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REVIEW OF PLUTONIUM PROCESS CHEMISTRY

AT ROCKY FLATS

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KWIC Index

- |                        |                      |
|------------------------|----------------------|
| Actinide               | Plutonium            |
| Americium              | Plutonium Recovery   |
| Dissolution            | Precipitation        |
| Electrorefining        | Pyrochemistry        |
| Fluorination           | Separation Processes |
| Hydriding              | Solvent Extraction   |
| Ion Exchange           | Waste Treatment      |
| Molten Salt Extraction |                      |

**MASTER**

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## ABSTRACT

Plutonium metal scrap, oxide, and other residues are processed at Rocky Flats using both pyrochemical and aqueous methods. The pyrochemical processes currently in production include electrorefining, fluorination, hydriding, molten salt extraction (MSE), calcination, and reduction operations. Aqueous processing and waste treatment methods involve nitric acid dissolution, ion exchange, solvent extraction, and precipitation techniques. An overview of the chemistry involved in these operations will be given. Research in progress to improve these operations, or develop new processes, will also be presented.

## INTRODUCTION

Rocky Flats is a Government-owned and contractor-operated facility which originated in 1952. The Plant's primary missions are metal fabrication, assembly, and chemical processing--with emphasis on production-related research and development. Chemical processing activities involve the recovery of plutonium from Rocky Flats Plant scrap, waste materials and residues, and effluent streams. The final product of this recovery and purification effort is high-purity plutonium metal for use in foundry operations.

Both pyrochemical and aqueous methods are used at Rocky Flats to process plutonium metal scrap, oxide, and other residues. The pyrochemical processes currently in production include electrorefining, fluorination, hydriding, molten salt extraction, calcination, and reduction operations. Aqueous processing and waste treatment methods involve nitric acid dissolution, ion exchange, solvent extraction, and precipitation techniques. A brief overview of the chemistry involved in these operations will be given. Research to improve these operations, or develop new processes, will also be presented.

## PLUTONIUM PROCESSING OVERVIEW

Figure 1 shows a simplified flow sheet for plutonium-239 recovery operations at Rocky Flats. Impure plutonium metal is sent through a pyrochemical process, called molten salt extraction (MSE), to remove the elemental impurity americium.\* The product plutonium metal, if it meets Plant purity requirements, is sent to the foundry. Metal that does not meet foundry requirements is processed further, either through an aqueous process using ion exchange, or through a pyrochemical electro-refining process. The waste chloride salt from MSE is dissolved; then the actinides are precipitated with carbonate and redissolved in 7M  $\text{HNO}_3$ ; finally the plutonium is purified by anion exchange.

Impure plutonium oxide residues are dissolved in 12M  $\text{HNO}_3$ -0.1M HF under refluxing conditions and then purified by anion exchange. Plutonium is leached from other residues, such as metal and glass, and is also purified by anion exchange. The purified eluate from the anion exchange process is precipitated with hydrogen peroxide. The plutonium peroxide is calcined to the oxide, and the plutonium oxide is fluorinated. The plutonium tetrafluoride is finally reduced to the metal with calcium.

Acid waste streams are processed through nitric acid recovery and then sent to a secondary plutonium recovery process which uses anion exchange. Acid, basic, and laundry waste streams are then combined and sent to Waste Treatment. A discussion of the process steps shown on Figure 1 follows.

### Molten Salt Extraction

Molten salt extraction has been used very successfully at Rocky Flats since 1967 to remove americium from plutonium.<sup>1,2</sup> Plutonium, in

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\* Americium grows in the plutonium-239 from the beta decay of plutonium-241.

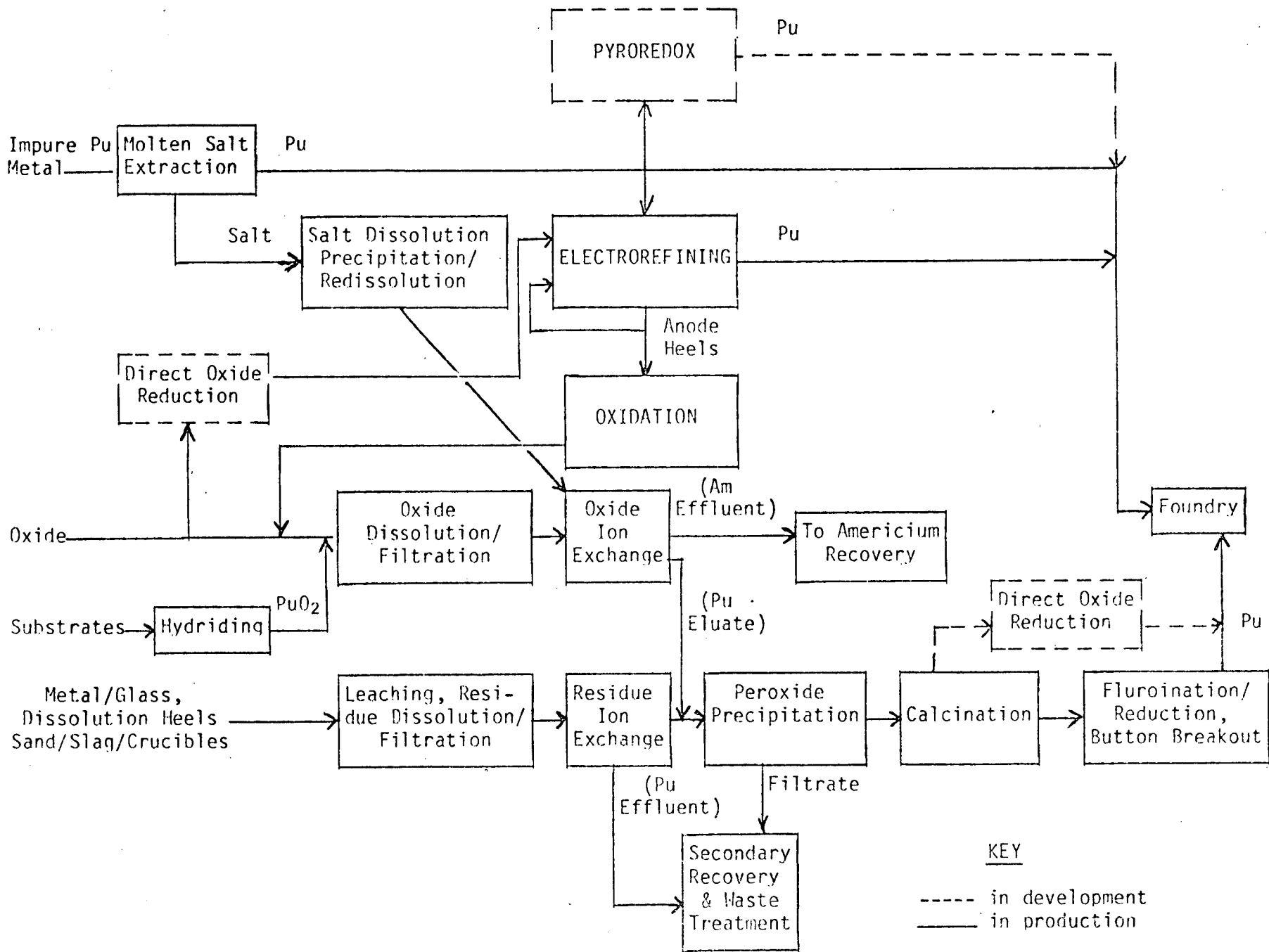


Figure 1. Plutonium Recovery Process

2-kg batches, is contacted at 750°C with a molten salt of 35 mole % NaCl-35 mole % KCl-30 mole % MgCl<sub>2</sub>. The MgCl<sub>2</sub> reacts with the americium according to the reaction:



In addition, some plutonium is also lost to the salt as PuCl<sub>3</sub>. A two-step counter-current extraction is used to minimize the amount of salt used in the MSE process, reduce plutonium losses to the salt, and achieve the proper level of americium removal.<sup>1</sup>

The spent salt from MSE is currently sent to an aqueous dissolution/carbonate precipitation process to recover plutonium and americium. Efforts to recover plutonium and americium from spent NaCl-KCl-MgCl<sub>2</sub> MSE salts using pyrochemistry have been partially successful.<sup>4</sup> Metallothermic reductions using Al-Mg and Zn-Mg alloys have been used in the past to recover plutonium and americium, and produce salts which meet Plant discard limits. Attempts at direct reductions of MSE salts using calcium metal have been less successful, with a discardable white salt phase, a nondiscardable black salt phase, and little or no metal produced.<sup>4</sup> Until recently, pyrochemical alloy products from salt cleanup have not been compatible with other Plant operations because of the difficulty in removing impurities, such as aluminum and calcium, from the americium during aqueous processing. Development of the CMP process (vide infra), which removes these impurities, has renewed the interest in pyrochemical recovery of spent MSE salt.<sup>3</sup> Other salt systems, such as NaCl-CaCl<sub>2</sub>-MgCl<sub>2</sub>, will again be investigated for MSE. Calcium reductions of CaCl<sub>2</sub>-based salts have been shown to be successful in the past and could lead to a more compatible salt system in the future at Rocky Flats for MSE.<sup>4</sup>

### Electrorefining

Impure plutonium metal from MSE and Direct Oxide Reduction (DOR) is sent to an electrorefining operation.<sup>6</sup> In plutonium electrorefining,

impure plutonium metal is placed in a molten salt electrolyte of equimolar NaCl-KCl and 3 mole % MgCl<sub>2</sub>. Trivalent plutonium ions, required to start electrolysis, are generated in situ by the MgCl<sub>2</sub> oxidation of plutonium metal. The impure plutonium metal is made anodic (positive) and a tungsten electrode is made cathodic (negative). When a direct current is applied, plutonium at the anode is anodically dissolved and plutonium metal is deposited at the cathode. The chemical basis for plutonium purification during electrorefining is the difference in the free energy of formation ( $-\Delta G_f$ ) for the chlorides of plutonium and the impurity elements. Elements with values of  $-\Delta G_f$  smaller than that for plutonium will remain in the anode. The transfer of impurities is set by the equilibrium distribution coefficient for each element partitioning between the molten anode-salt interface and the molten plutonium-salt interface at the cathode.<sup>4</sup>

Spent anode heels from electrorefining (which contain approximately 20-30 percent of the plutonium fed to the process) are either recycled back to electrorefining, or, if high enough in impurities, are oxidized and sent to oxide dissolution. The spent salt is sent to aqueous dissolution (see Figure 1).

Future work to be done in electrorefining includes evaluation of CaCl<sub>2</sub>-based salts, similar to those considered for use in MSE, which will allow direct reduction of plutonium from the salts. Past research and development using NaCl-CaCl<sub>2</sub>-MgCl<sub>2</sub> for electrorefining looked promising. In situ reduction of plutonium from the salt demonstrated the ability to recover the plutonium with the product metal and produce salt meeting the Plant's discard limits.<sup>4</sup>

The ability to reuse the salt will be investigated. Pyrochemical techniques to recover plutonium from spent anode heels will also be examined. One technique, called pyroredox (vide infra), utilizes ZnCl<sub>2</sub> in a diluent salt of 45 mole % KCl-54 mole % CaCl<sub>2</sub> to oxidize the plutonium to PuCl<sub>3</sub>.<sup>4</sup> The reduced zinc scavenges the impurities and separates from the salt. The salt is reduced in a diluent salt of



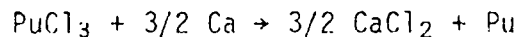
26 mole % KCl-74 mole % CaCl<sub>2</sub> to recover the purified plutonium which can be returned to electrorefining or, if pure enough, to the foundry. Pyroredox is also being investigated as a primary operation to purify plutonium, along with electrorefining.

### Pyroredox

Pyroredox is a three-step plutonium purification process.<sup>4</sup> Impure plutonium metal is reacted with ZnCl<sub>2</sub> in a solvent salt of KCl-CaCl<sub>2</sub>, as follows:



Impurities less chemically reactive than plutonium follow the zinc. The salt and zinc are allowed to solidify and are separated. The PuCl<sub>3</sub>, contained in the salt, is reacted with calcium, according to the reaction:



The plutonium reduces and separates from the salt phase. In the third step, distillation is used to separate the more volatile zinc and calcium from the plutonium.

Pyroredox is currently under development. Several problems have been identified and work is underway to overcome these obstacles.

As mentioned previously, this process has immediate application as a primary plutonium purification process and as a means to process spent electrorefining anodes for direct recycle back to electrorefining.

### Direct Oxide Reduction

Implementation of the Direct Oxide Reduction (DOR) process into production is currently underway. Plutonium oxide from foundry operations, hydriding, and other sources is calcined in air at 800°C to

remove any carbon or other volatile impurities. This oxide is then reduced by a 25 percent stoichiometric excess of calcium in a  $\text{CaCl}_2$  solvent. The salt-to-oxide ratio, by weight, is 4 to 1. The reaction takes place in a  $\text{MgO}$  crucible which is heated to approximately  $850^\circ\text{C}$ . Upon cooling to room temperature, a well consolidated plutonium product is obtained at better than 98 percent recovery, as well as salt and ceramics which are well below the Plant discard limits.

Recent development work has been done defining the above operating parameters and evaluating a  $\text{CaCl}_2$ - $\text{CaF}_2$  salt system.

### Hydriding

A hydride facility was constructed for recovering plutonium, as plutonium hydride, from various types of metallic substrates.<sup>9</sup> Hydriding does not damage certain types of reusable substrates, as does acid leaching. Hydriding also eliminates the use of large volumes of leaching acid solutions and the need for subsequent removal of plutonium from these solutions.

During the hydriding cycle, gaseous hydrogen reacts with plutonium in an oxygen-free reactor to produce plutonium dihydride. It is possible to produce other plutonium-hydrogen compounds having different hydrogen-to-plutonium ratios, depending on operating parameters. For this type of recovery process, however, the formation of nonstoichiometric plutonium hydride compounds is not significant.

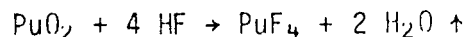
As plutonium hydride is produced during a hydriding operation, it falls free from the metallic substrate and drops into a tray. Since  $\text{PuH}_2$  is a pyrophoric powder, it is oxidized in air to  $\text{PuO}_2$ . This change permits safe handling of the material during additional processing.

Residual hydrogen that is not used in hydriding operations is pumped from the reactor to an apparatus where the hydrogen is burned in

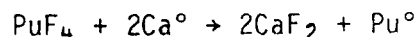
a natural gas flame. Plutonium has been selectively removed from metallic substrates that do not form hydrides with hydrogen. Plutonium has also been removed from metals that absorb hydrogen (i.e., tantalum), but do not produce a hydride under the hydriding operating conditions used. The hydriding apparatus is used to recover plutonium from (1) reusable equipment, (2) plutonium scrap, (3) plutonium-coated tools, and (4) plutonium melts from tantalum and tungsten crucibles. The hydriding apparatus is also used to oxidize such pyrophoric material as skull material, plutonium chips and turnings, mixtures of plutonium hydride and plutonium oxide, and plutonium hydride that is generated elsewhere on Plantsite.

#### Fluorination, Reduction, Button Breakout

Until recently, plutonium dioxide from the calcination of plutonium peroxide was contacted with HF in a rotary hydrofluorinator. The reaction converted  $\text{PuO}_2$  to  $\text{PuF}_4$ , according to the following reaction:



The  $\text{PuF}_4$  is then loaded in ceramic ( $\text{MgO}$ ) crucibles, where it is reacted with calcium to form  $\text{CaF}_2$  and plutonium metal as follows:<sup>7</sup>



The products of the reaction, once cooled to room temperature, are easily separated. The plutonium metal is sent to the foundry, while the  $\text{CaF}_2$  salt is stored until it can be dissolved in 9N  $\text{HNO}_3$  for recovery of residual amounts of plutonium.

Though both hydrofluorination and reduction were accomplished with relative ease, three significant problems were apparent. First,  $\text{PuF}_4$  is a neutron emitter, requiring considerable protective shielding and creating difficulty in handling. Secondly, the use of HF requires costly equipment which must be resistant to corrosion. Finally, the

salt from the reduction,  $\text{CaF}_2$ , is not discardable, and must be processed to recover residual plutonium.

In the last year, direct fluorination has been used to convert  $\text{PuO}_2$  to  $\text{PuF}_4$ , as follows:<sup>3</sup>



The problems previously discussed are basically the same, with an added problem--disposal of excess fluorine. Studies are underway to find a safe, efficient way to resolve it. Ultimately, the use of DOR, previously discussed, is expected to replace fluorination and reduction. This would result in one process step, rather than two. In addition, the problems previously discussed would be eliminated.

### Dissolution

Plutonium is solubilized in nitric acid solutions at Rocky Flats. The feed material consists of oxide, metal and glass, dissolution heels, incinerator ash and sand, slag, and crucible from reduction operations. The residues are contacted with 12M  $\text{HNO}_3$  containing  $\text{CaF}_2$  or HF to hasten dissolution. Following dissolution, aluminum nitrate is added to these solutions to complex the excess fluoride ion.

Complete dissolution of plutonium residues, especially high temperature calcined plutonium dioxide contained in residues such as incinerator ash, continues to cause problems, despite continued research on this problem since the Manhattan Project.<sup>9</sup> Methods to improve the Rocky Flats system include the use of additives (e.g., cerium) and electrochemistry, other solvents ( $\text{HCl-SnCl}_2$ ) as well as high-temperature fusion methods.<sup>10</sup> High pressure dissolution, HF preleaching, fluorination, and other methods are being investigated.

## Solvent Extraction

A modified, one-cycle purex process is used at Rocky Flats to recover plutonium from miscellaneous Pu-U residues.<sup>11</sup> The process utilizes the extraction of uranium (VI) into tributyl phosphate (TBP), leaving plutonium (III) in the raffinate. The plutonium is then sent to ion exchange for purification. An extraction chromatography method is being studied as a possible substitute for the liquid-liquid extraction process;<sup>12</sup> TBP is sorbed on an inert support so ion exchange column equipment can be used. Electrolytic valence adjustment could significantly improve this process.

Acid waste streams are sent through a nitric acid recovery process and then to a secondary plutonium recovery process using anion exchange (Figure 2). Another area of solvent extraction application involves the use of dihexyl-N,N-diethylcarbamoylmethylphosphonate for removing further amounts of plutonium and americium from the acid waste streams coming from the secondary plutonium recovery columns.<sup>3,13</sup> Alternative solvent extractants, sorbed or bonded on inert support materials so ion exchange column equipment can be used, are being studied to selectively extract only actinides and not impurities.

## Precipitation Processes

Plutonium peroxide precipitation is used at Rocky Flats to convert the purified plutonium nitrate solution to a solid;<sup>14</sup> the plutonium peroxide is then calcined to  $\text{PuO}_2$  and sent to the reduction step. The chemistry of the plutonium peroxide precipitation process is being studied, as well as alternative precipitation processes such as oxalate, carbonate, fluoride, and thermal denitration. The latter method shows the most promise for cost and waste reduction.

Molten salt extraction residues are processed to recover plutonium by an aqueous precipitation process. The residues are dissolved in dilute HCl, the actinides are precipitated with potassium carbonate, and

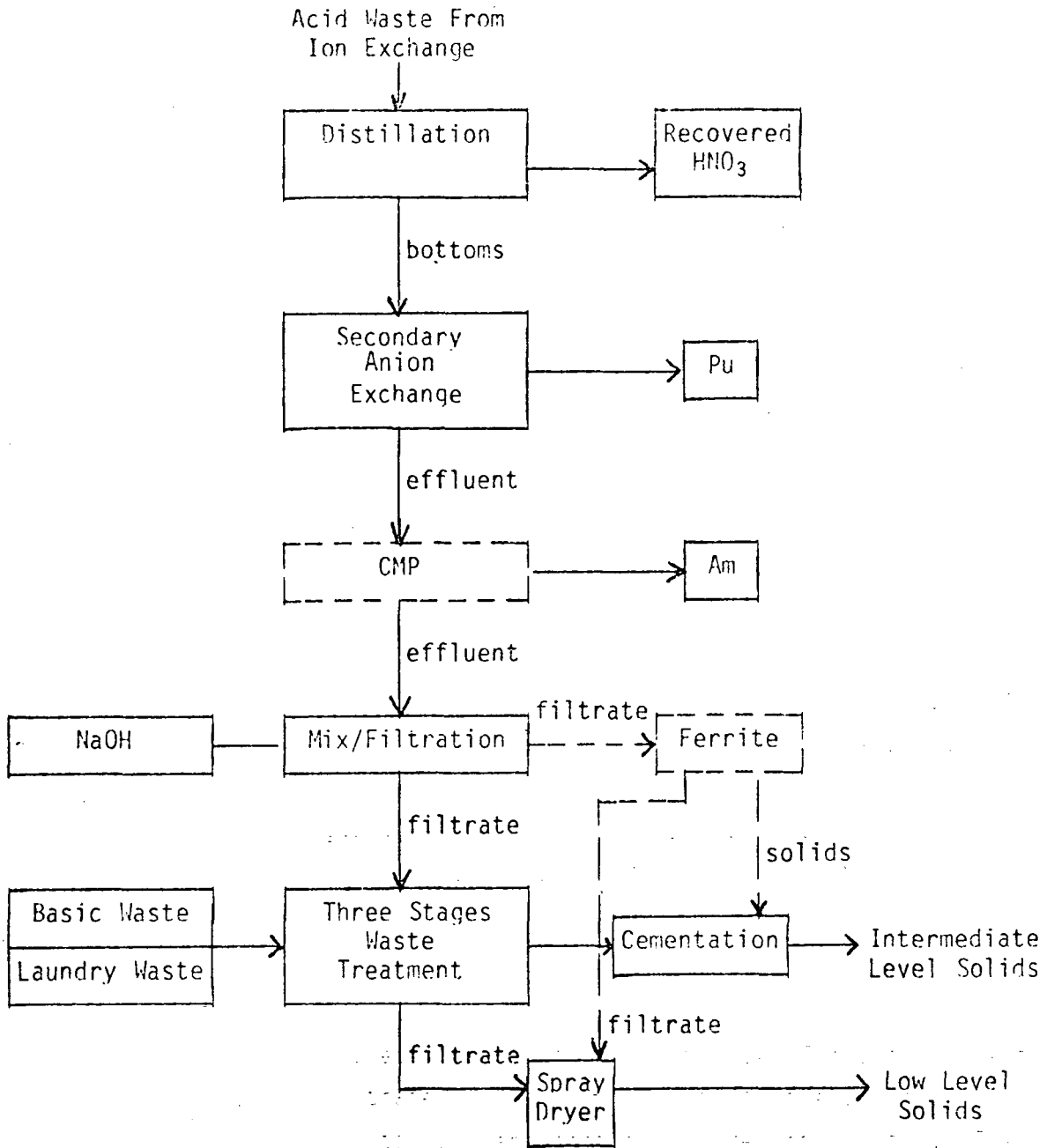


Figure 2. Aqueous Waste Recovery and Treatment Processes  
(broken lines represent processes under development)

the precipitate redissolved in nitric acid (7M) to convert from a chloride to a nitrate system. The plutonium is then recovered from the 7M HNO<sub>3</sub> by anion exchange and the effluent sent to waste or americium recovery. We are studying actinide (III) carbonate chemistry and looking at new cation exchangers as an alternative to carbonate precipitation.<sup>15,16</sup>

### Ion Exchange

Very few elements form anions in nitric acid solutions, thus anion exchange is a very effective procedure for purifying plutonium. The plutonium hexanitrate anion is sorbed on the resin from a 7M nitric acid solution. A nitric acid wash is used to remove residual impurities from the resin. Dilute nitric acid is used to elute the purified plutonium from the resin. We have a continuing resin evaluation program to test new gel and macroporous anion exchange resins, as well as inorganic ion exchangers.<sup>17</sup>

### Waste Treatment

Figure 2 outlines the current waste recovery and treatment processes, and proposed changes. Acid waste streams are sent through nitric acid and secondary plutonium recovery processes before being neutralized with potassium hydroxide and filtered. This stream is combined with basic and laundry waste streams, and sent to waste treatment. During waste treatment, the actinides in the aqueous waste are removed by three stages of hydroxide-iron carrier-flocculant precipitation. The filtrate solution is then evaporated to a solid with a spray dryer and the solids are cemented and sent to retrievable storage.

A ferrite waste treatment process is being investigated to determine if it can more effectively remove actinides from waste solution with less solid waste generation than the flocculant precipitation method presently used.<sup>18</sup>

Ferrite is introduced into the aqueous media by two techniques. With the in situ method, ferrite is formed within the actinide-containing solution by addition of Fe(II) , Fe(III), and sodium hydroxide. With the preformed ferrite method, ferrite solids are prepared separately and added to the actinide solution.

Both preformed and in situ ferrite lowered plutonium concentrations in simulated process waste from  $10^{-4}$  g/l to  $10^{-8}$  g/l in one treatment step. Two or three flocculant precipitations, as currently used for waste processing, were required to achieve the same result. Ferrite waste treatment produced 4.1 g/l solids, while production waste processing during the past year, using the flocculant process, produced 7.9 g/l solids.

The Chemistry Research and Development group has a large variety of actinide process chemistry projects underway. The work will certainly add to our understanding of actinide chemistry and will result in actinide process improvements.



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