

# Plutonium and Americium Processing Chemistry and Technology

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Plutonium processing originated at Hanford and Los Alamos as part of the Manhattan Project in 1943 [1]. Hanford separated plutonium from irradiated reactor fuel, whereas Los Alamos purified the plutonium, as well as recovered plutonium from residues and scrap. In the early 1950's, similar processing facilities were constructed at Savannah River and Rocky Flats.

The PUREX process (tri-n-butyl phosphate extraction) [2] is used at Hanford and Savannah River plants to separate plutonium from irradiated reactor fuel. At Los Alamos and the Rocky Flats Plant (RFP), both pyrochemical and aqueous processes are used to recover and purify plutonium. A by-product in the plutonium recovery processes is americium-241 from the beta decay of plutonium-241 present in the plutonium-239 stream. An overview of the americium and plutonium processing chemistry and technology at RFP is presented herein.

## Plutonium Processing

Chemical processing activities involve the recovery of plutonium from RFP scrap and residues. The final product of this recovery and purification effort is high-purity plutonium metal for use in foundry operations. The original plutonium recovery and purification processes were adopted from Los Alamos processes and are still similar today.

Fig. 1 shows a simplified flowsheet for plutonium processing at RFP. Impure plutonium metal is sent through a molten salt extraction (MSE) process to remove americium. The purified plutonium metal is sent to the foundry. Plutonium metal that does not meet foundry requirements is processed further, either through an electrorefining or aqueous process. The waste chloride salt from MSE is dissolved; then the actinides are precipitated with carbonate and redissolved in 7 M HNO<sub>3</sub>; and finally, the plutonium is recovered by an anion exchange process.

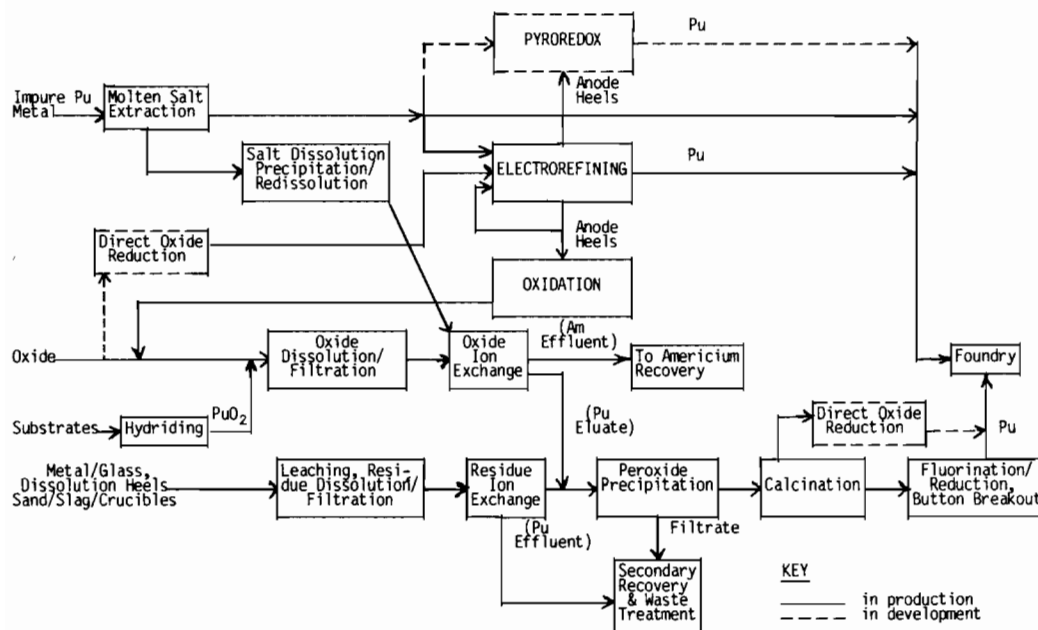


Fig. 1. Plutonium recovery process.

Impure plutonium oxide residues are dissolved in 12 *M* HNO<sub>3</sub>–0.1 *M* HF under refluxing conditions, and then the plutonium is recovered and purified by anion exchange. Plutonium is leached from other residues, such as metal and glass, and is also purified by anion exchange. The purified plutonium 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 sent through a nitric acid recovery process, and then to a secondary plutonium recovery anion exchange process. The acid waste streams are then sent to waste treatment.

#### *Plutonium Oxide Dissolution*

Dissolution of plutonium in many forms, such as the metal, oxide, or other compounds, is the first step in the aqueous process for recovery and purification of plutonium. Dissolution has been a persistent problem in plutonium recovery because the oxide is probably more difficult to dissolve than any other metal oxide. It is the high fired, or refractory, oxide that presents most of the operational problems [3].

There are two categories of materials in plutonium dissolution. The first involves dissolution of almost pure plutonium oxide, and the second involves dissolution of residues in which the plutonium is a minor constituent, such as incinerator ash. A dissolvent that is effective with one residue may not be effective with another because of the influence of the matrix.

Dissolution is conducted at RFP in a series of glass columns, containing steam coils (to heat solutions to 100–105 °C) and concentric tubes that allow for vertical mixing from the outer to the inner spacing. The solution in these cascade dissolvers flows from the top of one column or pot to another by gravity. The glass columns used for oxide dissolution have a diameter of 10 cm, a height of 60 cm and a volume of about five liters.

The most widely used dissolvent at RFP and most other plutonium processing plants is the nitric acid–hydrofluoric acid system. The HF is indispensable because dissolution in nitric acid alone is excessively slow. The advantages of this solvent are that (1) plutonium oxide dissolves readily if it has not been subjected to very high temperatures, (2) the resultant nitrate solution is well adapted for the subsequent purification steps, and (3) common process equipment materials can be used because the acid is not extensively corrosive at low fluoride concentrations. The most common concentration is 12 *M* HNO<sub>3</sub>–0.1 *M* HF. The disadvantage of the dissolvent is that dissolution is too slow in some residues that contain refractory oxide. Fluoride ion can be an interference in subsequent purification processes, but it does not

present any problems at RFP since aluminum nitrate is added after dissolution to complex excess fluoride.

The role of fluoride in this system is still not fully understood. It appears that free fluoride accelerates dissolution in two ways: (1) combining with plutonium on the surface of plutonium oxide and (2) forming plutonium fluoride complexes. As plutonium dissolves, fluoride is removed by plutonium complexing and the dissolution rate is retarded. Increasing the original fluoride concentration greater than about 0.1 *M* does not increase the rate because plutonium fluoride will begin to precipitate. This mechanism should be investigated further. The goal would be to prevent the initially high dissolution rate from decreasing with time. Of the many publications on this solvent, those by Tallent and Mailen [4], Barney [5], Ryan and Bray [6, 7], and others [8, 9] are recommended.

#### *Aqueous Separation/Purification Processes*

##### *Solvent Extraction*

A modified, one-cycle PUREX process is used at RFP to separate plutonium from miscellaneous Pu–U residues [10]. The process utilizes 16 liter air-sparged contactors and 30 vol% TBP (tri-*n*-butyl phosphate) in dodecane [11]. The plutonium is maintained in the trivalent oxidation state by ferrous sulfamate and does not extract appreciably. Uranium extracts into the organic phase, is washed with dilute nitric acid and is subsequently stripped with ammonium sulfate. The plutonium in the raffinate is sent to anion exchange for purification.

Another version of the process, using 20 vol% TBP-dodecane and York-Scheibel extraction columns, is presently being tested on a pilot-plant scale. An extraction chromatography method is also being studied as a substitute for the liquid–liquid extraction process [12]; TBP is sorbed on an inert support so ion exchange column equipment can be used. A small back-up column of support reduces losses of TBP in the effluent streams [13].

##### *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 7 *M* nitric acid solution. A 7 *M* nitric acid wash is used to remove residual impurities from the resin. Dilute nitric acid is then used to elute the purified plutonium from the resin. Presently Dowex<sup>®</sup> 11 and Amberlite<sup>®</sup> IRA-938 resins are used in production operations [14]. The resins are contained in 26 liter columns (15 cm diameter by 160 cm) and the plutonium(IV) feed is fed upflow. Prior to loading, the plutonium(IV) oxidation state is ensured by addition of ferrous sulfamate, then heated to destroy excess sulfamate ion and ferrous ion, and to oxidize plutonium(III) to plutonium(IV).

Acid waste streams are sent through a nitric acid recovery process and then to a secondary plutonium recovery process using anion exchange (Fig. 1). The use of a bifunctional organophosphorus extractant is being studied for americium as well as plutonium recovery from nitric acid waste [15].

#### Liquid-to-Solid Conversion Processes

Plutonium has been converted from a liquid to a solid by a variety of methods. The plutonium trifluoride process was developed at the Savannah River Plant [16], plutonium(III) oxalate and hydroxide precipitation were used at Los Alamos [17] and plutonium(IV) oxalate was employed at Hanford [18]. Various thermal denitration methods for plutonium nitrate to oxide conversion have also been studied [19].

Although we are now investigating the latter process, plutonium peroxide precipitation has been used at RFP since the Plant first started processing plutonium [20, 21]. This particular method was chosen over other methods because hydrogen peroxide adds no impurities to the process stream, and peroxide precipitation allows for greater metal impurity decontamination, especially for americium. RFP uses both a batch and a continuous operation for plutonium peroxide precipitation. Plutonium nitrate feed solution (~20–100 g/l Pu) is adjusted to ~4.0 M HNO<sub>3</sub> since acidities less than 2 M form an undesirable colloidal face-centered cubic phase precipitate. At acidities greater than 2 M, a hexagonal phase precipitate is formed that is more dense and easily filtered. Plutonium peroxide is soluble at acidities greater than 5 M. Precipitate formation is also dependent upon peroxide addition and mixing. A slow and uniform initial peroxide addition (3 l/hr), along with slow mixing, forms a more stable, easily filtered precipitate. For completeness of precipitation, a several-fold excess peroxide-to-plutonium ratio beyond stoichiometric is required.

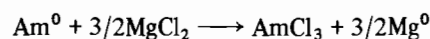
Sulfate (0.05 M) is sometimes added to the feed to aid in coagulating the colloids present in a cubic phase precipitate, improving filterability. However, sulfate present in a predominantly hexagonal-phase precipitate decreases precipitate density and filterability, altering the efficiency of the fluorination cycle by requiring higher temperatures to drive off the sulfate and decreases plutonium tetrafluoride density. The temperature of the solution during precipitation is cooled to less than 15 °C to prevent catalytic decomposition of peroxide caused by metallic impurities.

A rotary drum filter is used in continuous operation; however, a metal fritted filter is used in the batch operation. The precipitate cake in both cases is washed with 0.35 M HNO<sub>3</sub>. The cake is then calcined at 450 °C for 2 hours, to an oxide. The peroxide in

the filtrate solution is destroyed by boiling while the plutonium oxide is fluorinated, then reduced to metal with calcium.

#### Molten Salt Extraction

MSE has been used very successfully at Rocky Flats since 1967 to remove americium from plutonium [22, 23]. Plutonium, in 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 [22]. Work is in progress to use the process in production tilt-pour furnaces.

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 [24]. 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 RFP 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 [24]. 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 [25]. 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 RFP for MSE [24].

#### Direct Oxide Reduction (DOR)

Plutonium dioxide is reduced by calcium metal by the following overall reaction [26]:



The reaction is carried out in the presence of a molten CaCl<sub>2</sub> or CaCl<sub>2</sub>–CaF<sub>2</sub> salt. The salt provides at least two important functions: (1) the calcium metal is soluble in the salt, which provides a mechanism for transfer of calcium metal to the reaction site; and (2) the calcium oxide reaction product is

soluble in the salt, which provides a mechanism for removal of calcium oxide from the reaction site. Plutonium metal formed by the reduction has a high density and collects in the bottom of the crucible as a coalesced molten metal product.

This reduction is heterogeneous in that several separate phases may be present at various times during the reaction: (1) solid plutonium oxide; (2) calcium metal (either solid or liquid depending upon the reaction temperature); (3) molten salt; (4) solid CaO or CaO:2CaCl<sub>2</sub> (depending upon the CaO loading in the salt, the salt composition, and temperature); and (5) molten plutonium metal. To obtain rapid and efficient reduction, the system must be mixed with sufficient intensity to prevent the formation of pockets of unreacted material, to bring the reactants together, and to remove the reaction products from the reaction site.

The process has been used on a production scale at Los Alamos National Laboratory using CaCl<sub>2</sub> salt and stationary furnaces [27]. The process has recently been tested on a production scale at RFP, also using CaCl<sub>2</sub> salt and stationary furnaces. The lower melting binary CaCl<sub>2</sub>-CaF<sub>2</sub> salt may be required to use the process in tilt-pour furnaces at RFP.

### Electrorefining

Impure plutonium metal from MSE and DOR is sent to an electrorefining operation [28]. 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 [24].

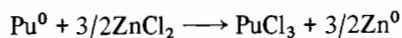
Spent anode residues from electrorefining (which contain approximately 20–30 percent of the plutonium fed to the process) are either recycled back to electrorefining, or, if high enough in impurities, are oxidized and sent to oxide dissolution. The spent salt is sent to aqueous dissolution (see Fig.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

Plutonium electrorefining was developed at Los Alamos and has been an established production operation since 1965 [29]. With minor modifications, the process has been used at RFP [30], Hanford, United Kingdom, and France with stationary furnaces. At

RFP, production electrorefining is conducted in induction heated, tilt-pour furnaces.

### Pyroredox

Pyroredox is an oxidation-reduction process for the removal from plutonium of impurity elements less chemically reactive than plutonium [31]. Zinc chloride oxidizes plutonium metal by the following reaction:



The impurity elements are taken up by the zinc metal reaction product. Plutonium chloride is taken up by a molten salt solvent. Plutonium is recovered from the salt by calcium reduction of PuCl<sub>3</sub> by the reaction:



A solvent salt is used to: (1) slow down the rates of the oxidation and reduction reactions by dilution of ZnCl<sub>2</sub> and PuCl<sub>3</sub> in the solvent salt, (2) form salt complexes to depress the volatility of ZnCl<sub>2</sub>, (3) provide a heat sink for reaction heat, and (4) provide a low melting point for the oxidation and reduction salt products.

Excess ZnCl<sub>2</sub> is used to drive the oxidation reaction, and excess calcium metal is used to drive the reduction reaction. The excess zinc (from excess ZnCl<sub>2</sub>) and excess calcium follow plutonium and collect in the plutonium metal reduction product. The excess zinc and calcium metal are separated from plutonium by distillation in a subsequent vacuum melting operation.

The process is presently under development at RFP and has been scaled up to a 2 kg batch of plutonium metal using a KCl-CaCl<sub>2</sub> solvent-salt heat sink. Additional small scale work (300 to 500 g plutonium) has been done using alternate salt solvents, high purity salts, and electrorefining anode heels as the feed metal.

Tilt-pour furnaces with metal crucibles (preferably tungsten) are required for production operation of the oxidation and reduction steps with 2 kg plutonium feed [31]. When ceramic crucibles are used, the reaction heat causes failure of the ceramics by thermal shock. High purity feed salts are required to avoid formation of salt and metal-insoluble impurities which are held up in the crucible upon pouring. Salt foaming during the oxidation step and dispersion of zinc metal (with impurities) in the oxidation product salt are major problems experienced in experiments conducted in tilt-pour furnaces. These problems appear to be minimized with the use of high purity salts.

Additional work is required on the distillation of zinc and calcium from plutonium. This work should be directed to determine conditions that maximize distillation rates and avoid splattering of molten plutonium metal.

### Americium Processing

Americium appears in all plutonium materials processed at RFP as the result of the beta decay of plutonium-241. Americium has been separated from plutonium process streams since the RFP plutonium recovery plant initiated operations in 1952.

Prior to 1960, americium was separated from plutonium by a peroxide precipitation process. Americium contained in the plutonium peroxide filtrate was precipitated with ammonia or caustic and stored. Americium was recovered from plutonium peroxide filtrate starting in 1960 using a thiocyanate ion exchange process [32]. In 1967, the MSE process was developed to extract americium directly from plutonium metal, eliminating the need to recover americium from plutonium peroxide filtrate [22, 23]. The MSE residues ( $\text{NaCl-KCl-MgCl}_2$ ) were first processed using hydroxide precipitation to isolate and concentrate americium from the chloride salts. Americium was then separated from plutonium by anion exchange and from impurities by the thiocyanate process; the americium was finally precipitated as the oxalate and calcined to the oxide. In 1975, the thiocyanate step was eliminated, the hydroxide precipitation process was replaced by cation exchange, and double oxalate precipitation of americium was introduced [33]. Recently, a carbonate precipitation process has replaced cation exchange (Fig. 2) [34, 35]. These process changes resulted in producing  $\text{AmO}_2$  of a purity comparable to that obtained by using the thiocyanate process since the MSE residues did not contain rare earths, aluminum, lead, calcium, zinc, and other interfering impurities. The  $\text{AmO}_2$  meeting specifications ( $>95$  wt.%  $\text{AmO}_2$ ,  $<1$  wt.% individual contaminant elements) was sent to the Department of Energy Isotope Pool at Oak Ridge National Laboratory.

### Present Americium Process

Processing of MSE waste salts (except those containing aluminum and zinc) is done by the RFP americium recovery process shown in Fig. 2. The process includes: (1) dissolution of the residues in dilute hydrochloric acid, (2) cation exchange or carbonate precipitation to convert from the chloride to the nitrate system and to remove gross amounts of monovalent impurities, (3) anion exchange to remove plutonium, (4) oxalate precipitation, and (5) calcination at  $600^\circ\text{C}$  to yield  $\text{AmO}_2$ .

The major problem encountered with the cation exchange process has been the large volume of acid required to elute the plutonium. Other problems have been with ion selectivity being less than expected. Consequently, residual cations such as magnesium, lead, calcium, and potassium are separated from the plutonium in the anion exchange step, but are carried to a limited extent into the americium oxalate precipitation. Lead and calcium contamination in americium continues to be a problem using carbonate precipitation.

### CMP Americium Purification Process

A variety of MSE residues and alloys has been generated from experimental runs and from changes in the salt mixtures used in the MSE process. These waste products can contain aluminum, calcium, zinc, and other minor impurities such as lead, which cannot be separated effectively from americium using the cation exchange or carbonate precipitation-oxalate precipitation processes. A new CMP process was developed using dihexyl-N,N-carbamoylmethyl phosphonate (DHDECMP) since it can separate trivalent actinides from the above impurity elements in  $5-7\text{ M HNO}_3$  (Fig. 3).

The use of the bifunctional organophosphorus extractant DHDECMP has been studied for actinide

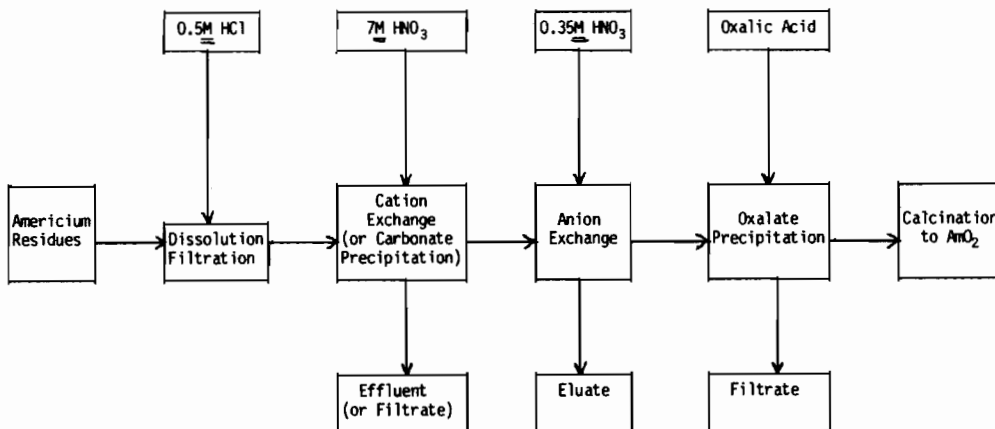


Fig. 2. RFP americium recovery process.

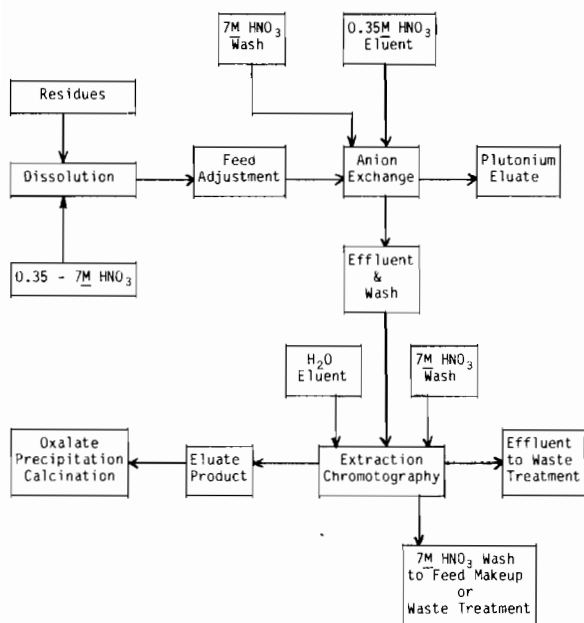


Fig. 3. Flow diagram of CMP process.

recovery processes for several years [36]. Following an earlier suggestion by Siddall [37], Schulz [38], and later others [9, 39–43] have demonstrated the usefulness of DHDECMP for the removal of actinides from radioactive acid wastes. Because DHDECMP extracts trivalent as well as tetravalent and hexavalent actinides and does not extract most other elements from 5–7 M HNO<sub>3</sub>, the extractant was tested for americium recovery and purification.

Preliminary laboratory scale studies at RFP have been reported using DHDECMP in the liquid-liquid extraction mode [44, 45]. However, since production scale ion exchange equipment is available at RFP, the extraction chromatography technique of sorbing DHDECMP onto a solid support has been developed. Various sorbents have been tested and Amberlite® XAD-4 has been selected for use [46]. Pilot plant studies of the combined anion exchange-extraction chromatography process for americium recovery and purification have been reported [25].

The process effectively separates and purifies americium from impurities such as aluminum, calcium, chloride, copper, fluoride, iron, lead, magnesium, plutonium, potassium, sodium and zinc. A total of 100 g of americium oxide was produced during pilot plant testing. The product oxide contained 96.5 wt.% AmO<sub>2</sub>, with 0.085 wt.% Pu and less than 0.15 wt.% of any other individual impurity element. No significant hydrolysis or radiolysis effects on the separation materials were observed. The resin capacity for actinides was essentially unchanged during the runs, and excellent recoveries, indicating adequate elution of actinides, were observed. Alpha radiation stability and the extent of acid hydrolysis

on DHDECMP-XAD resin have recently been determined [47].

The process is presently being tested on a production scale. Future work will examine the use of mixed extractants for the process; studies have shown that DHDECMP-TBP provide synergistic extraction of plutonium and americium [48, 49].

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