Separation of Plutonium from Chloride Salts is Demonstrated by High-Temperature Vacuum Distillation Method

Large quantities of contaminated salt residues have resulted throughout the DOE complex from pyrochemical processing of plutonium. This problem is most acute at the Rocky Flats Environmental Technology Site, where there are many tons of salt residues. These salts contain large amounts of plutonium and require treatment for disposal. Distillation of the salt matrix is a promising treatment technology for separating plutonium from the salts. This separation process should be capable of producing chloride salts that could be discarded as low-level waste (LLW) plus a concentrated plutonium oxide that would be stored as special nuclear material. Cost-benefit analyses have shown that disposal of the salts as LLW after separation by the distillation process can result in savings of hundreds of millions of dollars compared to merely stabilizing the residues and disposing of them at the Waste Isolation Pilot Plant (WIPP).

The basis for a vacuum distillation separation is the large difference in vapor pressure between chloride salts and plutonium oxides. Table 1 gives vapor pressures of common pyrochemical salt components at selected temperatures.

Figure 1. Top photo: a 1.5 kg (approx.) example of contaminated salt residue. Below left: After treatment using the high-temperature vacuum distillation method, the condensed salt distillate can be discarded as low-level waste. Below right: The plutonium contaminant, now in the form of a concentrated plutonium oxide, will be stored as special nuclear material.
The Actinide Research Quarterly

Separation of Plutonium from Chloride Salts is Demonstrated by High-Temperature Vacuum Distillation Method continued

The most common residue component in the pyrochemical salt residue is equi-molar sodium chloride and potassium chloride salts. This composition is a eutectic mixture with a melting point at 650 °C and was used for that reason. It is obvious from the vapor pressures listed in Table 1 that the best separation can be achieved between plutonium dioxide and the chloride salts. The difference in their vapor pressures is more than twelve orders of magnitude at 1050 °C. Calcium fluoride cannot be separated by distillation because of its low vapor pressure, but it is only a minor constituent and can be left with the plutonium heel.

A separation will not be obtained if plutonium trichloride is present in the system, so the residue salts are first treated by an oxygen sparge process to convert plutonium trichloride to plutonium dioxide or plutonium oxychloride. The discussion that follows will assume that the pyrochemical waste salts have been treated to convert all plutonium and americium species to the dioxide.

The rate of deposition of the various compounds can be calculated based on their vapor pressures. Actual experiments have shown that the rates are much slower than calculated results, sometimes by some orders of magnitude; nevertheless, it appears that all the chloride salts, except calcium chloride, can be distilled at acceptable rates below 900 °C. These same experiments have shown that temperatures above 1200 °C will probably be required to distill calcium chloride at acceptable rates. Those high temperatures will require extensive equipment modification and further developmental work. Since the NaCl-KCl salts constitute the majority of the waste stream, efforts have focused on treating sodium chloride/potassium chloride salts.

Deposition rates can be used to calculate the composition of the distillate salt under ideal conditions. For example, in a system with 100 cm² surface area that contains sodium chloride and plutonium dioxide being processed at 850 °C, the rate of deposition of sodium chloride is 4100 g hr⁻¹ while that of plutonium dioxide is 10⁻¹² g hr⁻¹. The distillate salt would then contain a weight concentration of 10⁻⁹ ppm plutonium. At 1050 °C the distillate salt would have a plutonium concentration of 10⁻⁷ ppm. (All these were calculated under ideal conditions.) Table 2 lists calculated plutonium concentrations at selected temperatures in a specific salt matrix. The americium content must be below 0.03 ppm for LLW, and this requirement can also be met assuming all the americium is present in the system as AmO₂.

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Table 1. The vapor pressure (torr) of pyrochemical salt components at selected temperatures.

<table>
<thead>
<tr>
<th>Compound</th>
<th>850 °C</th>
<th>950 °C</th>
<th>1050 °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaCl</td>
<td>10⁻⁰.₁</td>
<td>10¹</td>
<td>10¹</td>
</tr>
<tr>
<td>KCl</td>
<td>10⁰.₂</td>
<td>10¹</td>
<td>10²</td>
</tr>
<tr>
<td>MgCl₂</td>
<td>10⁰.₃</td>
<td>10¹</td>
<td>10²</td>
</tr>
<tr>
<td>CaCl₂</td>
<td>10⁻³</td>
<td>10⁻²</td>
<td>10⁻¹</td>
</tr>
<tr>
<td>CaF₂</td>
<td>10⁻⁸</td>
<td>10⁻⁶</td>
<td>10⁻⁵</td>
</tr>
<tr>
<td>Pu</td>
<td>10⁻⁸</td>
<td>10⁻⁷</td>
<td>10⁻⁵</td>
</tr>
<tr>
<td>PuCl₃</td>
<td>10⁻²</td>
<td>10⁻¹</td>
<td>10⁻⁰.₁</td>
</tr>
<tr>
<td>PuOCl</td>
<td>10⁻⁸</td>
<td>10⁻⁷</td>
<td>10⁻⁵</td>
</tr>
<tr>
<td>PuO₂</td>
<td>10⁻¹⁶</td>
<td>10⁻¹⁴</td>
<td>10⁻¹²</td>
</tr>
</tbody>
</table>

Table 2. Calculated Pu concentration (ppm) in distillate salt.

<table>
<thead>
<tr>
<th>Salt</th>
<th>850 °C</th>
<th>950 °C</th>
<th>1050 °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaCl</td>
<td>5.3E⁻¹⁰</td>
<td>1.4E⁻⁸</td>
<td>2.3E⁻⁷</td>
</tr>
<tr>
<td>KCl</td>
<td>2.4E⁻¹⁰</td>
<td>6.9E⁻⁹</td>
<td>1.2E⁻⁷</td>
</tr>
<tr>
<td>MgCl₂</td>
<td>1.9E⁻¹⁰</td>
<td>5.2E⁻⁹</td>
<td>8.6E⁻⁸</td>
</tr>
<tr>
<td>CaCl₂</td>
<td>2.4E⁻⁷</td>
<td>3.3E⁻⁶</td>
<td>3.1E⁻⁵</td>
</tr>
</tbody>
</table>

continued on page 9
The Laboratory has taken a dramatic step in changing the way it manages the execution of work. This new way may be called “the system approach.” At Technical Area 55 (TA-55), we have selected a number of project leaders whose job is to assure that projects are executed and products are delivered to customers on schedule. This change also highlights the cross-knitted nature of our projects across all Laboratory organizations. It ensures that the best set of Laboratory skills and abilities is employed in completing all tasks. Specialists come not only from the traditional science and technology organizations, but also from environment, safety, and health (ES&H); facilities; personnel; budgeting; program; and other operational functions. This integration of all the interacting parts of a project, all critical to its success, is defined as “the system approach.”

“Achieving success has always involved delivering high-quality products to our customers on time. Historically, cost has been important, but not a driving factor. Today, cost has become a very important driving factor. Adopting the system approach allows us to squeeze out redundancies, inefficiencies, shadow organizations, and activities that cause our costs to grow while not adding value or quality to our products. At TA-55 one can see the results of these efforts in many ways. For example, we have turned over the warehouse and property management functions to the Business Operations Division (BUS) professionals. They are employing modern warehousing techniques and beginning to use just-in-time purchasing methods. Their goal is to reduce overall costs, including the cost of maintaining inventory, and to provide timely delivery of materials.”

In another example, we are contracting with the ES&H organizations for expertise in the various health and safety professions of importance to TA-55. In the past these professionals were our critics; today they are becoming part of the solution. They are slowly being incorporated into the operations and are improving our safety posture. Other changes include incorporation of the BUS Team Leader and financial team, a security officer, a JCI (Johnson Controls, Inc.) craft coordinator, Audits and Assessments Office professionals, and a development team from the Human Resources Division.

The goal we keep in front of us is to use science and technology including the methodology of handling and disposing of plutonium, to reduce the nuclear danger. Therefore, the management methods we use must be linked with the actual science and engineering functions. The TA-55 management is encouraging increased coordination and integration of the line activities with the program functions so as to better serve the nation’s needs and to become more responsive to customer wishes. This will also allow us to raise important issues more quickly. We have recently had program management personnel from Nuclear Materials and Reconfiguration Technologies take up residence at TA-55, and their presence has already had a significant impact on improving our interactions with customers.

Project leaders will continue to identify the very best, properly trained personnel to complete project tasks, whether they are Nuclear Materials Technology Division employees or from other Laboratory divisions. By taking this “systems” point of view, everyone will have a stake in program success, we will become more efficient, and we will continue to deliver on our programmatic commitments to customers.
NMT Evaluates Extraction Chromatography for Removal of Pu and Am from HCl Effluents

The Task—Residue Recovery
The use of hydrochloric acid (HCl) for aqueous plutonium recovery offers good dissolution of many plutonium residue matrices. Following dissolution an extensive set of chemical separation options such as solvent extraction, ion exchange, extraction chromatography, and several precipitation techniques are presently available. Selection of the best treatment options for residue recovery depends on the type of residue to be recovered, the contaminants to be removed, and the purity and form of the product desired. The HCl processing of plutonium residues is a relatively new method with several potential benefits in process efficiency and waste reduction. This may present itself as a viable process alternative for residues whose disposition cannot be adequately addressed by other processes.

Minimizing the solid wastes and liquid effluents from plutonium processing and making them less hazardous are tasks of fundamental importance. Present goals for residue processing in HCl parallel the NMT Division goals for environmentally benign operations. These goals can be summarized for HCl operations as follows: producing concentrated actinide residues in forms suitable for safe long-term storage, forming stable solid wastes with acceptable disposal routes, and releasing liquid effluents with no radioactivity and low levels of other hazards.

Traditional Treatment
Liquid effluents from HCl operations at TA-55 have historically been treated by controlled hydroxide precipitation before they are transferred to the TA-50 Liquid Waste Treatment Facility. This hydroxide neutralization and precipitation operation has been necessary partially because of the corrosive nature of HCl, which requires that all effluent solutions containing significant amounts of chloride be made neutral or basic prior to transfer to TA-50. Hydroxide precipitation, combined with a filtration step, also recovers a fraction of actinides from process solutions in the form of a hydroxide cake. There are several problems, however, with hydroxide precipitation as a generic effluent treatment process: 1) many other metal hydroxides coprecipitate creating large cakes; 2) chloride salts can be entrained in the hydroxide matrix causing corrosion concerns for long-term vault storage of the hydroxide cakes; 3) many metal hydroxides are gelatinous, leading to slow filtration and high gamma exposure from americium (241Am) in this hands-on operation; 4) the filtrate from neutralization remains moderately high in radioactivity and requires special treatment at TA-50, producing more transuranic (TRU) solid wastes; and 5) almost all of the chloride from HCl operations is presently lost in the liquid effluent, causing the TA-50 outfall to the environment to exceed recommended National Pollutant Discharge Elimination System limits for chloride concentration.

Hydroxide precipitation remains a good choice for recovery of actinides from some specific processes, but it is not an acceptable choice as a generic treatment for all HCl effluents. Indeed, there is no single technology or unit operation that provides a panacea to resolve all
of the residue, liquid, and solid waste issues associated with HCl processing. The problems can be addressed by intelligently developing and applying better treatment technologies, directed toward the specific hazards of individual effluents.

A New Strategy

Recent waste minimization efforts have used the strategy of developing specific treatments for individual waste streams. Greatest effort has been expended on removing actinides from waste streams with high-molar HCl effluents including anion exchange effluents and solvent extraction raffinates. The chemical makeup of these streams includes all the americium in the process solutions (significant amounts in many residues), residual small amounts of plutonium left from purification, about 90% of the total amount of HCl used, and the soluble chloride salts of alkali, alkaline earth, and some transition metals. Americium is often the larger problem in waste streams because of its greater alpha activity compared to most plutonium isotopes and its associated 60-KeV gamma emission. Efficient recovery of the actinides in high-acid effluent streams would have a large impact on wastes from HCl operations.

Extraction chromatography, using ligands such as n-octyl(phenyl)-N,N-diisobutylcarbamoylmethylphosphine oxide (CMPO), diamyl amylphosphonate (DAAP) and/or tributyl phosphate (TBP) loaded on inert supports, has been used by others on an analytical scale to concentrate actinides for analysis. We are evaluating this technology for its adaptation to a much larger scale for removing actinides from high-acid effluent streams.

Recent Results

Our work began with small-scale experiments under carefully controlled conditions, using well-characterized HCl solutions of plutonium(IV), plutonium(III), and americium(III). Commercial resin formulations, (typical resins are formulated by coating inert support polymers with ligands having specific affinity for actinides) performed well at removing plutonium(IV) from high-molar HCl solutions but failed to remove plutonium(III) and americium(III). The preliminary studies also indicated that the resins will function at actinide-loading levels much higher than those recommended for analytical use, making them viable for a practical treatment process.

Work with different resin formulations has generated data indicative of how actinide distribution and kinetics change with various mixtures of extractants. These data have allowed us to tailor new formulations to more effectively remove the trivalent actinides. The more promising formulations have now been prepared in large quantity and tested at full scale with actual waste streams. Decontamination of gram quantities of plutonium and americium from anion exchange effluents and solvent extraction raffinates has been achieved with alpha decontamination results varying between 90% and 99.99% for the first ten attempts. The plutonium and americium are readily stripped from the resins with small elutriant volumes, providing relatively pure solutions. The actinides can then be recovered by oxalate or hydroxide precipitation, followed by calcination, to provide concentrated residues suitable for long-term vault storage.

The decontaminated effluent solutions were neutralized before their transfer to TA-50, producing hydroxide cakes of a radioactivity level that should allow fixation and discarding as TRU or low-level waste. Removal of americium from the processing stream as early and as efficiently as possible has the added benefit of reducing exposure to workers in all subsequent handling, treatment, and storage operations. Future plans are to use the decontaminated acid solution as feed for HCl recycling operations, which will further reduce activity, volume, and chloride content of effluents.

Efforts to implement this technology continue as we optimize resin formulations and alter process conditions for our specific applications. Other unique treatment strategies are being developed to dilute HCl process streams including filtrate from oxalate precipitation operations.
Noninvasive Chemical Concentration Analyzer (NCCA) Preserves Process Stream Purity

For years the chemical processing industry has needed a noninvasive, real-time method to measure the concentration of chemicals in process. The NCCA, developed by NMT scientists, uses Fourier transform analysis of high-frequency acoustic signals from ultrasonic sensors attached to the outside of a pipe or small tank to determine the concentrations of chemicals contained within. By taking concentration measurements without actually contacting the fluid, the NCCA prevents contamination of product streams, reduces or eliminates risks for workers who handle hazardous or radioactive materials, and decreases costs by eliminating the need to cut into the pipe or tank as required to install an invasive sensor.

Many industries seek to reduce worker exposure to toxic, radioactive, or other hazardous process streams and to preserve the purity of process streams during monitoring procedures. An important means of achieving both goals is the use of a process monitor that noninvasively determines concentrations of materials in sealed fluid containers, such as pipes and tanks, and provides reliable real-time analytical measurements. In Building PF-4 this is especially important because of the possibility that the inside of the container is radioactively contaminated.

The NCCA is a novel ultrasonic method for evaluating chemical concentrations noninvasively and in real time. It is based on the determination of the velocity of sound through a fluid inside a container, such as a pipe or tank. The velocity of sound is a concentration dependent parameter for binary aqueous or organic mixtures; measurements of sound velocity for many binary mixtures are well-known and can be used to determine the concentrations of such mixtures as they pass through a pipe or while they are stored in a tank. The NCCA analyzes the Fourier transform of the swept high-frequency acoustic spectrum after transmission through the container and its chemical fluid. For fluids of complex mixtures (such as gasolines and insecticides), this diagnostic technique cannot determine individual components, but it can determine the characteristic sound velocity of the total mixture. The mixture can then be compared to a norm, and its consistency can be validated.

For empty pipes and tanks, the acoustic response at low frequencies is strong, complex, and difficult to interpret. At ultrasonic frequencies greater than 100 kilohertz (or higher depending upon the geometry), these structural modes of the container become so closely spaced and weak that the spectrum (system response as a function of frequency) looks like “white noise.” However, when the container is filled with liquid, the ultrasonic spectrum changes, exhibiting a series of equally spaced peaks in the midst of the container’s white noise as shown in the upper panel of Fig. 3. These resonant peaks arise from standing waves (those acoustic reflections within the fluid that are in phase and additive) in the fluid between the walls of the container. The frequency between any two of these peaks, \( v \), is given by \( v = c/2l \), where \( c \) is the velocity of the sound of the fluid, and \( l \) is the inside diameter of the container. An accurate determination of the velocity of sound from the high-frequency ultrasonic spectrum requires an accurate measurement of the frequency between the peaks and accurate knowledge of the diameter of a container. The resonant peaks of sound filtered through a container exhibit a significant amount of superimposed structure, which is removed during Fourier transform analysis. Because the diameter of the container does not change with time, the calibration of \( l \) needs to be accomplished only once by measuring a fluid whose ultrasonic frequency is known.
A simple software package that Fourier-transforms the transmitted high-frequency acoustic response allows our inexpensive diagnostic system to be insensitive to the low-frequency acoustic signature associated with containment vessel geometry and composition. Using sensors glued to the outside of a 6-inch-diameter pipe, we have measured the fundamental frequency, and therefore the sound velocity, reproducibly to 7 parts in 100,000. To reach this accuracy requires concurrent temperature measurement to compensate for temperature-dependent velocity changes. Velocity measurements using the NCCA in nitric acid are compared to velocity measurements using a commercial instrument. Typically for nitric acid a velocity change of 1 m/s corresponds to a change in concentration of less than 0.1 molar. For the most favorable concentrations, we have demonstrated the ability of the NCCA to analyze nitric acid and sodium chloride solutions to 0.01-molar accuracy.

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Noninvasive Chemical Concentration Analyzer (NCCA) Preserves Process Stream Purity continued

The analyzer consists of a PC, a specialized PC card that simultaneously generates a swept high-frequency signal and detects system response, and two ultrasonic transducers attached to the outside of a pipe or tank. Software written by Dave Sanchez of NMT-6, for LabWindows, takes the Fourier transform of the data and determines the sound velocity of the fluid. We use algorithms that are specific to the chemicals known to be present in the fluid to calculate the concentration from the values obtained for the sound velocity. The analyzer can provide real-time concentration measurements for a wide variety of chemical systems and containers. It has been tested on pipes from 0.5 inch to 8 inches in diameter and on a rectangular tank whose dimensions are 6 inches by 24 inches by 12 inches. We currently have databases for nitric acid, hydrochloric acid and sodium hydroxide.

Sensors that must be immersed in the fluid they will assay add to the cost of monitoring and pose the risk of contamination. With its sensors attached to the outside of the process pipe or tank, the NCCA reduces cost by eliminating the need for special piping or flanges for sensor mounting and associated precision welding and construction. Further, its provision for external sensor mounting precludes the need for special construction materials that resist corrosion when immersed in the fluid. The NCCA can be used on any existing container geometry (arbitrary length, diameter up to 2 feet, any thickness, and any cross section) and composition (so long as it transmits high-frequency acoustic signals).

Chemical processing of nuclear material will continue to be required as an important part of global waste management efforts. The immediate benefits of this new analytical technique are a reduced risk of worker exposure to radioactive and hazardous materials; reduced cost of instrumentation, installation, and maintenance; and improved process efficiency. These substantial benefits can also be realized in a whole host of industries that handle or process hazardous or toxic materials. Strict regulation of industry requires that worker exposure to chemical hazards during processing be minimized. The NCCA can contribute to this effort even as it reduces assay costs by tracking concentrations in real time and eliminating traditional sampling methods. Industries such as chemical manufacturing, petrochemicals, agricultural chemicals, and photochemicals handle hazardous materials in large quantities and could benefit from this instrument.

D. Kirk Veirs, Noah G. Pope, David E. Sanchez, Vincente D. Sandoval are the developers of this diagnostic technique.
Separation of Plutonium from Chloride Salts is Demonstrated by High-Temperature Vacuum Distillation Method Continued

The LLW criterion for weapons grade plutonium translates to a plutonium concentration in the salt no more than 1.2 ppm. Therefore, vacuum distillation of a sodium chloride, potassium chloride, or magnesium chloride salt that contains only plutonium dioxide has the potential to produce a distilled salt with a plutonium concentration 10 orders of magnitude below the 100 nCi/g level.

It has been estimated that disposal of stabilized, undistilled salts at the WIPP would be one hundred to one thousand times more costly than disposal of salts treated by the high-temperature vacuum distillation method. A conservative estimate of the disposal cost of the present inventory, stabilized, would be hundreds of million dollars.

Experiments performed with oxidized sodium chloride salts and potassium chloride salts, along with plutonium, have shown that distillation separation is viable: the plutonium content of the salt has been reduced from tens of percent to the ppm and sub-ppm range in the distilled salts.

Analysis of the distilled salts showed that approximately one-fourth meet the LLW criterion. The remainder samples showed the same background contamination levels of the glove boxes in which they were handled and processed. Many control experiments were done with initially uncontaminated salts, and the analyses indicated nearly identical plutonium contamination levels. These results support the conclusion that essentially complete and clean separation of the salts from plutonium oxide can be achieved.

Project contributors include Eduardo Garcia, Vonda Dole, and James McNeese.

Figure 4. Schematic of the distillation separation apparatus. The two process streams are condensed salt distillates (left) and plutonium oxide.

Advantages of Distillation Process

- minimal generation of secondary waste
- compact unit process
- simple, low-cost equipment
- large pyrochemical experience pool
- cost-effective vs. other alternatives
For some time we have been preparing for NMT Division’s second Science and Technology Assessment scheduled for November 13-15, 1995. We issued the NMT Division Review Plan (Table 3) in March. The theme this year is “The Plutonium Roadmap,” which describes all current and future scientific and technological advances addressing the plutonium problem, and includes many of the elements depicted in the “fishbone” diagram (Fig. 5). Project personnel will report on several key projects under this theme, and other division-wide accomplishments will be presented in poster papers. The organizational self-assessment was issued in mid-June.

The NMT External Review Committee (ERC) has a new member, Dr. Robert Uhrig. Dr. Uhrig holds a joint appointment as Distinguished Professor of Engineering in the Nuclear Engineering Department at the University of Tennessee, and as Distinguished Scientist at the Oak Ridge National Laboratory. During the past few months all the ERC members have completed their scheduled first visits and discussions for this year’s review.
The following presentations were given at the 19th Annual Actinide Separations Conference, Monterey, CA, June 12-15, 1995.

E. Garcia and V. R. Dole, “Distillation Separation of Chloride Salts from Plutonium.”


R. E. Wieneke, “Transuranic Residue Treatment: Regulatory Considerations.”

R. E. Wieneke, “Computerized Waste Documentation at the TA-55 plutonium Facility.”


NMT Division has won one of the six R&D 100 Awards recently presented to the Laboratory. A first for NMT, the prestigious international award was earned for the Hydride-Dehydride Recycle Process. Principal developers were Bart Flamm and Garland M. Isom. The research team also included Joseph C. Martz and John M. Haschke, all of NMT-5. Details of the process were published in the last issue of Actinide Research Quarterly, spring 1995.

Division Seminar Speaker: Prof. Rod Ewing of UNM on the subject of “Zircon: A Host-Phase for the Disposal of Weapons Plutonium.”

Dr. Robert Uhrig is the new NMT Division External Review Committee member (see the related news article under the 1995 Division Review, page 10).


NMT Prepares Laboratory Directed Research and Development (LDRD) Proposals

March and April are the two busiest months in preparation for the coming year’s LDRD proposals. NMT produced about a dozen new proposals in the competency development (CD) program development (PD) and individual project (IP) components of LDRD. Several more idea papers were prepared jointly with investigators from other technical divisions and program offices. These idea proposals were reviewed by their respective category teams, and the following four were chosen to be prepared fully for final selection: “Integration of Advanced Nuclear Materials Separations Processes,” by Gordon Jarvinen; “Feasibility of a Standardized, Compact, Flexible, Portable, Modular Treatment System,” by Dana Christensen; “Stabilization of Nuclear Materials in Hybrid Materials,” by Nicholas Coppa; and “Radioactive Waste Remediation and Stabilization through Acoustic Cavitation,” by Pamela Benicewicz.


In addition to the above CD and PD proposals, two IP proposals have been submitted for consideration, but they have not yet been reviewed. FY 95 was a successful year: NMT obtained LDRD funding for four proposals. We hope that several more proposals will be successful in FY 96.