RECOVERY OF TRANSURANICS FROM PROCESS RESIDUES

by

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ABSTRACT

Process residues are generated at both the Rocky Flats Plant (RFP) and the Savannah River Plant (SRP) during aqueous chemical and pyrochemical operations. Frequently, process operations will result in either impure products or produce residues sufficiently contaminated with transuranics to be nondiscardable as waste. Purification and recovery flowsheets for process residues have been developed to generate solutions compatible with subsequent Purex operations and either solid or liquid waste suitable for disposal. The "scrub alloy" and the "anode heel alloy" are examples of materials generated at RFP which have been processed at SRP using the developed recovery flowsheets. Examples of process residues being generated at SRP for which flowsheets are under development include LECO crucibles and alpha-contaminated hydraulic oil.

INTRODUCTION

Molten salt extraction (MSE) is the primary pyrochemical process used to separate transuranics at RFP (Slide 1). Use of NaCl-KCl-MgCl₂ salt mixtures generates a purified plutonium product and a spent salt residue containing significant plutonium and most of the americium. MSE salt residues can be scrubbed with molten aluminum-magnesium to produce the Pu-Am-Al scrub alloy or processed directly using an aqueous flowsheet developed to recover both of the actinides from the wet salts.
Additional pyrochemical processes are used at RFP (Slide 2). Electrefining is used to produce high-purity plutonium metal when the quantities of impurities remaining in the metal product are relatively small. Anode heels, low in chloride content, and an oxide-chloride are two major residue categories resulting from electrorefining operations. Similar to the MSE salt residues, anode heels can be alloyed with aluminum to facilitate aqueous processing. Both the oxide-chloride and high-purity anode heel metal are suitable for aqueous processing without alloying.

Impure oxides generated during foundry operations can either be dissolved directly or first reduced to the metal by the direct oxide reduction (DOR) process. Again, depending on impurity levels, DOR metal product can be used for fabrication, purified by electrorefining, dissolved directly as the metal, or after alloying with aluminum, for aqueous processing.

Periodically, alpha-contaminated hydraulic oil is generated at SRP during metal finishing operations. In addition, alpha-contaminated LECO crucibles and combustibles are produced as a result of normal operations. Although these residue categories are not currently processed onsite, flowsheets are being developed for eventual processing and generation of discardable waste. Plans are underway to incinerate high plutonium content combustibles which will generate an ash requiring processing before disposal.

DISCUSSION

Presented in Slide 3 are some of the offsite residues which have been identified for flowsheet development. Some plutonium has already been recovered and purified at SRP from each of the
four major residue categories. Most has come from the "scrub alloy" (38.5%), the low n/g/s metal (20.4%), and the 6% (< 15% impurities) oxide (15.8%). Future major sources of offsite residues will come from the scrub alloy, Category III metal, and 6% oxide categories.

**Flowsheet Development**

- **Molten Salt Extraction Salt Residues**

  The aqueous process developed for recovery of transuranics from MSE salt residues (Slide 4) is an example of a flowsheet not ideally suited for use at SRP due to the high chloride content. In addition, dissolution of the MSE residues would be in HCl solutions. The insoluble residues need to be filtered and collected for dissolution and subsequent recovery operations. Cation exchange will be used to separate chloride and cation impurities from the filtered dissolver solutions. Essentially complete chloride removal is accomplished during the cation resin wash steps. When americium recovery is not required, cation column product solutions would be sent directly to the second plutonium cycle. To recover americium, anion exchange would be used to separate americium from plutonium. Plutonium in the anion column product solution would then be transferred to the second plutonium cycle for further processing. Utilization of this process at SRP would require an extensive new facility.
• **Scrub Alloy Buttons**

Kilogram quantities of scrub alloy buttons have already been dissolved at SRP. The aqueous flowsheet used for dissolving these scrub alloy buttons is given in Slide 5. The aluminum cans were dissolved in HNO₃ using Hg(NO₃)₂ as a catalyst. Upon breaching the cans, the scrub alloy buttons were dissolved using a solution of HNO₃ and HF. Residual chloride contained in the buttons was precipitated by adding Hg₂(NO₃)₂ and removed by centrifuging. The plutonium was extracted and purified by the standard Purex process as practiced at SRP.

• **Anode Heel Alloy**

Alloying anode heels with aluminum allowed the buttons to be processed as if they were scrub alloy. The aqueous flowsheet shown in Slide 6 for the anode heel alloy is less complicated than the one used for scrub alloy. This is due to the low chloride concentration found in the anode heel alloy which eliminated the need for the chloride removal step. A successful pilot demonstration has already been accomplished with a batch of anode heel alloy buttons using the large canyon dissolver at SRP.

• **Anode Heel Metal**

Anode heel metal not alloyed with aluminum can be dissolved directly in small metal dissolvers. Flowsheets were developed and tested using both sulfamic acid and HNO₃-N₂H₄-HF solutions (Slide 6). The sulfamic acid dissolver solutions require
additional heating at 70°C to completely dissolve any plutonium-bearing residues. Both dissolver solutions will require significant adjustment before blending into the solvent extraction process.

• Oxide-Chloride Residues

A third residue category generated from electrorefining operations is the oxide-chloride. This material results from the burn-out of electrorefining crucibles in tilt-pour furnaces. A proposed dissolution process for this residue category is presented in Slide 7. The initial process step is caustic dissolution, followed by dissolution of the plutonium-bearing solids in HNO₃-HF solutions. Most of the chloride will be contained in the NaOH waste solution. If additional chloride purification is required, it can be accomplished using either anion exchange or precipitation methods (similar to scrub alloy). Although this aqueous process has not been demonstrated, plans are being made to receive oxide-chloride residues for laboratory development.

• Direct Oxide Reduction (DOR) Metal

Initial DOR metal flowsheet development work began at SRP with impure oxides reduced to the metal at Los Alamos National Laboratory (LANL). The two candidate dissolver solutions tested in the laboratory were the same sulfamic acid and nitric acid-hydrazine-fluoride solutions evaluated for anode heel metal and are shown again in Slide 8. The presence of large amounts of impurities, primarily calcium metal, resulted in excessively fast dissolution and offgas generation rates using the HNO₃-N₂H₄-HF solutions. Because of the excessive amounts of heat and offgases that were generated, the sulfamic acid flowsheet has
been used to dissolve multi-kilogram quantities of DOR metal at SRP. The americium product separated from the dissolved DOR metal contained most of the calcium impurity.

• **Foundry Oxides**

Reduction to metal is not the only recovery approach for impure, relatively high-fired plutonium oxide generated during foundry operations. These oxide residues can be dissolved directly in boiling HNO₃-HF solutions *(Slide 9).* An ammonium bifluoride pretreatment of the oxide converted the samples to the tetrafluoride, but did not improve the overall dissolution; neither did the ammonium bifluoride treatment of the residues reduce the amount of insoluble material remaining after dissolution. This was due to the presence of tantalum as the major impurity which was unaffected by fusion with the ammonium bifluoride.

• **Refractory-Type Residues**

Flowsheet development for residues in this category have been directed toward the processing of incinerator ash and LECO crucibles. These materials (combustibles at SRP) are being generated both at SRP and at RFP. So far, LECO crucibles and incinerator ash from RFP have been used to develop a recovery process using ammonium bifluoride as the fluorinating agent *(Slide 10).* What has been accomplished using ammonium bifluoride is the conversion of insoluble refractory-type materials to the more soluble fluoride compounds. Additional work is planned using materials generated at SRP to resolve corrosion, offgas, and feed clarification concerns *(Slide 11).*
- **Hydraulic Oil**

Periodically, hydraulic oil containing significant quantities of plutonium is generated at SRP. A flowsheet involving the use of sodium hydroxide (NaOH) has been developed for treatment of this type residue (Slide 12). The initial caustic treatment step converts the oil phase by saponification to a water-soluble form and precipitates plutonium. After filtration and washing steps, the plutonium-bearing solids are dissolved by boiling HNO₃-HF solutions. Final purification of the product solutions is accomplished using anion exchange.

**SUMMARY**

A flowsheet summary is presented in Slide 13. Aluminum alloys require the use of mercury to catalyze the dissolution of the aluminum. The scrub alloy and anode heel alloy are two residues which have already been processed at SRP using this process. Other alloys are being studied for possible processing at SRP with this flowsheet.

Primarily due to the impurities present, most of the metals processed at SRP have used the sulfamic acid flowsheet. Only the high-purity anode heel metal containing greater than 90% plutonium will dissolve in HNO₃-N₂H₄-HF solutions at rates slow enough for use in small metal dissolvers.

All of the oxides already processed at SRP have been soluble in the HNO₃-HF solutions. Should significant quantities of high-fired oxide remain undissolved with the residues, treatment of the
residues with ammonium bifluoride to convert the insoluble oxide to soluble fluorides can be used. Further development of this process is planned.

Refractories present the most difficult type of residue to process effectively. A pretreatment step, whether it be with ammonium bifluoride or some other fluorinating agent, appears to be necessary. All of the actinides then dissolve easily in nitric acid.

Both the hydraulic oil and oxide-chloride residues use an initial NaOH pretreatment step before dissolving with the standard HNO₃-HF solutions. The caustic treatment of hydraulic oil solubilizes the oil whereas using NaOH is an effective way of removing the chloride from oxide-chloride residues. The MSE salt residues also have high chloride concentrations. Special corrosion resistant equipment would be necessary to process this type residue using the developed HCl-anion exchange flowsheet.
Pyrochemical Process
Flowsheet Development

Direct Oxide Reduction (DOR)

Foundry

Purified Pu Metal

Electrorefining

Anode Heels

Al Alloy at RFP

Oxide-Chlorides

FB-Line Metal Diss

> 3%

< 3%

Al Cans

SRP F-Canyon

> 3%

FB-Line Oxide Diss

(1)

(2)

(3)
Residues Identified for
Flowsheet Development and Processing

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<th>Residue Category</th>
<th>Actinide Recovery To Date</th>
<th>SRP Inventory (%)</th>
<th>Total Inventory (%)</th>
<th>Projected Generation (%)</th>
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<td>6%</td>
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<td>Graphite</td>
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<td>0.8</td>
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<td>Heels</td>
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<td>2.5</td>
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<td><strong>Total Pu (%)</strong></td>
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SLIDE 3
Aqueous Process Flowsheet for Molten Salt Extraction Residues

1. **Molten Salt Residue Dissolution**
   - 4 L 2 M HCl
   - Filter
   - Dilution ≤ 1 M HCl

2. **Dilute HCl**
   - H₂O, HONH₂NO₃

3. **Cation Exchange**
   - DOWEX 50X8 H⁺
   - DOWEX MSC-1

4. **Pu²⁴¹ Am Cation Product**
   - To Waste Tanks
   - (1) Cl⁻
   - (2) Na, K, Mg

5. **Anion Exchange**
   - Pu²⁴¹ Am
   - Anion Feed Prep

6. **Pu Oxide Conversion**
   - (1) Conc HNO₃
   - (2) Heat

7. **Purex Solvent Extraction**
   - 24¹Am to Waste

8. **Pu-²⁴¹Am Cation Product**
   - (1) 0.1 M HNO₃ Wash
   - (2) 1 M HNO₃ Wash
   - (3) 5 M HNO₃-0.35 M NH₂SO₃H Elution
Aqueous Process Flowsheet for Scrub Alloy Buttons

Scrub Alloy Buttons
Pu-Am-Al in Al Cans

(1) 7000 L HNO₃
(2) Hg(NO₃)₂
(3) HF

Dissolution F-Canyon Dissolver

Chloride Removal Head-End Centrifuge

(4) Hg₂(NO₃)₂

Pu-Am to Solvent Extraction

Hg₂Cl₂ to Waste Tanks
Aqueous Process Flowsheets for Anode Heels

- Anode Heel Alloy
  - Aluminum Alloy Packaged in Al Cans
  - Dissolved in HNO₃-Hg(NO₃)₂-HF Solutions
  - Canyon Dissolvers

- Anode Heel Metal
  - 1.4 to 1.6 M Sulfamic Acid, 40-45°C (~ 75°C for Residues)
  - 3 M HNO₃-1 M N₂H₄-10⁻² M HF, 55-60°C
  - Small Dissolvers
Aqueous Process Flowsheet for Oxide-Chloride Residues

NaOH Dissolution → Solid Separation → Nitric-HF Dissolution → Cl Ppt (if needed) & Filtration

Hg\(_2\)\(^{2+}\) or Ag\(^{+}\)

Pu as Nitrate Solution to Solvent Extraction

Solids to Waste

NaOH with Cl\(^{-}\)

Anion Exchange (Alt)
Aqueous Process Flowsheet for Direct Oxide Reduction Metal

- Sulfamic Acid
  - 1.4 to 1.6 M, 40-45°C
  - Residues, 70-75°C

- Nitric Acid - Hydrazine - Fluoride
  - 3 M HNO₃
  - 1 M N₂H₄
  - 10⁻² M HF
  - 55-60°C
Process Flowsheet for Foundry Oxides

- Nitric Acid - Fluoride
  - 14 M HNO₃
  - 0.1 M HF
  - Reflux Two Hours
  - Ta (major); Fe, Cr, Si, Ti, W (minor)

- Ammonium Bifluoride Pretreatment

- Ammonium Bifluoride Residue Treatment
Fluorinating by Fusion

Two Process Steps:

- Fusion with Ammonium Bifluoride
  - $\text{NH}_4\text{HF}_2$
  - 4 Hours at 140-170°C

- Dissolution in 14 M HNO$_3$
  - Boiling for 4 Hours
Future Studies

Incinerator Ash

- Process Demonstration
  - Two Types Complete
  - Two Types to be Investigated

LECO Crucibles

- Process Demonstration
  - Two Types Complete
  - Third Type to be Investigated

Problem Areas

- Corrosion
  - High Fluoride Content
- Crucible Crushing
- Bifluoride Mixing
- Offgas System
- Slurry Clarification
Aqueous Process Flowsheet for Hydraulic Oil

SLIDE 12
Flowsheet Development Summary

- Aluminum Alloys
  - $\text{HNO}_3$-Hg-HF

- Metals
  - $\text{NH}_2\text{SO}_3\text{H}$ (Sulfamic Acid)
    - DOR, LNGS, Cat III, (Anode Heel)
  - $\text{HNO}_3$-$\text{N}_2\text{H}_4$-HF

- Oxides
  - $\text{HNO}_3$-HF
  - $\text{NH}_4\text{HF}_2$ Treatment of Residues

- Refractories
  - $\text{NH}_4\text{HF}_2$ Pretreatment
  - $\text{HNO}_3$

- Other Residues
  - Hydraulic Oil
    - NaOH/$\text{HNO}_3$-HF
  - Oxide Chloride
    - NaOH/$\text{HNO}_3$-HF
  - MSE Salts
    - HCl/Ion Exchange