners would be needed to provide confidence that the 100-300 yr performance goal would be met. The following sections describe the materials evaluation conducted, and the GCD unit designs developed.

Materials Evaluation

An evaluation was carried out to identify materials suitable for use as inner shells and liners that would be capable of protecting the concrete pad and vaults used in the tumulus, and the mild steel and concrete used in the silos from corrosive degradation during the 100-300 yr control time period (Ref. 1). Metallics, metal ceramic composites, and plastics were reviewed. Four materials were determined to provide the desired corrosion/radiation resistance at reasonable cost.

1. Glass-lined steel is expected to provide an effective migration barrier for 300 years based on extrapolated degradation rates. Glass-lined steel provides the greatest radiolytic resistance and ultimate mechanical properties of the candidate materials. The major disadvantages of this material are limited impact resistance, handling difficulties and highest cost among the candidate materials.

2. Filament-wound vinyl ester resins (glass-filled) offer excellent chemical resistance and radiation stability. Cross-linking with novalac and incorporation of a large degree of phenyl structures in the backbone increases radiation stability and reduces oxidative degradation. Outgas rate from radiation-induced scission is very low. This material is the most cost-effective with respect to other candidate materials. Disadvantages are that the mechanical properties are slightly reduced at high dose (10^8 rads) and are less than steel initially.
3. Vinyl ester resin linings on mild steel substrate appear to meet the design criteria of no migration for 300 years. Chemical resistance and radiation stability are expected to be similar to that provided by vinyl ester resin filament-wound vessels. The primary disadvantages of this composite are a limited tendency to spall which may increase with long-term exposure, the lack of standardization in the industry which will require extensive quality assurance, and the labor-intensive application process which elevates cost relative to filament-wound vessels.
4. Vessels of rotationally cast molded cross linked polyethylene (CLPE) are considered a potential material for inner liner application in the GCD silo. CLPE is the current standard in HIC applications, offers low cost and good chemical resistance to the anticipated leachate. The primary disadvantages are a high outgas potential, susceptibility to oxidative degradation and stress crazing, difficulties in the fabrication of large vessels, and the least strength among the candidate materials.

Each of these materials is planned to be used in at least one of the GCD silo units to develop experience with, cost, constructability, and performance. The filament-wound vinyl ester resin material was judged to offer the best cost/performance combination and was selected as the liner material for the casks to be used in the tumulus disposal unit and as the inner shell for six of the silos.

Tumulus Disposal Unit Design

The existing tumulus demonstration disposal unit is planned to receive 60 of the 80 waste forms to be produced in the initial solidification campaign. The tumulus disposal unit is described in more detail in Ref. 2 and consists of a 65-ft X 105-ft, curbed, epoxy coated steel reinforced concrete pad. The pad surface is drained through two lines to a monitoring station. A 30 mil high density polyethylene (HDPE) liner isolates the gravel layer under the pad, and provides additional monitoring capability through a separate drain line.

The tumulus pad will initially be loaded with low activity waste contained in rectangular concrete vaults. The vaults will be placed in a single row, two vaults high, around the perimeter of the pad, creating an open space in the center of the pad, surrounded by a "shield" wall (Fig. 1). The shield wall will provide an access barrier and radiation shielding during the solidified waste loading operations. The solidified waste disposal casks, described in more detail in the following section, will be covered by a layer of low activity vaults following waste loading. Ultimately, the stacked waste will be covered with a layered earthen mound.

The solidified waste disposal cask will consist of steel reinforced (epoxy coated), pre-cast concrete with a filament-wound vinyl ester resin (glass filled) liner (Fig. 2). The cask will have a fixed internal cavity, with varying wall thicknesses (40 units with 8-in., 10 units with 10-in., and 10 units with 12-in. walls) to provide the ability to handle waste form surface dose rates up to 2 r/hr and still achieve <200 mr/hr cask surface dose rates.

The solidified waste is currently planned to be transported to SWSA 6 in a Department of Transportation (DOT) approved shipping cask. The waste will be removed by crane from the shipping cask and placed in the disposal cask, which will have already been placed on the tumulus pad.

The cask will be sealed by two separate covers. An internal vinyl ester resin lid will be placed and sealed to the liner to completely enclose the waste form. This cover will include a pressure relief vent with check valve. A 1-ft thick concrete cover will be placed and sealed with bitumen.

Silo Disposal Unit Design

The remaining 20 waste forms will be placed in below-grade silos which are based on the concept currently being utilized in SWSA 6. The current SWSA 6 concept involves excavation of a trench, placement of two concentric corrugated metal pipes (CMP) in the trench, and filling of the bottom and annulus with concrete to create a concrete silo. As described below, three types of silos are planned to be built as a part of the GCD demonstration/MVST disposal activities. The silos will be constructed in three modules of five units each, with two waste forms to be placed in each silo of two modules. The third module is intended for bulk LLW from routine plant operations. Each silo will include an access pipe to sample the inner silo cavity directly, and an external gravel sump for monitoring and removal of water which may infiltrate around the silos.

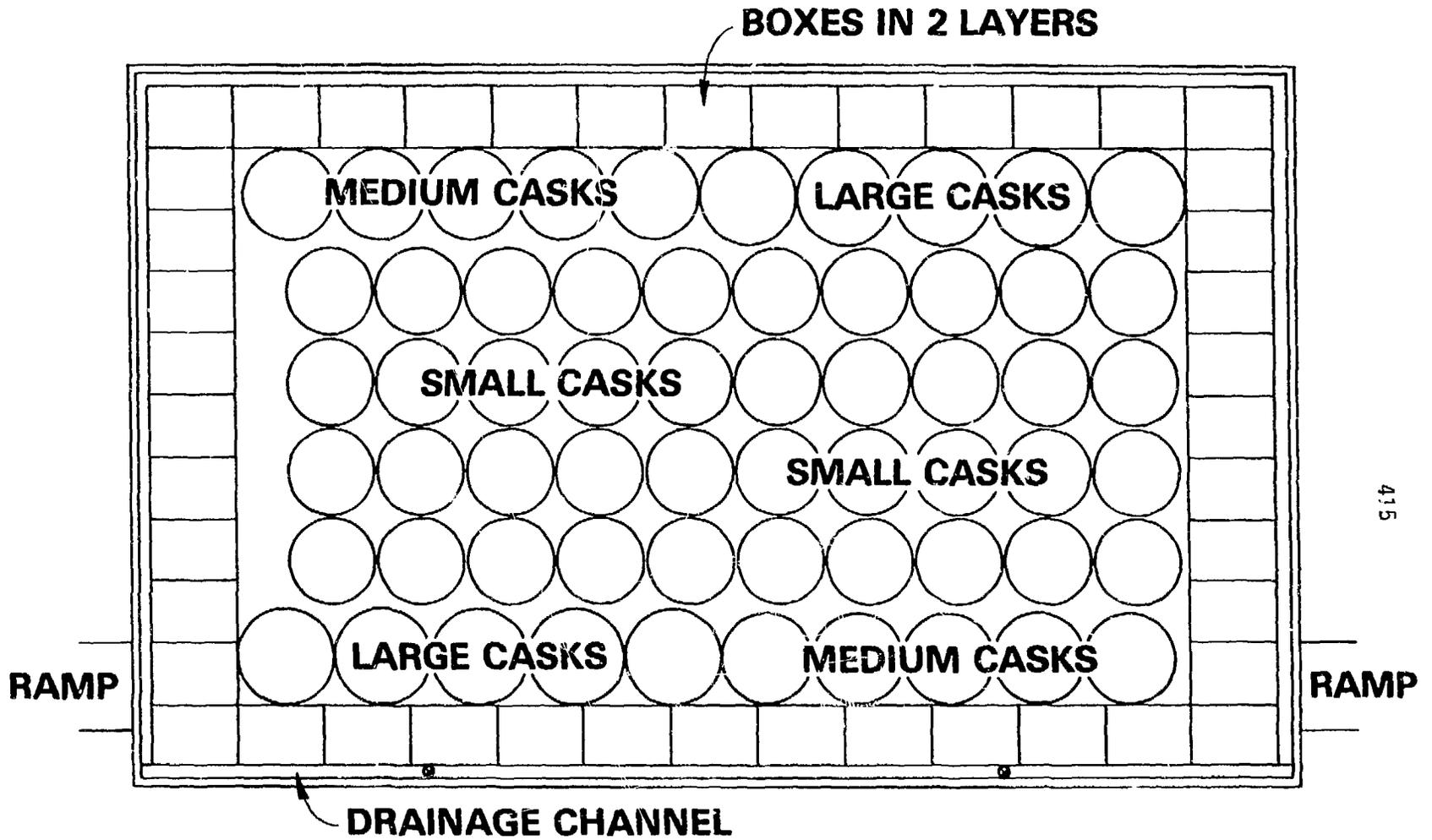
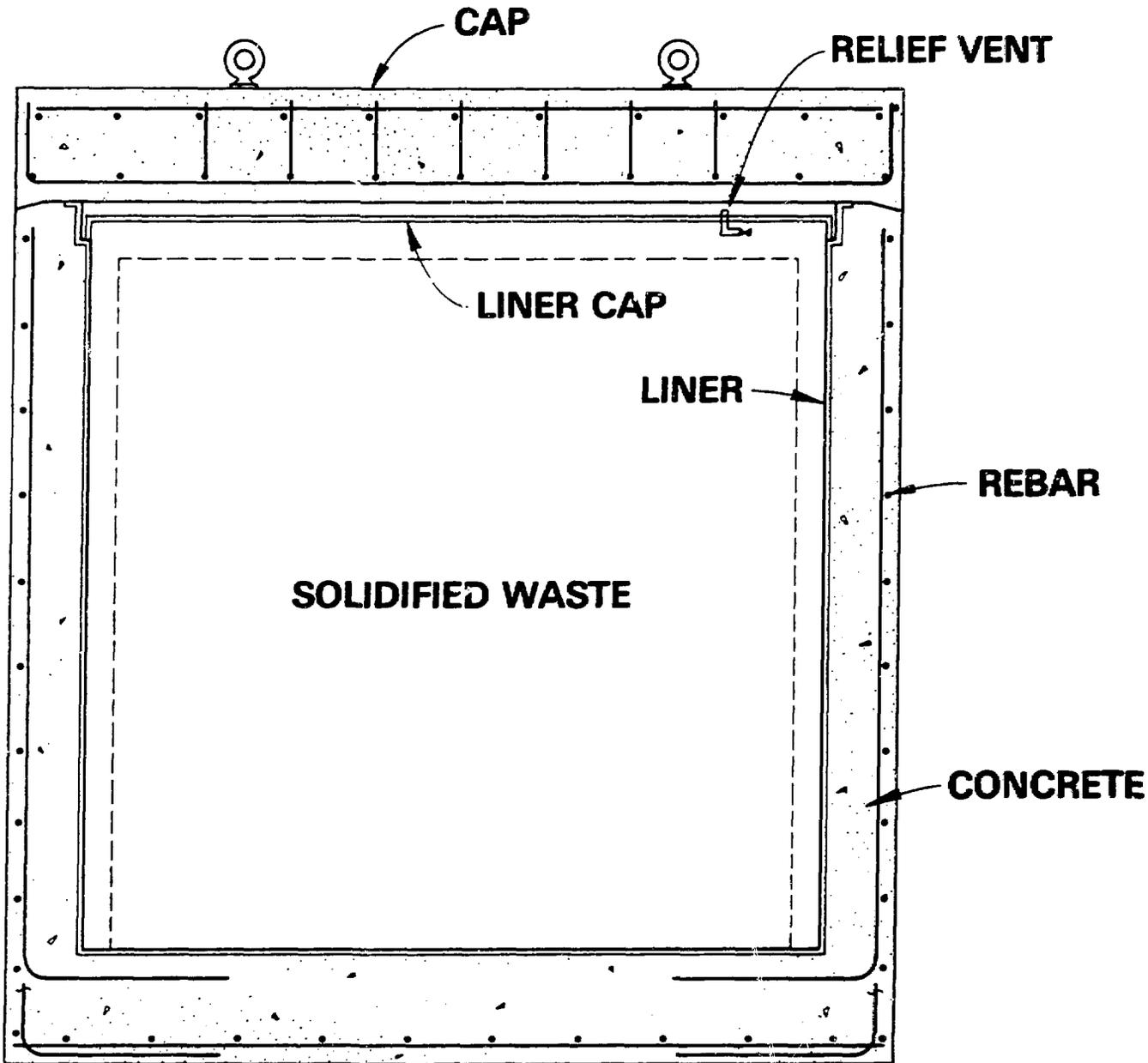


FIG. 1. TUMULUS LOADING PLAN

**FIG. 2. DISPOSAL CASK**

Type I Silo

The Type I silo is aimed at providing a retrieval capability to allow for long-term monitoring and examination of the waste form to be produced in the MVST solidification efforts. Two non-radioactive, surrogate waste forms will be produced during initial checkout and testing of the MVST solidification system and placed in the Type I silo.

The silo will be constructed by placing a 10-ft diameter X approximately 20-ft long CMP in the prepared trench (Fig. 3). An 8-ft diameter painted mild steel shell with attached sampling and vent tubes, and associated steel reinforcing will be suspended inside the CMP by a hold down structure. Concrete will be placed in the annular space creating an integral concrete silo. A 7-ft diameter X 14-ft long filament wound, vinyl ester resin tank will be placed in the silo and the void space between the silo and the tank will be backfilled with sand. A layer of sand will be placed in the bottom of the tank, a waste form placed, and backfilled and covered with a layer of sand, then the second waste form will be placed and backfilled with sand. The waste forms will be equipped with handling fixtures designed to provide capability for long-term retrieval. The tank will also be designed with handling capability to allow it to be "retrieved" from the silo to provide back-up capability for long-term waste form examination. Prior to closure a vinyl ester resin cover, with sampling/vent relief capability will then be temporarily sealed to the tank. An interim concrete cover with penetrations for the sampling lines will then be placed.

Type II Silo

The Type II silos will be designed for disposal of solidified radioactive MVST waste. The basic approach will be similar to the Type I silo, except that the free standing, inner tank be eliminated. Instead, the inner mild steel shell will be replaced with a shell made of corrosion resistant materials. One Type II silo will be constructed using each of the four materials described previously - glass lined steel, filament-wound vinyl ester resin (glass filled), vinyl ester resin lined steel, and CLPE - for the inner shell. These four Type II silos plus the one Type I silo will be placed in a single module (5 silo unit). In addition, one module (5 silos) using the filament wound vinyl ester resin (glass filled) inner shell will also be constructed.

The Type II silos will be 9-ft outside diameter, 7-ft inside diameter, by approximately 20-ft long (Fig. 4). Sampling and vent relief capabilities similar to the Type I silo will be provided. Waste loading will also involve the use of sand backfill. Inner corrosion resistant lids sealed to the inner shell, and interim concrete covers will be used. The Type II silo will include a rebar dowel insert in the top edge of the silo wall which will allow for construction of an integrally reinforced, permanent concrete cover in the future.

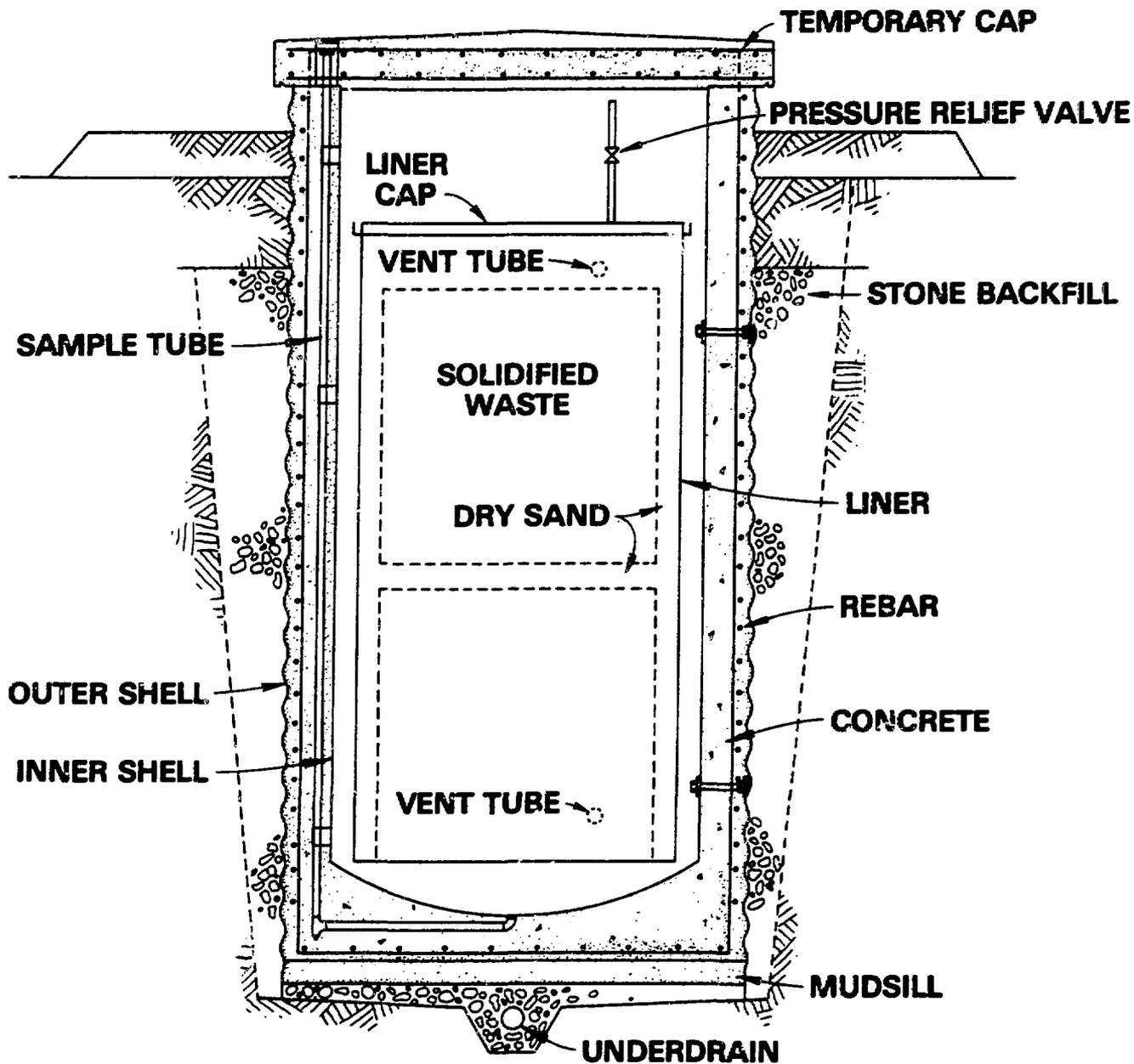


FIG. 3. SILO - TYPE I

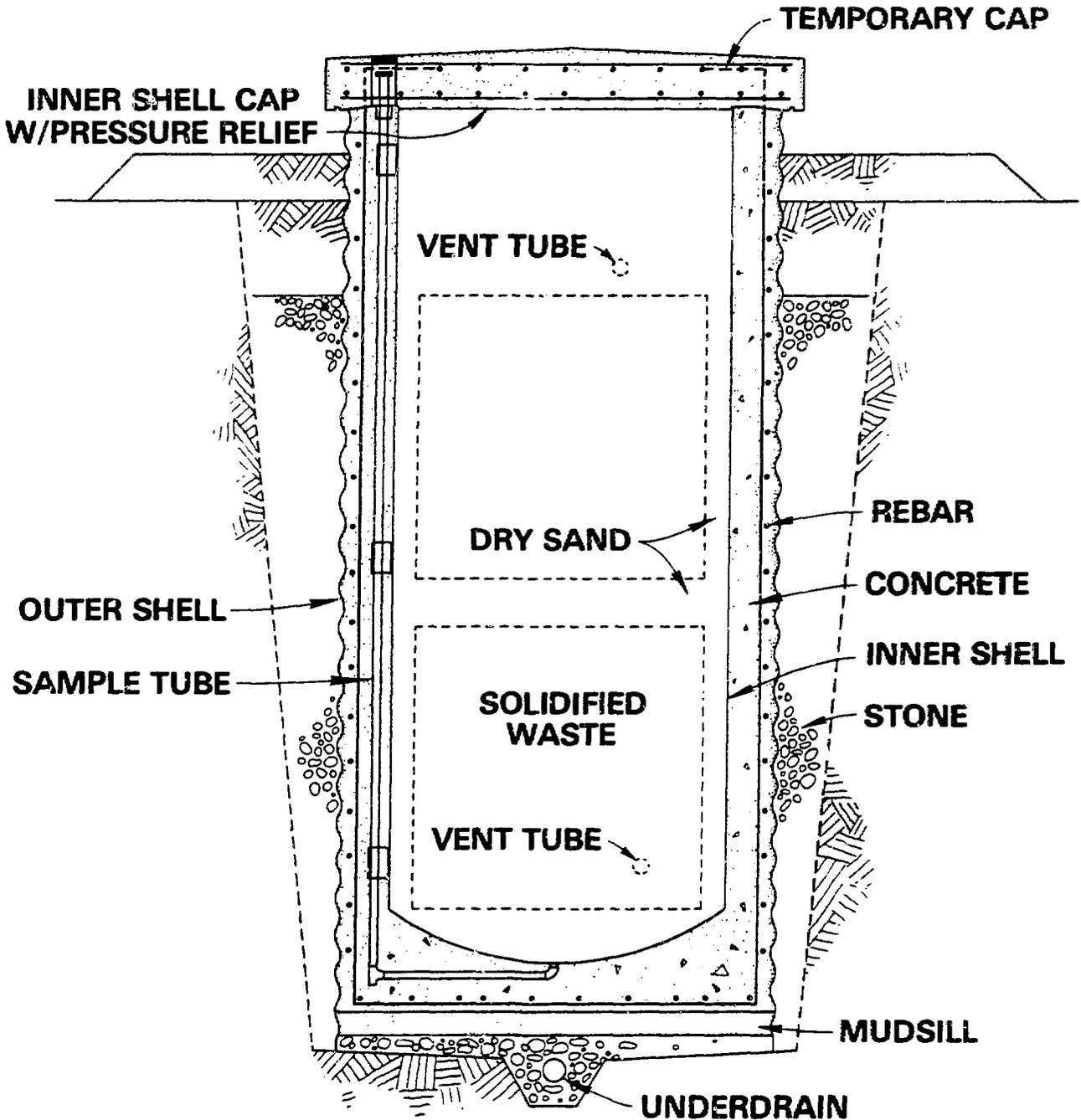


FIG. 4. SILO - TYPE II

Type III Silo

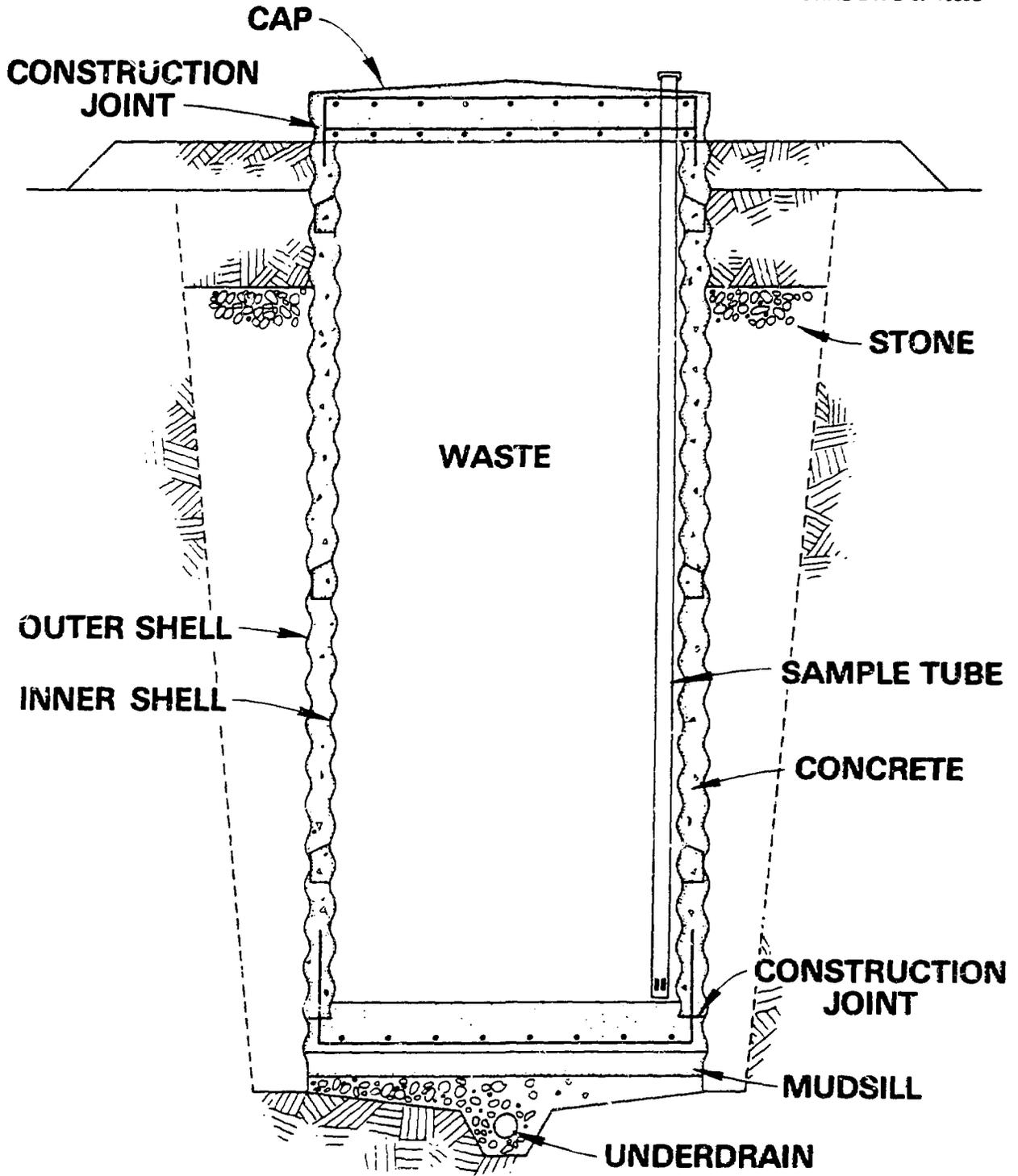
The Type III silo design is based on the existing SWSA 6 silo concept. These silos are intended for use for the disposal of non-corrosive bulk solid LLW. An 8-ft diameter by 20-ft long CMP will be placed in the trench, and the drainage system installed (Fig. 5). A 7-ft diameter CMP with centering devices will be placed inside the larger CMP with its bottom edge above the mudsill. Reinforcing steel will be placed to tie the silo bottom and sides together. Concrete will be poured for the silo base and allowed to harden. The silo walls will then be poured with a construction joint at the wall-base interface. Rebar will be placed in the upper portion of the wall to provide a connection point for the cap rebar. A temporary rain cover (and possibly radiation shielding) will be provided during waste loading operations. Upon completion of waste loading, the cap rebar will be tied to the wall rebar, and the permanent concrete cap constructed.

IV. Demonstration Performance Monitoring

A program to monitor the occupational exposures, waste form/disposal unit performance, and environmental performance of the GCD units is planned. The program is currently being developed and will likely be revised as additional information and experience becomes available.

Due to the elevated radiation fields associated with the solidified waste form (1-2 r/hr estimated), occupational exposure evaluations will be a prime focus of the monitoring plan. Preliminary analysis of doses resulting from waste form handling operations have been performed to provide information for use in identifying equipment (e.g., remote disconnect rigging, shields, etc.) and operations modifications needed to keep doses ALARA. A worker exposure monitoring program will be conducted which is aimed at providing information to validate the predictive models used initially, and to ensure that workers are protected.

Several provisions have been included in the silo units to allow monitoring of the performance of the waste forms and disposal unit materials. Each silo will include an inner cavity sump and monitoring line to allow collection and analysis of any liquids and corrosion products that may accumulate in the disposal units. Two vent tubes are also provided which are intended to provide the means to monitor for any gas generation that may result from radiation damage to the waste form or silo materials. One Type I silo will be constructed which will include provisions for direct retrieval of the non-radioactive surrogate waste forms which will be placed in that unit.

**FIG. 5. SILO - TYPE III**

Environmental monitoring capabilities have been provided for the silos and the tumulus. The silo's inner cavity sump will provide a means to collect and analyze any leachate which may form in the disposal unit. The external gravel sump in the bottom of each trench will provide a means to detect and monitor any release of radionuclides from the disposal unit. Ground water monitoring wells will also be placed around the disposal unit area. The tumulus unit includes pad surface drainage provisions to allow collection and monitoring of water which may have contacted the waste. In addition, the HDPE liner which encloses the area directly beneath the pad is also monitored to allow detection of any leaks through the pad.

REFERENCES

1. Selection of Materials for the Greater Confinement Disposal Silo Inner Liner, W. P. Teichert, Lee Wan & Associates, Inc., 1987, pg. 1-4.
2. S. D. Van Hoesen and R. B. Clapp, "SWSA 6 Tumulus Disposal Demonstration," Oak Ridge Model Conference, February 3-5, 1987.

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Field Analytics, A Faster Way to the Answer

Presented by:

Dr. Earl M. Hansen, Roy F. Weston, Inc.

"Field Analytics, A Faster Way to the Answer"

Earl M. Hansen, Ph.D., Vice President & Technical Director
Weston Analytics - Roy F. Weston, Inc.

Analytical requirements are a significant component of site assessments and cleanups due to the need for larger data bases to define the extent of contamination. This increased data requirement typically increases the samples required to provide the information necessary to characterize a site.

The technical complexity and extensive quality control requirements for current analytical protocols and associated reporting requirements can result in significant cost increases and possibly extend RI/FS and cleanup completion schedules due to typical 4-8 week analytical turnaround time. The growing requirement for validation of analytical data used to select appropriate remedial action alternatives and/or declare a site clean, adds to the complexity of this issue.

There is growing interest from regulatory agencies and data users to develop rugged and sensitive field analytical methods for selecting samples for broad scale chemical analyses used to provide timely information about extent of contamination and/or achievement of cleanup criteria, and for application to emergency response activities when typical need for analytical information may be 24 hours or less.

This presentation separates the "myths and realities" of field analyses, summarizes a variety of "field" analytical methods, and describes WESTON's experience in the development, validation and use of several methods.

429/430

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Soil Gas Screening: Its Theory and Applications to Hazardous Waste Site Investigations

Presented by:

Lynne Preslo, Roy F. Weston, Inc.

SOIL-GAS SCREENING: ITS THEORY AND APPLICATIONS
TO HAZARDOUS WASTE SITE INVESTIGATIONS

By

Walter M. Leis, Lynne M. Preslo
and Raphe Pavlick
ROY F. WESTON, INC.
1001 Galaxy Way, Suite 107
Concord, California 94520

During the last three years, soil-gas sampling has grown from a virtually unknown, seldomly used technique, to become one of the main-stays and an essential tool in the geosciences field for site investigations. Soil-gas screening, if conducted properly, is a very effective and comparatively inexpensive technique for the following applications:

- o Source-area identification: Source area of volatile chemicals within the vadose, or unsaturated, zone can be identified using soil-gas techniques.
- o On-site vs. off-site sources: Soil-gas screening can assist in the delineation of on- and off-site sources.
- o Plume-tracking: Soil-gas screening can be used to track plumes of chemicals within the groundwater, depending upon site conditions.
- o Migration of Landfill Gases: Soil-gas screening can also be used to identify the type of chemicals present in and the migration patterns of landfill gases (e.g., Calderon Bill Requirements in California).
- o Optimize Subsequent Monitoring Points: Soil-gas screening is used to optimally locate, and therefore reduce the total number of, the more expensive and more intrusive monitoring points (eg., soil borings and groundwater monitoring wells).

This paper discusses the theory behind soil-gas screening, its applications at various sites, and its limitations depending on site conditions.

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437/1139

FEDERAL BUREAU OF INVESTIGATION
DEPARTMENT OF JUSTICE

**Methodology for the Characterization of Low-Level
Radioactive Waste at the Oak Ridge National Laboratory**

Presented by:

D. A. Costanzo, ORNL

Methodology for the Characterization of Low-Level
Radioactive Waste at the
Oak Ridge National Laboratory

D. A. Costanzo
F. J. Peretz

Low-level liquid radioactive waste originates from a number of different source facilities at the Oak Ridge National Laboratory (ORNL). Sources include reactors, radioactive fuel and target processing facilities, decontamination operations, hot cells, and analytical laboratories. Waste generated at these source facilities are collected in storage tanks distributed throughout ORNL. Many of the source facilities generate acidic nitrate wastes which are neutralized with sodium hydroxide in the collection storage tanks. The stored waste is essentially a high-pH, sodium nitrate, salt solution with smaller concentration of potassium, calcium, and magnesium cations, and sulfate chloride, fluoride, and phosphate cations. The principle radionuclides are strontium-90, cesium-137 and cobalt-60.

Data on the chemical and physical form of the waste are needed to evaluate the practicality of various processing options and to analyze the resulting waste forms. Data on radiochemical concentrations are needed to predict dose rates and shielding requirements around processing equipment and waste packages and to provide a data base for leach tests and other immobilization requirements. This paper describes chemical and physical measurement techniques that have been used to characterize low-level waste at ORNL.

441/442

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**Detection and Delineation of Waste Trenches
by Geophysical Methods at ORNL**

Presented by:

Robert J. Selfridge, Maxima Corporation

Detection and Delineation of Waste Trenches
by Geophysical Methods at
Oak Ridge National Laboratory

By Robert J. Selfridge
The MAXIMA Corporation

Detection and delineation of waste trenches at hazardous waste sites are needed before actual implementation of site corrective measures. In a field study conducted in Solid Waste Storage Area 4 (SWSA4) at Oak Ridge National Laboratory (ORNL), surface geophysical techniques were used to assist in the delineation of waste trenches. A magnetometer/gradiometer survey was used to detect ferrous metals buried at the site. An electromagnetic ground conductivity survey was used to measure the electrical conductivity of the subsurface and aided in supporting the magnetometer/gradiometer results. Results from the two techniques were complimentary and easily integrated into a final interpretation. The reliability, efficiency, and worker safety benefits of these techniques offer a nondestructive surface technique for locating buried waste trenches.

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449/450

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Investigations to Determine the Origin of Toxic Constituents in ORGDP Liquid Effluents

Presented by:

M. A. McGaha, ORGDP

INVESTIGATIONS TO DETERMINE THE ORIGIN
OF TOXIC CONSTITUENTS IN
ORGBP LIQUID EFFLUENTS

M. A. McGaha

Systems and Equipment Technology Department
Quality and Technical Services Division
Oak Ridge Gaseous Diffusion Plant
Oak Ridge, Tennessee 37831

Operated by Martin Marietta Energy Systems, Inc.
for the U.S. Department of Energy
under Contract No. DE-AC05-84OR21400

INVESTIGATIONS TO DETERMINE THE ORIGIN
OF TOXIC CONSTITUENTS IN ORGDP LIQUID EFFLUENTS

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Systems and Equipment Technology Department
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Operated by Martin Marietta Energy Systems, Inc.
for the United States Department of Energy

ABSTRACT

The National Pollutant Discharge Elimination System (NPDES) permit for the Oak Ridge Gaseous Diffusion Plant contains requirements for a Biological Monitoring Plan and Abatement Program for the surface stream above the K-1700 discharge point as well as a Toxicity Control and Monitoring Program for the discharges from listed outfalls. Toxicity tests are conducted at the Oak Ridge National Laboratory according to Environmental Protection Agency protocols using sensitive aquatic organisms. In support of these programs, portions of water samples have been retained for laboratory analysis of constituents which might contribute to observed toxicity. This presentation describes efforts underway to correlate toxicity observations with water quality data and investigations to identify process and area source discharges from which toxic constituents originate. The feasibility of potential long-term measures to ensure acceptable test results will also be discussed.

INTRODUCTION

The National Pollutant Discharge Elimination System (NPDES) permit for the Oak Ridge Gaseous Diffusion Plant (ORGDP) contains requirements for a Biological Monitoring Plan and Abatement Program for the surface stream above the K-1700 discharge point as well as a Toxicity Control and Monitoring Program for the discharges from listed outfalls. Toxicity tests are conducted at the Oak Ridge National Laboratory according to Environmental Protection Agency protocols using sensitive aquatic organisms. In support of these programs, portions of water samples have been retained for laboratory analysis of constituents which might contribute to observed toxicity.

DESCRIPTION OF PLANT AREA AND SAMPLING POINTS

Biological monitoring at ORGDP (Figure 1) was conducted in the small surface stream known as the Mitchell Branch (Figure 2). This stream is located in the northeast corner of ORGDP and flows into Poplar Creek which empties into the Clinch River.

Sampling has been conducted at ten points along the branch. These points are described in Table 1.

Table 1

| | |
|---------|--|
| Site 1 | Before Mitchell Branch enters plant |
| Site 2 | After branch passes TSCA area |
| Site 3 | After storm drain 170 enters stream |
| Site 4 | After effluents from K-1407B pond and storm drain 180 enter stream |
| Site 5 | After storm drain 190 enters stream |
| Site 6 | K-1700 - NPDES monitoring point as Mitchell Branch exits plant |
| Site 7 | Storm drain 170 before it enters stream |
| Site 8 | K-1407B pond effluent |
| Site 9 | Storm drain 180 before it enters stream |
| Site 10 | Storm drain 190 before it enters stream |

Scheduled sampling involves sampling predetermined sites for a week each month. Sites 1-6 are sampled together every other month. Site 8 is

Biological monitoring has only been used at ORGDP for ten months. We are still in the process of understanding how to interpret the data and use the results to meet NPDES requirements.

REFERENCES

1. Short-term Methods for Estimating the Chronic Toxicity of Effluents and Receiving Waters to Freshwater Organisms, Section 13: Ceriodaphnia Survival and Reproduction Test Method 1002.0 and Section 11: Fathead Minnow (Pimephales promelas) Larval Survival Growth Test Method 1000.0, EPA-600/4-85-014.

FIGURE 1

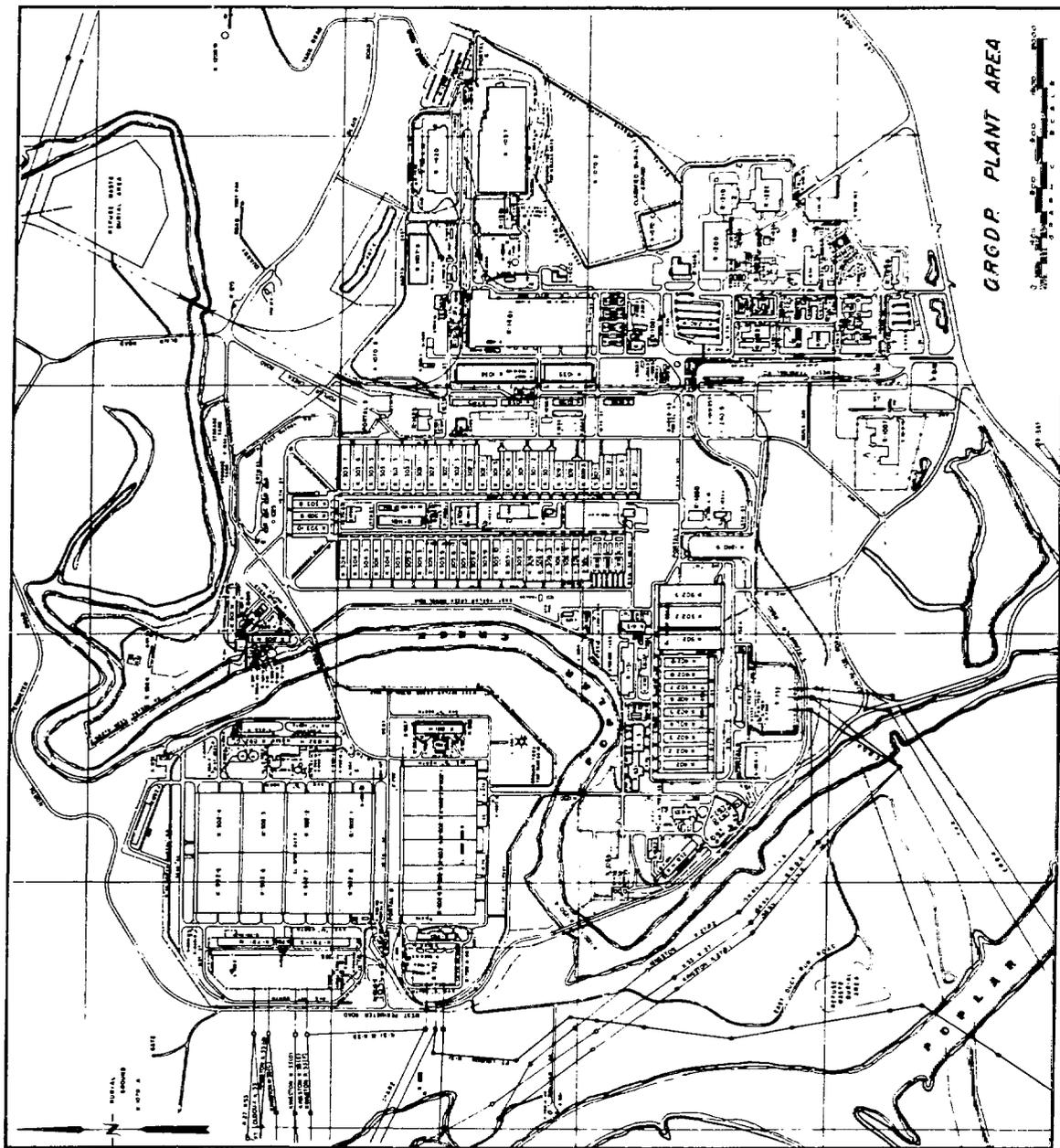
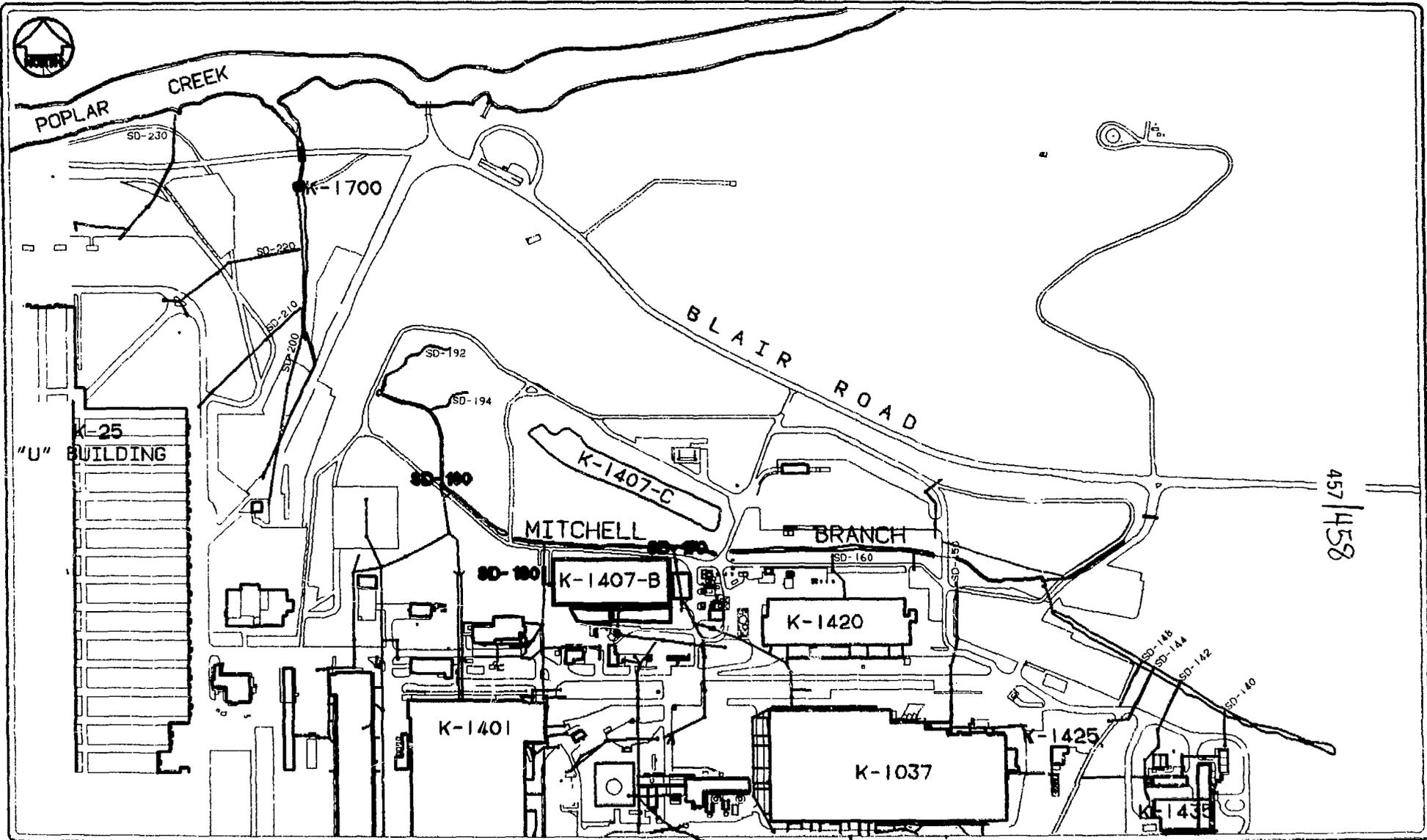


FIGURE 2



STORM DRAINS ON MITCHELL BRANCH

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**Use of On-Site Chemical Analyses in the
Identification of Groundwater Contamination Sources
Affecting the Rockaway Borough Well Field**

Presented by:

**Kevin R. Boyer,
Science Applications International Corporation**

USE OF ON-SITE CHEMICAL ANALYSES IN THE IDENTIFICATION OF GROUNDWATER CONTAMINATION SOURCES AFFECTING THE ROCKAWAY BOROUGH WELL FIELD - Christopher S. Manikas and Kevin R. Boyer, PE, Science Applications International Corporation, McLean, Virginia

ABSTRACT

The contamination of groundwater aquifers by chlorinated solvents in the Rockaway River Valley of northern New Jersey has become a major public health concern in municipalities that rely on the glacial aquifer in this area as a sole-source water supply. Selecting time- and cost-effective approaches to locating sources of groundwater contamination in urban and industrialized areas such as the Rockaway River Valley presents a challenge for conventional site investigation strategies. The integration of on-site, high-sensitivity chemical analyses into a field investigation program to provide timely feedback to field investigators can be a valuable tool for application to such sites.

Field chemical analyses were applied to an investigation of the Rockaway Borough well field and the designated sole-source glacial aquifer supplying the well field. The aquifer and the Borough water supply were found to be contaminated with up to 680 parts per billion (ppb) of tetrachloroethylene (PCE) and 172 ppb of trichloroethylene (TCE) in 1980. The sources of the contaminants had not been identified in 1982 when the well field was placed on the USEPA National Priorities List (NPL) of uncontrolled hazardous waste sites. A limited site investigation was conducted using on-site chemical analyses of groundwater samples and soil sample headspace gases. The investigation identified optimal monitoring well locations, provided cost-effective time series sampling data, and identified the locations of three potential contaminant sources.

INTRODUCTION

The degradation of the quality of groundwater withdrawn from the glacial aquifer underlying the Rockaway River Valley in northern New Jersey has heightened concerns in recent years regarding the protection and maintenance of safe drinking water supplies for populations in this area. With increasing frequency since 1979, municipalities within the Rockaway River Valley have reported organic contamination affecting well fields that are supplied by the sole-source drinking water aquifer. A mixture of older urban and industrialized areas are located within the valley, thereby providing numerous potential sources of groundwater and surface water contamination. Identification of contaminant sources in areas that contain a large number of past and present potential sources that are widely distributed may become both costly and time-consuming using conventional site investigation techniques. The use of laboratory-quality gas chromatography equipment in field investigations can provide timely, cost-effective chemical data to site investigators. These data can then be used to support and guide progressive field activities. Such techniques can also

provide the capability for collection of time-series chemical data for the environmental media of concern. The resulting data are used to guide ongoing investigations and are used in conjunction with the results of laboratory analyses and hydrologic data to identify source areas that have contributed to the observed contamination.

SITE BACKGROUND

The Rockaway Borough well field draws groundwater from a sole-source glacial aquifer that supplies drinking water to areas in Morris County, New Jersey (see Figure 1). The well field consists of three large-diameter wells that combined produce approximately 1.2 million gallons daily. The detection of volatile organic contaminants in well water from the nearby Township of Rockaway in 1979 prompted the New Jersey Department of Environmental Protection (NJDEP) to extend water quality testing of well water to neighboring communities. In 1980, the presence of PCE and TCE contamination was confirmed in Rockaway Borough's three water supply wells (Nos. 1, 5, and 6 on Figure 2) and at points within the Borough's water distribution system. PCE concentrations as high as 678 ppb and TCE concentrations as high as 172 ppb were subsequently identified in the well water. Lower concentrations of 1,1,1-trichloroethane, trans 1,2-dichloroethylene, toluene, methylene chloride, chloroform, trichlorofluoromethane, carbon tetrachloride, benzene, chlorobenzene, 1,1-dichloroethylene, bromodichloromethane, and 1,1,2-trichloroethane were also identified. The highest initial concentrations of PCE and TCE were observed in Well Nos. 1 and 6 and lower concentrations were observed in Well No. 5.

In 1981, concern for public health prompted Rockaway Borough to install a granular activated carbon adsorption system that reduced contaminant concentrations in the distributed water to State of New Jersey requirements. The persistence of the PCE and TCE contamination in the aquifer and the cost to the Borough of operating and maintaining the treatment system warranted that the source of the contaminants be located and, if possible, abated. The source(s) of the contaminants had not been identified in 1982 when the well field was placed on the USEPA National Priorities List (NPL) of uncontrolled hazardous waste sites. A field investigation of the Rockaway Borough well field was initiated by Science Applications International Corporation (SAIC) in 1985 under contract with the NJDEP.

Because these wells provided virtually all of the water used by the public within the Borough and supplemented the supplies of neighboring Rockaway and Denville Townships, the NJDEP directed the Borough of Rockaway to: (1) give immediate preference to the use of Well No. 5, to use Well No. 6 only as a backup source, and to use Well No. 1 only for peaking purposes; (2) provide an acceptable water-supply treatment technique; and (3) sample each well monthly and analyze for volatile organic compounds. Well No. 1 was removed from the distribution system in September 1980, and a water emergency was declared in

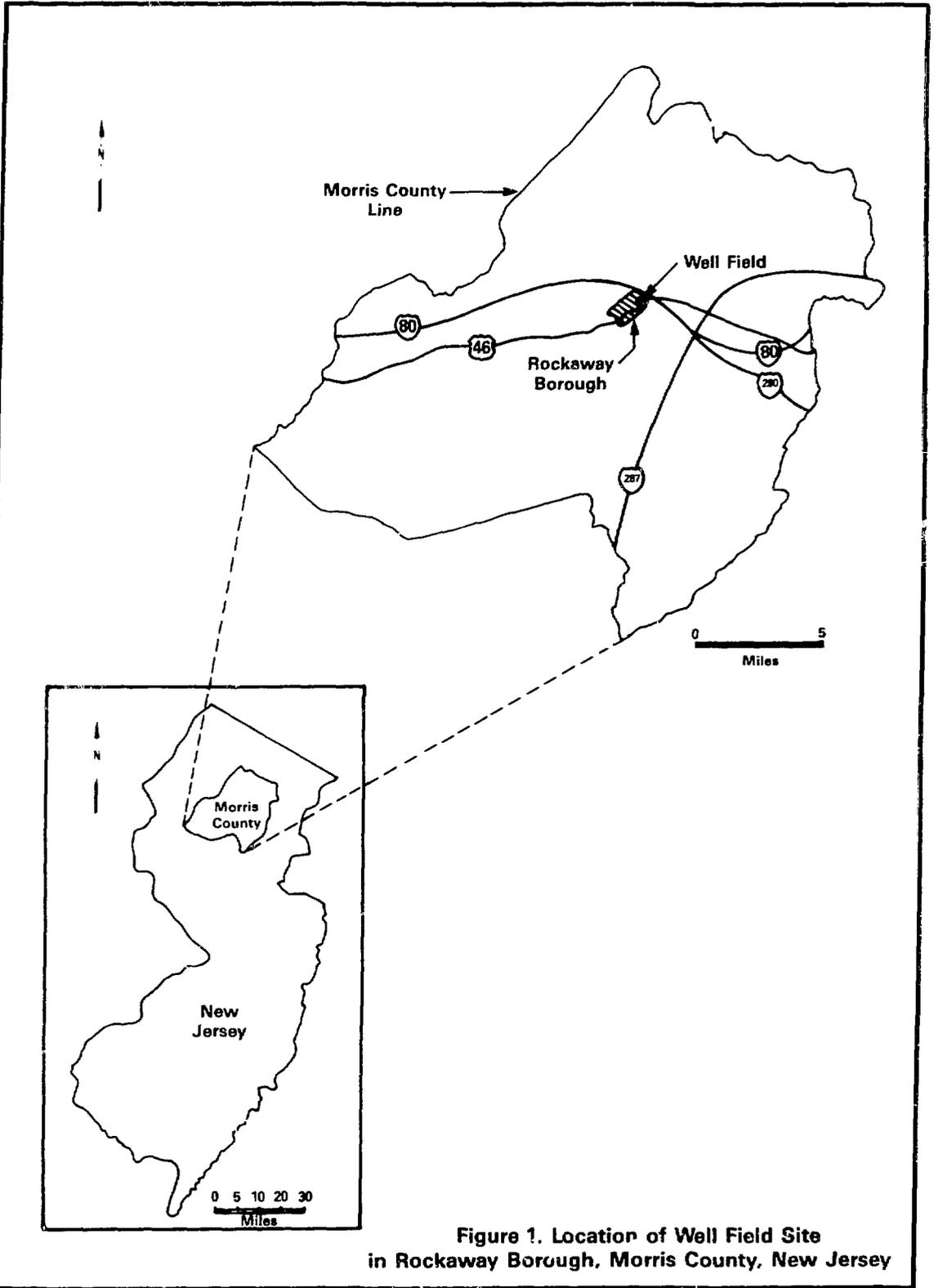


Figure 1. Location of Well Field Site in Rockaway Borough, Morris County, New Jersey

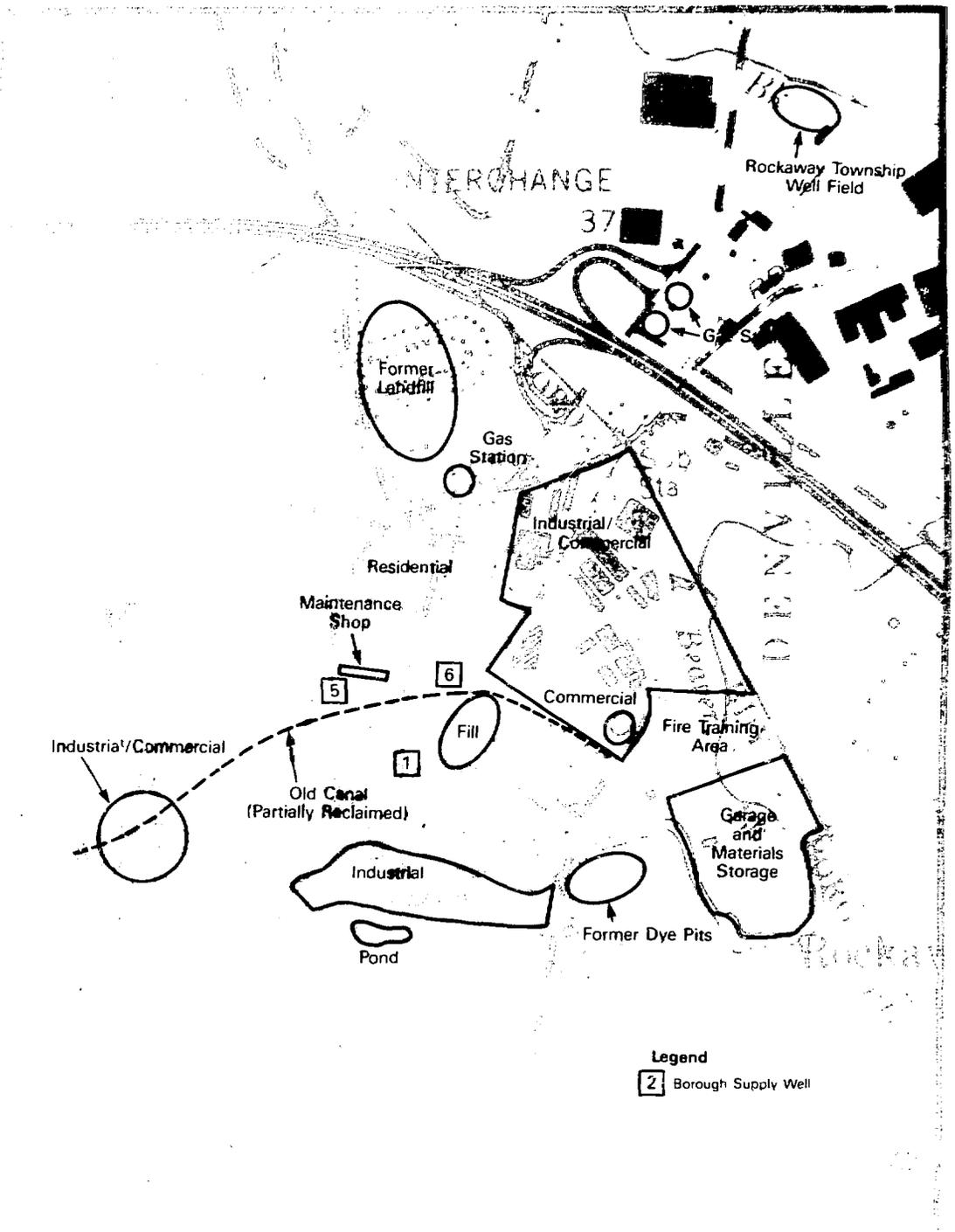


Figure 2. Potential Contaminant Source Locations in the Vicinity of the Rockaway Borough Well Field

February 1981 when Well No. 6 showed high concentrations of PCE and TCE. The Borough of Rockaway constructed a three-bed granular activated carbon adsorption treatment system during the water emergency period with the assistance of Calgon Carbon Corporation. The system began treating raw water pumped from the Borough wells in July 1981.

The variation of PCE and TCE concentrations in the supply wells over time is shown in Figure 3. In general, PCE concentrations were initially highest at Well No. 1 (up to 568 ppb), but showed marked decline after pumping at Well No. 1 was stopped in 1980. Approximately coincident with the shutdown of Well No. 1, PCE concentrations rose sharply in Well No. 6 from an average pre-shutdown concentration of approximately 15 ppb to a post-shutdown peak concentration of 678 ppb. PCE concentrations in Well No. 5 (up to 400 ppb) were variable and showed a more gradual increase over time than in the other Borough wells. TCE concentrations were generally low (less than 10 ppb) in Well Nos. 1 and 5, with the exception of a 76 ppb peak observed in Well No. 5 in August 1980. TCE concentrations in Well No. 6 were substantially higher and more persistent (5.7 to 172 ppb) than those observed in Well Nos. 1 and 5 (Figure 3).

The strategy for identifying the sources of the groundwater contaminants considered that the contaminants could have emanated from a single point source, multiple unrelated point sources, or non-point sources located within the area surrounding the well field. Several of the types of industries and commercial establishments that are likely to have used PCE and TCE in their operations are located or have historically been located in Rockaway Borough in the vicinity of the well field. Other, non-industrial possible sources included: a sanitary landfill, uncontrolled dumping areas, local septic system drain fields, contaminated surface waters, and fill materials in reclaimed portions of a former navigation canal. Potential sources of groundwater contamination that were preliminarily identified prior to initiating the field investigation are shown on Figure 2.

SITE GEOLOGY AND HYDROGEOLOGY

The Borough of Rockaway is located within the New Jersey Highlands Physiographic Province and is underlain by Pre-Cambrian igneous, metamorphic, and metasedimentary bedrock. Overlying the bedrock over most of the area are Quaternary sediments deposited as a result of Pleistocene glaciation. A terminal moraine of the Wisconsin glacial stage deposited in the vicinity of the Borough is the southern-most extent of the glacial advance in that area. The terminal moraine is not topographically conspicuous, largely because of the extensive relief on the underlying bedrock surface.

Groundwater resources in the area are extensively developed for private, commercial, and industrial uses. Groundwater is withdrawn from both Pre-Cambrian bedrock and Quaternary glacial aquifers, typical of usage throughout much of western Morris County. Groundwater occurs under unconfined conditions in the absence of low-permeability

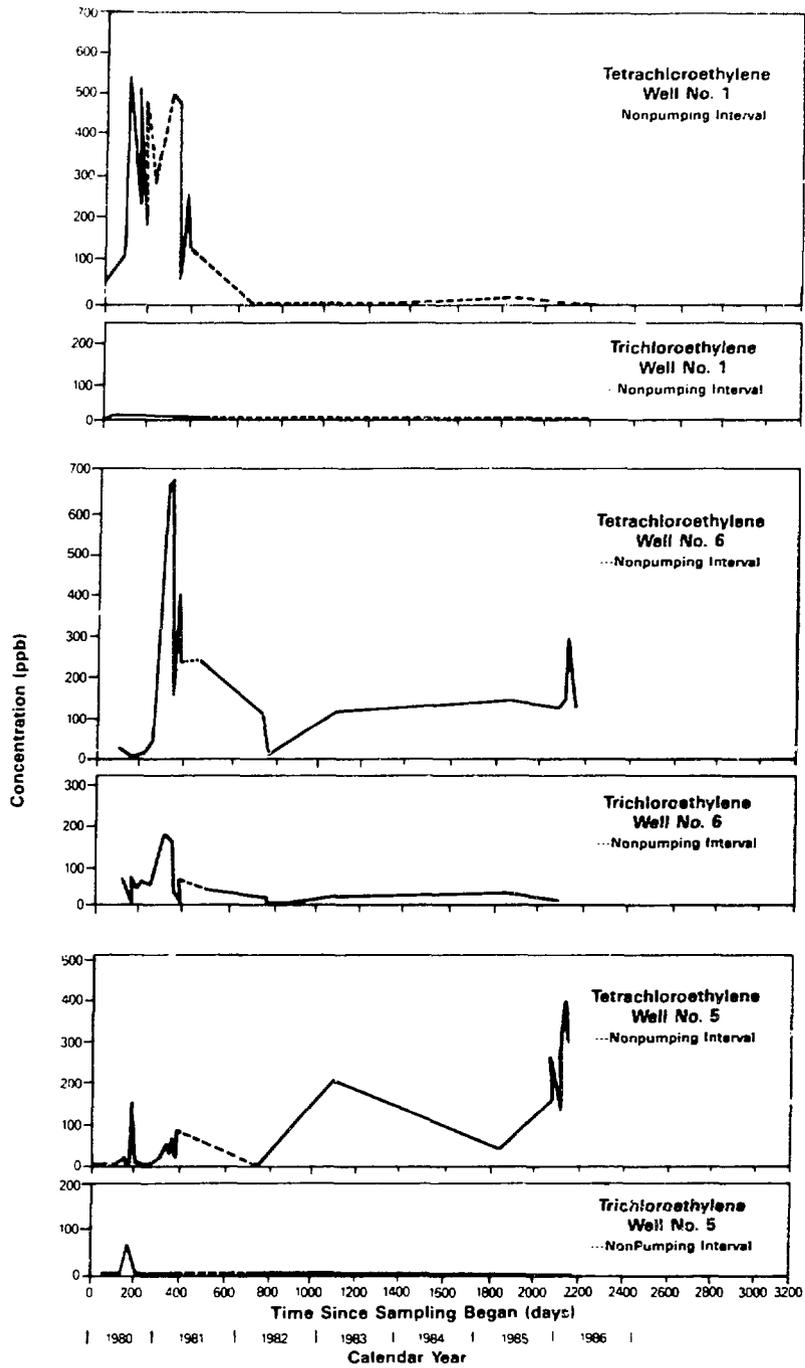


Figure 3. PCE and TCE Concentrations in Rockaway Borough Supply Wells

layers and under confined or semi-confined conditions where relatively thick, low-permeability till is present over the drift deposits. Local confining conditions may also occur within stratified drift deposits, caused by the presence of low-permeability clay and silt interbeds. Aquifer properties within the glacial aquifer are variable with hydraulic conductivity ranging from 18 to 400 ft/day, transmissivity ranging between 177 and 42,900 ft²/day, and storage coefficients ranging between 1.0×10^{-3} and 9.2×10^{-4} (Gill and Vecchioli 1965; Meisler 1976; Summers et al 1979; Canace et al 1983). Confined drift deposits are recharged in part from water entering at outcrop areas and from water entering bedrock fractures, with subsequent migration to the stratified drift deposits. Artificially induced recharge from the nearby Rockaway River caused by pumping provides another means of locally recharging the stratified drift aquifers by substantially increasing the amount of groundwater available in the area.

In Rockaway Borough, groundwater is the only source of potable water and is also withdrawn for commercial and industrial purposes. The Borough operates three water supply wells, which are located in the north/central part of the Borough within 1,200 feet of the Rockaway River. The wells range in depth from 53 to 84 feet and static water level depths range from 12 to 15 feet. Groundwater flow in the vicinity of the Rockaway Borough well field converges on the pumping wells from all directions. The mapped equipotential surface (Figure 4) is concentrically located around Borough Well Nos. 5 and 6. Hydraulic gradients flatten significantly to the east and northeast of the well field, possibly attributable to interaction between the cones of groundwater depression generated by the Rockaway Borough well field to the southwest and the Rockaway Township well field to the northeast, or to increased sand layering in this area.

FIELD INVESTIGATION

A field investigation of the Rockaway Borough well field contamination was initiated in 1985 by SAIC under contract with the NJDEP. The investigation was conducted to determine the concentrations of contaminants in the aquifer and the well field, to trace the contamination from the well field toward the direction of the contaminant source, and, to the extent possible, identify the sources of the contaminants. The field program consisted of the following activities:

- Soil gas sampling and analysis using on-site gas chromatography.
- Soil boring, soil and groundwater sampling, and analysis of groundwater and soil headspace gases using on-site gas chromatography.
- Installation and sampling of groundwater monitoring wells.

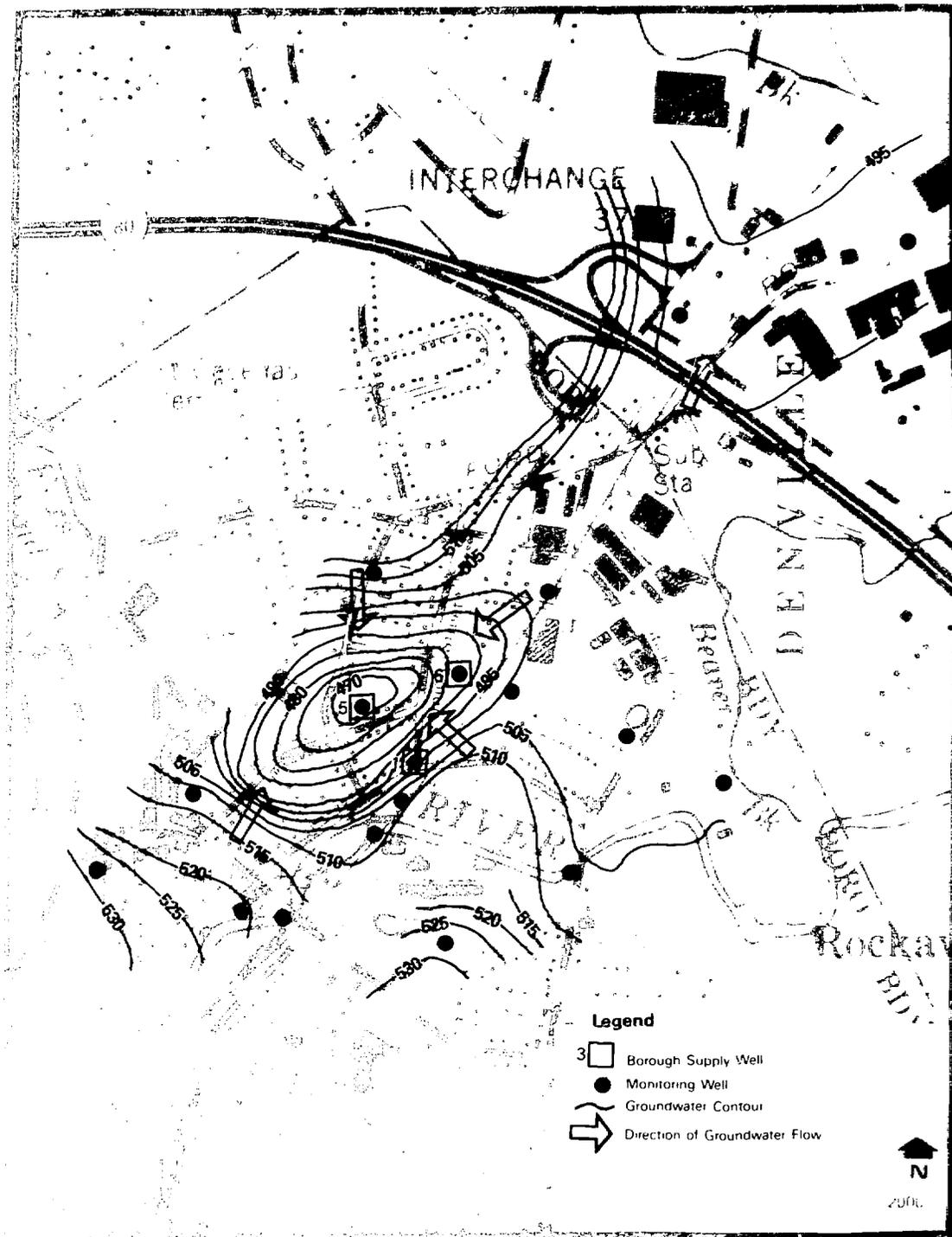


Figure 4. Map of Potentiometric Surface in the Vicinity of the Rockaway Borough Well Field

- Laboratory analysis of samples obtained from the installed monitoring wells.

In addition, water samples were frequently collected from the pumping supply wells and analyzed by on-site gas chromatography through the course of the field program.

Gas chromatography (GC) analyses were conducted in the field using laboratory-quality Varian 3300 and Tracor 540 gas chromatographs equipped with electron capture detectors (ECD). Peak integrations were automatically computed in the field using a Spectra-Physics SP4270 computing integrator. Concentrations for the various compounds of concern were calculated using calibration standards (external standards) that were run daily or more frequently as necessary. Detection limits using the GC/ECD apparatus were approximately 0.0005 ug/l for gas samples and 0.05 ug/l in water for chlorinated solvents. The reported detection limits are a function of the injection volume and the detector sensitivity for individual compounds. Halocarbon compounds detected in gas and water samples were identified by chromatographic retention time. Verification of the compound identity was obtained by chromatographic analysis using GC columns of differing selectivity. A "drying column" composed of ionic polymer material installed on the gas chromatograph allowed the direct injection of water samples without the use of purge-and-trap or preconcentration techniques (Tracer Research Corporation 1986).

Soil Gas Sampling and Analysis

Shallow soil gas samples were collected and analyzed at 62 locations within Rockaway Borough. Soil gas samples were collected by hydraulically pushing a hollow steel probe fitted with a detachable drive point to the sampling depth (commonly 2 to 5 feet beneath the ground surface) and evacuating 5 to 10 liters of soil gas with a vacuum pump. During the soil gas evacuation, samples were collected by inserting a syringe needle through a silicone evacuation line and down into the steel probe. Soil gas was subsampled (duplicate injections) in volumes ranging from 1 ul to 2 ml, depending on the concentrations of volatile compounds at a particular location. The concentrations of PCE, TCE, and 1,1,1-trichloroethane (TCA) in the soil gas were quantified using an electron capture detector in the gas chromatograph. System blanks were run periodically to confirm that contamination in the probes, adaptors, or syringes was not occurring, and analytical instruments were continually checked for calibration using chemical standards.

The areal distribution of PCE and TCE identified in the soil gases (Figures 5a and 5b) was inferred to reflect the directions of contaminant movement and thereby provide indications of the locations of potential contaminant sources. The highest soil gas contaminant concentrations observed at the site were inferred to indicate close proximity to a potential contaminant source and, conversely, lower concentrations were inferred to indicate lesser proximity to a

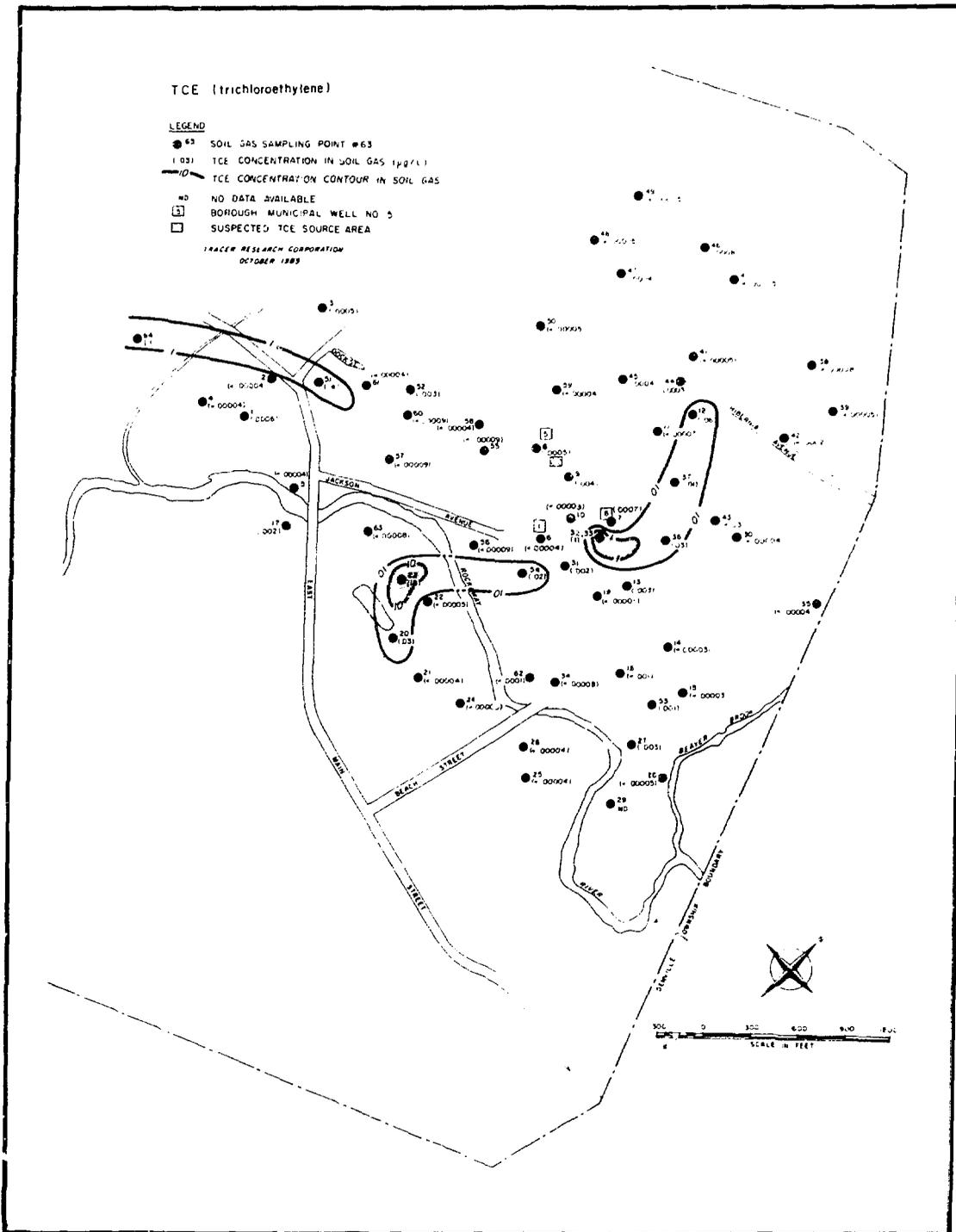


Figure 5b. Soil Gas Concentration Contours for TCE

potential source. On this basis, high-concentration areas, shown on Figures 5a and 5b, were identified for further investigation to narrow the areas of the potential contaminant sources to:

- Commercial areas west of the well field.
- Commercial/industrial area south of the Rockaway River and directly across the river from the Borough well field.
- Commercial/industrial/residential area northeast and southeast of Borough Well No. 6.

The patterns of the on-site soil gas contaminant distribution, preliminary estimates of groundwater flow directions, and the results of historical and preliminary groundwater chemical analyses were collectively used to identify areas of possible groundwater contaminant sources and to determine optimal locations for the installation of groundwater monitoring wells.

Soil and Groundwater Sampling and Analysis

Confirmation of potential contaminant distribution within the aquifer required the drilling of a limited number of monitoring wells. A conventional monitoring well location strategy in this situation might have consisted of a radial distribution of monitoring wells around the well field within a relatively small area to determine directionality of the contaminant distribution surrounding the well field. The disadvantage of such a configuration is that groundwater flow directions and contaminant concentrations could be addressed only in the immediate vicinity of the well field, given the limited number of monitoring points, and could not be adequately determined for potential source areas beyond the locations of the monitoring wells. Based on background records and literature, preliminary groundwater analyses of wells in the vicinity of the well field, and the quantitative soil gas results, the following factors influenced the siting of borings and monitoring wells available for the study:

- Locations of points of known contamination
- Locations of suspected potential sources of contamination
- Inferred directions of groundwater flow
- Soil gas contaminant distribution
- Pumping and contamination histories of supply wells.

With these factors in mind, seven borings and monitoring well locations, shown on Figure 6, were selected to provide information that could establish connections between the well field contamination and the suspected sources and to aid in evaluating potential contaminant migration pathways. An additional consideration was to place wells

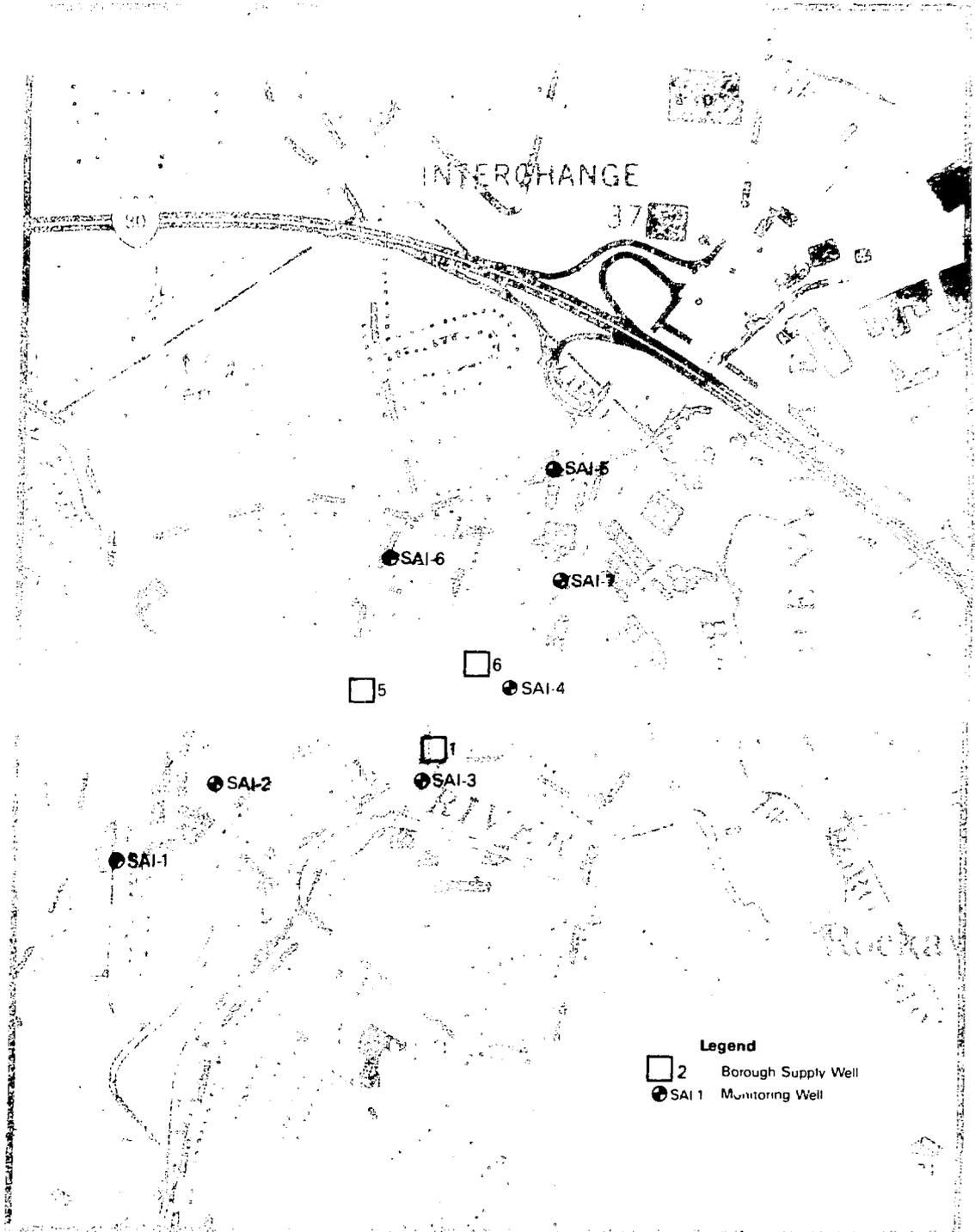


Figure 6. Installed Monitoring Wells

to provide optimum locations for delineating groundwater flow patterns over an area that encompassed all of the suspected sources of contamination.

Boreholes were drilled using mud rotary methods with drilling fluids consisting of mixtures of treated Borough water and bentonite. Split-spoon soil samples were obtained at approximately five-foot intervals in the boreholes, except where cobbles and boulders prevented the retrieval of representative samples. Approximately 20 grams of each soil sample were placed into a 40 ml VOC vial containing 10 ml of distilled water, which was then sealed with a teflon septum cap. The soil/water mixtures were shaken for one minute and headspace gases were extracted by syringe from the vials for analysis for PCE, TCE, and TCA as relative indicators of the presence of contaminants in the soil samples and thereby in the aquifer. The sampled gases were then injected into a Varian 3300 gas chromatograph supported by a Spectra Physics SP4290 integrator. The chemical quality of the distilled water and the potable rinse waters was quality controlled through periodic on-site GC analyses of distilled and potable water samples. This procedure allowed for early detection and screening of contaminated potable and distilled (bottled) water sources that contained organic constituents. Without the capability for on-site detection, these potential sources of contamination error may have gone undetected and could have adversely impacted the field results. Each analysis was duplicated or triplicated and the average of the multiple runs for a sample was reported. The concentrations and vertical distribution of PCE and TCE in headspace gases from soil samples obtained from the seven test borings are shown in Figure 7. Concentrations of TCA were consistently less than 0.01 ppb and are not shown in the figure. In general, observed headspace gas PCE concentrations were higher than headspace gas TCE concentrations.

Discrete groundwater samples were also obtained during drilling at progressive depths in the boreholes. Twenty-two attempts were made to retrieve groundwater samples, of which 18 attempts were successful. Four attempts did not produce sufficient water for a useful sample to be obtained. Discrete groundwater sampling was conducted by driving a stainless steel, two-inch-diameter wellpoint two to four feet below the depth of the bottom of the borehole at the time of sampling. Once seated at the target depth, the wellpoints were developed by air surging until the water produced was clear or until enough water was produced so that a representative sample could be obtained. In some instances, turbid samples were collected after extended air surging did not produce clear water. Groundwater samples were obtained from the developed wellpoints using Teflon point source bailers. Each sample was collected in a 40 ml VOC vial and sealed with a septum cap. The samples were analyzed by direct aqueous injection into the on-site gas chromatograph. Turbid samples were refrigerated and allowed to settle for up to two days after sample collection prior to analysis. The results of field analyses for PCE and TCE in groundwater samples obtained during drilling are summarized in Table 1.

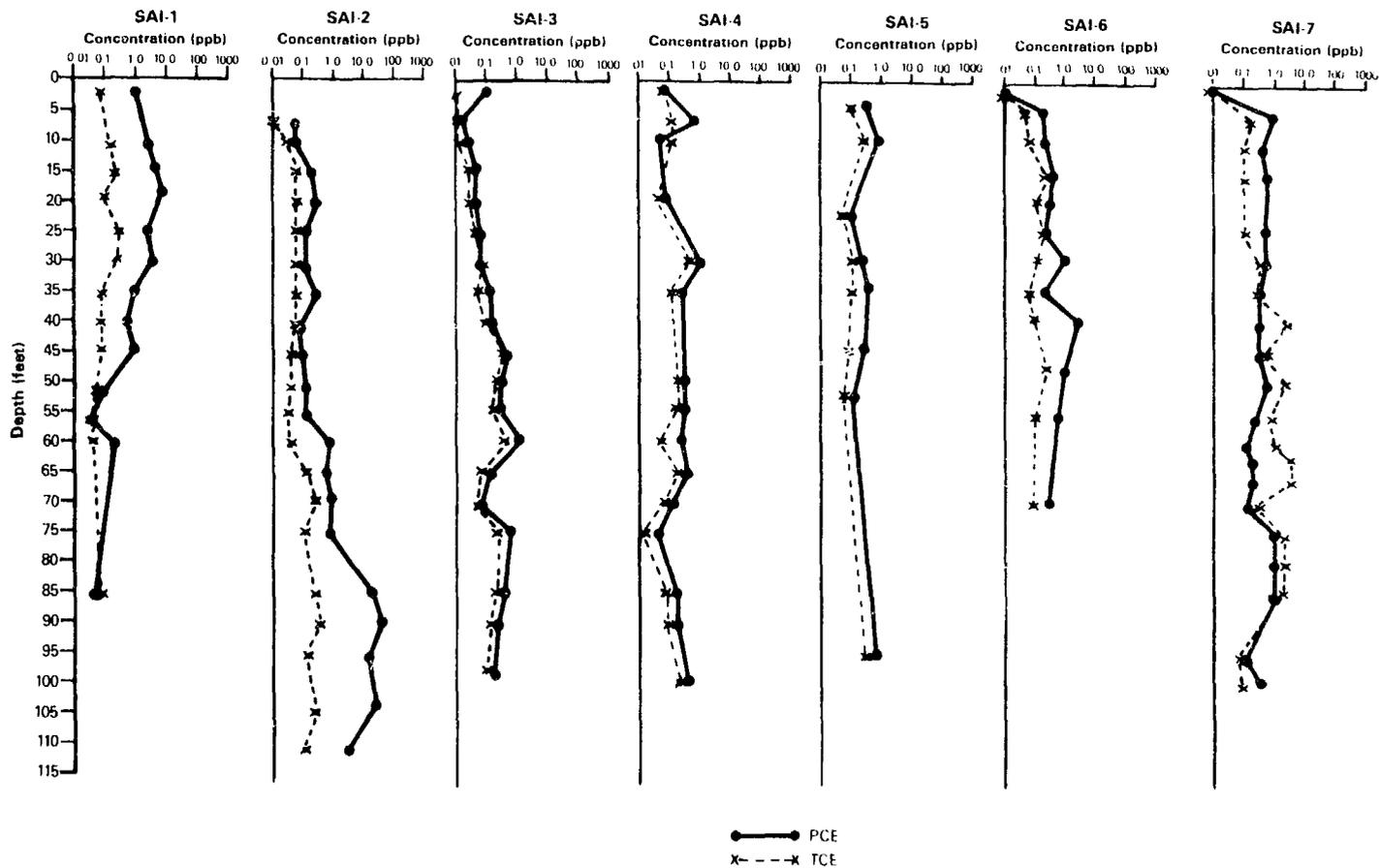


Figure 7. Concentrations of PCE and TCE in Soil Sample Headspace Gases

TABLE 1

RESULTS OF ON-SITE ANALYSES OF GROUNDWATER SAMPLES
OBTAINED DURING DRILLING

| Boring No. | Depth of Sample (ft) | Compound Concentration (ppb) | | |
|------------|----------------------|---------------------------------|-------|-------|
| | | PCE | TCE | TCA |
| SAI - 1 | 17-20 | <0.06* | <0.09 | <0.06 |
| | 87-91 | 0.1 | 0.06 | 0.03 |
| | 91-95 | 0.3 | <0.1 | <0.07 |
| SAI - 2 | 21-21.5 | 0.3 | 0.3 | <0.05 |
| | 45-47.5 | No sample obtained | | |
| | 65-68 | 3.0 | <0.08 | 0.06 |
| | 80-82 | 12.0 | 0.6 | <0.1 |
| | 105-108 | 1.0 | <0.1 | <0.1 |
| SAI - 3 | 17.5-19.5 | 0.22 | <0.2 | <0.1 |
| | 50-53.3 | 0.19 | 0.13 | 0.26 |
| | 86-88 | 5.2 | <0.08 | <0.06 |
| SAI - 4 | 21-23 | 0.6 | 0.31 | 0.13 |
| | 51-53 | <0.1 | 0.43 | 0.26 |
| | 90-91 | <0.1 | <0.08 | <0.06 |
| SAI - 5 | 35-38 | No sample obtained | | |
| | 55-58 | <0.1 | <0.1 | <0.09 |
| | 97-99 | <0.1 | <0.2 | <0.1 |
| SAI - 6 | 30-30.5 | No sample obtained | | |
| | 50-53 | No sample obtained | | |
| SAI - 7 | 25-27.5 | <0.05 | 1.0 | <0.04 |
| | 55-57.0 | <0.5 | 1000 | <0.5 |
| | 75-78.0 | <0.1 | 2.0 | 0.6 |

* < indicates concentration was less than indicated value. These values represent detection limits for the compound in the particular sample as a function of the GC instrument response factor and the injection volume.

Quantitative (linear) correlation was not observed between headspace gas concentrations and groundwater contaminant concentrations, although higher headspace gas concentrations generally provided a qualitative indication of higher groundwater contaminant concentrations. Boreholes showing the highest contaminant concentrations in the groundwater samples also showed the highest concentrations of corresponding contaminants in headspace gases of soil samples. A cross-section through selected Borough supply wells and monitoring wells indicating zones where PCE and TCE were detected in soil sample headspace gases and in groundwater samples is shown in Figure 8. On-site analyses were also conducted on groundwater samples from the three Borough supply wells. The samples from the supply wells were collected at the well head while the wells were being pumped. The results of on-site analyses of groundwater samples from Rockaway Borough's supply wells are summarized in Table 2.

Seven monitoring wells were installed and developed following completion of the borings. Well screen settings were selected to include the zone of maximum observed contamination based on the results of the on-site chemical analyses of soil sample headspace gases and discrete groundwater samples collected from each borehole. Groundwater samples were collected from the wells for laboratory analysis. The results of laboratory analyses for detected volatile organic compounds in groundwater samples collected from the seven installed monitoring wells are summarized in Table 3. The observed contaminant distribution in the groundwater samples is consistent with the contaminant distribution observed during drilling using the on-site GC analyses.

CONCLUSIONS

The results of the investigation of the Rockaway Borough well field indicate that the contamination of the well field with volatile organic compounds, first observed in 1980, has persisted over time. The observed concentrations of PCE in the well field are persistent and considerably greater (approximately seven times greater on average) than TCE contamination and PCE has affected all three Borough supply wells. Termination of pumping of Borough Well No. 1 in 1980 reduced PCE concentrations in the well to low (less than 2 ppb) concentrations. TCE contamination in the well field has largely been confined to Borough Well No. 6 and has been persistent over time.

The results of laboratory and field chemical analyses of soil, groundwater, and soil gas samples from Rockaway Borough indicate that the contamination affecting the well field may have emanated from multiple sources within the Borough. The lateral distribution of PCE and TCE in the groundwater, based on observed concentrations in monitoring wells and on field analyses, shows a trend of PCE detection limited to areas southwest of Borough Well No. 6 and TCE detection generally confined to areas northeast to southeast of Borough Well No. 6. The TCE concentrations that have been observed at Borough Well Nos. 1 and 5 have generally been low (less than 10 ppb). The average PCE concen-

TABLE 2
 RESULTS OF ON-SITE ANALYSES OF SAMPLES FROM
 ROCKAWAY BOROUGH SUPPLY WELLS

| Date Sampled | Compound Concentration (ppb) | | | | | |
|--------------|------------------------------|-----|------------|--------|------------|------|
| | Well No. 1* | | Well No. 5 | | Well No. 6 | |
| | PCE | TCE | PCE | TCE | PCE | TCE |
| 12/10/85 | NA | NA | 170 | <2.0** | 130 | 8.0 |
| 12/13/85 | 2.0 | 0.9 | 250 | <2.0 | 130 | 17.0 |
| 01/08/86 | NA | NA | 170 | <0.1 | 153 | 13.0 |
| 01/09/86 | 2.8 | 0.4 | 140 | <0.4 | 140 | 8.7 |
| 01/10/86 | 2.5 | 0.7 | 240 | <0.5 | NA | NA |
| 01/27/86 | 2.0 | 0.6 | 340 | <0.7 | 300 | 17.0 |
| 01/30/86 | 2.0 | 1.0 | 380 | <2.0 | 260 | 18.0 |
| 02/06/86 | 2.0 | 0.9 | 400 | <2.0 | 190 | 18.0 |
| 02/13/86 | 1.0 | 0.8 | 310 | <2.0 | 170 | 16.0 |
| 02/19/86 | 1.0 | 0.9 | 295 | <1.0 | 150 | 13.0 |

Analyses conducted by Tracer Research Corp. using Varian 3400 Gas Chromatograph with ECD detector

NA - not analyzed

* Well No. 1 has been inoperative since 9/12/80 except for brief trial startups

**< indicates concentration was less than indicated value.

Samples obtained 3/18/86.

TABLE 3

RESULTS OF LABORATORY ANALYSES OF GROUNDWATER SAMPLES
FROM MONITORING WELLS

| Sample No. | Compound Concentration (ppb) | |
|--------------------------------|------------------------------|--------------------------|
| | <u>Tetrachloroethylene</u> | <u>Trichloroethylene</u> |
| SAI-1 | ND | ND |
| SAI-2 | 365 | ND |
| SAI-2 (Dup) | 1170 | ND |
| SAI-3 | 4.83 | ND |
| SAI-4 | ND | ND |
| SAI-5 | ND | ND |
| SAI-6 | ND | ND |
| SAI-7 | ND | 253 |
| Field blank | ND | ND |
| Trip blank | ND | ND |
| Method de- tection limit | 4.1 | 10.0 |

ND = compound not present at detectable concentrations

Dup = duplicate sample; monitoring well was sampled a second time
on the same occasion to obtain this sample

Samples obtained 3/18/86.

tration historically affecting the well field is approximately seven times the average TCE concentration.

The distribution of the contaminants in the well field, particularly PCE, is affected by the pumping wells. For example, contaminant concentrations at Borough Well No. 1, which initially contained the highest PCE concentrations observed, decreased substantially after the pumping of the well was terminated in 1980. However, PCE concentrations in Borough Well Nos. 5 and 6 gradually increased as the contaminant plume apparently was drawn toward these wells, although TCE concentrations remained low (less than 5 ppb since September 1980) in Well Nos. 1 and 5. Further examination indicates that the observed variations in contaminant concentrations within the Borough supply wells were appreciably parallel over time. The corresponding rise and fall in chemical concentrations shown by the plots of PCE versus time for these wells at approximately 300 days after initiation of the program illustrate this observation and reflect the balance achieved between the well field pumpage and the contaminant distribution in the wells.

The majority of the contamination occurs at moderate depths in the aquifer, ranging between approximately 55 and 95 feet. PCE concentrations (5 ppb) detected at SAI-3 may be indicative of a deeper (75 to 95 feet) migratory path by which the compounds are transported. Although the headspace gas and water sample analyses conducted during drilling were integral in determining the vertical distribution of the contaminants in the aquifer, the presence of subsurface boulders and cobbles limited the acquisition of samples that would have allowed a more complete determination of the vertical distribution of contaminants at particular locations, notably at SAI-5 and SAI-6.

The available data pertaining to contaminant distribution in and around the Rockaway Borough well field are not sufficient to identify specific locations of the contaminant sources affecting the well field. However, possible sources that may have contributed to contamination of the well field appear to be located in one or more of the following areas:

- Commercial area west of the well field (Area 1 on Figure 9) - possible PCE source.
- Commercial/industrial area northeast of the Borough well field (Area 2) - possible TCE source.
- Commercial/industrial area south of the Rockaway River and across the river from the well field (Area 3) - possible PCE and/or TCE source as inferred from soil gas monitoring results and the results of data provided by NJDEP from a separate investigation.

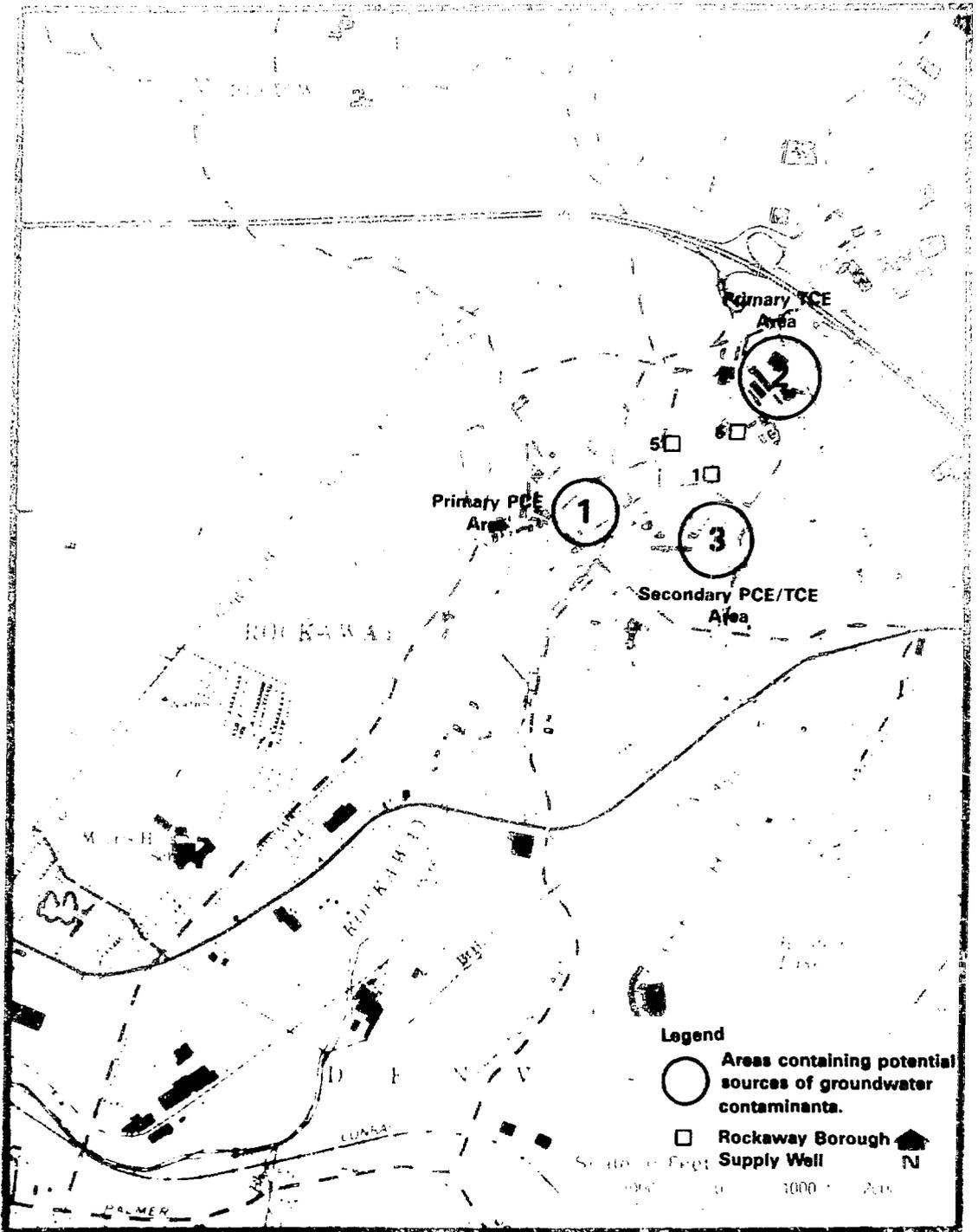


Figure 9. Areas that May Contain Sources of Contaminants Affecting the Rockaway Borough Well Field

The application of high-sensitivity field chemical analyses to site investigations can provide semi-quantitative data regarding the lateral and vertical distribution of contaminants in an aquifer. The approach of using headspace techniques to delineate subsurface contaminant distribution in soils (and, by inference, in groundwater) provides a cost-effective method for evaluating aquifer contamination in three dimensions. The Rockaway Borough well field investigation used field headspace techniques and field direct-injection water analyses that do not involve preconcentration or purge-and-trap steps and that are generally conducted under ambient room conditions. This methodology has been successful in providing semi-quantitative data regarding subsurface soils and groundwater contamination and has been shown to be cost-effective. Field laboratory analyses of groundwater samples using laboratory-quality gas chromatographs have provided chemical data that are generally comparable in quality to data obtained from a testing laboratory. More rigorous preconcentration and analysis techniques, instrumentation (mass spectrometer, atomic absorption spectroscope), and temperature controls can also be applied in the field with increased costs for services and instrumentation. Data collected using less sophisticated headspace and soil gas techniques, while quantitative, provide only an indication of the presence of a particular contaminant in a sample. Also, order-of-magnitude variations in the headspace concentrations may be significant in terms of groundwater contamination. Recognition of these limitations is integral to the effective application and interpretation of the field data, and additional experience is needed regarding the relationships between soil sample headspace concentrations, soil gas concentrations, associated groundwater concentrations for individual contaminants, and site-specific conditions such as lithology, soil moisture, and depth to groundwater.

The inclusion of field chemical analyses into the investigation of the Rockaway Borough well field contamination added flexibility that greatly enhanced the capabilities for delineating potential sources of contaminants and, to a limited extent, three-dimensional contaminant distribution within the aquifer. By using high-sensitivity, on-site chemical analyses, the field data that were generated provided an improved understanding of the temporal and spatial aspects of the contaminant distribution surrounding the well field. The data also contributed to the identification of three potential sources in an industrial area consisting of numerous potential contaminant sources.

REFERENCES

- Canace, R., Hutchinson, W.R., Saunders, W.R., Andres, K.G., 1983, Results of the 1980-81 Drought Emergency Groundwater Investigation in Morris and Passaic Counties, New Jersey, New Jersey Geological Survey Open-File Report No. 83-3.