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LOS ALAMOS NATIONAL LABORATORY

1992

NUCLEAR MATERIALS TECHNOLOGY

WEAPONS COMPLEX 21 RECONFIGURATION

C O V E R

Eric Vigil of Information Services Division created the aerial view drawing of TA-55, using Alias software on a Silicon Graphics work station.

NUCLEAR MATERIALS

TECHNOLOGY

WEAPONS COMPLEX 21

RECONFIGURATION

Annual Report
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Los Alamos
NATIONAL LABORATORY

C O N T E N T S

C O N T E N T S

FOREWORD

F O R E W O R D

by Delbert R. Harbur

Division Leader
Delbert R. Harbur

Most of the nuclear materials activities at the Los Alamos National Laboratory are done in the Nuclear Materials Technology Division. The Division is responsible for the Plutonium Facility located at Technical Area 55 (TA-55). With our expert research and development in the fields of metallurgy, chemistry, engineering, and solid state physics, we examine the complex chemistry associated with plutonium and other actinides in various physical states.

To remain at the forefront of important areas of actinide chemistry and materials science, we maintain a strong and vital base of scientific research. Our materials research is directed at understanding the relationships among processing, composition, structure and properties of materials and ultimately at discovering how these materials respond to external environments. Our chemical processing research is aimed at understanding the basic chemistry involved together with the complex interactions found in real systems.

In the national defense arena, we support nuclear weapon design, development, and testing programs by developing safe, efficient, and environmentally acceptable technologies for manufacturing and processing of plutonium in the nation's production complex. In addition, the division's energy programs focus on nuclear reactors for space power and radioisotope heat sources.

The Laboratory's technology leadership role for the nation's plutonium production complex has been well established over the last decade. Rapid, significant changes in world events and within the nation's weapons production complex indicate a strengthening of this role. The nation's nuclear materials production complex is widely perceived as at the end of its useful life and as no longer sized nor technologically equipped to meet future needs.

"Technologies that we researched and demonstrated as prototypes at TA-55 will make up the base technologies for the future Plutonium Manufacturing Plant in the Weapons Complex Reconfiguration (Complex 21)."

For the last decade, we have been upgrading the manufacturing and processing technologies developed at TA-55 to meet the proessing need to decommission and decontaminate older facilities and to reconfigure the weapons complex into properly equipped facilities for their future missions. Using the Laboratory's strong research and development base, we initiated these upgrades to address problems inherent in the inability of the older technologies to properly deal with the growth of regulatory, compliance, and waste issues confronting the Department of Energy.

Technologies that we researched and demonstrated as prototypes at TA-55 will make up the base technologies for the future Plutonium Manufacturing Plant in the Weapons Complex Reconfiguration (Complex 21). Fortunately, many of these technologies will also be the ones required to decommission older facilities and to stabilize residues.

This year focuses on the processing technologies that we have developed for Complex 21. Most of these technologies are quite mature, and the associated metallurgy and chemistry are well understood. We are now emphasizing process integration, real-time sensors, and process-control systems. Automation is applied only to mature, fully-integrated, and optimized process systems.

This publication provides a brief review of the scientific and technical activities in each of our operating groups, as well as a compilation of our accomplishments during the past 18 months, including awards, patents, and publications. ◆

OVERVIEWS

P R E F A C E

Weapons Complex Reconfiguration: The Future of Plutonium Technology

by Dana C. Christensen

Deputy Division Leader
Dana C. Christensen

Weapons Complex Reconfiguration Concerns

Recent unforeseen changes in the global balance of power have prompted a reevaluation of the entire nuclear weapons complex, including research and development in the area of nuclear materials technology. National defense concerns related specifically to plutonium processing include

- stockpile security and surety,
- existing production and supply infrastructure, and
- future production and supply infrastructure.

In the area of stockpile security and surety, we must maintain a safe but robust arsenal of nuclear weapons while reducing the numbers of various types of weapons. Constant surveillance of stockpile components and materials is essential to ensure that devices will work when called upon and that they will remain in a safe and secure condition until that time.

As to the existing production and supply infrastructure, the nation currently owns a significant quantity of plutonium; it exists in the form of weapon components, oxides and metals, miscellaneous lean residues, and contaminated equipment. However, most of the production facilities are more than 35 years old and have reached the end of their useful lives.

Of utmost concern is managing the plutonium supply so as to avoid environmental contamination and to prevent loss of material to a proliferant group. We must have available safe, secure facilities in which to store the material returned from stockpile disassembly activities as well as the material recovered from residues. The mandated shrinking stockpile and the reduced reliance on the nuclear deterrent as a key to national defense mean that our excess and aging facilities must be decontaminated and decommissioned. Existing environmental damage resulting from the activities conducted in these facilities must also be ameliorated.

Finally, the future production and supply infrastructure requires technical support for the stockpile (at whatever level it finally reaches), the capability to fabricate improved components and upgrades of the stockpile, and the means to survey the stored inventory of material to ensure accountability and safety. The primary concern will continue to be the minimization of hazardous waste and the management of necessary waste so as to preclude release to the environment. Future facilities must formalize operations in compliance with increasingly stringent federal requirements, thereby providing a high degree of safety to employees, the public, and the environment.

The Los Alamos Plutonium Facility

The successful reconfiguration of the nuclear weapons complex requires that the above key areas be addressed. Although some technical developments at Los Alamos uniquely address only one area, many others contribute

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Fig. 1. Baseline flow sheet for the Plutonium Processing Facility for the reconfigured weapons complex.

This emphasis on advanced technology, including the successful demonstration of plutonium production, ensures that the Los Alamos Plutonium Facility will continue to refine the technologies of the 1990s as it plans the developments of the 2000s.

Baseline Flow Sheet for Plutonium Processing

Pivotal to selecting the appropriate development activities is the effective charting of a direction that ensures progress by setting a defined goal. All of our activities focus on the plutonium processing facility of the future. Fig. 1, a baseline flow sheet for that facility, highlights the key technical areas of emphasis for processing and, in addition, identifies technology developments needed for the entire complex reconfiguration.

to all three areas. The pervasively multidisciplinary nature of the Laboratory makes it uniquely suited to address the entire spectrum of concerns associated with the reconfiguration of the nuclear weapons complex. The Laboratory's formula for continued success comprises an educated and experienced staff possessing detailed knowledge of the important issues and specially designed equipment and facilities unparalleled throughout the world.

For more than a decade, the mission of plutonium operations at Los Alamos has included

- conduct of fundamental and applied research,
- development of advanced processes,
- full-scale demonstration of those processes in a plutonium environment, and
- exchange of technology with other DOE contractors and industry.

Weapons Complex Reconfiguration:
The Future of Plutonium Technology (continued)

Improvements designated as applicable to the future plutonium complex will assist in meeting existing cleanup requirements as well as facilitate the management of future material inventories. The five chapters in this section provide detailed attributes of projects as they apply to the Fig. 1 flow sheet.

Site Return Processing

The chapter on site return processing provides details of the problems being addressed and of a new suite of technologies being implemented as solutions. The processing approach is elegantly simple but involves the integration of a number of processing steps, each of which uses unique and different chemistries. The goal of this work is to demonstrate that complex site-return processing operations can be integrated into a flow loop in which safety, accountability, and processing complement each other.

Because no acceptable technology for performing this task presently exists, the successful integration of site-return operations at Los Alamos will be a landmark achievement. Further, the waste generated in this fully integrated approach is near zero. Developments in this area will apply directly to needs in stockpile security and surety and future production and supply infrastructure.

Advanced Manufacturing Technology

The chapter on advanced manufacturing technology addresses significant changes in techniques for fabricating weapon components while minimizing waste and promoting safety. Plutonium manufacturing processes, which require the use of chlorinated and fluorinated hydrocarbons, has historically been responsible for the production of mixed waste; however, new operations now under development will eliminate the problem of mixed waste.

Improvements in this area will also significantly reduce the amount of residues and the quantity of plutonium in residues, thereby reducing the need for aqueous recovery. The major goals in the manufacturing area center on maximizing the utilization efficiency of plutonium metal and on minimizing the generation of residues and waste. Developments in manufacturing will directly impact stockpile surety and future production and supply infrastructure.

Nitrate Recovery and Chloride Recovery

The chapters on nitrate recovery and chloride recovery address the aqueous recovery of residues resulting from the site-return- processing and manufacturing functions. The recovery operations generally involve the dissolution of residues in acids, the separation and purification of plutonium, and the conversion of the plutonium into foundry-acceptable metal.

"The overall goal of Complex 21 is 'zero discharge,' that is, no release of plutonium to the environment."

The bane of aqueous systems has been the volume of waste liquids and sludges generated. The goal of recent developments in the process control area is to operate the process chemistries as closely as possible to the stoichiometric limits, thereby minimizing the need for excess reagents and ultimately reducing the volume of waste. Scientists are also developing element- or ion-selective systems capable of plucking plutonium out of a scrap matrix without the help of reagents. Finally, a key goal of nitrate and chloride recovery operations is to demonstrate process integration in an environment where the synergism of unit operations can be measured. The work described in these two chapters will have a profound impact on all aspects of future plutonium processing.

In particular, the existing residue and waste inventory is not now capable of being packaged for long-term storage. Technologies in nitrate and chloride recovery will provide the basis for developing processing and packaging techniques for long-term storage of residues.

Waste Management
The final chapter covers waste management. The essential focus of all nuclear materials processing is the minimization or elimination of waste wherever possible. Although not all waste can be eliminated, the goal in waste management is either to remove all activity before discharge or to immobilize the waste so as to preclude any uncontrolled release. To the extent possible, reagents as well as any recovered plutonium will be reconstituted and recycled.

The important types of waste that must be managed include liquids, sludges from liquid treatment, combustibles, plastics (especially polyvinyl chlorides), stack gases, and various solids, such as tools, glove boxes, and process equipment.

The overall goal of Complex 21 is "zero discharge," that is, no release of plutonium to the environment. The extent to which that goal can be met is a measure of our success in this key area of operations. Los Alamos has addressed this goal by consistently subscribing to a very direct and logical approach to waste processing:

1. Identify the problem and develop an approach for solving it that begins at the initial stages of all related processes.

2. Identify and understand the related fundamental chemistry and metallurgy.

3. Develop process control mechanisms such as sensors.

Weapons Complex Reconfiguration:
The Future of Plutonium Technology (continued)

4. Engineer processing equipment to meet process and process control requirements and constraints.

5. Adapt engineered equipment to facility operating constraints, or, in the case of a new facility, engineer the facility around processing requirements and constraints.

Experience shows that when process engineering precedes a clear understanding of the problem or of the process chemistry involved, failure is certain. Projects can be successfully brought to fruition only when knowledge precedes action. A unique strength of research, development, and demonstration activities at the Los Alamos Plutonium Facility is that they follow the five-step logical approach in a healthy range of activities.

The Role of the Nuclear Materials Technology Division

In conclusion, the Los Alamos Plutonium Facility is an unequaled national resource because it is the only site that hosts technologies covering the entire spectrum of plutonium needs. The Nuclear Materials Technology Division is responsible for applying this capability to meet weapon complex reconfiguration requirements and to respond to changing needs in a manner that adheres to the premise of safe conduct of operations and full compliance with regulatory requirements. ◆

Site-Return Processing Overview

by John Haschke
Plutonium Metallurgy Group

Scope and Options

Because nuclear reactors are unlikely to be operated for the purpose of producing additional supplies of plutonium, the only remaining source of plutonium metal for future weapons fabrication is site-return components. Consequently, site-return processing is the key element of the flow sheet for the plutonium processing facility for Complex 21 (see the introductory article) because all metal entering the facility will be subject to such processing. The objective of site-return processing is to produce required quantities of War Reserve metal from site-return feed materials while minimizing waste generation and worker radiation exposures and maximizing safety and efficiency.

Site-return processing incorporates both mechanical and chemical operations. The initial mechanical operation is disassembly of site-return units into basic components; subsequent mechanical operations are concerned with converting plutonium-containing components into a form suitable for chemical reprocessing. The chemical operations include a sequence of process steps that produce purified metal for use in fabricating new components.

Selection of the best process technologies is of utmost importance. All baseline technologies should be adequately demonstrated and should reflect state-of-the-art technology. In contrast to the well-established process for mechanical operations, several process alternatives are proposed for chemical operations. The selection of baseline methods for chemical processing of plutonium-bearing materials isa somewhat controversial issue, complicated by the fact that the initial chemical operation fol-lowing mechanical operations largely determines the structure of the entire flow sheet.

Only two chemical processing options, aqueous recovery and pyrochemical purification, are sufficiently developed to merit serious consideration as baseline flow sheet technologies for plutonium recovery. Alternative purification methods, such as fractional distillation of the halides, are viewed as competing options that must be adequately demonstrated and evaluated with regard to flow sheet impact before serious consideration as an alternative to the two proven processes.

Aqueous and pyrochemical methods represent substantially different purification options. Aqueous processing, the more traditional approach, requires several steps. The plutonium-bearing metal is first dissolved in aqueous nitric acid, and the plutonium is then separated from impurities by ion exchange or solvent extraction methods.

Plutonium is removed from the purified solution by precipitation, and metal is regenerated by calcium reduction of the oxide or fluoride. All residues are redissolved for recycle through the process.

In contrast, pyrochemical purification is a two-step approach in which the plutonium retains its metallic form throughout the process. Molten salt extraction to remove americium is followed by electrorefining to eliminate other impurities. Because both of these pyrochemical processes use molten metal chlorides as solvents, the reprocessing of their residues requires that an aqueous chloride facility be provided in addition to the aqueous nitrate facility used for reprocessing oxide residues.

Pyrochemical purification has been adopted as the baseline recovery process because the combination of purification and support technologies is considered superior to the technologies for aqueous nitrate recovery. Important considerations in the selection of the baseline process include the quantity of waste generated, the level of radiation exposure, the complexity and cost of equipment, and the process efficiency. Although such issues are best addressed for the respective flow-sheet options using available data and process modeling, certain key issues merit brief consideration. The main disadvantage of the aqueous process is the generation of large amounts of waste. The use of aqueous nitrate and chloride facilities to support pyrochemical operations would be an unnecessary duplication of capability.

The advantages of the pyrochemical method are realized in reduced waste generation and in a high single-pass process efficiency. A comparable single-pass efficiency is realized in aqueous nitrate recovery, but that operation requires several steps and is significantly less cost-effective and energy efficient than pyrochemistry because a chemical reduction step is required to regenerate the metal. Incorporation of aqueous chloride and nitrate facilities with pyrochemical methods can be viewed as advantageous because it provides a balanced capability for handling the many types of residues stored for recovery and accommodates the flexibility needed to exploit the waste-stream polishing potential of aqueous methods.

"The baseline flow sheet provides a basis for formulating relevant research and development strategies and for effectively directing resources to support the most promising options."

The baseline flow sheet provides a basis for formulating relevant research and development strategies and for effectively directing resources to support the most promising options. As implied in the preceding discussion, two categories of effort are recognized: efforts to modify the baseline process and efforts to provide alternatives to it. A decision to pursue an activity falling in the second category must weigh the potential payback from the alternative method against its complexity and development time and against its impact (positive or negative) on the flow sheet and on facility design. Although pursuit of promising alternatives is necessary, allocation of limited resources to enhancing baseline technologies seems most prudent because modification of a baseline technology neither

changes the facility footprint nor significantly alters equipment design. Baseline improvements can be accommodated at a point well beyond the date for final process definition and they guarantee that a usable process will always be available for implementation.

Baseline Processes
Disassembly

The baseline process for component disassembly incorporates standard precision machining techniques. The need for residue reprocessing is avoided because precision methods are capable of selectively removing materials without including turnings from adjacent components. Further development is not needed.

The decontamination of enriched uranium components is an ancillary disassembly process. Plutonium-containing particles must be removed from a component before it can be returned to the uranium reprocessing facility.

The baseline decontamination process is a demonstrated manual operation in which dilute nitric acid solution and abrasion are used to remove plutonium oxide particles from uranium surfaces. The process generates large volumes of liquid waste that must be treated by a currently undefined method.

Consolidation

A baseline method for consolidating plutonium components also remains undefined. Demonstrated alternatives include compaction, casting, and in-process fusion of component fragments.

Molten Salt Extraction

Molten salt extraction is the baseline process for removing americium-241 from aged plutonium metal. Ingrowth of the americium isotope from beta decay of plutonium-241 (half-life of 13.2 years) present in the original metal presents a significant radiation hazard for workers handling aged metal.

Americium-241 (half-life of 458 years) undergoes alpha decay, but a large fraction of the process forms an excited-state neptunium-237 daughter that emits a penetrating 60-kiloelectron-volt gamma ray. The maximum activity of aged metal is reached after approximately 75 years. Immediate separation of americium is essential for reducing radiation exposures.

Americium is extracted into a molten salt phase that is physically separated from the americium-free metal in a subsequent breakout step. When plutonium trichloride is added to a molten calcium dichloride phase that is in contact with molten plutonium, americium in the metal is exchanged for plutonium in the salt by an ensuing redox reaction. Although molten salt extraction is an established production method, significant upgrades are possible.

The production of plutonium trichloride reagent for molten salt extraction and electrorefining is an essential support operation of the site-return flow sheet. The baseline process is a demonstrated technology that involves preparation of plutonium hydride. The hydride is subsequently converted to plutonium trichloride by reaction with gaseous hydrogen chloride at elevated temperatures.

Electrorefining

Electrorefining is the baseline process for producing high-purity plutonium. The technique uses molten calcium dichloride rich in plutonium trichloride as a transport medium for an electrolysis process that removes plutonium from an impure plutonium anode and deposits pure metal at a second electrode. The anode residues constitute a major portion of the reprocessing

load for the aqueous chloride facility. However, only a portion of the site-return metal must be purified by electrorefining; War Reserve metal is obtained by blending the high-purity product with americium-free metal from molten salt extraction.

Baseline Modifications and Alternatives

The baseline site-return processes provide several opportunities for modification and substitution. Such efforts include the development of reusable crucibles for various pyrochemical applications and several larger development activities that have potential for significantly upgrading processes.

Baseline flow sheet for the Plutonium Processing Facility for the reconfigured weapons complex.

An *in situ* chlorination process for use in molten salt extraction and electrorefining is one of the larger activities being pursued. Plutonium trichloride is generated within the pyrochemical apparatus by bubbling a stoichiometric amount of chlorine gas into the molten metal. The potential payback is large because process operations are simplified and the need for a facility to prepare plutonium dihydride and plutonium trichloride is eliminated. Application of the technique has been demonstrated for molten salt extraction. A detailed description of the effort is included in the chapter on chloride recovery operations.

The use of a fluorine-rich plasma as an alternative method for decontaminating uranium components is also being investigated. Fluorine atoms generated from inert fluorocarbons in a radio-frequency field react with particles contaminated with plutonium oxide to form gaseous plutonium hexafluoride that is collected in a downstream trap. The technology will replace the acid decontamination process with a method that produces minimal solid residue. This replacement will eliminate the need for a leachate treatment facility and will not negatively affect the flow sheet because decontamination is a terminal flow-sheet process. The conditions and kinetics for etching plutonium oxide have already been defined.* A detailed report on plasma processing is included in this chapter.

Automation

An important and unifying initiative of site-return activities is their automation and integration, as detailed here in a separate article. Although this concept is not indicated on the baseline flow sheet, consolidating operations are expected to reduce radiation exposures, enhance safety, and increase efficiency. Negative impact on the flow sheet is not introduced because the approach being developed does not alter the fundamental chemistry of the baseline process; the effort attempts only to exploit opportunities that currently exist. In addition to accomplishing improvements cited above, the automation and integration program will provide a unique and necessary opportunity for unifying individual technologies and demonstrating their chemical and process compatibility before final flow sheet definition. ◆

* J. C. Martz, D. W. Hess, J. M. Haschke, J. W. Ward, and B. F. Flamm, "Demonstration of Plutonium Etching in a CF_4/O_2 RF Glow Discharge," *J. Nucl. Mater.* **182**, 277 (1991).

SITE - RETURN

PROCESSING

Automation and Integration of Site-Return Processing

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The next-generation nuclear materials processing complex will require new technologies to dismantle site-return components and recover the nuclear materials. By integrating baseline technologies with proven techniques in robotics and automation, we can create a safe, environmentally friendly operation that will eliminate mixed wastes, reduce waste generation to theoretical minimums, reduce personnel radiation exposure to as low as reasonably achievable, and place process safety above all other operational concerns. A secondary objective of this technology development is to maximize process efficiency.

The three key processes in the site-return operation are disassembly of the weapon component, recovery of its nuclear material, and purification of the recovered metal to meet War Reserve specifications.

The component forms the input to the process. Exit streams include nonnuclear component materials, salt from the purification step, and nuclear material in a form suitable for long-term storage or immediate reuse. Added reagents include stoichiometric quantities of oxidant for removal of americium and calcium dichloride for pyrochemical operations.

The high radiation levels resulting from americium build-up in the weapons stockpile make remote handling highly desirable for site-return material. Specifically, the high-radiation-exposure operation of salt breakout after molten salt extraction can be automated to reduce worker exposures. In addition, the pyrochemical methods envisioned for site-return processing are amenable to automation. Increases in process safety and efficiency are an added benefit of system integration.

Reconfiguration of the nuclear weapons complex provides a unique opportunity to apply the concepts of concurrent engineering to site-return disassembly. In the past, automation technologies—usually involving the application of commercial equipment in a glove-box enviornment—have been applied to preexisting processes and process equipment with mixed results. Los Alamos has been involved in developing automated technologies for almost a decade. This extensive experience has led to the identification of the important issues that influence glove-box automation. Thus, Los Alamos expertise, combined with knowledge of the important process chemistries, has led to the development of a system requirements document that outlines the key issues and technologies involved in the successful implementation of an automated site-return processing system. Engineering analysis

" By integrating baseline technologies with proven techniques in robotics and automation, we can create a safe, environmentally friendly operation that will eliminate mixed wastes, reduce waste generation to theoretical minimums, reduce personnel radiation exposure to as low as reasonably achievable and place process safety above all other operational concerns."

and design are currently in progress. Individual process technologies have matured over the past several years so that they are now amenable to integration and process automation.

Separation of site-return components is accomplished through the use of intelligent modules optimized to perform this task. A specially designed parting system consisting of a parting lathe and custom tooling receives the intact pit. Design of the parting system addresses such typical glove-box operational issues as maintenance within the inert atmosphere, reliability of components, accessibility for routine service, and optimum use of glove-box space. Important features of the system include modular x- and y-axes, a telescoping z-axis, externally mounted electronics, and dust-proof construction. The intent of this effort is to develop a flexible, modular handling system in partnership with private industry.

Certain assemblies require consolidation before material purification. An intelligent station is used to perform this task. This modular approach follows closely the development of automated chemical analysis technologies for the Department of Energy's Office of Environmental Restoration and Waste Management. Software architecture and control structures already in place allow a facile and rapid development effort.

In the purification stages of the site-return system, intelligent stations perform the requisite process chemistry. Fixed automation stations provide repeatable process control that enables automation of highly repetitive process operations. The automation system provides a means of transport between these stations. Individual processes are coordinated to the extent that the product from one operation provides the feed for the next. In addition, each chemical operation will be optimized such that its by-products will not negatively impact subsequent process operations.

A single glove box accommodates all process operations. A centrally located parting system separates intact assemblies into hemishells. The automated material-handling system transports individual hemishells to the chemical recovery and purification operations. A single parting and material transport system serves two separate recovery stations.

The changing culture in the Department of Energy with respect to environmental and safety awareness demands that all new operations generate minimal wastes, avoid mixing different types of waste, minimize personnel radiation exposure, and operate to the highest standards of safety and security. The automated site-return processing system described here meets these requirements while ensuring high process efficiency.◆

SITE-RETURN

PROCESSING

Advanced Cleaning Technologies

by John M. Haschke
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Introduction

Plutonium components are exposed to a variety of organic compounds during fabrication. In normal production practice, a protective flow of hydrocarbon oil is directed over a part during machining. Residual oil must be removed by an in-process cleaning procedure to facilitate handling and inspection of a part. During these operations a component is exposed to other organics that are removed by a final cleaning procedure immediately before assembly. Hydrocarbon residues remaining on plutonium surfaces are radiolytically decomposed during stockpile storage of weapon assemblies and cause detrimental corrosion of nuclear components.

As in many other established manufacturing processes, chlorocarbon solvents are used to degrease plutonium components. The in-process operation uses a carbon tetrachloride spray rinse, and an ultrasonic cleaning/vapor degreasing method. A 111-trichloroethane (TCA) solvent is used for final cleaning.

These chlorocarbon solvents (which deplete ozone, pose a carcinogenic hazard, and generate mixed waste) are subject to regulation limiting their continued use and availability. During recent production cycles, the combined annual usage of these chlorocarbons has approached 100,000 liters, a large part of which is released as atmospheric emissions.

Although anticipated decreases in weapons production will result in substantial reductions in solvent usage, chlorocarbon-based processes must be eliminated. The use of dry machining techniques precludes the need for in-process cleaning. However, final cleaning is necessary because components are exposed to oils and other hydrocarbons during subsequent manufacturing operations. Advanced cleaning techniques are being investigated to identify and develop environmentally acceptable alternatives to chlorocarbon-based methods. In addition to satisfying all environmental,

safety, and health requirements, suitable alternative technologies must not generate mixed waste, must be economically feasible and process compatible, and must satisfy requirements for component cleanliness. Although the levels of cleanliness achieved by the existing TCA-based process are unknown, the maximum allowable level of hydrocarbon residue calculated from evaluation of data from stockpile systems is 5 micrograms per square centimeter of component surface area.

Results of joint development efforts with collaborators from EG&G Rocky Flats are presented here. Technologies based on supercritical fluid (SCF) carbon dioxide and on aqueous media are described along with efforts to establish analytical methods for defining surface cleanliness. A third cleaning alternative based on plasma processing is described in the article titled "Plasma Chemical Processing."

"Advanced cleaning techniques are being investigated to identify and develop environmentally acceptable alternatives to chlorocarbon-based methods."

Baseline Cleaning Process

Unlike most baseline technologies in the flow sheet for the Complex 21 Plutonium Processing Facility, the process for final cleaning of plutonium components has not been demonstrated for production. Use of SCF carbon dioxide is recommended because of its potential cleaning capability and its anticipated process compatibility. However, because pursuit of a single alternative technology for replacing the chlorocarbon cleaning method is imprudent, the cleaning potential of aqueous media is also being investigated.

Supercritical Fluid Cleaning

Background

Supercritical carbon dioxide is the primary candidate for replacing TCA in the final cleaning of plutonium components. A recycle SCF carbon dioxide process satisfies both the letter and the spirit of environmental regulation.

Carbon dioxide occurs naturally, is nontoxic and unreactive, and poses minimal risk to the environment and to the health and safety of employees and the public. Supercritical conditions are attained at modest conditions (above 31°C and 74 bar pressure), and the high volatility of carbon dioxide facilitates the separation of solvent and solute. SCF carbon dioxide technology is well developed and widely used for extracting organics in the food, polymer, pharmaceutical, and synthetic-fuel industries. Large SCF systems are commercially available.

Prior work suggests that SCF carbon dioxide is an effective cleaning medium. Results of initial studies of SCF cleaning conducted at Rocky Flats show that comparable levels of carbon-containing residues remain on steel and uranium surfaces after cleaning with carbon dioxide and with TCA.[1] Tests conducted at a vendor laboratory show that 20-centimeter-diameter steel hemispheres are cleaned to levels well below the limit for plutonium at reasonable temperatures, pressures, flow rates, and times.[2] These studies, which are consistent with earlier extraction work showing that the solvent properties of SCF carbon dioxide are strongly dependent on solvent density, establish tentative conditions for cleaning (temperature of 35°C to 40°C and pressure of 150 to 200 bars). At these conditions, the fluid density is in the range of 0.80 to 0.85 grams per cubic centimeter. Cleaning times for hemispheres are less than 20 minutes at a fluid flow of 1.0 liter per minute.

Advanced Cleaning Technologies (continued)

Fig. 1. Diagram of a closed-loop SCF cleaning system.

Glove Box — Pressure — Temperature — Flow — Heated Cleaning Chamber — Part — Preheater — Pump — Heated Expansion Valve — Residue Collection Vessel — CO$_2$ Supply — CO$_2$ Collector — ◄— Mechanical or Thermal Compression —◄

Concept

The concept of an SCF carbon dioxide cleaning apparatus is illustrated in Fig. 1. The part is contained in a heated cleaning chamber with a clearance of 2 to 3 millimeters on each side of the part to minimize fluid volume and to direct flow over the part surface. Liquid carbon dioxide is drawn from the supply, pumped to the desired pressure, and heated to the desired temperature in the supercritical range before flowing over the part at a controlled rate. Organic residues dissolve in the solvent phase and are carried out of the chamber and through a heated expansion valve. The decrease in density accompanying expansion forces dissolved organics to precipitate in a collection trap. The carbon dioxide is condensed and re-cycled to the supply vessel. Important cleaning parameters such as temperature, pressure, flow rate, and time are readily controlled.

Several advantages of the concept are evident. In addition to using a solvent posing minimal risk, the process concentrates all cleaning residues for disposal or processing. If in-line filters do not remove plutonium-containing particles entrained by the fluid stream, they also will collect with the residue. The recycle potential of the process is particularly attractive; no wastes or emissions are produced other than the concentrated organic residue.

Status

A laboratory-scale SCF system has been constructed and installed. In this system, an air-driven pump delivers 18 milliliters of solvent per minute at a density of 0.85 grams per cubic centimeter through a 20-cubic-centimeter cleaning chamber. Parallel chambers are installed inside a glove box for plutonium studies and outside the glove box for nonnuclear samples. Sample surface areas up to 50 square centimeters are accommodated by these chambers.

"The recycle potential of the process is particularly attractive; no wastes or emissions are produced other than the concentrated organic residue."

Important compatibility issues are resolved by initial studies with plutonium. Although the reaction of plutonium with carbon dioxide to form plutonium dioxide is thermodynamically favorable and highly exothermic, reaction is not anticipated because of slow kinetics.[3] Numerous chemical compatibility tests conducted within the projected cleaning range show that burnished plutonium remains untarnished after exposure to SCF carbon dioxide for several hours. The metal also shows no evidence of reaction with the solvent after one hour at extreme conditions of 100°C and a pressure of 310 bars.

The effects of water contamination in the solvent are also established. The solubility limit of water in SCF carbon dioxide at 40°C is approximately 0.5 mass percent. Although commercial carbon dioxide contains water at ppm levels, the flow procedure exposes the plutonium surface to large amounts of water whose chemical nature is unknown. If it exists as carbonic acid, plutonium may dissolve and cause dimensional changes in the component and contamination of the equipment. Visual observation of the surface, mass gain data, and downstream contamination surveys show that a 1-hour exposure of clean metal to static SCF carbon dioxide containing 0.13 mass percent water resulted in formation of a passive surface film.

Cleaning studies with SCF carbon dioxide are in progress. Attempts to use gravimetric methods for quantifying residual levels of hydrocarbon oil on cleaned samples show that such techniques are not sufficiently sensitive. An infrared spectroscopic method of analysis is necessary to establish cleaning efficacy. Future experiments will investigate effects of such parameters as temperature, pressure, flow rate, time, and residue type in order to identify the optimal condition for cleaning.

The results will be used to define specifications for a pilot-scale SCF system. The effects of the cleaning process on the chemistry and storage behavior of the metal must also be determined.

A pilot system will establish the cleaning parameters for a production process. Procurement and installation of commercial equipment is planned. Experiments will be conducted to define cleaning parameters for full-sized parts, develop solvent recycle methods, and address safety issues.

Aqueous Cleaning
Background
Aqueous cleaning methods provide an alternative to the baseline SCF carbon dioxide process. The environmental, safety, and health risk is low, but the compatibility of an aqueous system with the plutonium recovery process is uncertain.

Advanced Cleaning Technologies (continued)

A major concern is the chemical compatibility of plutonium metal with aqueous media. The corrosion of plutonium by water and dilute salt solutions is a rapid reaction that produces hydrogen and a series of oxide hydrides and oxides.[4] The possibility of using aqueous cleaning media arises because plutonium apparently does not corrode if the pH is greater than 8.[5]

Concept

The concept of an aqueous cleaning process closely parallels that of the SCF carbon dioxide sytem. Although the use of a basic detergent solution in an ultrasonic bath is an attractive option, the potential for corrosion from release of water vapor into the process facility is unacceptable. Use of a closed-loop cleaning system is preferred. The apparatus resembles that shown for SCF carbon dioxide in Fig. 1. After being placed in a small-volume cleaning chamber, a component is subjected to a three-step cleaning procedure.

In the first step, a high-pH detergent solution is heated and pumped over the part to remove organic residues from the surface. The cleaned component is then rinsed with distilled water or a selected buffer solution before being vacuum dried during the final step.

Several advantages of the process are recognized. The system operates at low pressure, and the equipment requirements and the safety concerns are less than with carbon dioxide cleaning. However, although the process is likely to generate only low levels of waste, a processing facility will still be required to concentrate organic and detergent residues, to purify water, and to prepare fresh detergent solutions.

Status

Initial experiments designed to determine the feasibility of an aqueous cleaning process will establish the chemical compatibility of plutonium with water and high-pH detergent solutions. Measurements are complete for a test matrix designed to assess the effects of pH, temperature, detergent type, and time on the aqueous corrosion of plutonium. Burnished samples of plutonium were weighed and placed on the desired aqueous media for extended periods of time. Periodic visual inspections were made, and mass changes were measured after approximately 2 weeks.

Results of the compatibility tests are consistent with earlier reports indicating that corrosion is negligble in high-pH solutions. Tests at 22°C show that the metal remains untarnished after more than 24 hours in buffered solutions having pH values of 7.0, 10.0, and 10.2 and in high-pH commercial detergents. Tests with the same solutions at 49°C show that the metal surface becomes only lightly tarnished during that time period. Although distilled water produced localized areas of extensive reaction after 24 hours, the surface was untarnished after 1 hour at 22°C.

"The success of efforts to define advanced cleaning methods hinges on the ability to determine the cleanliness levels attained by different procedures."

These findings show that plutonium is compatible with warm cleaning solutions and that cleaned components can be rinsed with distilled water at room temperature.

Construction and installation of a laboratory-scale system must be completed before cleaning studies can be initiated. Cleaning efficacy will be evaluated using infrared spectroscopic methods, and optimal cleaning conditions will be defined. The decision to construct a pilot facility is contingent on the results of studies of SCF carbon dioxide cleaning.

Analytical Procedures

The success of efforts to define advanced cleaning methods hinges on the ability to determine the cleanliness levels attained by different procedures. Fourier transform infrared (FTIR) spectroscopy is being developed for indirect and direct measurement of the organic residue remaining on a surface after cleaning. Indirect measurement follows a standard procedure in which a solvent rinse of the cleaned surface is followed by infrared analysis of the solution. Although easily accomplished, this technique is based on the assumption that the solvent is ideal and removes all residues. Reflectance and diffuse-reflectance FTIR techniques are being investigated as possible means for directly quantifying hydrocarbon residues on surfaces.

Development of a rinse method using Freon 113 solvent is complete. The technique analyzes for the total carbon hydrogen concentration from all organic species by integrating the 2800- to 3000-cm^{-1} spectral range and defines hydrocarbon levels as low as 0.3 ppm. With samples from laboratory-scale cleaning studies, the method can determine residue levels of 0.1 microgram of hydrocarbon per square centimeter. The apparatus and procedures for transferring rinse samples from the glove box to the spectrometer are demonstrated with nonnuclear samples. Reflectance equipment for directly analyzing residues is now in design and fabrication. ◆

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SITE-RETURN
PROCESSING

Plasma Chemical Processing

by Joseph C. Martz
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Background

Over the past 20 years, plasma processing has become increasingly important in the fabrication of microelectronic devices. Since the late 1960s, semiconductor manufacturers have exploited the characteristics of plasmas to create increasingly complex circuits. Application of plasma processing to other manufacturing operations has increased in recent years. Diverse operations such as tool hardening, industrial and cosmetic coating, medical instrument sterilization, component cleaning, solar cell manufacture, analytical determination, and archaeological restoration have benefited from advanced plasma processing techniques. Plasmas offer a unique chemical environment in which to deposit, alter, and pattern a wide variety of materials. The plasma environment offers an otherwise unattainable combination of reactive chemical species and energetic particle bombardment, all at room or near-room temperatures (300 to 600 K).

Extension of plasma processing techniques to plutonium production operations offers many advantages. Plasma processing consists primarily of gas/surface reactions conducted at low pressure (1 to 1000 millitorr). For this reason, by-product formation is minimized (minimizing waste generation), feed chemical use is reduced, remote operation is readily accommodated, and process automation is easily implemented. Specific application of plasma processing to plutonium production includes decontamination of items exposed to plutonium and other actinides, plasma-based cleaning of plutonium and nonplutonium components, selective removal of plutonium compounds (such as the selective etching of plutonium dioxide from plutonium), and the growth of novel chemical layers on plutonium surfaces.

Plasma Fundamentals

Plasmas may be generated by a wide variety of excitation sources. Radio-frequency (rf) excitation is the most common source, and plasmas created in this manner are often called rf glow discharges. Energy is coupled into the gas by ionization of gas species, and transfer of energy is accomplished by electron impact. Because electrons are accelerated in the plasma by the presence of electrical fields, they have considerable kinetic energy. Subsequent collision of these energetic electrons with other gas-phase species results in substantial energy transfer.

Examination of the collision process reveals that electronic states of atoms and molecules are selectively excited. If the collision is entirely elastic and occurs without a change in internal energy of the species, the electron will simply rebound from the massive neutral species with little transfer of energy.

"The plasma environment offers an otherwise unattainable combination of reactive chemical species and energetic particle bombardment, all at room or near-room temperatures (300 to 600 K).

Thus, elastic collisions are incapable of imparting a significant translation energy to neutral species. Because the average translation energy of a neutral species is a measure of its temperature, electron impact results in little or no temperature rise. Conversely, if the collision is inelastic and occurs with a change in internal energy, the efficiency of energy transfer increases remarkably. A change in internal energy of an atom or molecule is equivalent to an excitation of the electronic states of that species. Thus, the efficient transfer of energy to the neutral species from electron impact results in an excitation of the electronic states of the molecule or atom.

Electron-impact excitation is sufficient to completely remove one or more electrons from the outer electronic shells of these species, thereby resulting in ionization. The degree of ionization in the plasma is small, however—rarely occurring for more than 0.001% of all species in the plasma.

A more prevalent result of electron impact is dissociation of molecular species caused by excitation of electrons in bonding orbitals to higher-energy antibonding orbitals, resulting in species dissociation. In some diatomic plasmas, the degree of dissociation can reach 60%. In addition, most free-radical recombination occurs as a three-body process, nearly all of which occurs heterogeneously at interfaces. Therefore, free radicals have a long gas-phase half-life, and most surfaces exposed to the plasma are subjected to a significant free-radical flux.

The free radicals resulting from molecular dissociations define the unique chemical environment of the plasma.They are often highly reactive species, such as free-radical halogens, that provide a powerful chemical reagent in which to process a wide variety of materials.

Translational, vibrational, and rotational temperatures have been measured at or near room temperature in most plasma systems. However, thermally equilibrated systems with temperatures of several thousand kelvins would be required to achieve dissociation fractions comparable with those of the plasma. Thus, the plasma is a nonequilibrium thermal environment.

Though the concentration of ions is low compared with the concentration of neutrals, charged species play an important role in many reactions by breaking surface bonds, creating reaction sites, and enhancing product desorption. Ion bombardment provides a directional component to many plasma reactions, allowing anisotropic pattern transfer. Heating effects arising from ion bombardment can play an important role in the kinetics of many important chemical reactions.

Plasma Chemical Processing (continued)

Fig. 1. Schematic of reaction pathways within the carbon tetrafluoride plasma. Circled species indicate stable reaction end products. Arrows indicate reaction of carbon-containing species. Note that most reactions produce atomic fluorine.

Despite the widespread use of plasma processing in the manufacture of solid-state devices, many fundamental aspects of the processes are poorly understood. Simple two-component mixtures of reactant gases in the plasma can give rise to complex chemistries involving dozens of different reactions.[1,2] Optimization of the plasma environment often starts with enhancement of the active reactant concentration. Plasma parameters, such as pressure, applied plasma power, and system residence time, can have a dramatic effect on the production of desired atomic and molecular radicals.

The classic example of gas-phase optimization is the addition of oxygen to carbon tetrafluoride discharges to enhance fluorine production.[3] For more than 20 years, semiconductor manufacturers have known that the addition of small amounts of oxygen (~10%) to carbon tetrafluoride can result in a significant increase in fluorine production.

Figure 1 is a schematic of the important chemical reactions within the carbon tetrafluoride/oxygen discharge.[4] Major products from these reactions include carbon dioxide, carbon monoxide, carbonyl fluoride, and large quantities of atomic and molecular fluorine.

The efficient generation of useful quantities of fluorine gives rise to a whole class of etching reactions based on the formation of volatile metal fluorides. In principle, any material that forms a volatile compound on reaction with fluorine may be etched. Tungsten, tantalum, niobium, carbon, germanium, titanium, molybdenum, boron, sulfur, uranium, plutonium, and, of course, silicon are all candidates for fluorine-based plasma etching.

"In principle, any material that forms a volatile compound on reaction with fluorine may be etched."

Other etching chemistries are possible. The most important of these is the chlorine-based etching of aluminum and gallium arsenide. Although aluminum and gallium do not form volatile fluorides, they do form volatile chlorides. Oxygen-based etching of organic materials (plasma ashing) represents another important class of etching reactions.[5]

Plasma chemistry can be used to selectively etch certain materials in preference to others. For example, numerous oxides (such as silicon dioxide) are readily etched in perfluoro-propane plasmas, whereas the corresponding metals (such as silicon) do not etch appreciably in these environments[6,7] (because of the tendency for carbon-rich discharges to form polymeric films on surfaces).

If the ratio of carbon to fluorine in the feed gas is within a certain critical range, only the polymeric film created by the discharge is etched. In such an equilibrium condition, the net result is neither etching nor deposition. If this process occurs on an oxide surface, the oxygen present in the surface helps to volatilize the carbon-rich polymeric film, yielding an excess of fluorine atoms. This excess fluorine is available to etch the underlying substrate material. Thus, the oxide is etched, but the metal is not. This process yields selectivities as high as 200 to 1 for silicon dioxide-to-silicon etching. Application of this technology to the selective cleaning and restoration of actinide surfaces appears promising.

Oxygen- and water-based plasmas are often used as cleaning agents. The strong oxidizing potential of these discharges serves to ash nearly all organic materials to carbon dioxide and water. Materials traditionally resistant to solvent-based techniques, such as radiolytically cross-linked polymers, are readily removed by these plasmas. This feature is particularly important in plutonium processing because of the radiolytic reactions occurring at plutonium surfaces. Plutonium parts exposed to machining and other oils (for longer than a few days) are usually difficult to clean. Plasma cleaning offers the benefit of cleaning these components while generating only minimal quantities of additional waste.

Plasma Chemical Processing (continued)

Fig. 2. Plutonium etch rate versus reactor pressure in carbon tetrafluoride/ 10% oxygen discharge. Power is 50 watts, system residence time is 10 seconds, and temperature is 298 kelvins.

Plasma Decontamination

The potential advantage of applying carbon tetrafluoride/ oxygen plasma technology to generate volatile plutonium hexafluoride is clear. Efficient generation of fluorine by the plasma, in addition to the enhanced reaction rates available in the glow discharge, offers significant potential for actinide processing and decontamination. The application of plasma processing to plutonium volatilization has been described elsewhere.[8] Figure 2 shows the etch rate of plutonium versus reactor pressure in a carbon tetrafluoride/10% oxygen discharge. Fluorine atom concentration increases linearly with reactor pressure across the range shown in Fig. 2. Thus, the etch rate appears to increase with increasing fluorine concentration (possibly showing first-order kinetics).

Figure 3 compares the etch rate of plutonium with that of plutonium dioxide for several samples processed at a pressure of 200 millitorr. The etch rate of plutonium dioxide is typically 5 to 10 times higher than that measured for plutonium metal. Several factors may account for the high etch rate of the oxide.

Plutonium dioxide has a high surface area when prepared at either room or elevated temperatures. Stakebake and Dringman[9] report a surface area of 16.9 square meters per gram and a crystallite size of 9.7 nanometers for low-temperature, unsintered plutonium dioxide, whereas the sintered oxide is reported to have a surface area of 3.48 square meters per gram and a crystallite size of 68.2 nanometers. A large surface area provides a large etch area for the heterogeneous reaction of fluorine with plutonium dioxide, leading to enhanced reaction rates.
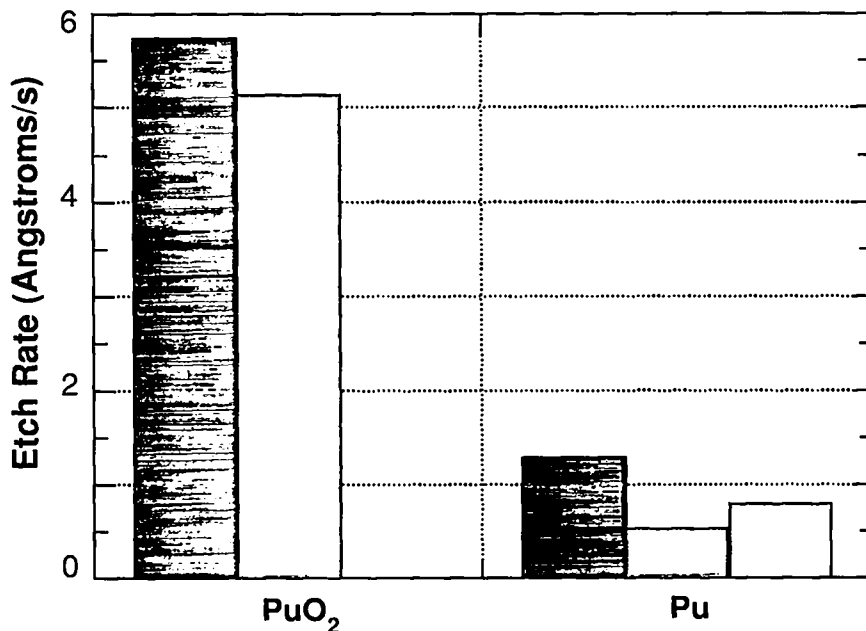
Fig. 3. Comparison of etch rates of plutonium and plutonium dioxide for several etch runs. Pressure is 200 millitorr, power is 50 watts, and residence time is 10 seconds.

volatilization of plutonium hexafluoride proceeds considerably faster than the purely chemical reaction between fluorine and plutonium.[12,13] Several reasons exist for these differences in the etch rate. Chemical sources of fluorine typically rely on surface dissociation of a parent molecule and subsequent surface diffusion before reaction with plutonium can proceed. Conversely, the plasma produces fluorine in the gas phase. A flux of fluorine atoms impinges on all surfaces exposed to the plasma, resulting in a high reaction probability without the need for surface diffusion. In addition, ion bombardment plays an important role in the plasma by creating adsorption sites, promoting reaction and surface activation, and enhancing plutonium hexafluoride desorption. All of these factors may contribute to the high etch rate for plutonium dioxide observed in the plasma (as compared with the etch rate with chemical sources).

Further, it is possible that an oxyfluoride of plutonium may exhibit a higher vapor pressure than pure plutonium hexafluoride, which would account for the increased reaction rate for plutonium dioxide. This is unlikely, however, as the vapor pressures of all known oxyfluorides of plutonium are several orders of magnitude below the vapor pressure of highly volatile plutonium hexafluoride, for which the vapor pressure is 43.35 kilopascals at 52°C.[10,11]

A third possibility to account for the increased oxide etch rate involves the fluorocarbon film model described previously.

Because of the high fluorine content of plutonium hexafluoride, the fluorine-to-carbon ratio for plutonium dioxide etching should be larger than that for silicon dioxide; the equilibrium fluorine-to-carbon ratio for selectively etching plutonium dioxide in preference to plutonium should be nearer 4:1 (as for carbon tetrafluoride feed gas). This effect may also contribute to the observed increase in the etch rate for plutonium dioxide.

The observed plasma etch rate of plutonium dioxide compares favorably with that reported for purely chemical sources of fluorine; plasma

Plasma Chemical Processing (continued)

Fig. 4. Schematic of plasma decontamination reactor. Main reactor body is 2.25-in.-thick glass. Radio-frequency power at up to 300 watts is inductively coupled into the plasma by external copper electrodes.
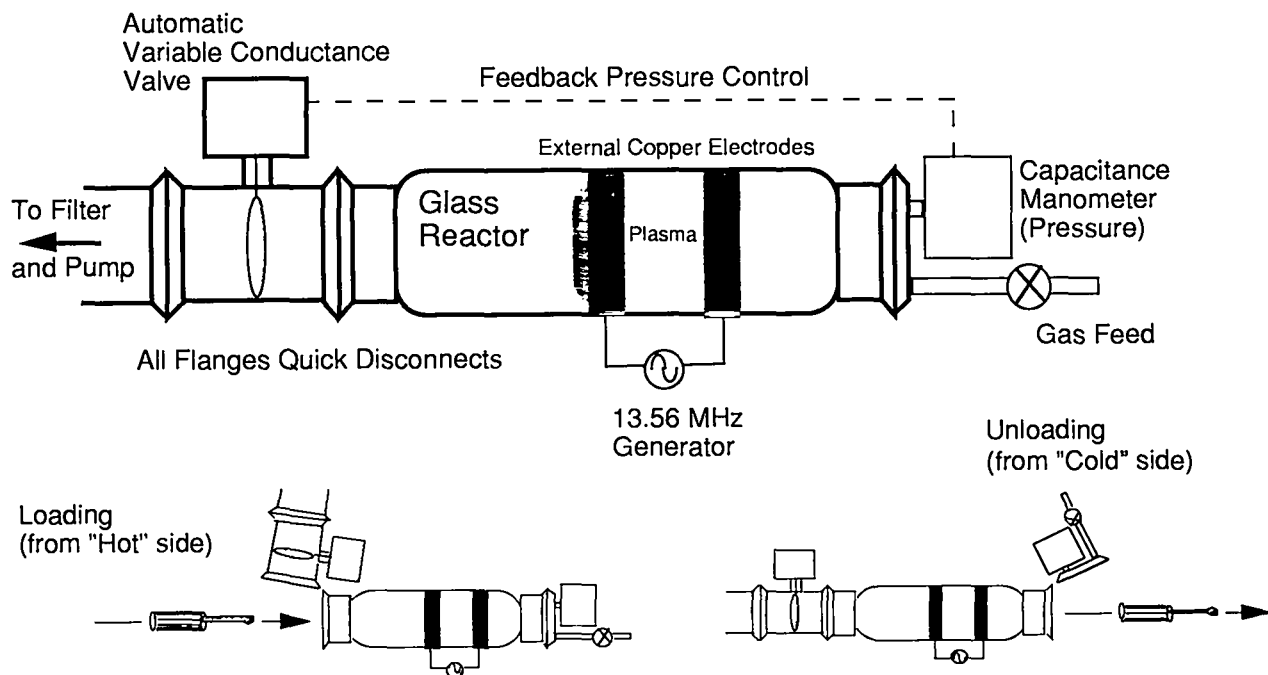

Fig. 4 is a schematic of a plutonium decontamination reactor currently in operation at TA-55. Radiolytically contaminated items are placed in the reactor at one end and, after decontamination, are removed at the other end. This procedure is used to avoid cross-contamination of plutonium during the operation. The plasma reactor is self-cleaning. Established operating conditions ensure that all interior surfaces of the reactor are exposed to the discharge.

Demonstration of the ability to decontaminate "real-world" items is proceeding with this equipment, and initial results are expected in early spring 1992. Plutonium contamination typically consists of small particulates of plutonium dioxide. Further, the quantity of plutonium dioxide present on a contaminated item is often less than a few nanograms. The measured etch rate of plutonium dioxide and the surface areas and particle sizes reported for low-temperature oxide[11] indicate

that processing times of only several seconds are likely to be needed to remove and recover plutonium at typical levels of contamination. Well-established procedures are followed to readily recover and contain off-gas from this operation.

Plasma decontamination has an immediate application in the flow sheet for the Complex 21 Plutonium Processing Facility. Plutonium must be removed from enriched uranium components before they are returned for reprocessing.

"Plasma decontamination of uranium in weapons disassembly should result in substantial waste elimination, a reduction in process times, and near elimination of radiation exposure."

The acid-wash process currently used generates many liters of mixed waste, requires several hours of manual scrubbing with an abrasive pad, and results in considerable personnel radiation exposure. Plasma decontamination of uranium in weapons disassembly should result in substantial waste elimination, a reduction in process times, and near elimination of radiation exposure. The advantages of plasma processing in this application are numerous.

Other Applications of Plasma Processing

The use of plasmas for final cleaning operations in weapons manufacture offers considerable promise. Oxygen-based plasmas could easily remove the machining oils used during production of weapon components. Further, the ability to remove even radiolytically polymerized oils is a distinct advantage of the plasma. An added benefit of oxygen-plasma-based final cleaning is the potential to modify the plutonium surface to a corrosion-resistant state.

Evidence exists that a uniform plutonium dioxide film will passivate the metal to further oxidation. Previous work has shown that dioxide plasmas can grow uniform, adherent oxides on many metals. Therefore, it may be possible to both clean the plutonium surface and grow a well-characterized, uniform oxide film that passivates the plutonium to further oxidation. This process may be of benefit for long-term storage of plutonium.

Other novel compounds such as oxychlorides and oxyfluorides have been produced by plasma exposure. Uniform layers of plutonium oxydifluoride and plutonium oxydichloride are of interest for use in numerous reaction studies. Previous work at Los Alamos has shown that tantalum surfaces exposed first to carbon tetrafluoride discharges and then to dioxide plasmas grow a uniform, adherent tantalum oxyfluoride film. This technique may be extended to plutonium. ◆

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ADVANCED MANUFACTURING

TECHNOLOGY

Advanced Manufacturing Technology Overview

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The manufacturing of plutonium components for nuclear weapons has traditionally used a wrought processing scheme wherein plutonium is cast in a form suitable for subsequent rolling and hydroforming to a near-net shape. These shapes are then further processed by precision machining to reliably produce a part with tightly held dimensional tolerances and a high degree of reproducibility. This processing scheme was chosen because of the wide industrial familiarity with wrought processing and some limited processing conveniences.

At the time wrought processing of plutonium components was implemented, capital investment and maintenance, radiation exposure to personnel, and waste streams and residues generated were not important considerations. Recently, however, a reexamination of the manufacturing scheme, using prototype production experience from Los Alamos and Lawrence Livermore national laboratories

and process development experience from the Rocky Flats Plant, has led to a baseline manufacturing scheme that addresses these wider health, environmental, and capital-intensity issues.

The principal guiding philosophy in this effort has been to substitute modern near-net-shape casting for the traditional wrought processing scheme. In near-net-shape casting, a premeasured and alloyed charge of molten plutonium is direct-gravity cast into a reusable metal or graphite mold. This technique has been in use at both weapon design laboratories for the fabrication of components for Nevada Test Site experiments and other development projects. Additionally, the Rocky Flats Plant used shape casting for several production projects for which wrought processing was unsuitable.

At Los Alamos, we use a custom-designed induction casting process featuring separate coils for both an upper crucible and the lower mold. In operation, a manually operated stopper rod and stirring paddle hold the melt in the crucible. When ready for casting, the operator pulls the stopper and the metal pours onto a metal runner tray that feeds the molten metal into the mold gating system. We have traditionally used graphite molds in nested configuration with calcium difluoride as a mold coating to protect against reaction between the plutonium and the graphite.

Current development work focuses primarily on improving the customized casting furnace by adapting a design begun collaboratively between Rocky Flats Plant and Retech, Inc., a specialty furnace manufacturer.

"The principle guiding philosophy in this effort has been to substitute modern near-net-shape casting for the traditional wrought processing scheme."

During 1992 we will be installing a new version of an induction-heated tilt-pour furnace that will allow us to conduct casting experiments under high-vacuum conditions. The new design will eliminate operator radiation exposures by allowing for remote operational control of the furnace during melting.

Ongoing experiments focus on development of a split mold design that will facilitate easy removal of the part and reuse of the mold. We have also begun development of special fixtures for "creep" annealing of pluto-nium parts following casting. Such a process will allow the part to more closely assume the necessary final dimensional contours before machining. These and other details of our casting development work are covered in more detail in the article "Plutonium Casting and Forming."

Immediately following part casting and heat treatment, the part is moved directly to pre-liminary inspection stations for visual, radiographic, density, and dimensional examination and then to machining. There, another subtle but very impor-tant difference in technique is employed. In the past, machin-ing of plutonium parts included flood cooling and lubrication of the part/tool interface with a light oil. These processes neces-sitate cleanup with organics such as carbon tetrachloride, a suspected carcinogen, and 1,1,1-trichloroethane, a chlorof-luorocarbon slated for elimina-tion. The Los Alamos Plutonium Facility (TA-55) has long prac-ticed "dry" machining of pluto-nium, which requires no organic cutting aids or solvents. The lathes used to dry machine plutonium are enclosed in well-engineered and isolated inert glove boxes not only to pre- serve the metallic finish of freshly machined parts but also to prevent combustion of the finely divided and pyrophoric plutonium turnings.

To further reduce residues (that is, to prevent plutonium oxide accumulation) and control fire hazards, we have also been investigating machine chip management methods. The essential idea is to collect the machine chips in real time using a vacuum-generating device, such as a venturi tube, and then package the chips for rapid delivery to a pyrochemical processing station where they are molten processed under calcium chloride with calcium metal, resulting in a recovery of more than 99.9% of the plutonium metal. This metal is then directly returned for foundry feed, with minimal residue stream generation.

Another important aspect of successful plutonium ma-chining is rapid turnaround to the machinist of accurate gauging information so that the control software can be corrected to compensate for tool wear, temperature instabili-ties, and machine inaccuracies.

Advanced Manufacturing Technology Overview
(continued)

Today, this information is gathered by removing the part and gauging it at a separate station. Plutonium metallurgy personnel at Los Alamos have explored the use of on-machine gauging, a technique in which a noncontacting transducer mounted to the tool post would provide, without part removal, gauging information of equivalent quality. Ultimately, with the proper signal processing and interfacing to the tool positioner, this technique may allow for *real-time* compensation and control of the machining process, guaranteeing true part contours time after time. The details behind successful dry machining of plutonium are discussed at greater length in the article "Plutonium Dry Machining."

Joining technology used in later stages of nuclear primary fabrication has been based principally upon electron-beam welding methods, the state-of-the-art technology when Rocky Flats began production, and its application has been largely successful. In recent years, however, powerful, compact laser systems capable of delivering focused energy deposition suitable for welding or machining applications have matured to the point where obvious advantages are available. As a result, the Los Alamos Plutonium Facility has purchased a 1-kW, pulsed Nd:YAG laser for multipurpose joining applications in nuclear weapons research.

In the past, the use of large electron-beam welding facilities required special handling procedures and the maintenance of associated vacuum systems. Duplicate welders were required for plutonium and nonplutonium applications, and secondary joining and brazing apparatus was required to finish unit fabrication. The laser welding facility at TA-55 will feature an enclosed room containing three glove boxes in which all joining operations for prototype fabrication can be accomplished. These gloveboxes will require only inert gas environments, as opposed to expensive vacuum chambers, and a single laser will service each box through fiber-optic cables switched through a multiplexer station.

"For more than 40 years, as it manufactured prototype test components, Los Alamos has been continuously investigating manufacturing improvements."

Previous development work at Lawrence Livermore National Laboratory has shown that this class of laser couples well to plutonium and other materials of interest and can accommodate filler metal feed, consumable shims, or autogenous joining applications. Additionally, the tuning of such a laser can be altered for special drilling and/ or machining applications, perhaps further minimizing the number of work stations necessary for manufacturing.

Researchers at the Los Alamos Plutonium Facility (TA-55) have also been investigating a new method for accurately measuring the density of plutonium components, termed gas pycnometry. Traditionally, plutonium component density must be determined by immersing the part in a compatible fluid of known density and by then weighing it. By comparing the weight in air with the weight in the fluid, we can ascertain the density of the component.

Unfortunately, the preferred fluids include Freon and monobromobenzene, organics slated to be discontinued for various reasons. In gas pycnometry, helium gas is charged into a space with the plutonium and then evacuated into a calibrated volume. The displaced volume of the part is thus accurately measured, and this volume combined with the weight reveals the density. Preliminary tests with small metal samples have been successful thus far.

For more than 40 years, as it manufactured prototype test components, Los Alamos has been continuously investigating manufacturing improvements.

While helping to define a baseline manufacturing scheme for the modern nuclear weapons complex, we are developing many of the new technologies that will result in lower capital equipment expenditures, reduced radiation exposure to personnel, smaller waste-stream volumes, and actual elimination of waste in some cases. Importantly, Los Alamos does this in a pilot-scale manufacturing environment using weapons-grade plutonium, thereby ensuring that many factors related to implementation and utility are addressed in a suitable environment. ◆

ADVANCED MANUFACTURING TECHNOLOGY

Plutonium Casting and Forming

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Introduction

Plutonium fabrication processes incorporate a wide variety of complex and precise techniques. Most of these techniques were established during the 1950s and 1960s and now require upgrades to meet the technology needs of the 1990s. Of particular concern are efforts to simplify processes and minimize waste while maintaining product quality. Current research, design, and development activities in the areas of near-net-shape gravity casting and final forming of plutonium seek to reduce by half or more personnel radiation exposure, generation of plutonium scrap and secondary waste, production floor-space requirements, and environmental pollution.

Background

Casting is a necessary and versatile part of all plutonium fabrication schemes. The casting methods of the future will meet requirements for minimization of waste as well as for efficiency of plutonium use.

To meet the challenge of environmental, safety, and health considerations, Los Alamos scientists have been rethinking plutonium casting procedures to develop techniques that simplify the wrought fabrication process characteristic of operations at the Rocky Flats Plant. The wrought process typically required multiple steps as follows:

1. Cast plate
2. Heat treat
3. Roll
4. Shear circle
5. Heat treat
6. Form shape
7. Heat treat
8. Machine

The wrought-fabrication method at Rocky Flats was tailored to produce flat parts for rolling, forming, and machining processes developed decades ago. Although a die-casting program was initiated about 10 years ago to improve efficiency and minimize waste, the resulting die-casting machine was complex, cumbersome, and difficult to maintain.

Efforts to die cast near-net-shape hemishell parts contributed to machine and mold complexity; therefore, die casting never reached production status at Rocky Flats.

A proposed new process, based on die-casting experience at Rocky Flats and gravity-casting experience at Los Alamos, involves shaped gravity casting and final forming during heat treatment with reusable metal molds and heat-treatment fixtures. The process comprises only three steps:

1. Near-net-shape gravity cast
2. Simultaneous homogenize and creep form
3. Dry machine

The creep-forming step (step 2) will increase flexibility and reduce tolerance requirements of the initial shaped casting. Such a casting process is simple and relatively free of problems; the casting equipment requires only minimal maintenance, and the simplified mold design will improve mold life.

"The casting methods of the future will meet requirements for minimization of waste as well as for efficiency of plutonium use."

Implications for environmental issues are also favorable, as the near-net-shape process requires less plutonium alloy than does the wrought process. Therefore, it should generate less primary plutonium waste in the form of plutonium-bearing residues. Reuse of molds and hardware will result in lower quantities of secondary waste. Also, better casting-furnace design and improved glove-box atmospheres will significantly decrease plutonium oxide formation. At Rocky Flats most plutonium waste was generated during recovery of plutonium metal from plutonium oxide, and the plutonium foundry was the single largest generator of plutonium oxide.

Approach

Los Alamos scientists are undertaking a number of technical activities in parallel to develop a process using graphite molds and fixtures now but integrating reusable metal molds and fixtures later. These activities include

1. Development of a subscale plutonium casting and forming process using graphite molds and fixtures.
2. Development of metal molds by saturable carburizing or nitriding and by coating with ceramics.
3. Finite-element modeling to optimize casting parameters and mold and fixture design.
4. Conduct of casting experiments using nonradioactive surrogate alloys to shorten development time.
5. Process flow modeling of casting and forming to quantify predictions of total waste generation and to identify areas needing improvement; incorporation of results into larger process models for the Complex 21 Plutonium Facility to follow.
6. Full-scale plutonium casting and forming to verify all work defined in 1 through 5 above.

Recent Results

Casting, heat treating, and final forming of a subscale part have been completed. Gravity-casting equipment similar to that already proved in a production environment was used.

The results of the subscale work are:

1. Calculations predicted correctly that the decrease in density during heat treatment would significantly change the dimension of the plutonium part. The calculated dimensional change values were used to design the mold and the heat-treatment fixtures.

2. A split-mold design allowed easy removal of the cast plutonium part, thereby increasing mold life, decreasing damage of the part during break out, and reducing waste.

3. Inspection on a coordinate-measuring machine showed that the contour of the heat-treated part closely follows the contour of the heat-treatment fixture.
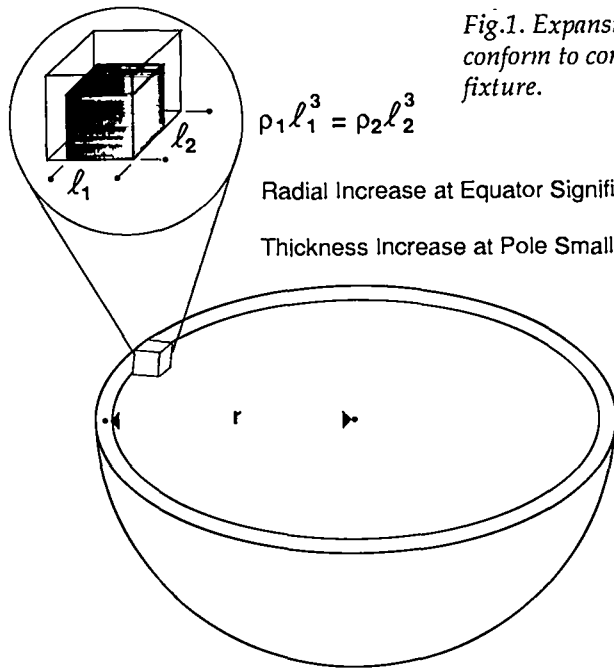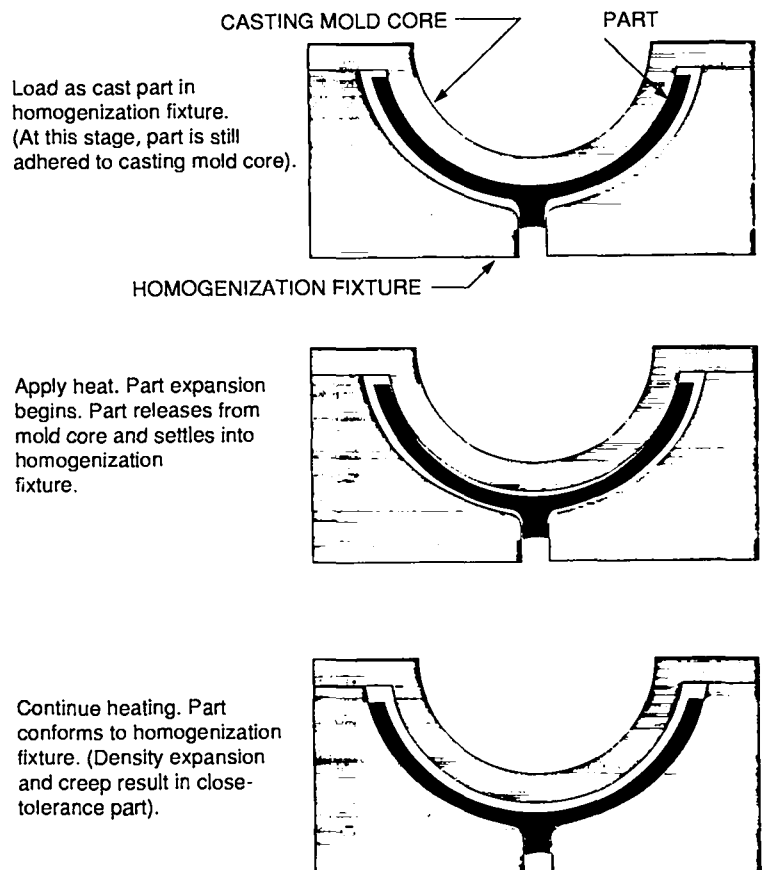
Plutonium Casting and Forming continued)

Fig.1. Expansion of plutonium to conform to contour of heat-treatment fixture.

$$\rho_1 \ell_1^3 = \rho_2 \ell_2^3$$

Radial Increase at Equator Significant

Thickness Increase at Pole Small

Fig. 2. Simplified depiction of density expansion and creep forming during heat treatment.

CASTING MOLD CORE ⟶ PART

Load as cast part in homogenization fixture. (At this stage, part is still adhered to casting mold core).

HOMOGENIZATION FIXTURE ⟶

Apply heat. Part expansion begins. Part releases from mold core and settles into homogenization fixture.

Continue heating. Part conforms to homogenization fixture. (Density expansion and creep result in close-tolerance part).

The split-mold design allows easy release of the plutonium cast part from the outer case. Figure 1 shows how expansion during the phase change resulting from heat treatment causes the part to move out radially and closely conform to the contour of the heat-treatment fixture. Figure 2 shows how the core of the plutonium casting mold is positioned in the heat-treatment fixture and how the plutonium casting releases from the mold core during heat treatment and settles into the heat-treatment fixture.
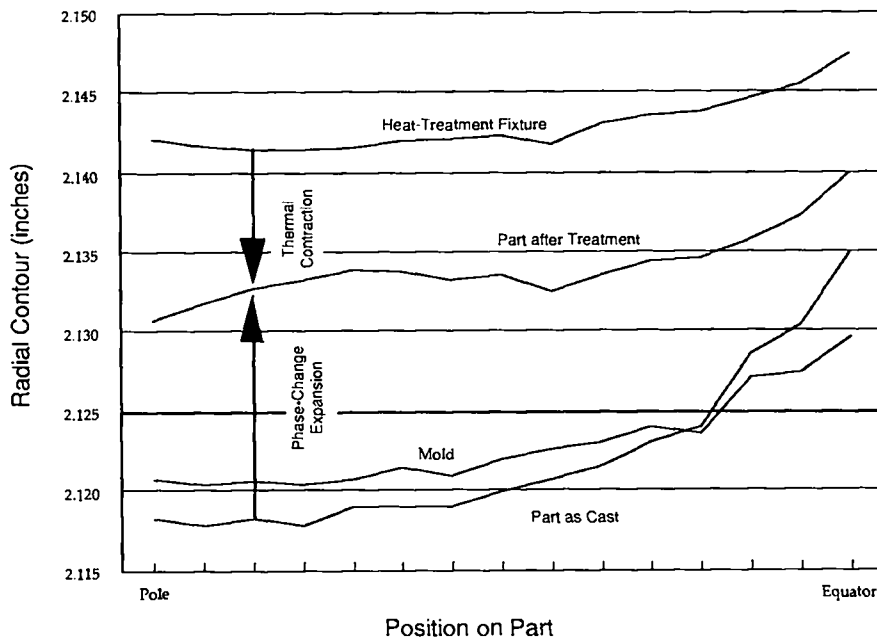
Fig. 3. Inspection data at various stages of the subscale casting process.

The creep of the plutonium part caused by gravitational force contributes to this hot forming process. In the future we wil lbe testing a low-thermal-expansion metal fixture.

Figure 3 summarizes the inspection data recorded at various stages of the subscale process. The contour of the plutonium part after heat treatment closely follows the contour of the heat-treatment fixture.

Summary

Los Alamos scientists are developing a production process for near-net-shape gravity casting, heat treatment, and forming of plutonium parts. Key elements in the process are gravity casting to shape, split-mold design for easy part release, and use of phase change and creep during heat treatment (homogenization) to expand the plutonium part into a close-tolerance heat-treatment fixture.

By using bottom-pour and tilt-pour plutonium casting furnaces, the process applies existing technology rather than developing major new equipment, as would be required in a die-casting process. ♦

ADVANCED MANUFACTURING TECHNOLOGY

Plutonium Dry Machining

by Rueben L. Gutierrez
Plutonium Metallurgy Group

Introduction

The machining of plutonium parts to exact specifications is crucial in the development of nuclear weapon designs. Because plutonium metal is pyrophoric and the cutting operation performed during machining produces heat from friction, the metal is susceptible to ignition and combustion when exposed to air during the process. Before 1986, machining of plutonium parts for weapons research and development at Los Alamos required the use of freon for cooling during machining. Also, the Rocky Flats process for machining production quantities of plutonium parts required that plutonium parts be flood cooled with oil. The oil added to cool the part during production machining not only prevents combustion of the plutonium metal but also minimizes expansion of the part.

However, in 1986, the Plutonium Metallurgy Group, developed a dry machining technique that eliminates the need for solvents and oils during glovebox operations involving machining of plutonium metal. Implementation of the dry machining process at Rocky Flats would have significantly reduced the waste streams being generated during the production operations for the manufacture of nuclear weapons. Use of dry machining rather than flood cooling with oil would have eliminated the need for 2,500 gallons of cutting oil and 15,000 gallons of trichloroethylene, which is used as a cleaning solvent, annually.

Combustion during dry machining of plutonium parts is prevented by performing the operation in an inert glove-box atmosphere in which the maximum upper limit for oxygen is 3000 ppm. By using a low-oxygen atmosphere, machine turnings do not undergo surface oxidation.

Machining Support Operations

Two other areas presently under development will enhance the dry machining operation. One is application of a vacuum technique for collecting chips produced during machining, and the other is an in-process technique for gauging the contours of produced parts.

Plutonium Dry Machining (continued)

Before production operations at Rocky Flats stopped, personnel there had initiated a technique for removing plutonium chips as the part was being machined. Called Vortex, the technique involves using a vacuum to suck the metal chips away and siphon them into a canister. Before this method was introduced, machinists pulled the chips away with a pair of tweezers and dropped them into a canister. The Vortex system minimizes radiation exposure by allowing personnel to withdraw from the glove box. This technique is being refined and will be incorporated into the TA-55 plutonium machining operations.

An in-process method for gauging machine performance will provide precise gauging information of the part being machined. The technique involves the use of a variable impedance transducer (VIT) to measure the machined surface of the part. The VIT works in unison with the tool bit and the lathe's preprogrammed controller. Once this technique is fully developed and implemented, we will no longer need to remove parts from the lathe to confirm accuracy. This will minimize the number of times a part must be handled, thereby reducing the potential risks of damage to the part and of personnel radiation exposure.

Current and Future Developments

Although dry machining is ready for production operation, a few enhancements are being addressed. For instance, we are investigating thermal cooling of the pot chucks, which hold the part, and the tool bit. The technology for vacuum collection of machine chips is nearing completion. However, in-process gauging of machined parts is in the seminal stage of development and will be ready for production operation in about 2 years. It is fully expected that dry machining, chip collection and management, and in-process gauging will be fully developed as a cohesive operation within the next 2 to 4 years. ◆

Nitrate Recovery Overview

by Bill McKerley

Nuclear Materials Processing Group: Nitrate Systems

The Plutonium Facility of the Future, commonly referred to as "Complex 21," will include the disassembly of site-return pits, purification of site-return metal, assembly of product pits, recovery of plutonium from residues generated in the production and recovery operations, and processing and packaging of the wastes for shipment and disposal. This overview focuses on the nitrate recovery baseline flow sheet, which is an integral part of the overall baseline plutonium facility flow sheet outlined on page 9. The current nitrate recovery operations at TA-55 provide the basis for the nitrate recovery baseline flow sheet envisioned for Complex 21.

The nitrate recovery baseline flow sheet consists of the following unit operations:

- Pyrolysis and Calcination
- Pretreatment
- Acid Decontamination, Leachate Treatment
- Leaching
- Cascade Dissolution
- Anion Exchange
- Precipitation
- Calcination
- Evaporation

At the Los Alamos Plutonium Facility as well as Complex 21, the primary feed source will be plutonium process residues from the recovery, manufacturing, and analytical laboratory operations.

A large quantity of bulk materials generated from other operations will also require some processing. The goal of the nitrate recovery baseline flow sheet is to recover the plutonium, to produce a pure oxide for conversion to metal, and to ensure that the resulting residues are in a form that meets all waste acceptance criteria.

The pyrolysis and calcination operations will support several flowsheets. As currently envisioned, these operations will produce an ash from combustible materials for further chemical recovery of the residual plutonium. An incineration-type capability is a critical step in the flowsheet but presently is not considered to be a licensable/permittable process. Consequently, we are investigating several alternatives, such as a thermal decomposition unit that is performed in an inert atmosphere, molten-salt thermal decomposition, and supercritical water oxidation.

"The Plutonium Facility of the Future, commonly referred to as 'Complex 21,' will include the disassembly of site return pits, purification of site return metal, assembly of product pits, recovery of plutonium from residues generated in the production and recovery operations, and processing and packaging of the wastes for shipment and disposal."

Pretreatment operations include sorting, milling and grinding operations, that are used to segregate and size-reduce residues, as needed, before dissolution. Also, we are collaborating with researchers in NMT-3 to develop and demonstrate (on a production scale) magnetic separation techniques such as magnetic-roll or drum-type separators and high-gradient magnetic separation. This physical separation technique supports waste minimization efforts by allowing only plutonium-rich residues to be sent for aqueous recovery. The plutonium-lean portion is suitable for transfer to waste management for disposal. Other physical processing methods may be necessary, and we continue to investigate new approaches.

The acid decontamination and leachate treatment operations chemically remove plutonium surface contamination from Oralloy parts. These parts are leached with nitric acid to remove residual plutonium contamination. The clean, nonplutonium metal will then be acceptable for return to the uranium handling facility.

The solution (leachate) will be transferred to ion exchange or waste treatment for further processing, depending on the plutonium content.

Nitrate leaching/dissolution processes produce plutonium nitrate solution by dissolving and/or leaching plutonium oxide from plutonium-containing materials using nitric acid and fluoride ion. Dissolution takes place in dissolver pots or cascade dissolution systems where the flow rate of feed and reagents differs with the different feed materials.

Process analytical chemistry developments will allow the real-time determination of key parameters, such as acid concentration, fluoride ion concentration, and plutonium concentration. This will allow better process control, which directly affects the ability to reduce waste, provides better materials control and accountability, and greatly increases process efficiency.

The nitrate solution is filtered, and the undissolved solids are collected and dried. The undissolved solids are either recycled or disposed of as waste, depending upon plutonium content. Dissolution techniques such as the catalyzed electrochemical plutonium oxide dissolver are being evaluated to determine their application on hard-to-dissolve residues. The filtered solution is stored in tanks and analyzed for subsequent processing in the anion exchange system.

The purpose of the anion exchange process is to concentrate and purify plutonium in nitrate solution. The nitrate solutions are first analyzed for acid concentration, plutonium valence, and plutonium concentration. The acid concentration is adjusted to 7 $\underline{M}$ by adding either concentrated or dilute nitric acid (HNO_3) as required. The Plutonium is stabilized in the (IV) valence by the addition of reagents such as hydrogen peroxide. In 7 $\underline{M}$ nitric acid, plutonium(IV) forms an anionic complex that will adsorb on anion exchange resin. The anion exchange operation is essentially a four-step process— loading, washing, eluting, and reconditioning.

In the loading cycle, plutonium is adsorbed on the anion exchange resin. The effluent from a load cycle contains the elemental impurities and is transferred to the acid recycle system after being analyzed for plutonium.

If the plutonium content is above the discard limit, the effluent is recycled. The nitric acid wash cycle removes residual impurities from the columns. The wash solution is also analyzed before transfer to the acid recycle system.

During the elution cycle the plutonium is removed from the ion exchange resin by the addition of a reducing agent such as hydroxylamine nitrate or with the use of dilute nitric acid. The eluate, containing the purified plutonium, is sent to the precipitation step. After elution, the resin is returned to a nitrated state by reconditioning the columns with 7 $\underline{M}$ nitric acid. The ion exchange columns are now ready to repeat the entire cycle. Current R&D activities in resin development, process analytical chemistry, process chemistry, and process control and instrumentation are yielding results that are directly applicable to the needs of today's plutonium recovery operations as well as the requirements for Complex 21.

The addition of solid oxalic acid to a plutonium nitrate solution results in the formation of an insoluble complex that precipitates from solution. This solid plutonium oxalate complex is collected by filtration and is transferred to the calcination operation where excess nitric acid and water are removed and the plutonium oxalate is converted to plutonium dioxide. The thermal decomposition of the oxalate ion takes place at approximately 600°C or above.

Enhanced precipitation techniques such as homogeneous oxalate and hydroxide precipitations are being investigated. These precipitation techniques hold the potential for easier filtration and lower actinide levels in the filtrates.

The product from this process, the dry plutonium dioxide, would then be transferred to the chloride recovery area for conversion to metal using multicycle direct oxide reduction (MCDOR).

"These advances in process control will not only allow an enhanced capability to manage our recovery operations, but will also support a superior materials control and accountability program."

The nitric acid recycle portion of the nitrate recovery baseline flow sheet incorporates evaporation, oxalate ion destruction, nitric acid fractionation, and nitrate destruction unit operations. Solutions such as ion-exchange effluents and oxalate filtrates are transferred to an evaporator in preparation for nitric acid recycle. This requires several process steps:

1) oxidation of oxalic acid to CO_2 and H_2O;
2) recovery of HNO_3 from evaporator bottoms;
3) fractionation of recovered nitric acid to form a dilute nitric acid waste stream and a concentrated and purified nitric acid stream for recycle;
4) catalytic conversion of excess HNO_3 to benign N_2 gas; and
5) disposal of the dilute acid evaporator bottoms to waste.

The product from this process (pure, reusable 12 M HNO_3) will be used, as required, throughout the nitric acid recovery system. The waste streams from this process are CO_2 and N_2 off-gasses, evaporator bottoms containing concentrated impurities, and a dilute nitric acid stream from the fractionator.

Reagent recycle is obviously an important component of our waste minimization efforts. We are currently demonstrating nitric acid recycle on the Advanced Testing Line for Actinide Separations (ATLAS). This advanced line will be the site where many of the development and demonstration activities will take place.

In many of the operations described above, there is a need for real time information regarding acid concentration, anion concentrations, plutonium valence, impurity concentrations, etc. By providing this important information to the process engineer in real time or near real time, decisions can be made to tailor the processing parameters to the appropriate conditions. In addition, this process information is being combined with a modern computer-based process monitoring and control system that will allow processes to be operated for reduced waste, decreased personnel exposure, and purer product.

Nitrate Recovery Overview (continued)

These advances in process control will not only allow an enhanced capability to manage our recovery operations, but will also support a superior materials control and accountability program. These factors are vital for the plutonium facility of today and are even more important for the plutonium facility of the future, which will most likely be required in a much more restrictive environment.

This overview of the nitrate recovery baseline flow sheet has summarized the unit operations that will support Complex 21. In addition, a brief glimpse has been provided into the research development and demonstration activities that are ongoing at Los Alamos to ensure that the plutonium facility of the future will have the capability to respond to a wide range of processing requirements. ◆

NITRATE

RECOVERY

Process Analytical Chemistry

by Rick Day
Nuclear Materials Processing Group: Nitrate Systems

The waste challenge for facilities in the DOE complex engaged in the aqueous recovery of plutonium from residues is largely a chemical processing issue. In fact, one important way to minimize or eliminate waste is to address the problem at its source: in the process. The close monitoring of process parameters and the early identification of process upsets are key features of any system that seeks to minimize waste generation and reduce cost, both in dollars and worker exposure. Laboratory studies indicate that many of the parameters that govern process operation can be measured successfully using the on-line and at-line techniques of process analytical chemistry. Processing information thus acquired can

• lower reagent consumption, thereby reducing the amount of waste generated,
• reveal levels of actinides in waste streams, thereby facilitating more efficient recovery operations based on real-time processing information,

• eliminate the need to reprocess out-of-specification material,
• identify process inefficiencies, and
• better characterize and monitor waste stream compositions.

The Advanced Testing Line for Actinide Separations (ATLAS) provides the means for testing, evaluating, and incorporating into residue recovery processing those process analytical chemistry technologies that have been proved in principle. ATLAS emphasizes the integration of analytical methods into a single system for supplying real-time chemical information and applying that information to processing refinements. The formulation of developmental strategies for all processing modules requires that analytical methods be combined with statistical process control and experimental design.

The following baseline technologies are now being demonstrated on ATLAS:

• an ion chromatograph for monitoring anion impurities,
• an automated titration system for measuring free acid,
• a visible, near-infrared, fast-scanning spectrophotometer for on-line measurements of plutonium oxidation state, nitrate concentration, and interfering anions,
• an on-line x-ray fluorescence spectrometer for impurity metal analysis, and
• specific chemical sensors, including a chloride sensor and the R&D 100-award-winning high-acidity sensor developed by the Nuclear Materials Process—Nitrate Systems Group, NMT-2; the Materials Technology Polymers and Coatings Group, MST-7; and the Analytical Chemistry Group, CLS-1.

Process Analytical Chemistry (continued)

Instrumentation of three types is applied during the development of process analytical chemistry technologies: specially modified instrumentation for at-line use in a glovebox environment, commercially available instrumentation for on-line use for real-time monitoring, and chemistry-specific sensors developed at Los Alamos for on-line use during plutonium processing.

At-line technologies such as the ion chromatograph and automated titration consist of standard laboratory instruments modified to work in a glove-box environment. At-line instruments in glove boxes are located adjacent to the processing locations and supply near-real-time information. The analysis they provide also serves as a "reference method" to guide the development of more advanced on-line and sensor methodologies.

Current on-line technologies use advanced data analysis techniques, including partial-least-squares analysis, fundamental-parameter analysis, and commercially available instrumentation. A fast-scanning spectrometer multiplexed by fiber-optic cables to remote sampling locations performs visible spectroscopy during anion exchange feed treatment, column wash make-up, oxalate precipitation, and waste stream monitoring. Chemometric methods are used to analyze spectral scans that measure total plutonium, plutonium oxidation state, nitrate concentration, and interfering anions. An x-ray fluorescence spectrometer not only operates at the line to categorize various feed materials but also monitors the ion exchange effluent on-line to optimize wash volumes and track the actinide concentrations coming off the ion exchange column.

Several compact chemistry-specific sensors are either already in use or close to completion. The recently developed high-acid sensor consists of a Hammond indicator bound in a polymer coating and an optical flow cell monitored by the fiber-optic spectrophotometer. A new chloride sensor applies a commercial ion-selective electrode to concentrations outside its normal operating range; a similar fluoride sensor is under development. An electrochemical sensor is being designed for use in solutions containing mixtures of uranium and plutonium.

The continuing development and use of process analytical chemistry technologies and the resulting knowledge of process parameters and analytic ranges will remain evolutionary, as new methods and sensors continue to be explored and evaluated.

"The waste challenge for facilities in the DOE complex engaged in the aqueous recovery of plutonium from residues is largely a chemical processing issue."

An inductively coupled plasma mass spectrometer being acquired to aid in the monitoring of waste streams will also be used in near-line fashion to analyze solutions before a concentration step such as precipitation is performed. Detection of out-of-specification material at this point can substantially reduce waste by eliminating the need to rework out-of-specification oxide.

Research in the area of sensors and related techniques, such as flow injection analysis, will continue. As industrial process analytical chemistry continues to grow as a field, the resulting new instrumentation will be evaluated for application to the special requirements of actinide process stream analysis within the confines of the glove-box environment.

Process Analytical Chemistry Applications to Complex 21.

The instrumentation and methods being developed on ATLAS are designed to supply near real-time chemical analysis on virtually all of the aqueous unit operations found in the Complex 21 flow sheet for nitrate recovery of plutonium scrap. The measurements being developed on ATLAS supply information on important processing parameters including plutonium oxidation states, free-acid concentration, interfering anions and trace metal impurities. These process analytical techniques can also be applied to the Complex 21 flow sheets for chloride recovery and aqueous waste streams, which share many of the same parameters that need monitoring.

Process Analytical Chemistry Benefits to Complex 21.

Closer monitoring of process parameters and early identification of process upsets in Complex 21 will ensure that product quality and waste minimization goals are met. Additional benefits include better understanding of the chemistry involved in the processing, characterization of process and waste streams, and minimizing the need to rework out-of-spec products. ◆

Nitrate Recovery

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NITRATE

RECOVERY

Process Measurement and Control

by Noah G. Pope
Nuclear Materials Processing Group: Nitrate Systems

For many years, aqueous processing at TA-55 and other nuclear materials facilities has been conducted with a hands-on, operator-based approach. Recently, however, an effort to incorporate modern industrial computer-based process monitoring and control systems has been initiated. Complex 21 plays a vital role in this program. Most, if not all, of the processes planned for Complex 21 will require some form of computer-aided process control or automation. Clearly, a strong control and automation program is essential to accomplish these technical challenges. Modern control technologies will strengthen Complex 21 by reducing operator radiation exposures to levels as low as reasonably achievable, minimizing the generation of waste by optimizing operations, increasing the understanding of the chemical processes by applying iterative techniques of data acquisition and modeling, and increasing overall safety by incorporating computer-supervised systems of alarms and monitors.

A strong control effort is required for administrative reasons as well. At TA-55, these issues include the increase in auditing requirements that has resulted from new DOE orders related to conduct of operations and quality assurance. The availability of computers alongside the processes also allows technical reports to be compiled in a more convenient and timely manner.

It is vital that NMT Division maintain a viable industrial control and automation capability. Towards this end, we have selected proven reliable and commercially available technologies that are common throughout other, more mainstream chemical process industries. At TA-55 these capabilities are being introduced incrementally to increase the overall safety, reliability, and efficiency of the operating environment.

By emphasizing process control as well as automation, we rely on the experience of the process operators and plant environment testing to constitute the foundation on which automatic control may be successfully instituted. In anticipation of the requirements of the Complex 21 control environment, we have instituted a program that covers the majority of processes within the nitrate flowsheet. The effort began by applying industrial control techniques to the nitrate evaporation unit operation. Using the experience gained there, the program was recently expanded to include other unit operations common to both TA-55 and Complex 21. In addition to evaporation, the unit operation control systems under development include dissolution, ion exchange, feed preparation, acid recycle, eluate and oxalate precipitation, and calcination.

"By emphasizing process control as well as automation, we rely on the experience of the process operators and plant environment testing to constitute the foundation on which automation control may be successfully instituted."

From the experiences gained on these projects and on a fundamental understanding of current control technologies, a number of important development principles have been established. These principles and the projects to which they have been applied are outlined as follows:

Information Flow. Information should be shared between unit operations for the total operation to flow smoothly from start to finish. Thus, a common information data base should be accessible from a variety of processors and software languages. Because process parameters derived during one operation may be of value in a subsequent process, such information should by readily available. For example, during plutonium processing, the amount of oxalic acid added by a technician to complete the precipitation step directly affects the performance of the downstream waste evaporator, a system operated by different technicians.

A multitasking environment that allows on-line, real-time access to such information would be ideal.

Hardware Selection and Configuration. Hardware should be decentralized to avoid reliability problems common to large single-processor systems. A network of several small computers, which are considerably less expensive and easier to replace than a single large computer, provides several layers of back-up processor power should power fluctuations, contamination, or other facility problems cause a computer to fail. Although small computers lack the speed common to large systems, personal computers with 80386- and 80486-type processors have proved to be fast enough to handle most industrial processing situations.

Software Selection. Commercial software should be used so that scientists, engineers, and operators spend their time configuring the system rather than writing custom software and drivers. Their expertise lies in process operations, not in the inner workings of a computer. Therefore, operators and line supervisors should be able to customize and modify their process screens without in-depth knowledge of computer programming.

Control System Concept. Because process operators possess by far the greater control intelligence, the control system should serve as an extension of, rather than a replacement for, their capabilities. Operators stabilize the environment by exerting an intelligence and flexibility that far exceed the qualities of even the most advanced computers. Thus, the control system's function would be to increase the operators' ability to interact with a process.

Process Measurement and Control (continued)

However, the control system should be sufficiently flexible to accommodate unforeseen circumstances because most processes have a finite life expectancy, and modifications may be required to meet new processing needs. The control system should be layered so that it has at least two back-up modes of operation, one of which would be a manual override capability to ensure that all operations continue even without computer control. Preservation of the excellent manual control operations at TA-55 is essential because of their proven track record and their contribution to the training effort.

Current Development Projects. NMT-2 presently has under way several process control and measurement projects that embody the features specified above: the enhanced evaporator process, the metal preparation line, the Advanced Testing Line for Actinide Separations (ATLAS), and the multipurpose cascade dissolvers. These projects use similar computer hardware and software and similar input/output hardware.

The enhanced evaporator process, which is a technology common to both TA-55 and Complex 21, has more than two dozen inputs and has operated successfully for more than 2 years. The system throughput is nearly double that previously achieved, and the number of operators required has been reduced by half. The data-logging capability has proved valuable for the diagnosis of process upsets.

Of the control projects in progress, ATLAS has by far the most advanced capabilities. Designed to encompass most of the unit operations on the Nitrate Recovery flow sheet for Complex 21, ATLAS presents control challenges common to large, multiple process plants. To meet these challenges, three 80386- and 80486-based Compaq computers running the OS/2 operating system are networked together to run a commercial control software package. Each computer is located near a different unit operation, and a network link to other areas of TA-55 allows system design and supervision to be performed outside the laboratory. Each piece of input/output hardware uses a commercially supplied software driver. A network security system tracks manpower usage and helps ensure that only qualified personnel are allowed access to the system.

"Designed to encompass most of the unit operations on the Nitrate Recovery flow sheet for Complex 21, ATLAS presents control challenges common to large, multiple process plants."

All ATLAS operators have been trained to create their own custom control screens. A complete, automatic data-logging capability allows large quantities of information to be collected for on-line or post-process analysis. ATLAS includes both batch and recipe control capabilities, and an on-line statistical quality control package will be incorporated to assist operators in process diagnostics. A complete supervisory process alarm system is available. Development time has been reduced to a minimum by the use of proven, commercially available technology.

NMT-2 has developed a clear methodology for upgrading Los Alamos' process capabilities to include a process measurement and control system of the type described here. The transition from computerized process control to automation of the process itself requires careful deliberation based on experience gleaned from work with simpler systems. Future processing systems should be designed with control system constraints in mind. The challenges presented by Complex 21 demand that technical developments be based on sound engineering and scientific experiences. NMT-2 has made the required investment in the area of process control and automation as part of our continuing effort to meet the needs of the nuclear weapons complex. ◆

N I T R A T E

R E C O V E R Y

Process Chemistry

by Gordon D. Jarvinen
Nuclear Materials Processing Group: Nitrate Systems

The innovative separations chemistry needed for the DOE to accomplish its goals of cleanup of the nuclear weapons complex and more efficient operations in Complex 21 guarantees that research, development, and demonstration (RD&D) activities in process chemistry at Los Alamos will remain essential. The next generation of production facilities, regardless of type or location, will integrate advances in separations technology with on-line sensors and computer control systems to increase safety, reduce personnel radiation exposure, minimize waste, and improve product quality and yield. Developments at the Los Alamos Plutonium Facility will lead to the prototype systems to be integrated into the reconfigured production complex. Even now, the cleanup of a wide variety of actinide-contaminated wastes and sites within the DOE complex requires the ability to tailor separations chemistry to address widely different conditions.

The ongoing RD&D work in the nitrate systems group (NMT-2) covers a broad range of activities, from short-term improvements in operating processes to long-term efforts to obtain fundamental knowledge of separation processes and metal coordination chemistry. The improvements in operating processes that can be implemented in the near future will be incorporated into the baseline flowsheet for Complex 21. The longer range RD&D efforts will provide alternative processing methods that enhance the Complex 21 baseline. The following paragraphs summarize recent progress by tracking the flow of a plutonium-containing residue through the nitrate recovery operation, which includes the following steps:

- sorting, decontamination, and dissolution,
- feed pretreatment,
- metal ion separations,
- product preparation,
- recycling of reagents, and
- waste treatment.

Many of the accomplishments described briefly here are the result of collaborations with other groups in the Nuclear Materials Technology Division, groups from other Laboratory divisions, and employees of other DOE facilities, universities, and industrial firms.

Sorting, Decontamination, and Dissolution. Several new technologies related to the first step in the plutonium recovery process are in various stages of development.

- Magnetic separation of certain finely divided plutonium-containing solids into a small fraction that is relatively rich in plutonium and a large fraction that can be discarded as low-level waste has been demonstrated on a process scale, using a commercially available open-gradient device. After separation, the plutonium-rich fraction can be dissolved and the plutonium recovered by aqueous processing methods.

> *"Developments at the Los Alamos Plutonium Facility will lead to the prototype systems to be integrated into the reconfigured production complex."*

Results from preliminary tests using a high-gradient magnetic separation system are very encouraging. Advantages of the high-gradient system relative to the open-gradient device include the capability to separate smaller particles and operate on aqueous suspensions.

• An electrolytic cell constructed in a plutonium glovebox line now enables researchers in NMT-2 to examine the use of the silver(I)/silver(II) couple to promote the dissolution of plutonium oxide in nitric acid under relatively mild conditions.

• Collaborators in the Isotope and Structural Chemistry Group, INC-4, have found that siderophores and synthetic analogues of siderophores show promise in the removal of actinide contamination from soils and surfaces. The siderophore enterobactin was found to be more effective than 0.1 M nitric acid and a variety of other chelating agents in dissolving an aged plutonium hydroxide polymer.

Feed Pretreatment. Fluoride is usually present in the nitric acid solutions from the dissolvers because hydrogen fluoride is added to increase the dissolution rate of plutonium oxide. Presently, aluminum nitrate is added to complex the fluoride to prevent interference with the subsequent ion exchange purification of the plutonium. An octaazacryptand synthesized by INC-4 appears to bind fluoride very selectively and strongly, even in the presence of a great excess of nitrate. NMT-2 is testing the use of this material to remove fluoride from the processing solutions and to eliminate the need to add aluminum nitrate, which adds to the volume and complexity of the waste solutions.

Metal Ion Separations. A number of investigations are contributing to efforts to facilitate the separation of plutonium and americium ions from aqueous solutions.

• Reillex HPQ is a polyvinylpyridine-based anion exchange polymer developed at Los Alamos in collaboration with Reilley Industries. For several years this polymer has been routinely used at TA-55 for the ion exchange purification of plutonium in nitric acid solutions. Recently, we found that resin in use for 3 years and beginning to lose effectiveness could be largely regenerated by treatment with 1 M sodium hydroxide. The regenerated resin showed improved kinetics of plutonium sorption relative to new resin, and the improved kinetics of the regenerated material is being studied in the hope of improving the kinetics of new resin as well.

Process Chemistry (continued)

- Spectroscopic studies of plutonium nitrate complexes in aqueous and organic solutions sorbed on ion exchange membranes are providing more information on the plutonium complexes involved in the ion exchange process. Careful analysis of the visible spectra of plutonium(IV) in 1 to 13 M nitric acid indicates that three major complexes or groups of complexes are present in various concentrations of nitric acid. The complex that exists at intermediate nitric acid concentrations has not been previously studied, but the intensity of its absorption spectrum correlates with the distribution coefficient of plutonium(IV) on anion exchange resin as a function of nitric acid concentration. Thus, this unstudied species may be the complex most crucial to the ion exchange sorption process. Further studies include measurements of ultraviolet, visible, and nuclear magnetic resonance spectra images.

- The use of chelating polymers and extractants sorbed on polymeric supports to remove plutonium and americium from the ion exchange effluent and the oxalate filtrate solutions is being investigated. Duolite C467 (made by Rohm & Haas) shows promise for reducing the amount of plutonium remaining in the oxalate filtrate to quite low levels. We are also studying several novel extractants of actinides [tetradentate bis(acylpyrazolones), tridentate triphosphoryl and phosphoryl/ N-oxide ligands, and octadentate tetrahydroxamates] for application in process operations.

- We tested the liquid-liquid extraction capability of a membrane contactor module sold by Hoechst-Celanese using tributylphosphate in an aromatic solvent to extract uranium(VI) from nitric acid. Under test conditions, the 25-centimeter module performed as the equivalent of one to two-and-a-half theoretical stages.

These promising initial results indicate a need for further examination of the use of such contactors to extract plutonium and americium from waste and process streams.

Product Preparation. Our group has been responsible for two important contributions in the area of product preparation.

- A recently completed new-generation metal preparation line is now in operation. It produces plutonium metal from plutonium oxide by two-step hydrofluorination to plutonium tetrafluoride followed by reduction to metal using calcium. The new design incorporates computer-controlled equipment to minimize labor-intensive operations and subsequent neutron exposure. We are testing use of a stirred-bed fluorinator to reduce hydrogen fluoride consumption and yield a free-flowing product.

"The ATLAS facility is being used to examine the recycling by evaporation of a considerable portion of the nitric acid used in nitrate recovery operations."

We examined a technique that eliminates the corrosion problems caused by iodine by using a carbon dioxide laser to initiate the plutonium tetrafluoride/calcium reaction. Helium tubes in the furnace monitor the alpha-neutron reaction in plutonium tetrafluoride, thus improving process control. Presently, an alternative method is under investigation for the recycling of unreacted hydrogen fluoride in which sorption occurs in a stirred bed of sodium fluoride. Such a method would eliminate the need for the large volume of aqueous potassium hydroxide solution now used to trap the excess hydrogen fluoride.

• Downstream waste treatment operations will benefit from an investigation of the homogeneous precipitation of plutonium(IV) hydroxide as an alternative to precipitation of plutonium(III) oxalate after elution of plutonium from the ion exchange column.

The major advantage of the hydroxide precipitation is the much lower concentration of plutonium remaining in the supernatant solution. The decomposition of formamide and urea homogeneously generates hydroxide in the nitric acid solution. Unlike precipitations using alkali or alkaline earth hydroxide solutions, formamide and urea decomposition generates a readily filterable solid. Because the bench-scale studies have been quite promising, this method will be compared with oxalate precipitation in the course of operations on the Advanced Testing Line for Actinide Separations (ATLAS).

Recycling of Reagents. The recycling of reagents used in plutonium processing will result in reduced waste production.

• The ATLAS facility is being used to examine the recycling by evaporation of a considerable portion of the nitric acid used in nitrate recovery operations.

Recycling by evaporation will significantly reduce the volume of nitrate effluents that must be treated by the Waste Treatment Facility (TA-50). The Los Alamos-developed high-acid sensor will allow rapid monitoring of nitric acid concentration in the distillate.

• The recycling of hydrogen fluoride in metal preparation line operations, described previously under *Product Preparation*, is also an important accomplishment in this area.

Waste Treatment. Although waste treatment activities are described in another chapter, some nitrate recovery operations are directly applicable to this increasingly important concern.

• Some residues generated during processing operations are presently processed without being considered "waste."

Process Chemistry (continued)

For example, cotton cloths used to clean glove boxes often become partially nitrated and can contain significant quantities of plutonium. At present, the regulatory situation prohibits incineration. With the agreement of state regulators, we are now testing a thermal decomposition operation to reduce the inventory of nitrated rags and generate a solid residue that can be leached to recover plutonium should the amount warrant the effort.

• We are collaborating with Rockwell International in the preliminary testing of a molten salt reactor for destroying rags, paper, plastic, and other combustible materials contaminated with plutonium. A molten salt system based on calcium dichloride/calcium difluoride or sodium chloride/potassium chloride is being considered because both salt systems are wastes generated from the oxygen sparging of electrorefining salts or from the multiple-cycle direct oxide reduction process. Substantial waste reductions, in addition to the volume reductions resulting from the destruction of the organics, could be achieved by multiple use of these salts. This "thermal treatment" method may prove acceptable where incineration is prohibited.

The implications of process chemistry studies and technology innovations are enormous for the nuclear weapons complex of the next century. The contributions of the nitrate systems group at Los Alamos will continue to play a major role in the development of acceptable plutonium processing capabilities. ♦

NITRATE

RECOVERY

Systems Integration

by Bill McKerley
Nuclear Materials Processing Group: Nitrate Systems

Los Alamos efforts to develop and demonstrate efficient and effective nuclear materials processing and recovery technologies applicable throughout the DOE complex have already been proved beyond the bench, or pilot, scale. Research, development, and demonstration work at the Los Alamos Plutonium Facility at TA-55 centers around three primary activities:

• optimizing existing processes to minimize waste generation and operator exposure,
• developing additional treatment or polishing operations that will convert a large fraction of the total waste volume to benign effluents that can be discharged with reduced impact on the environment, and
• evolving new technologies that will result in significantly lower total waste generation and reduce operator exposure.

These activities can be conducted successfully only if researchers in several areas combine their efforts to resolve the complex issues involved in plutonium recovery operations. Therefore, the Nuclear Materials Processing Nitrate Systems Group, NMT-2, conducts an innovative process engineering program that brings together specialists in process chemistry, process analytical chemistry, and process control.

The conduct of many operations within DOE's nuclear weapons and nuclear power programs requires many different processing steps, and process upsets in one operation can adversely affect other operations.

For example, the fluoride added to facilitate the nitric acid dissolution of oxide may result in higher levels of plutonium in the ion exchange effluence because fluoride interferes with plutonium. This conflict can be resolved by integrating the process elements through appropriate planning and by developing prototype integrated experimental facilities. The concept integrating the various processes in plutonium recovery operations is successfully demonstrated in the Advanced Testing Line for Actinide Separations (ATLAS), a testing facility that can process and recover a wide variety of actinide-bearing scrap. Such a broad capability is necessary because each process in the recovery operation produces its own unique plutonium-contaminated residue, such as metal shavings, crucibles, oxides, pyrochemical salts, and ash.

Systems Integration (continued)

ATLAS plays a dominant role in such DOE programs as complex reconfiguration and radioisotope recycle and recovery. It incorporates such technologies as enhanced process control and on-line analytical chemistry to optimize the plutonium recovery process and to minimize waste produced at the source and reduce waste treatment and storage requirements. Waste is further reduced by coupling such optimized processing with improved processing methods in dissolution, ion exchange, precipitation, waste polishing, and final treatment techniques. Once these technologies have been properly demonstrated on ATLAS, they can be easily integrated into the current processing facilities at Los Alamos, the Rocky Flats Plant, and Westinghouse Hanford.

The solid operating data provided by ATLAS experiments will accomplish primary goals in waste minimization and will support activities in the reconfiguration of the DOE complex. Furthermore, ATLAS, other equipment and instrumentation at the Plutonium Facility, and the integrated systems approach at Los Alamos ensure the smooth transfer of information among Laboratory scientists and personnel at other DOE sites. ♦

CHLORIDE

RECOVERY

Chloride Recovery Overview

by Joel Williams
Nuclear Materials Processing Group: Chloride Systems

Many of the processes planned for the Complex 21 Plutonium Processing Facility are chloride-based unit operations. These include americium extraction from the feed metal, electrorefining of the impure metal, dissolution in HCl media, aqueous chloride purification using solvent extraction and ion exchange, precipitation, calcination of the precipitate to oxide, and conversion of the oxide to metal through multiple cycle direct oxide reduction.

These unit operations can be grouped into two major categories: high-temperature, molten-salt, pyrochemical processes and the more conventional chloride-based aqueous operations. A brief review of chloride recovery operations, as envisioned for the Complex 21 Plutonium Processing Facility, includes all of the aforementioned processes except americium extraction and electrorefining. For purposes of process grouping, these two unit operations are included in the site-return processing discussion.

Current chloride recovery projects that support Complex 21 cover a broad range of activities. In the area of aqueous chloride processing, the most important process improvement is the alternative diluent work for solvent extraction. This work has been ongoing for approximately a year and replaces tetrachloroethylene (TCE), an environmentally objectionable chemical, with an acceptable organic diluent for tributyl phosphate. This work uses dodecane as the primary diluent with decanol as a phase modifier. The most significant operational effect of this change has been the reversal of the light and heavy phases from the replacement of the TCE. As a result, extensive cold testing has been required to confirm the performance of the centrifugal contactors with the new diluent system.

The use of an alternative diluent has created the need for a more sophisticated technique for evaluating the composition of the organic phase.

A method that shows great promise is the use of gas chromatography to analyze the organic stream. Private industry has long used this technique safely and reliably for just such applications.

Other major projects currently under way that will impact the design of any new facility include

1. dissolution studies to quantify process efficiencies for a variety of matrices,
2. additional work on chloride ion exchange, and
3. the application of sensors for process monitoring and control.

For some of this work, we are collaborating with the process development section of the Nuclear Materials Processing—Nitrate Systems Group. This approach has allowed our aqueous chloride operations to use research being done to support ATLAS in the nitrate area.

Chloride Recovery Overview (continued)

Future plans for the aqueous chloride operations include the replacement of virtually an entire glove box line. The experimental chloride extraction line (EXCEL) project calls for the removal of the existing solvent extraction glove boxes and their replacement with chloride-compatible, plastic-lined boxes as the start of this upgrade.

Another part of our long-range plan is to incorporate on-line analytical techniques and specialized process diagnostics. Because of special materials requirements in a chloride environment, the development of wet chemistry techniques and other noninvasive methods such as sensors and spectrophotometric measurements must be modified and adapted to the glove boxes that will use the new technologies. These new diagnostic and process-monitoring capabilities will be incorporated into unit operations as they are demonstrated and will become a part of the design of any new Complex 21 facility.

The sole pyrochemical process included in the chloride recovery portion of the Complex 21 flow sheet is the multiple cycle direct oxide reduction (MCDOR) operation. This process for converting oxide from aqueous operations to metal has undergone several significant changes during the past few years. The introduction of chlorine sparging to convert the reaction by-product, calcium oxide, to the calcium chloride process salt has resulted in dramatic reductions in waste. In addition, the use of chlorine in high-temperature operations has opened the door to new technologies such as *in situ* generation of the plutonium trichloride necessary in americium extraction.

This technology improvement has also required the development of more sophisticated off-gas monitoring capabilities. The use of a newly installed spectrophotometric technique for detecting chlorine will become an important tool for optimizing the regeneration step of the MCDOR process.

Once demonstrated, this same diagnostic technique can be implemented in any process that uses chlorine as a reagent or that may generate chlorine as a by-product. Because the technique is noninvasive, we need only a simple modification of the off-gas piping to implement the technology.

Optimization of the MCDOR process is under way to reduce overall cycle time, further minimize waste generation, and improve the purity of the metal product. The off-gas monitoring system has already been discussed as one of the optimization efforts. Automation of feed preparation, handling, and introduction into the reaction cell is under current development. The aim of this effort is to improve MCDOR through increased product consistency and decreased personnel radiation exposure. Additional automation will configure and operate cells and remove and produce the final products.

"The implementation of a universal salt system for all pyrochemical operations has long been a goal of our process development."

After the completion of a set of reductions, the chlorination of the calcium oxide to calcium chloride results in a salt excess. This salt, however, is free of the impurities found in commercially available calcium chloride and could be used to produce product metal with the same chemical composition as the feed oxide. An initial set of experiments to determine product metal purity produced mixed results. Most of the metal showed no increase in impurity levels compared with the feed oxide. Some runs, however, showed elevated levels of impurities that were not in the feed material. In the future, careful evaluation of product purity requirements will be necessary to produce a product with the same chemical composition as the feed oxide.

The implementation of a universal salt system for all pyrochemical operations has long been a goal of our process development. Calcium chloride has been implemented as the salt-of-choice in americium extraction and is currently being demonstrated in electrorefining. Potential advantages of a universal salt include consolidation of some pyrochemical unit operations, simplification of the aqueous recovery flow sheet, and reduction in the volume of aqueous solutions processed because calcium chloride is significantly more soluble in HCl media than the sodium chloride/potassium chloride salts historically used in americium extraction and electrorefining.

A program is being developed to demonstrate an integrated chloride processing scheme. However, production-scale aqueous chloride processing is relatively new; and changes in the pyrochemical operations, such as oxygen sparging of electrorefining salts, have also resulted in changes in the composition of the feed to recovery. Although all of the individual unit operations have been fully demonstrated, no evaluation has been made of the overall, integrated flow sheet performance. Not only will such a demonstration confirm the high level of confidence for success, but also the use of the exact feed stream specified for Complex 21 will demonstrate the direct applicability of the entire flow sheet for the future facility.

The purpose of this program is the demonstration of each sequential process step:
1. americium extraction of the site-return feed metal,
2. electrorefining,
3. recovering all chloride-based residues, and
4. converting the recovered product oxide to metal in MCDOR.

Chloride Recovery Overview (continued)

The goals of this work include the evaluation of process efficiencies on a known feed, the demonstration of an integrated flow sheet for residue recovery, and the conversion of oxide to metal based on the pyrochemical processing of that feed. This demonstration will identify problems and provide an opportunity for process improvement.

Overall waste generation rates will be determined from a specified throughput of typical site-return feed. This will give more accurate information to help specify waste stream content and quantities. Such information will be invaluable in sizing waste-handling requirements and may identify potential problems with specific waste constituents. By taking this approach, the program will exactly duplicate the waste-stream characteristics expected from the Complex 21 flow sheet.

Issues not fully evaluated in the existing flow sheet include the requirements for analytical or nondestructive assay equipment, materials surge-capacity requirements, critical process equipment redundancy requirements, and the effect of differing reliability, availability, and maintainability (RAM) characteristics of the specific operations. One of the significant problems with Building 371 at Rocky Flats was the incompatibility of some process unit operations. This building could not perform at its design capacity because unit operations with different RAM histories were implemented in lock-step fashion.

In conjunction with processing, materials control and accountability (MC&A) requirements must be carefully evaluated before finalizing any process flow sheet. As part of MC&A requirements, we will need surge capacity and assurance of safeguards for such excess material storage.

The integrated demonstration of the chloride flow sheet will provide information and insight into these areas and help identify potentially significant problems. ◆

CHLORIDE

RECOVERY

In Situ Chlorination of Plutonium Metal

by Eduardo Garcia
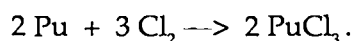Nuclear Materials Processing Group: Chloride Systems

Introduction

Plutonium trichloride is used as a reagent in the molten salt extraction (MSE) and electrorefining (ER) processes. Presently, plutonium trichloride is made by combining plutonium oxide and highly toxic phosgene. Because of this toxicity, an alternative synthetic route to plutonium trichloride is highly desirable. By making plutonium trichloride during the processes in which it is used, with less toxic reagents, we can gain in overall safety, decrease waste generation, reduce radiation exposure, and reduce the number of accountability steps.

A simple way to accomplish this goal is by direct reaction of elemental plutonium and chlorine. Although chlorine is a toxic material, it is an order of magnitude less toxic than phosgene.

Furthermore, the reaction between chlorine and plutonium metal is expected to be much more efficient than the reaction between phosgene and plutonium dioxide, thus smaller amounts of gas are needed to generate equivalent amounts of plutonium trichloride. Preliminary work shows the feasibility of *in situ* chlorination for producing the required plutonium trichloride.

Approach

In the conventional MSE process, quantities of calcium chloride, plutonium trichloride, and plutonium metal are loaded into a crucible. *In situ* chlorination generation, however, eliminates the need to add plutonium trichloride at the beginning of a run and will be accomplished by sparging chlorine gas through the molten plutonium. Conceptually, the chemical reaction is very straightforward and simple:

$$2\,Pu\ +\ 3\,Cl_2\ \longrightarrow\ 2\,PuCl_3.$$

Unfortunately, although the chlorination reaction is very highly thermodynamically favored, the reaction is so exothermic that there must be careful control of chlorine flow rates in order to prevent unwanted temperature excursions. In the direct chlorination of plutonium metal for purification purposes, the reaction temperature can be maintained at acceptable levels by proper flow control of the chlorine.[*]

Another concern that chlorination of plutonium metal introduces, and a concern of pyrochemistry in general, is that of materials compatibility. Chlorine gas is a highly corrosive oxidizing agent, but molten plutonium metal is a highly corrosive reducing agent.

In Situ Chlorination of Plutonium Metal (continued)

This kind of environment presents materials compatibility problems because materials that can withstand highly oxidizing conditions are usually chemically incompatible with highly reducing conditions and vice-versa.

There are two possible solutions to this problem. The first is to use magnesia crucibles because they have demonstrated minimal chemical attack in plutonium pyrochemical processes and are, of course, inert to chlorination. A magnesia crucible has the disadvantage of not being reusable because it must be broken in order to recover the product.

The second solution is to use tantalum crucibles, which are currently used in MSE, because they are reusable. Tantalum, or any other metal, would seem inappropriate as container material because it is attacked readily by chlorine at elevated temperatures. However, it may be possible to have a complete reaction between the chlorine and plutonium metal so that the

tantalum crucible never comes in contact with chlorine gas.

There are two possible methods by which contact between chlorine and plutonium can be maximized. One of these would involve redesign of the crucible to increase contact time between the two reagents and minimize the amount of unreacted chlorine escaping from the melt. The second method uses stirring while sparging, which maintains intimate contact between the gas and the metal throughout the melt, thus optimizing the reaction.

In situ production of plutonium trichloride for MSE would have several benefits. It would reduce accountability steps currently required for separate plutonium trichloride production. Although chlorine is a toxic material, it is much less toxic than the phosgene currently used, and the reaction with the metal is predicted to be much more efficient, reducing both the time required to effect the reaction and the amount used.

Another advantage is that no additional glove boxes and space for separate MSE oxidant synthesis would be required. Because very little, if any, chlorine will escape from the furnace during *in situ* generation of plutonium trichloride in MSE, gas scrubber waste that is normally generated from these processes will be minimized to a large extent. This process will not increase the personnel radiation exposure normally received from the MSE process but will, of course, eliminate the exposure received from a separate plutonium trichloride synthesis procedure.

MSE is the logical process for investigating *in situ* chlorination because of the simplicity of the process. Electrorefining is another process that would benefit from *in situ* generation of plutonium trichloride, but the increased number and complexity of the mechanical components render this process less suitable. After *in situ* generation has been perfected for MSE, the knowlege and experience gained will be applied to ER. ◆

CHLORIDE

RECOVERY

Opportunities for Magnetic Separation Applications in Complex 21

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The Magnetic Separation Process

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

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 material.

Because all actinide compounds are paramagnetic (Table 1), 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. The advent of reliable superconducting magnets makes magnetic separation of weakly paramagnetic species attractive.

Table 1. Magnetic susceptibility of selected compounds and elements.

Compound/Element	Susceptibility, 10^{-6}
Paramagnetic	
FeO	+7200
Fe_2O_3	+3586
Cr_2O_3	+1960
UO_2	+2370
PuF_4	+1760
Am	+1000
PuO_2	+730
Ni_2O_3	+660
Pu	+610
U	+409
PuF_3	+173
Th	+134
CrO_3	+40
Ca	+40
Al	+16
Diamagnetic	
Si	-4
Graphite	-6
MgO	-10
CaO	-15
ThO_2	-16
MgF_2	-23
CaF_2	-28
SiO_2	-30
NaCl	-30
Al_2O_3	-37
K Cl	-39
$CaCl_2$	-54
CaI_2	-109

Opportunities for Magnetic Separation
Applications in Complex 21 (continued)

Magnetic Separation Methods

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

A diagram of a roll separator is shown in Fig. 2. In practice, a powder is delivered onto a thin belt that moves over rollers. The front roller is fabricated from a permanent 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. The operation results in a separation.
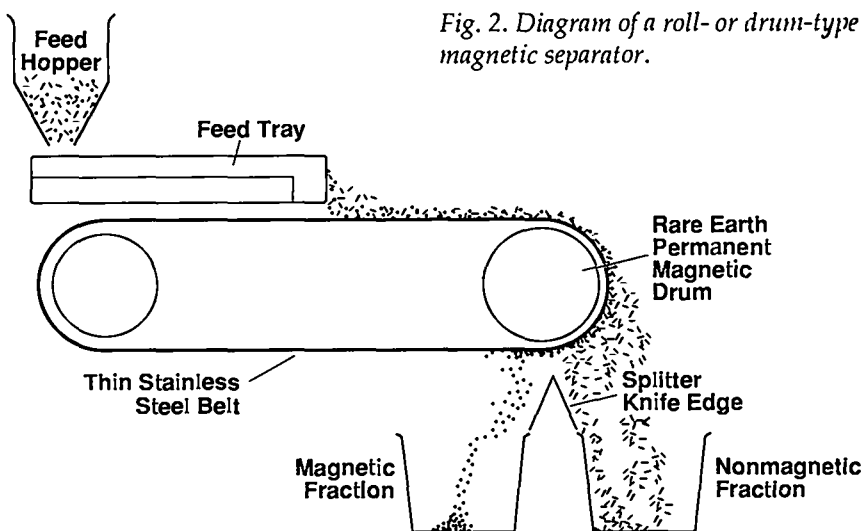

Fig. 2. Diagram of a roll- or drum-type magnetic separator.

The roll separator we are currently using contains the latest in permanent magnet technology: a neodymium-iron-boron rare-earth magnet. The roll is constructed of rare-earth magnetic disks separated by ferromagnetic spacers. This generates high field gradients on the surface of the roll. The roll separator has been installed in a glove box for a demonstration with actual residues.

The HGMS method is used to separate magnetic fractions from gases or liquids. A diagram of the method is shown in Fig. 3. Most commonly, the feed is slurried with water and passed through a magnetized volume. Field gradients are produced in the magnetized volume by a ferromagnetic matrix material. The matrix can be steel wool, steel balls, nickel foam, etc.
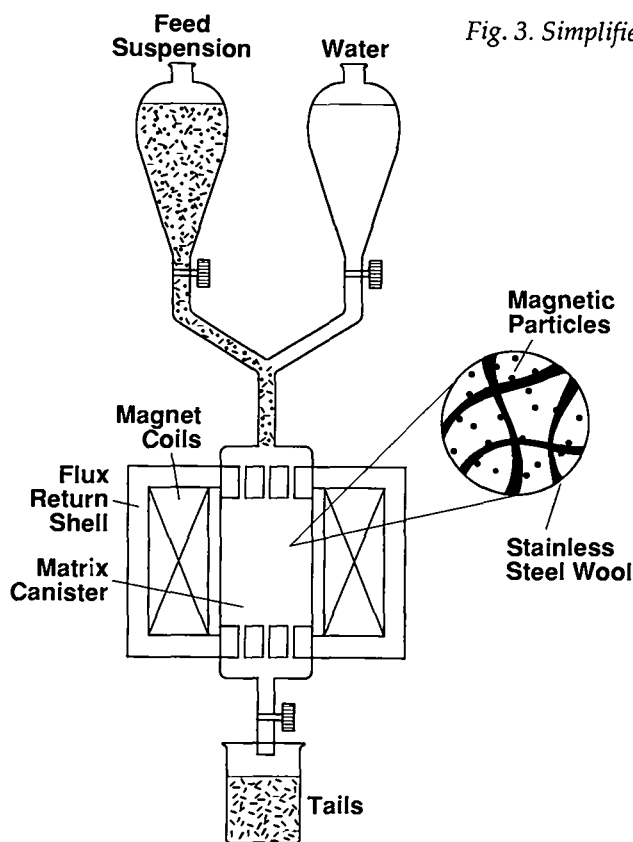
Fig. 3. Simplified HGMS Diagram.

Feed Suspension **Water**

Magnetic Particles

Magnet Coils

Flux Return Shell

Matrix Canister

Stainless Steel Wool

Tails

Ferromagnetic and paramagnetic particles are extracted from the slurry while the diamagnetic fraction passes through the magnetized volume unaffected. 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.

Much higher electromagnetic fields are routinely available with today's superconducting magnet technology.

Higher fields offer the possibility of a broader range of HGMS applications than is afforded by conventional electromagnets, which are limited by the saturation of iron.

For our HGMS work at Los Alamos, we have a laboratory-scale 1-inch-bore, cross-field, conventional magnet and a larger, warm-bore superconducting magnet.

Magnetic Separation Applications in Complex 21

Several applications of magnetic separation will be examined for Complex 21:

1. concentration of recycled-plutonium, chemical processing residues,
2. extraction of actinides from liquid wastes, and
3. development of reusable magnetic gas filters.

We have shown that chemical process residues, such as reduction slags, crucibles, graphite, and silica, can be segregated into a plutonium-rich and a plutonium-lean fraction. The plutonium content of the lean fraction from these demonstration experiments is sufficiently low in plutonium that it is uneconomical to recover the plutonium value. Therefore, the plutonium lean fraction can be discarded directly in grout. Processing of dry residues is important not only for Complex-21 processing but also for volume reduction of the current DOE backlog.

Opportunities for Magnetic Separation
Applications in Complex 21 (continued)

HGMS might also be useful as a selective filter for fluid waste generated during actinide chemical processing. Our magnetic separation model predicts that HGMS can reduce the actinide concentration in liquid waste streams by several orders of magnitude.
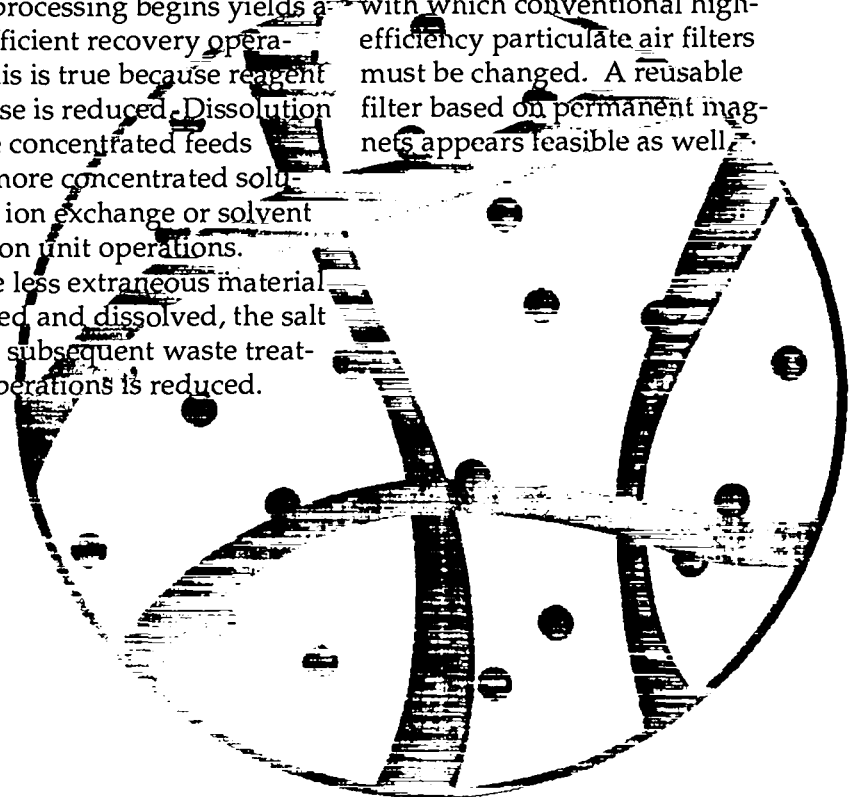
An identified need in uranium and plutonium operations is the reusable filter for glove box and hood exhaust. A reusable high-efficiency magnetic filter for paramagnetic particulates appears feasible, but only a small amount of work has been conducted in this area.

Benefits of Magnetic Separation in Complex 21

The benefits of interjecting magnetic separation as a head-end unit operation include the generation of only a very small volume of secondary waste. The ability to concentrate the actinides from extraneous materials before processing begins yields a more efficient recovery operation. This is true because reagent (acid) use is reduced. Dissolution of more concentrated feeds yields more concentrated solutions to ion exchange or solvent extraction unit operations. Because less extraneous material is leached and dissolved, the salt load on subsequent waste treatment operations is reduced.

Magnetic filtration of fluid waste may be a method to cut transuranic (TRU) effluents from DOE facilities to near zero. This would greatly reduce waste treatment cost.

Magnetic gas filters on glove box process exhaust would also greatly reduce the frequency with which conventional high-efficiency particulate air filters must be changed. A reusable filter based on permanent magnets appears feasible as well.

"A cooperative research and development agreement was recently signed with AWC/Lockheed to examine paramagnetic separation for soil decontamination."

Project Status

Cold testing of the roll separator has been completed and it has been installed in a glove box. Soon, process demonstration will begin. The roll separator represents a pilot-scale demonstration for this technology. Data obtained from this unit can be used, to design and fabricate a full-scale processing unit with virtually any number of separation stages and processing rates.

The conventional HGMS unit at Los Alamos is currently being used in cold testing. Through the use of
1. various nonradioactive surrogate materials with different magnetic susceptibilities,
2. different surrogate particle sizes,
3. parameter variation such as flow rate, solids loading in the slurry, fluid viscosity, etc.
4. magnetic matrix parameters, and
5. magnetic field strength,
a performance-based HGMS model is being developed. The hope is that given a separation problem, we will have the ability to select the processing criteria that will achieve a necessary per-formance level. Currently, numerous experiments must be conducted to determine optimum performance.

The superconducting HGMS is due in Los Alamos very soon. After cold testing and model development, one of the HGMS separators will be relocated for plutonium residue processing tests.

There are other important aspects of magnetic separation work at Los Alamos that do not strictly involve Complex 21. A cooperative research and development agreement was recently signed with AWC/ Lockheed to examine paramagnetic separation for soil decontamination. In addition, a soil decontamination study with Rocky Flats is anticipated. Use of HGMS to segregate underground storage-tank waste, a problem at the Hanford site, is also being studied. ◆

CHLORIDE
RECOVERY

Oxygen Sparging

by Eduardo Garcia
Nuclear Materials Processing Group: Chloride Systems
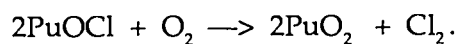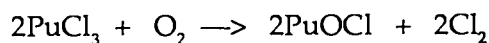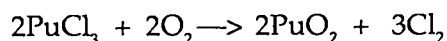
Introduction

Before the advent of oxygen sparge as a recovery process, calcium salt was used to strip plutonium from salt residues. In the resulting sodium chloride/potassium chloride salts, excess calcium produced metallic and potentially pyrophoric alkali metals. These waste salts, though below the economic discard limit, did not meet Waste Isolation Pilot Plant (WIPP) criteria because of their potentially pyrophoric nature. To make these molten waste salts acceptable to WIPP, work was started in 1988 on air sparging because with this process any pyrophoric material would be converted into a more inert oxide. In the course of these experiments, it was noted that even further plutonium was being recovered than before. Literature[*] surveys revealed that oxygen sparging work had been conducted as early as the 1960s.

Although this earlier effort had concentrated on actinide separation and not specifically on plutonium recovery, it was still a good foundation on which to build.

Air sparging of salts was replaced by oxygen sparging in which a controlled mixture of oxygen and argon was used to provide improved process control. As new information was gained, process parameters were continually changed in order to improve performance. Oxygen sparging has now almost completely replaced calcium salt stripping as the method of choice for treating electrorefining salt residues.

Approach

Oxygen sparging has been used to treat salt residues, mainly from electrorefining, on the kilogram scale. Sodium chloride/potassium chloride or calcium chloride salts derived from this process contain plutonium in the form of dissolved plutonium trichloride as well as some uncoalesced metal. To minimize the quantity of material that must be treated to recover this plutonium, and thereby minimize waste from the recovery process, plutonium is concentrated into a fraction of the volume of the residue salt by oxygen sparging. The major portion of the salt is thereby made suitable for discard. Concentration of the plutonium is accomplished by oxidation of the soluble chloride species into an insoluble oxide species. Chemical reactions of interest are as follows:

$$2PuCl_3 + 2O_2 \longrightarrow 2PuO_2 + 3Cl_2$$

$$2PuCl_3 + O_2 \longrightarrow 2PuOCl + 2Cl_2$$

$$2PuOCl + O_2 \longrightarrow 2PuO_2 + Cl_2.$$

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[*] L. J. Mullins and J. A. Leary, "Molten Salt Method of Separation of Americium from Plutonium," U.S Patent No. 2,420,639 (1967).
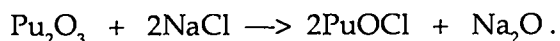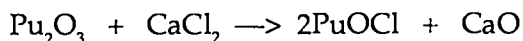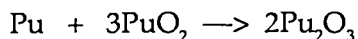
"Oxygen sparging has now almost completely replaced calcium salt stripping as the method of choice for treating electrorefining salt residues."

Oxygen sparging has undergone several modifications and indeed continues to evolve as information and experience gained are applied towards process optimization. However, the basic process has remained the same.

This basic procedure typically results in a multilayered product. At the bottom of the crucible can be found metallic plutonium, usually poorly coalesced. Above the metal is a solidified "black salt" matrix layer that contains plutonium dioxide, plutonium oxychloride, and plutonium metal. Above this black layer is usually a brownish layer of plutonium dioxide that is considered part of the "black salt" layer. Finally, the uppermost layer that makes up 50% to 75% of the bulk volume is the "white salt" that contains only very small amounts of plutonium and is suitable for discard.

Plutonium oxychloride is more easily handled in the aqueous hydrochloric acid recovery process. In 1991, work was started on efforts to maximize plutonium oxychloride production with respect to plutonium dioxide. This effort resulted in a closer look at the chemistry and kinetics of the oxygen sparging process. The first thing that became clear was that the product is not at chemical equilibrium because plutonium metal and plutonium dioxide cannot coexist in chemical equilibrium. Depending on the limiting reagent, the equilibrium products of a mixture of metal and dioxide should be either metal and ß-plutonium sesquioxide or α-plutonium sesquioxide and plutonium dioxide. Another mystery was the location of plutonium oxychloride in a layer below plutonium dioxide. Because plutonium dioxide has a density of 11.5 g/cc, significantly higher than that of plutonium oxychloride at 8.8 g/cc, it should sink to the bottom of the molten salt.
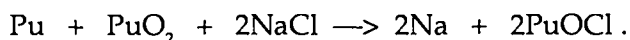
In order to overcome the perceived kinetic barriers to the reaction between plutonium and plutonium dioxide, a procedure for stirring was added to the basic process. The anticipated chemistry was

$$Pu \ + \ 3PuO_2 \ \longrightarrow \ 2Pu_2O_3$$

$$Pu_2O_3 \ + \ CaCl_2 \ \longrightarrow \ 2PuOCl \ + \ CaO$$

$$Pu_2O_3 \ + \ 2NaCl \ \longrightarrow \ 2PuOCl \ + \ Na_2O \ .$$

Stirring did indeed eliminate plutonium dioxide in cases where there was a metal excess. The product typically consisted of a well-coalesced metal button, a "black salt" layer (plutonium oxychloride) that had a pronounced blue-green color, and a "white salt" layer.

Oxygen Sparging (continued)

The chemistry occurring during stirring in the case of calcium chloride salts was as expected. However, in the case of sodium chloride, the actual chemistry is

$$Pu + PuO_2 + 2NaCl \longrightarrow 2Na + 2PuOCl.$$

After stirring, a second oxygen sparge oxidizes the pyrophoric metallic sodium that deposits on the furnace head.
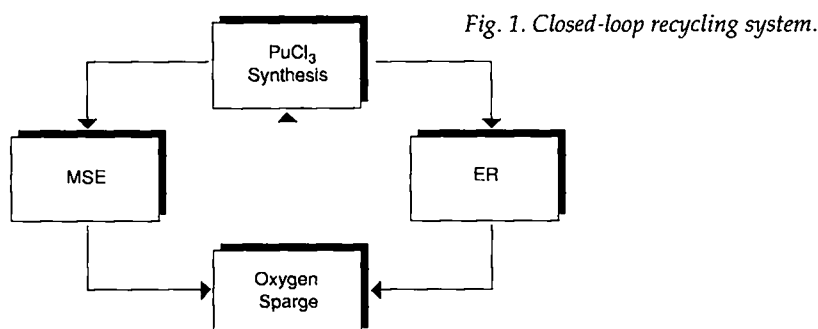
Oxygen sparge experiments on clean calcium chloride salts containing pure plutonium trichloride revealed that only plutonium dioxide is produced when plutonium trichloride reacts with oxygen. The large amounts of plutonium oxychloride in oxygen-sparged electrorefining salts can be attributed only to the presence of plutonium metal in those salts. A possible reaction scheme that explains experimental observations has been theorized below.

When the salts are first melted, some coalescence of metal occurs, but a large fraction of elemental plutonium remains suspended in a "black salt" layer. After sparging is initiated, plutonium dioxide begins to precipitate and initially is intimately mixed with plutonium metal in the black salt layer. Some of the plutonium dioxide will be in sufficiently close contact to react and produce plutonium oxychloride. Although the mixture is probably not adequate to cause a complete reaction between all the precipitated oxide and metal, some of it will be in sufficiently close contact to produce plutonium oxychloride. As the sparging continues and plutonium dioxide continues to precipitate, the "black salt" layer becomes so viscous that plutonium dioxide begins to pile up on top of the "black salt" layer. This is the oxide layer that was usually observed in traditional oxygen sparging. The material in the "black salt" layer is a mixture of plutonium metal, plutonium oxychloride, and plutonium dioxide. These have all been observed by powder x-ray diffraction. This scheme explains why plutonium oxychloride is

found below the oxide layer even though it is much less dense than plutonium dioxide. Furthermore, the variability of the size of the oxide layer can be understood because it is a function of the amount of uncoalesced plutonium metal in the electrorefining salts that seems to vary widely.
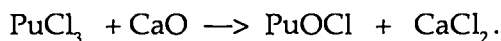
Future Work

An improvement to the process will be made by adapting a chlorine spectrophotometric in-line detector developed for multiple cycle direct-oxide reduction, thereby providing real-time analytical capabilities for detecting chlorine. A by-product of the oxygen sparge process is chlorine, and a diminishing concentration of this chemical substance in the off-gas stream will signal completion of the run. Eventually this detector will be connected to a computer that will automatically terminate oxygen flow.

Fig. 1. Closed-loop recycling system.

Plutonium oxychloride is easier than plutonium dioxide to recover by aqueous chloride methods. This was the initial impetus for optimization of plutonium oxychloride production. There is now another reason for producing a homogeneous plutonium oxychloride product. If plutonium trichloride can be produced from plutonium oxychloride, then a closed-loop recycling system can be set up as shown in Fig. 1. If the conversion step can be accomplished with a minimum of waste generation, then this closed-loop system will lower overall waste generation associated with plutonium trichloride synthesis and recovery. Preliminary experiments using ammonium chloride to convert plutonium oxychloride to plutonium trichloride are very encouraging.

Molten salt extraction is envisioned as a baseline process for Complex 21. Residue salts from this process contain dissolved plutonium trichloride but very little metal. Because oxygen sparging requires plutonium metal as a reagent to produce plutonium oxychloride, oxygen sparging would not be a process of choice for the closed-loop recycling system described above, but a similar process could be used. Instead of using elemental oxygen to produce a plutonium oxide species, calcium oxide can be used according to

$$PuCl_3 + CaO \longrightarrow PuOCl + CaCl_2.$$

There is no oxidation agent in this reaction; therefore, plutonium must remain in the +3 oxidation state, and no plutonium dioxide will be produced. With calcium chloride salts, all the compounds are soluble except plutonium oxychloride, so a clean reaction can be expected. In several successful experiments that used sodium chloride/potassium chloride salts, calcium oxide remained in the "black salt" layer. An issue that must still be addressed is americium separation.

To produce plutonium trichloride from plutonium oxychloride, americium must first be separated. Otherwise, unacceptably high levels of radiation exposures will be encountered. Separation does occur with oxygen sparging where the americium remains in the "white salt." We have not yet explored americium separation with calcium oxide.◆

CHLORIDE
RECOVERY

Materials Development for Pyrochemical Applications in the Weapons Complex Reconfiguration

by Keith M. Axler

Nuclear Materials Processing Group: Chloride Systems

Introduction

Currently, a large contribution to the volume of contaminated waste is from nonreusable crucibles and ancillary furnace components that fail in service. The objective of our work is to identify alternative construction materials that will reduce waste by providing extended service and that will improve process quality by remaining nonreactive in the chemical system.

Compared with analogous industrial studies, materials development for plutonium applications presents exceptional considerations because of the reactivity of plutonium and the hygroscopic salts. With an extensive array of capabilities, the Nuclear Materials Technology (NMT) Division at Los Alamos is uniquely suited to conduct materials development research in this field.

1. The Los Alamos plutonium facility is the only currently operating laboratory equipped for complete experimental testing of materials for plutonium pyrochemistry.

Specifically, this testing combines the abilities to conduct experimental work both with reactive gases and with salt and alloy systems containing actinide elements.

2. State-of-the-art analytical and metallographic capabilities in support of research on radioactive materials are fully operational at Los Alamos.

3. NMT Division maintains the most advanced capabilities for thermodynamic modeling of complex chemical systems. Computer modeling is used to evaluate potential candidate materials from a standpoint of chemical thermodynamics. Thermodynamic modeling also serves in process optimization studies to identify effects caused by variances in process conditions.

Candidate Materials Evaluation: Methodology

The criteria for alternative materials are defined by the specific conditions of the selected process application.

Each pyrochemical process performed in the weapons complex presents a different set of materials requirements. Among other considerations, the criteria for materials selection are based upon the process thermal profile, chemical composition, and the functions of internal furnace components. Additionally, product purity specifications are carefully considered in materials selection because of the strictly defined tolerances for specific elements in our product.

An evaluation process has been designed to use time and resources and to obviate unnecessary experimental use of plutonium. This is accomplished through a demonstrated series of tests.

1. First, an evaluation of current materials performance is conducted. This often requires examination of the final product to characterize materials interactions.

"...in the examination of product metal in plutonium electrorefining, electron microscopy revealed an oxychloride surface phase associated with the uncoalesced metal."

2. Computer modeling is then conducted to determine the viability of candidate materials based on system thermodynamics. Computer models are constructed for each pyrochemical process and reflect the chemical environments in which the candidates must perform.

3. If positive results are obtained in the modeling, "cold" testing is conducted to partially confirm the modeled predictions by compatibility testing without plutonium. This includes high-temperature salt containment and thermal cycling tests.

4. If promising performance has been indicated in the initial stages of the evaluation process, work will proceed with "hot" testing of the candidate. At this stage, small-scale exposure tests are conducted with plutonium in chemical environments simulating actual service conditions.

5. Finally, successful candidates are then demonstrated in service application. This provides thoroughly documented performance for final consideration.

Evaluation of Current Materials Performance.

Current incompatibilities between pyrochemical systems and construction materials are identified by studying the reaction products of the selected processes. Interactions with the crucible or furnace hardware are indicated by the appearance of interfering species in the products. For example, in the examination of product metal in plutonium electrorefining, electron microscopy revealed an oxychloride surface phase associated with the uncoalesced metal. This observation was consistent with the partial reduction of magnesium oxide components predicted by computer modeling.

In addition, failed components are examined to identify the mechanisms of corrosion that define the microstructural properties desired in a viable candidate. Materials selection for the multiple cycle, direct oxide reduction of plutonium dioxide presents one example. Based upon the characteristic corrosion mechanisms of chlorine gas and liquid plutonium, metallographic techniques were used to interpret their relative contributions to the corrosion of internal furnace hardware. This data narrowed the field of candidate materials by establishing required microstructural characteristics.

Materials Development for Pyrochemical Applications in the Weapons Complex Reconfiguration (continued)

Computer modeling

System thermodynamic calculations are used to provide a cost-effective initial evaluation of candidates. Many proposed containment materials have been disqualified by thermodynamic models and dramatic savings realized by obviating experimental evaluations. These computer models utilize rigorous calculations to predict equilibrium compositions based on free-energy minimization for complex, heterogeneous chemical systems. The models require input in the form of Gibbs energies for all possible species and phases as well as initial composition, temperature, and pressure. Large data banks,[1] which are updated on a continuous basis, provide the required thermodynamic data.

Processes are modeled with alternate materials for crucibles and ancillary furnace components.[2,3] The modeling results reveal possible side reactions with the crucibles or the hardware. Verification tests have been conducted to establish the viability of the computer models. This involved the experimental confirmation of results obtained in the modeling.[4] In addition to utilizing these computer codes to evaluate candidate materials, they are used to model phase equilibria in higher-order systems to aid in process optimization.[5,6]

Cold Testing

Thermal cycling tests are particularly valuable in the evaluation of coated materials. To date, we have examined an extensive matrix of refractory coatings, prepared by a variety of deposition techniques.[7]

Many candidates that appear promising because of their thermodynamic stability have been disqualified because of their inability to maintain integrity through a sufficient number of thermal cycles. Cold testing also includes salt release tests in which compatibility with molten pyrochemical salts is examined.

Hot Testing

Experimental work with plutonium is indicated only for candidates that have performed well in the previous stages of the campaign. Small-scale crucibles of the candidate material are fabricated and tested by their use in the containment of liquid plutonium and molten salt over extended time.

Also at this stage, differential thermal analysis has been conducted to determine the rate and extent of the candidate material's reactivity with plutonium.[8]

" The importance of minimizing radioactive waste volumes continues to promote interest in alternate construction materials"

Demonstration work

Demonstration involves using the candidate material to construct components used in actual pyrochemical processing. Currently, several candidates are under evaluation in this advanced stage of materials selection:

1. Carbon-saturated tantalum is being tested for use in the multiple cycle direct oxide reduction process. This material will also be tested in advanced-concept electrorefining and in the americium extraction process performed on aged plutonium.

2. Silicon nitride is being tested for use in reactive gas sparging during the *in situ* regeneration of spent salts.

3. High-density yttria is being used in plutonium electrorefining.

Other materials are at more preliminary stages of evaluation for selected applications. These include carbon-saturated niobium and yttria-stabilized zirconia.

Summary

The importance of minimizing radioactive waste volumes continues to promote interest in alternative construction materials. As work continues in this area, we will develop a suite of materials for pyrochemical operations that will provide extended service without compromising product quality.

As part of our investigations, we are collaborating with scientists in related fields to remain apprised of current developments in advanced materials. One example is the recent industrial collaboration with W.R. Grace & Co. and CERMET on the advanced processing of thorium-based ceramics.[9] Other joint investigations have included studies of engineered materials[10] and refractory ceramics[11] involving scientists at Lawrence Livermore National Laboratory, Westinghouse Savannah River Laboratory, and Westinghouse Science and Technology Center. ◆

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CHLORIDE

RECOVERY

Pyrochemical INtegrated Actinide Chloride Line (PINACL)

by James A. McNeese
Nuclear Materials Processing Group: Chloride Systems

NMT-3 has identified a need to develop a glove box process and development facility, the Pyrochemical INtegrated Actinide Chloride Line (PINACL), as a means of totally integrating pyrochemical process technology. This versatile system will facilitate process development and technology enhancement for processes that will be included or have the potential for inclusion in the Complex 21 reconfiguration effort. PINACL will include design features minimizing space requirements, personnel exposure, and waste generation while maximizing personnel efficiency, material throughput, process reliability, safeguards and security, and safety. Process automation will be used where beneficial. State-of-the-art analytical nondestructive array equipment for monitoring and controlling the process will be incorporated into the design. This facility will be used as a test bed for bench-scale through production demonstration for pyrochemical processes and processing techniques.

Our current pyrochemical process facility was developed for production support throughput and not as a development/demonstration facility. Some of the glove boxes were transferred from TA-21 after several years of use and then installed into TA-55. With the changing missions and modes of operation at TA-55, the present facility is not adequate for present priorities, which include process development and demonstration for Complex 21, development of new methods for pyrochemical separations, basic chemistry investigations of current processes, and development of diagnostic techniques for molten salt systems. We are designing a versatile process facility that will adequately test chemistry, equipment, and processing techniques for pyrochemical processes and that will incorporate automation testing facilities within the facility.

The design and reconfiguration will be done by stages. First, we will specify general glove box conditions for atmosphere, workstation size, material transport systems, utility needs, and estimated floor-space usage. The resultant design will be a modular glove box system. This modular concept will allow enough versatility to continually change the configuration of the layout (removing and replacing glove boxes) to meet the needs of projects and demonstration goals. We are beginning the conceptual design of the project. Design, fabrication, and installation will take several years to complete.

Facility integration is closely tied to process chemistry integration efforts. Pyrochemical processing has always had the goal of becoming a stand-alone operation that would treat all of its residues and recycle its reagents to reduce dependence on the aqueous recovery processes.

"PINACL will include design features minimizing space requirements, personnel exposure, and waste generation while maximizing personnel efficiency, material throughput, process reliability, safeguards and security, and safety."

Historical pyrochemical operations used different salt systems and process chemistries for each individual process. Currently, we are perfecting a common salt system that will tie all the pyrocemical operations together into an integrated system. Studies for several years have shown that calcium chloride can be used in the molten salt extraction (MSE) process and, in the electrorefining (ER) process. The major pyrochemical salt user has been calcium chloride in direct oxide reduction (DOR). This process has been improved and now is the present multiple cycle direct-oxide reduction (MCDOR) process that is a net calcium chloride generator. Salt produced in the MCDOR process can be used in MSE and ER because each process has been demonstrated using the calcium chloride system.

Our approach is to develop equipment that is compatible with use of the salt product from MCDOR and to demonstrate the feasibility and effect of this salt in the other operations. From a gross chemistry standpoint, there is no difference in recycled salt, but small impurities removed from the salt during the reduction step in the MCDOR process may contribute to salt behavior differences.

The salt from MCDOR is enriched in calcium chloride because initial impurities are reduced into the product metal during the first reduction. As the salt is reused, some impurities are introduced from corrosion of the equipment and occasionally the salt product is completely friable and does not hold a cast shape. These concerns must be addressed by determining the cause and effect of the observed behavior. Process and product purity data will be collected and analyzed when the tests are completed on the MSE and ER processes using salt from the MCDOR process.

Success of the concept will depend on the actual process efficiencies and product purities from the systems. Finding a method of shaping the regenerated salt is also a topic that will be addressed. The feed salt to the ER process is presently a cast cylinder that is smaller than the MCDOR crucible. Methods for casting the salt after regeneration or a method for loose-salt-loading into the ER cell will be developed. In the interim, salt will be loaded as pieces into an ER cell and melted. Additional salt will then be added to the molten salt.

Chemistry-based concepts are also being combined with equipment-based integration schemes. In addition, process systems can and will be combined in future development efforts. A recent example of this concept has been the new initiative to combine separate Complex 21 processes into one operation. This operation will combine several differing process chemistries so that we can take advantage of the consecutive processing sequence.

Pyrochemical INtegrated Actinide Chloride Line (PINACL) (continued)

The individual processing steps are combined into a sequential single-location processing flow array that will minimize handling operations, waste generation, and operator exposure. Automation techniques will be applied to repetitive operations where feasible. The intent of this project is to address a pertinent Complex 21 mainline processing sequence and to develop handling techniques and operational flows into a coherent whole.

The benefit will be to develop a system of processes that can be demonstrated as a module and that can be inserted into the design of the Complex 21 flow sheet while using less floor and glove box space for a separate processing flow sequence. ◆

W A S T E

M A N A G E M E N T

Waste Management Overview

by Larry R. Austin
Nuclear Materials Processing Group: Nitrate Systems

Introduction

All waste streams generated in the site return, recovery, and manufacturing areas are sent to the waste management area. The waste management part of the baseline flow sheet is divided into two main areas. The first waste management area handles the liquid wastes, and the second area processes and treats solid wastes.

As a rule, processing operations that would involve the recovery and recycle of usable materials would not be a part of the waste management area. These operations would be included in the appropriate part of the site return, recovery, or manufacturing areas. Waste management is one of the more critical areas: All materials processed in this area must comply with all DOE, state, and federal treatment, storage, and disposal regulations.

In addition, discharges from this facility must meet the federal Clean Air and Water Act, and solid waste shipped off site must meet transportation and Waste Isolation Pilot Plant Waste acceptance criteria.

Flow sheet Considerations

The waste management part of the flow sheet has been one of the more difficult parts to develop for several reasons.

1. The development of the flow sheet depends, to some extent, on the amount and type of material that is being sent to the waste management area. The feed streams to the waste management location are the discharges from the manufacturing, site return, and recovery areas. Thus, the flow sheet for these sites must be sufficiently developed to define discharges so that the technical details of the development programs in the waste management flow sheet can be addressed.

2. The waste management location has several steps wheree acceptable technologies, have been shown to be "production ready" but do not exist today.

3. The waste management location has numerous operating steps as shown by the number of boxes on the flow sheet.

4. Within the DOE complex, fewer technology development programs are aimed at solving some of these difficult problems.

On the positive side, for most of the waste management flow sheet, the operations are relatively straightforward, and the development programs are under way.

Critical Flow Sheet Concerns

On the baseline flow sheet, the areas of critical technological concern for waste management are the destruction of waste organics and the immobilization of residues and liquids for shipment to WIPP. The technology of choice for destroying waste organics is controlled air incineration (CAI). The major reason for the technical uncertainty is concern over the ability of sites to obtain licensing and permits for CAI. Several sites are planning to obtain licenses and permits to perform CAI, but if these efforts are unsuccessful, the Complex 21 facility would not be able to operate.

There are numerous alternatives and backups for CAI, but one of the problems is that none of the alternatives would replace CAI directly. For example, existing methods for destroying hazardous liquid organics would not perform very well on solid organic waste. Therefore, technology development for destroying organic waste is made more difficult.

The second major concern is immobilization or fixation. The baseline technology for fixation is cementation. This process is very sensitive to the composition of the material to be immobilized. If the cement sets too rapidly, the cement can easily dewater after a few months.

Also, radiolysis might generate hydrogen gas that can push free liquid from the cement matrix and result in surface water. Of the several alternatives to cementation, none are now "production ready."

Four technical areas will be highlighted with feature articles under the waste management section. These are super critical water oxidation, waste stream monitoring, and waste stream polishing (removal of heavy metals). ◆

WASTE

MANAGEMENT

Destruction of Hazardous Wastes by Supercritical Water Oxidation

by Steven J. Buelow
Photochemistry and Photophysics Group

Introduction

Supercritical water oxidation (SCWO) is a relatively low-temperature process that destroys a wide variety of hazardous chemical wastes effectively and efficiently. It is applicable to the destruction of most organic compounds and some inorganics and therefore could be used to destroy toxic organic waste and to treat contaminated water, soil, and sludges. A SCWO system can treat aqueous streams containing organics in relatively low concentrations (<20%) and offers complete control over emissions, thus meeting the Environmental Protection Agency's concept of a "totally enclosed treatment" facility.

In SCWO, the waste is mixed with an oxidant (oxygen, air, or hydrogen peroxide) in water at pressures and temperatures above the critical point of water (374°C and 218 atm).

Under these conditions, water is a fluid with densities high enough for reasonable process throughput to be achieved, but its transport properties are like those of a gas, allowing rapid chemical reaction.

Supercritical water is a unique solvent medium in which oxidation can take place at temperatures lower than those of incineration, limiting the production of unspecified nitrogen oxides and char. The reaction is carried out entirely in an enclosed pressure vessel containing dilute reactants, so that the heat of reaction is absorbed by the solvent and the temperature can be maintained at any desired level, typically in the range of 400°C to 650°C. Rapid oxidation occurs within seconds or minutes and produces simple products (ideally, carbon dioxide, water, and nitrogen).

In principle, any organic compound—that is, any compound composed of carbon and other elements such as hydrogen, nitrogen, phosphorus, sulfur, and the halogens— can be completely oxidized to relatively innocuous products. Because water is the reaction medium, the process can be used for a variety of organic wastes containing water or for water contaminated with organic compounds. The optimum concentration of organic compound in water depends on the heats of oxidation of the particular organic compounds present and the engineering design of the apparatus. An engineering tradeoff to be considered in the design of a plant is the organic concentration that generates enough heat to maintain the reaction but not more heat than can readily be removed from the processing vessel.

Destruction of Hazardous Wastes by Supercritical Water Oxidation (continued)

Pure or highly concentrated organic wastes can be diluted with water. Conversely, fuel or other organic wastes can be added to contaminated water. Other factors that influence the engineering design include the residence time in the reactor (determined by the chemical kinetics of oxidation of the waste), the physical state of the waste and its oxidation products, and the amounts of waste to be processed.

Our current research at Los Alamos National Laboratory aims to determine the advantages or problems with using SCWO to treat high-risk wastes. Such wastes include explosives, propellants, and the complex mixed wastes found in the underground storage tanks at Hanford, Washington.

This work evaluates reactor design, determines destruction efficiencies and products of destruction, and models chemical and physical processes in supercritical water. Some of our results concerning reactor operation for several waste streams, in particular, mixing of organic wastes and oxidizers, destruction of explosives, and treatment of Hanford waste simulants are summarized here.

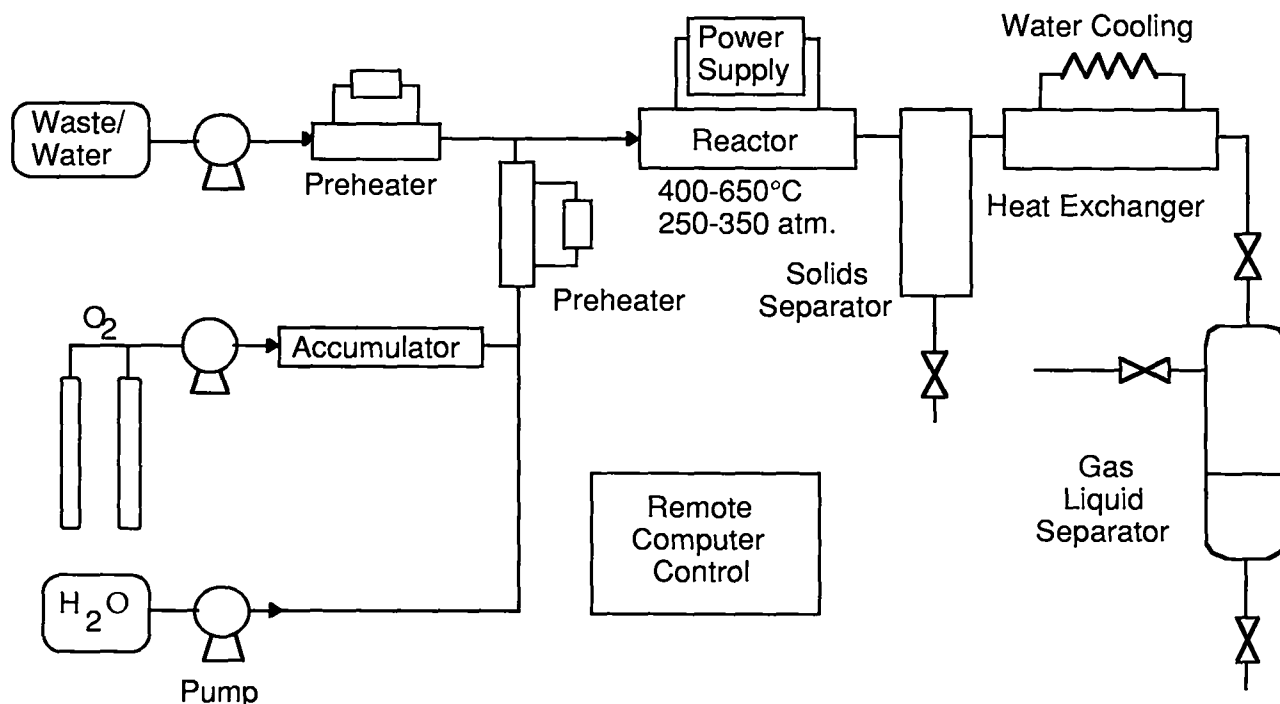## Reactor Design and Operation

A general schematic for an SCWO reactor is shown in Fig. 1. The waste, oxidant, and fuel (if needed) are compressed, preheated, mixed, and injected into the reactor, which ideally converts the waste to water, carbon dioxide, nitrogen, salts, and insoluble solids. The reactor temperatures and pressures are typically 400°C to 650°C and 250 to 350 atm. The solid, liquid, and gaseous effluents are separated, depressurized, and if needed, post-processed.

All effluents can be contained and collected so that they can be tested before release to the environment; unreacted oxygen can be segregated and recycled, and energy can be recovered and used to heat incoming waste.

A number of different reactor designs have been proposed and put into practice, including both vessel and tubular reactors. A great range of sizes appears to be possible for SCWO plants. Standard pressure-vessel technology can be used to provide both small mobile units and permanent medium-sized surface installations for processing of laboratory or manufacturing wastes. Plants with very large capacities have also been proposed. These plants consist of a cylindrical heat exchanger and reaction vessel emplaced in the ground by using oil-field drilling technology.

Fig. 1. Simplified schematic of supercritical water oxidation unit.

To date, our experiments have examined tubular reactors. Our largest SCWO unit has a capacity of 50 gal./day, is transportable, and operates by remote control by computer.[1] All important operating parameters, such as temperature, pressure, and flow rate, are continuously monitored and recorded. The unit is modular so that reactors of various designs can be easily interchanged. Fig. 2 shows the temperature distribution along a 55-ft-long tubular reactor measured during a test using acetone as a surrogate waste.

Temperatures are measured using thermocouples attached to the outside of the reactor tubing. For the test shown in Fig. 2, the acetone/water and oxygen/water feed streams were mixed and then heated to the desired temperature by direct, electrical-resistance heating of the first 20 ft of the reactor; heaters on the last 35 ft of the reactor helped to balance conductive heat losses.

The total flow was 1 gal./h at 273 atm. The acetone concentration after mixing was 2 wt%, and oxygen was present at twice the stoichiometric concentration needed to convert the acetone to carbon dioxide and water. At a distance of 10 ft, a temperature plateau occurred (Fig. 2) because of the behavior of water near the critical temperature. In this temperature range, the heat capacity of water is relatively large, and the temperature rise decreases with constant heating.

Destruction of Hazardous Wastes by Supercritical
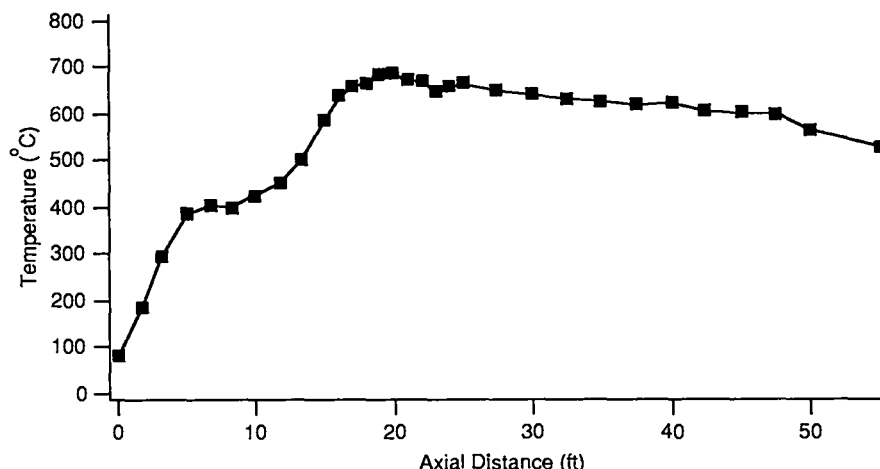# Water Oxidation (continued)

Fig. 2. Reactor-tube temperature as a function of distance from the reactor inlet under steady-state conditions. The total flow was 1 gal./h at 273 atm. The acetone concentration after mixing was 2 wt%, and oxygen was present at twice the stoichiometric concentration needed to convert the acetone to carbon dioxide and water.

At a distance of about 15 to 20 ft (450°C to 700°C) the reaction rate of acetone with oxygen increased, and the temperature rose more rapidly because of the energy release from the oxidation reaction. The lack of further temperature increase after 20 ft indicates that most of the oxidation reaction was complete and that the temperature slowly decreased from the heat loss through the reactor insulation. Because the reactor was not cooled, the maximum temperature is determined by the heat content of the waste and the heat capacity of the fluid. A heat exchanger at the end of the reactor rapidly cooled the effluent to ambient temperature.

Analysis of the aqueous effluent yielded a destruction efficiency for acetone of 99.99985% under these conditions.

Mixing the waste and oxygen before heating the fluid is convenient and allows the oxidation reactions to begin at lower temperatures (which may diminish pyrolysis reactions). However, it is not safe to do so for all wastes. Similar tests using 2% hexane solutions produced detonations in the first several feet of the reactor and in a room temperature filter located upstream of the reactor.

Hexane, oxygen, and water are not miscible at low temperatures and in the subcritical portion of the reactor, they remain separated into three phases, producing an explosive mixture. This problem does not occur when the waste/water and oxidizer/water streams are heated above the critical temperature before being mixed.

Figures 3 and 4 show the temperature distributions along a reactor with separate preheater sections for the waste and oxidant under steady-state conditions. The preheaters are 12 and 13 ft long for the feed streams, and are heated by direct electrical resistance. Oxidation occurs in a 6-ft insulated tube following the mixing region.
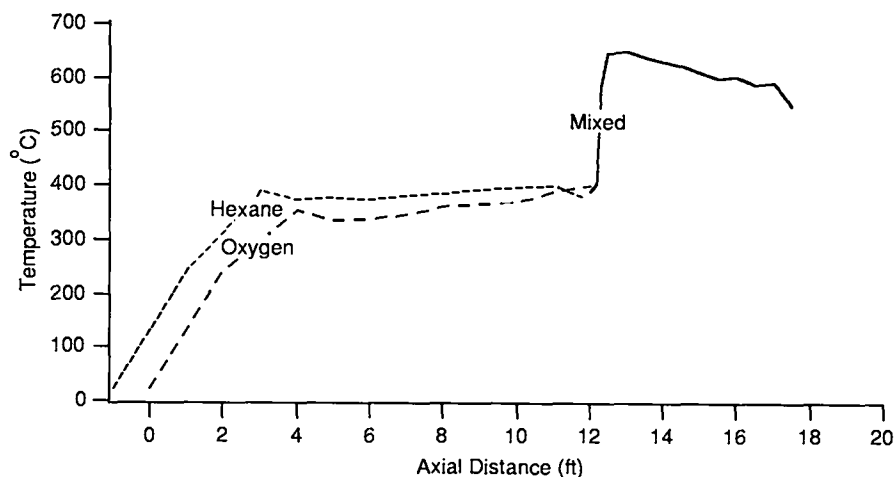
Fig. 3. Reactor-tube temperatures as a function of distance from the oxygen preheater tube inlet. The total flow was 1gal./h at 248 atm. The acetone concentration after mixing was 3 wt%, and oxygen was present at twice the stoichiometric concentration needed to convert the acetone to carbon dioxide and water.
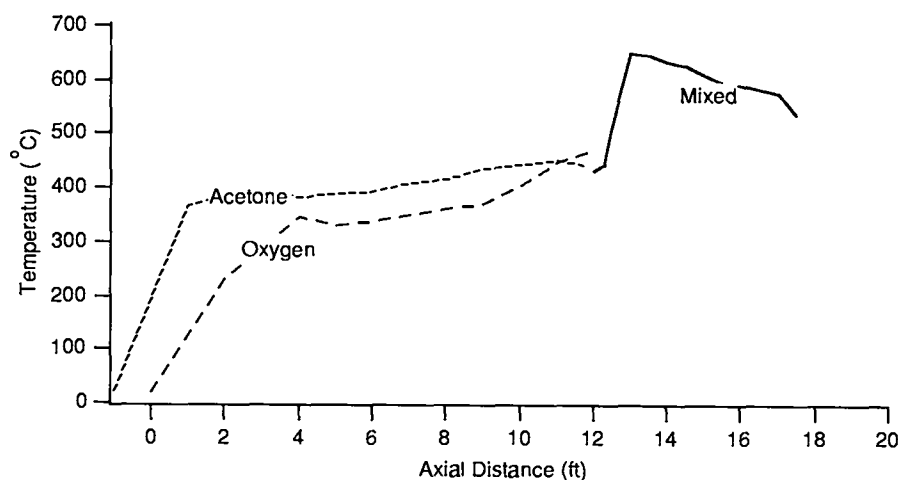

Fig. 4. Reactor-tube temperatures as a function of distance from the oxygen preheater tube inlet. The total flow was 1.1 gal./h at 253 atm. The acetone concentration after mixing was 2.5 wt%, and oxygen was present at 1.5 times the stoichiometric concentration needed to convert the hexane to carbon dioxide and water,

For tests using acetone (Fig. 3), we heated the acetone and oxygen feed lines above 450°C before mixing in order to initiate a rapid oxidation reaction. The heat of reaction released after mixing increased the fluid temperature from 450°C to 650°C within 12 in. of the mixer and produced rapid and complete destruction of the acetone.

At mixing temperatures below 450°C, a temperature increase after mixing did not occur and acetonewas not effectively destroyed. The hexane oxidation rate was noticably faster. For hexane, the temperature reached a maximum only 4 in. after the mixer.

Thus far, we have not tested a wide range of organic wastes

to determine which materials can be safely mixed in the sub-critical region. However, we suspect this may be a problem only for volatile, water-insoluble, flammable organics such as hexane. Furthermore, the prob-lem may not occur when air is used as the oxidant because a pure oxygen phase will not be present in the subcritical region.

Destruction of Hazardous Wastes by Supercritical Water Oxidation (continued)

Table I. Results for the SCWO Explosive

	PETN	HMX	RDX	TNT	NQ
Initial conc. (ppm)	3.8	2.6	35.2	65.5	1700.
Destruction efficiencies	>0.9825	>0.99	>0.9992	>0.9998	>0.9999
NO_3[a]	0.187	0.124	0.101	0.366	0.0003
NO_2[a]	0.060	0.053	0.141	0.285	0.0004

[a] Given as fraction of initial nitrogen.

Destruction of Explosives

The traditional disposal methods for explosives are open-air burning and open detonation. Regulatory agencies, however, are likely to prohibit these methods because of the associated uncontrolled air emissions, in particular the huge quantities of unspecified nitrogen oxides that are commonly formed. In addition to conventional forms of explosives wastes, soils and groundwater at manufacturing plants and military bases have been contaminated with explosives from normal operating procedures. Incineration with the associated air pollution may be used for decontamination of such soils, but few satisfactory and economic methods exist for decontamination of ground water.
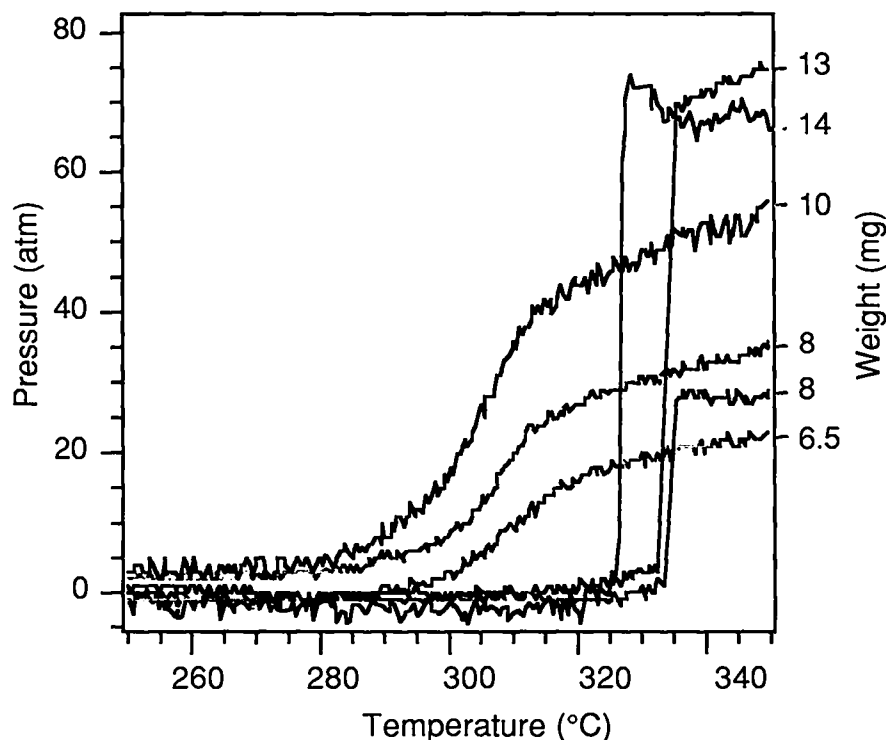
We have investigated the feasibility of oxidation in supercritical water as an alternative method for the destruction of explosives and propellants.[2] In Table I, the destruction efficiencies for five explosive compounds—pentaerythritol tetranitrate (PETN), cyclotetramethylene tetranitramine (HMX), cyclotrimethylene trinitramine (RDX), trinitrotoluene (TNT), and nitroguanidine (NQ) in supercritical water—are given along with the fraction of the initial nitrogen converted to nitrate and nitrite in the aqueous effluent. The initial concentrations of the explosives were kept low, less than half their room-temperature solubilities, to prevent precipitation and accumulation of explosive material in the feed lines leading to the reactor. Hydrogen peroxide was used as the oxidizer and was mixed with the feedstock containing explosive before the fluids were heated. In all cases, the oxidizer was in excess of that needed to convert the explosive to carbon dioxide, water, and nitrogen. Typical experimental conditions were pressures near 340 atm, reactor temperatures near 600°C, and residence times near 7 s. For all of the explosives investigated, the aqueous effluents did not contain detectable amounts of explosives. The measured destruction efficiencies were limited by the sensitivity of the analysis method (50 ppb) and the low initial concentration of the explosives. Carbon dioxide and nitrous oxide were identified in the gaseous effluents using Fourier transform infrared spectroscopy with a multipass white cell.

Fig. 5. Reaction of TATB in water. The pressure rise because of the heating of the water has been subtracted.

Carbon monoxide, methane, nitric oxide, and nitrogen dioxide were not observed. We estimate detection limits for these species as a fraction of starting weight to be 0.1 for PETN and HMX to 0.005 for NQ. It is interesting to note the wide variation in the fraction of initial nitrogen that is converted to nitrate and nitrite ions. For TNT, the amount of nitrogen converted to nitrates and nitrite is over 60%, whereasfor NQ it is less than 0.1%. The amount of nitrate and nitrite produced also varies with reactor temperature and oxidizer concentration. This chemistry is being investigated further in order to minimize nitrate and nitrite production.

Destroying explosives using SCWO at concentrations at or below the solubility limits is not practical except for the treatment of contaminated ground water. In order to increase the throughput of the destruction process for bulk explosives, other methods for introducing the explosives into the supercritical water reactor are being developed. We are currently investigating two alternatives.

The first approach uses slurries to continuously feed high concentrations of explosives into a supercritical water reactor. To evaluate the hazards associated with heating slurries above the critical temperature, we are examining the behavior of small particles of explosives as they are heated in water. These experiments are performed using a small batch reactor (200 µl). A small quantity of explosive is added to 100 ml of water, with the balance of the reactor volume filled by air. The pressure is measured at 1- s intervals as the reactor is heated.

To determine the pressure rise caused by the reaction of the explosive, a baseline test using an equal quantity of water in the absence of the explosive is performed. The difference in the measured pressures at a particular temperature for the two tests is the pressure of the gases produced by the reaction of the explosive. This pressure difference gives a qualitative measure of both the extent and the rate of the reaction of the explosive. Fig. 5 shows preliminary results for the behavior of triaminotrinitrobenzene (TATB) as it is heated.

Destruction of Hazardous Wastes by Supercritical Water Oxidation (continued)

For small quantities (<7 mg) of TATB, the reaction proceeds slowly as the water is heated, producing a controlled release of energy. For quantities greater than 13 mg, the reaction starts at slightly higher temperatures but proceeds much more rapidly. In the 8-to-10-mg range, the behavior is not reproducible and probably depends on the morphology of the particle. These preliminary results indicate that the behavior of the slurries may vary and that the slurry particles can react rapidly. Such uncertainties raise concerns about using slurries to feed supercritical water reactors.

The second method for introducing large quantities of explosives into a supercritical water reactor involves processing the explosive by hydrolysis at ambient pressures and low temperatures (50°C to 100°C). Thus far, we have demonstrated that NQ, HMX, and nitrocellulose can be decomposed rapidly into water-soluble nonexplosive products through hydrolysis under basic conditions.

We then processed the products of the hydrolysis through a supercritical water reactor, producing carbon dioxide, water, nitrous oxide, and nitrogen. For HMX and NQ solutions with starting concentrations between 1 and 8 wt%, this two-step treatment produced over 99.999% destruction of the explosive and less than 1 ppm total organic carbon (TOC) in the liquid effluent. We are examining the possible problems, such as self-heating, associated with hydrolyzing large pieces of explosives. Thus far, none have been encountered.

Treatment of Hanford Waste Simulants

Storage tanks at the Hanford reservation in Washington contain millions of gallons of mixed wastes composed of highly concentrated soluble inorganic compounds and organic components.

SCWO has been identified as an attractive method of nonselectively destroying the organic components of the complexant concentrate waste before that waste is fed into the Grout Treatment Facility or the Hanford Waste Vitrification Plant Feed.

Although SCWO has been proved efficient for the removal of organic matter, the ability to treat highly concentrated inorganic waste streams has not been fully demonstrated.[3] In the case of the Hanford tank wastes, thermodynamic calculations show that the nitrate already present in the wastes can serve as an oxidant for organics and other oxidizable compounds such as ferrocyanides. Preliminary experiments indicate that nitrate may be an acceptable oxidant for other components of the waste.
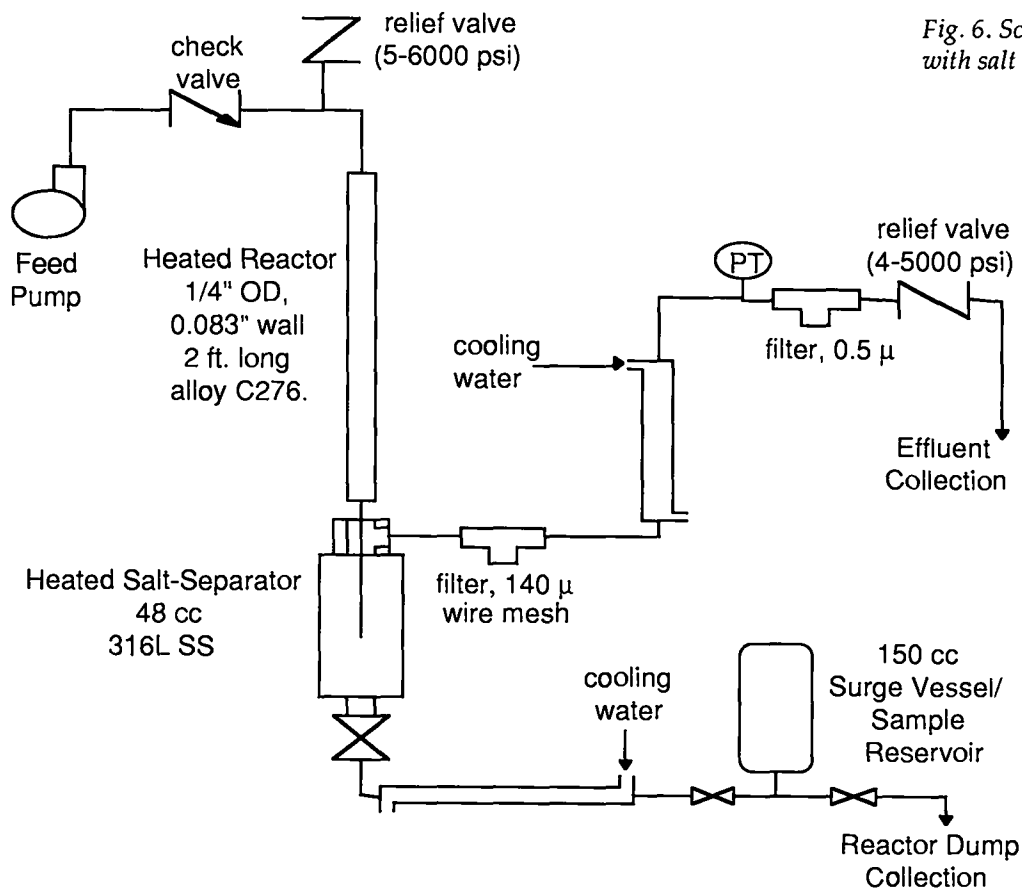
Fig. 6. Schematic of SCWO reactor with salt separator.

To explore the feasibility of SCWO treatment of the Hanford tank wastes, a simulant was prepared and treated. The constituents of the simulant (Table II) are mainly sodium nitrate (5 wt%), with some organic matter (sodium acetate and EDTA), other sodium salts (chloride, sulfate, and bicarbonate), heavy metals (chromium and nickel), aluminum nitrate, and nuclides of concern (cesium and strontium).

A schematic of the apparatus used for this experiment is shown in Fig. 6. The heated portion of the reactor consists of a short linear tube that flows into a heated salt separator. The reactor is mounted vertically so that precipitating solids will settle into the separator. The mass flow rate was 7 g/min, producing a 51-s residence time in the reactor. The formation and breakdown of plugs during the experiment produced some temperature and pressure fluctuations at about 508°C and 286 atm.

During the experiment, the effluent was collected and measured for volume and pH. At the end of the experiment, the reactor tube was drained into the salt separator. The separator was then cooled and the contents collected. The system was washed with water, followed by a 1.0 N sulfuric acid solution. Finally, solids were filtered from the rinse solutions, dried, and weighed.

Destruction of Hazardous Wastes by Supercritical Water Oxidation (continued)

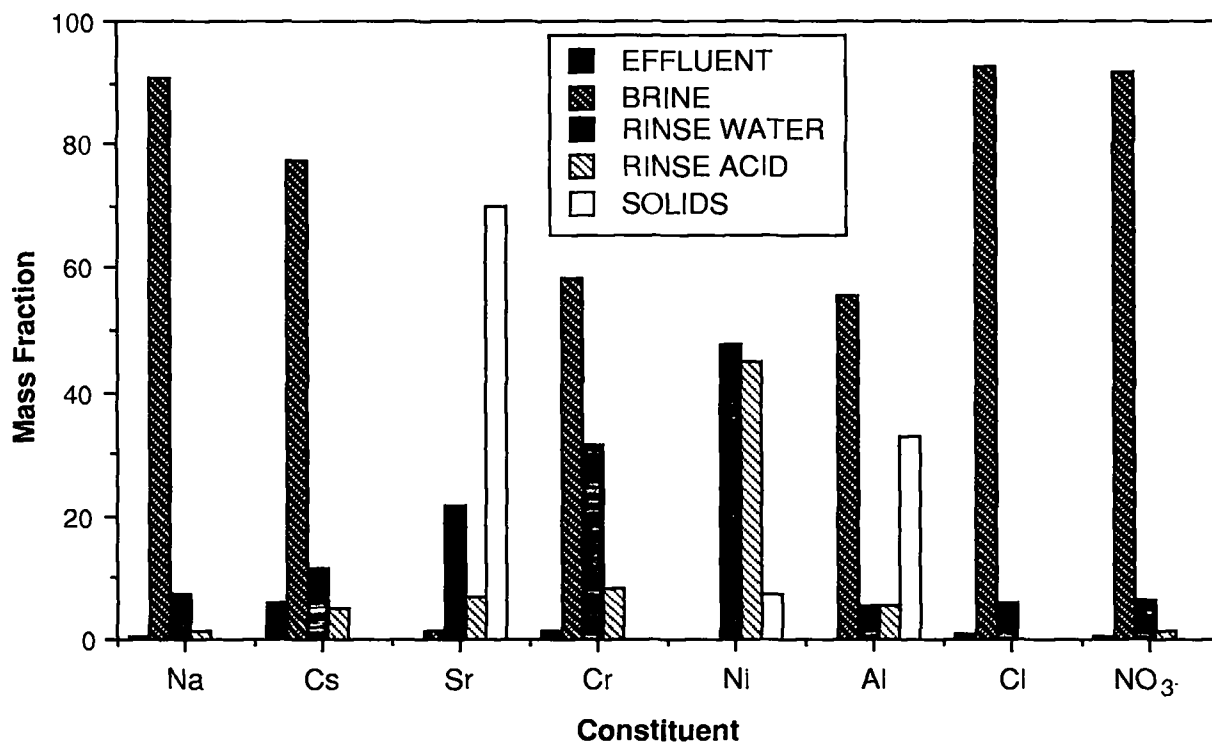Table II. Results of Hanford
Waste Simulant Processing

Experiment/ Constituent	Feed mg/l	Effluent mg/l	Brine mg/l	Rinse Water mg/l	Rinse Acid mg/l	Solids μg
Volume (L)	----	0.347	0.023	0.202	0.206	----
pH	7.0	6.3 - 6.4	12.4	10.0	----	----
Cs	5.5	0.2	41.6	0.7	0.3	BDL
Na	19100	71 - 72	254000	2360	473	BDL
Sr	6.0	BDL	1.10	1.90	0.60	1240
Al	463	0.2	1800	20.8	20.4	24600
Cr	12.9	0.55 - 0.64	340	21	5.3	14.5
Fe	BDL	BDL	BDL	0.9	12.5	1330
Ni	12.8	BDL	BDL	6.20	5.70	193
NO_3-	37420	156-167	491000	3990	806	----
Cl-	681	8.5	11300	85.7	----	----
NO_2-	BDL	46 - 59	38600	382	----	----
Acetate	2220	1 - 3	100	211	----	----
TOC	4300	1 - 7	23	157	50	----
TIC	4	75 - 127	0.1	203	0.1	----

The results from processing the Hanford waste simulant are given in Table II. The content of the sodium, nitrate, and organic matter in the effluent was reduced by over 99.5% from the feed. Strontium concentrations in the effluent were below detection limits whereas the cesium concentration was reduced by over 96%.

The aluminum concentration was reduced by 99.95% and the chloride concentration was reduced by 98.7%. Most of the constituents were recovered in the brine.

This result is illustrated in Fig. 7, which shows the constituent distribution in the various streams. The large fraction of the aluminum and strontium in the solid phase suggests that they formed insoluble aluminum oxide and strontium carbonate.

Fig. 7. Partitioning of constituents for processed Hanford waste simulant.

Chloride and bicarbonate most likely precipitated as sodium salts. The majority of the sodium and cesium likely precipitated as nitrates. The pH of the brine was quite high (12.4), possibly because of the precipitation of sodium hydroxide and bicarbonate. The feed pH was 7.0 whereas the pH of the effluents varied from 6.3 to 6.4. After processing for 30 min, plugs began to form in the heated reactor tube, and the experiment was halted after 50 min.

Aluminum and nickel were difficult to remove by rinsing and were not fully recovered. It is possible that oxides of these metals caused the plugging.

Summary

The use of SCWO to treat hazardous wastes such as organic compounds, explosives, and mixed wastes has been investigated. This relatively low-temperature process has been proposed as a means of destroying both fuels and oxidants, with full control of effluents.

The results presented in this paper show that explosives such as HMX, PETN, RDX, TNT, and NQ can be rapidly destroyed by reaction in supercritical water. The problems associated with introducing large concentrations of explosives into a supercritical water reactor have not yet been fully solved. The use of slurries may be viable, but preliminary experiments indicate unpredictable behavior.

Destruction of Hazardous Wastes by Supercritical Water Oxidation (continued)

Preprocessing the explosives using hydrolysis in low-temperature basic solutions has been demonstrated for NQ and HMX. A Hanford underground-storage tank waste simulant was processed successfully using SCWO. At temperatures near 500°C, over 99.5% of the organic matter, sodium, and nitrate are removed from the reactor effluent. The resulting waste brine (nearly 1.4 kg/liter of sodium nitrate) was less than 3% (by volume) of the total volume processed.

Cesium was also efficiently removed (>90%), indicating a significant waste reduction and the potential of SCWO for activity reduction of the radiocesium in mixed wastes. Tests of different reactor designs showed that volatile, flammable organics that are immiscible in water can be safely processed in a supercritical water reactor. Our results for hexane oxidation demonstrate that separate preheating of such organics and of the oxidant before mixing allows for safe and efficient destruction of the organic compound. ◆

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2. S. J. Buelow, R. B. Dyer, C. K. Rofer, J. Atencio, and J. D. Wander, "Destruction of Propellant Components in Supercritical Water," Proceedings of JANNAF Safety and Environmental Protection Subcommittee Workshop, Tyndall Air Force Base, Florida, March 27-28, 1990, CPIA Publication 540, March (1991).

3. T. T. Bramlette, B. E. Mills, K. R. Hencken, M. E. Brynildson, S. C. Johnston, J. M. Hruby, H. C. Feemster, B. C. Odegard, and M. Modell, "Destruction of DOE/DP Surrogate Wastes with Supercritical Water Oxidation Technology," Sandia National Laboratories report SAND90-8229 (1990).

WASTE

MANAGEMENT

Waste Stream Monitoring

by Rick Day
Nuclear Materials Processing Group: Nitrate Systems

In light of the new regulations and restrictions imposed on facilities for discharge or transfer of liquid waste, the ability to monitor, ensure SNM accountability, and characterize waste streams is crucial. As a lead DOE facility for the development of special nuclear materials process technology, TA-55 has a responsibility to set a standard in the DOE complex for effluent monitoring and control for environmental protection. Waste solutions generated from plutonium processing need to be characterized. Flow rates need to be monitored to ensure regulatory comliance and to confirm that a minimum amount of waste is generated. We also need to verify the extent of waste reduction achieved through process optimization initiatives.

A Waste Stream Monitoring Program has been initiated using experts from NMT-2, NMT-3, NMT-7, NMT-8, and CLS-1 to address the technical challenges. The program's emphasis is on

1. determining the volumes of liquid waste generated at TA-55/PF-4 in a given time period;

2. identifying suitable sampling techniques for representative sampling, accurate flow measurements, temperatures, and so forth;

3. characterizing the composition of the various liquid waste streams; and

4. applying the appropriate instrumentation to allow TA-55 to properly respond to waste monitoring requirements both now and in the future.

Characterization of the liquid waste streams (acid, caustic, and industrial) that leave TA-55 is being performed by CLS-1.

The analyses being performed include

1. radiochemistry,

2. trace elements using inductively coupled plasma-emission spectrometer (ICP-ES) and inductively coupled plasma-mass spectrometry (ICP-MS),

3. ion chromatography to determine anions, and

4. chemical oxygen demand (COD). When instrumentation becomes available, total organic carbon will replace COD. All the results are entered into a spreadsheet for tracking purposes.

Waste Stream Monitoring (continued)

Thirteen flow meters are in place at various locations throughout the basement of PF-4 to monitor the solution flows generated by the various processes. To track total gamma activity, sodium iodide gamma detectors have been placed at various locations on the process piping in the PF-4 basement. To handle the unscheduled flow into the industrial waste line that goes to the waste-handling facility at TA-50, a surge tank was installed in the basement immediatel;y preceeding the point where this line leaves the facility.

To monitor the various outputs of the waste stream system, an industrial PC-based control system has been installed with access in the operations center. Four data concentrators capable of accepting 32 input channels and providing up to 8 output channels are routed through single communication cables to the operation center.

TA-55 is implementing appropriate instrumentation and methods to ensure better monitoring of waste streams.

An inductively coupled ICP-MS will be acquired to complement the ICP-ES currently on site to aid in the monitoring of the waste streams. The process control is upgraded continually to ensure monitoring of new locations and instrumentation as they are added. New level sensors will be installed on the surge tank to provide more accurate measurements. This proactive approach to waste management will demonstrate our commitment to minimizing the environmental impact of our operations while optimizing plutonium recovery.◆

W A S T E

M A N A G E M E N T

Waste Treatment: Chelating Polymers for Removal of Heavy Metals from Aqueous Waste Streams

by Gordon D. Jarvinen

Nuclear Materials Processing Group: Nitrate Systems

Alternative technologies are urgently needed for the treatment of waste waters to reduce the concentration of contaminating metal ions to meet increasingly stringent regulatory limits and to decrease waste disposal costs. We are developing a series of polymer-supported, ion-specific extraction systems for removing actinides and other hazardous metal ions from waste water streams. Our work focuses primarily on metal contaminants (especially plutonium and americium) in waste streams from TA-55, at the Waste Treatment Facility at TA-50, and at the Rocky Flats Plant. We are testing ligands to identify the compounds having the required selectivity and binding constants to remove the target metal ions from the waste streams. Selected ligands are then incorporated into poly-meric structures that will allow ready separation of the target metal ions from the waste water stream.

The separation properties of the polymer-supported ligands are being evaluated to allow a complete engineering assessment of these polymer systems in combination with complementary technologies and to compare them with competing technologies.

These new polymer materials can provide a cost-effective replacement for sludge-intensive precipitation treatments and yield effluents that meet more stringent discharge requirements. At Los Alamos, we are striving for a 95% reduction of low-level sludge volume and a 50% reduction in transuranic (TRU) sludge volume at TA-50. These systems could also be applied at Rocky Flats, Hanford and other DOE facilities.

The exploratory work done by our R&D team has demonstrated the effectiveness of this approach to cleaning up waste waters. Collaborators in this work include the Los Alamos Laboratory groups INC-1, CLS-1, MST-7, and EM-7; Reilly Industries; the University of New Mexico; Texas Tech University; New Mexico State University; and the University of Tennessee.

Removal of metal ions from aqueous solution is a major industrial activity that includes processes such as water softening, hydrometallurgical recovery from ores, and detoxification of waste waters and contaminated natural waters. The concept of attaching metal-ion-specific ligands to polymers is an important approach to solving such problems and has received considerable attention over the past 20 years. Separations involving transition metals have dominated the work in this area.

Waste Treatment: Chelating Polymers for Removal of Heavy Metals from Aqueous Waste Streams (continued)

Relatively little work has been done for the actinides and lanthanides, with the exception of a rather large body of work dealing with the use of chelating polymers to recover uranium from seawater. Chelating polymers are the basis of a number of successful industrial separations including removing calcium to part-per-billion levels from brine and removing radioactive cesium from alkaline waste waters.

Reducing the concentration of a target metal ion to the desired level will require that the chelating polymer have a binding strength that is high enough to accomplish the desired separation. However, in the presence of other cations, the ligand will require a large selectivity if the target metal ion is to overcome the competition from these other cations for the ligand binding sites.

In many of the waste streams to be addressed, the target metal ion is present in very low concentration compared with metals such as sodium, potassium, calcium, magnesium, and iron.

Polyhydroxamate Chelators

We have evaluated several polyhydroxamate chelators for their ability to bind thorium(IV) and have obtained preliminary results with plutonium(IV). Some results for thorium(IV) are shown in Fig. 1. Desferrioxamine-B (DFB) is a naturally occurring chelator that is commercially available, and OZ-118 is a new synthetic chelator prepared by Prof. A. Gopalan, our collaborator at New Mexico State University.

The pM value is defined as $log[Th]$, where $[Th]$ is the amount of free thorium remaining in solution at any given pH starting with equal quantities of metal and chelator (both in solution). In this case we are treating 1 ppb, a typical plutonium concentration in the TA-50 waste-stream influent. The figure illustrates the potential of these chelators, at near-neutral pH and above, for reducing the amount of plutonium in low-level waste streams to levels well below 2pCi/liter for plutonium 235. The value of 2pCi/liter has appeared in at least one EPA proposal as a limit for alpha-emitting isotopes in drinking water. These calculations indicate that upon attachment of these chelators to solid supports, it should be possible to reduce the amount of plutonium to extremely low levels.
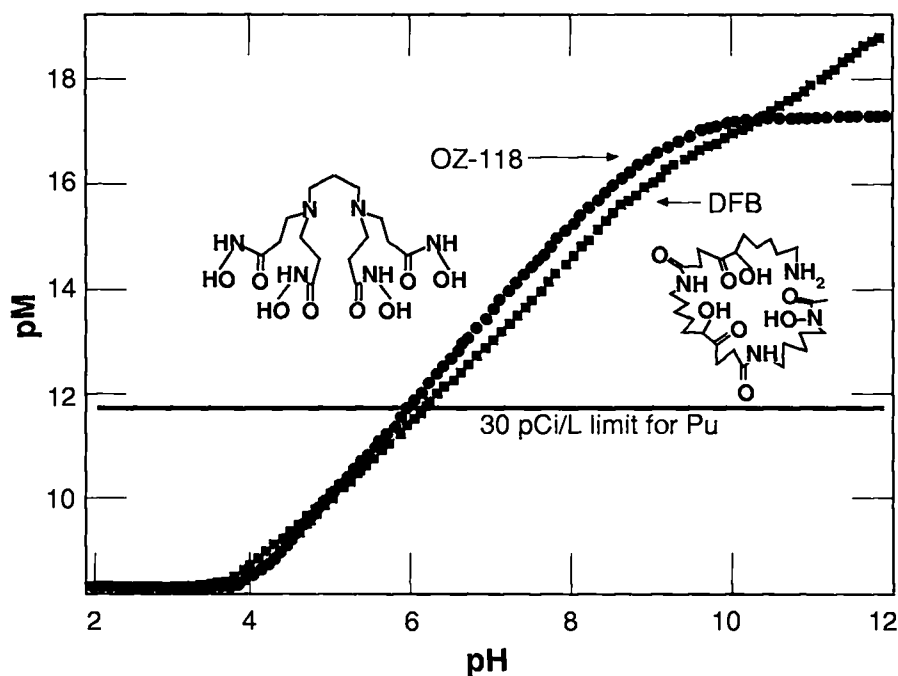
Fig. 1. Calculations for amount of uncomplexed thorium in the presence of polyhydroxamate chelators indicate that thorium and plutonium can be reduced to very low levels.

Polyhydroxamate chelators such as those illustrated above are selective for highly charged metal ions such as plutonium(IV) and americium(III). Therefore, they are not likely to bind metals such as magnesium, calcium, or sodium even in the presence of large excesses of these metals, as is often the case in waste process streams. However, they would normally be expected to bind iron(III) as well as or better than plutonium(IV).

Iron is typically found in waste waters at part-per-million levels, which may be enough to saturate the polymeric chelating resin with iron. This behavior might be expected for the chelator DFB, which has evolved in microbial systems to bind iron(III) in the environment. However, the tetrahydroxamate chelators have been designed to be selective for plutonium(IV) over iron(III).

Gopalan's group has also synthesized the compound OZ-184, which has a *meta*-xylene bridge in place of the propylene bridge of OZ-118. The thorium(IV)-and iron(III)-binding constants of this compound have been measured and show that this compound indeed binds thorium(IV) 3.5 orders of magnitude more strongly than iron(III). We expect plutonium(IV) to bind even more strongly to OZ-184 than thorium(IV); therefore, OZ-184 should have even larger selectivity for plutonium (IV) over iron (III).

Waste Treatment: Chelating Polymers for Removal of Heavy Metals from Aqueous Waste Streams (continued)

Bis(acylpyrazolones) with High Selectivity for Tetravalent Actinides

The 1,3-diketones have been extensively studied as extractants for actinide and lanthanide ions. The linking of multiple 1,3-diketone units to give compounds with increased binding constants for divalent metal ions, uranium (VI), and some lanthanide ions has been reported. However, data on metal complexation for such compounds are rather limited. In a systematic study seeking to enhance actinide ion binding by preorganization, we have synthesized a series of acylpyrazolone ligands linked with four to eight methylene units (see Fig. 2) and have investigated their complexation chemistry.

A large increase in selectivity ($>10^3$) for plutonium(IV) and thorium(IV) over uranium(VI), americium(III), europium(III), iron(III), and aluminum(III) was found relative to closely related bidentate compounds.

The extraction system was also highly selective for plutonium(IV) over thorium(IV). The high selectivity for tetravalent actinides over iron(III) results from the very slow kinetics of iron extraction. The selectivity of these compounds has potential uses in novel sensors and separations, and a patent application has been filed.

Because these systems have demonstrated an enhanced selectivity and high binding constants for tetravalent actinides, they will be evaluated for removing plutonium(IV) from the waste streams. At pH > 2, they will also be evaluated for removing americium(III).

Malonamides

A liquid-liquid extraction process proposed by French workers for removing trivalent actinides from PUREX waste streams based on malonamides, $RR'NC(O)CH(R'')C(O)NRR'$, has potential advantages over the TRUEX process.
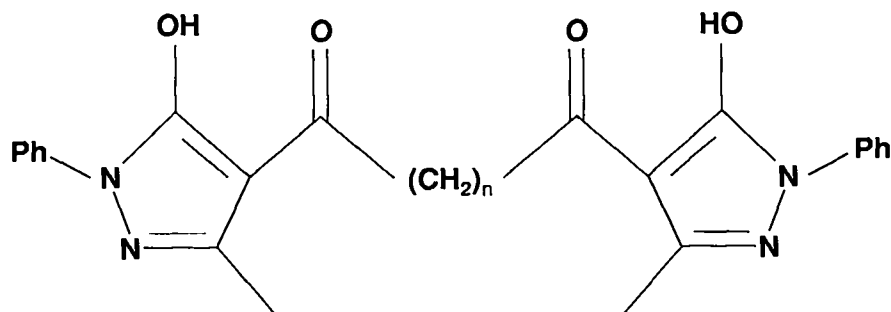
We have attached some of these compounds to polymers such as polybenzimidazole through the R" group on the methylene carbon. The extraction properties of these chelating polymers is under investigation.

Synthetic Methods for Preparation of Chelating Polymers

The major synthetic methods used in the preparation of chelating polymers are

1. polymerization of functionalized monomers,
2. polymerization of nonfunctionalized monomers followed by chemical modification,
3. graft polymerization of a functionalized monomer on a prepared polymer, and
4. physical entrapment of hydrophobic chelating extractants during poly merization or postpolymerization.

Fig. 2. Bis(acylpyrazolones) have a high selectivity for tetravalent actinides.

We have used all of these routes in our exploratory studies. Most of our polymer extractants will be prepared by attachment of ligands to a prepared polymer, such as polybenzimidazole. However, we feel the graft polymerization route will yield chelating polymers with some greatly improved properties. These materials will be discussed in more detail below.

Advanced Chelating Polymers

We have an approach that will advance chelating polymers beyond current technology. Chelating polymers are cross-linked, insoluble, porous polymer beads with functional chelating groups. They have high surface areas and exchange capacities that range from less than 0.1 to about 10 meq/g.

Our approach is to improve the performance of the polymer beads by designing several new features into the polymer structure. The surface area will be increased by graft polymerization of chelating groups onto the surface. This arrangement differs from that of standard chelating polymers in that a long chain of chelating groups will extend away from the surface rather than be fixed into the rigid interior of the resin.

The flexibility of the long chains will have several benefits over fixed sites. Frequently two or more chelating sites are required to bind a metal. In rigid polymers, many sites may be unable to chelate because nearby ligands are not oriented properly to allow chelation and many sites are unavailable. Long, flexible chains of ligands will make many more sites available.
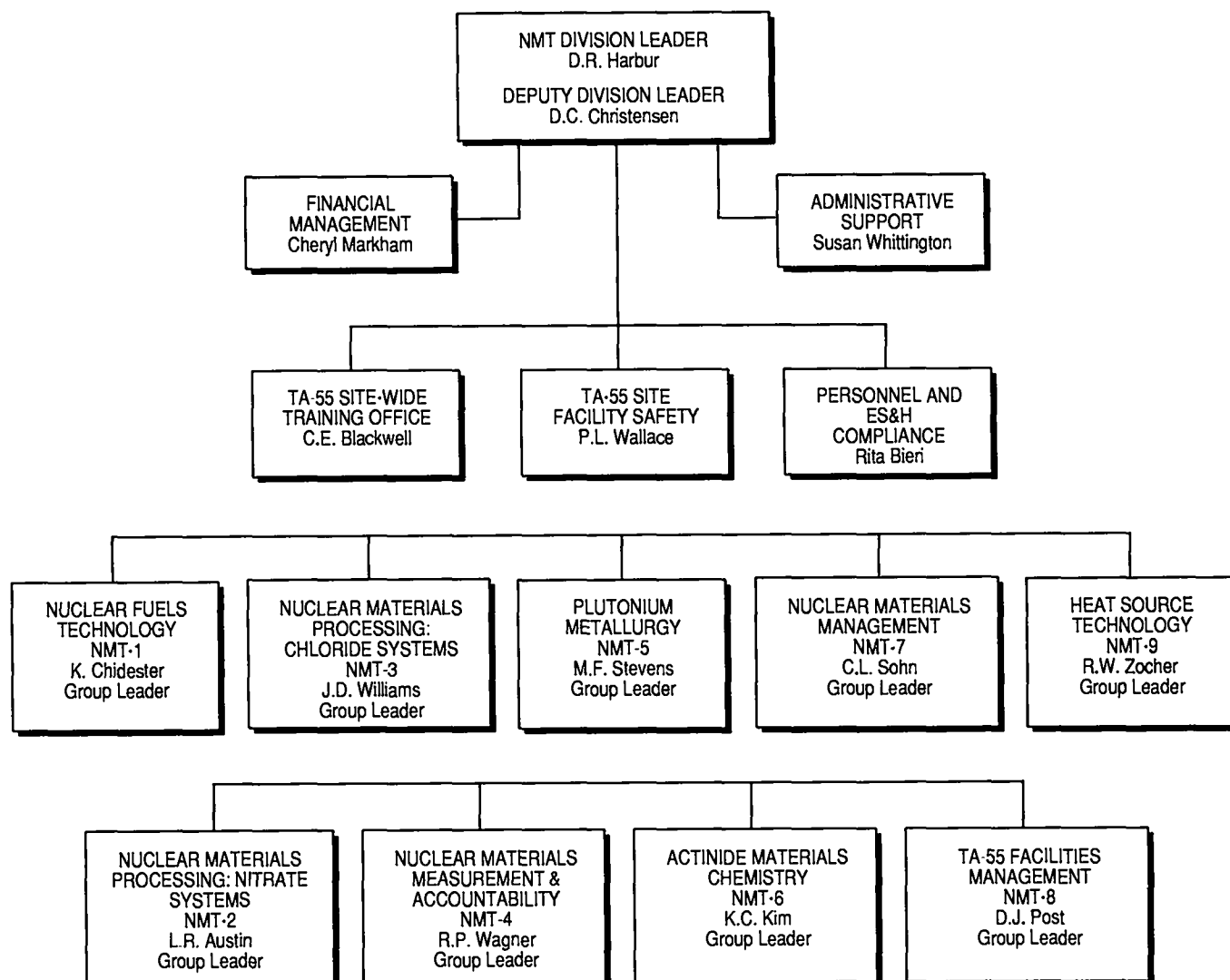
Copolymerization with other monomers can incorporate other features. Hydrophilic groups can be incorporated into the grafted chains so they will extend freely into the aqueous medium. The kinetics of binding will be enhanced by these chains, which are essentially water soluble but bound to a polymer base. Other factors can be designed into the graft polymer such as spacer groups to optimize chelation.

The ultimate in selectivity of complexation can be achieved by use of a ligand preorganized for a specific metal ion at each functionalized site in the grafted polymer chain. For example, this ligand could be one of the tetrahydroxamates discussed over or a crown ether with acidic arms developed to encapsulate a particular ion. In this case, cooperation between binding sites located at different points along the chain or on different chains would not be required. ◆

GROUP

PROFILES

NMT-DO

NUCLEAR MATERIALS
TECHNOLOGY DIVISION
ORGANIZATION CHART

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┌─────────────────────────────┐
│     NMT DIVISION LEADER      │
│        D.R. Harbur           │
│                              │
│   DEPUTY DIVISION LEADER     │
│       D.C. Christensen       │
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TA-55 SITE FACILITY SAFETY
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NMT-3
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Division Leader
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Deputy Division Leader
Dana C. Christensen

Nuclear Materials Technology Division conducts scientific and technical work within the nine operating groups shown in the organizational chart. The title of each group indicates the group's major functions or responsibilities. However, most of our groups carry out a variety of efforts to support our national defense and energy programs, and most groups conduct active research programs to support their main technological or programmatic emphasis. Our operating groups range in size from approximately 20 to nearly 70 employees.

The NMT Division Office, along with group managers, provides technical leadership, managerial guidance, and administrative support to the division's operating groups. The Division Office is also a focal point for nuclear materials issues within the Laboratory. Along with materials and chemistry staff elsewhere in the Laboratory, the NMT Division Office provides overall direction and leadership to the Laboratory's materials and chemistry efforts.

The Division Office management team works directly under the division leader and deputy division leader to provide programmatic and administrative support to the division's staff and management. One of the team's most important tasks is to maintain effective communication between NMT Division and other Laboratory divisions, Laboratory program offices, and upper management. The management team also works closely with funding agencies and other external organizations. The real strength of NMT Division is our people. At present, NMT Division employs approximately 500 people, including part-time and temporary employees. More than 87 percent of the division's employees are staff members or technicians, the vast majority of whom are working on scientific or technical activities.

Approximately 5 percent of our people are postdoctoral appointees, graduate research assistants, or undergraduate summer students. The remainder of our employees provide very necessary administrative and nontechnical management and support functions for the division.

Materials science has a multidisciplinary focus that requires insight and support from many different professional disciplines. Included among our staff are chemists, metallurgists, physicists, mathematicians, ceramists, and engineers with many specialities. Almost all of our staff members have scientific or engineering degrees; 72 percent have either a Ph.D. or M.S. in their respective specialties. Our technicians also represent a wide range of disciplinary interests, including mechanical, chemical, and materials technology.

NUCLEAR FUELS
TECHNOLOGY

Our group has 28 employees: 7 staff members, 13 technicians, 1 support person, 5 consultants, 1 graduate research assistant, and 1 postdoctorate researcher.

Group Leader
Kenneth Chidester

Deputy Group Leader
Walter A. Stark

The Nuclear Fuels Technology Group, NMT-1, specializes in research, development, irradiation testing, and fabrication of uranium- and plutonium-based ceramic fuels. Our group backs up the disciplines of chemical synthesis, ceramic fabrication, and metallurgy with expertise in materials characterization, analytical chemistry, nondestructive examination, and quality assurance. We initiate high-risk/high-payoff research and development for national advanced reactor programs. An example is the development and fabrication of high-quality pelleted uranium nitride for the SP-100 space power reactor. We develop advanced fuel and cladding fabrication techniques, measure fundamental properties, build fuel pins for irradiation testing, analyze performance, and demonstrate fabrication procedures. Our ultimate goal is to turn over demonstrated fuel technologies to private industry for potential commercial development.

Our nuclear-fuels-development laboratories support a wide range of R&D activities, including phase transformations and diagrams, high-temperature diffusion studies; fuel/liner/cladding/coolant capability measurements, kinetics of high-temperature interactions, development of novel synthesis and fabrication methods, refractory alloy weld development, irradiation testing, and postirradiation analysis of fission products migration, fission gas release, swelling, and thermochemical interactions.

Our group has four sections: Fuel Research, Fuel Development, Fuel-Pin Assembly, and Materials Characterization.

The Fuel Research Section studies high-temperature performance of various fuel/cladding combinations. Knowledge of high-temperature interactions is essential to choices of new ceramic-fuel/refractory-alloy combinations for use at high temperatures and/or high burnups. We are currently developing and characterizing high-melting-point carbide compounds for nuclear propulsion reactors. Before commitments can be made to reactor designs that call for various fuel types, fuel cladding combinations must be tested. We test ex-pile compatibility and in-reactor performance on such combinations as niobium, rhenium, and tungsten with uranium nitride and uranium carbide.

"The Nuclear Fuels Technology Group, NMT-1, specializes in research, development, irradiation testing, and fabrication of uranium- and plutonium-based ceramic fuels."

Fuel-development activities include researching advanced processes and fabricating fuel for terrestrial- and space-based reactor concepts. NMT-1 has developed and supplied pelleted uranium nitride fuel for the SP-100 space reactor and uranium carbide for the liquid-metal fast breeder reactor. We are currently developing a cryochemical process to fabricate spherical fuels for space propulsion reactors. We synthesize oxide feedstocks to carbide or nitride powders by carbothermic reduction at up to 15 kg per week. We can fabricate up to 15 kg per week of nitride or carbide fuel pellets or 30 kg per week of oxide fuel pellets by conventional cold pressing and sintering.

Thirty-five atmosphere-controlled gloveboxes, powder-preparation equipment, four automatic pellet presses, three large-capacity synthesis furnaces, and three large-capacity sintering furnaces are available for production. A small-scale fabrication line is also available for developing novel fabrication techniques.

Our Fuel-Pin Assembly Section develops and qualifies refractory alloy welds, anneals cladding components, and fabricates fuel pins for irradiation testing of pin-type reactor concepts. Up to 60 full-length fuel pins per week can be loaded with fuel pellets, welded, cleaned, annealed, wire-wrapped, examined, and packaged for shipment. Fabrication techniques include vacuum-annealing, electron-beam and gas-tungsten arc welding, profilometry, eddy current testing, gamma scanning, and x-radiography.

Our Materials Characterization Section examines fuel and cladding components for advanced fuels and heat-source programs, as well as plutonium metal and alloy samples for weapons programs. This section also provides general photographic support to other NMT groups. Capabilities include ceramography, metallography, x-ray diffraction, residual gas analysis, surface area analysis, and image analysis. ♦

NUCLEAR

MATERIALS

PROCESSING:

NITRATE SYSTEMS

NMT-2 has 73 employees: 22 staff members, 1 limited-term staff member, 37 technicians, 4 support personnel, 1 data base manager, 6 Laboratory associates, 1 Laboratory consultant, and 1 postdoctoral researcher.

Group Leader
Larry R. Austin

Deputy Group Leader
Bill J. McKerley

The Nuclear Materials Processing Group (Nitrate Systems), NMT-2, develops and demonstrates processing technology for plutonium and other actinides by primarily using aqueous-based operations. Our mission has three major components; First, we support the Department of Energy (DOE) complex by developing new and improved methods for plutonium recovery that are safe, efficient, and environmentally sound. Second, we demonstrate new operations on a sufficiently large scale to make them attractive to the plutonium facilities of the future, thus improving future overall operational effectiveness and efficiency.

Third, we support the Los Alamos Plutonium Facility by recovering and purifying plutonium from scrap residues and producing a pure metal that can be used for weapons fabrication development activities. The major goals of these efforts are to improve process safety and efficiency, including minimization of all wastes leaving our facility.

We possess the facilities and expertise to demonstrate on a production scale the recovery and purification of plutonium from a wide range of contaminants and scrap matrices. Our feed materials also consist of residues generated at off-site facilities. Frequently, these facilities do not have the specialized capabilities to handle the more exotic contaminants, and consequently we provide this service for the DOE complex.

Our primary process flow sheet consists of nitric acid/hydrofluoric acid dissolution or leaching followed by purification with anion exchange. The plutonium in the concentrated ion exchange eluate is precipitated with oxalic acid, then filtered, dried, and thermally decomposed to form plutonium oxide. The plutonium oxide may then be converted to a tetrafluoride by reaction with HF and reduced to metal by calcium in a high-temperature reduction furnace.

Our group's research, development, and demonstration efforts directly support all major processing operations at TA-55.

"The Nuclear Materials Processing Group (Nitrate Systems), NMT-2, develops and demonstrates processing technology for plutonium and other actinides by primarily using aqueous-based operations."

We continue to improve our understanding of the underlying chemistry of all the processes, which enables us to improve operations. Our process-development activities are concentrated in four major areas:

1) process chemistry,
2) process analytical chemistry,
3) process monitoring and control, and
4) process engineering.

Scientists in these major areas focus on specific projects. For example, a sensor for high-acid concentrations was developed by our personnel and was selected as one of the top 100 developments of the year, earning an RD100 award.

In the area of waste minimization, we are developing selective extraction systems to reduce radionuclides in aqueous waste streams to very low levels. In addition, we are evaluating opportunities to recycle many of our reagents, such as nitric acid, to also reduce the waste streams leaving TA-55. All of these technologies arebeing developed and tested in the Advanced Testing Line for Actinide Separations (ATLAS). This integrated pilot plant operation, housed in six interconnected gloveboxes, encompasses all the major unit operations currently used for the nitrate aqueous processing of actinide scrap. These include dissolution, anion exchange, precipitations (oxalate, peroxide, and hydroxide), calcination, and evaporation for waste treatment.

The ATLAS uses a distributed process-control scheme based on a PC network running a process-control software package, and analytical support provides near real-time results for both the actinide and impurity content of the various streams that are used to optimize process efficiency. Integrating all of the major aqueous unit operations, along with the process control and the analytical support, is a first for the industry. It will be used to optimize process efficiency for minimizing waste generation. Progress in these areas results in purer product, decreased waste generation, and lower personnel radiation exposure. These activities have far-reaching potential for aiding modernization and environmental cleanup efforts within the DOE complex and in industry. ♦

NUCLEAR MATERIALS PROCESSING: CHLORIDE SYSTEMS

Our group has 52 employees: 17 technical staff members, 30 technicians, 1 support person, 2 postdoctoral researchers and 2 Lab associates.

Group Leader
Joel D. WIlliams

Deputy Group Leader
S. Mark Dinehart

For the most part, the Nuclear Materials Processing Group, NMT-3, (Chloride Systems), supports the residue elimination program at the Rocky Flats plant and process development and demonstration for Complex 21. However, we also have an important role in the weapons program at the Lab.

Within the group, we are developing an integrated approach to chloride-based processing technologies. This encompasses both the aqueous systems and the high-temperature, molten salt systems. New equipment, new reagents, and advanced process diagnostics are all being incorporated into this integrated approach. We have also broadened the emphasis of our weapons program support activities to include demonstration of new equipment and technologies for removal of low levels of actinides from process streams.

Within the group, the scrap recovery activities center around the use of hydrochloric acid media as the basis for process chemistry. Dissolution of scrap matrices, including actinide metal, results in a solution that is processed through either solvent extraction or chloride ion exchange. The solution assay is the determining factor; rich solutions go through solvent extraction for purification, and lean solutions go through ion exchange. A new set of corrosion-resistant, Kynar-lined gloveboxes have been installed to contain the solvent-extraction equipment. Development work of the new dodecane/decanol/tributyphosphate-extraction system is well underway. These solvent extraction glove boxes will begin processing scrap from the TA-55 vault in late FY92. Further upgrades to the aqueous chloride processing line include new, corrosion-resistant boxes to house the ion-exchange process and, eventually, a set of gloveboxes for off-gas scrubbing and other process/facility interface support.

Long-range plans in the area of aqueous recovery include at-line analytical capabilities. One such technique, gas chromotography, is already being evaluated as support for the solvent-extraction process. Recent changes to this process have necessitated sampling and analysis of the organic stream to assure proper composition. Gas chromotography, a technique used widely in industry, provides an at-line analysis that will help assure optimal process performance.

Improved diagnostic and monitoring techniques have also been incorporated into the pyrochemical operations. The use of a spectrophotometer to monitor chlorine in the off-gas from the multicycle direct-oxide reduction process is an excellent example. Enhanced diagnostic techniques, such as the use of a high-temperature reference electrode in electrorefining, are also being explored.

"For the most part, the Nuclear Materials Processing Group, NMT-3, (Chloride Systems), supports the residue elimination program at the Rocky Flats plant and process development and demonstration for Complex 21. However, we also have an important role in the weapons program at the Lab."

Process optimization, through improved monitoring capabilities, is one of the benefits we expect this work to facilitate.

Process development in the area of pyrochemistry includes not only equipment improvements but also the definition of process parameters. One example is the *in situ* chlorination work in the molten-salt extraction process. This uses plutonium trichloride as the oxidant to extract decay-product americium from plutonium metal. Rather than adding the oxidant as a separate reagent, we are evaluating the use of gaseous chlorine sparged through the molten metal to generate the plutonium trichloride.

Specific goals of this work include the definition of the relationship between gas flow rates and the production of the plutonium trichloride, and the subsequent americium extraction. During the past 3 years, Savannah River person-nel performed foundation experiments for this work at Los Alamos.

Finally, we are expanding the emphasis of our direct weapons program support to include the incorporation of the latest recovery technologies for dealing with low levels of actinides.

This change is a natural outgrowth of our efforts in the areas of waste minimization and programmatic support of the WRD&T activities within the Lab. The recovery capabilities required to support the weapons program provide an excellent test bed for demonstrating new techniques for the removal of the very low-level actinides present. Although we have just implemented this change in direction, we believe the work in this area will point the way to the future for Complex 21. ♦

NUCLEAR MATERIALS MEASUREMENT & ACCOUNTABILITY

Our group has 35 employees: 12 staff members, 21 technicians, and 2 support personnel.

Group Leader
Raymond P. Wagner

Deputy Group Leader
Dennis L. Brandt

Nuclear Materials Measurement and Accountability, NMT-4, is a service group that uses nondestructive assay methods to measure nuclear materials at the TA-55 Plutonium Facility. Our group also helps TA-55 comply with Los Alamos and regulatory agency policies regarding nuclear materials accountability. Successful accountability of nuclear materials results in quality process controls, increased production, timely availability of nuclear materials, and increased safety and safeguards.

Specifically, we provide services in nuclear materials control and accountability, nondestructive assay, and measurement control.

Our nuclear materials control activities include coordinating and acting as the focal point for internal and DOE audits, originating and maintaining process-accountability flow diagrams, investigating and resolving inventory differences, interacting with the Laboratory's Program Director for Safeguards Assurance, and verifying that TA-55 personnel are trained to use material surveillance procedures. Our group is responsible for determining and investigating any shipper/receiver differences.
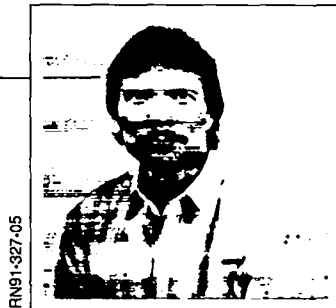
Nondestructive assays are essential to any safeguards program. They confirm and verify the presence and stated quantities of nuclear materials. We also use NDA measurements in isotopic blending operations.

We operate two neutron counters, five gamma-ray assay counters, five gamma-ray isotopic counters, and seven calorimeters. Our Instrumentation Section maintains and calibrates these instruments, as well as the accountability instruments used in the process lines.

We are installing and operating robotic and automated systems to increase our throughput of assayed materials, as well as to enhance safety and security. A full-scale automated assay system (robotic calorimeter, RbobCal) is being used to assay process materials. An automated low-level solid waste handling and measuring system is being built. ◆

PLUTONIUM

METALLURGY

Our group has 54 employees: 19 staff members, 31 technicians, 2 office support, 2 graduate research assistants, and 2 Laboratory associates.

Group Leader
Michael F. Stevens

Deputy Group Leader
Rueben L. Gutierrez

The Plutonium Metallurgy Group, NMT-5, is a multi-disciplinary organization engaged in prototype weapon primary fabrication, metallurgical and chemical properties studies of plutonium and other actinides, and surveillance and stockpile evaluation technologies in support of Laboratory and the Department of Energy (DOE) weapons programs. Our group is principally supported through the Laboratory's weapons research, development, and testing programs, although significant technology support and development efforts are funded through production and surveillance and environmental restoration sources from within DOE. A major new functional responsibility for the Plutonium Metallurgy Group will be to perform pit evaluation studies on stockpile return pits.

Our Fabrication Section constructs the prototype pits that are primarily used in Nevada Test Site research. We use modern casting, machining, and assembly technology to provide war-reserve-type plutonium components in support of this highly important Laboratory activity. We are constantly upgrading and expanding our capabilities in fabrication, as exemplified by our installations of advanced vacuum-induction casting and Nd:YAG laser-welding (1-kW, pulsed) systems. Our flexibility in metal processing and fabrication serve as an excellent proving ground for development of modern complex, or Complex-21, methodologies.

In addition to pit fabrication capabilities, the fabrication section maintains a unique facility for manufacturing isotope detector packages, used in postshot diagnostic studies. This facility features a robot-operated, isotope-powder filling station, unique within the DOE weapons complex. Besides accurately manufacturing these detectors, our studies of radiation-exposure reduction to workers resulting from the use of this robot will serve as a pilot study for the appropriate use of other such automated stations in the complex of the future.

The Process Research and Development Section continues to expand its role in weapons safety, surety, and reliability research. We are completing installation of a comprehensive furnace system for simulated accidental fire testing of nuclear primaries in vacuum, inert gas, and oxidizing atmospheres.

"The Plutonium Metallurgy Group, NMT-5, is a multi-disciplinary organization engaged in prototype weapon primary fabrication, metallurgical and chemical properties studies of plutonium and other actinides, and surveillance and stockpile evaluation technologies in support of Laboratory and the Department of Energy (DOE) weapons programs."

In the meantime, we continue to conduct fire-resistance tests for engineering qualification of not only Los Alamos system designs, but also designs from the United Kingdom, with whom we share other nuclear safety technology. In a similar vein, we will also be conducting safety verification tests in support of Lawrence Livermore National Laboratory systems presently in the stockpile. Our materials scientists are also conducting various experiments in order to elucidate the consequences of aging on the properties of plutonium and to extend these findings to support weapon-reuse studies.

Our Actinides Chemistry and Physics Section continues world-recognized work ranging from fundamental surface chemistry to solid-state physics research on the actinides. We have extended our findings on the nature of radio-frequency plasmas to develop unique methods for removing trace quantities of actinides from the surface of various substrates, providing a decontamination method that produces little or no waste stream. The push to eliminate chlorofluorocarbons (CFCs) in manufacturing has led us to study the use of supercritical carbon dioxide as a solvent for residue surface oils on plutonium, as well as preliminary studies into the use of aqueous cleaning agents, such as detergents and other surfactants, to remove residues.

To complement this work, we have adapted our capabilities in Fourier transform infrared spectroscopy (FTIR) to quantify the presence of contaminants on plutonium and other metal surfaces. In addition, we continue fundamental studies into the mechanisms of surface chemical reactions and the electronic structure of plutonium, the actinides, and their compounds.

We are also responsible for the successful installation and operation of the 40-mm gas/powder launcher at the Plutonium Facility. The launcher will offer DOE researchers a unique opportunity to investigate *in situ* dynamics mechanical properties of plutonium. Data from such testing will enable weapon design codes to more accurately predict performance. ◆

ACTINIDE

MATERIALS

CHEMISTRY

Our group has 24 employees: 14 technical staff members, 8 technicians, 1 office support person, and 1 graduate research assistant. In order to accomplish our group's multidisciplinary mission, our scientific staff's expertise ranges broadly in inorganic and physical chemistry, materials science, and chemical engineering.

Group Leader
Kyu C. Kim

Deputy Group Leader
Thomas W. Blum

The Actinide Materials Chemistry Group, NMT-6, conducts fundamental and applied research in actinide chemistry to develop and maintain diverse scientific expertise and capabilities and to apply the technology base in support of nuclear materials processing and process development activities in Nuclear Materials Technology (NMT) Division.

Technical and scientific tasks are distributed between the Process Chemistry and Advanced Separation Concepts sections. Main activities include organo-actinide chemistry, plutonium chlorination and fluorination, plutonium thermochemical studies, process control and diagnostic development, actinide spectroscopy, waste gas treatment, and chemical and physical plutonium separation and purification technology development.

Our group focuses on new and emerging technologies and on improving existing technologies with strong emphasis on waste reduction, safety, environmental improvement, and efficiency.

Our group has established broad collaborations with other groups, implemented new and improved recovery and purification process concepts and advanced diagnostic techniques, and applied our research expertise, especially in spectroscopy and thermodynamics. In addition, we are active in technology transfer and consultation with other nuclear materials production sites and other national laboratories. ◆

NUCLEAR

MATERIALS

MANAGEMENT

Our group has 39 employees: 10 staff members, 28 technicians, and 1 support person.

Group Leader
Carol L. Sohn

Deputy Group Leader
Charles L. Foxx

Nuclear Materials Management, NMT-7, manages the movement of nuclear materials within the TA-55 boundaries. Group programs include waste management, nuclear materials storage, roasting/blending, shipping/receiving of nuclear materials, and coordination of nuclear materials.

Waste management is one of our most important functions at NMT-7. Our handling of liquid waste ensures that acidic and caustic waste solutions meet the applicable discard limits and are suitable for processing by the Laboratory's central waste treatment plant. Our solid waste activities involve cement fixation of the treated liquid wastes that meet pertinent discard limits. In addition, we develop the procedures to meet Waste Isolation Pilot Project certification requirements for solid waste.

We manage the secured vault in which nuclear materials not in process are stored. This operation includes safely introducing and removing material and maintaining the required documentation. In addition, we blend, sample, roast, and consolidate various feed materials for metal preparation and aqueous recovery.

We also coordinate the shipping and receiving of nuclear materials, including packing and unpacking shipments in compliance with the current Department of Energy regulations. We routinely ship and receive product and process feed materials, scrap, analytical samples, and waste.

Our coordination of nuclear materials includes diverse activities in support of programmatic requirements. We have developed a site-wide nuclear materials model that forecasts future inventories of scrap and waste generation and that examines the impacts of new technologies on the TA-55 Plutonium Facility. In support of the model, we have created a waste generation data base that provides detailed information about waste origins. We are initiating electronic transmission and generation of the voluminous records associated with our operations. ◆

TA-55 FACILITIES MANAGEMENT

Our group has 51 employees: 11 staff members, 15 technicians, 19 support personnel, and 6 casual employees.

Group Leader
David J. Post

Deputy Group Leader
Richard A. Briesmeister

The TA-55 Facilities Management Group, NMT-8, oversees all engineering operations and maintenance at the TA-55 plant and manages the engineering design and construction of new facilities and renovations of existing facilities.

Our site administration responsibilities include warehouse operations, safety operations, change rooms, access control, telecommunications, computer systems, equipment inspections, and financial management. We also communicate on behalf of NMT Division with the Operational Security and Safeguards Division and the Laboratory's protective force.♦

HEAT SOURCE
TECHNOLOGY

RN91-331-08

Our group has 38 employees, 9 staff members, 22 technicians, 4 support personnel, and 3 casual employees.

Group Leader
Roy Wayne Zocher

The Heat Source Technology Group, NMT-9, has long-term experience with radioisotope heat-source development for terrestrial and space electrical generators. Heat sources developed at Los Alamos have been used on radioisotope thermoelectric generators (RTGs) to supply electrical power for NASA spacecraft, including the Pioneer 10 and 11, Voyager 1 and 2, Galileo, and Ulysses deep-space exploration missions. Some of the spacecraft also required small radioisotope heaters, developed and produced at Los Alamos, for thermal input to critical components.

Processing of Plutonium 238, which began at Los Alamos in the late 1950s, has expanded to include
1. design of radioisotope heat sources,
2. development of fuel fabrication processes,
3. fabrication of a variety of heat-source fuel forms,
4. safety tests and postmortem examinations of tested heat sources,
5. safety assessments of radioisotope power generators, and
6. heat-source materials research, development, and service evaluation for space and terrestrial applications.

Our group is supporting the upcoming Cassini mission by
1. requalifying the general-purpose, heat-source (GPHS) fuel-fabrication process,
2. performing independent safety assessments on the components and RTGs to be used, and
3. fabricating lightweight, radioisotope heater units.

These heat sources will thermally stabilize scientific equipment and critical valves during the missions.

Our group evaluates the high-temperature and impact response of candidate heat-source materials, including graphite composites, noble metal alloys, fuel simulant, and alternative insulating materials. We are also investigating methods to decontaminate iridium and return the material to the national stockpile.

Our group recently ceased fabrication of mW-generator (MWG) heat sources that are used in RTGs for weapon components, but we will continue to perform stockpile surveillance on these heat sources. We are currently transferring the mW stockpile surveillance and storage characteristics activities at General Electric Pinellas Plant to Los Alamos. ◆

AWARDS

HONORS

PATENTS

A W A R D S

H O N O R S

P A T E N T S

During the year, NMT Division's people achieved many notable scientific and technical accomplishments and received awards recognizing their efforts. Some of our employees who were recognized for distinguished contributions in scientific or technical areas are listed here. The individuals within NMT Division who were awarded patents during the year are listed also. Here, too, we applaud these individuals for their contributions in areas that have high potential to benefit not only the Laboratory but our nation.

H. L. Nekimken (NMT-2), FY 1991 R&D 100 Award for development of the "Optical High-Acidity Sensor," (issued September 1991).

H. L. Nekimken (NMT-2), Federal Laboratory Consortium Award for Excellence in Technology Transfer for 1992 (issued February 1992).

H. L. Nekimken (NMT-2), "Optical High Acidity Sensor," S-72,805, S.N. 07/770,388 (patent application filed October 3, 1991).

Q. Fernando, N. Yanagihara, *J. T. Dyke*, K. Vemulapalli, (NMT-2), "Formation of Rare Earth Carbonates Using Supercritical Carbon Dioxide," U.S. Patent 5,045,289 (issued September 3, 1991).

S. F. Fredric Marsh (NMT-2), Member of the DOE Red Team (Phenomenology Subteam) assigned to provide an independent assessment of WHC plans and strategy for the Hanford Tank Waste Project to Leo Duffy, DOE Headquarters.

S. F. Fredric Marsh (NMT-2), Member of DOE delegation sent to France, August 26–30, 1991, to evaluate French technology that might be applicable to the Hanford Site Restoration Project, at the request of John Tseng, DOE Headquarters.

S. F. Fredric Marsh (NMT-2), Invited presenter of "The Effects of External Gamma Radiation and *InSitu* Alpha Particles on Five Strong-Base Anion Exchange Resins," at the 1987 Godon Research Conference on Reactive Polymers, Ion Exchangers, and Adsorbants, Newport, Rhode Island, August 19-23, 1991.

S. F. Fredric Marsh (NMT-2), One of three invited Los Alamos participants to the First Hanford Separations Science Workshop, Richland, Washington, July 23–25, 1991.

S. L. Yarbro (NMT-2) ATW Chemistry Team Leader, Accelerator Transmutation of Waste Program.

Heat Source Technology Group (NMT-9), 1991, National Aeronautics and Space Administration, Group Achievement Award for Galileo Safety for Contributions to Design, Analysis, Testing, and Documentation required to ensure safe use of radioisotopic thermoelectric generators and radioisotope heater units for the Galileo Ulysses missions.

R. W. Zocher (NMT-9), Certificate of Recognition for Achievements in "Nuclear Fuel Elements," US Patent No. 5,002,723 (issued March 26, 1991).

PUBLICATIONS

PUBLICATIONS

Another important component of our scientific and technical effort is the communication of results and conclusions to our sponsors and the scientific community at large. During the past year, our staff published many scientific papers and reports (listed on the following pages). Documents of unlimited distribution cannot cite classified or limited access publications. For this reason, this is not a complete listing of NMT-Division publications.

Nuclear Fuels Technology (NMT-1)

In the following publications list, the single underline identifies the author as a group member. If you would like to contact any of these authors, please write to them in care of the Nuclear Fuels Technology Group, Mail Stop E505, Los Alamos National Laboratory, Los Alamos, New Mexico 87545.

1. "Advancing Liquid Metal Reactor Technology with Nitride Fuels," R. B. Baker, R. D. Legget, W. F. Lyon, R. B. Matthews, *International Fast Reactors and Related Fuel Cycles*, Los Alamos National Laboratory document LA-UR-90-4343 (December 1990).

2. "Reactor Fuel Production in Western Europe," R. B. Matthews, H. T. Blair, K. M. Chidester, *SAIC Study of Western European Reactor Capabilities*, Los Alamos National Laboratory document LA-UR-91-0481 (February 1991).

3. "Ceramic Fuel Development For Space Reactors," R. B. Matthews, *Ceram. Bull.* **71**, 96 (January 1992).

4. "Experimental Investigation of Uranium Dicarbide Densification and The Influence of Free Carbon Diffusion," K. M. Chidester, Thesis, Los Alamos National Laboratory document LA-11954-T (April 1991).

5. "Review of Experimental Observations About the Cold Fusion Effect," E. K. Storms, *Fusion Technol.* **20**, 433 (December 1991).

6. "Carbide Fuels For Nuclear Thermal Propulsion," R. B. Matthews, H. T. Blair, K. M. Chidester, K. V. Davidson, W. A. Stark Jr., E. K. Storms, *Proc. AIAA/NASA/OAI/Advanced SEI Technologies*, Los Alamos National Laboratory document LA-UR-91-2317 (July 1991).

7. "Effect of Fuel Geometry on the Lifetime-Temperature Performance of Advanced Nuclear Propulsion Reactors," E. K. Storms, D. L. Hanson, W. L. Kirk, P. Goldman, *Proc. AIAA/NASA/OAI/Advanced SEI Technologies*, Los Alamos National Laboratory document LA-UR-91-2428 (July 1991).

8. "SP-100 September Quarterly Report," C. W. Hoth, N. A. Rink, Jet Propulsion Laboratory, Los Alamos National Laboratory document LA-UR-91-3199 (October 1991).

9. "Behavior of ZRC 1-X and UYZR 1-Y C1-X in Flowing Hydrogen at Very High Temperatures," E. K. Storms, Los Alamos National Laboratory document LA-12043-MS (January 1992).

10. "Relationship Between Surface Curvature and Local Active-To-Passive Transitions During Oxidation," D. P. Butt, *Proc. Am. Ceram. Soc.*, Los Alamos National Laboratory document LA-UR-92-0307 (January1992).

11. "Directional Zone Sintering In UC_2 Compacts," K. M. Chidester, *Proc. of the Am. Ceram. Society*, Los Alamos National Laboratory document LA-UR-92-0111 (January 1992).

12. "Diffusion of Carbon Through The Niobium Carbides (Niobium Carbide and Diniobium Carbide)," R. W. Schmude, T. C. Wallace, *Nuclear Materials*, pending, Los Alamos National Laboratory document LA-UR-92-0016 (January 1992).

Nuclear Materials Processing: Nitrate Systems (NMT-2)

In the following publication list, the single underline identifies the author as a group member. If you would like to contact any of these authors, please write to them in care of the Nuclear Materials Processing: Nitrate Systems Group, Mail Stop E501, Los Alamos National Laboratory, Los Alamos, New Mexico 87545.

1. "Evaluation of Different Solvent Extraction Methods for Removing Actinides From High Acid Waste Streams," S. L. Yarbro, S. B. Schreiber, S. L. Dunn, and J. D. Rogers, Los Alamos National Laboratory document LA-UR-91-3253 (1991).

2. "Homogeneous Precipitations for Separations and Waste Treatment," S. L. Yarbro, S. B. Schreiber, and S. L. Dunn, Los Alamos National Laboratory document LA-UR-91-2409 (1991).

3. "Los Alamos Technology Office Assessment of the Rocky Flats Plant Criticality Alarm System," D. Smith, S. Vessard, R. E. Malenfant, and A. F. Muscatello, Los Alamos National Laboratory document LA-UR-91-1118 (1991).

PUBLICATIONS

4. "Optical High Acidity Sensor," B. Jorgensen and H. Nekimken, *1992 Research Highlights* (1992).

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In the following publication list, the single underline identifies the author as a group member. If you would like to contact any of these authors, please write to them in care of the Nuclear Materials Processing: Chloride Systems Group, Mail Stop E511, Los Alamos National Laboratory, Los Alamos, New Mexico 87545

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In the following publication list, the single underline identifies the author as a group member. If you would like to contact any of these authors, please write to them in care of the Nuclear Materials Measurement and Accountability Group, Mail Stop E513, Los Alamos National Laboratory, Los Alamos, New Mexico 87545.

1. "A Versatile Passive/Active Neutron Coincidence Counter for In-Plant Measurements of Plutonium and Uranium," J. R. Wachter, J. E. Stewart, R. R. Ferran, H. O. Menlove, E. C. Horley, J. Baca, and S. W. France, European Safeguards Research and Development Corporation, Avignon, France, Los Alamos National Laboratory document LA-UR-91-1566 (1991).

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In the following publication list, the single underline identifies the author as a group member. If you would like to contact any of these authors, please write to the Plutonium Metallurgy Group, Mail Stop E506, Los Alamos National Laboratory, Los Alamos, New Mexico 87545.

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Actinide Materials Chemistry (NMT-6)

In the following publication list, the single underline identifies the author as a group member. If you would like to contact any of these authors, please write to them in care of the Actinide Chemistry Group, Mail Stop E510, Los Alamos National Laboratory, Los Alamos New Mexico 87545.

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Nuclear Materials Management (NMT-7)

In the following publication list, the single underline identifies the author as a group member. If you would like to contact any of these authors, please write to them in care of the Nuclear Materials Management Group, Mail Stop E524, Los Alamos National Laboratory, Los Alamos, New Mexico 87545.

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Heat Source Technology (NMT-9)

In the following publication list, the single underline identifies the author as a group member. If you would like to contact any of these authors, please write to them in care of the Heat Source Technology Group, Mail Stop E502, Los Alamos National Laboratory, Los Alamos, New Mexico 87545.

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