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POLLUTION PREVENTION TECHNOLOGIES FOR PLUTONIUM PROCESSING

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Preface

Preventing Pollution From Plutonium Processing

K. K. S. Pillay
Nuclear Materials Technology

Introduction

Pollution is a dirty word. No one has to make a case anymore for the need for pollution prevention or the related concept of environmental management. Although the history of pollution control legislation in the United States dates back to the River and Harbor Act of 1899, the past four decades have been most active in developing and administering numerous environmental regulations. This process of administering environmental regulations has accelerated in recent years and has become a critical factor in the quality of life in these United States.

Since the passage of the Atomic Energy Act in 1954, the Congress of the United States has promulgated numerous environmental statutes. Figure 1 shows the accumulation of environmental statues and their amendments that are presently applicable to nuclear defense facilities. These statutes have been codified into over 9000 regulations by federal agencies.[1] The Environmental Protection Agency (EPA) alone has over 125,000 employees administering these statutes and regulations. There is an equal number of environmental regulators at the state and local government levels.

Although radioactive wastes have been accumulating in the United States for the past half century, only during the last two decades has there been a concerted effort to address the problems of long-term isolation of these wastes from the human environment. After considerable study and debate, the U.S. program for radioactive waste management was codified in the Nuclear Waste Policy Act of 1982.[2]

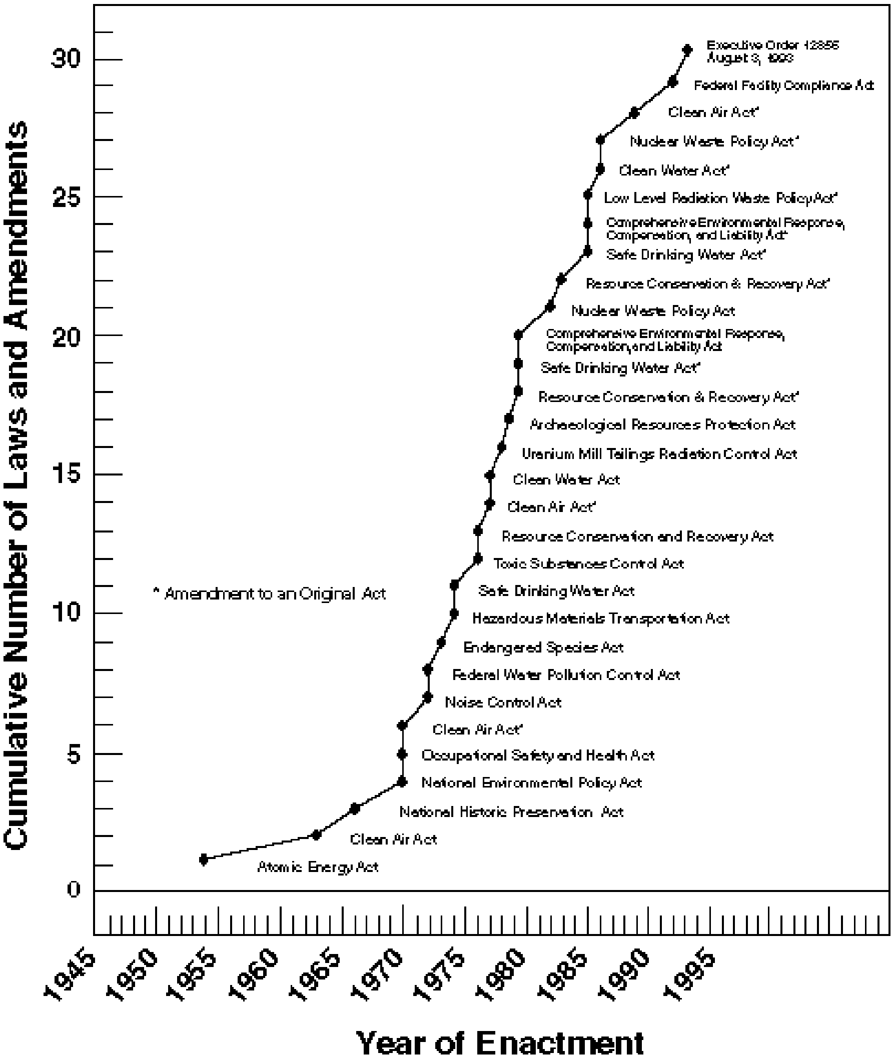

Fig.1. Accumulation of environmental statutes and their amendments since the passage of the Atomic Energy Act in 1954.

According to this legislation, the U.S. Department of Energy (DOE) has the responsibility to develop strategies, systems, and technologies for the long-term isolation of all spent nuclear fuels, high-level wastes, and transuranic wastes in the United States. Because of the unique socio-political atmosphere surrounding radioactive waste management, there are considerable challenges to the scientific community for developing technological solutions that are acceptable to a concerned free society.

For nearly four decades, the U.S. nuclear defense facilities sought refuge under the Atomic Energy Act and claimed sovereign immunity from compliance with most of the environmental regulations. In response to increasing public pressure during the past few years, the defense sector has undergone a cultural shift that has changed past attitudes toward complying with environmental regulations. This shift has culminated in the passage of the 1992 Federal Facility Compliance Act (FFCA) and other complementary regulations and executive orders.[3,4] The FFCA gives federal facilities a three-year period to develop detailed plans for complying with all applicable environmental regulations. This particular legislation has been a great motivator to all federal facilities, including the Los Alamos Plutonium Processing Facility, to modify past practices and to become conscious of the environmental impacts of all its activities.

The Nuclear Materials Technology (NMT) Division, in this new cultural climate, adopted a strategic goal to systematically eliminate the adverse environmental impacts associated with operating the Los Alamos Plutonium Facility. This ambitious goal of a committed group of people in the Los Alamos nuclear technology community is the theme of this compilation of technology initiatives. Our strategic goal is not only part of a survival strategy but also represents our readiness to solve national environmental problems associated with nuclear processing facilities and, thereby, help alleviate public and governmental concerns.

Since September 1992, several activities within NMT Division have been postponed because of the FFCA and the long and laborious negotiations that are required to reach a facility-specific agreement with the EPA. On July 19, 1993, DOE Secretary Hazel O'Leary approved the Los Alamos agreement with Region 6 of the EPA. According to this agreement, full compliance with the FFCA is expected by the year 2000. During these negotiations, NMT Division began to implement its strategic plan to meet all regulatory requirements of waste minimization and pollution prevention and to transform the Los Alamos plutonium processing operations into an environmentally benign activity. In developing those technologies required to meet our goals, we will also serve the needs of the weapons complex of the next century.

The following paragraphs examine the legacy of nuclear waste, the new priority of waste minimization, responsible waste management, and technological challenges for the future.

The Legacy of Nuclear Waste

The term "nuclear waste" is generally used to represent all radioactive waste materials regardless of their origin, material form, or radioactivity levels. Nuclear wastes originate from a multitude of activities involving nuclear technologies in both the civilian and defense sectors. The steady accumulation of nuclear wastes over the past half century has attracted considerable public attention during the past two decades. Following the reactor accidents at Three Mile Island and Chernobyl, there have been overwhelming expressions of public concerns over safety of all nuclear facilities and the safe management of accumulated nuclear wastes as well as those that are being generated.

Studies have shown that the public's perception of risk from nuclear waste is similar to those of highly energetic, catastrophic events. This perception is qualitatively incorrect because radioactive wastes have far lower energy levels in comparison with reactor accidents, earthquakes, volcanic eruptions, etc. An educational process that conveys realistic risks of nuclear wastes has to be a necessary part of an overall program of nuclear waste management.

Arguments about the costs and benefits of nuclear technologies continue to dominate public discussions. Attitudes of both governmental agencies and nuclear industries based on artificial cost-benefit analyses have contributed enormously to the negative attitudes surrounding nuclear wastes in the United States. Unfortunately, these analyses do not factor in the significant costs arising from environmental impacts considered unacceptable by the general public.

The unmaking of nuclear wastes and the abrogation of all uses of nuclear technologies are not in the realm of reality. As we approach the 21st Century, we cannot afford to forgo the many peaceful uses of nuclear technologies. Considerable resources have been devoted during the past two decades to the design of technical solutions for long-term management of nuclear wastes and isolation of this waste from the biosphere. There is a world-wide scientific consensus that deep geologic disposal is the best option for disposing of existing inventories of high-level and transuranic radioactive wastes.[5] However, it is now abundantly clear that the public and its representatives will not be satisfied until releases of radioactive nuclides from man-made sources to the environment are completely eliminated. The DOE has recognized that if it is to successfully achieve its long-term goals, this agency must first find a way to change public perceptions about nuclear waste. Focusing on waste minimization and responsible waste management are steps in the right direction.

Waste Minimization

Waste minimization is any action that avoids or reduces the generation of wastes. For nearly a decade, defense nuclear facilities have been voluntarily making efforts to reduce nuclear waste generation. In recent years, DOE identified environmental restoration and waste management as a major mission area.[6] The primary objective of the fourth annual Environmental Restoration and Waste Management Five-Year Plan for 1994-98 is the reduction of wastes from DOE facilities.[7]

Waste reduction can be accomplished through source reduction, recycling potential waste materials that cannot be eliminated or minimized, and treating all wastes to reduce their volume, toxicity, or mobility prior to storage or disposal. The significant reduction in nuclear weapons requirements represents a major source reduction mechanism. Recycling of a number of waste stream components is a technical possibility now and can accomplish additional waste reduction. Waste treatment to reduce volume, toxicity, and mobility are all in various stages of development and implementation.

DOE's ambitious plan for waste minimization can be taken a step further using new technologies essential to new nuclear facilities that will have little or no impact on the environment. Liquid waste-stream polishing to eliminate radioactive and hazardous components of wastes from nuclear materials processing facilities for the weapons fuel cycle is feasible and can be implemented in large-scale nuclear materials processing facilities. Approaches to minimizing radioactive and hazardous components in solid waste streams are being developed, and the costs for implementing such technologies are not expected to be prohibitive. Because a modern nuclear material processing facility is necessary to maintain a nuclear deterrent capability, a vigorous technology development program for waste minimization is essential to maintain public confidence in nuclear programs and to change present attitudes toward nuclear waste.

Responsible Waste Management and Future Challenges

Future nuclear processing facilities have a major responsibility to properly treat and dispose of their wastes. These facilities must be able to function without the release of radioactive and hazardous materials to the environment. Dilution and dispersion of wastes practiced in the past are not acceptable solutions any longer. Immobilization and isolation of wastes from the biosphere will have only a limited role in the long-term management of nuclear wastes. Repository construction and geologic disposal as a solution to nuclear waste problems cannot be continued forever; however, stabilization and storage have to be seriously considered as an option so that valuable resources are not discarded for political expediency. Managed storage of concentrated nuclear materials may become the policy for the national defense sector.

The scientific community faces numerous other challenges resulting in part from present public perceptions of nuclear technologies. These challenges include meeting the conflicting needs of nuclear proliferation control and nuclear energy production. Increasing concerns over the proliferation of nuclear materials and its impact on our future is an international political problem with no obvious solutions. Achievements in the area of nuclear arms reduction are eclipsed by the increasing likelihood of nuclear proliferation. Although we can propose to control proliferation through systematic reduction in fissile material inventories worldwide, the need for energy production in many parts of the world using fissile and fertile materials must be met.

These challenges are opportunities for NMT Division to develop and apply technologies that can prevent environmental pollution. Technology transfer initiatives now being actively promoted by DOE offer opportunities for NMT Division to develop university and industry partnerships that can be mutually beneficial. Technology initiatives detailed in the following pages of this report are steps toward achieving our overriding goal of an environmentally benign plutonium processing facility at Los Alamos.◆

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Off-Gas Scrubbing

W. Brad Smith
*Nuclear Materials Processing:
Chloride Systems*

Introduction

Effectively handling corrosive off-gases produced by aqueous-based processing of Special Nuclear Materials is an enigma for most facility operations. Resolving the problem is not just limited to scrubbing the corrosive off-gases. Project research and design must also consider containment design, ventilation control, the effects of radiation and other contaminants, monitoring and control systems, maintenance, and waste minimization. The comprehensive plan for the aqueous recovery operations at the Los Alamos Plutonium Facility incorporates a minimum of local corrosion-resistant material, the capture of all corrosive acid vapors near the source, and monitoring of the glove-box exhaust system. The first phase of the plan consists of consolidation of all chloride-based processing to minimize the number of containment systems requiring special materials and maintenance. The second phase involves the design and evaluation of the corrosion-resistant containment systems such as glove-box linings, dispersion-coated ventilation systems, and lined process piping. The third phase is comprised of various efforts to protect the local utility support systems; these efforts include the use of an off-gas central scrubber for the chloride recovery glove-box exhaust system and local caustic scrubbers for the chloride and nitrate vacuum transfer systems. This paper first examines the extent of corrosion caused by acid vapors in the Los Alamos Plutonium Facility, reviews the history of integrating aqueous-based chloride processing into our nuclear processing facility, and then focuses on the operation of the off-gas central scrubber, vitally important to implementing the third phase of the Los Alamos plan for aqueous recovery operations.

> *"The comprehensive plan for the aqueous recovery operations at the Los Alamos Plutonium Facility incorporates a minimum of local corrosion-resistant material, the capture of all corrosive acid vapors near the source, and monitoring of the glove-box exhaust system."*

Acid Vapor Corrosion at the Plutonium Facility

Concerns about acid vapor corrosion at the Plutonium Facility have grown with the increase in applications for acid-based aqueous processing, the buildup of local corrosion, and the trend toward shorter-lived HEPA (high efficient particulate air) filters. Other facilities are concerned about the corrosion problems caused by the increased use of hydrofluoric acid, hydrochloric acid (HCl), chlorine, and caustics.[1] Acidic liquid corrosion may cause more problems than acid vapor corrosion; however, the problems caused by acid vapor corrosion can be more serious. Effects such as chloride stress cracking of stainless-steel systems, HEPA filter seal or material failures, and acid-level buildup in the utilities can be more difficult to contain, monitor, or evaluate as compared to liquid-based corrosion effects.

Since most standard industry techniques for determining the extent and rate of corrosion are not feasible in a plutonium processing facility, the Los Alamos plan for aqueous recovery operations is based on process knowledge and the specific system's susceptibility to corrosion. Visual inspection of the enclosures and the glove-box exhaust plenums provides the only evidence of the extent of corrosion. With the exception of some nonstainless appurtenances, the glove boxes have experienced the greatest corrosion. The location is typically near the glove-box bottom, where liquids collect. Similarly, the local ducts are significantly more pitted near the duct bottoms than the duct tops. The scale buildup is highest nearer the glove-box exhaust, most probably due to condensation and the subsequent ferric precipitates from dissolved iron components. The rate of corrosion is also extremely difficult to evaluate due to the variations in operating times, concentrations, and chemical interactions. Specific upsets with processes and equipment, such as the evaporation process for nitrate-based operations, dissolution processes, loss of condenser cooling water, or liquid carryover from vacuum transfer operations, may cause more corrosion than the continuous release of low-concentration fume gas. Currently, no system or procedure is in place to monitor these upset conditions.

The selective application of corrosion-resistant material in the second phase of the plan has been technically and economically feasible primarily because of the first-phase consolidation of aqueous chloride operations, which routinely vent low, but significant, concentrations of HCl vapors. The Plutonium Facility was originally designed for nitric acid (HNO_3) operations, so even these low concentrations pose a long-term problem for the Facility. Corrosion problems do exist with other operations, but the impact from chloride corrosion presents the biggest potential for failure due to stress-corrosion cracking. Although the Plutonium Facility has not experienced any primary containment failures because of corrosion, many factors such as general process knowledge, scale buildup in the local ducts, and localized glove-box corrosion indicate material incompatibilities exist. Furthermore, because of the variety of process operations and the size of the Facility, replacing all exposed systems with special corrosion-resistant materials would not be economically feasible and, thus, preventative measures become necessary. Preventative measures at Los Alamos consist of off-gas scrubbing at the various sources of acid vapor combined with selective material upgrades and real-time, in-line monitoring to ensure the performance of these scrubbers.

History of Integrating Aqueous-Based Chloride Processing

The Los Alamos graded approach to implementing and demonstrating an integrated aqueous chloride flow sheet was governed by the severity of the effects from HCl corrosion. This graded approach proceeded as follows: early emphasis on new liquid-processing equipment and transfer systems, followed by secondary containment of liquids, then ventilation system upgrades, and finally point-source off-gas scrubbing.

New liquid processing equipment and transfer systems were developed using chlorinated and fluoropolymer-based plastics, such as CPVC (chlorinated polyvinyl chloride) end plates, commercial-grade plastic piping and valves for internal glove-box transfer systems, PVDF (polyvinylideneflouride) slab tanks for process storage, and plastic-lined piping for all external liquid transfer systems. This use of plastics reduced corrosion at the most susceptible points, provided a level of safety and reliability similar to typical metal systems, and actually improved accessibility and flexibility in processing.

Aqueous batch processing in a research and development facility can result in spills of minor amounts of process liquids because of process-tubing changes and routine operations or maintenance; thus, secondary containment of liquids is essential.

Drawing on experience gained with fluoropolymers for process equipment, we used fluoropolymer-based plastics to protect enclosures, appurtenances, and utilities. The glove-box shell, which provides the secondary containment, has historically been fabricated of 316 stainless steel, as are most appurtenances. The published corrosion rate for 316 stainless steel in concentrated (10 *M*) aqueous HCl is at least 0.05 inches per year[2] (versus a rate of 0.002 inches per year for aqueous HNO_3). This corrosion rate only provides for an approximate 10-year life cycle for 7-gauge stainless steel. Evaluation and testing of several different glove-box linings led to a new specification[3] for the fabrication and installation of fluoropolymer enclosure linings, which provide both mechanical and chemical protection.[4]

Ventilation equipment has been modified for compatibility with low concentrations of acid vapors. All mild steels used for HEPA fire screens and supports have been replaced with stainless-steel components. However, recent studies[5] have shown a decrease in the efficiency of the three-stage Facility HEPA filters for the aqueous chloride processing ventilation system. Trends toward higher DOS* penetration rates are evident for the first-stage HEPA filters but are still an order of magnitude below the design failure point. Although the exact cause has not been determined, the decrease in filter efficiency corresponds to an increase in aqueous operations in this area. To trace possible causes, access ports for periodic sampling of the ventilation exhaust for acid gas, for measurement of exhaust flow rates, for corrosion coupon tests, and for visual examination of scale buildup have been incorporated into the local glove-box exhaust ducts, where the acid gas concentrations should be the highest.

Point-source off-gas scrubbing was originally implemented to protect the vacuum transfer system. Fume gas was originally vented directly to the glove-box atmosphere from dissolution, feed treatment, and evaporator processes. These concentrated fumes, which condense on and etch the glove-box windows, reduced visibility. The humidity also caused the local HEPA filter to swell and plug prematurely. Local scrubbers now capture approximately 90% of all HCl acid vapors and 50% of all HNO_3 vapors.

HCl Central Scrubber Design

For some processes the vacuum transfer system cannot provide the necessary volume to collect the acid vapors. These fugitive emissions are vented through the glove-box exhaust system and continuously diluted by exhaust from other areas. Although the local scrubbers remove a majority of the fumes, some concern about the effects of chlorides on stainless-steel systems, neoprene seals, and HEPA materials still exists. The consolidation of the aqueous chloride operations provides the opportunity to collect and treat all HCl fugitive emissions with a central scrubber and enhances the life cycle of the Plutonium Facility systems that don't use chloride-resistant material.

An evaluation of commercial fume gas scrubbers found one system that met the stringent requirements for integration with the Plutonium Facility systems. Some of the features provided by this system include automatic, unattended operation; low maintenance; critically safe liquid waste storage; waste minimization; and fail-safe shutdown. The system is sized to treat the exhaust from four to fifteen glove boxes and has a total system pressure loss about half the available static pressure of the glove-box exhaust system. Because this scrubbing process provides a utility support function, which only enhances the safety and life cycle of the Facility, it can be easily automated without the burden of a "safety class" designation.

The HCl central scrubber is designed to remove acid gas fumes from twelve glove boxes. The process equipment will be installed in specially designed enclosures to meet ALARA (as low as reasonably achievable) contamination control goals associated with maintenance operations and instrument calibration. Fumes will be collected in a local corrosion-resistant exhaust duct, removed by liquid absorption in a packed column scrubber, and then vented to the glove-box exhaust system. (Refer to Fig. 1 for this and other design details that follow.)

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* di (2 ethylhexyl) sebacate, which replaces DOP (dioctyl phthalate).

The maximum static pressure for the glove-box exhaust is a negative 1.3-inch water column (WC). The maximum scrubber system pressure loss is a 0.7-inch WC. Therefore, a very sensitive instrumentation system is required to monitor and control the pressure loss. Initially, the pressure will be maintained by allowing the flow to decrease as the HEPA filters and scrubber packing plug up. As the pressure loss increases above a predetermined set point, the system will go into a bypass mode (see Flow Control Valves, designated as FV, in Fig. 1). Upset or maintenance conditions will also force the system into a bypass mode. Emergency Shutdown (ESD) logic will be developed and monitoring installed to insure proper system response. Sufficient local gauges and manual overrides will be provided to insure fail-safe operation. However, failure of any component will still not affect the glove-box exhaust system flow and pressure stability, minimizing the need for redundant or “safety-class” systems.

As HCl vapor is absorbed, the pH of the scrubber solution will decrease. Batch processing causes the influent concentration of HCl to vary over a wide spectrum. Therefore, the scrubber liquid discharge rate (see pH Control Valve, AV) will be proportional to changes in the HCl concentration, which is monitored by measuring the pH. This sidestream of scrubber solution will be piped to a set of slab tanks, and an equal amount of fresh water will be added (see Level Control Valve, LV) to maintain an optimum pH of 2.

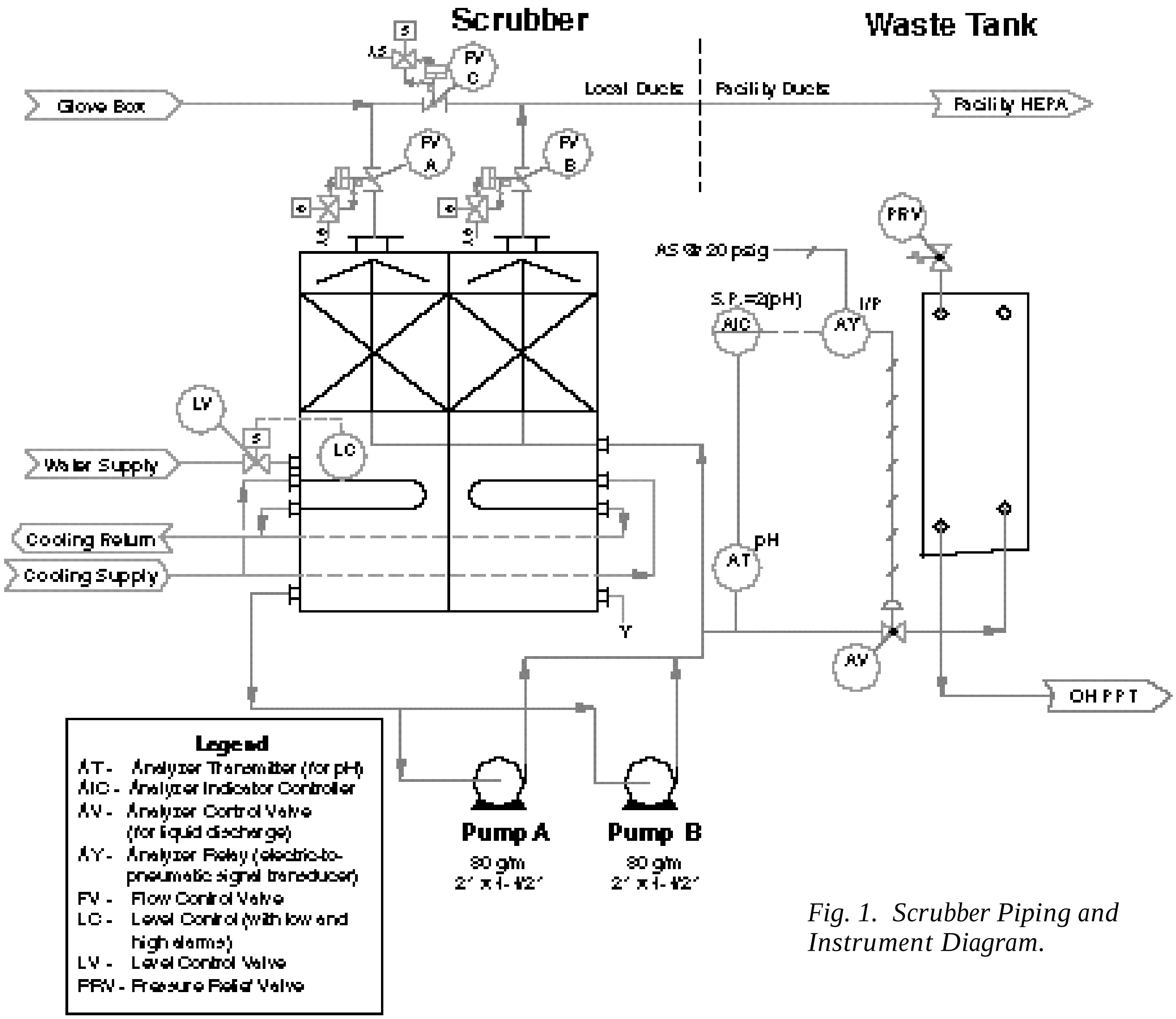

Fig. 1. Scrubber Piping and Instrument Diagram.

The water level in the scrubber sump will have redundant monitors. One system (see Level Control, LC) will be an analog signal used as an override for the pH control to maintain proper pump suction with alarm indication for high and low levels. A second set of level switches (not shown), high-high and low-low, will be used to shut down the scrubber and place the ventilation Flow Control Valves in a bypass mode. A tertiary level control, consisting of an open drain line, shall be used to prevent any possibility of liquid depths above 4 inches (because of criticality concerns). A flow-limiting device may also be considered to limit the total amount of water used on a periodic basis.

The primary contamination control for glove boxes is the negative pressure for the glovebox exhaust system in the aqueous chloride processing area. Therefore, the pressure will be monitored (not shown), and any excursions beyond set point will override the bypass Flow Control Valves. A redundant pressure switch will activate an alarm and also place the ventilation Flow Control Valves in a bypass mode.

The exhaust from the scrubber may be saturated with water; the resultant humidity will affect HCl detectors and air flow monitors, and condensation will increase the possibility of corrosion in the main ducts. Using a local chiller to cool the scrubber solution will lower the dew point as well as increase the removal efficiency of the scrubber.

A mass spectrometer is the most feasible method to monitor the effectiveness (HCl removal) of the scrubbers. This type of continuous, on-line instrumentation is required to evaluate multiple acid-gas concentrations, provide wide rangeability to determine upset conditions, and provide detailed glove-box exhaust air analysis on a continuous basis.

Waste Minimization

To minimize liquid waste, the central scrubber will have a liquid discharge rate that is proportional to changes in the system pH, as previously discussed. This control system will reduce the projected waste from 4000 gallons per month to approximately 120 gallons per month. This waste stream will be neutralized and then sent through the caustic waste line to the Los Alamos Liquid Waste Treatment Facility. One possible alternative to treating the waste is to recycle or reuse the scrubber solution and thereby eliminate liquid waste altogether.

Another approach being considered for solid waste minimization is to replace local glove-box HEPA filters, which require frequent changing because of swelling due to the absorption of moisture from the aqueous operations, with corrosion-resistant roughing filters and a post-scrubber HEPA. Roughing filters will prevent alpha contamination of the local ducts due to particulates, provide more consistent flow and more consistent pressure control, and reduce plugging of the proposed post-scrubber HEPA. The use of a post-scrubber HEPA (which could be installed in one of the utility support enclosures to simplify change out and disposal) between the central scrubber exhaust and the main ducts would help insure that no contamination would spread to the Facility exhaust ducts.♦

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Acid Recovery and Recycle

Thomas R. Mills
Actinide Materials Chemistry

"Minimizing the concentrations and amounts of plutonium and neutralized salts sent to waste disposal supports the Nuclear Materials Technology Division's vision of zero radioactive and hazardous discharges."

Introduction

Plutonium processing, both for waste handling and for recovery, uses large amounts of nitric and hydrochloric acids. Typical processes involve dissolving some form of plutonium in these acids for purification. These acid-based processes effectively accomplish needed separations, but they generate large volumes of waste acid solution.

The previous approach to handling these solutions has been to neutralize them with caustic and then partition radioactive components from the bulk of the solution. The radioactive fraction is put into a concrete matrix (saltcrete), and the remaining solution is discharged to the environment, after treatment to remove radioactivity. At Los Alamos, the bulk of nitric acid (HNO_3) is separated from nonvolatile salts (including most of the plutonium), but both fractions are presently disposed of rather than recovered and recycled.

This approach leads to environmental and storage problems. With both our heightened commitment to protecting the environment and future regulatory requirements, reduction of generated wastes is essential. Including handling, inspection, packaging, shipping, and actual storage, the cost of producing waste units can be tremendous. Beyond cost implications, concerns over long-term storage of radioactive waste dictate that both the amounts be minimized and that the storage forms be highly stable. In particular, a potential for leaching of soluble salts from saltcrete exists, and such leaching could render the storage form less stable.

Recycling acids from waste solutions helps solve many of these problems because this method eliminates most of the waste generated by plutonium processing. Hazardous chemical discharges (notably nitrates) are greatly reduced, and already low levels of radioactive discharges are further reduced. This reduction in the total number of radioactive waste units requiring storage lowers disposal costs significantly; for example, acid recycle would save over $50 million in waste disposal costs in five years for a facility operating at levels similar to the previous levels of the Rocky Flats Plant. The reduced salt content in radioactive wastes, an additional benefit of acid recovery and recycle, reduces the potential for leaching of stored radioactive wastes.

Minimizing the concentrations and amounts of plutonium and neutralized salts sent to waste disposal supports the Nuclear Materials Technology (NMT) Division's vision of zero radioactive and hazardous discharges.

Our three-year goals are
  1) a 90% recycle of HNO_3,
  2) a 90% reduction of acid concentration in waste streams, and
  3) a 10-fold reduction of nitrate concentration in effluent liquid.

Our five-year goals are
  1) an operating recycle system for both acids that will eliminate effluent acid streams,
  2) a reduction of nitrate wastes by a factor of 500, and
  3) a reduction of chloride wastes by a factor of 10.

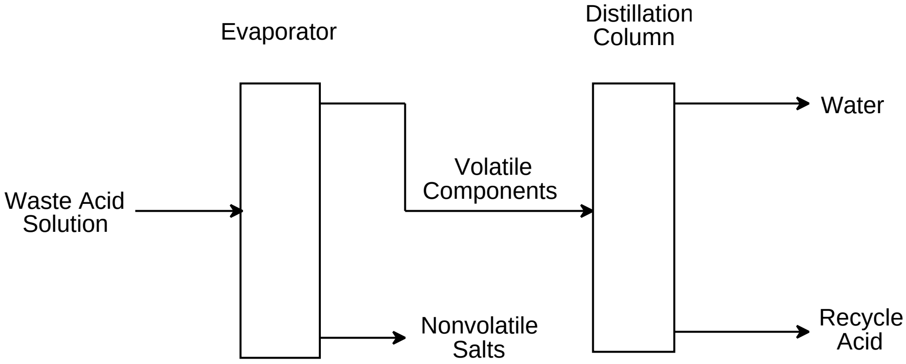

Fig.1. Block diagram of acid recovery and recycle system.

Approach

A two-stage recovery and recycle process is planned. First, each acid waste stream is evaporated to separate volatiles (primarily acid and water) from dissolved radioactive solids and other inorganic salts. Second, the evaporated acid and water are separated in a fractional distillation column to yield a concentrated acid and a water stream. This two-stage process is shown by the block diagram in Fig. 1.

The nonvolatile salt residue from evaporation, which contains any plutonium and inorganic salts from solution, represents a small fraction of the original acid solution. This fraction will be neutralized and dried and may receive further treatment (e.g., denitration or freeze drying[1]) before disposal. The resulting solid will be disposed of in a concrete matrix or an alternative ceramic form.

The acid / water vapor mixture from the evaporator will be separated in the distillation column to yield a concentrated acid (≥12 *M* HNO_3, 6 *M* HCl) at the column bottom and a very dilute acid stream (“water”) at the column top. The separated acid will be sufficiently concentrated to be reused for processing, and it will contain minimal plutonium or other constituents.
The water stream will require pH adjustment to neutrality prior to discharge to the environment. This effluent stream will have a negligible plutonium content and will have a salt content much less than at present.

Nitric and hydrochloric acid recovery and recycle will be demonstrated at the Los Alamos Plutonium Facility using the two integrated demonstration lines: Advanced Testing Line for Actinide Separations (ATLAS) for HNO_3 and Experimental Chloride Extraction Line (EXCEL) for HCl. ATLAS already has a thermosyphon evaporator as an integral part; a distillation column will be added as an upgrade. HCl recycle is at an early stage; thus, characterization of HCl processes (which includes flow balances) and bench-scale evaporation and distillation experiments are needed. Both an evaporator and a distillation column will be added to EXCEL.

Following demonstrations using these systems, full-scale systems will be built to handle all acid waste streams from the Plutonium Facility. The acid recovery and recycle effort will have active participation from members of the Nitrate Systems (NMT-2), the Chloride Systems (NMT-3), and the Actinide Materials Chemistry (NMT-6) groups.

Project Status

The Nitrate Systems Group, using the ATLAS thermosyphon evaporator, has already conducted valuable initial experiments with HNO_3. Promising results indicate that acid recycle is feasible. A simulated process waste solution containing 4.5 *M* HNO_3 was evaporated with the goal of separating the maximum possible fraction of contained acid. At evaporation rates of 0.7–0.8 L / min, over 82 mol % of the HNO_3 was recovered for further concentration. The volume of solution remaining in the evaporator was only 2% of the amount fed to the evaporator, and this solution was flushed from the evaporator before the acid concentration process was begun. In a second pass of clean distillate through the evaporator, steady HNO_3 concentrations were reached within 30 minutes. In this second pass, 43 mol % of the original nitric acid feed was concentrated to 10.7 *M* HNO_3. In a third pass, 21 mol % of the original nitric acid was collected as 12 *M* HNO_3.

A physical design for acid recycle systems has been developed for use in the present ATLAS system. The HNO_3 distillation column is closely coupled to the ATLAS evaporator to take advantage of thermal energy invested. Vapor exiting the evaporator becomes the feed to the column. The existing thermosyphon evaporator uses a steam bundle to produce vigorous boiling and liquid circulation through the boiler. Important to retention of radioactive components, a demister bed in the evaporator minimizes entrainment of fine droplets with dissolved solids.

The distillation column contains loose-poured packing to support a dispersed liquid phase trickling downward. The packing provides maximum interfacial area for vapor-liquid equilibrium but offers minimal resistance to upward vapor flow. The column has a steam boiler for vapor boilup and a partial condenser for liquid reflux. A schematic diagram of the evaporator and column is shown in Fig. 2. The evaporator and column combination for EXCEL will have a similar configuration.

Preliminary designs have been made for HNO_3 and HCl distillation columns for ATLAS and EXCEL. The design for a HNO_3 distillation system is based on handling 1 L / min of 4–6 *M* HNO_3. A 6-inch-diameter, 6-foot-tall distillation column can concentrate at least 95% of the HNO_3 in this stream to 12 *M* HNO_3. The waste stream will have less than 5% of the acid feed, and plutonium activity will be lower than that obtained using evaporation only. "Cold" tests are under way on the HNO_3 distillation column to determine packing performance for flow capacity and separating ability. Following these tests, the column will be installed in ATLAS.

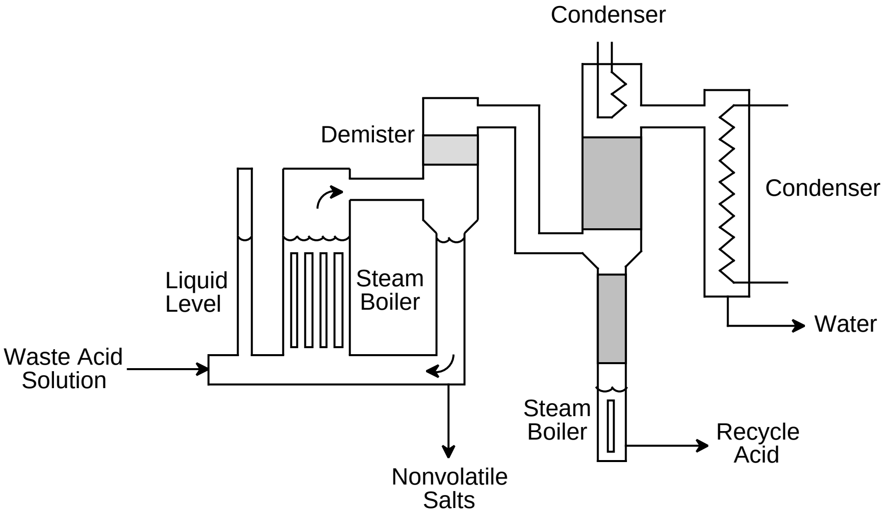

Fig. 2. Schematic of thermosyphon evaporator and acid distillation column.

(In parallel, we are discussing with a vendor possible purchase of acid recovery systems that use technology developed at Pacific Northwest Laboratories.) A similar system for HCl distillation is expected to produce 6 *M* HCl from a feed of 1 L / min of 2–4 *M* HCl.

The highest volume of the HNO_3 effluent stream from the Plutonium Facility in recent years was about 75,000 liters per year. Although the capacity of ATLAS (~0.75 L / min) might conceivably handle this stream, the required duty cycle of 80% (1667 hours) is unrealistic for a plutonium facility. Full-scale acid recycle systems will be designed and built using experience gained from the ATLAS and EXCEL demonstrations. These systems will address the five-year goals.

Summary

Development of acid recovery and recycle will enable NMT Division to reduce wastes on a facility-wide basis. Our research will demonstrate that hazardous and radioactive chemicals can be reduced and eliminated from liquid effluent streams in an existing plutonium facility. In addition, this important technology will be available for the plutonium facility yet to come — Complex 21.✥

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Hydrochloric Acid Waste Stream Polishing

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Introduction

Aqueous processing of plutonium residues in hydrochloric acid (HCl) produces waste effluent streams that require several treatment steps before the liquids may be discharged to the environment. Effluents from HCl processing streams are currently combined and routed to controlled hydroxide precipitation as the first step in actinide decontamination. This step neutralizes the entire inventory of process acid, coprecipitates many other metal salts with the actinides, and produces a solid cake that is often too high in americium and plutonium for eventual WIPP (Waste Isolation Pilot Plant) disposal. The liquid effluent from controlled hydroxide precipitation (usually about 10^9 dpm per liter) is the largest contributer of alpha activity for solutions sent to the TA-50 Liquid Waste Treatment Facility. Final treatment steps at TA-50 include a ferric flocculation process, which produces additional barrels of transuranic (TRU) solid waste.

The purpose of this work is to evaluate extraction chromatography techniques and materials as an alternative method to removing actinides from aqueous Hcl effluent streams. Part of the challenge has been to develop and match extraction methods to specific waste stream requirements for best overall actinide decontamination. Effluent streams may be categorized as “high-acid streams” (~6 *M* HCl) which originate from solvent extraction raffinate or anion exchange effluent, or “low-acid streams” (~1 *M* HCl) which may come from the filtrate of plutonium(III) oxalate precipitation or the eluate of an anion exchange “guard column” used to remove iron from the process stream. The advantages of applying chromatographic techniques to decontamination of radioactive aqueous effluents include generation of smaller quantities of solid residues in forms suitable for storage, reduction of TRU waste volumes, and more efficient decontamination of aqueous effluents.

> *“The advantages of applying chromatographic techniques to decontamination of radioactive aqueous effluents include generation of smaller quantities of solid residues in forms suitable for storage, reduction of TRU waste volumes, and more efficient decontamination of aqueous effluents.”*

High-Acid Effluent Streams

The majority of our early research has concentrated on high-acid streams for several reasons:

1) high americium content presents the greatest decontamination challenge,
2) increasingly low limits on activity content of grout waste forms indicate the need for isolation of the americium in a stable form for storage or vitrification,
3) removal of americium early in the processing flowsheet will reduce personnel irradiation exposure from subsequent waste handling steps,
4) decontamination of the effluent would provide feed for a simple acid recycle scheme for about 90% of the HCl used in plutonium processing, and

5) segregation of the high-acid stream from other effluent streams simplifies some aspects of waste polishing design.

Separation of actinides from the other elements in the waste stream, mostly alkali or alkaline earth metals, appears feasible using present-generation technology. CMPO (n-octyl(phenyl)-N,N-diisobutylcarbamoylmethylphosphine oxide) and related molecules have been examined for use in liquid-liquid extraction schemes in hydrochloric media to remove actinides.[1, 2] Extraction chromatography, using similar extractants physically sorbed to a solid support, has been successfully used to concentrate actinides on an analytical scale; however, testing of these techniques for larger-scale applications has received scant attention.[3–5] Our work has demonstrated extraction of sizable quantities of actinides from HCl media containing alkali or alkaline earth metals and shows promise for development into a reversible chromatographic system.

Several resins coated with CMPO diluted in either DAAP (diamyl amylphosphonate) or TBP (tributyl phosphate) were tested. Contact studies with plutonium(IV) demonstrated a distribution coefficient (Kd) of ~10^4 in 6 *M* HCl, and a Kd near 1 when reduced to plutonium(III) in 1–4 *M* HCl (see Fig. 1). Kd is defined as actinide quantity per gram of resin ÷ actinide quantity per milliliter of solution. Flow studies of plutonium(IV) have shown decontamination factors (DF) of up to 10^4. DF is defined for a particular solution as actinide concentration before treatment ÷ actinide concentration after treatment. Elution of plutonium(IV) from the loaded columns in flow experiments has been slower than desired but is expected to be improved by altering the elution conditions. Loading studies with plutonium(IV) indicate that the resins should be useful for HCl process stream decontamination. The maximum plutonium loading observed in this study was 107 mg per gram of resin, a loading capacity approaching one-half that of a standard anion exchange resin (typically about 1 millimole per gram of resin or ~240 mg actinide per gram of resin).

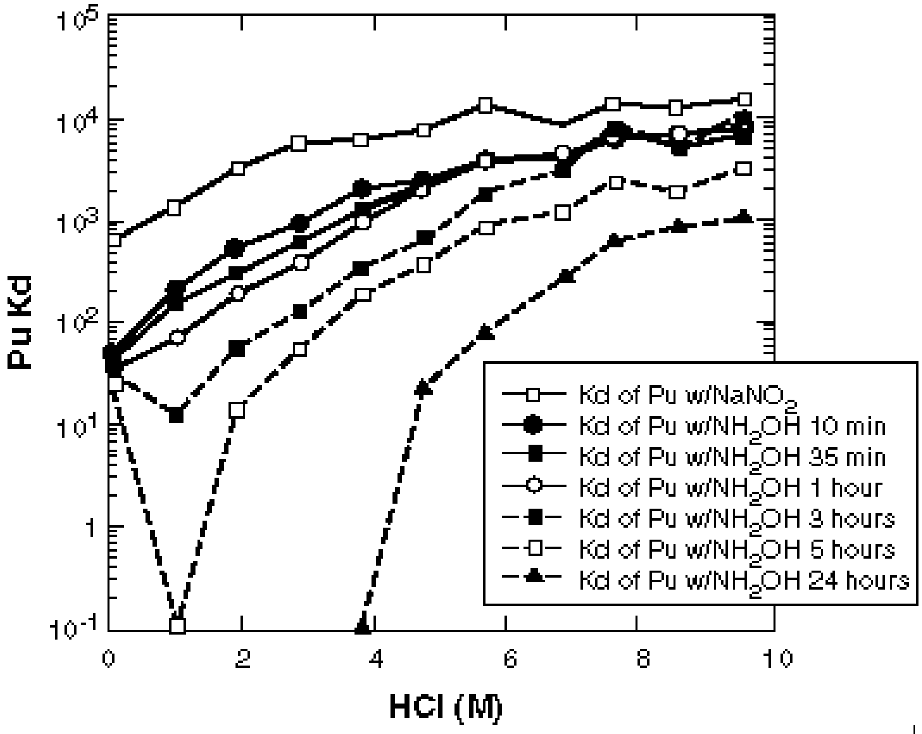

Fig. 1. Changes in Pu retention on 20:20 CMPO/DAAP resin with $NaNO_2$ and NH_2OH additions.

Americium(III) removal has proven more difficult. Contact studies of several CMPO-bearing resins with americium(III) have shown dramatic variation in observed Kd, dependent upon the amount and type of diluent used to disperse CMPO on the bead. Contact studies to remove americium(III) on a resin loaded with pure CMPO (no diluent) in 6 *M* HCl demonstrated the largest Kd (~10^3), but this resin was kinetically too slow to be useful in a flow system. Other resins with better kinetic properties gave a Kd of about 10^2, high enough to retain significant americium(III) but with breakthrough larger than desired in flow experiments. We are continuing to design and test new extractive resin materials tailored to more effectively remove americium(III) from these high-acid effluent streams.

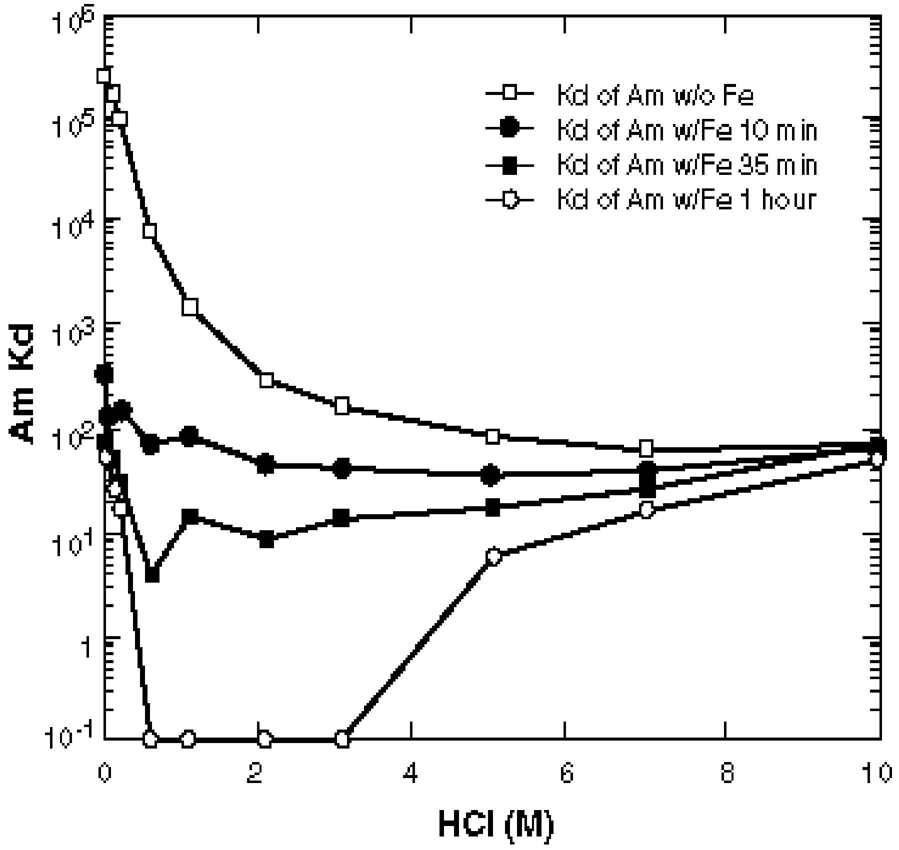

Fig. 2. Changes in Am(III) retention on Diphonix with Fe(III) addition.

Low-Acid Effluent Streams

The low-acid effluent streams will require a fundamentally different approach for decontamination because of the presence of additional chemical interferents. Oxalic acid competes with neutral ligands like CMPO in complexation of actinides in HCl, especially at low-acid concentrations. Iron(III) and certain other transition metal elements, present in the effluent stream from the guard column, act as interferents for CMPO-type ligands. For these reasons we are examining Diphonix,* a commercial polystyrene resin containing covalently-bound gem-diphosphonic acid groups, for these applications. Preliminary experiments with this resin have shown a very good uptake of americium from dilute HCl solutions with a measured contact Kd of about 10^5 (see Fig. 2). Other workers have demonstrated that the Diphonix resin is capable of selectively removing actinide(III) ions from most other elements in acidic solutions and with little interference from oxalate.[6,7] Elution of actinide(III) elements from the column may be accomplished with very strongly coordinating diphosphonic acid ligands (not desirable for our process) or by flooding the column with selected stable elements in dilute acid.[8] Our preliminary displacement experiments indicated that Am^{+3} should be effectively eluted using Al^{+3} or Fe^{+3}. Further work is required to fully evaluate the promising potential of Diphonix resin for low-acid waste stream treatment.

Conclusions

Major improvements in the form and quantity of actinide wastes generated from HCl plutonium processes are possible. Treatment of specific process effluents at the source, with extraction methods tailored for the individual stream, offers the best chance of successful actinide decontamination. The payoff will be concentration of actinides into smaller volumes of storable or treatable solid forms, decontamination of high-acid stream effluents to activity levels that allow facile HCl recycle, reduction in alpha activity in waste solutions released to TA-50, and reduction in the volume of TRU solid waste generated.✥

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* Diphonix resin is commercially available from EIChroM Industries, Inc., Darien, Illinois.

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A Novel Liquid-Liquid Extraction Technique

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Nuclear Materials Processing:
Nitrate Systems

Introduction

The cleanup of sites where nuclear materials were used and the treatment of wastes accumulated during the Cold War require the development of cost-effective and efficient technologies for the processing of radioactive wastes. Such technologies separate radioactive materials from the nonradioactive materials that make up the bulk of the wastes. The radioactive materials are sometimes further partitioned into their long-lived and short-lived radioactive components. The wastes can then be disposed of in a less expensive fashion and in a manner that significantly reduces their potential threat to the environment. Some of the radioactive materials may also be suitable for reuse.

"LLE is a process in which two immiscible liquids (commonly an aqueous and an organic phase) are allowed to come in contact so that a solute present in one of the phases can be transferred to the other."

A variety of liquid-liquid extraction (LLE) technologies are used for the processing of nuclear materials. LLE is a process in which two immiscible liquids (commonly an aqueous and an organic phase) are allowed to come in contact so that a solute (substance dissolved in a solvent) present in one of the phases can be transferred to the other. The overall process is composed of two separate steps — extraction and back-extraction. In the extraction step, an aqueous acidic stream, in which is dissolved a mixture of radioactive and nonradioactive species, comes in contact with an organic stream containing an extractant specifically designed to remove these radioactive metals. In the back-extraction step, this organic stream comes in contact with a less acidic stream into which the extractant liberates these radioactive metals. The metals from both aqueous effluent streams (leaving the extraction and back-extraction steps) are then recovered by evaporation, precipitation, electrodeposition, or other methods.

An LLE technology best suited for the applications of interest to this research must satisfy a variety of criteria. The technology must operate in a continuous mode so as to process large amounts of wastes in a reasonable amount of time. It must be resistant to the highly acidic and radioactive environments to which it will be exposed. And, because many applications will be in a contained environment, the technology must require little space, be safe and simple to use, and require little or no maintenance. LLE technologies being considered for these applications include mixer settlers, pulsed columns, spray columns, and centrifugal contactors. Each of these technologies uses its own mode of phase mixing to expedite mass transfer of the solute between the two phases.[1,2] But unfortunately, this mixing promotes aqueous/organic phase dispersions that not only deplete the organic from the LLE process but also reduce its overall extraction and back-extraction capabilities.

This dispersion problem can be avoided by using a recently developed technology called a microporous hollow fiber (MHF) membrane module. This technology does not require phase mixing for good mass transfer. Instead, the aqueous and organic phases come in contact with each other through a rigid, thin, and porous membrane as illustrated in Fig. 1. The membrane in this diagram is made of a hydrophobic material which allows the organic phase to enter its pores or "wet" the membrane. When a slight positive pressure is induced on the aqueous phase, the organic phase is held within the pores, and a region of stable and intimate contact between the two phases is established where dispersion-free mass transfer can take place. An MHF module is illustrated in Fig. 2. It consists of an outer casing containing a large number of hollow fibers fabricated from this porous membrane material. The aqueous phase is passed through the inside of the hollow fibers (on the tube side), and the organic phase is passed over the fiber bundle (on the shell side).

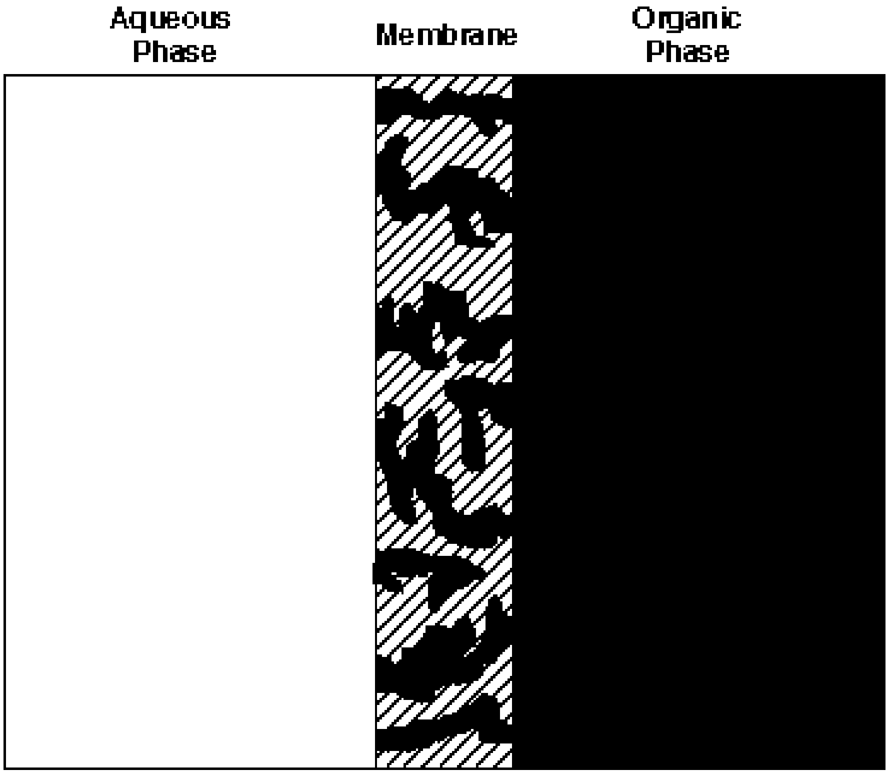

Fig. 1. Diagram of a porous hydrophobic membrane. The membrane provides a region of stable and intimate contact between the aqueous and organic phases where dispersion-free mass transfer can take place.

MHF modules possess a number of features that make them an attractive technology for LLE processes.[3-5] The small size of the hollow fibers permits a design that achieves a very high interfacial area in a given volume, which helps to minimize the size of the LLE process. Extractions and back-extractions are conducted in a dispersion-free fashion, thus avoiding phase coalescence problems commonly found in other technologies. There is no need to have a difference in aqueous and organic phase densities, allowing for a wider array of organic systems to be taken into consideration. The aqueous/organic phase ratios can be easily varied over a wide range by merely adjusting the flow rates. The modular nature of the units makes it easy to accurately scale up experimental results to process applications and to engineer any multiple module configuration that would optimize the process. Finally, the modules are inexpensive (capital costs are low); they have no moving parts (maintenance costs are low); and once running, they require little supervision, monitoring, or external control (operational costs are low).

The purpose of this research is to evaluate the potential for using MHF modules for the processing of radioactive wastes. This is to be accomplished by analyzing the extraction and back-extraction capabilities of the modules for different organic systems over a range of aqueous and organic flow rates.

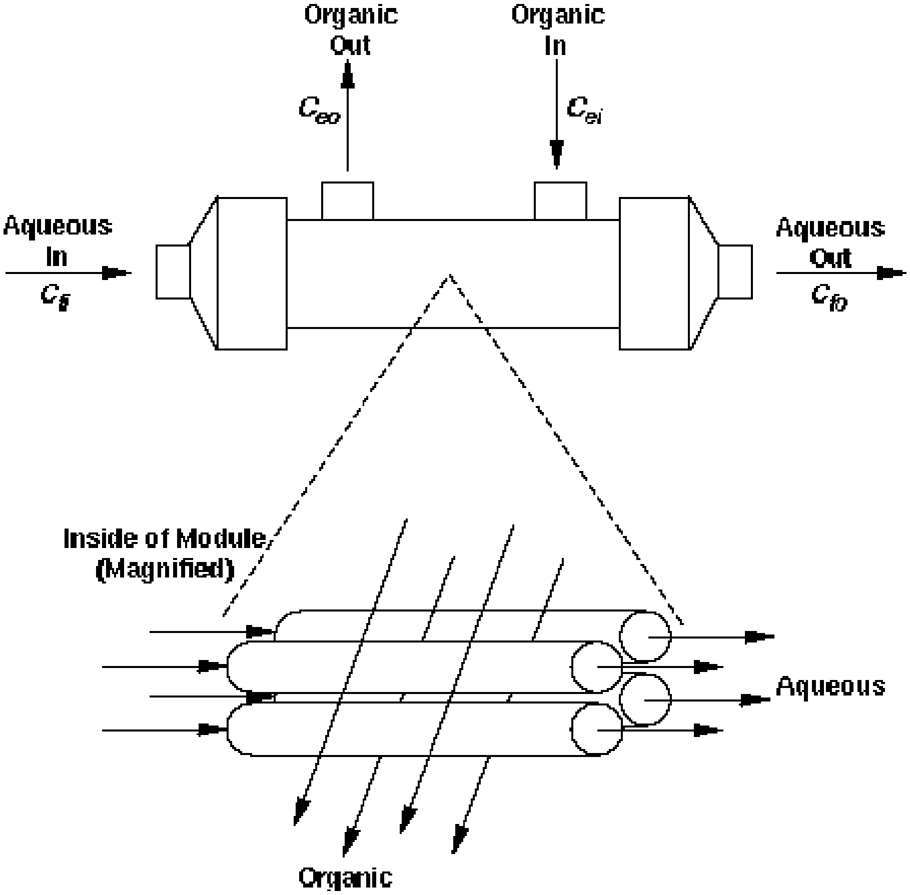

Fig. 2. Diagram of an MHF module. The design achieves a high interfacial surface area per unit volume and allows the aqueous and organic phases to contact in a continuous-flow fashion. C_{fi} and C_{fo} are the respective solute concentrations in the aqueous feed and effluent, and C_{ei} and C_{eo} are the respective solute concentrations in the organic feed and effluent.

The results are used to determine the number of modules required to achieve one theoretical extraction stage, and to provide valuable insights as to how this technology can be improved and optimized for process-scale applications.

In this work, MHF modules are used to extract neodymium from an aqueous 2 *M* nitric acid stream and to concentrate the neodymium into a different aqueous stream by back-extracting it into 0.01 *M* nitric acid. Although neodymium is not radioactive, its behavior is similar to that of trivalent americium (a long-lived actinide) and thus serves as a surrogate for this evaluation. DHDECMP (dihexyl N,N-diethylcarbamoylmethylphosphonate) and CMPO [n-octyl(phenyl)N,N-diisobutylcarbamoylmethylphosphine oxide] are the organic phase extractants used in this study. These two extractants are chosen for their ability to extract neodymium at modest acid concentrations (2 *M* nitric acid) and for their high selectivity for actinides over fission products. Each of these extractants removes trivalent metal ions from the aqueous phase by forming a complex as shown in Fig. 3. The reverse reaction occurs during the back-extraction process. Additional information about these extractants is available in the literature.[6-9]

Fig. 3. The complexation of neodymium with CMPO. Three extractant molecules are required to complex each neodymium ion.

$$\underbrace{Nd^{3+} + 3NO_3^-}_{\substack{\text{Neodymium Nitrate}\\\text{(Aqueous Phase)}}} + \underbrace{3CMPO}_{\text{Extractant}} \rightleftharpoons \underbrace{Nd(NO_3)_3 \cdot 3CMPO}_{\substack{\text{Neodymium Complex}\\\text{(Organic Phase)}}}$$

Theory and Definitions

General Equations

The MHF module illustrated in Fig. 2 permits a continuous-flow countercurrent extraction (or back-extraction). The rate at which the solute is transferred from the aqueous phase to the organic phase can be determined by conducting a material balance around the aqueous stream. Doing so yields

$$\dot{M} = Q_{aq}\left(C_{fi} - C_{fo}\right) , \qquad (1)$$

where $\dot{M}$ is the rate of mass transfer from the aqueous to the organic phase, Q_{aq} is the aqueous flow rate, and C_{fi} and C_{fo} are the respective solute concentrations in the aqueous feed and effluent. The rate of mass transfer can also be determined by conducting a material balance around the organic stream. This approach yields

$$\dot{M} = Q_{or}\left(C_{eo} - C_{ei}\right) , \qquad (2)$$

where Q_{or} is the organic flow rate, and C_{ei} and C_{eo} are the respective solute concentrations in the organic feed and effluent. An additional way to characterize the rate of mass transfer is in terms of an overall mass transfer coefficient. For an extraction in which the aqueous phase is flowing through the inside of fibers fabricated from a hydrophobic membrane material, this rate is expressed as

$$\dot{M} = K_w A_i \Delta C_{lm} \quad , \qquad (3)$$

where K_w is the overall mass transfer coefficient of the module based on the aqueous phase, A_i is the total membrane surface area of the module based on the internal fiber diameter, and ΔC_{lm} is the logarithmic mean concentration difference given by

$$\Delta C_{lm} = \frac{\Delta C_1 - \Delta C_2}{\ln\left(\Delta C_1 / \Delta C_2\right)} . \qquad (4)$$

ΔC_1 is the driving force for mass transfer at the aqueous inlet and is equal to the solute concentration in the aqueous feed minus the interfacial aqueous phase solute concentration at the aqueous inlet:

$$\Delta C_1 = C_{fi} - C_{fi}^{\text{interface}} \quad . \qquad (5)$$

Determining $C_{fi}^{\text{interface}}$ is far from trivial, and its value is commonly approximated as the concentration that is in equilibrium with the solute concentration in the organic effluent. This is expressed as

$$C_{fi}^{\text{interface}} \qquad \frac{C_{eo}}{m} \quad , \qquad (6)$$

where m is the distribution coefficient defined as

$$m = \left(\frac{\begin{matrix}\text{solute concentration} \\ \text{in organic phase}\end{matrix}}{\begin{matrix}\text{solute concentration} \\ \text{in aqueous phase}\end{matrix}} \right)_{\text{equilibrium}} . \qquad (7)$$

Equation 5 can thus be expressed as

$$\Delta C_1 = C_{fi} - \frac{C_{eo}}{m} \quad . \qquad (8)$$

ΔC_2 is the driving force for mass transfer at the aqueous outlet and (in a manner consistent with the determination of ΔC_1) is expressed as

$$\Delta C_2 = C_{fo} - \frac{C_{ei}}{m} \quad . \qquad (9)$$

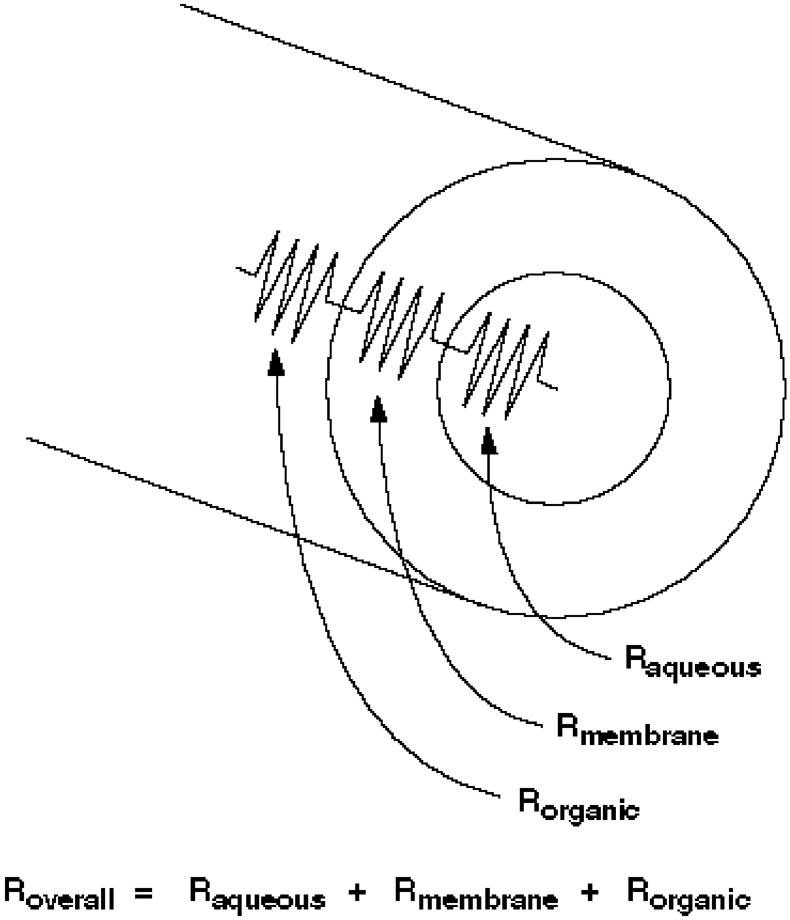

Fig. 4. Resistances to mass transfer in the extraction and back-extraction processes.

A more comprehensive development of the general equations that characterize two-phase countercurrent flow extraction and back-extraction processes can be found in Bennett.[10]

Resistances to Mass Transfer

Mass transfer of a solute through a porous hydrophobic membrane occurs in three fundamental steps. First, the solute travels through the aqueous phase to the aqueous/organic interface where complexation takes place. Second, the solute complex diffuses through the membrane pore. Third, the solute complex travels through the organic medium. Expressing Equation 3 as

$$\dot{M} = \frac{\Delta C_{lm}}{1/\left(K_w A_i\right)} \qquad (10)$$

shows that the rate of mass transfer is equal to a driving force term, ΔC_{lm}, divided by a resistance term, $1/K_w A_i$. The latter term incorporates the individual resistances to mass transfer existing in each of the three fundamental steps and i s thus referred to as the overall resistance to mass transfer. These resistances are illustrated in Fig. 4. Equations provided by Prasad[3,4] and Sirkar[3-5] make it possible to quantify these resistances.

For modules fabricated with hydrophobic membrane fibers and assembled for tube side aqueous flow and shell side organic flow, these resistances can be expressed as

$$\underset{\substack{\uparrow\\ \text{Overall}\\ \text{Resistance}}}{\frac{1}{K_w A_i}} = \underset{\substack{\uparrow\\ \text{Aqueous}\\ \text{(Tube Side)}\\ \text{Resistance}}}{\frac{1}{k_{wt} A_i}} + \underset{\substack{\uparrow\\ \text{Membrane}\\ \text{Resistance}}}{\frac{d_i \ln\left(d_o / d_i\right)}{2 \ mD_{c,or} A_i}} + \underset{\substack{\uparrow\\ \text{Organic}\\ \text{(Shell Side)}\\ \text{Resistance}}}{\frac{d_i}{d_o m k_{os} A_i}} \quad . \qquad (11)$$

In this equation, k_{wt} is the mass transfer coefficient of the solute in the aqueous phase inside the fibers, k_{os} is the mass transfer coefficient of the solute complex in the organic phase outside the fibers, d_i is the internal diameter of the fiber, d_o is the outer diameter of the fiber, $D_{c,or}$ is the diffusion coefficient of the solute complex in the organic,   is the membrane porosity, and   is the tortuosity of the membrane pores. Although Equation 11 is presented here in terms of the extraction process, its applicability is equally valid for the back-extraction process as well.

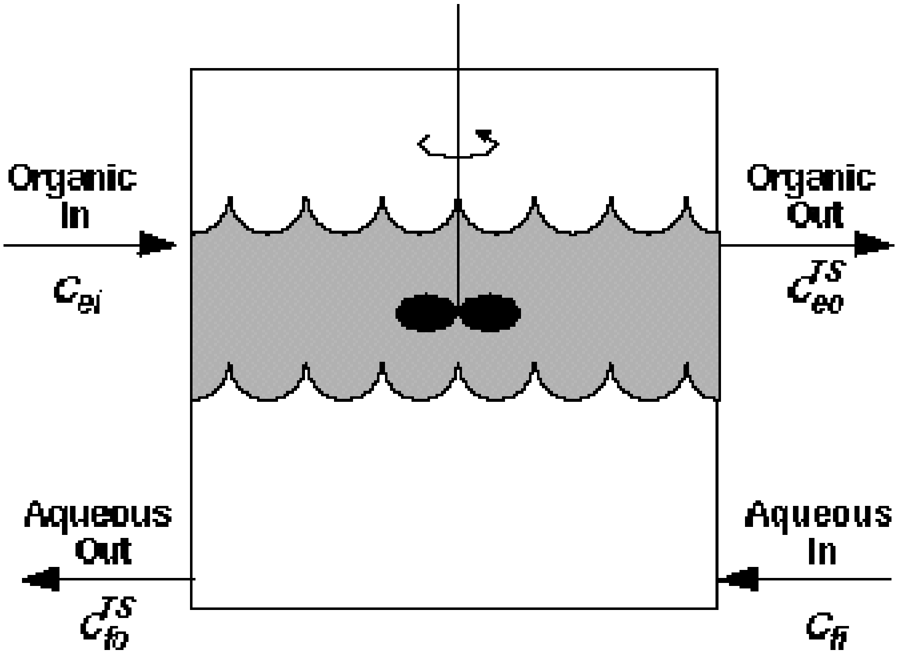

Fig. 5. An ideal theoretical stage in a continuous-flow LLE process. C_{fi} and C_{ei} are the respective solute concentrations in the aqueous and organic feed streams entering the theoretical stage, and C^{TS}_{fo} and C^{TS}_{eo} are the respective solute concentrations in the aqueous and organic effluent streams leaving the theoretical stage.

Number of Modules per Theoretical Stage

A theoretical stage in an LLE process is one that first allows mass transfer between the aqueous and the organic phases to reach equilibrium and then allows complete (i.e., dispersion-free) separation of the two phases to occur before they exit the process. A theoretical stage with continuous aqueous and organic flow is illustrated in Fig. 5. The rate at which solute is transferred from the aqueous to the organic phase can be determined by conducting a material balance around the aqueous stream. Doing so yields

$$\dot{M}^{TS} = Q_{aq}\left(C_{fi} - C^{TS}_{fo}\right) , \qquad (12)$$

where $\dot{M}^{TS}$ is the rate of mass transfer from the aqueous to the organic phase in the theoretical stage, and C^{TS}_{fo} is the solute concentration in the aqueous effluent leaving the theoretical stage. Conducting a material balance around the organic stream yields

$$\dot{M}^{TS} = Q_{or}\left(C^{TS}_{eo} - C_{ei}\right) , \qquad (13)$$

where C^{TS}_{eo} is the solute concentration in the organic effluent leaving the theoretical stage.

Equations 12 and 13 can be used with the distribution coefficient equation, $m = C_{eo}^{TS} / C_{fo}^{TS}$, to solve for C_{fo}^{TS} and C_{eo}^{TS} as a function of inlet concentrations and flow rates. Doing so yields

$$C_{fo}^{TS} = \frac{Q_{aq}C_{fi} + Q_{or}C_{ei}}{Q_{aq} + mQ_{or}} \tag{14}$$

and

$$C_{eo}^{TS} = \frac{Q_{aq}C_{fi} + Q_{or}C_{ei}}{Q_{aq}/m + Q_{or}} \quad . \tag{15}$$

For a number of modules connected in series that provide the total membrane surface area required for a theoretical stage, the rate at which mass transfer occurs is

$$\dot{M}^{TS} = K_w A_i^{TS} \Delta C_{lm}^{TS} \quad , \tag{16}$$

where A_i^{TS} is the total membrane surface area of these modules based on the internal fiber diameter and ΔC_{lm}^{TS} is the logarithmic mean concentration difference in a theoretical stage. The latter term is given by

$$\Delta C_{lm}^{TS} = \frac{\Delta C_1^{TS} - \Delta C_2^{TS}}{\ln\left(\Delta C_1^{TS} / \Delta C_2^{TS}\right)} \quad , \tag{17}$$

where

$$\Delta C_1^{TS} = C_{fi} - \frac{C_{eo}^{TS}}{m} \tag{18}$$

and

$$\Delta C_2^{TS} = C_{fo}^{TS} - \frac{C_{ei}}{m} \quad . \tag{19}$$

Dividing Equation 16 by Equation 3 yields

$$\frac{\dot{M}^{TS}}{\dot{M}} = \frac{A_i^{TS}}{A_i} \frac{\Delta C_{lm}^{TS}}{\Delta C_{lm}} \quad . \tag{20}$$

Substituting Equation 12 for $\dot{M}^{TS}$ and Equation 1 for $\dot{M}$, and solving for A_i^{TS} / A_i yields

$$N^{TS} = \frac{A_i^{TS}}{A_i} = \left(\frac{C_{fi} - C_{fo}^{TS}}{C_{fi} - C_{fo}}\right) \frac{\Delta C_{lm}}{\Delta C_{lm}^{TS}} \quad . \tag{21}$$

where N^{TS} is the number of modules required for a theoretical stage.

Experimental Details

Preparation of Aqueous and Organic Solutions

Three different organic systems are considered in this analysis: 0.25 *M* CMPO in DIPB, 0.81 *M* DHDECMP in DIPB, and 0.25 *M* DHDECMP in DIPB. A total of 5 L of organic solution is prepared for each extraction (or back-extraction) experiment. Additional information about these chemicals is provided in Table I.

Table I. Extractants and Solvent used to Make the Different Organic Systems

Extractant #1:		
	Chemical	dihexyl N, N-diethylcarbamoylmethyl phosphonate
	Abbreviation	DHDECMP
	Supplier	Occidental Chemical Corporation
Extractant #2:		
	Chemical	n-octyl (phenyl)-N, N-diisobutylcarbamoylmethylphosphine oxide
	Abbreviation	CMPO
	Supplier	M&T Chemicals, Inc.
Solvent:		
	Chemical	diisopropylbenzene, 98% (approximately 50% meta, 40% para, and 10% ortho)
	Abbreviation	DIPB
	Supplier	Eastman Laboratory Chemicals

The aqueous solution for the extraction experiments is prepared by dissolving 2.5 g of neodymium nitrate hexahydrate in 5 L of 2 *M* nitric acid resulting in a neodymium concentration of 166 mg/L. The organic solution is prepared by equilibrating it against an equal volume of 2 *M* nitric acid. This equilibration prevents nitric acid mass transfer from affecting the neodymium extraction process.

The aqueous solution for the back-extraction experiments is prepared by making 5 L of 0.01 *M* nitric acid. The organic solution is first equilibrated against an equal volume of 0.01 *M* nitric acid and is then added to 15 g of neodymium nitrate hexahydrate, resulting in a neodymium concentration of 996 mg/L. The organic is later decanted from the trace water liberated during the dissolution process.

Extraction and Back-Extraction Experiments

The experiments are conducted using the Hoechst Celanese Liqui-Cel Laboratory LLE System. The MHF modules subject to analysis are Hoechst Celanese Liqui-Cel High Efficiency Phase Contactors. These modules are small laboratory-scale versions that are specifically designed for experimental purposes. Their small size makes it possible to evaluate the performance of the technology without having to prepare large amounts of aqueous and organic feed solutions. Additional information about the Hoechst Celanese Liqui-Cel module is provided in Table II.

A schematic of the experimental setup is illustrated in Fig. 6. In the experiment, the aqueous feed is pumped through the tube side of the MHF module where it comes in contact with the organic feed and neodymium mass transfer takes place. Upon exiting the module, the aqueous stream is passed through a flowmeter and then through a flow cell present in a diode array spectrophotometer programmed for continuous, on-line neodymium concentration measurement. The stream is then collected in the aqueous effluent reservoir. The organic feed is pumped through the shell side of the module, is passed through a flowmeter, and is ultimately collected in the organic effluent reservoir. Valves and pressure gauges are present to control the flow rates and to ensure that a positive pressure of approximately 5 psig is maintained on the aqueous side of the membrane.

Table II: Characteristics of Hoechst Celanese Liqui-Cel MHF Module

Model No.:	5PCM-100
Description:	High Efficiency Phase Contactor
Shell Characteristics:	
Material	polypropylene
Length	20.3 cm
Internal Diameter	2.43 cm
Outer Diameter	3.34 cm
Fiber Characteristics:	
Material	polypropylene (Celgard X-10)
Number of Fibers	3600
Effective Length	15.9 cm
Internal Diameter	240 mm
Outer Diameter	300 mm
Effective Surface Area	4300 cm^2
Effective Pore Size	0.05 μm
Membrane Porosity	0.30
Membrane Tortuosity	2.6

During the first half of each experiment, the organic flow rate is held constant at 5 mL / minute, and the performance of the module is observed over a range of aqueous flow rates. For the second half, the aqueous flow rate is held constant at 8 mL / minute, and the module's performance is observed over a range of organic flow rates. After a particular aqueous flow rate and organic flow rate are established, a period of time must elapse for the system to reach steady state. This point is determined when the aqueous effluent neodymium concentration (measured as spectrophotometric absorbance at 578 nm) becomes constant with respect to time. At this point, 5 mL of the aqueous effluent is removed from the sample port with a syringe and is placed in a 20-mL screw-cap scintillation vial for subsequent determination of its neodymium concentration. To ensure repeatability, three 5-mL samples are taken at each steady state.

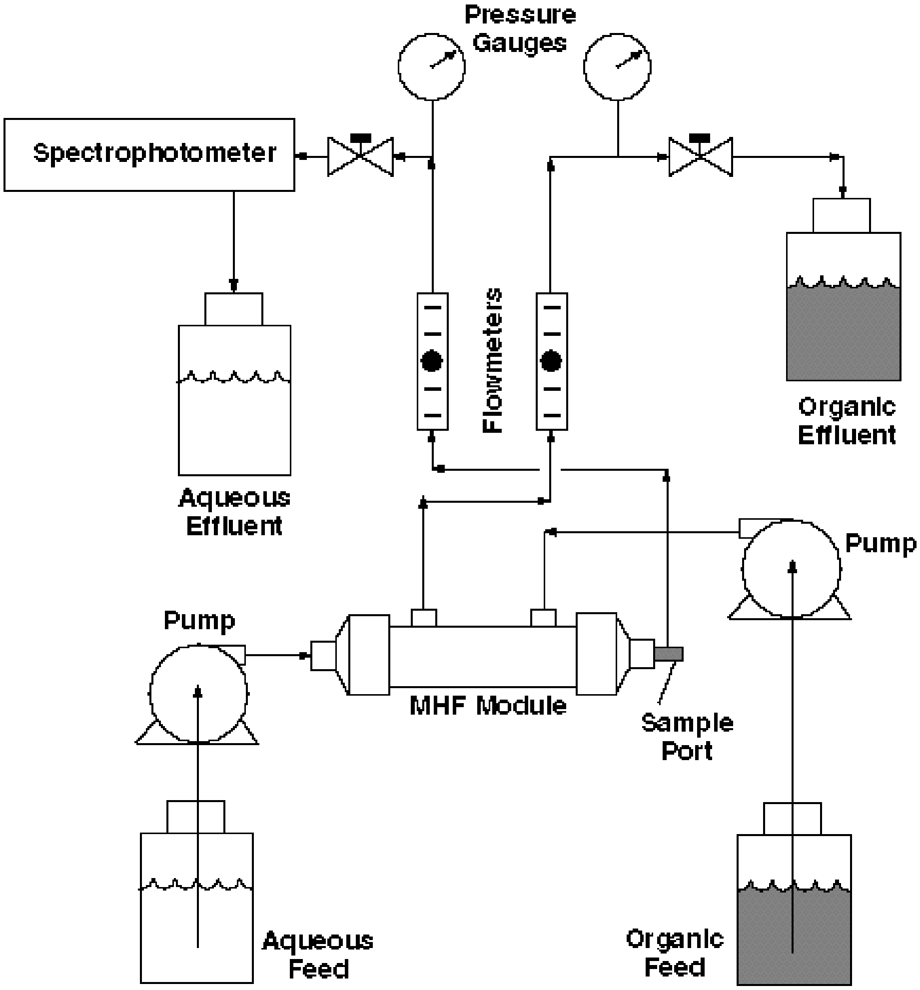

Fig. 6. Experimental setup used to evaluate the extraction and back-extraction capabilities of the MHF modules.

Evaluation of Distribution Coefficients

The distribution coefficients are determined by using small amounts of the aqueous and organic feed solutions prepared for the extraction and back-extraction experiments. In this determination, 10 mL of the aqueous solution and 10 mL of the organic solution are placed in a 20-mL screw-cap scintillation vial and are thoroughly mixed for one minute using a vortexer. The mixture is then allowed to sit for two days to ensure that complete phase separation has taken place. Using a syringe, 5 mL of the aqueous fraction is removed and is placed in a new screw-cap scintillation vial for subsequent determination of its neodymium concentration. Four distribution coefficient determinations are conducted for each aqueous/organic system.

Neodymium Concentration Determination

Each extraction (or back-extraction) experiment generates more than 36 aqueous samples of unknown neodymium concentration. Because the absorbance peak for neodymium (exhibited at 578 nm) is very weak, an acceptably precise determination of its concentration in these samples is not feasible by direct spectrophotometric measurement. However, neodymium does form a complex with arsenazo III that exhibits a strong absorbance peak at 655 nm.[11] Taking advantage of this, the unknown concentrations can be accurately determined.

In this approach, 0.1 g/L of arsenazo III is added to a buffer solution of 1 *M* glacial acetic acid and 0.5 *M* sodium acetate. A 10-mL aliquot of this solution is placed in a 20-mL screw-cap scintillation vial followed by 500 μL of the aqueous sample of unknown neodymium concentration. The resulting solution is thoroughly mixed for one minute using a vortexer and is allowed to sit for one day to ensure that complexation has reached equilibrium. The absorbance at 655 nm is then measured with the spectrophotometer. The neodymium concentration of each unknown is determined by comparing its measured absorbance with those obtained from a series of calibration standards.

Table III. Distribution Coefficients of Neodymium for Three Different Organic Systems

Organic System	Distribution Coefficient for Extraction (2 *M* HNO_3)	Distribution Coefficient for Back-Extraction (0.01 *M* HNO_3)
0.25 *M* CMPO in DIPB	8.8	3.2×10^{-2}
0.81 *M* DHDECMP in DIPB	3.6	1.3×10^{-3}
0.25 *M* DHDECMP in DIPB	0.25	5.8×10^{-5}

Results and Discussion

All extractions and back-extractions conducted with the MHF modules were clean, easy to run, and absolutely dispersion-free. No measurable loss of organic was detected during any of the experiments.

The distribution coefficients for the different organic systems are shown in Table III. A superior organic system for extraction is one in which the solute preferentially dissolves in the organic phase and thus exhibits a large distribution coefficient. From the organic systems considered, the best for this purpose is the 0.25 *M* CMPO in DIPB, next is the 0.81 *M* DHDECMP in DIPB, and last is the 0.25 *M* DHDECMP in DIPB. An organic system best suited for back-extraction is one in which the solute preferentially dissolves in the aqueous phase and thus exhibits a small distribution coefficient. The best system for this purpose is the 0.25 *M* DHDECMP in DIPB, next is the 0.81 *M* DHDECMP in DIPB, and last is the 0.25 *M* CMPO in DIPB. Under the conditions used, the organic system with the greatest affinity to remove neodymium during the extraction process is also the one least inclined to liberate the neodymium during the back-extraction process.

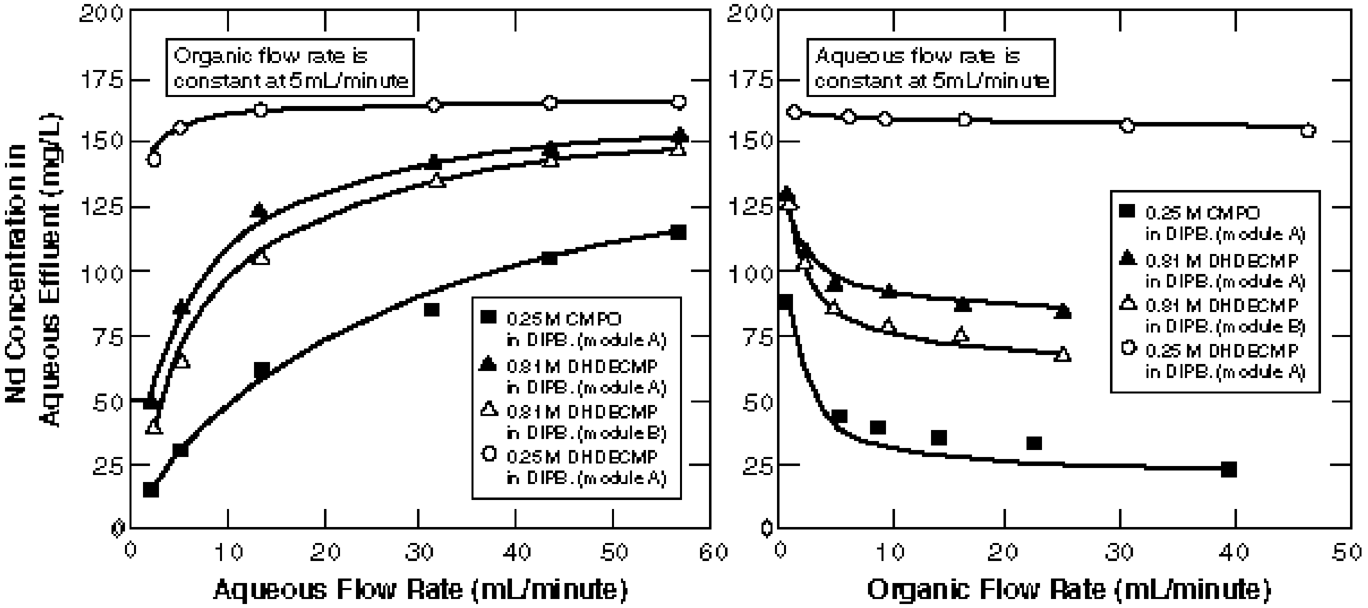

Fig. 7. Extraction of neodymium from 2 M nitric acid. Neodymium concentration in aqueous effluent is shown as a function of aqueous flow rate (left) and as a function of organic flow rate (right) for the different organic systems. Aqueous feed concentration is 166 mg/L.

The results of the extraction and back-extraction experiments are illustrated in Figs. 7 and 8. As shown in the graphs, low aqueous flow rates and high organic flow rates are best for extractions, whereas low organic flow rates and high aqueous flow rates are best for back-extractions. The low flow rates of the solute-laden streams (those from which the neodymium is to be removed) provide the high residence times necessary for substantial mass transfer to take place. In addition, the high flow rates of the solute removal streams (those that enter the process with no solute) maintain low concentrations of solute in those streams and thus maximize the concentration gradients for high mass transfer rates.

Figure 7 shows that an organic system with a larger distribution coefficient provides for a better extraction. This behavior can be explained by analyzing the individual resistances to the mass transfer process. As shown in Equation 11, the membrane resistance and the shell side resistance are both smaller for an organic system having a larger value of m. In addition, as shown in Equations 4 through 9, such a system also has a greater value of ΔC_{lm} – the driving force for the mass transfer process. These two factors (a decreased resistance and an increased driving force) increase the mass transfer rate and thus result in a superior extraction process.

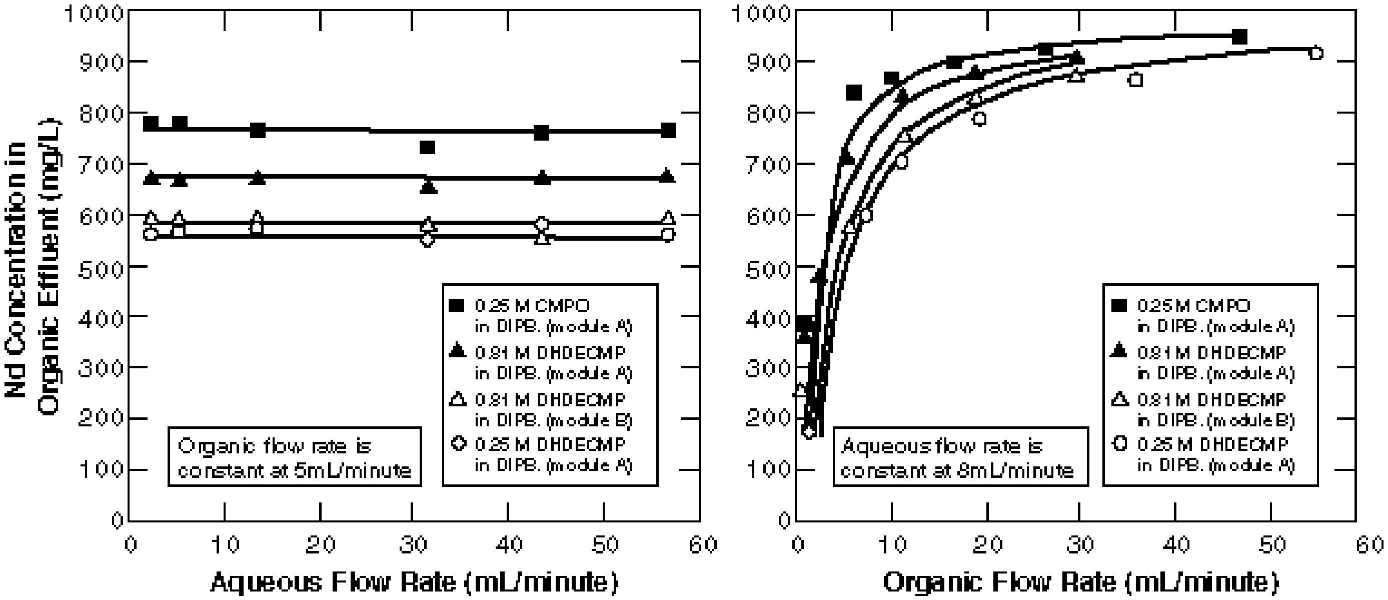

Fig. 8. Back-extraction of neodymium into 0.01 M nitric acid. Neodymium concentration in organic effluent is shown as a function of aqueous flow rate (left) and as a function of organic flow rate (right) for the different organic systems. Organic feed concentration is 996 mg/L.

As shown in Fig. 8, superior back-extractions are achieved with an organic system exhibiting a smaller distribution coefficient. Equation 11 shows that such a system does possess higher membrane and shell side resistances. However, the value of ΔC_{lm} (which is inherently negative for back-extraction processes) is more negative for smaller values of m and thus provides a stronger driving force for the back-extraction process. For the systems considered, the increased magnitude of this driving force is much greater than the increased resistance. As a result, the systems with smaller distribution coefficients exhibit higher mass transfer rates for the back-extraction processes.

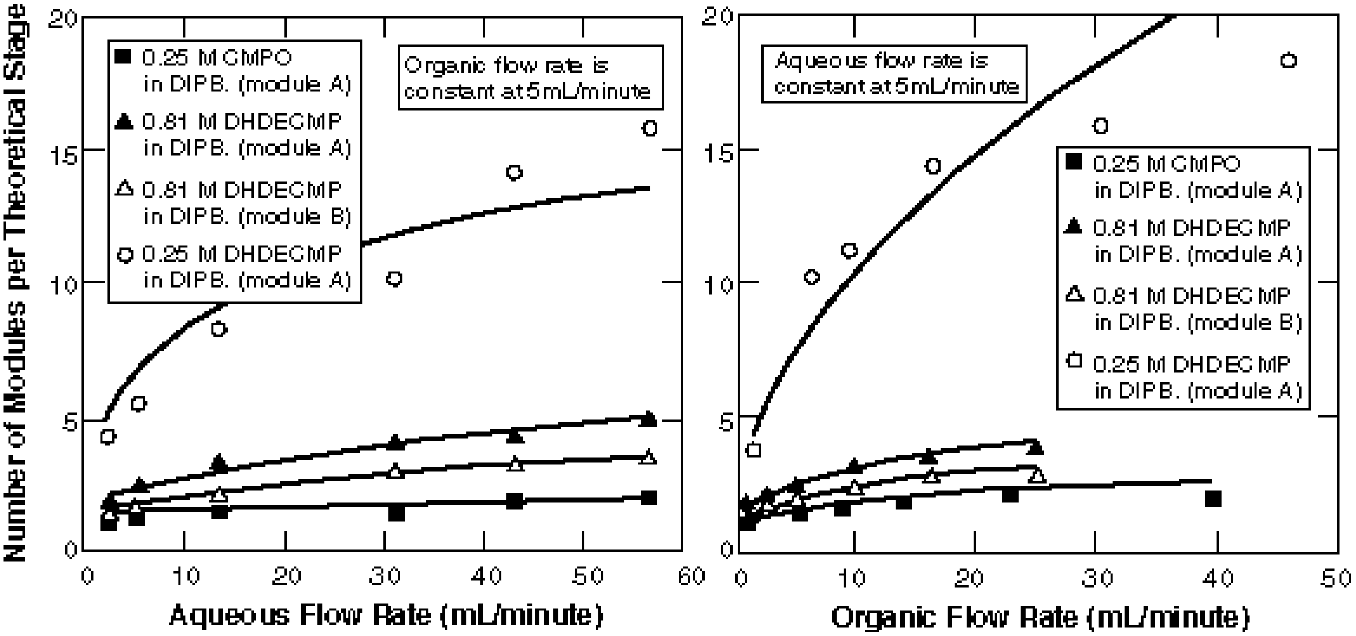

Fig. 9. Extraction of neodymium from 2 M nitric acid. The number of modules required for one theoretical stage is shown as a function of aqueous flow rate (left) and as a function of organic flow rate (right) for the different organic systems.

Experimental data are used with Equation 21 to determine the number of modules required for a theoretical stage. As shown in Figs. 9 and 10, this number increases with both aqueous and organic flow rates. Thus, longer aqueous and organic residence times are conducive to fewer modules.

For the two stronger extraction systems (the 0.25 *M* CMPO in DIPB and the 0.81 *M* DHDECMP in DIPB), between one and five modules are required for a theoretical stage. For the weaker system (the 0.25 *M* DHDECMP in DIPB), between five and twenty-five modules are required. This provides another reason for using a strong organic system for extraction. Not only does such a system remove more solute in a theoretical stage, but also fewer modules are required for that theoretical stage to be achieved.

Comparing Figs. 9 and 10 shows that for a given organic system, the number of modules required for back-extraction is much greater than that required for extraction. This large difference is due to the increased membrane resistance existing in the back-extraction process. From Equation 11, the ratio of these two resistances can be expressed as

$$\frac{\left(\begin{array}{c}\text{membrane resistance}\\ \text{for back-extraction}\end{array}\right)}{\left(\begin{array}{c}\text{membrane resistance}\\ \text{for extraction}\end{array}\right)} = \frac{m_{\text{extraction}}}{m_{\text{back-extraction}}} \quad . \qquad (22)$$

This ratio is between 200 and 4500 for the organic systems in this analysis. Suggestions on how this membrane resistance (and therefore the number of modules) can be reduced are provided in our conclusions.

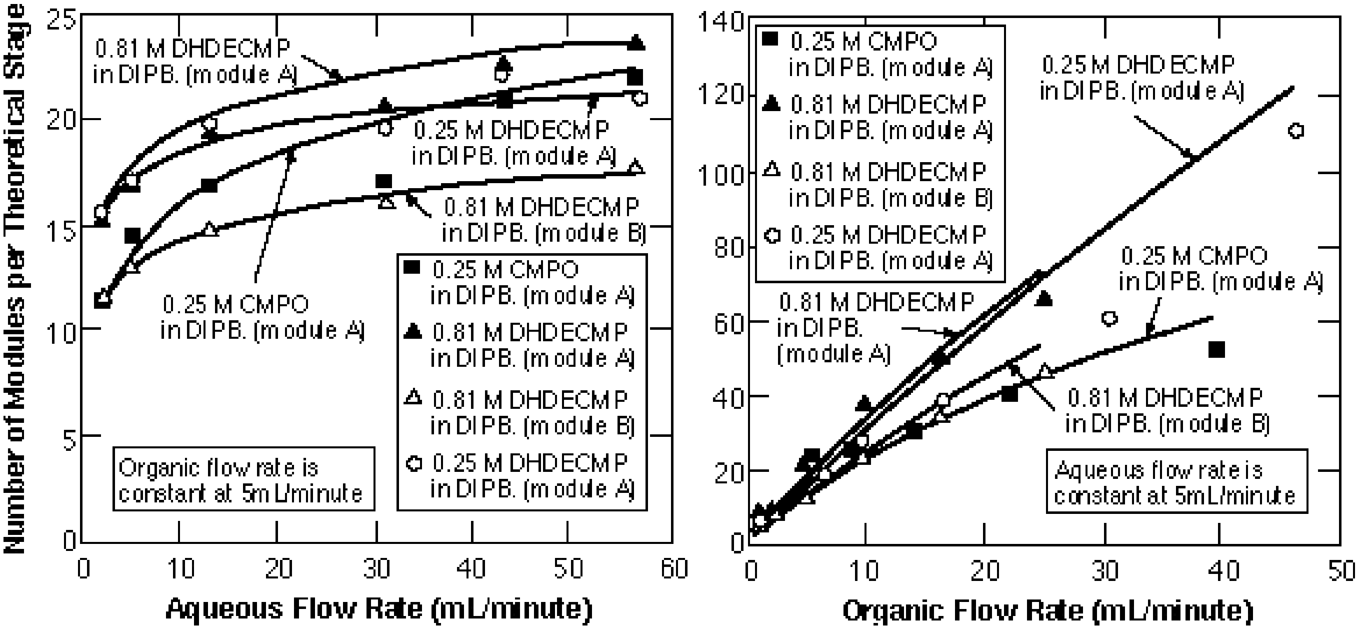

Fig. 10. Back-extraction of neodymium from 0.01 M nitric acid. The number of modules required for one theoretical stage is shown as a function of aqueous flow rate (left) and as a function of organic flow rate (right) for the different organic systems.

Conclusions

MHF modules provide a cost-effective and convenient means by which to conduct metal separations. But initial inspection of the experimental data seems to indicate that reasonable separations can be achieved only at flow rates that are much lower than those found in conventional, process-scale metal separation applications. But by modifying the number or type of modules, the organic extraction systems, or the membrane material, this technology can also perform well at the higher flow rates typically found in process-scale applications.

The modules used in this analysis are small laboratory-scale versions specifically designed for experimental purposes. In an actual process application, pilot-scale (or larger) modules can be used, each of which provides as much as 10 times the membrane surface area of a laboratory-scale version. Additional surface area can also be achieved by connecting a number of modules in series. These approaches would make it possible to conduct reasonable separations at the high flow rates normally found in process applications.

In addition, the modules for this analysis use an early version of a fiber bundle design that is not conducive to good shell side flow. According to Seibert,[12] this poor flow causes a significant portion of the fibers to be bypassed by the organic and keeps the surface area available for mass transfer from being fully utilized. Newer modules are now being produced with an advanced fiber mesh that allows the organic to flow more uniformly throughout the fiber bundle. A new shell side baffle technology has also been recently introduced that may significantly improve the module's performance.

The technology may also be improved by modifying the organic system. For extraction, this could be achieved by using a more powerful extractant or by using a higher concentration of the extractant in the organic phase. Such an approach would reduce the membrane resistance and would increase the concentration driving force for the mass transfer process. But there is a drawback to this approach. As mentioned in the previous section, an organic system that is more inclined to capture metals during the extraction process may be less inclined to liberate those metals during the back-extraction process. Comparison of Figs. 7 and 8 shows that this behavior is observed in our experimental results. Because a process-scale application of this technology would undoubtedly encompass both extraction and back-extraction, the performance of the organic system in both processes must be taken into consideration when choosing an improved organic system.

The performance of the modules may also be improved by changing the membrane from a hydrophobic to a hydrophilic material. In a hydrophilic membrane, the aqueous phase fills the pores, and the neodymium passes through the membrane in its ionic form. In a hydrophobic membrane (like the polypropylene membrane used in this analysis), the organic phase fills the pores, and the neodymium passes through the membrane in its complexed form (see Fig. 3). The diffusivity of neodymium through an aqueous phase is significantly greater than that of an inherently large and sterically hindered neodymium complex through a viscous organic phase. The greater diffusivity means less membrane resistance and results in a greater mass transfer rate. Changing the membrane material may also reduce the large number of modules presently required for a theoretical stage in the back-extraction process. As mentioned in the previous section, this comparably large number of modules is due to the small distribution coefficient (and thus large membrane resistance) found in the back-extraction process. Using a hydrophilic membrane would make the membrane resistance independent of the distribution coefficient and would significantly reduce the size of the process. Flat sheet hydrophilic membranes fabricated from polybenzimidazole have demonstrated good extraction capabilities for neodymium and copper[13] and are reputed to have significant acid and radiation stability. MHF modules made from this polymer may thus be potentially well-suited for the process applications of interest to nuclear facilities.❖

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Electrochemical Treatment of Mixed Hazardous Waste

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and Aaron L. Swanson
Nuclear Materials Processing:
Nitrate Systems

Introduction

Strong oxidizing agents such as Ag(II) or Co(III) ion can be generated electrochemically in nitric acid (HNO_3) at the anode of a divided cell. These species are capable of oxidizing insoluble actinide oxides to the more soluble higher oxidation state and are being investigated as a method to recover actinides from various scrap matrices.[1] The electrogenerated oxidants are also capable of oxidizing various organic molecules to carbon dioxide and water and thus can serve as a potential alternative to the treatment of mixed wastes by incineration.[2-5]

In the treatment process, the substrate of interest is added directly to the anolyte where the catalyst is generated at a fixed rate by constant current electrolysis. The Ag(II) or Co(III) ion that is formed oxidizes the organic substrate and is itself reduced back to Ag(I) or Co(II). These ions migrate back to the anode surface where the oxidizing agents are regenerated and the cycle is repeated. Once the organic component of the waste is destroyed, the radioactive component may be recovered by standard actinide recovery techniques.

"The most basic conclusion of direct oxidation research is that each class of organics reacts differently to a given set of oxidation conditions; indeed, some types resist oxidation altogether."

Much is known about the electrochemical behavior of many organics in broad areas such as electrosynthesis, reaction mechanisms, and kinetics. Extensive research has focused on the direct electrochemical oxidation of organics, especially methanol oxidation because of its importance in fuel-cell technology.[6] The most basic conclusion of direct oxidation research is that each class of organics reacts differently to a given set of oxidation conditions; indeed, some types resist oxidation altogether. [7]

These unique reactions to oxidation have led us to study the mediated electrochemical oxidation (MEO) of several classes of organics, beginning with isopropanol. Isopropanol is a commonly used organic solvent and has some probability of appearing in a mixed waste. It also has only three carbon atoms, which limits the number of possible intermediates that may be formed in the course of oxidation to carbon dioxide. This molecular structure should make it easier to measure the mechanistic pathway and produce some insight into the overall oxidation process of alcohols in general. However, the complete conversion of isopropanol to carbon dioxide and water involves the transfer of 18 electrons :

$$(CH_3)_2CHOH - 18\ e^- + 5\ H_2O \longrightarrow 3\ CO_2 + 18\ H^+ . \qquad (1)$$

Thus, considerable complexity still characterizes the oxidation of this relatively "simple" molecule.

MEO is a two-step process, the heterogeneous electrochemical generation of the catalyst at the electrode surface and the homogeneous reaction between the catalyst and the organic substrate. In order to obtain a clearer understanding of the overall reaction, we have attempted to study these reaction components individually. Specifically, we investigated the effect of several critical reaction parameters, such as current density, anolyte temperature, acid concentration, and cell separator type, on the efficiency of catalyst generation in the absence of an organic substrate. We then repeated those experiments with the isopropanol present, looking at the effect of these variables on the catalyzed destruction of the organic compound. Finally, we investigated the direct electrochemical oxidation of isopropanol in the absence of an electron transfer catalyst.

Catalyst Generation

The first step in the catalytic oxidation of organics is electrochemical generation of the catalyst at the anode of a divided electrochemical cell. Typically, the kinetics and mechanism of these oxidation processes would be studied using a small area electrode and modern electrochemical techniques, such as cyclic voltammetry, rotating ring-disc voltammetry, etc. However, utilizing these techniques usually requires a fairly clean system in which the electron transfer process of interest is far removed from other redox processes in solution. Unfortunately, both the Ag(I) to Ag(II) and Co(II) to Co(III) oxidations occur at the anodic solvent oxidation limit so that neither gives a well-resolved voltammetric response.

To study the efficiency of catalyst generation, we then had to use a combined electrochemistry-spectroscopy method in which a constant current density is applied to the anode to carry out the oxidation reaction, and the amount of the catalyst generated is monitored by measuring the amount of light absorbed at the wavelength maximum of the oxidized species. Measurement of the catalyst concentration was accomplished by using a flow-through cell in the spectrophotometer and pumping the solution from the electrochemical cell.

All of the measurements made on the two catalyst systems were carried out in 6 *M* HNO_3. When we attempted to do the electrolyses at lower solution acidities, the catalysts formed insoluble oxide salts at the electrode surface and fell to the bottom of the reaction cell.

As seen in Figs. 1 and 2, the efficiency for generation of both Ag(II) and Co(III) decreases with increasing current density. The oxidation potential of Ag(I) is slightly less positive than the solvent itself, whereas the oxidation potential of Co(II) is slightly more positive than the solvent. Therefore, the generation of Co(III) is impossible without simultaneous oxidation of the solvent, whereas there is a small potential range in which Ag(II) may be generated without oxidation of the solvent. In either case, increasing the current density does result in increasing the fraction of the current going toward the solvent oxidation process, decreasing the overall current efficiency of catalyst generation.

The effect of temperature on current efficiency was determined by performing the electrolysis at a fixed current density but at three separate temperatures: 20, 35, and 50 °C. As the temperature was increased, the generation of both Ag(II) and Co(III) decreased, although this effect was more pronounced for Ag(II). Both catalysts have limited lifetimes in aqueous solution because of their ability to oxidize water with subsequent reduction back to the original oxidation state. As the temperature is increased, these parasitic reactions proceed at a faster rate so that the steady state concentration of the catalyst appears to decrease, even though the rate of generation remains essentially constant.

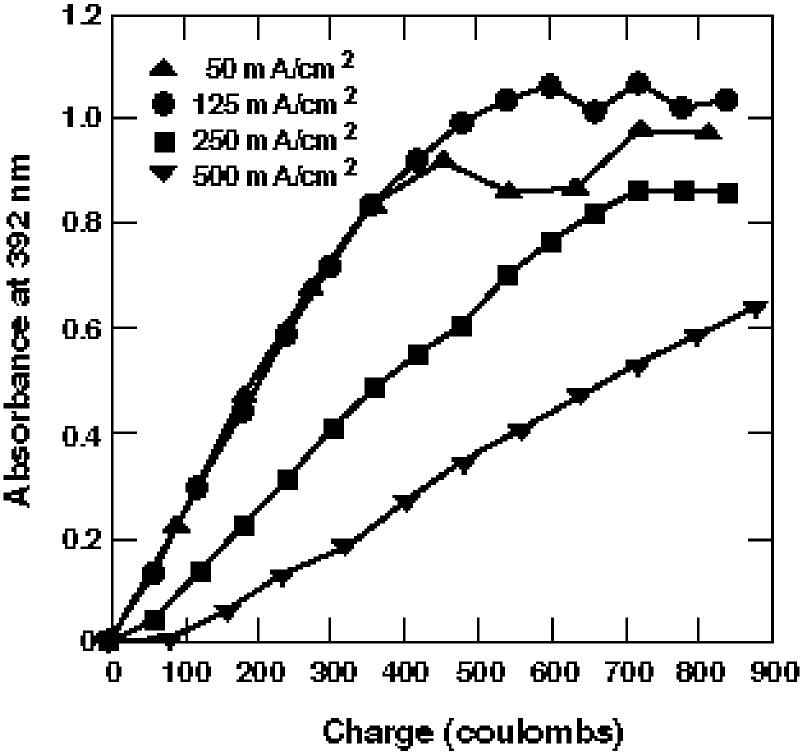


Fig. 1. Effect of current density on Ag(II) generation in 6 M HNO_3.

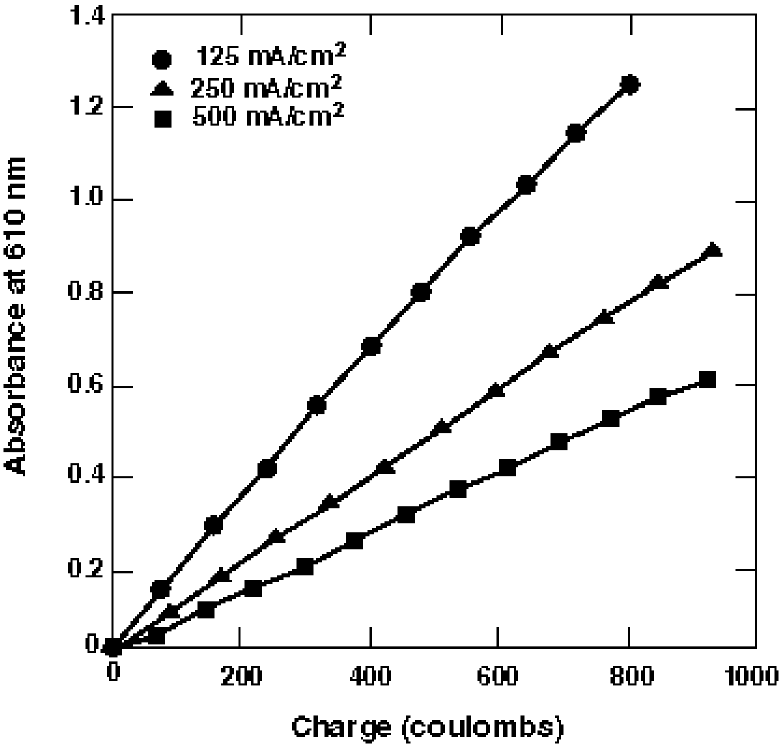


Fig. 2. Effect of current density on Co(III) generation in 6 M HNO_3.

Carrying out this reaction in a divided electrochemical cell is necessary to prevent the material that is oxidized at the anode from being re-reduced at the cathode. Typically, a ceramic frit, glass frit, or ion exchange membrane is used to separate the two cell compartments. We have found that a ceramic frit separator gives a higher catalyst yield than either a Nafion 117 or Nafion 324 cation exchange membrane.

The most likely explanation for this observation is charge balance within the cell. During electrolysis, positive charge builds up in the anolyte while negative charge accumulates in the catholyte. With a ceramic frit, this charge imbalance is alleviated by the movement of positively charged ions from the anolyte to catholyte and negatively charged ions from catholyte to anolyte. All ions in solution will cross the barrier at rates proportional to their ionic mobility and concentration. Protons that are highly mobile and in high concentration will carry the greatest fraction of the current in moving to the catholyte, while the remainder will be carried by the movement of nitrate ions to the anolyte. The movement of catalyst ions across the membrane will be minimal.

With a cation exchange membrane, alleviation of charge imbalance is restricted to the movement of cations. Therefore, all of the current will be carried by cation migration from anolyte to catholyte. Whereas protons will continue to be the primary charge carrier, an increasing fraction of the current will be carried by catalyst ion migration. This process is readily observed when cobalt is used as the catalyst. With a frit in place as a separator, no cobalt enters the catholyte. When a cation exchange membrane is used, the catholyte quickly becomes pink, the characteristic color of Co(II) in HNO_3 solution.

To summarize, the efficiencies of both Ag(II) and Co(III) generation are improved by use of low current density, low temperature, a ceramic frit rather than a cation exchange membrane separator, and in highly acidic media.

Isopropanol Oxidation

Electrochemical oxidation of isopropanol in a well-stirred solution was carried out at fixed current density at a platinum anode. Products and intermediates of the reaction were monitored by extracting a small sample of the anolyte during the run and injecting this sample directly into a gas chromatograph (GC).

Because HNO_3 is itself an oxidizer, we first determined if solvent oxidation of the organic substrate was contributing to the electrochemical oxidation process. A small amount of isopropanol was mixed with 6 *M* HNO_3, and the solution was stirred for several hours. Samples for GC analysis were taken every half-hour from this solution. The fact that there was no change in isopropanol concentration and no evidence of other substances forming during the time period suggested that isopropanol is not attacked by HNO_3.

Under an applied constant current with no catalyst present, isopropanol was oxidized very quickly and efficiently to acetic acid (Fig. 3). The GC analysis clearly showed an initial buildup of acetone, the two-electron oxidation product, followed by a decrease in acetone concentration when acetic acid, the four-electron oxidation product, began to appear. Evidence also existed for the formation of formic acid and formaldehyde in the reaction mixture. However, the reaction appeared to stop with the formation of acetic acid, which occurred when approximately 10 equivalents of electrons per mole of isopropanol had been removed from the solution.

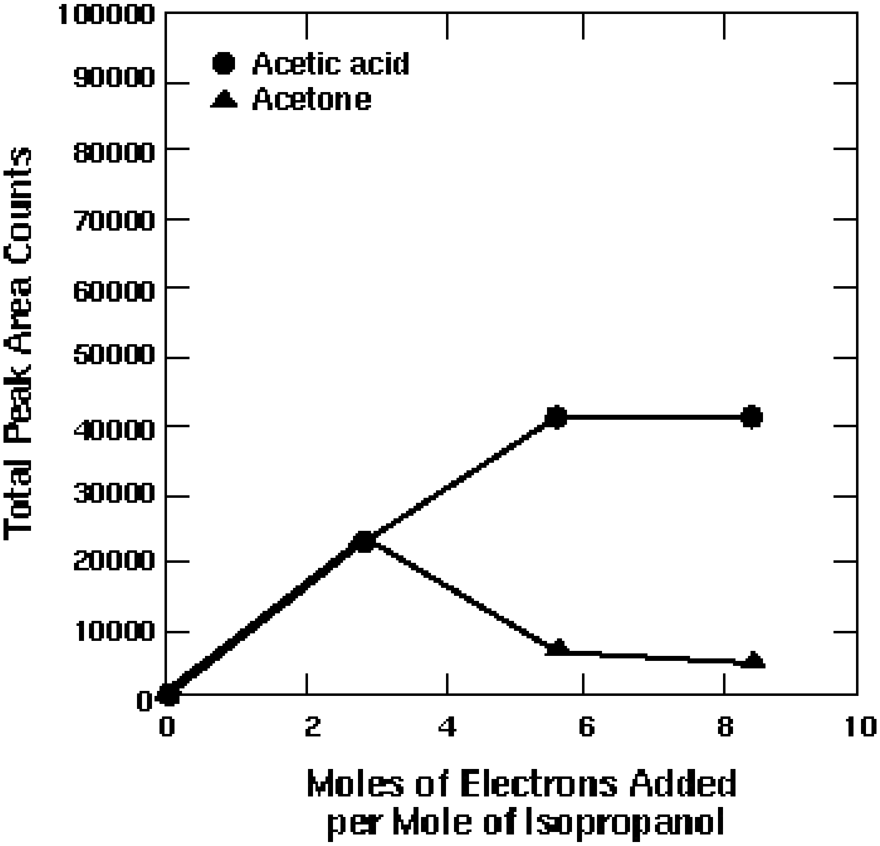


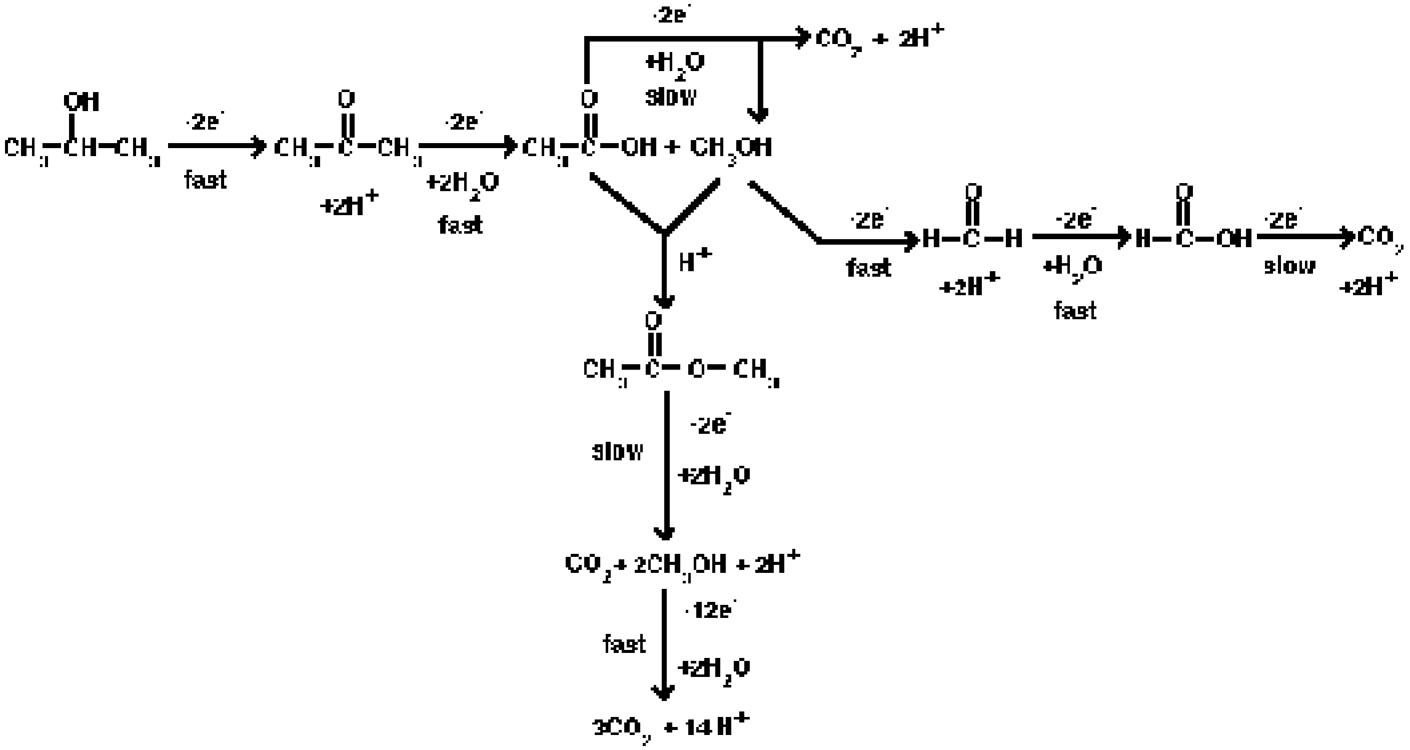
Fig. 3. Electrooxidation of isopropanol at 500 mA/cm^2.

This number is consistent with the partial oxidation of isopropanol to one equivalent of acetic acid and one of carbon dioxide, as per the following equation:

$$(CH_3)_2CHOH - 10\ e^- + 3\ H_2O \longrightarrow CH_3COOH + CO_2 + 10\ H^+. \quad (2)$$

To further verify this result, we conducted a separate experiment starting with acetic acid. After passing 10 equivalents of electrons per mole of acetic acid, we detected no change from the original concentration.

These results are explained in the reaction mechanism that follows:



The ease of oxidation of organic compounds by class appears to be alcohols > ketones, aldehydes > carboxylic acids. Isopropanol is very rapidly oxidized to acetone and more slowly to acetic acid. But a product of the second oxidation step is an equivalent of methanol. Because methanol is even more easily oxidized than isopropanol, it is immediately converted to formaldehyde, formic acid, and ultimately carbon dioxide. Thus, only a small quantity of these substances is present in the reaction cell at any time during the reaction. If there were an appreciable concentration of methanol, the acid-catalyzed esterification of acetic acid would be expected. The product, methyl acetate, does not appear in the chromatogram.

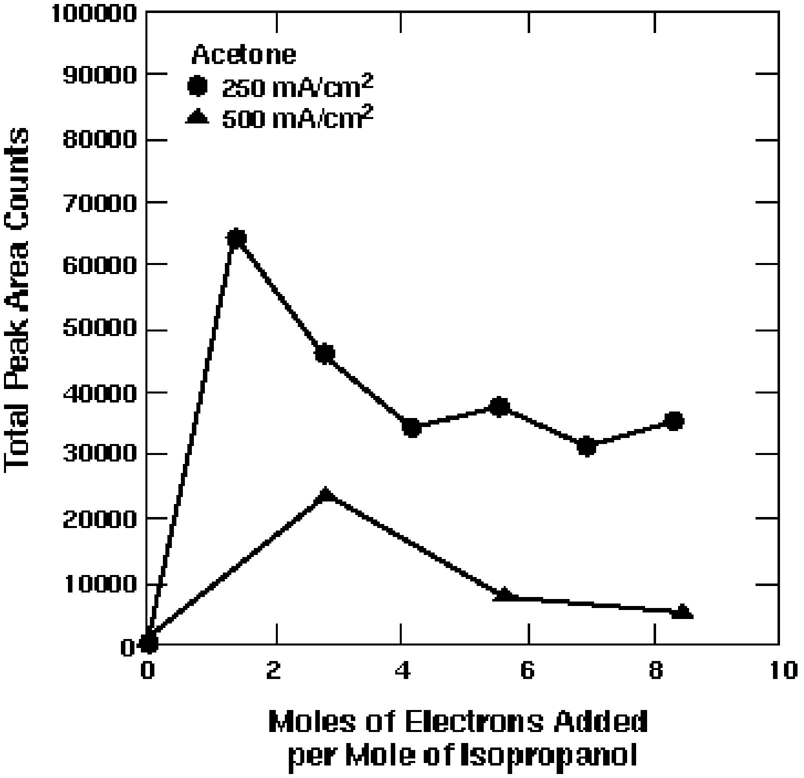


Fig. 4. Effect of current density on oxidation of isopropanol to acetone.

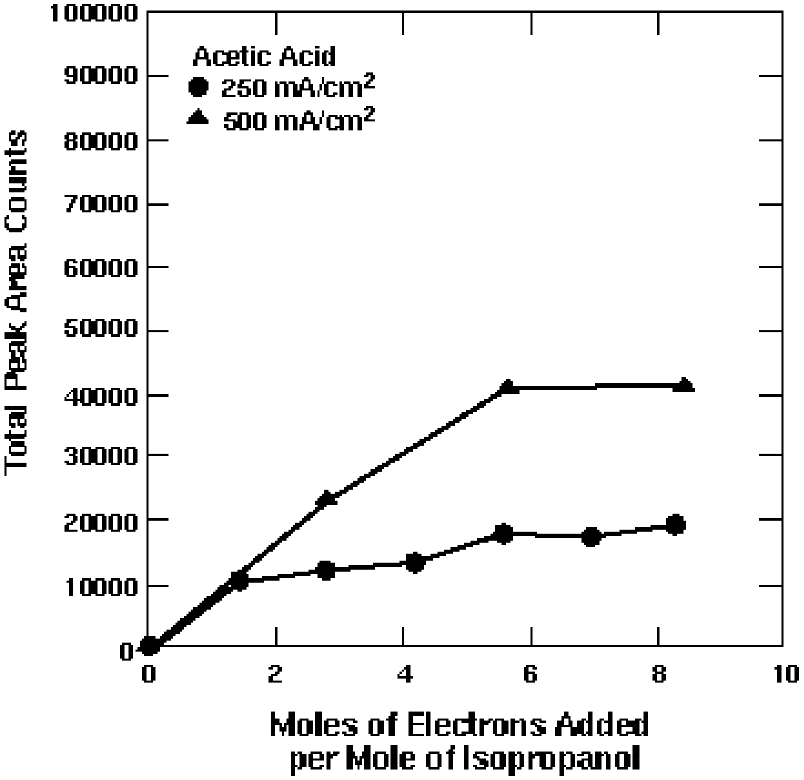


Fig. 5. Effect of current density on oxidation of isopropanol to acetic acid.

Conversion of isopropanol to acetone and / or acetic acid occurs more efficiently at higher current density (Figs. 4 and 5). This higher efficiency may be due to (1) the higher acquired potential of the working electrode, which could more effectively oxidize the acetone intermediate, or (2) the generation of hydroxyl radicals by direct water oxidation, which may contribute to the overall oxidation mechanism.

Temperature has a significant influence on the oxidation rate. At room temperature some fraction of the acetone still remains in the reaction mixture even after the passage of 18 equivalents of electrons. At 50 °C the acetone is completely oxidized to acetic acid well before 18 electrons have been added. More elevated temperatures may be necessary to achieve further oxidation of the acetic acid to carbon dioxide. These experiments are currently underway.

Finally, the oxidations were repeated using optimal conditions (high current density, high temperature, and high acidity) in the presence of a catalyst.
We found that the addition of Co(III) improved the oxidation efficiency, whereas the addition of Ag(II) led to a decrease. The most likely explanation for this phenomena can be attributed to the relative redox potentials of the systems: Ag(II) < solvent < Co(III).

The results of our investigations suggest that the optimum conditions for electrochemical oxidation of isopropanol are high current density, elevated temperature, high solution acidity, and Co(III) as an electron transfer catalyst. However, even under optimum conditions, oxidation to carbon dioxide is incomplete. We are still investigating those conditions necessary to achieve complete conversion.❖

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Waste Minimization Technologies

Application of Freeze Drying Technology to Decontamination of Radioactive Liquids

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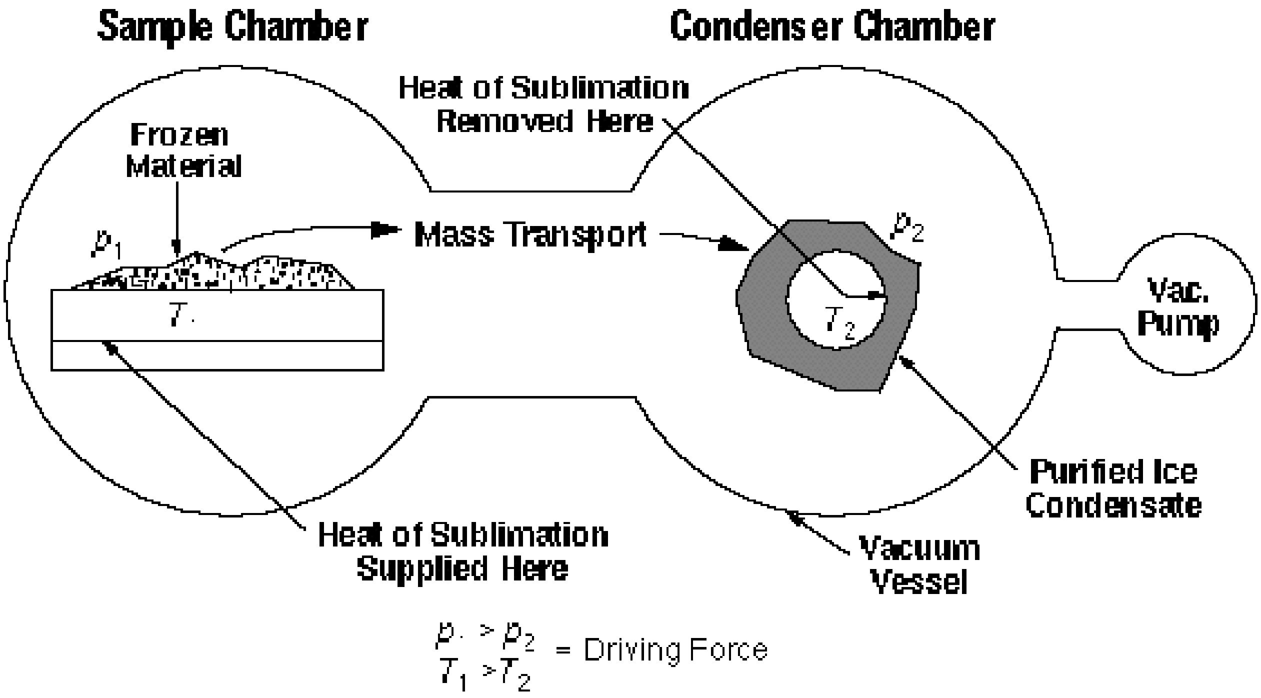
Introduction and Background

Freeze drying is the removal of solvent or volatile components by sublimation from a frozen solution, suspension, or multicomponent material. The freeze drying process, or lyophilization when it refers to biological materials, includes two independent steps: the freezing of the material and the removal by sublimation (*drying*) of the volatile component. The removal of a solvent from a material under these conditions often results in the preservation of the solid portion of the material. This preservation aspect of freeze drying technology (FDT) has led to diverse applications that have resulted in the processing of tons of materials daily throughout the world. The objective of this work is to demonstrate the applicability of FDT to the decontamination of complex radioactive materials including liquids, slurries, and sludges containing a wide variety of constituents in which the decontamination levels are in excess of 100 million. When FDT is applied to the decontamination of multicomponent radioactive materials, the product *is* the condensate (as opposed to the solid portion of the material). This is the first application of FDT where primary importance is given to the condensate, and this new twist has drawn the attention of several commercial manufacturers and developers to this work. Our focus in applying this technology is the elimination of radioactive discharges from the Los Alamos Plutonium Facility; however, successful demonstration here will most likely lead to nuclear industry-wide applications.

"Our focus in applying this technology is the elimination of radioactive discharges from the Los Alamos Plutonium Facility; however, successful demonstration here will most likely lead to nuclear industry-wide applications."

Separation of an aqueous nonradioactive solvent and a radioactive solid (solute) during the freeze drying process occurs in the following manner (please refer to Fig. 1 throughout the following discussion). The solution is frozen and situated in the proximity of a condenser surface. The radioactive material in the left chamber of the freeze drying apparatus is held at a higher temperature than the condenser in the right chamber ($T_1 > T_2$). A concentration gradient develops between the two chambers due to the difference between the temperature-dependent vapor pressures (p_1 and p_2) of the solvent at the two locations. This concentration gradient drives the transport of the nonradioactive solvent from the sample chamber to the condenser. Heat is supplied to the frozen material to allow sublimation to occur. Because the vapor pressures can be quite low, a vacuum is applied to assist the diffusion of the sublimed solvent. Solvent removal is fully achieved by supplying enough heat to the frozen material to complete the sublimation process while removing enough heat at the condenser to maintain the concentration gradient.[1]

Fig. 1. Schematic of a freeze drying apparatus. The sample chamber contains the frozen radioactive material (speckled) and the condenser chamber houses the cold condenser surface onto which the purified ice (gray) condenses. The temperature of the frozen material (T_1) is maintained higher than that of the condenser (T_2). The vapor pressure of ice at the two locations (p_1 and p_2) is dependent on these temperatures, and the resultant concentration gradient causes mass transport. Supplying the heat of sublimation at the sample and removing it at the condenser maintains the transport conditions.



The drying rate can be determined through the simultaneous solution of the Fourier heat law, the Knudsen equation, and the appropriate conductance relationship for the geometry of the apparatus.[2,3] (See Reference 2 for an in-depth discussion of transport phenomena, including the Fourier, Fick, Dufour, and Sorret relationships.) Such analysis indicates that this rate is strongly dependent on the temperature difference between the frozen solution and the condenser, the frozen solution temperature, surface area and concentration, and the geometry of the apparatus. Nuclear waste streams have a relatively low solute concentration in comparison to, for example, foods. Consequently, the greatest impediment to the freeze drying rate, for nuclear waste solutions, is the thermal conductivity of ice. This fundamental limitation is circumvented through engineering solutions, such as maximizing the surface area, minimizing the thickness of the sample, and supplying radiant energy directly to the surface of the frozen material.

Freeze dryers are extremely versatile and broad in their applications. Laboratory freeze dryers are usually designed to sublime kilograms of solvent per day, whereas industrial freeze dryers are capable of drying thousands of kilograms per day.[4] The factor that most greatly influences the cost of a freeze dryer is the performance required by the particular application.

Application of FDT to Nuclear Materials

FDT has been applied to the decontamination of waste streams containing nuclear and hazardous materials with great success. Acidic solutions containing uranium, iron chromium, and nickel originating from nuclear power plant operations have been decontaminated such that the concentration of radioactive materials was 1 pCi per liter (four times lower than current Environmental Protection Agency [EPA] emission levels) while the decontamination factor was 60 million.[5] (The decontamination factor is equal to the ratio of the initial and final concentrations.) Waste solutions containing sodium and potassium nitrates, cesium-137, strontium-90, yttrium-91, cerium-144, ruthenium-106, and iodine-131 were reduced to dry residues while the condensate was decontaminated by 10 million times.[6] Other radioactive elements, such as iodine,[7] plutonium,[8] and ruthenium,[9] have been concentrated in the freeze-dried solid residues to produce radiochemically pure water. Organic solvents have been separated from radioactive solids.[10] Tritium oxide has been separated from solids, but, in that case, the condensate contained the radioactive fraction. Zinc, cadmium, molybdenum, selenium, ruthenium, iron, chromium, and nickel also have been separated from radioactive solids.[11,12] Pilot plant-scale operations for the concentration of radioactive materials (throughput of 25 L per hour) with decontamination factors of 100 thousand have also been reported.[13]

FDT is versatile in that its application is not limited to aqueous solutions. Organic solvents can be separated from other liquids or solids. Liquids processed in this way may be reused or discarded as nonradioactive.

FDT drastically reduces the volume of the waste since the volume of solute or solid component is smaller than the solution or wet volume. Volume reduction factors greater than one thousand have been achieved in aqueous nitrate / nitric acid solutions ($pH < 0.5$),[14] but the exact volume reduction of nuclear waste depends on the particular moisture content. Volumes may also be reduced through the elimination of neutralization steps in transuranic (TRU) processing. Processing of plutonium- and uranium-contaminated scrap often involves the dissolution of the scrap using nitric acid. These solutions are usually neutralized using sodium hydroxide for compatibility with subsequent process steps. A significant percentage of the wastes stored at Hanford was a result of chemical neutralization. The application of FDT may eliminate the use of sodium hydroxide neutralizing agents and consequently greatly reduce the quantity of contaminated solids at later process steps. During the freeze drying of salt / nitric acid solutions, the nitric acid and water vapors are transported to the condenser leaving behind a neutral salt.[14] Furthermore, the acidic condensate may be recycled. This aspect of FDT is being integrated with the current acid-recycle effort[15] in the Nuclear Materials Technology (NMT) division.

Other decontamination methods such as ion exchange, precipitation, or chelation have high ion specificity but require multiple stages, regeneration, neutralization, and / or filtration. They involve the addition of other components (resins, chelating agents, precipitating agents, etc.) that also require remediation. Integration of FDT into these processing lines may greatly increase process efficiency and decontamination effectiveness.

Distillation and / or evaporation decontamination processes involve continuous, often turbulent, flow; thus, entrainment of the radioactive component is an unavoidable consequence. Decontamination factors of ten thousand are theoretically achievable for distillation, but values of about one to three hundred are typical in practice. The freeze drying process differs from distillation in that the transport process during freeze drying involves molecular flow and the thermal energy of the radioactive material is much lower. These features are responsible for the virtual elimination of solute entrainment; consequently, decontamination factors obtained using FDT are extremely high.

FDT can be considered safe and compact. No high temperatures or pressures are used. Furthermore, because the freeze drying process occurs in a vacuum, the failure of a component would lead to an inward leak, which reduces the potential for contamination outside the system.

A system occupying an area of about 225 sq ft would be capable of processing 375,000 kg per year (based on 1500 L per day and 250 days per year) while maintaining a decontamination factor greater than 100 million. More conventional approaches would require considerably larger space investments to achieve equivalent performance characteristics.

Plutonium Facility Demonstration

The FDT demonstration in the Plutonium Facility consists of two phases:

1) studies using a freeze drying apparatus in a glove box to demonstrate performance and to obtain design criteria for a plant-scale system, and
2) integration of FDT into the existing Plutonium Facility liquid waste processing line.

In the first phase, data will be acquired using mock plutonium solutions for the purpose of determining extreme performance characteristics. With these extrema known, tests will be conducted using aliquots of real solutions obtained from various steps along the Plutonium Facility processing line. This work will enable process engineers at the Facility to determine the best place(s) to employ FDT and at what scale.

The integration of FDT into the Plutonium Facility waste processing line, the second phase, will require engineering and manufacturing capabilities beyond those available at Los Alamos. To meet this engineering and manufacturing need, Los Alamos has entered into a CRADA (cooperative research and development agreement) with Edwards Freeze Drying, a commercial manufacturer of plant-scale freeze dryers (1500 liters capacity per unit per day) based in upstate New York. Edwards Freeze Drying will work with the NMT staff in the design, fabrication, and installation of the glove-box system to ensure that the operating parameters can be scaled to a plant-sized system.

In this partnership, both parties have the opportunity for substantial benefit and gain. Edwards Freeze Drying considers NMT Division’s knowledge and experience with nuclear materials and the Plutonium Facility to be vital for the development of this new FDT application. They see this partnership as the foundation for the development of a new product line and possibly new worldwide markets. The successful demonstration of FDT at the Plutonium Facility is crucial to meeting the Laboratory’s immediate and long-range discharge goals. Furthermore, particular nuclear waste problems facing other Department of Energy (DOE) facilities such as Rocky Flats, Savannah River, and Hanford are also being considered in the demonstration of this technology, and solutions to those problems will be integrated into the Edwards Freeze Drying product development. The DOE will gain indispensable technology for the environmental restoration of its nuclear facilities, and the nuclear industry in general will have at its disposal the technology to meet discharge limits that are becoming increasingly more stringent.

In order to understand how FDT might be integrated into the Plutonium Facility’s waste stream processing line, the plutonium recovery operation from scrap is used as an illustration.[16] (See References 17–19 for more in-depth descriptions of the waste stream processing line at the Plutonium Facility.) Plutonium scrap is defined as any material that has a plutonium component; usually other metals are present. The plutonium scrap is dissolved in either an acid or base depending on the chemical composition of the scrap. This solution enters a processing line where other metals are separated by methods such as ion exchange or precipitation. Three effluents are discharged from this processing line. Each varies in the concentration of the radioactive and nonradioactive elements. The plutonium concentrations for the three lines are typically 0.05, 0.08, and 0.15 g plutonium per liter. Usually the radioactive component is a small fraction of the total volume, but even these small amounts are not allowed to be discharged into the environment.

In an effort to further concentrate the radioactive component and to pass an effluent that has a lower radioactive concentration, the three effluents exiting from the ion exchange and precipitation process are sent to an evaporator. The evaporator effluent has a concentration of about 7×10^{-7} g plutonium per liter and is sent to the Liquid Waste Treatment Facility (TA-50) at Los Alamos for further processing.

The residues after evaporation (called *bottoms*) are stabilized in cement. The cements are sent off-site for disposal and / or storage. Figure 2A illustrates the evaporator feeds, evaporator products, and storage and disposal paths.

Two of the possible application points for FDT in the processing line are (1) as a replacement for the evaporator or (2) in series after it. Either of these applications may also feature a means for stabilizing the solid residues that uses atomically mixed ceramic or cement precursors (see next section). Figures 2B and 2C illustrate these FDT application configurations. An analysis and comparison summary of evaporator performance and the performance of configurations using FDT is given in Table I and discussed in the following paragraph. Of the three evaporator feeds, the solutions with a concentration of 0.15 g plutonium per liter represent only a small fraction of the total waste processed; the largest fractions contain only 0.05 – 0.08 g plutonium per liter. Because the relative fractions are variable over time, the worst case scenario was chosen for the performance analysis; that is, we assumed that 100% of the feed has a concentration of 0.15 g plutonium per liter.

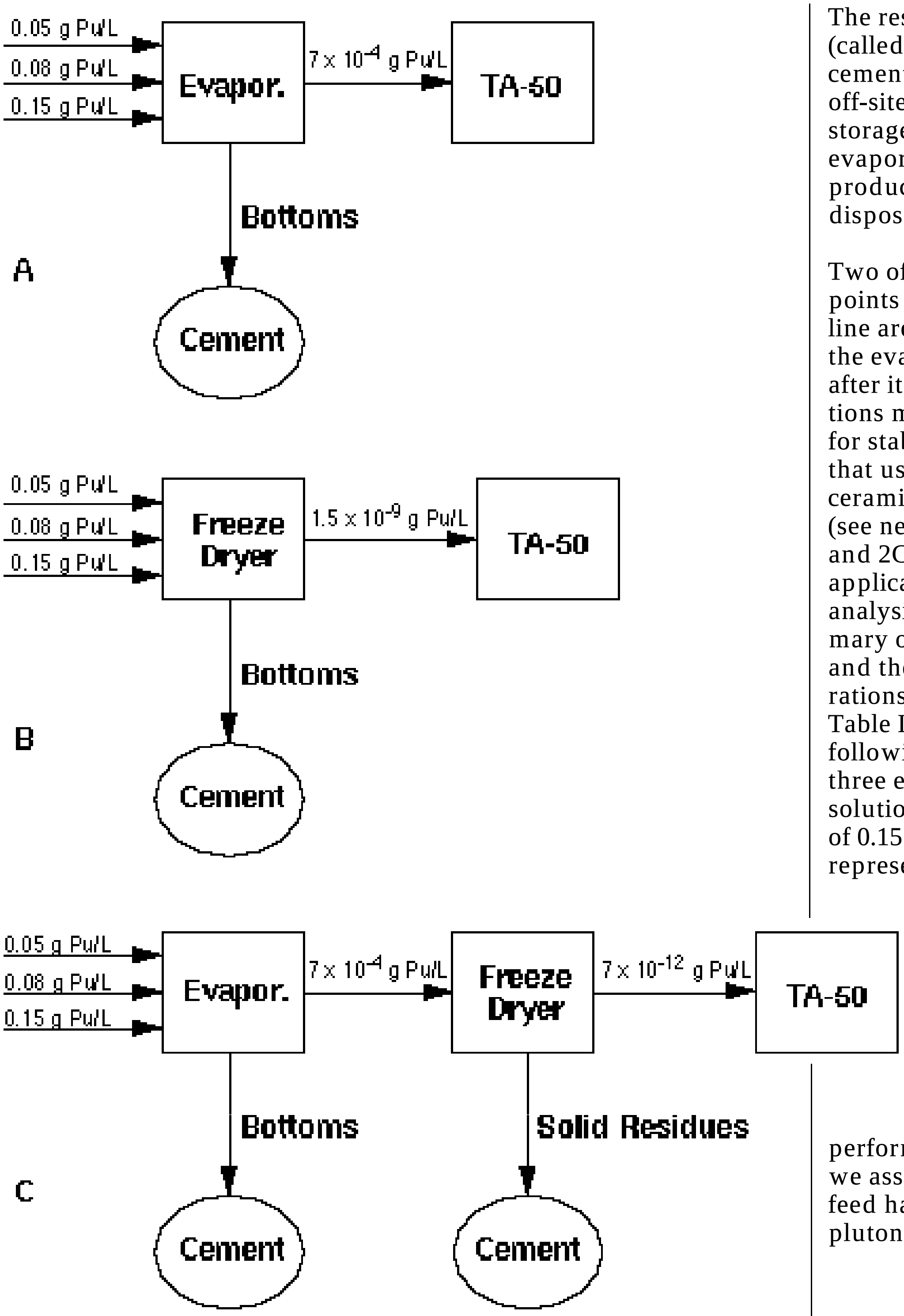


Fig. 2. Configurations for plutonium effluent processing line: (a) current processing line for plutonium scrap at the Plutonium Facility and performance characteristics, (b) proposed simple substitution of a freeze dryer and its performance characteristics, (c) proposed evaporator and freeze dryer in series and their performance characteristics.

Table I. Comparison of Present Evaporator Performance to FDT and to Their Performance in Series.[a]

	Present Evaporator Performance		FDT Performance[b] (alone)		Evaporator and FDT[b] (in series)	
	(g Pu l^{-1})	(dpm l^{-1})[c]	(g Pu l^{-1})	(dpm l^{-1})	(g Pu l^{-1})	(dpm l^{-1})
Input	0.15[d]	2.0×10^{10}	0.15[d]	2.0×10^{10}	0.15[d]	2.0×10^{10}
Output	7.0×10^{-4}[d]	9.3×10^{7}	1.5×10^{-9}	200	7.0×10^{-12}	1.0
Decontamination Factor	210	210	10^{8}	10^{8}	2×10^{10}	2×10^{10}

[a] Evaporator is placed upstream relative to a freeze dryer.

[b] In light of new proprietary developments, the actual decontamination factors may be substantially greater (1000 times) than those cited here.

[c] Disintegrations per minute per liter, assuming a plutonium-239 half-life of 24,100 years.

[d] Maximum input values and minimum output values were chosen from Ref.16; in practice, actual values will probably be lower by a factor of 3 or greater.

Using FDT as a replacement for the evaporator at the Plutonium Facility and assuming a decontamination factor of 100 million, the liquid effluents would contain 1.5×10^{-9} g plutonium per liter or 93 pCi per liter.

A decontamination factor of 100 million is not at all optimistic because other developments made in conjunction with our industrial partner have indicated that decontamination factors far in excess of one billion should be achievable. (The details of these developments were proprietary at the time of the writing of this paper and could not be disclosed.)

If a freeze dryer is placed in series and downstream from the evaporator at the Plutonium Facility, the effluent would contain 7×10^{-12} g plutonium per liter, which is 0.4 pCi per liter or 10 times lower than the current EPA discharge limits.

In that case, discharges may not have to be sent to TA-50, and this could have a significant positive impact on that waste facility's operations as well. In calendar year 1991, the plutonium-239 effluents from TA-50 averaged 43 pCi per liter.[20]

Current decontamination factors at TA-50 are on the order of about 1000 (based on the average 1991 monthly influents and effluents for all radioactive materials). Clearly, if FDT enjoyed a successful demonstration at the Plutonium Facility, this success would imply that decontamination factors at TA-50, as well as at other DOE facilities, would be lower (by factors in excess of 1000) than current EPA discharge limits.

In conjunction with the preparation of atomically mixed ceramic precursors (see the next section), FDT may prove dually advantageous: first, the liquid wastes would be greatly decontaminated; second, the solid residues may be more easily stabilized, which would result in the simplification or elimination of some post-evaporator operations.

Stabilization of Radioactive Solids Using Freeze-Dried Atomically Mixed Precursors

A freeze drying process for the preparation of ceramic precursors that are atomically mixed has been developed and proven to be very useful for overcoming kinetic and thermodynamic barriers encountered during conventional ceramic materials processing. By integrating the separation aspects of FDT with the preparation of atomically mixed precursors (AMPs), the radioactive solid residues from the separation process can be transformed into materials with exceptional environmental stability. These materials can be synthesized faster, at lower temperatures and pressures, and in a fashion compatible with the glove-box environment on an industrial scale.

Atomic mixtures are a mixture of two or more components lacking both long- and short-range structural and compositional order. Atomic mixtures are prepared by rapidly freezing (dT/dt = one million °C per second) a solution containing the appropriate salts followed by freeze drying.[14] (See Fig. 3 for a diagram of this freeze drying process.) The high freezing rates trap solute molecules in a disordered state in a matrix of ice. Then, by freeze drying, the ice matrix is removed, and the disordered state of the original solution is preserved in the residual solid. These atomic mixtures are extremely reactive, and the kinetics for product formation are unlike those of conventional ceramic processing. A microscopic picture for the behavior of these mixtures is being developed in conjunction with the staff from several other Laboratory divisions* using time- and temperature-resolved neutron and x-ray scattering and Monte-Carlo simulations of the molecular dynamics. The calcine temperature of AMP materials has been shown to be lower (by greater than 100 °C)[21] than those of conventional ceramic processes, while the reaction times are also drastically reduced.

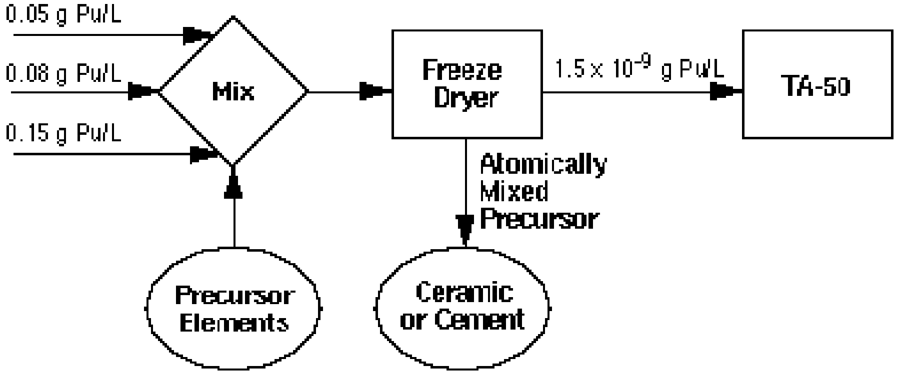


Fig. 3. Schematic for the preparation of atomically mixed precursors of either ceramics or cement, which contain the solid, freeze-dried residues. Using this approach, solid residues would be rendered more stable as well as liquid wastes decontaminated.

As indicated in Fig. 2A, cements are currently mixed with the radioactive evaporator bottoms for the purpose of stabilization. While this composite allows for safe temporary storage and transportation, these cements may not be considered suitable for long-term storage because of new performance requirements imposed by regulating agencies (EPA) and are not considered to be stable on time scales of geological porportions. Other materials such as glasses and mineral analogues, for example synroc, are, or have been, candidates for long-term, permanent storage of nuclear materials, but these candidates also have problems. Although the manufacturing process for glasses is compatible with the radiological environments and procedures, serious disadvantages exist; for example, borosilicate glass is metastable with respect to a crystalline-phase assembly of the same composition[22] and, thus, readily devitrifies when subjected to elevated temperatures and pressures.[23] Crystalline materials such as synroc have been shown to have far superior environmental stability compared to that of either borosilicate glasses or supercalcine materials,[24] but the high temperatures and pressures required for their synthesis have made these materials unattractive as a waste form. Because of the unique characteristics of AMPs, we are applying them to the stabilization of uranium- and plutonium-containing solids resulting from the FDT decontamination process. There are many crystalline phases into which uranium, plutonium, and other radioactive elements can be incorporated.[25] High temperatures and/or pressures may be eliminated. Cements with a dispersion of the radioactive component that is homogeneous on nanometer-length scales, without the use of mechanical mixers, may also be prepared. Formulations based on existing mineral or cement compositions using chemical surrogates for actinide materials, such as those found at the Plutonium Facility, are currently being developed and the products characterized.

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* Participants include Los Alamos Neutron Scattering Center (LANSCE) and the Materials Division.

The synthesis and characterization of actinide-containing materials are planned for the near future. Research using AMPs that contain nuclear materials is focused on the development of several high-performance ceramics and cements, but this research will also advance the frontier of multication, solid-state actinide materials.♦

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Nuclear Applications for Magnetic Separations

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Magnetic Separation Process

Magnetic separation is a physical separation process that segregates materials on the basis of magnetic susceptibility.[1] Because the process relies on physical properties, separations can be achieved while producing a minimum of secondary waste.

Table I. Volume Magnetic Susceptibility of Selected Compounds and Elements

Compound/Element	Susceptibility x 10^{6*}
FeO	7178.0
Fe_2O_3	1479.0
UO_2	1204.0
Cr_2O_3	844.0
NiO	740.0
Am	707.0
Pu	636.0
U	411.0
PuO_2	384.0
CuO	242.0
RuO_2	107.0
Th	41.0
UO_3	41.0
CrO_3	14.0
Si	-0.3
CaO	-1.0
ZrO_2	-7.8
MgO	-11.0
KCl	-13.0
$CaCl_2$	-13.0
NaCl	-14.0
CaF_2	-14.0
SiO_2	-14.0
MgF_2	-14.0
Graphite	-14.0
Al_2O_3	-18.0

*SI Units

When a paramagnetic particle encounters a nonuniform magnetic field, the particle is urged in the direction in which the field gradient increases. Diamagnetic particles react in the opposite sense. When the field gradient is of sufficiently high intensity, paramagnetic particles can be physically captured and separated from extraneous nonmagnetic material.

Because all actinide compounds are paramagnetic (Table I), magnetic separation of actinide-containing mixtures is feasible. Magnetic separation on recycle plutonium chemical process residues has been demonstrated on an open-gradient magnetic separator.[2] The advent of reliable superconducting magnets also makes magnetic separation of weakly paramagnetic species attractive.

> *"Magnetic separation is a physical separation process that segregates materials on the basis of magnetic susceptibility."*

Magnetic Separation Methods

Although numerous magnetic separation methods exist, we have currently selected two methods for development: magnetic roll (or drum-type) separation and high-gradient magnetic separation (HGMS). The usefulness of the open-gradient separation method used in the early work is limited by its low processing rate.[2]

The magnetic roll separation method is used to separate magnetic particles from dry powders. A diagram of a roll separator is shown in Fig. 1.

In practice, a dry powder is delivered onto a thin belt that moves over rollers. The front roller is fabricated from a neodymium-iron-boron rare earth magnet. Ferromagnetic and sufficiently paramagnetic particles are attracted to the magnet and adhere to the belt in the region of the magnet. As the belt moves away from the magnet, the ferromagnetic and paramagnetic particles disengage from the belt and are collected in a catch pan. Diamagnetic and nonmagnetic particles pass over the magnetic roller relatively unaffected and are collected in a different catch pan. This method effectively extracts particle sizes ranging from 90 to 850 µm.

The HGMS method is used to separate magnetic components from solids, liquids, or gases. A diagram of the method is shown in Fig. 2. Most commonly, the solid is slurried with water and passed through a magnetized volume. Field gradients are produced in the magnetized volume by a ferromagnetic matrix material, such as steel wool, iron shot, or nickel foam. Ferromagnetic and paramagnetic particles are extracted from the slurry by the ferromagnetic matrix, while the diamagnetic fraction passes through the magnetized volume. The magnetic fraction is flushed from the matrix later when the magnetic field is reduced to zero or the matrix is removed from the magnetized volume. The HGMS method effectively extracts particle sizes ranging from ~0.3 to 90 µm and, thus, is complementary to the roll separator.

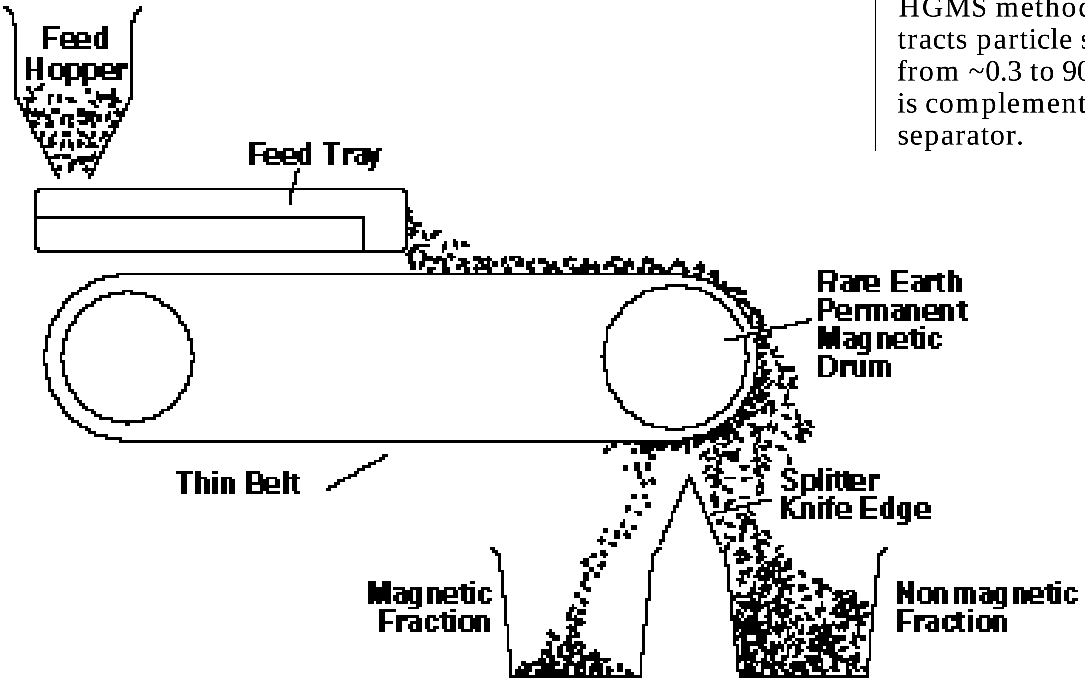

Fig. 1. Diagram of a roll magnetic separator.

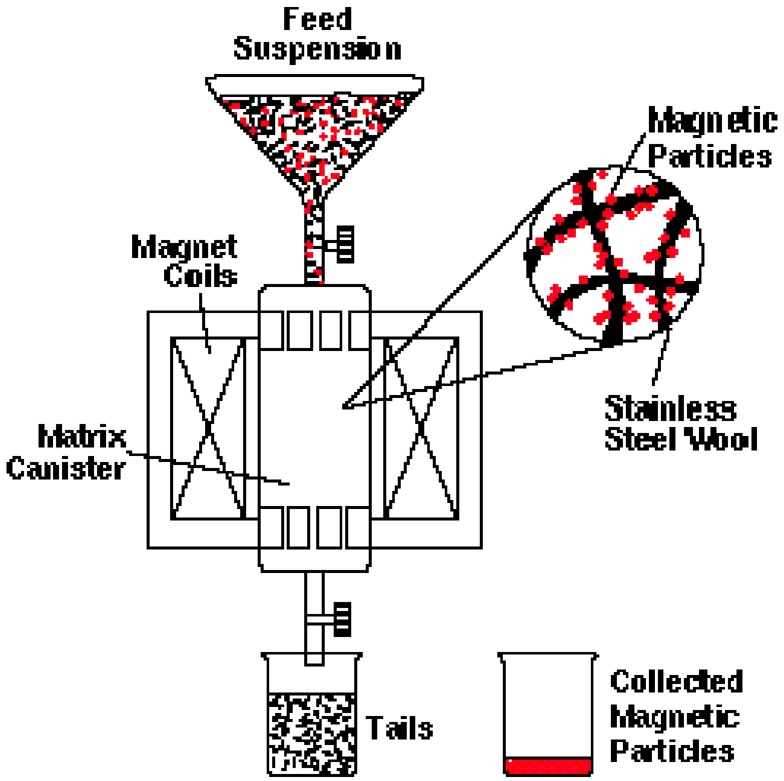

Fig. 2. Simplified HGMS diagram.

The development of the HGMS method has been the central focus of Los Alamos National Laboratory's magnetic separation research.[3-5] Today's superconducting magnet technology produces much higher electromagnetic fields than is possible with conventional electromagnets, which are limited by the saturation of iron to a magnetic field strength of about two tesla. This availability of high fields permits a broad range of HGMS applications, including liquid waste stream treatment, underground storage-tank waste treatment, chemical processing residue concentration, and soil decontamination.

Our current experimental HGMS equipment includes one conventional-coil separator and three superconducting high-gradient separators. We are using the 1-inch-bore conventional coil and one 3-inch-bore superconducting magnet, installed on a vent hood in the Plutonium Facility, for low-activity samples such as contaminated soils and uranium-containing surrogates. A second 3-inch-bore superconducting magnet, installed at our waste treatment facility, will be used to study waste stream treatment applications and will eventually be interfaced to a glove box in the Plutonium Facility for tests of chemical processing residue concentration. Finally, a 6-inch-bore magnet, installed in an open area, is being used for nonradioactive tests and for prototype development of soil decontamination applications.

High-Gradient Magnetic Separation (HGMS) Model

More than 10 variables independently affect the HGMS process; thus, an analytical model for the process is needed to select appropriate bench-scale experiments and to effectively analyze the resulting data. In addition, a validated analytical model supports prototype design and process scale-up. Much work[6-12] by others has been done to model the behavior of the paramagnetic particles as they interact with the magnetized matrix. Areas investigated include the dynamic effects of particle trajectories in homogeneous materials, the influence of particle buildup on the matrix elements, and the particle buildup effect on the flow field. These studies, though requiring simplifying assumptions, identify appropriate independent variables that form the basis for this investigation.

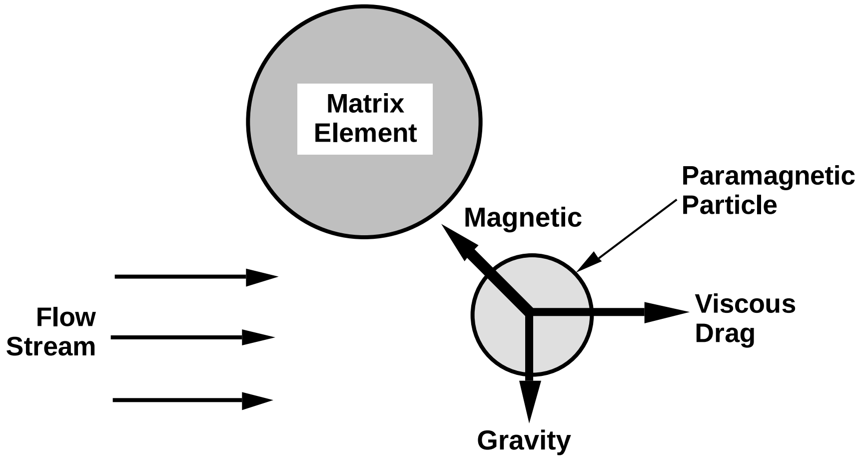

Fig. 3. Force balance of magnetic, viscous drag, and gravity forces on a paramagnetic particle in the vicinity of a matrix element.

The matrix materials currently used for HGMS are inhomogeneous and have a complex cross section. In addition, the paramagnetic particles are nonspherical and include a range of particle sizes. All of these factors preclude precise analytical treatment. If the particles are physically liberated from the host material and are not electrically charged, the principal forces governing their behavior are magnetic, viscous, and gravitational.

The performance of the magnetic separator is modeled using a static force balance on an individual paramagnetic particle in the immediate vicinity of a matrix element, as shown in Fig. 3. The model assumes that if the magnetic capture forces are greater than the competing viscous drag and gravity forces, the particle is captured and removed from the flow stream.

We propose a rate model for this process that depends on a separation coefficient, which we define in terms of a capture cross section and a potential function defined by the force balance on the particle. A series of tests was performed to evaluate separator performance as a function of the independent variables in the separation process. The results were used to determine the separation coefficient in the proposed rate model and were correlated using physically meaningful, dimensionless groups.

We assume that there exists for each matrix element a capture height, wherein each magnetic particle entering the window defined by the capture height and the matrix element diameter will be captured by the matrix element. We then define a capture cross section λ for a matrix element to be the ratio of the capture height to the matrix element diameter, as shown in Fig. 4. The separation coefficient is related to the capture cross section, and if the capture cross section is known, the separation efficiency can be calculated.

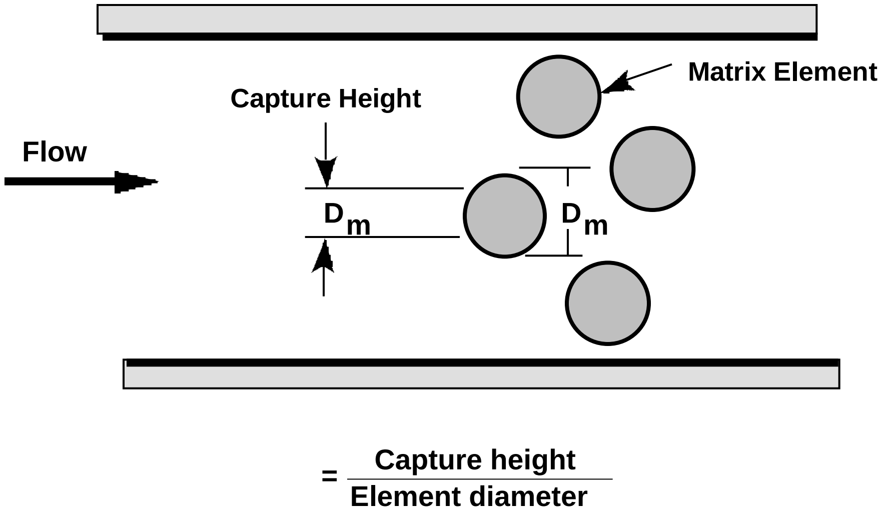

Fig. 4. The matrix capture cross section λ defined as the ratio of capture height to matrix element diamter D_m.

Table II. Independent Variables Investigated

Material Characteristics	Separator Parameters
Particle Size: 0.5−50 μm	Matrix Element Size: 5−100 μm
Impurity Concentration: 0.4−400 ppm	Matrix Element Spacing: 80−1200 μm
Solids Concentration: 5−30 wt %	Magnetic Field Strength: 0.5−7.5 T
Volume Magnetic Susceptibility* ($x10^6$): 129−1478	Matrix Material: 43D Stainless Steel & Ni
Surfactant Concentration: 0.05−0.2 wt %	Residence Time: 1.0−8.0 s
Slurry pH: 7−10	Superficial Velocity: 0.25−4.0 cm/s

*SI units

HGMS Data Correlation

A comprehensive series of experiments was performed to determine the capture cross section as a function of the independent variables. Table II lists the variables investigated and their range. For convenience, the list has been divided into material characteristics and separator parameters. A total of 120 experiments were conducted; 76 involved water/contaminant mixtures and 44 involved water/soil/contaminant mixtures.

The capture cross section λ for each test was determined experimentally based on the measured feed and effluent concentrations, the particle force balance, the matrix geometry, and the contaminant particle size.

The capture cross section is significantly less than 1.0, which implies that particles are swept around the matrix elements by the fluid flow even if the particles enter the region defined by the projected frontal area of the matrix element. In addition, the capture cross section is proportional to the magnetic force and the contaminant particle diameter and inversely proportional to the matrix element diameter and the matrix element spacing. These results are consistent with our observations. The capture cross section λ is inversely proportional to the superficial velocity, which is the ratio of the separator length and the slurry residence time in the matrix.

Intuitively, one expects to have to maximize both the separator length and the matrix residence time for optimum performance; however, only their ratio has to be considered, and this fact makes superficial velocity the more fundamental parameter.

HGMS Results

We have completed a comprehensive series of HGMS experiments with nonradioactive surrogates, as discussed in the previous section, and have progressed to tests with radioactive material. The results to date are very promising.

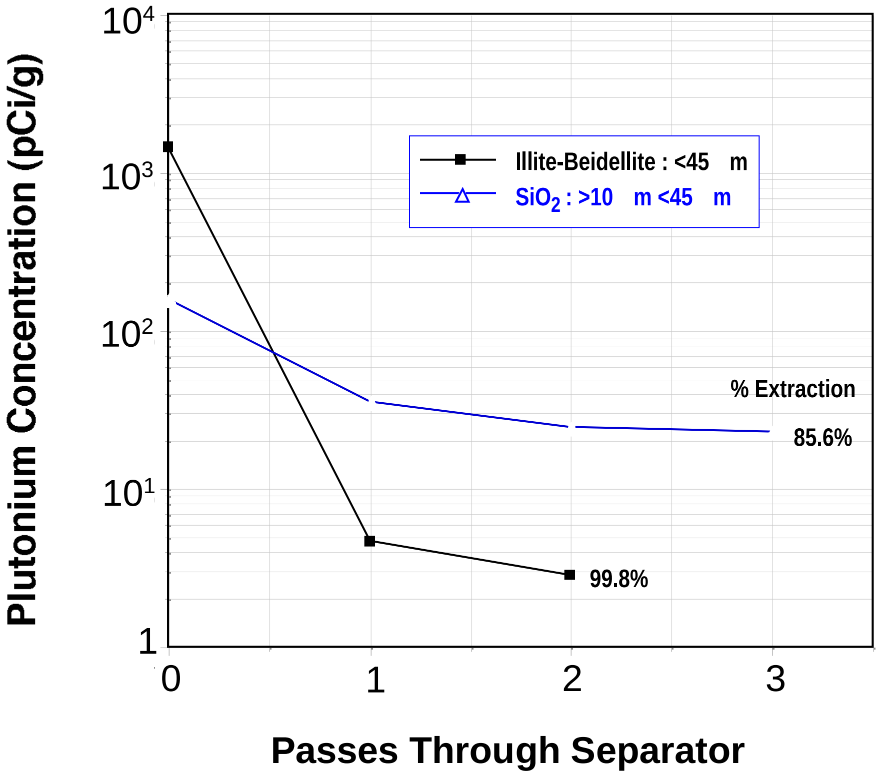

Fig. 5. HGMS extraction of plutonium oxide from soils (external magnetic field strength of 2.0 tesla ; 2–5 µm PuO_2 particles).

To investigate soil decontamination applications, we worked closely with Lockhead Environmental Systems and Technologies in a CRADA (cooperative research and development agreement) effort. Our first tests with a spiked clay-type soil showed almost three orders of magnitude decontamination — from about 1500 pCi/g to less than 4 pCi/g with an applied field of two tesla (see Fig. 5).

With silica, however, ~86% of the plutonium in a spiked sample was removed by HGMS at two tesla. Surface adsorption appears to cause silica sand to bind plutonium oxide particles to the surface. We also are planning HGMS soil tests with the 3-inch superconducting magnet located in the Plutonium Facility. Model predictions and surrogate work suggest increased decontamination levels at field strengths above two tesla.

To investigate chemical processing applications, we experimented with contaminated graphite residues. These series of tests revealed that HGMS performance is strongly influenced by the graphite solids content. Copper oxide serves as the surrogate for plutonium oxide. Figure 6 illustrates the effect of magnetic field and solids fraction on the separation effectiveness for particles less than 90 µm. The highest separation efficiency is observed under conditions of low solids fraction (<5% solids), with a fairly minor effect from external field strength. As discussed earlier, the effective particle size range for the roll separator on dry powders is greater than 90 µm; thus, the coupling of HGMS with the roll separator would be advantageous for treatment of chemical processing residues.

Our application of HGMS to the Tank Waste Remediation System (TWRS) indicates that we may be able to reduce certain types of tank waste directly to non-transuranic (non-TRU) levels in one step. The initial tank waste target is Neutralized Cladding Removal Waste (NCRW), which is formed from the chemical decladding of Zircaloy-clad metallic uranium fuel that has been made alkaline for storage. It contains zirconium hydrous-oxide solids, TRU elements (~1000 nCi/g in sludge), and mixed fission products. Our surrogate components for NCRW tank waste were generated from PUREX reagents used in NCRW production.[13]

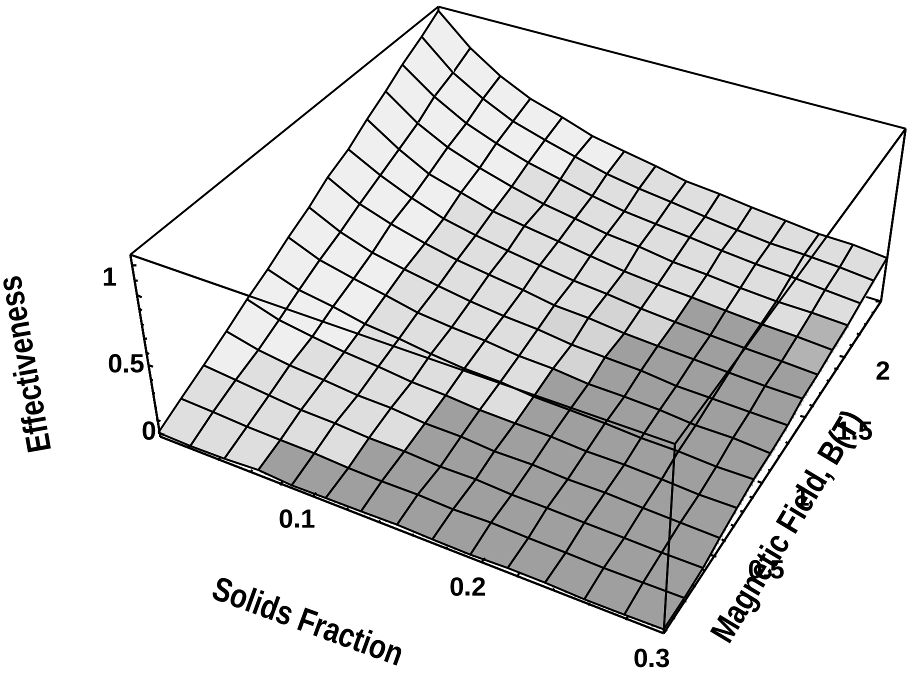

Fig. 6. HGMS effectiveness for contaminated graphite slurries as a function of magnetic field strength and graphite solids fraction. The plutonium surrogate was 4-μm copper oxide particles, and the graphite solids were sized < 90μm for the experiments.

Prior to precipitation of the hydrous oxides, uranyl nitrate or iron nitrate was added to the acidic solution serving as the NCRW TRU surrogate. HGMS tests of aged and unaged slurries containing precipitated iron and zirconium have been conducted at a one-tesla field, and results indicated that 84% of the aged ferric hydrous oxides can be captured from a slurry. Because of this favorable outcome using the iron solutions, HGMS tests are planned on zirconium / uranium / hydrous-oxide solutions.

HGMS is also being developed for magnetic filtration of fluid waste streams generated during actinide chemical processing and for those generated at the waste treatment facility. The analytical model predicts that HGMS can reduce the actinide concentration in liquid waste streams by several orders of magnitude.

Magnetic Roll Separation Results

A variety of hot tests have been conducted on a lab-scale roll separator in a glove box. Several lots of graphite powder, bomb reduction sand (MgO), and sand, slag, and crucible (SS&C) residues have been processed with variable results. The best results were obtained with graphite processing, in which 85% of the plutonium was concentrated into 4% of the bulk material. Particles were sized greater than 125 μm. The plutonium content of the lean fraction was sufficiently low in plutonium so that it could be discarded directly to grout.

The roll separator results were not as favorable with MgO or SS&C residues. In the best case for MgO, 68% of the plutonium was concentrated in 44% of the bulk material. For SS&C, the results were inconclusive with no discrete separation. Yet, in the past, we have shown that magnetic separation can achieve higher performance with these residues; for example, with the open-gradient magnetic separator, we were able to concentrate 81% of the plutonium in 33% of the SS&C bulk material.[2]

We feel that, if we can increase the magnetic field intensity, a viable roll separation technology can be developed. The magnetic field intensity acting on the feed particles in magnetic roll separation is inversely proportional to the thickness of the belt.

In the glove-box environment, belt changes and roller alignment are very difficult with our current roll separator. A second roll separator of improved design that uses a very thin (0.005 inch) stainless-steel belt has been obtained. This separator will be tested in a nonradioactive environment and modified for convenient glove-box use.

Benefits of Magnetic Separation

We have shown that HGMS, open-gradient magnetic separation, and magnetic roll separation can be used to concentrate plutonium and uranium in waste residues and contaminated soils. One of the major benefits of magnetic separation technology is that it only partitions the existing waste volume. A high contaminant concentration of a primary component and a low contaminant concentration of a secondary component are created.

If the separation efficiency is high, the secondary component can be discarded, and the primary component, with reduced volume, can be further processed or packaged for disposal. Concentration of the actinides from extraneous materials before further processing yields more efficient recovery or treatment operations; for example, concentrating the contaminants reduces the volume of chemical reagents (acids) necessary for subsequent operations. Furthermore, increased concentration of contaminants in dissolved feeds allows a more efficient ion exchange or solvent extraction unit operation. Because less extraneous material is leached and dissolved, the salt load on subsequent waste treatment operations is reduced.

Magnetic separation could be applied to on-site decontamination of radioactive spills. However, development of a mobile magnetic separation unit would be required. Portable superconducting magnet systems do exist for mobile Magnetic Resonance Imaging. Development of magnetic filtration may be a method to cut to very low levels the TRU effluents from Department of Energy facilities and, thereby, greatly reduce waste treatment cost. ✦

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Distillation Separation of Actinides from Waste Salts

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Nuclear Material Processing:
Chloride Systems

Introduction

Plutonium-bearing residue salts resulting from past pyrochemical processing have accumulated in the Department of Energy (DOE) weapons complex. This problem is especially acute at Rocky Flats, where approximately 20 metric tons of salt await disposition. Pyrochemical salt wastes will also be generated in the future by Complex 21. In addition to containing plutonium with its attendant hazards, these salts may contain reactive metals. The reactive component places the salts in the category of mixed waste and unacceptable under Waste Isolation Pilot Plant (WIPP) acceptance criteria. Because of restrictions on plutonium loading in individual waste drums, WIPP may not even have the capacity for the number of drums that would be generated, even if the waste were acceptable. The salts must therefore be treated to remove as much plutonium as possible and render inert any reactive components.

Physical separation processes, such as distillation separation, are more attractive than chemical or dissolution processes because physical processes generate much less secondary waste. A physical separation of waste salts from plutonium is theoretically possible because of a large difference in vapor pressure. A high-temperature distillation process can be used to volatilize the alkali and alkaline-earth chloride salts from essentially nonvolatile actinide oxides. An oxygen sparging process developed at Los Alamos pretreats the salts to convert actinide species to oxides or oxychlorides and simultaneously converts reactive metals into inert oxides so that they are no longer mixed waste. The salt is then evaporated to leave a plutonium dioxide heel suitable for storage. Waste volume will be essentially limited to the salts themselves. Moreover, the greatly reduced plutonium content of the salts will result in a greatly reduced number of waste drums for WIPP disposal and a large reduction in the cost of disposal. It is theoretically possible to remove plutonium below the 1 ppm level, which would then classify the salts as low-level waste (LLW) rather than transuranic (TRU) waste and result in even greater cost savings and a more benign waste form.

> *“It is theoretically possible to remove plutonium below the 1 ppm level, which would then classify the salts as low-level waste rather then transuranic waste and result in even greater cost savings and a more benign waste form.”*

Distillation Separation Process

The distillation separation process can be modeled by the kinetic theory of gases.[1] From this theory, one can show that the rate of the mass of a gas incident on a unit area per unit time is

$$W = CP\left(\frac{M}{2\pi RT}\right)^{\frac{1}{2}} \tag{1}$$

where

W = gas incident rate (g cm^{-2} sec^{-1}),
M = molecular weight (g mol^{-1}),
R = gas constant (8.325×10^{7} ergs K^{-1} mol^{-1}),
T = temperature (K),
P = vapor pressure (torr) at temperature T, and
C = conversion factor (1333 dyne cm^{-2} torr^{-1}).

Substituting the values for the gas constant and the conversion factor produces the rate equation

$$W = 0.0583P\left(\frac{M}{T}\right)^{\frac{1}{2}} \tag{2}$$

Table I. Vapor Pressure of Pyrochemical Salt Components

Compound	850 °C	950 °C	1050 °C	Ref. No.
NaCl	$10^{-0.063}$	$10^{.0.64}$	$10^{1.2}$	2
KCl	$10^{0.23}$	$10^{0.90}$	$10^{1.5}$	3
$MgCl_2$	$10^{0.27}$	$10^{0.97}$	$10^{1.6}$	4
$CaCl_2$	$10^{-2.9}$	$10^{-1.9}$	$10^{-1.0}$	4
CaF_2	$10^{-7.7}$	$10^{-6.1}$	$10^{-4.7}$	5
Pu	10^{-8}	10^{-7}	10^{-5}	6
$PuCl_3$	$10^{-1.8}$	$10^{-0.86}$	$10^{-0.086}$	7
PuO_2	$10^{-15.7}$	$10^{-13.5}$	$10^{-11.7}$	8
PuOCl	10^{-6}	10^{-5}		9

If the temperature of the surface that the gas strikes is much colder than the temperature of the gas vapor, then condensation will occur with a sticking coefficient of 1. Under these conditions, the condensation rate is equal to the incident rate, and, thus, the amount of material deposited can be estimated by using the calculated incident rate. In the case of molten salt distillation, the condenser temperature will be much lower than the temperature at which the material is evaporating, so that estimating the amount deposited will be possible. Most importantly, calculations can be made for the rate of deposition of pyrochemical salts because the vapor pressure of the various components, with one exception, is known.

Table I lists vapor pressures of common pyrochemical salt components at selected temperatures.[2-9] The extremely low vapor pressures for plutonium dioxide and calcium fluoride are extrapolations from higher temperature data. Table I shows that the best separation can be achieved between plutonium dioxide and the chloride salts; it also shows that a good separation between the salts and plutonium trichloride cannot be achieved. To ensure optimal separation, Los Alamos pretreats the pyrochemical waste salts using an oxygen sparging process, or alternate oxidation processes, to convert plutonium and americium species to oxides or oxychlorides.

Table II. Deposition Rate (g hr^{-1}) from 100 cm^2 Surface Area

Compound	850 °C	950 °C	1050 °C
NaCl	4100	20000	75000
KCl	9100	41000	140000
$MgCl_2$	11000	55000	200000
$CaCl_2$	9	85	560
CaF_2	$10^{-3.9}$	$10^{-2.3}$	$10^{-1.0}$
AmO_2	10^{-11}	$10^{-9.0}$	$10^{-7.2}$
PuO_2	10^{-12}	$10^{-9.6}$	$10^{-7.8}$
Pu	$10^{-3.7}$	$10^{-2.4}$	$10^{-1.4}$

Table II lists the rate of deposition (at selected temperatures) of various compounds. Figure 1 shows calculated deposition rates as a function of temperature. These are calculated rates, however, and actual rates can be slower by some orders of magnitude. Nevertheless, all the chloride salts, except calcium chloride, can be distilled at acceptable rates below 900 °C. Calcium chloride can be distilled at 1100 °C. Even at 1100 °C, the vapor pressure of plutonium and americium dioxide is low enough to still get an excellent separation from the salt.

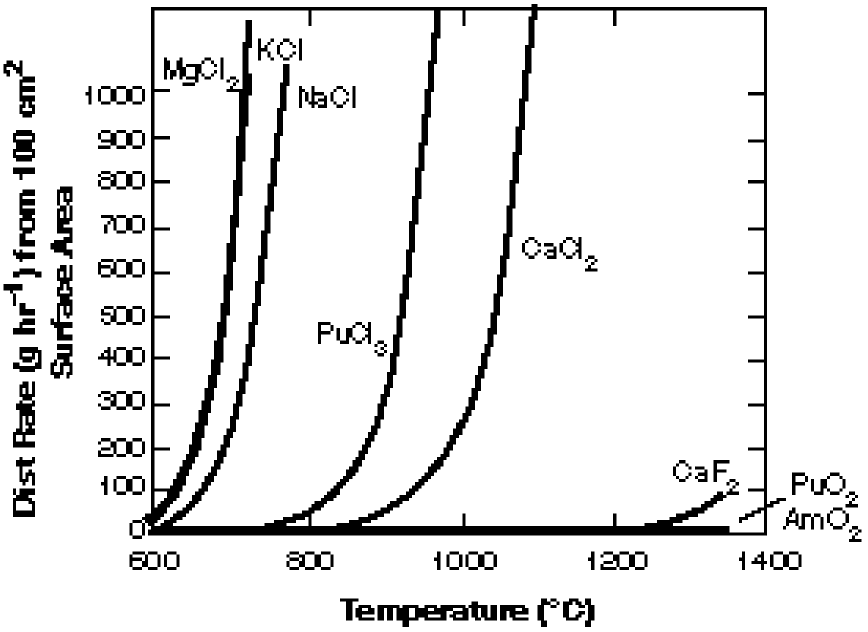

Fig. 1. Distillation rates as a function of temperature.

The deposition rates can be used to calculate the composition of the distillate salt under ideal conditions. For example, in a salt that contains only sodium chloride and plutonium dioxide at 850 °C with a 100 cm^2 surface area, the rate of deposition of sodium chloride is 4100 g per hour while that of plutonium dioxide is 10^{-12} g per hour. The distillate salt would then contain a weight concentration of 10^{-10} ppm plutonium. At 1050 °C, the distillate salt would have a plutonium concentration of 10^{-7} ppm. The LLW criterion for plutonium-239 is on the order of 1 ppm. Therefore, vacuum distillation of a sodium chloride, potassium chloride, or magnesium chloride salt that contains only plutonium dioxide has the potential to produce a waste salt with a plutonium concentration 10 orders of magnitude below the LLW criterion. In the case of calcium chloride, the calculated concentration is 10^{-5} ppm at 1050 °C. Figure 2 shows a plot of plutonium concentration in various distilled pyrochemical salt components as a function of temperature. As shown in this plot, even at 1200 °C all the chloride salts will be considerably below the 1.6 ppm LLW cutoff for plutonium. The americium content must be below 0.03 ppm for LLW, and this requirement can also be met assuming all the americium is present as AmO_2.

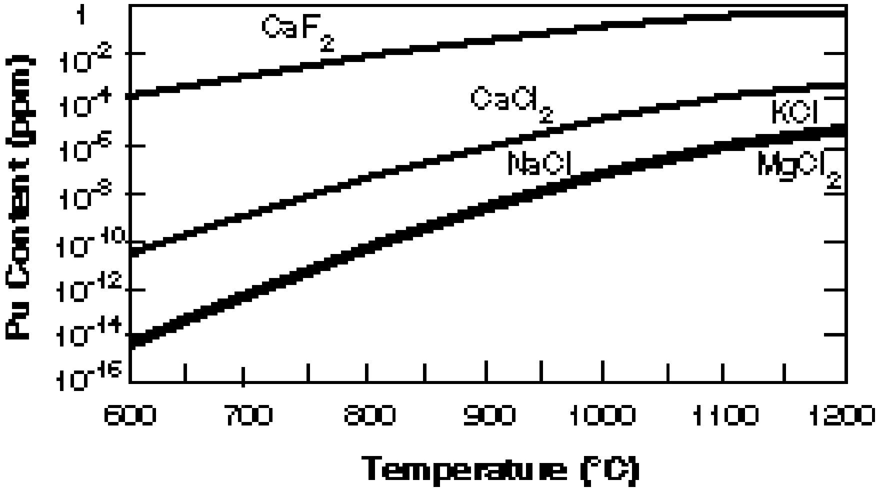

Fig. 2. Calculated plutonium concentration in distilled salts assuming only PuO_2 *present.*

Pretreatment of Waste Salts

The calculations in the previous section assumed that the waste included only chloride salt and plutonium dioxide. Actual waste salts may also contain plutonium metal and plutonium trichloride and must be pretreated to convert all actinide species to oxides. Oxygen sparging can convert plutonium trichloride to plutonium dioxide. However, because neither plutonium metal nor oxygen is soluble in the chloride salts to a significant extent, using oxygen sparging to convert plutonium metal to plutonium dioxide is more difficult. Plutonium oxychloride is also generally a product of oxygen sparging and, based on preliminary vapor pressure measurements,[9] may not be desirable. Alternate oxidation agents that are soluble in the salt are being examined experimentally and modeled theoretically.

Results

We are still in the early stages of distillation experiments and are using equipment that was easily available but not necessarily designed for our purposes. Nevertheless, early results have been extremely encouraging. Greater than 95% of the salt was recovered from plutonium-rich fractions of sodium chloride-potassium chloride salts pretreated by oxygen sparging. The plutonium concentration was reduced from approximately 50% to the range of hundreds of ppm. Although still significantly above the LLW cutoff, this concentration is low enough to allow very significant savings in costs for WIPP disposal of Rocky Flats salts. Experiments with “cold salts” in the glovebox indicate that the level of contamination in the distilled salts may be the result of handling in the glove-box environment, not the distillation process itself. The distillation heels left in the crucible consisted of loose powders that could be poured out.

A picture of the waste salt before vacuum distillation is shown in Fig. 3, and the resulting distilled salt and plutonium-dioxide heel are shown in Fig. 4.

Preliminary experiments with alternate oxidation pretreatments have also been very encouraging. Many different oxidation agents were considered, but sodium carbonate and calcium carbonate were selected because of desirable solubility and stability properties. They are also essentially nonhazardous materials. Tests with plutonium metal in molten salts have shown them to be effective in converting the metal to the dioxide. Experiments with waste salts have also produced plutonium dioxide as the only plutonium species. Thermodynamic modeling predicts that the only materials that will be left in the distillation heel will be plutonium dioxide and graphite. A final calcination step can be incorporated into the process to convert the graphite to carbon dioxide, leaving a plutonium-dioxide heel suitable for storage.

Future Work

Preliminary results with nonoptimized equipment have already demonstrated that distillation can be used to purify sodium chloride-potassium chloride salts so that they contain plutonium in the range of hundreds of ppm. Our ultimate objective is to produce salts that can be disposed of as LLW. Better equipment is being designed to achieve this objective.

Fig. 3. Plutonium-rich fraction of an oxygen-sparged salt before vacuum distillation.

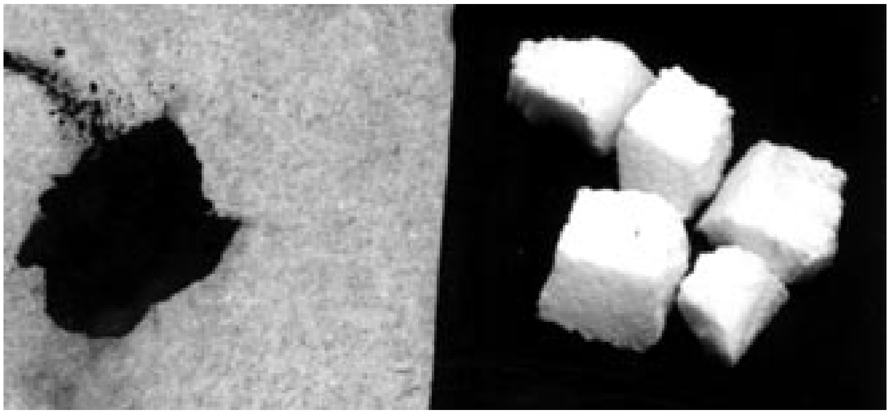

Fig. 4. Plutonium-dioxide powder heel and purified condensate salt.

Calcium chloride salts constitute another major fraction of the stockpiled waste salts, and equipment is being obtained to carry out the distillation process at the higher temperatures required for calcium chloride.

Experiments are also being carried out on "cold" salts to help optimize processing parameters such as time, temperature, and pressure. These experiments will aid condenser and other equipment design. Surrogate metal oxides will be mixed with salts to help determine the extent to which the salts can be purified in a noncontaminated environment. Experiments with carbonate oxidation agents will also continue.

The encouraging preliminary results and the calculations predicting an extremely low plutonium concentration of the distillate salt lead us to conclude that the ambitious goal of converting plutonium-bearing waste salts to low-level waste is achievable.❖

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Evaluating Existing Partitioning Agents for Processing Hanford High-Level Waste Solutions

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“Los Alamos National Laboratory has been asked by DOE to support the Hanford Tank Waste Remediation System mission, which is to 'store, treat, and dispose of all tank waste in a safe, cost-effective, and environmentally sound manner.'”

Introduction

The Hanford Reservation in Washington State incorporates 177 underground storage tanks that contain over 165 million curies of radioactivity in more than 65 million gallons of waste. Many different processes were used at Hanford during the half-century these wastes were accumulated from nuclear materials processing for national defense requirements. As a result, many different reagents and waste streams were neutralized and combined in underground tanks, often with insufficient concern about the compatibility of the components being stored. The resulting wastes are an extremely complicated and sometimes unstable mixture of sludges, saltcakes, slurries, and supernates. Adding significantly to the stored waste problem is the fact that 67 tanks are known, or are suspected, to have leaked.

The U.S. Department of Energy (DOE) is committed to the environmental remediation of hazardous wastes stored at the Hanford Site. Los Alamos National Laboratory has been asked by DOE to support the Hanford Tank Waste Remediation System (TWRS) mission, which is to “store, treat, and dispose of all tank waste in a safe, cost-effective, and environmentally sound manner.” An essential requirement for achieving the TWRS mission is identifying suitable partitioning agents and technologies to accomplish this challenging goal.

Experimental Program

The objective of our study was to evaluate the performance of a large number of potentially useful absorber materials, including many not previously studied, in realistic waste simulants of acid-dissolved sludge and acidified supernate solutions found in Hanford high-level waste (HLW) Tank 102-SY. Relatively few absorber materials have been evaluated with media approaching the complexity of Hanford HLW solutions. Nor have other investigators evaluated the distribution of such a large number of elements onto so many absorbers.

We evaluated 60 commercially available or experimental absorbers for partitioning high-level radioactive waste. We use the term “absorbers” to represent solid materials that remove ionic species from aqueous solutions, whether by ion exchange, chelation, ion trapping, molecular sieving, or other mechanisms. Absorbers in our study included cation and anion exchange resins, inorganic exchangers, composite absorbers, and a series of liquid extractants sorbed on porous support beads. We measured the distributions of 14 elements onto these absorbers.

The selected elements, which represent fission products (Ce, Cs, Sr, Tc, and Y), actinides (U, Pu, and Am), and matrix elements (Cr, Co, Fe, Mn, Zn, and Zr), were traced by radionuclides and assayed by gamma spectrometry. Distribution coefficients for each of the 1680 element / absorber / solution combinations were measured for dynamic contact periods of 30 minutes, 2 hours, and 6 hours to provide sorption kinetics information for the specified elements from these complex media. We measured more than 5000 distribution coefficients.

Absorbers

Many organic and inorganic absorbers are more resistant to chemical attack and radiation damage than are most liquid extractants. Moreover, solid absorbers can readily be used in compact, low-cost columns that provide rapid multistage separations. A typical operation cycle for a solid absorber column consists of loading the absorber and elution of the sorbed element(s), followed by regeneration and reuse of the absorber. At times, the targeted elements are sorbed so strongly that elution is difficult; in such cases, the loaded absorber becomes a candidate for the final waste form.

Although most of the absorbers we evaluated are cation exchangers, we included some anion exchange resins and a series of liquid extractants (sorbed on porous carbon beads) to obtain more comprehensive data, as well as to supply convenient reference points to other studies. We also included some experimental absorbers to provide guidance for future research activities.

Waste Simulants

We recognize that no waste simulant will exactly represent the contents of an HLW tank. Nevertheless, we have used the best information available in our effort to prepare realistic simulants. Ultimately, the most promising absorbers must be tested with actual waste. However, because actual waste samples are expensive and difficult to obtain, we suggest that screening of promising candidate absorbers precede tests with actual Hanford tank waste.

Flow Sheet Options

Our identification of suitable partitioning agents was also intended to help designers develop reliable flow sheets. The selection of agents will, of course, depend on the particular objectives of the flow sheet. Although our study initially was intended to support the flow sheet development program for Hanford Tank 102-SY,[1] many of our experimental findings are applicable to other flow sheet proposals, such as the so-called “Clean Option.”[2] Decisions about whether the targeted elements should be recovered individually, or grouped for subsequent disposal, are properly left to the flow sheet designers. Whichever flow sheet is adopted, we expect that our experimental data will help the designer anticipate the performance of existing partitioning agents.

Results

Only a brief summary of our results is presented here. A detailed description and all experimental data have been published elsewhere.[3]

Behavior for many absorber / element combinations was substantially different from what would be expected, based on published measurements from relatively clean solutions; this finding demonstrates the importance of using realistic simulants. In some cases, we found that inexpensive commercial partitioning agents outperform specialty products whose costs are orders of magnitude higher.

In addition to identifying promising existing partitioning agents, we determined which partitioning agents and technologies, including some of those that have been designated as the Hanford baseline technologies, are marginal or inadequate. Table I summarizes how well each of the 14 elements is sorbed, from the two acidic solutions, by showing the number of effective absorbers in each of the six distribution coefficient (Kd) categories. Where acceptable absorbers have been identified, we recommend that these absorbers be tested with other simulated tank compositions and with actual waste. Where acceptable absorbers have not been identified, we recommend an accelerated effort to identify or develop satisfactory partitioning agents.

Table I. Number of Identified Absorbers in Various Kd Categories for Each of 14 Elements, from Two Solutions Simulating Hanford HLW Tank 102-SY

Medium	Kd Element	Kd >1000	Kd 300-1000	Kd 100-300	Kd 20-100	Kd 10-20	Kd 5-10
Acid-Dissolved Sludge	Ce	0	0	0	5	1	1
	Cs	7	0	0	11	1	4
	Sr	0	0	0	0	0	0
	Tc	0	0	1	11	2	5
	Y	0	0	0	0	0	0
	Cr	0	0	0	0	0	0
	Co	0	0	0	0	1	0
	Fe	0	0	0	0	0	0
	Mn	0	0	0	0	0	0
	Zn	0	0	0	0	0	0
	Zr	0	1	3	10	4	3
	U	0	0	0	6	8	5
	Pu	2	5	6	2	8	2
	Am	0	0	0	0	0	6
Acidified Supernate	Ce	1	3	3	10	3	6
	Cs	8	1	5	2	4	2
	Sr	0	0	0	0	3	4
	Tc	0	7	7	9	3	1
	Y	1	0	1	9	0	5
	Cr	0	0	0	2	2	5
	Co	0	0	0	1	3	4
	Fe	0	0	0	0	0	3
	Mn	0	0	0	0	1	5
	Zn	0	0	0	5	3	2
	Zr	0	0	0	1	4	3
	U	0	1	4	15	8	8
	Pu	0	0	0	0	0	1
	Am	0	3	2	13	1	5

Elements that show good-to-excellent sorption from the simulant solution of acid-dissolved sludge are cerium, cesium, technetium, zirconium, uranium, and plutonium (Table II). Elements that show low sorption from this solution are strontium, yttrium, chromium, cobalt, iron, manganese, zinc, and americium.

Table II. Absorbers* Whose Measured Distribution Coefficients Exceed 20 for the Specified Elements, from Simulated Acid-Dissolved Sludge Solution

Medium	Element	Absorbers
Acid-Dissolved Sludge	Ce	JSK-1, JSK-2, JSK-3, Purolite™ A-520-E, Ionac™ SR-3
	Cs	SNL/CSTs, AMP-PAN, M315-PAN, NiFC-PAN
	Tc	Reillex™ HPQ, Ionac™ SR-3, Purolite™ A-520-E Sybron™ $(Et)_3N$, LANL TiO_2, LANL ZrO_2, LANL Nb_2O_5
	Zr	NaY-PAN, SNL/CSTs, Duracil™ 230, TiO-PAN, Ionsiv™ TIE-96, M315-PAN, Duolite™ CS-100, Cyanex™ 272
	U	TRU-Spec™, Sybron $(Et)_3N$, Ionac™ SR-3, Purolite™ A-520-E
	Pu	JSK-3, JSK-2, JSK-1, Reillex™ HPQ, TRU-Spec™, Sybron SR-3, Purolite™ A-520-E, Cyanex™ 923

* Detailed descriptions of these absorbers, whose trade names are used here, have been published elsewhere (see Reference 3).

Elements that show good-to-excellent sorption from the simulant solution of acidified supernate are cerium, cesium, technetium, yttrium, zinc, uranium, and americium (Table III). Elements that show poor-to-marginal sorption from this solution are strontium, chromium, cobalt, iron, manganese, zirconium, and plutonium.

Applications to Los Alamos Plutonium Facility Waste

The Los Alamos Plutonium Facility at TA-55 has assigned a high priority to waste minimization. Because the acidic waste streams generated at TA-55 are in some ways similar to the simulant solutions selected for this study, some of the most promising absorbers identified in this study may have applications at TA-55. This is especially likely for those absorbers and extractants that sorb americium strongly. Testing of likely absorbers with TA-55 acidic and alkaline waste is planned.

Future Studies

Our screening study has met its objective of identifying specific absorbers that appear capable of partitioning targeted elements from Hanford HLW Tank 102-SY. The best absorbers from this study and perhaps a few promising new materials should be evaluated with simulated compositions that represent other Hanford tanks, especially those on the safety watch-list. The 14 elements whose distributions have been measured should be carefully examined to determine if any should be dropped or if additional elements should be included in future measurements. Finally, radioactive tracers, shown to provide a rapid, reliable, and inexpensive way to obtain large amounts of distribution data, should be used in such studies.

The effects of radiation on the most promising absorbers from our present and future studies should be determined, when such information is not already available,[4] before partitioning agents are selected or before any large-scale recovery flow sheet is selected.

Table III. Absorbers* Whose Measured Distribution Coefficients Exceed 50 for the Specified Elements, from Simulated Acidified Supernate Solution

Medium	Element	Absorbers
Acidified Supernate	Ce	Cyanex™ 923, TRU-Spec™, SNL/HTO, CMPO-DIPB, Amberlyst™ 15, DHDECMP, MgO-PAN, Diphonix™, SNL/CST111, Amberlyst™ XN-1010
	Cs	SNL/CSTs, NiCF-PAN, AMP-PAN, M315-PAN, Durasil™ 230, SRS resorcinol, Ionsiv™ TIE-96
	Tc	Sybron (Pr)$_3$N, Cyanex™ 923, Aliquat™ 336, Sybron (Et)$_3$N, Reillex™HPQ, Purolite™ A-520-E, Ionac™ SR-6, Ionac™ SR-3, TRU-Spec™, LIX™-26, DHDECMP, CMPO-DIPB, LANL TiO$_2$, LANL ZrO$_2$, LANL Nb$_2$O$_5$
	Y	Cyanex™ 923, TRU-Spec™, Amberlyst™ 15, MgO-PAN, CMPO-DIPB, Amberlyst™ XN-1010
	Zn	NiFC-PAN, Duolite™ C-467, NaTiO-PAN
	U	Cyanex™ 923, Diphonix™, TRU-Spec™, TiO-PAN, SNL/HTO, CMPO-DIPB, SNL/CST35, Cyanex™ 272, Duolite™ C-467, Amberlyst™ 15
	Am	Cyanex™ 923, TRU-Spec™, SNL/HTO, CMPO-DIPB, Amberlyst™ 15, SNL/CST111, AMP-PAN, Bone char, Amberlyst™ XN-1010, LIX™-1010

* Detailed descriptions of these absorbers, whose trade names are used here, have been published elsewhere (see Reference 3).

Conclusions

Our experimental data indicate that many existing partitioning agents may be suitable for HLW tank remediation. If reliable partitioning agents can be identified, Hanford HLW tank processing might begin and reach completion sooner, and at a lower cost, than would otherwise be possible. We therefore feel that the findings of our study could have a major beneficial impact on environmental remediation efforts at Hanford and elsewhere within the DOE complex.❖

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Gas Pycnometry for Density Determination of Plutonium Parts

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Introduction

Traditionally, determination of plutonium component density has been accomplished by measuring the apparent weight loss when the object is immersed in a liquid of known density (Archimedes' principle). Liquids that are compatible with plutonium, and that have been successfully used in the past, include freon and monobromobenzene. However, these fluids have undesirable characteristics that present health and environmental hazards. Furthermore, the spent fluid stream is environmentally undesirable. Gas pycnometry eliminates the liquid waste as well as the gaseous emissions from volatiles. The focus of current gas pycnometry research and development is to prove that this technique can reliably determine the density of plutonium subscale shapes to the desired accuracy. If this goal is met, gas pycnometry can be expanded to address all plutonium density determination needs.

Background

The accurate determination of part density is an important parameter in plutonium fabrication. Densities of solids are routinely determined by the hydrostatic technique of measuring the apparent weight loss when the solid is submerged in a liquid of known density.[1] When the sample volume, determined from Archimedes' principle, is combined with the true weight of the sample, its density is readily calculated. However, the hydrostatic technique is subject to error if the sample surface has cracks that are not completely filled by the liquid. Similarly, trapped air bubbles can introduce errors. Furthermore, the thermal effects of heat-generating materials such as plutonium can induce thermal currents or raise the temperature of the fluid and thus affect the accuracy of the results. If the fluid chemically reacts with the sample, or adsorbs on the surface of the sample, the sample will be physically altered, and results will be inaccurate.

> *"The focus of current gas pycnometry research and development is to prove that this technique can reliably determine the density of plutonium subscale shapes to the desired accuracy. If this goal is met, gas pycnometry can be expanded to address all plutonium density determination needs."*

Accuracy of the hydrostatic technique for determining plutonium part density thus depends, in large part, on the choice of fluid. Freon and monobromobenzene, the traditional fluids of choice for plutonium, are less attractive now because of emerging environment, safety, and health regulations. Freon production is being curtailed by the Montreal Protocol, whereas monobromobenzene is a suspect carcinogen. Searches for other liquids were conducted, and some were found that provided adequate results. Unfortunately, these liquids required the use of a solvent to remove them from the plutonium surface when density determination was complete. The increasing regulation of liquid waste disposal prompted efforts to identify a method of density determination that is not dependent upon the hydrostatic technique.

Gas pycnometry is used successfully in industries that are ill-suited for hydrostatic density determination. These industries typically process powders, such as metal powders, ceramic powders, and dry cement. To use this technique, a volume of gas is allowed to expand in a calibrated sample chamber, and the pressure difference caused by the sample volume is calculated. Different implementations are possible, but all rely upon the fundamental gas law. Equation 1 is the fundamental gas law at constant temperature and solving for the new volume V_2 yields Equation 2:

$$P_1V_1 = P_2V_2 \qquad (1)$$

and

$$V_2=V_1(P_1/P_2). \qquad (2)$$

The application of gas pycnometry to density determination of plutonium parts is more complicated than normal industrial applications, primarily because plutonium is self-heating and will increase the temperature of the gas in the pycnometer. The fundamental gas law at nonconstant temperature and its solution for volume V_2 are shown in Equations 3 and 4:

$$(P_1V_1)/T_1=(P_2V_2)/T_2 \qquad (3)$$

and

$$V_2=V_1(P_1/P_2)(T_2/T_1)\,. \qquad (4)$$

In addition, the precision desired for plutonium fabrication is much higher than standard industrial practice. Considering these factors, we concluded that a system designed specifically for use with plutonium would be required.

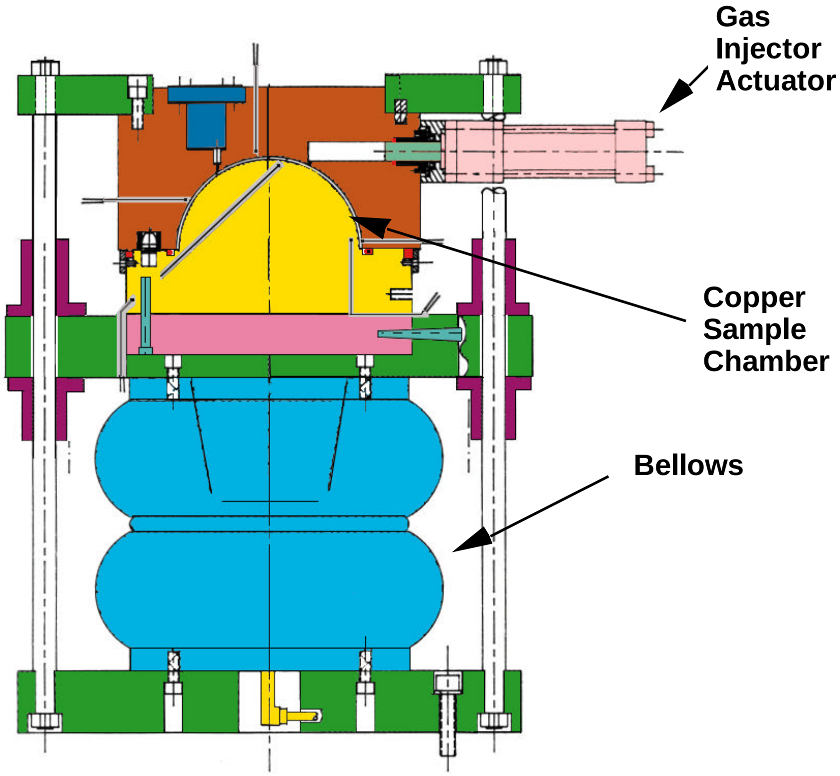

Fig. 1. Schematic of prototype gas pycnometer.

Los Alamos researchers entered into a technology development partnership with equipment development specialists from the Savannah River Technology Center (SRTC), a division of the Westinghouse Savannah River Company. The goal of this partnership was to design, build, and test a prototype system to demonstrate the application of gas pycnometry on a subscale plutonium shape. Requirements developed for the gas pycnometer system were as follows:

- determines density within ± 0.05%,
- does not leave residues or contaminants on part,
- accommodates self-heating of plutonium,
- operates in a glove-box environment, and
- completes measurement cycle in less than two hours.

Prototype Gas Pycnometer System

A schematic of the device developed by SRTC is shown in Fig. 1. The sample chamber is made of a solid block of copper to provide the required heat transfer characteristics for the temperature control system. The designers selected a simple-to-machine, hemispherical shell for the sample part. The chamber closely matches the shape of the sample so that the sample will occupy a significant portion of the available volume. The chamber volume should be within 50% of the volume of the part to allow a sufficiently large change in gas pressure and thus provide reasonable accuracy. Other notable features of the device include the rubber bellows in the bottom portion for opening and closing the chamber and the side-mounted actuator for injecting the gas charge.

To achieve the ± 0.05% repeatability specification for part density, variations from one measurement cycle to the next had to be carefully controlled. An analysis of measurement uncertainties indicated that one of the major design challenges was closure of the sample chamber to achieve a highly repeatable volume. A rubber bellows actuator was selected to lower and raise the male portion of the chamber in order to open and close the chamber. The pressure in the bellows is controlled to within 0.05 psi to assure consistent compression of the O-ring seal. Also, the bellows accommodates angular misalignment, and this inherent property ensures that pressure is applied uniformly around the O-ring circumference.

Temperature is controlled through a feedback control loop. Thermistors are used to measure the temperature within ± 0.001 K. The thermistor values are read by the control computer, which controls the heat removal rate by adjusting the voltage output to the thermoelectric coolers. Heat must be constantly removed from the device to maintain the temperature within ± 0.01 K of the set point. The set point is selected by the computer to ensure that heat is always being removed. In addition to maintaining the device at the set point temperature, the thermoelectric coolers have sufficient capacity to remove the heat generated by a plutonium sample.

An actuator on the side of the device injects a known, repeatable amount of gas into the chamber. The pressure increase caused by the gas injection is used to calculate the chamber volume from the fundamental gas law. The difference between pressures in the chamber with the sample present and absent is used to calculate the sample volume. Pressure is measured with a highly accurate quartz pressure transducer. The computer reads the transducer for twenty measurements before releasing the actuator to relieve gas injection pressure, and then twenty low pressure readings are taken. Readings are taken multiple times to establish stability and give statistical significance to the values used in subsequent calculations.

A computer running custom data collection and device control software controls the entire system. The computer does not allow a measurement cycle to begin if temperature stability is not achieved. Once a measurement has been initiated, no user interaction is required; thus, operator variability is not a factor in the measurement process.

An aluminum hemispherical shell was fabricated for initial out-of-glove-box testing of the device. In addition, a stainless-steel shell encircled by resistance heating wire was constructed to simulate the self-heating properties of plutonium. A plutonium shell has been designed and is to be fabricated at Los Alamos.

Savannah River cold-tested the gas pycnometer with both the aluminum and stainless-steel shells. The device was then transported to Los Alamos where it was cold-tested again with the aluminum shell.

Aluminum Shell Test Results at Savannah River

The aluminum shell was used for most of the Savannah River experiments. Its true volume was determined by the hydrostatic technique, using water as the working fluid. The immersion was performed in a vacuum so that air bubbles could not form and bias the results. The mean of the results of a number of trials was used as the best estimate of the true part volume. The standard deviation of the hydrostatic measurements was 0.08%.

A number of trials were then performed using the aluminum shell in the gas pycnometer. The repeatability of the results was superior to the hydrostatic technique (0.01% at 1 std dev). However, an offset of the mean was noted. Analysis of the results indicated that the swept volume of the actuator, and hence the volume of the gas injection, was different than the theoretical value because of mechanical tolerances in mounting the actuator. The correct value for the actuator volume was then calculated and used in future measurements.

Stainless-Steel Shell Test Results at Savannah River

The stainless-steel shell had a series of concentric grooves machined into the outer surface. Resistance heating wire was wound into these grooves and connected to a power supply. By varying the supply voltage the power of the heater was adjusted to approximate the power generated by a plutonium shell. The power dissipation during trials with the stainless-steel shell was 2.5 watts.

As anticipated, trials conducted on the heated stainless-steel shell showed a loss in precision. The loss is attributed to uneven heat generation, which leads to variations in the temperature of the gas in the annular space. However, the observed precision of 0.03% is still better than the goal of 0.05%. Uniform heat generation from plutonium should reduce the variability somewhat.

Aluminum Shell Test Results at Los Alamos

After transport of the gas pycnometer to Los Alamos, testing with the aluminum shell was repeated to confirm that the device was not damaged in transit. Repeatability within 0.01% was achieved, confirming proper operation of the device and reconfirming the results from Savannah River. The results of this testing are presented in Fig. 2.

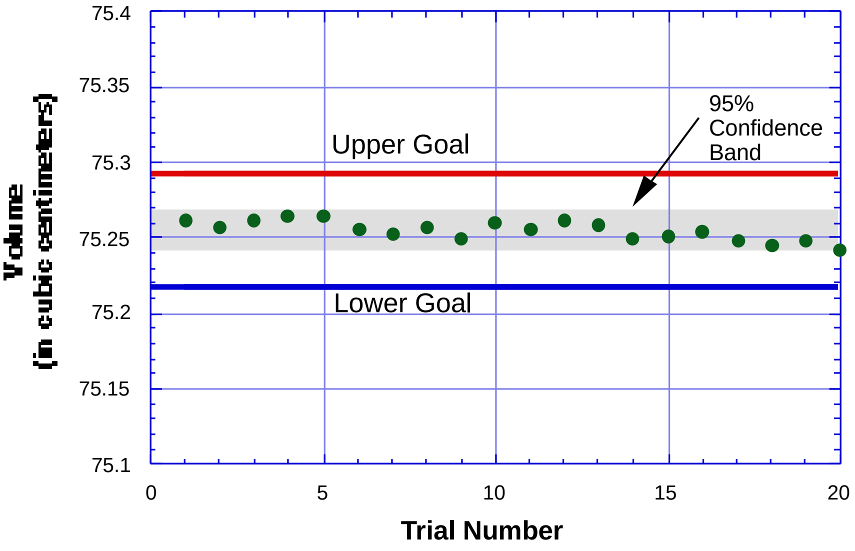

Fig. 2. Los Alamos aluminum shell data compared to experimental goals.

Future Directions

Preparations are in progress for installing the gas pycnometer in a glove box in the Los Alamos Plutonium Facility. After installation, the aluminum shape will again be measured with the gas pycnometer and then measured with the hydrostatic monobromobenzene method. No further testing is planned with the heated stainless-steel shell; instead, the plutonium shell will be used. The plutonium shell will be measured with both the gas pycnometry and hydrostatic monobromobenzene methods to determine the success of the pycnometer system.

The pycnometry method is inherently less flexible than the hydrostatic technique because of the geometric constraints of the pycnometer sample chamber. Near-term efforts include fabricating a pycnometer system that will accommodate specific part geometries for Los Alamos missions. A longer-term effort will examine alternative methods of increasing robustness, such as replaceable chamber inserts or premeasured gas volumes at higher pressures. Eventually, gas pycnometry will replace hydrostatic density determinations for plutonium.

Summary

Los Alamos scientists, in cooperation with their SRTC partners, are evaluating gas pycnometry for determining density of plutonium parts. This replacement for the current hydrostatic immersion technique will eliminate a liquid waste stream and support the vision of an environmentally benign plutonium facility. Initial testing of gas pycnometry with surrogate materials indicates the technique can provide results that are superior to those from existing methods. Density of aluminum hemispherical shells can be determined to ± 0.01% of the actual density. Testing with plutonium shells will commence in the near future.✥

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Plutonium Dry Machining

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"Reducing or eliminating hazardous wastes from plutonium machining processes at Los Alamos National Laboratory is critical to ensure continued operations under current and increasing legislative demands."

Introduction

Reducing or eliminating hazardous wastes from plutonium machining processes at Los Alamos National Laboratory is critical to ensure continued operations under current and increasing legislative demands. In the past, Los Alamos machining processes used an argon and freon mist system to lubricate and cool the plutonium parts and to act as a fire inhibitor (plutonium is pyrophoric). Current U.S. legislation requires the elimination of all chloro-fluorocarbons, such as freon, by 1996; therefore, switching to plutonium machining methods that are environmentally friendly is crucial. Dry machining is one possibility because it does not require the use of coolants or oils, and, thus, mixed waste byproducts can be minimized or eliminated. The impact of this method is realized downstream as well, because the material recovery processes receive cleaner feed material.

Dry machining tests at Los Alamos on various plutonium parts, which included features similar to weapon components, showed that plutonium can easily be dry machined, practically eliminating the need for cutting fluids. Results indicated a significant reduction in the use of oils and solvents for research and development activities as well as for production processes. This reduction and eventual elimination of hazardous solvents and oils for plutonium machining processes will complement activities at the future plutonium production facility, Complex 21.

Background

Metal machining has traditionally used cutting fluids to lubricate or cool parts at the cutting tool interface during the material removal process. These fluids have a number of benefits, such as reducing friction and wear (thus extending tool life and improving surface finish), cooling of the cutting zone, and removing metal chips from the immediate work area. The fluids are generally water-based oil, organic oils, or solvents. However, plutonium machining has been associated only with compatible organic oils or solvents, because water acts as a neutron reflector that decreases the amount of plutonium needed to sustain a nuclear chain reaction.

Cutting fluids can be used as lubricants or coolants depending on their applications. High-speed machining requires coolants to reduce heat that occurs from increased cutting speeds, whereas slower-speed machining requires lubricants to reduce material buildup on tooling and to improve surface finish. Past plutonium machining processes have used cutting fluids for both purposes, to lubricate and to cool parts.

The plutonium shapes typically machined require that the cutting tool begin at the spindle center line and proceed outward to some specified diameter, or the reverse of this process. The operations are analogous to a facing operation performed from the center line outward. A direct relationship exists between the cutting speed and the radius of the part; as the radius (distance from the center line) increases during machining, the part surface speed increases in relation to the cutting tool.[1] Therefore, close to the spindle center line, a rotating plutonium part has very low surface speed and the cutting process acts as a low-speed machining operation. As the tool progresses outward, the surface speed of the part increases and the cutting process behaves more like a high-speed operation. This direct relationship between the cutting speed and the part radius is expressed as

$$V_c = \pi r \times \omega ,$$

where

V_C = cutting speed (ft / min),
r = radius (ft), and
ω = rotational speed (rpm).

Plutonium is a material that must be processed in a controlled environment in order to prevent plutonium contamination, limit radiation exposure to personnel, and reduce the amount of oxygen present. Because plutonium is pyrophoric, heat created from processing must be regulated, along with oxygen, to prevent igniting the metal. Reducing oxygen content is also necessary to inhibit oxide growth (plutonium reacts with oxygen to create plutonium oxide). Oxygen reduction within a glove box requires purging it with either nitrogen or argon.

Los Alamos and the Rocky Flats Plant each have used a different approach for cooling and lubricating the plutonium parts. Production machining methods at Rocky Flats used oil as a cutting fluid that was applied by flood cooling. This method served not only to cool and lubricate the parts but also limited the amount of oxygen in contact with the material at the tool and part interface. However, the oil, once in contact with plutonium, is considered a mixed waste and was difficult to dispose of properly. Additionally, the oil had to be cleaned from the surface of the parts, chips, and equipment with large amounts of carbon tetrachloride, approximately 7800 gallons per year. This solvent, when contaminated with plutonium, is considered a mixed hazardous waste and requires very strict disposal procedures. Research and development plutonium machining methods at Los Alamos used argon to propel a freon mist onto the tool and part interface for the same reasons as at Rocky Flats. Freon usage at Los Alamos was approximately 50 liters per year. Because freon is a chloro-fluorocarbon, its use will soon be eliminated in the United States. Clearly, alternatives to these environmentally harmful practices at Rocky Flats and Los Alamos were desperately needed.

Rocky Flats investigated alternative solvents for carbon tetrachloride while Los Alamos searched for methods to eliminate freon; however, Rocky Flats was shut down before an alternative could be found. The research performed at Los Alamos revealed that by reducing the oxygen content low enough in the glove box, plutonium could be dry machined, reducing the need for cutting fluids. Currently, this process is applied in approximately 85% of all machining operations at Los Alamos. The remaining operations are carried out with a light, thin coat of oil applied to the surface of the material for finish cuts.

Methodology

Tests at Los Alamos were performed as an engineering study to investigate the feasibility and practicability of plutonium dry machining for research and development purposes as well as for production processes. Experiments included upper oxygen limit and plutonium machining tests. In addition, the formation of nitrogen and plutonium compounds were investigated in the current literature.

Establishment of an upper oxygen limit for dry machining was critical to the prevention of a plutonium fire. Two methods were used to test the oxygen limit at which plutonium would ignite under various machining conditions. The first machining tests were performed on an engine lathe. A series of cuts were taken on a 0.75-inch, delta-stabilized plutonium rod while the oxygen content in the glove box was increased. Another series of tests were performed in a furnace to verify the temperature as well as oxygen content required for plutonium combustion. In both approaches, only small amounts of plutonium were used in order to prevent a large fire from occurring.

The machining investigations were conducted on various phases of plutonium, including delta-stabilized material. The tests concentrated on turning (the shaping process) and were performed on computerized numerical control T-base lathes. Various shapes were machined including component parts that were designed for, and tested at, the Nevada Test Site. These full-size parts were of the type that would be manufactured for weapons production.

Results

Upper Oxygen Limit Tests

Test results for the safe upper oxygen limit during a plutonium machining operation showed that the glove-box oxygen level must increase to approximately 4.5% before plutonium ignition could occur. At this oxygen level the burning of the plutonium was concentrated in the turnings (metal chips) as they fell from the part. As the turnings burned, they quickly changed to Pu_2O_3 as the heat caused by the friction of the cutting tool in combination with the 4.5% oxygen created the critical mix of plutonium, heat, and oxygen needed for combustion. Experience with plutonium machining and occasional “fires” has shown that fires are indeed associated with chips only. This concentration of heat energy, approximately 80%, occurs because of the friction between the cutting tool rake face and the chip, typically resulting in tool crater wear. Because maximum temperatures are located away from the cutting tool edge,[2] the plutonium part does not receive the frictional heat energy that is carried away with the chips. The experimental results, in combination with plutonium chip fire experience, were used to establish a maximum oxygen level of 3% for dry machining of plutonium parts.

Machining Tests

Results from the machining tests showed no detectable differences in quality between parts machined without cutting fluids and those machined with fluids. The dry-machined parts were inspected on a AA-gage, a rotary contour inspection machine, that produced inspection data consistent with data from parts machined with cutting fluids. No quantitative surface finish data could be gathered because no equipment exists in glove boxes at Los Alamos to perform this inspection. However, experienced inspectors estimated the surface finish to be as good as parts machined with cutting fluids.

Test parts, along with production parts, showed that, when facing operations are required, dry machining plutonium can gall (or tear) the material at the center line of the rotating part. Generally, the size of this defect was approximately 0.050 inches wide by 0.000080 inches deep, and this defect appeared in approximately 30% of all parts that required this type of operation. Although these plutonium parts pass inspection criteria, they do not meet the approval of the Los Alamos user. The physicists and engineers who design the components for testing at the Nevada Test Site require these components to surpass weapons-grade specifications, physically and visually. This anomaly may cause a part to be rejected even though the part meets weapons-grade specifications. However, a small amount of light oil swiped on the surface eliminated any galling.

The positive test results for machining convinced Los Alamos to adopt dry machining as the alternative to producing parts with an argon / freon mist system for all Nevada Test Site components and for related Los Alamos machining activities. About 85% of all plutonium components are dry machined. The remaining 15% require a light coat of oil to eliminate the potential for microinch tearing during the final cut.

The light coat of oil is brushed on the part just prior to performing the finish cut. The oil-contaminated chips, kept separate from the dry-machined chips, are cleaned with a small amount of freon. The oil-free chips are then melt-consolidated under calcium chloride to produce a plutonium button ready for further processing.

Nitride Investigations

Exposing plutonium to a nitrogen atmosphere at elevated temperatures for extended periods of time can create a compound called plutonium nitride. Plutonium nitride is extremely unstable in air and readily forms a hydrated oxide. Plutonium oxide can deteriorate the plutonium metal surface, reduce density, and increase part weight.

However, the temperatures and time required to form even small amounts of a nitride compound are quite high. Experimental results have shown that 3% nitride is formed at 625 °C after 16 hours of exposure to nitrogen.[3] Estimates of temperatures at the tool part interface are significantly lower, approximately 300 – 400 °C, while cutting tool contact times are approximately microseconds.[2,4] Therefore, even at 400 °C the creation of any significant amount of plutonium nitride is highly improbable because the nitride does not have adequate time to form. Additionally, no rapid formation of oxide has been observed on dry-machined plutonium. Observations of dry-machined parts have taken place over time periods of up to one year. Certainly, if significant amounts of nitride were formed during dry machining a yellow-green oxide growth would quickly attack the outer surface and would be readily visible. The empirical and physical evidence clearly shows that the formation of plutonium nitride during the dry-machining process is insignificant.

Waste Minimization and Other Benefits

Benefits from dry machining of plutonium parts include improved part quality, a significant decrease in chlorofluorocarbon releases, and significant mixed waste reduction.

Part quality at Los Alamos was enhanced by eliminating the freon mist that produced a localized cooling effect. This localized cooling physically reduced the part size in the immediate area of coolant application during machining and thus produced out-of-tolerance conditions.

Currently, plutonium dry machining activities at Los Alamos use approximately one liter of freon annually, as contrasted with the 50 liters required for the argon/freon mist system. The 20 cubic centimeters of oil now introduced annually into the machining process easily meets current regulations.

Flood cooling techniques at Rocky Flats created 2500 gallons of mixed waste oils each year and required the use of approximately 7800 gallons of carbon tetrachloride to clean the oil-contaminated chips, machine tools, and parts. Application of the dry machining techniques outlined in this report (adjusted for the number of units machined at Rocky Flats) would entirely eliminate hazardous (carcinogenic) carbon tetrachloride use, reduce the amount of mixed waste oils to approximately 1.25 gallons per year, and produce approximately 50 gallons of waste freon each year. Obviously, dry machining techniques will complement the future plutonium production processes.

Ongoing Research

The current trend in environmental legislation clearly shows that the small amount of oil and freon required for the dry machining process should be eliminated. Plutonium machining research and development efforts are addressing this issue. Efforts include the investigation of diamond turning techniques to increase the cutting tool edge quality and to reduce friction on the rake face. These performance improvements should produce a better surface finish as the tool approaches the center line of a rotating part. Changing spindle speeds and cutting tool feed rates should improve the surface finish in a slow-speed cutting operation. Alternative cutting fluids are also being explored, and this search has lead to a solvent called SF2I, developed by the 3-M Company. This solvent, originally tested at the Atomic Weapons Establishment in Aldermasten, England, shows promising results for plutonium machining operations. It will be further tested at Los Alamos for application as a coolant for machining operations, such as sawing, drilling, and milling.♦

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Technical Issues in Plutonium Storage

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Plutonium Metallurgy

Introduction

The retirement of large numbers of nuclear weapons necessitates the management of an unprecedented quantity of excess plutonium. Surplus materials from production and reprocessing operations will add to the amount of concentrated plutonium that must be stored on an interim basis until a decision regarding ultimate disposition is made. Traditionally, the weapons complex faced a scarcity of plutonium. Thus, the future course is unfamiliar. An evaluation of technical issues is needed to develop a basis for storage decisions. Identification of acceptable storage options is a prerequisite to the definition of standards, procedures, and facilities for storage.

The selection of suitable storage options is a complex task impacted by political and economic concerns as well as technical issues. Many factors influence decisions on plutonium storage; however, emphasis is often placed on a narrow set of issues, such as perceived proliferation resistance or some specific hazard. A comprehensive examination should include topics such as the potential for remediation of hazards, the maintenance of flexibility for ultimate disposition, and the cost of implementation.

A consideration of cost must extend beyond the initial expenditures for research, development, and capital investment in facilities to other factors that contribute to the total expense of the operation. A thorough assessment must include not only the cost of addressing radiation exposure and contamination control but also the cost of other environmental, safety, and health (ES&H) issues. For example, disposal of radioactive waste constitutes a major and increasingly larger fraction of the total operating cost of a plutonium facility. The amount of waste that must be considered includes that produced during normal facility operation as well as that generated during facility modification and decommissioning.

In this report, an assessment of issues relevant to plutonium storage is presented in order to provide a *technical* basis for addressing complex interfaces with political and economic issues and for identifying suitable storage options for excess plutonium. An effort is made to summarize the merits of alternative approaches and to establish a qualitative ranking of options for an interim storage period of up to one hundred years. This work focuses on plutonium extracted from weapons. It is important to note that this source represents the minority of available plutonium. Considerable quantities of reactor-grade plutonium are found throughout the world and represent a significant environmental and proliferation risk. Narrow solutions that only address material extracted from weapons may fail in the larger context of a worldwide plutonium economy.

> *“In this report, an assessment of issues relevant to plutonium storage is presented in order to provide a technical basis for addressing complex interfaces with political and economic issues and for identifying suitable storage options for excess plutonium.”*

Technical Issues

Consideration of a broad range of issues is necessary for assessing plutonium storage options. A summary of the major issues is included to provide a comprehensive perspective.

Proliferation of nuclear weapons capability by major nuclear states, aspiring nations, or subnational groups presents a serious threat to world order and stability. The selection of storage options is complicated by political pressures demanding that a technical remedy be found to prevent proliferation. The level of interdiction required to prevent an existing nuclear state from rapidly reconstructing a nuclear arsenal from intact pits differs from that required to prevent a subnational group from fabricating a nuclear device from diverted plutonium. The goal is simple: select a physical or chemical storage form that cannot be directly used in fabricating a fission weapon and that cannot be processed into a usable form. Unfortunately, there is no technical solution that achieves this result.

ES&H issues encompass a spectrum of issues that extend well beyond identification of hazards and waste streams. A credible evaluation must examine possible methods of hazard remediation and weigh the advantages of their implementation against the disadvantages. An important means for minimizing ES&H risk is the avoidance of all unnecessary process operations.

Credible interim storage options must be technically feasible and capable of near-term implementation. Even if an option is technically feasible, it may be impractical due to excessive costs or limited availability of key resources or material. Evaluation of a storage option is hindered by lack of knowledge about material properties, hazards, or process operations. Previous experience with a given option is particularly valuable and is given appropriate consideration in this assessment.

Storage options that change the chemical form of the plutonium have especially far-reaching impacts on the total cost. In all likelihood, the interim storage form will not be identical to that chosen for final disposition. Additional processing may ultimately be necessary. Interim conversion from one form to another amplifies this problem, particularly if the form is significantly diluted. The advantage of avoiding chemical processing is clearly reflected in the cost because a unique facility is usually required for each process. Such facilities are necessary because most chemical processes are cyclic instead of reversible. For example, the technologies and process equipment used for converting metal to oxide are different from those for reducing oxide to metal. The processing facility must first be configured for preparing the desired storage form and then reconfigured for preparing material for reuse or final disposition. Finally, a realistic assessment must include decontamination and decommissioning of interim processes as well as installation, operation, and decommissioning of any subsequent facilities. The impact of such operations on cost, including waste generation during the entire cycle, must be weighed against that of storing material in its existing form until specifications for final disposition are defined.

The issue of special nuclear material (SNM) control also merits examination. In addition to existing standards for accountability and verification of plutonium inventory, increased transparency requirements are anticipated during an extended storage period. Certain options are more amenable to accountability than others because the chemical form of the stored material is homogeneous. Whereas plutonium metal and compounds formed by gas-solid reactions tend to be homogeneous, compounds prepared by condensed-phase reactions or pyrolysis of precipitates are frequently inhomogeneous and thus more difficult to inventory and verify. Such assay and measurement is particularly difficult for dilute plutonium forms, especially those mixed with other radioactive elements.

A final consideration involves contingency planning and preservation of flexibility for final disposition. Certain physical and chemical forms are more suitable for a rapid, low-cost response than others. Maximum flexibility is achieved by storing a form that requires minimum processing for interim storage, but this ability to respond stands in conflict with a desire for increased proliferation resistance. Existence of the necessary technology base for processing and verification within Complex 21 are important factors.

The options examined for storage of excess plutonium fall into three categories:

1) storage as intact pits,
2) storage as altered pits, and
3) storage as extracted material.

An assessment of each category is presented below.

Intact Pits

Storage of plutonium as intact pits is an approach that employs the intrinsic characteristics that made the pit suitable for extended storage in a weapon configuration. These features include a critically safe plutonium geometry, a known nuclear material inventory, and a durable, hermetically sealed containment vessel with certified closures. A plutonium facility is not needed for implementation of this option but is required for surveillance and disassembly of pits that are identified as unsuitable for continued storage.

Storage as intact pits has distinct advantages for all technical issues. Hazards and ES&H risks are minimal. The pit is a well-certified containment vessel, and feasibility is certain and supported by an extensive and excellent history of storage in the weapons stockpile. The desirability of intact pit storage is reflected in the comments of a long-time production worker from the Rocky Flat’s Plant: “We don’t build triggers for nuclear weapons. We build the safest, most certified, best characterized storage containers for plutonium known to man.” This option preserves maximum flexibility and is the most cost-effective option due to limited facility requirements and the absence of radioactive waste generation.

In terms of proliferation resistance, pit storage is often considered highly undesirable because of the possibility for diversion and use in a nuclear device. However, the potential for utilizing diverted plutonium from other storage configurations is comparable to that for an intact pit. The availability of intact pits for reconstruction of a large arsenal by a major nuclear state may not be of concern because the production rate of weapon systems is influenced by operations other than pit fabrication. Indeed, experts in nonproliferation and arms control point to the fabrication of delivery systems as the rate-limiting step in the reconstruction of a superpower’s nuclear arsenal. Fabrication of the warhead has little if any impact on the time required to reconstitute a large stockpile. In fact, this very observation is reflected in the numerous arms control treaties signed by the United States and the former Soviet Union. START I, START II, and the INF treaties all address the disposition of delivery vehicles but have no provisions or protocols for destruction of actual nuclear warheads.

Storage of plutonium as intact pits is preferred by the scientific community over all other options under consideration. Nonetheless, the political cost and perceptions associated with storage of intact pits may override the technical issues and prevent its ultimate implementation.

Altered Pits

Pit alteration is an approach that focuses on retaining advantageous pit features such as nuclear material containment while destroying the suitability for direct reuse. Two levels of alteration are proposed:

1) modification of nuclear geometries by mechanical or physical methods, and
2) modification of nuclear geometries and material properties by chemical methods.

Whereas mechanical and physical methods include deformation and insertion of inert materials to prevent direct reuse in weapons fabrication, chemical methods are designed to hinder or deny reuse by also forming plutonium compounds that are difficult to reconstitute to a usable form. Suggested chemical methods include *in situ* formation of a product such as hydride, oxide, nitride, or alloy.

A detailed discussion of specific methods is beyond the scope of this paper.

Alteration methods may be capable of denying the rapid reconstruction of an arsenal under very specific scenarios, but the utility of alteration as a means of preventing proliferation by nonnuclear states and terrorist groups is doubtful. To varying degrees, mechanical, physical, and chemical alteration methods only extend the length of time between diversion and reconstitution of material into a usable form. Estimates of the time required for such reconstitution have been made, but in no case do they provide a significant barrier to extraction and purification of nuclear material. The technologies required to reform metal and to reprocess suggested chemical forms into metal are well known and can be implemented at low cost, especially if ES&H risks are disregarded.

Although pit alteration methods may provide a small measure of proliferation resistance (essentially in the political message they might send), this gain must be weighed against the disadvantages. As noted previously, an important advantage of pit alteration is retention of the pit as a storage vessel; however, the certified integrity of the container is destroyed by all methods requiring access to the pit interior. The potential for release of nuclear materials during those operations will undoubtedly require use of a plutonium-handling facility and implementation of a certification procedure for reclosure.

Verification of pit disablement could be accomplished by a number of nonintrusive methods that would not compromise classified information.

Risk and cost are significantly increased by use of chemical methods that involve injection of reactive solids, liquids, or gases into the pit. Useful reactions must be complete in a reasonable time period to maintain process throughput. Difficulties arise because of thermodynamic and kinetic factors. In some cases, the reactions are highly exothermic (for example, $\Delta H°_f$ of PuO_2 = -252 kcal/mol), and the likelihood of excessive temperatures would require control of processing rate and heat flow to prevent thermally induced failure of pits as containment vessels. Other reactions proceed at prohibitively slow rates, and excessively high temperatures would be required to promote those processes. None of the proposed chemical reactions has an appropriate rate at room temperature, and none of the methods is sufficiently developed to permit a thorough assessment of hazards, assessment of stability during extended storage, identification of the difficulties in reprocessing for final disposition, or estimation of waste generation levels.

Extracted Material

Extraction of plutonium destroys the pit configuration and permits a broad range of candidate forms to be considered for storage. The absence of classified shapes facilitates transparency in storage, but verification of material transfer during extraction remains a concern.

The thermodynamic and kinetic complications cited for *in situ* alteration are eliminated by flexibility in the design of process equipment. As with chemical alteration, the desirability of storing selected material forms resides in the potential for preventing reuse and/or reprocessing of plutonium. Placement of plutonium in a dilute form such as a fused silica matrix or as a mixture containing high-level radioactive waste does not prevent its recovery by a motivated group but would significantly hinder further United States processing because of stringent ES&H concerns. A decision to store plutonium in such forms is essentially equivalent to selecting an option for final disposition and must be carefully considered as an option for interim storage.

A qualitative assessment of issues for candidate storage forms of extracted plutonium is presented in Table I. In addition to the plutonium compounds mentioned in the discussion of chemical alteration, the candidate storage forms include plutonium metal, plutonium dicarbide, and a mixed plutonium-uranium oxide. Results of the evaluation are particularly significant; none of the candidate forms prevent proliferation, and differences in time periods required for reprocessing are small.

Table I. Qualitative Assessment of Issues for Candidate Storage Forms of Extracted Plutonium

Candidate Forms	Proliferation Resistant	Potential Hazards	Remediation Available	Anticipated Total Cost	Ease of SNM Accountability	Storage Experience	Flexibility
metal	no	yes	yes	low	high	extensive	high
oxide	no	yes	yes	moderate	good	high	reduced
mixed oxide	no	yes	yes	high	reduced	modest	low
dicarbide	no	yes (?)	no (?)	high	very low	limited	reduced
nitrite	no	yes (?)	no (?)	high	low	limited	reduced
hydride	no	yes*	no	low	low	limited	high
alloys	no	yes (?)	no (?)	high	very low	none	low

(?) Insufficient data is available.

*Candidate form is especially hazardous because of pyrophoricity.

Since all candidate forms have potential ES&H hazards, the selection of suitable storage forms hinges on the remaining issues in Table I. The deciding factors are availability of methods for hazard remediation, total cost, and storage experience. The assessment of cost includes the loss of flexibility and the economic impact of first processing for storage and then reprocessing for final disposition. Cost is driven by the need to develop both processing and reprocessing technologies, to install and replace process facilities, and to dispose of associated radioactive waste. The low assessment of flexibility for mixed oxide and alloys arises because reprocessing involves dissolution in aqueous media and subsequent isolation of plutonium by ion exchange or solvent extraction. Other candidate forms are directly recovered by pyrochemical methods.

Results in Table I suggest that two storage forms, metal and oxide, are the favored candidates for interim storage. The remaining discussion of extracted plutonium focuses on these materials.

Plutonium metal is an acceptable form for interim storage. Although metal is often viewed as a highly undesirable storage form because of proliferation concerns, the technical assessment indicates that its proliferation resistance is comparable to that of oxide. Potential hazards identified for metal storage include chemical reactivity, dispersal of radioactive contamination, and pressurization of the storage container. The primary hazard is the chemical reactivity of metal in air and the potential for pyrophoric ignition.

The oxidation rate of plutonium metal is modest and controlled by a protective oxide layer at temperatures up to 450 °C. The oxidation rate in air is constant (0.2 g $PuO_2/cm^2/min$) at temperatures above 500 °C.[1] A recent analysis of ignition data from literature sources shows that massive (greater than 0.2-mm-thick) plutonium becomes pyrophoric only at temperatures near 500 °C.[2] Plutonium fines and foils ignite when heated to 150–200 °C and are not suitable for storage. Oxidation of plutonium is prevented by storage in sealed metal containers with certified closures.

The remaining potential hazards identified for storage of plutonium metal do not present serious ES&H risks. Metal is not a dispersible form of plutonium and must be oxidized before entrainment is possible. The oxidation rate at room temperature is such that dispersible particles are released from clean metal only after several days in moist air at room temperature.[3] Above 500 °C, air oxidation of a typical 4-kg metal casting by the constant-rate process is complete after several hours, but less than 0.1 mass percent of the oxide product exists as particles with sizes in the dispersible range below 10-µm geometric diameter.

Hydrogen and other gases formed by alpha radiolysis of plastics and organic materials in the storage environment are not a hazardous pressurization source because they are gettered by reaction with plutonium. The products of these reactions frequently include plutonium hydride and sesquioxide that present pyrophoricity hazards upon exposure to air. Rupture of a storage container is possible if it is not hermetically sealed and pressure is exerted by expansion of the oxide product.

Assessments of the remaining issues for metal storage are favorable. Experience gained from storage of thousands of pits defines the conditions required for extended storage of metal and demonstrates that such storage is remarkably free of problems. SNM accountability is facile, maximum flexibility is preserved, and minimal waste is generated by storage of metal. The cost of a processing facility is minimal because metal storage is compatible with the pyrochemical technologies of the Complex 21 baseline. If any extracted form (metal, oxide, or other) is selected for storage, the throughput capacity of the metal extraction facility must be appropriate to process the inventory of retired pits in a timely manner that cannot exceed the projected lifetime of the facility.

Plutonium dioxide is also an acceptable storage form. The proliferation risk of oxide is considered equivalent to that of plutonium because the metal is readily reconstituted by methods such as direct oxide reduction (DOR) using commercially available chemicals and equipment. Plutonium dioxide is generally considered to be a stable and inert material, but concerns arise because of the high surface area and tenacious adsorption of molecular species including water, organic compounds, and atmospheric constituents. Process oxides formed by pyrolysis of precipitates such as oxalate, nitrate, or peroxide have specific surface areas from 20 to 60 m^2 per gram[4] and chemisorb several mass percent of water.[5] The removal of adsorbates including water is accomplished by heating the oxide at 1000 °C.[6]

Potential pressurization hazards during oxide storage arise from gases generated by radiolytic and chemical reactions. Alpha-induced decomposition of adsorbates and organic materials forms gaseous products including H_2, CO, and HCl. A single monolayer of water, which can be readily readsorbed on an oxide surface if adequate precautions are not taken after firing, is capable of generating 5 to 10 atm of pressure in a typical storage container over time.[3] Although the dioxide is generally considered to be thermodynamically stable, a recent study shows that the dioxide reacts with water to form H_2 and $PuO_{2.2}$, a compound containing Pu(VI).[7] Although the kinetics of these radiolytic and chemical processes are unknown and cannot be accurately predicted, the rate of helium formation from decay of plutonium-239 is well defined.[8] This decay product, which is retained as bubbles in massive plutonium metal and released from oxide powder, increases the internal pressure of an oxide container by about 1 atm over a hundred-year period. An additional pressurization hazard encountered during short-term storage and transportation arises from desorption of molecular species at elevated temperatures created by self-heating or fire.[3] Use of vented storage containers provides a method for releasing pressure during storage, but radiolysis of air produces high concentrations of gaseous nitrogen oxides that are highly corrosive in the presence of moisture.

Assessment of hazards associated with plutonium storage indicates that the greatest environmental risk arises from dispersal of process oxide following a container rupture or a spill.[5] This conclusion is based on particle size data showing that 100 mass percent of a process oxide is in the dispersible range. The dispersal risk is a thousand times greater for process oxide than for the worst-case incident with metal. Possible methods of remediation include sintering of oxide powders to increase the effective particle size and hot-pressing of oxide into briquettes; however, the cost and waste consequences of these operations must be carefully evaluated.

Remaining issues related to oxide storage include nuclear materials accountability, storage experience, and flexibility. To varying degrees each of these issues impacts the others and the cost. Variations from 1 to 10 mass percent are observed in the plutonium content of process oxides because of differences in the amount of unpyrolyzed anions remaining after firing.[4] Although such complications with material accountability are well known, storage experience for oxide is limited and procedures for outgassing and certifying oxides prior to storage are poorly defined. If oxide is adopted as the only storage form for extracted plutonium, the processing facility must be appropriately sized and include an additional capability for efficiently converting extracted metal to oxide. The aqueous recovery technologies in the Complex 21 baseline produce oxide but are designed for treating residues and pyrochemical salts, not for oxidizing large quantities of metal. If only oxide is stored, the potential impact on cost and waste will be large.

Conclusions

The selection of an option for interim plutonium storage on the basis of proliferation resistance cannot be justified on a technical basis. Alteration measures are considered effective in forcing a nuclear state to refabricate pits before reconstructing a large arsenal, but that delay may not limit the rate at which weapons are produced. The value of chemical alteration of pits and reaction of extracted plutonium to form proliferation-resistant material forms is questionable because reconstitution of candidate materials to usable forms is facile. Furthermore, most candidate forms could probably be used for constructing a nuclear device without being reconstituted. Adequate safeguards and security provide the only effective method for preventing diversion and reuse of nuclear materials.

The formulation of a comprehensive strategy is essential for achieving the goal of plutonium processing with minimal waste. Storage of excess plutonium must be included in that strategy. Development and implementation of advanced technologies that reduce the quantities of radioactive waste produced and those that provide capability for decontaminating waste are essential components of the strategy. The maximum impact on waste generation may be realized by applying a simple intuitive approach: avoid all unnecessary processing. Consequently, plutonium that is to be placed in interim storage should remain in its existing form; reprocessing and interconversion of chemical forms should be avoided unless a potentially hazardous situation exists.

A comprehensive strategy must also consider forms of plutonium that are not part of the present assessment. Such materials include incinerator ash, pyrochemical salts, anode heels, etc., that are presently in storage at several DOE sites. The situation is extremely complex and application of general guidelines may not be appropriate. Further evaluation of these areas is clearly needed.

The present technical assessment provides a basis for general recommendations on interim storage of plutonium. Both metal and oxide are acceptable storage forms. Storage of metal as intact pits is preferred. In the absence of a suitable plutonium handling facility, intact storage is the only near-term option. If interim storage of intact pits is deemed unacceptable, storage as extracted metal is preferred. Storage as altered pits is the least desirable option. If alteration of pits is necessary, only mechanical or physical methods that preserve the integrity of containment are acceptable. Metal and process oxide should be stored in their existing forms after preparation and certification for storage. All storage vessels should be hermetically sealed and should exclude organic and other covalently bound materials. Regardless of the storage option(s) employed, adequate and continuing surveillance will be necessary to identify potential problems.

Several technology areas need further definition and development. Continuation of efforts to upgrade process technologies for efficiency and waste minimization are essential. Additional work on the kinetic and equilibrium behavior of oxide adsorption is needed with emphasis on the conditions required for preparing, certifying, and packaging material for storage. Studies to define the chemical and radiolytic reactions between water and oxide are needed to predict long-term storage behavior. The merits of removing americium from extracted material prior to storage also requires evaluation. The storage of plutonium-containing residues needs to be addressed, and the consistency of storage decisions and Complex 21 design must be monitored.

In addition to providing a technical basis for selection of storage options, the present study helps to place waste issues and the role of technology development in perspective. Although development of new technologies for minimization and processing of radioactive waste is necessary, development of technical input for policy decisions is also essential to ensure that the objectives are consistent and complementary.◆

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Waste Management at Technical Area 55: A Historical Perspective and Status Report

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Nuclear Materials Processing:
Nitrate Systems

Introduction

In August 1992, the transuranic (TRU) waste management operations for the Nuclear Materials Technology (NMT) Division were transferred into the Nitrate Systems Group (NMT-2), one of nine operating units within the Division. In February 1993, all waste management activities at Technical Area 55 (TA-55) were consolidated. The areas of immediate concern were backlogged legacy waste items (low-level, TRU, and hazardous) stored in the basement of the Los Alamos Plutonium Facility in TA-55, cemented TRU waste drums stored at an off-site location, experimental radioactively contaminated vessels stored on the Plutonium Facility grounds, and oversized waste items stored in the Plutonium Facility basement. Communication was initiated with the Laboratory's Waste Management Group (CST-7) to discuss options for resolving these issues. This report describes the technical, regulatory, and administrative actions and accomplishments that allowed NMT Division to effectively address these important issues. Activities in the pursuance of waste minimization goals are also reviewed.

"The areas of immediate concern were backlogged legacy waste items (low-level, TRU, and hazardous) stored in the basement of the Los Alamos Plutonium Facility at TA-55, cemented TRU waste drums stored at an off-site location, experimental radioactively contaminated vessels stored in the Plutonium Facility yard, and oversized waste items stored in the Plutonium Facility basement."

Background

Waste management at the Plutonium Facility was one function of the old Nuclear Materials Management Group (NMT-7). The group was responsible for such diverse activities as shipping and receiving, nuclear material storage, roasting and blending of reactor fuels, and the development of a site-wide nuclear materials model (in support of Complex 21 planning) to forecast the impact of new technologies on scrap inventories and waste generation. With limited personnel resources and diverse operations, group staff could not keep up with the steadily increasing requirements and demands of waste management regulations. Likewise, personnel resources were not available to assign additional technicians to waste management activities as needed to address the resulting operational demands and problems. Thus, waste management personnel were faced with a variety of seemingly insoluble problems without the resources to explore and implement solutions.

Waste Management Issues

A variety of difficulties in several operations had developed in the waste management program at the Plutonium Facility. These problems, outlined below, threatened waste certification and shipment of TRU, mixed, and low-level waste to the Laboratory's interim storage facility and low-level waste disposal site, TA-54.

Water Release from Cemented TRU Waste. In June of 1989, free liquid was found on the top of a drum of cemented TRU waste in the basement of the Plutonium Facility. Analysis indicated that this liquid worked its way up through the carbon filter from the inside of the drum. This clear violation of the Waste Acceptance Criteria for the Waste Isolation Pilot Plant (WIPP), criteria that bar free liquids from waste packages, immediately brought into question the integrity of the 350 waste drums that had been immobilized using the gypsum cement process.

Prohibitive Packaging Limits for ^{238}Pu Waste. Transportation safety requires that materials moved by highway, in this case TRU wastes transported in the TRUPACT II overpack (Department of Transportation Type B shipping package), must not contain flammable or explosive mixtures of gasses. A primary source of flammable gas in TRU waste is hydrogen from alpha radiolysis of hydrogenous materials in the waste matrix. Plutonium-238 has the highest specific activity (which is directly proportional to the gas generation rate) of the plutonium isotopes handled at TA-55 and, consequently, has the lowest allowable concentration limits in WIPP waste packages. Packaged TRU wastes, especially those in multilayer packaging configurations, did not meet the Waste Acceptance Criteria for WIPP and, therefore, were not certifiable or suitable for storage at TA-54.

Lack of Suitable Nondestructive Assay Capabilities for ^{235}U Waste. Another complex issue involved the nondestructive assay of waste packages containing uranium-235 as a co-contaminant with plutonium from mixed oxide fuel processing operations. At the time of this waste generation, no suitable nondestructive assay capability existed at the Plutonium Facility. But the Safeguards Assay Group (N-1), who is the vanguard of nuclear material detection technology development at the Laboratory, assayed about two dozen of these drums for uranium-235 content. This operation was outside of the domain of the Laboratory TRU waste program and, consequently, outside of the integral quality assurance program. This technicality had to be resolved before the uranium Special Nuclear Material (SNM) assays could be judged acceptable and waste could be certified for storage at TA-54.

Nonconforming ^{239}Pu Waste Drums. An inventory of two dozen nonconforming plutonium-239 waste drums (due to either SNM or weight comparison discrepancies) had accumulated in basement storage areas of the Plutonium Facility. The particular discrepancies could not be investigated and resolved due to limited staffing and the pressures of keeping up with the steady stream of waste generated from plutonium processing operations.

Accumulation of Oversized TRU Waste. An accumulation of oversized waste items (bigger than would fit in 55-gallon drums), requiring either size reduction or packaging in standard waste boxes, filled storage areas in the basement of the Plutonium Facility. Shortage of personnel available to support the TRU oversized waste operation also contributed to this waste problem.

Accumulation of Contaminated Experimental Vessels. A collection of radioactively contaminated experimental vessels dating back to the 1960s was being laboriously decontaminated by a team of NMT-2 technicians and was accumulating in the yard of TA-55. Methods of preparing the vessels for transportation and storage at TA-54 had not been established with the CST-7 Waste Management Group. Additional requirements that had to be met to transfer the vessels out of the Plutonium Facility needed to be negotiated as well.

Accumulation of Contaminated Glove Boxes. For four years, glove boxes from decontamination and decommissioning operations in the Plutonium Facility had been crated in plywood crates and moved out into the TA-55 yard for interim storage. As in the case of the experimental vessels, additional documentation or preparation that would be required to move the glove boxes off-site had not been established.

The destination of the glove boxes would be the TA-50 Size Reduction Facility where they would be cut into pieces and consequently repackaged in acceptable waste containers (55-gallon drums or standard waste boxes). Water had accumulated in some boxes from prolonged exposure to the elements and would have to be analyzed and removed from the packages before shipment.

Accumulation of Low-Level Oversized Waste. Low-level oversized waste, packaged in 4-ft x 4-ft x 8-ft plywood boxes, had likewise accumulated in the TA-55 yard, totaling thirty-six boxes. These waste packages added to the congestion of materials in the yard and occupied valuable space.

Thus, waste items were stalling in the "pipeline" that processed, packaged, and funneled waste items to the waste management storage and disposal site at TA-54. As a result of these difficulties, waste operations at TA-55 were coming to a halt and were threatening the research programs that generated the waste. Resources had to be reallocated immediately to alleviate this situation.

New Regulatory Setting

In the spring of 1992 both the Department of Energy (DOE) and the Environmental Protection Agency (EPA) realized that an agreement must be reached concerning Resource Conservation and Recovery Act (RCRA) compliance (which dealt with hazardous waste issues) at DOE Weapons Complex sites; therefore, a commitment to draft a Federal Facility Compliance Agreement (FFCA) was made. The DOE also made an agreement with the EPA to cease generating hazardous and, consequently, mixed wastes from all defense operations. This decision effectively shut down most radiochemical processes at the Plutonium Facility as of May 8, 1992. The moratorium on mixed waste generation presented both a challenge to and an opportunity for the TA-55 mission. At a time when waste management needed manpower to resolve growing waste problems, processing operations were curtailed, resulting in idled personnel that, potentially, could be reassigned to address this need.

Group Reorganization

Division resources were immediately put to work on waste management problems at TA-55. The TRU liquid and solid waste operations were transferred to the NMT-2 Nitrate Systems Group and placed under the Nitrate Processing Team Leaders. This decision was based upon the fact that NMT-2 produced most of the waste being processed, and nitrate operations personnel had intimate knowledge of the waste produced. NMT-2 group management also had a no-nonsense reputation for defining and solving problems; furthermore, many of the personnel idled by the moratorium on mixed waste generation were NMT-2 employees. Responsibility for the Plutonium Facility basement storage and low-level waste activities and the TA-55 yard storage areas was transferred to the NMT-8 Facilities Management Group, since these functions matched NMT-8's mission better. And the shipping and receiving operations were transferred to the NMT-4 Nuclear Materials Measurements and Accountability Group.

Not all aspects of the reorganization were positive. The dissolution of the NMT-7 Nuclear Materials Management Group resulted in time-consuming attempts to coordinate interrelated Facility waste management operations that were now located in separate Laboratory host groups. The reorganization also resulted in the loss of experienced waste management personnel; out of thirty personnel originally in the NMT-7 Group, approximately half chose to transfer to other types of positions rather than move with the waste management functions assigned to other NMT groups. New technicians and staff hired to replace them required site- and operation-specific training before assuming their duties.

Waste Management Solutions

The concentration of NMT-2 resources on waste management problems at TA-55 over the past year and a half has yielded dramatic results. Waste management operations are staffing up to realistic levels to handle the workload, and personnel are being certified in their operations.

Dialog has been reestablished with the Laboratory waste management and environmental compliance organizations, providing a means of resolving problems in a mutually agreeable manner. And legacy waste issues are being resolved: old wastes are being remediated and sent to TA-54 for storage, and procedures are being modified to avoid similar future problems. Solutions to the waste management problems outlined earlier in this paper are given below.

Repackaging of Cemented TRU Waste Drums. Drums of cemented TRU waste suspected of containing free liquid were returned to TA-55 (point of generation) from interim storage at TA-54. Because there was not enough room for the returning drums in the Plutonium Facility basement, additional space for drum storage was arranged at the Chemical and Material Research (CMR) building. The first challenge was to determine the extent of the problem; the next challenge was to find the cause of the water release from the cement monoliths. Three drums were found to contain significant quantities of free water attributable to variances in the cement mixing process. Small quantities of water vapor are normally released during the cement curing process by the heat of hydration and sometimes condense on the inside of the plastic liner. Samples of the liquid were found to contain very little radioactivity. The plutonium is effectively immobilized in the cement, even though free liquid may appear. NMT personnel negotiated with the CST-7 Waste Management Group for a waiting period of 84 weeks before shipment to TA-54, the approximate time for the cement curing process based upon earlier research by NMT personnel. Waste management personnel would then visually confirm the absence of free liquids before shipment to TA-54. Any packages in which moisture was observed or that could not be inspected (such as drums containing one-gallon cans) would require overpacking. The drums stored in the CMR building were visually examined where possible and then overpacked in polyethylene-lined 83-gallon drums, and the annulus was filled with absorbent materials. CMR repackaging operations were conducted in September and October 1993; shipment of all 218 of the CMR drums was completed the first week of October. To date, 107 drums in the Plutonium Facility basement storage areas have been held the requisite time, visually examined, and shipped to TA-54 for storage; the remaining drums should be shipped out shortly after the beginning of 1994.

Research on the gypsum cement process and on the alternative return to portland cement is being conducted. Research into the portland cement process requires addressing the control of process-related ammonium nitrate emissions. Experimental work is also being conducted on toxic metal retention, since the evaporator bottoms (the radioactive residues resulting from evaporation) contain RCRA-regulated concentrations of chromium, lead, and nickel.

Safe Storage Limits for ^{238}Pu Waste Drums. The NMT-9 Heat Source Technology Group has been conducting a research effort to determine the safe quantity of plutonium-238 allowed in waste packages. They have been researching existing literature, conducting experiments under controlled conditions, and doing headspace gas sampling (with the cooperation of NMT-2 waste management personnel) on legacy waste packages in the basement of the Plutonium Facility. Work that involves CST-1 Analytical Chemistry and CST-7 Waste Management and Benchmark will establish a reasonable storage limit that will ensure safe storage of plutonium-238 containing waste but that will exceed conservative TRUPACT-II Content Code (TRUCON) limits for shipment to WIPP. Storage requirements will be based upon waste matrix and containment layers. Legacy waste drums are being opened to confirm packaging configuration, and the first 10 drums of plutonium-238 waste are being prepared for shipment to TA-54 for interim storage.

Nondestructive Assay Capabilities for ^{235}U at TA-55. The WIPP waste program allows evaluation of certifiable wastes by instruments that can be proven to be equal in integrity to those used for waste assay within the approved TRU Waste Certification Program, including its integral quality assurance program. The N-1 nondestructive assay instrumentation and methods used in the uranium assay of the mixed plutonium/uranium drums were rated as equivalent to those used in the TRU Waste Certification Program.

These assays were then used to complete the paperwork packages, which were circulated for review and approval. In addition, the NMT-4 Nuclear Materials Measurements and Accountability Group completed programming and certification of one of the Segmented Gamma Scanning instruments, capable of assaying 55-gallon waste drums for uranium. This instrument was used to assay drums with low atomic weight waste matrices. Approximately half of the 40 mixed uranium/plutonium waste drums were assayed, the paperwork packages were completed, and the waste drums were sent to TA-54 for storage.

Inspection/Repackaging of ^{239}Pu Waste Drums. Nonconfirming plutonium-239 drums were organized into two major groups: (1) those for which the final gross drum weights did not match the sum of the individual item weights and the package tare (empty container weight), and (2) those for which the total drum SNM assay did not agree with the sum of the individual item SNM assays. Paper work was first examined for errors; if none could be found, then the drums were carefully opened and the items reweighed or reassayed as appropriate until the discrepant item was found. The package paperwork was then corrected and routed for reviews and approvals, allowing shipment to TA-54 for interim storage.

Decontamination/Repackaging of Oversized TRU Waste. Work is progressing on the disposal of oversized TRU waste items stored in the basement of the Plutonium Facility. In early 1993, a concerted effort was made to identify and categorize waste items in this area. Approximately a dozen items were decontaminated, repackaged, and disposed of as low-level waste. Seven items that were too large to fit in standard waste boxes were crated and are in the process of being assayed for SNM content by NMT-4. They will be shipped to TA-54 for interim storage pending the availability of the TA-50 Size Reduction Facility for processing waste.

Analysis/Decontamination of Experimental Vessels. The decontamination work being conducted by NMT-2 personnel on the experimental vessels has made steady progress, and at present, twenty vessels have been decontaminated. Two major determinations that had to be made prior to disposal were these:

(1) whether the vessel waste residues were TRU or low-level waste and
(2) whether the residues included mixed waste.

To make these decisions, NMT-2 personnel assumed that the contamination on the inside of the vessels was uniform and that the waste residues removed were representative of the contamination. Samples of these residues were sent to CST-1 for analysis, but analysis was delayed due to limited analysis capacity and low priority. Some of the samples took a year to be analyzed. Nondestructive assay of the vessels was challenging due to the thick steel walls and consequent attenuation of the radiation used to detect and quantify the radioisotopes in the waste. NMT-4 ran calibration tests and determined uncertainties based upon a series of experiments conducted on an uncontaminated vessel with a known source placed inside. This information was used to devise the counting scheme for the vessels, and the clean vessels were then assayed. Calculations were made based upon the weights of the vessels, the results of the RCRA constituents' analysis, and the nondestructive assay. Then the vessels were classified for disposal. In September, twelve 3-ft-diameter vessels were shipped to TA-54 for interim storage until the TA-50 Size Reduction Facility is able to process them. They will eventually be placed inside standard waste boxes, which are acceptable primary containers for TRUPACT II shipment to WIPP.

Removal of Contaminated Glove Boxes and Oversized, Low-Level Waste Boxes. The problem with the glove boxes and the 4-ft x 4-ft x 8-ft low-level waste boxes centered upon assembly of the proper documentation necessary for review and acceptance by the CST-7 Waste Management personnel. After consultation with CST-7, paperwork packages were prepared by NMT-2 waste management personnel, and shipments were scheduled. Some of the glove boxes that had been in storage and exposed to the environment for several years had water inside the crates, which had to be drained in a manner acceptable to waste management and health physics personnel. The thirty-six 4-ft x 4-ft x 8-ft boxes were shipped to TA-54 in March 1993, freeing considerable space in the yard for other purposes. The glove boxes, which required more preparation than the low-level waste boxes, were not shipped off-site until July 1993.

Waste Minimization

Waste in any form is expensive to package, document, treat, and dispose of; costs are escalating as regulations become more stringent, treatments become more exotic, and landfill space disappears. Waste minimization serves to reduce the expense of waste operations by avoiding or minimizing waste in the first place. It is also mandated by DOE Order 5820.2A, “Radioactive Waste Management,” and the Resource Conservation and Recovery Act.

The philosophy of waste minimization at the Los Alamos National Laboratory is defined by Administrative Procedure 10-8, “Waste Minimization.” To date, waste minimization efforts at TA-55 have been the responsibility of the waste generators. Personnel are encouraged in waste generator training to utilize waste minimization as the most desirable method of waste management in their operations. The generator has the responsibility to reduce waste not only in every day operations but also in designing future processes.

In the past, the need for waste minimization was addressed in each Safe Operating Procedure (SOP) as a self-contained section, but no coordinated effort was made to provide comprehensive and consistent guidance to all operations at TA-55.

Currently, a waste minimization plan for TA-55 is being written. This plan will provide guidance to all personnel (from office workers to plutonium processing technicians) whose operations generate waste on-site. The redundancy of addressing waste minimization in each SOP will be eliminated, and waste minimization information for all personnel and all operations will be consolidated into one source that can be revised expeditiously as warranted.

Performance indicators (PIs) are being investigated that would provide a measure of waste minimization at the Plutonium Facility. Information on past program performance has been largely qualitative because only information on waste leaving that facility has been recorded. Incorporation of PIs at TA-55 to measure waste minimization will require the commitment of manpower and computer time to track the requisite variables that comprise each PI.

Epilogue

Dramatic progress has been made in the waste management program at TA-55 over the past year. Reorganization of the waste management team and support by NMT-2 operations personnel and management has restored operational viability. Communication, vital in dealing with continually changing rules and regulations, has been reestablished and enhanced. Problematic legacy wastes have been addressed and remediated where possible, and the root causes have been identified to prevent recurrence. The number of technical staff and operations technicians is being increased to handle the workload, and new personnel are being trained on both regulations and practical aspects of operations. Much work has been accomplished over the past year, but even more waste issues are yet to be resolved. The waste management organization must learn to anticipate mandated changes and must plan for facility operation changes in such a way as to minimize the impact and burden to the primary objective of the Plutonium Facility: to provide to the DOE Weapons Complex first-rate research and development in actinide processing.♦

Future of Waste Management at the Los Alamos Plutonium Facility

Ronald E. Wieneke
Nuclear Materials Processing:
Nitrate Systems

"We must find innovative ways of complying with environmental regulations while maintaining flexibility of operations and an emphasis on research."

Introduction

With the enactment of the Federal Facility Compliance Act of 1992 (FFCA), the national laboratories within the Department of Energy (DOE) weapons complex are no longer immune to fines for violating Environmental Protection Agency (EPA) hazardous waste regulations. The Federal Facility Compliance Agreement between the laboratories and their respective states will establish a timetable to achieve full compliance with existing requirements. If the agreed-upon milestones are not met, facilities and managers will be subject to civil and possibly criminal penalties for violations. Those who oversee operations that generate hazardous waste must move quickly to implement waste management systems, but restraint and good judgment will be required to avoid overburdening operations with excessive documentation.

The Plutonium Facility at Los Alamos National Laboratory strives to meet existing environmental regulations and to anticipate future requirements. We must find innovative ways of complying with environmental regulations while maintaining flexibility of operations and an emphasis on research. This enormous task can only be accomplished with a spirit of cooperation among those who generate, manage, and regulate waste. This requires cooperation among (1) waste generators and waste management personnel within the Plutonium Facility, (2) waste management and environmental compliance groups at Los Alamos, and (3) external regulatory agencies. A reasonable approach to the interpretation of regulations as they apply to the complexities of radiochemical processing operations is required at all levels.

The Plutonium Facility must look ahead and anticipate changes in requirements for the management of hazardous waste. Careful planning will be needed to give us time to act in harmony with our mission, rather than being forced to react to new requirements in ways that merely minimize adverse consequences.

Deadlines for Proper Storage and Treatment of Los Alamos Mixed Waste

The Federal Facility Compliance Act (FFCA) waives the doctrine of sovereign immunity for federal facilities, such as DOE contractors, with respect to enforcement of environmental regulations. This waiver allows civil and possible criminal penalties to be levied by the EPA. The FFCA in essence gives the EPA the teeth that it needs to enforce compliance with the Resource Conservation and Recovery Act (RCRA) for hazardous and mixed waste operations. Furthermore, the DOE has agreed to negotiate agreements with the respective state environmental agencies on how to implement RCRA at each facility.

Los Alamos must certify compliance with the storage criteria for transuranic (TRU) mixed waste by the end of January 1995 and must present a plan to the New Mexico Environmental Department (NMED) to establish treatment priorities for low-level mixed waste by the end of May 1995. The treatment and disposal of this waste is significantly complicated by the presence of radioactivity, as has already been demonstrated by the problems encountered with stored mixed waste at other DOE facilities. The ultimate treatment and disposal of mixed waste, which must be accomplished in a manner that protects employees, the public, and the environment, presents both a technological and financial challenge to the entire DOE weapons complex.

Cost and Complexity of Waste Disposal

Each kind of waste generated at the Plutonium Facility has its own set of complex requirements that must be met to allow disposal. Ever growing requirements will continue to escalate the costs related to characterization and disposal of waste. Even low-level radioactive waste, a relatively uncomplicated waste stream, will be more difficult and costly to dispose of in coming years as the Los Alamos low-level waste acceptance criteria become more stringent and landfill space is depleted. All personnel who generate waste must assure that no RCRA hazardous components have been inadvertently included in their low-level radioactive waste and must demonstrate control over their waste streams.

Mixed waste, waste that has both radioactive and hazardous components, is a much larger problem. DOE is severely limited in its ability to process mixed waste to meet the EPA waste treatment standards due to a finite number of viable mixed waste treatment options and a shortage of accessible treatment facilities. Despite these problems, waste must be treated in accordance with the EPA standards before disposal. Low-level mixed waste is required to be treated in accordance with 40 CFR Part-268, “Land Disposal Restrictions,” and disposed of in specially designed hazardous waste landfills. The landfills must incorporate all specified design features such as double liners, leachate collection and treatment systems, a leak detection system, and monitoring wells.

Disposal of TRU mixed waste should be easier, provided the Waste Isolation Pilot Plant (WIPP) is successful in obtaining a no-migration variance for the disposal phase. WIPP currently has a no-migration determination from the EPA for the test phase only. The disposal of mixed waste (both low-level and TRU) is costly, and those who generate waste must avoid the production of additional mixed waste whenever possible.

Documentation of Waste Through Process Knowledge

Process knowledge is the documented evidence provided by cognizant operating personnel of the presence or absence of hazardous compounds in their waste streams. This documentation is most effective when the process is very well defined and the composition of incoming process streams is well known. Documentation saves a significant amount of money by eliminating analytical tests for compounds that have not clearly been associated with the process. On the other hand, it is particularly damning when a hazardous compound or condition is discovered that was not disclosed in the process knowledge proclamation. Such a discovery throws a shadow of doubt over all wastes so characterized. For this reason, control over process knowledge documentation must be rigorously exercised.

The Plutonium Facility must document its processes carefully. All radioactive wastes must be precisely characterized to verify that no hazardous constituents other than radioactivity are present. DOE Order 5820.2A, “Radioactive Waste Management,” requires that waste disposal facilities know the contents of the waste that they are burying by establishing waste acceptance criteria for those sites that generate and ship the waste to them for disposal. In addition, generators must also know the hazardous component of the waste so that appropriate handling, storage, and treatment methods can be implemented.

Mixed waste must be carefully analyzed for both hazardous and radioactive constituents because disposal facilities must satisfy two sets of disposal site criteria. One of these is the prescriptive criteria of RCRA, which covers the hazardous component of the waste. The other is the performance-based criteria of 40 CFR 191, "Environmental Radiation Protection Standards for Management and Disposal of Spent Nuclear Fuel, High-Level and Transuranic Radioactive Wastes," which covers the radioactive components in the waste. To meet both of these criteria for a waste from an unknown source, the generator would have to perform a full spectrum RCRA analysis on mixed waste in accordance with EPA's SW-846, "Test Methods for Evaluating Solid Waste," as well as perform a comprehensive radioassay. Estimated cost of the RCRA analysis alone for a mixed waste could reach tens of thousands of dollars per sample. This estimate is not unreasonable considering the possible number of hazardous components, employment of techniques to reduce radiation exposure to operators, and the quality assurance requirements for samples and sampling protocols (including chain of custody). Process knowledge documentation is, therefore, an extremely important consideration from the aspect of cost reduction.

Impact of Waste Management on Research

As the requirements of waste management at the Plutonium Facility grow, the program must become more efficient. The Plutonium Facility mission is to perform basic and applied research in actinide chemistry and materials research in support of plutonium processing needs within the DOE weapons complex. Research at the Plutonium Facility benefits current operations involving cleanup and recovery of plutonium-bearing scrap, safe decommissioning of weapons components, and preparations for long-term Special Nuclear Material (SNM) storage. Research at the Plutonium Facility also provides the basis for the design effort of the next generation of DOE plutonium manufacturing facilities (Complex 21).

Meanwhile, requirements for handling, storing, and certifying waste are increasing the workload of process operations personnel. More time is required to complete the necessary documentation and maintain control over waste collection and storage at the Plutonium Facility. Every dollar that is spent for the documentation, treatment, handling, packaging, or disposal of waste is a dollar that cannot be used for research. In this age of shrinking research budgets and growing competition for assignments and funding between sites in the DOE complex, making optimum use of every funding dollar is essential. For this reason, new programs are being planned and initiated that will increase the effectiveness of the waste management operations at the Plutonium Facility.

Problems with Conflicting Regulations

The complexity of the operations at the Plutonium Facility can bring regulations from different agencies into conflict with each other. For example, what one agency may consider radioactive waste, another may view as valuable, recoverable scrap material. A significant portion of the material stored at the Plutonium Facility contains economically recoverable quantities of plutonium, but it may also fall under the RCRA definition of waste. This material, which is known as "scrap" with respect to plutonium recovery, is being stored until processing can resume. This situation has been aggravated by the changing mission of the DOE complex, which has brought the concept of economic discard limits for plutonium into question. The absence of a demand for plutonium in weapons production and the surplus from the decommissioning of retired weapons have resulted in plutonium being considered by some as a liability.

When the requirements of the Atomic Energy Act (AEA) and the RCRA are both applied to mixed wastes, the result is often conflicting requirements. The storage requirements for radioactive scrap material classified as mixed waste present particular challenges: the AEA storage criteria for SNM emphasize security, personnel radiation safety, and criticality safety.

Several of these safety principles for handling fissile materials are in conflict with EPA guidance and RCRA requirements for hazardous waste storage. Specifically, the periodic inspection of items and the labeling of existing stored containers as required by the EPA increase personnel exposure significantly, and the EPA requirement to confine water used in putting out fires in storage areas could present a criticality hazard.

Another example of conflicting guidance is the TRUPACT-II Content Code (TRUCON) limitations, Radioactive Material Management Areas (RMMAs), and waste minimization requirements. Radioactive wastes are disposed of on a volumetric cost basis; therefore, it is beneficial to minimize waste volumes to decrease disposal costs, including transportation and handling. TRUCON limits the quantity of plutonium-238 to 0.049 grams per drum by specifying the allowable activity in organic waste contained within a 55-gallon drum with three levels of containment. This limit, which is based on what many consider to be an overly conservative transportation safety analysis, may only amount to one contaminated tissue in a 55-gallon drum.

The premise behind the RMMA concept is that all waste coming from a radiation control area is potentially contaminated and should be disposed of as radioactive. This premise is in direct conflict with waste minimization principles. Because neither the DOE nor EPA has issued *de minimis* radiation standards, nuclear facilities have had to use the strict interpretation of a “no radioactivity added” doctrine for the segregation of waste streams. This overly conservative stance will result in the generation of more suspect radioactive waste than is necessary. Solutions that will allow reasonable operating parameters to be implemented without compromising safety and environmental concerns must be found.

Improving Communication and Interaction at Los Alamos

Communication must be enhanced and encouraged among personnel from the various Los Alamos organizations that are engaged in waste management activities. Waste management personnel in the Plutonium Facility have been forced to interact closely with Laboratory waste management and environmental management groups because of the number and complexity of regulations pertaining to radioactive, hazardous, and mixed wastes. This interaction has resulted in several benefits to the Laboratory and the Plutonium Facility. For example, the Laboratory’s environmental management organization plans to send a representative to work and reside at the Plutonium Facility. This representative will gain an intimate understanding of the needs of those who generate the waste, and communication will be enhanced. A communication network is also being developed to translate requirements from the federal regulations to understandable directions at the operating level. Monthly meetings are being held to discuss issues of mutual interest. Although all personnel have full work schedules and have difficulty committing time for additional activities, the time required for these meetings is well spent.

Operating personnel must be convinced that waste management regulations are not trivial and must be observed consistently. Waste certification and characterization and waste stream control require additional manpower and financial expenditures. Operating personnel must clearly understand the significance of this additional work, even if their principal interest is in research. Specific training must be developed for all those who generate waste at the Plutonium Facility. The training program must be well organized and must use knowledgeable waste management personnel as instructors.

Need for Planning and Scheduling Waste Management Activities

Scheduling waste management activities has become essential because the waste handling process has become complex, requiring the support of dozens of personnel. Waste can no longer be collected and disposed of as it is accumulated. Planning must begin before the waste is generated, and scheduling must allow personnel to plan and coordinate their activities. Special activities, such as glove-box removals, must be scheduled to optimize use of limited waste management resources and to avoid conflicts with normal Facility activities. Groups are experiencing staffing shortages, which limit the availability of backup personnel for waste support activities. When unplanned activities do occur, they must be handled with special care to prevent surprises that can derail normal waste disposal operations.

The Plutonium Facility Waste Management Team

The waste management process at the Plutonium Facility must be performed in a cost-effective manner while meeting all regulatory requirements. A waste management team has been formed to coordinate efforts at TA-55 to attain these goals. The team provides an interface between regulations and operations by providing guidance to those generating waste. This guidance includes how to certify and package waste according to established waste acceptance criteria. Waste management activities are conducted in a way that minimizes the impact on operations as much as possible. Waste management personnel must be careful to respect and understand the interests of those who generate waste and try to avoid restricting their operations unnecessarily. At times, innovative ways of complying with regulations must be implemented.

Shortcomings of the Current Waste Management Program

The waste management program must be able to react expediently to regulatory changes. For example, the TRU waste program at Los Alamos consists of a hierarchy of documents. EPA regulations, Department of Transportation and Occupational Safety and Health Administration regulations, AEA requirements, and DOE orders are the highest-level documents. Below them are second-level documents telling how the applicable regulations and orders will be implemented at disposal facilities (WIPP) and the Laboratory. The third and final level of documents are those written at the Plutonium Facility such as waste stream attachments to the Laboratory certification plans and the Safe Operating Procedures (SOPs), which describe how work is to be performed. Changes to higher-level documents must be reflected in lower-tier documents in a timely manner, down to the operating level. The revision and review process for a Plutonium Facility SOP can easily take a year. Much of this time is spent on resolving comments and questions from reviewers. With three levels of program documents to update, it could take three years for changes to filter down to the working level. This time span is clearly unacceptable. Something must be done to expedite the review and approval process if operations are to keep current with changing requirements.

With increasing frequency, the demand for manpower to keep up with paperwork requirements is being met by the use of contractors. If contractors are used, it is imperative that they

1) demonstrate regulatory expertise regarding the document that is being written and
2) possess knowledge of the operations for which the documents are being written.

The sponsor cannot simply pay the contractor and walk away from the project expecting to receive a satisfactory product. If anything, extra attention must be given to the development of contractor-generated program documents. Program documents must be written realistically. It is very easy to make a commitment that looks good on paper but is impossible to carry out. These unrealistic commitments are usually the first findings to be identified during an audit.

Evolution of Waste Management at the Plutonium Facility

Several projects are currently underway to improve the efficiency of the Plutonium Facility waste management program. The first is the computer-based Nuclear Materials Technology (NMT) Waste Management System. This system will take the place of the current paper system, which requires standardized forms, manual transfer of data, and operator calculations. The hard-copy form used in the current system must accompany the waste and functions as the data package for the completed container. The form must then be physically circulated for review and approval. The new computer-based program will either reside on one of the file servers distributed around the network or on the individual personal computers connected to the network and used for data entry in the field. A user-friendly interface will prompt the user for data, check the input, do calculations automatically, and disallow the entry of improper information. Hard-copy forms for data packages will be generated outside of the processing area, eliminating paper transfer across the radiation control areas. Approvals will be electronic, expediting the review process. This system should be ready for testing in May of 1994. In conjunction with this system, a bar code labeling scheme will be instituted. Waste items will be labeled with identification (ID) stickers and scanned as they are transferred between operations. Data will be entered under the item ID and transferred electronically into the NMT Waste Management System.

The Plutonium Facility waste management team is working to improve the waste management system at the Facility, not only to meet the needs of the present but also to meet the challenges of the future. Unencumbered communication is being encouraged. For example, personnel at the Plutonium Facility have been issued waste management telephone cards to help them get in touch with the right person to assist them. Organizations outside the facility have been given information about how the Plutonium Facility waste management team is organized. A new facility-specific training course for those who generate waste is being planned. The course will be interactive and will be required for all personnel who currently generate waste as well as new employees. Guidance on process knowledge documentation will be emphasized. The Plutonium Facility is taking advantage of the DOE Mentor Program, a program by which DOE offers assistance from experts in specialized areas, including environmental compliance. These personnel, who are familiar with regulatory issues within the DOE complex, are investigating compliance problems and are discussing resolution strategies. Their recommendations are currently being evaluated by Facility management.

Summary

The Plutonium Facility at Los Alamos is striving to come into full compliance with all environmental regulations for the storage, treatment, and disposal of radioactive and hazardous waste. The complexity of the regulations paired with the uniqueness of radiochemical processing operations presents challenges and frustrations to those involved in the waste management process. Mutually agreeable solutions to waste management problems must be found: the EPA and DOE must come to agreement on solutions for the DOE complex as a whole, and the NMED and Los Alamos must agree on solutions for the Plutonium Facility in particular. Funding shortfalls and budgetary constraints are placing a growing emphasis on minimizing waste generation and maximizing the efficiency of waste management practices. The waste management team is making steady progress in improving the quality of the waste management program at the Plutonium Facility. These improvements will not only result in enhanced operational safety and a reduction in environmental risk but will also ultimately result in full compliance with environmental regulations and efficient utilization of taxpayer dollars.◆