ORNL/TM-2004/174

Development and Evaluation Study for the Production of ^{238}Pu

December 2004

Prepared by

R. M. Wham
A. S. Icenhour
W. D. Bond
R. R. Brunson
T. D. Hylton
L. M. Toth
J. F. Birdwell

DOCUMENT AVAILABILITY

Reports produced after January 1, 1996, are generally available free via the U.S. Department of Energy (DOE) Information Bridge:

Web site: http://www.osti.gov/bridge

Reports produced before January 1, 1996, may be purchased by members of the public from the following source:

National Technical Information Service
5285 Port Royal Road
Springfield, VA 22161
Telephone: 703-605-6000 (1-800-553-6847)
TDD: 703-487-4639
Fax: 703-605-6900
E-mail: info@ntis.fedworld.gov
Web site: http://www.ntis.gov/support/ordernowabout.htm

Reports are available to DOE employees, DOE contractors, Energy Technology Data Exchange (ETDE) representatives, and International Nuclear Information System (INIS) representatives from the following source:

Office of Scientific and Technical Information
P.O. Box 62
Oak Ridge, TN 37831
Telephone: 865-576-8401
Fax: 865-576-5728
E-mail: reports@adonis.osti.gov
Web site: http://www.osti.gov/contact.html

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

ORNL/TM-2004/174

Nuclear Science and Technology Division

DEVELOPMENT AND EVALUATION STUDY FOR THE PRODUCTION OF ^{238}Pu

R. M. Wham
A. S. Icenhour
W. D. Bond
R. R. Brunson
T. D. Hylton
L. M. Toth
J. F. Birdwell

Date Published: December 2004

Prepared by
OAK RIDGE NATIONAL LABORATORY
P.O. Box 2008
Oak Ridge, Tennessee 37831-6283
managed by
UT-Battelle, LLC
for the
U.S. DEPARTMENT OF ENERGY
under contract DE-AC05-00OR22725

CONTENTS

LIST OF FIGURES

ACRONYMS AND ABBREVIATIONS

ATR	Advanced Test Reactor
CEPOD	catalyzed electrolytic plutonium oxide dissolution
DBP	dibutyl phosphoric acid
GPHS	General Purpose Heat Source (flowsheet)
HAN	hydroxylamine nitrate
HFIR	High Flux Isotope Reactor
MBP	monobutyl phosphoric acid
NPH	normal paraffin hydrocarbon
ORNL	Oak Ridge National Laboratory
REDC	Radiochemical Engineering Development Center
SEPHIS	Solvent Extraction Processes Having Interacting Solutes (model)
SRS	Savannah River Site
TBP	tributyl phosphate

ABSTRACT

Plutonium-238 is used as a heat source in radioisotope thermoelectric generators for deep space missions and other applications. This material can be produced by irradiating ^{237}Np in a nuclear reactor.

Studies have been undertaken at the Oak Ridge National Laboratory to evaluate the flowsheet for ^{237}Np target fabrication and irradiated target processing. The equipment and processes are similar to those that have been used for the past 35 years at the Radiochemical Engineering Development Center (REDC) in the production of transuranium elements. Consequently, the facilities and processes designed for target fabrication and processing are based closely on the proven methods used at REDC.

This report describes the processes to be used in ^{238}Pu production. Conceptual flowsheets from previous reports have been updated and modified based on experimental results and additional evaluation. The flowsheets for recovery and separation of neptunium and plutonium are based on coextracting these two transuranics in their quadrivalent (extractable) states and then partitioning the plutonium by reducing it to inextractable Pu(III). The production of ^{238}Pu is described from the process of target fabrication through ^{238}Pu pellet production. For some of the process steps, more than one option has been evaluated. Additionally, an option to directly produce the ^{238}Pu pellets has been added. This pellet production step, if adopted, would eliminate the concerns with handling dusty ^{238}PuO$_2$ powders.

1. INTRODUCTION

Plutonium-238 is used as a heat source in radioisotope thermoelectric generators for deep space missions and other applications. This isotope is produced by the irradiation of ^{237}Np targets in a nuclear reactor, followed by post-irradiation chemical processing to separate the plutonium. In a 2001 Record of Decision, the U.S. Department of Energy selected the Radiochemical Engineering Development Center (REDC) at the Oak Ridge National Laboratory (ORNL) as the location for target fabrication and processing (Federal Register 2001).

Studies have been undertaken at ORNL to evaluate the flowsheet for target fabrication and processing. Previous reports have provided a detailed description of the facilities available at ORNL as well as conceptual flowsheets (Wham et al. 2004a, 2004b, 2004c). The equipment and processes are similar to those that have been used for the past 35 years at the REDC in the production of transuranium elements. Consequently, the facilities and processes designed for target fabrication and processing are based closely on the proven methods used at REDC.

This report describes the processes to be used in ^{238}Pu production. Conceptual flowsheets from previous reports have been updated and modified based on experimental results and additional evaluation. The production of ^{238}Pu is described from the process of target fabrication through ^{238}Pu pellet production. For some of the process steps, more than one option has been evaluated. Additionally, an option to directly produce the ^{238}Pu pellets has been added. This pellet production step, if adopted, would eliminate the concerns with handling dusty $^{238}PuO_2$ powders.

An overview of these processes is provided in Fig. 1.1, while more details on each of the individual operations are provided in subsequent sections. A detailed conceptual flowsheet is provided in Appendix A.

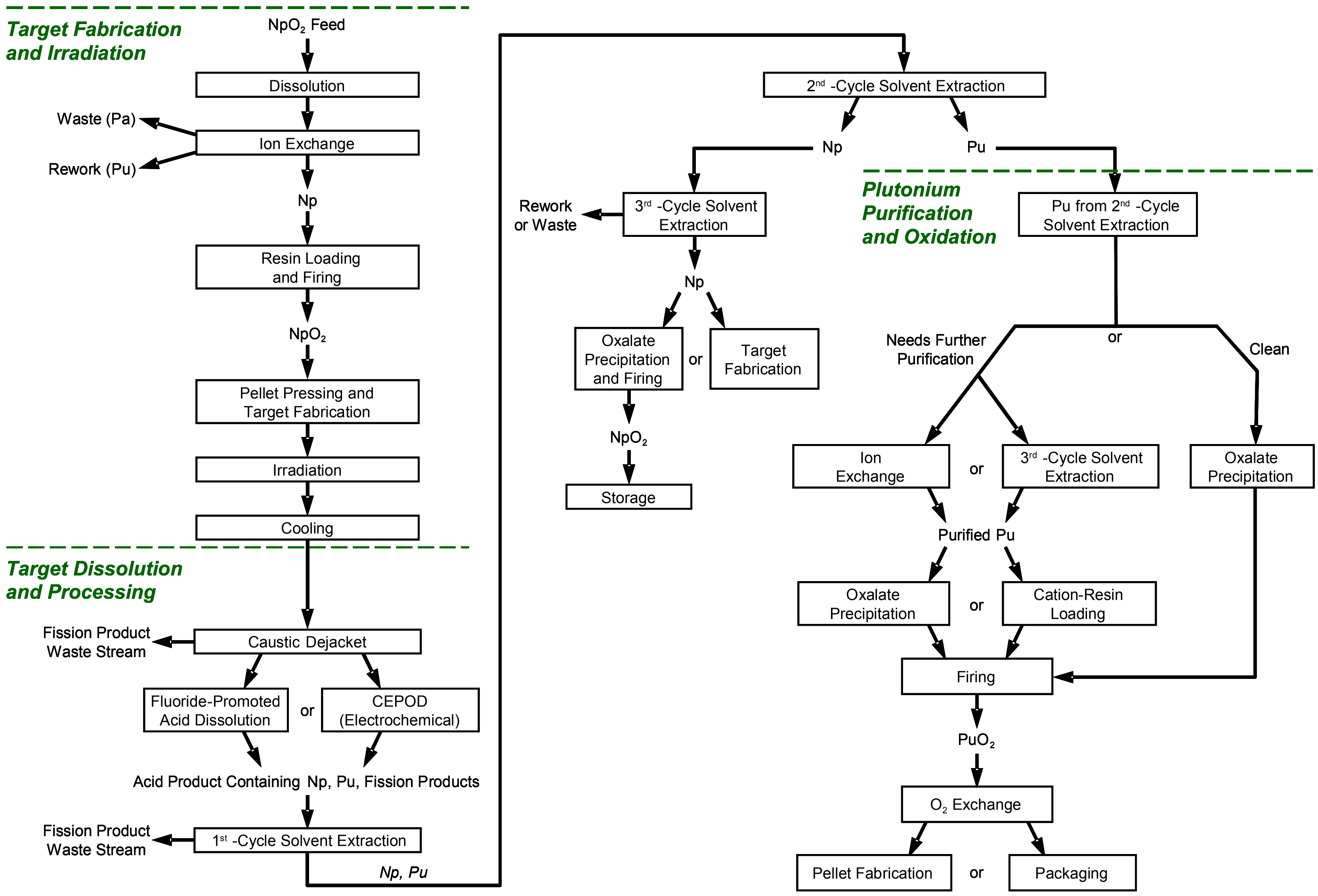


Fig. 1.1. Overview of ^{238}Pu production process.

2. TARGET FABRICATION AND IRRADIATION

Targets containing NpO_2 distributed in an aluminum matrix will be fabricated using methods similar to those used at ORNL for ^{244}Cm targets. The neptunium feedstock must be purified to lower the radiation hazard from the daughter product ^{233}Pa. A resin-loading process, based on the process to produce curium oxide, will be used to produce the NpO_2 for the target pellets. The fabricated targets will be fully tested prior to irradiation. The targets will be irradiated for multiple cycles in either the Advanced Test Reactor (ATR) or the High Flux Isotope Reactor (HFIR) to produce the desired amount and quality of product.

2.1 CONCEPTUAL TARGET DESCRIPTION

Targets will consist of pellets that are prepared from a mixture of NpO_2 and aluminum powder. The pellets will be contained inside an aluminum-clad rod of nominal dimensions 48 in. long and 0.25-in. ID. Based on irradiation experiments performed at ORNL to evaluate the loading of NpO_2 in the pellets (Icenhour et al. 2003; Wham et al. 2004a, 2004d), 10 vol % NpO_2 in the pellets has been chosen as the base case for production. This selection is driven primarily by the amount of ^{236}Pu production during irradiation. More experiments are planned to evaluate other target loadings.

For the 10 vol % NpO_2 targets, after two irradiation cycles, it was found that about 11 to 16 mol % of the neptunium had been converted to plutonium. The ^{238}Pu content ranged from 85 to 90 wt % of the total plutonium, while the ^{236}Pu content ranged from 3 to 4 ppm. Assuming that 14 mol % of the irradiated neptunium is converted to plutonium, of which 85 wt % is ^{238}Pu, 1200 to 1300 targets would need to be processed each year to produce 5 kg of ^{238}Pu. This number will vary based on the final target design and dimensions. Higher neptunium loadings would result in fewer targets; however, longer post-discharge decay time may be needed because of increased ^{236}Pu production. Fabrication of the targets would be based on techniques developed at ORNL and used for over 35 years for the production of transuranic isotopes.

2.2 NpO_2 PREPARATION

The preparation of the NpO_2 target material consists of dissolution, purification, and resin loading and firing. This material can then be formed into pellets (as an aluminum/NpO_2 mixture) and loaded into targets.

2.2.1 Acid Dissolution

The neptunium oxide stock from the Savannah River Site (SRS) will require purification to remove ^{238}Pu, ^{233}Pa, and fission products. The initial neptunium oxide feedstock will be dissolved in 8 M HNO_3–0.02 M NaF, which dissolves the actinides and most of the remaining fission products. The solution is filtered to remove solids and produce an acid-product feed for purification and conversion to an oxide.

The proposed facilities for conversion of neptunium to an oxide form and subsequent target fabrication are alpha glove boxes. The close coupling of the target-fabrication activities with the removal of the in-grown ^{233}Pa is very important. The protactinium reaches 90% of the equilibrium activity in ~10 weeks, which contributes significantly to the radiation doses in the target-fabrication line. Removal of the protactinium prior to oxide conversion and target fabrication will allow a few weeks to work with the material at lower dose rates.

2.2.2 Purification

The best approach for the removal of the protactinium, and possibly the easiest to implement, is to pass the neptunium solution through silica gel, which adsorbs the protactinium. This material would be regenerated or converted to a solid waste form for disposal. Due to the relatively short half-life of the ^{233}Pa (27 days), the radioactivity from this waste should be minimal. After ^{233}Pa removal, the purified neptunium solution can then be transferred to the target-fabrication glove-box line and the conversion of the neptunium to the oxide can be initiated.

2.2.3 Resin Loading and Firing

The desired form for the target fabrication is currently assumed to be oxide microspheres. The flowsheet is illustrated in Fig. 2.1. This form has been used for a number of years in the fabrication of curium recycle targets for irradiation in the HFIR at ORNL to produce the heavy transcurium radionuclides. To obtain this microsphere form, the neptunium is loaded on a cation-exchange resin—Dowex 50W-X8 has been used successfully—of selected particle size range (typically 60–80 μm). The loaded resin is washed with dilute acid and dried. To convert the loaded resin to the oxide, a multistep heating cycle with ramp and hold times using both air and 4% H_2–Ar streams is employed. The preferred method is to use heated air to burn the resin (providing the stoichiometric oxygen for the oxide conversion) and form the oxide microspheres. The heated air results in better heat transfer and reaction than that achieved by heating the resin with an external heat source such as a tube furnace. Also, with this method, the high-temperature heat sources could be located outside the glove box and the heated air could be piped into the resin column via insulated lines. The heating cycle would be similar to that used to produce curium oxide.

One drawback to the resin-loading process is the volume of waste generated by the feed loading and washing steps. As an alternative, NpO_2 derived from an oxalate precipitation process might be used directly for pellet production. With this method, oxalic acid is added to a dilute acid solution containing the valence-adjusted neptunium to form an insoluble neptunium oxalate that is recovered by filtration, air dried, and then calcined to yield a purified neptunium oxide. However, further testing of pellets fabricated from such material would be required to evaluate its performance under irradiation.

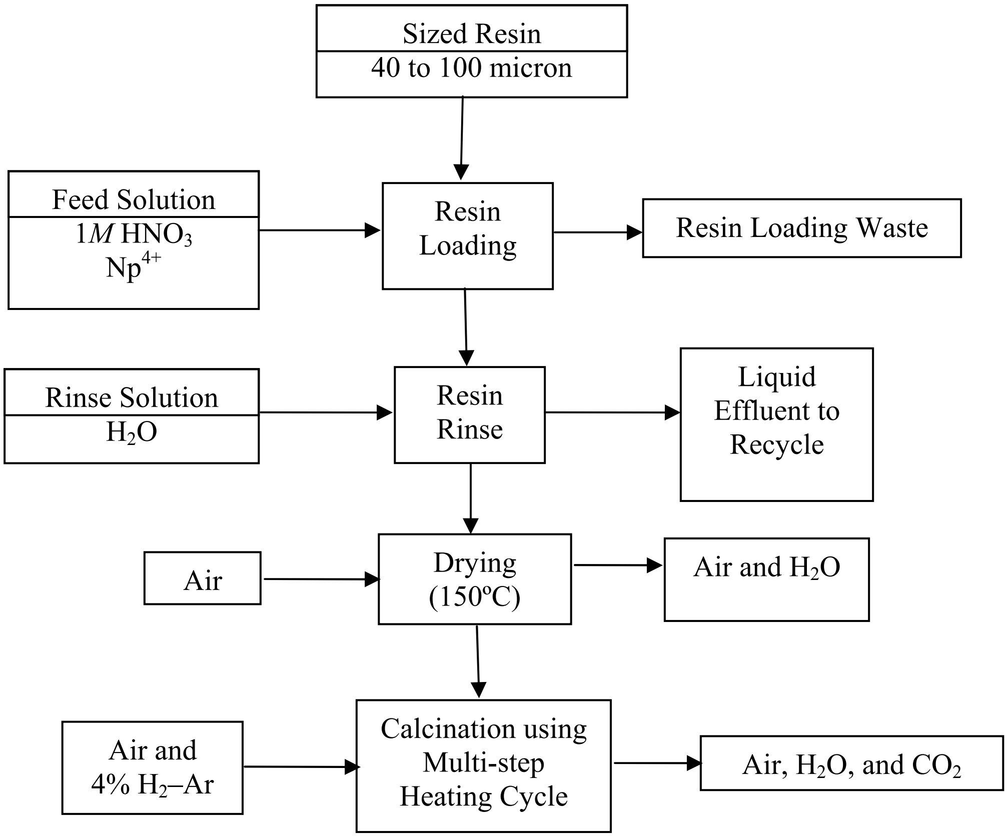


Fig. 2.1. Overview of resin-loading process for NpO_2 production.

2.2.4 Pellet Pressing and Target Fabrication

The target is an aluminum tube containing a stack of NpO_2 pellets. The pellets are fabricated with NpO_2 in an aluminum powder matrix. Target fabrication involves neptunium oxide preparation, oxide and aluminum powder blending, powder weighing, pellet fabrication, pellet cleaning, pellet examination, target tube fabrication, target tube loading, target examination/inspection, and target cleaning. A number of ORNL studies have been performed on the fabrication of targets for irradiations in the HFIR and the ATR (Wham et al. 2004d, 2004e).

An essential aspect of pellet fabrication is the development of a powder mixture of NpO_2 and aluminum that is not only homogeneous but also not readily segregated during powder-handling operations. Blended powders of different densities and particle sizes tend to segregate when tapped or shaken. Pellets will be pressed in a commercial press of capacity adequate to produce 1200 to1300 targets per year. Pellets will be pressed to ~90% theoretical density and then fired to remove impurities (e.g., stearic acid lubricant). After firing, the pellets will be inspected and tested to ensure that they meet specifications.

Loaded target tubes will be sealed by welding the top end cap in a positive-pressure helium-atmosphere glove box. After welding, the targets will be helium leak tested and radiographed. The targets will be compressed in a hydraulic chamber by applying 20,000 psig to put the tube wall in contact with the pellet stack. The targets will be radiographed again after compression to verify that a gap between the pellet stack and the inside wall does not exist. (Such a gap could serve as an insulator, reducing the heat transfer rates and causing the centerline temperature of the target to overheat.) The final radiographs will also serve as a recheck of both welded end caps for damage during compression. A final helium leak test and dye penetrant weld test will be performed on each target before the targets are cleaned and ready for shipment.

2.3 IRRADIATION

Targets will be irradiated in either the ATR or the HFIR. A number of configurations and cycles may be used for the irradiation, and these parameters will be optimized to achieve the desired ^{238}Pu production. The number of cycles impacts both the ^{238}Pu and ^{236}Pu yields, each of which must be considered in obtaining the required product attributes. For design purposes, the minimum ^{238}Pu content is taken to be 82 wt % of the total plutonium, while the maximum ^{236}Pu concentration is taken to be 2 ppm. Both of these values apply at the time of processing, so some decay may occur after discharge from the reactor.

Depending on the irradiation configuration used and the number of cycles, the targets will need to cool after discharge from the reactor to allow for the decay of ^{131}I and ^{236}Pu. A period of about 0.5 to 1 year should be sufficient for the ^{131}I decay. However, longer periods may be required depending on the

^{236}Pu concentration. Because of the short ^{236}Pu half-life (2.85 years), the targets may be held for a reasonable period (up to 3 years) to reach the ^{236}Pu specification, while not having a significant impact on the longer-lived (87.74-year half-life) ^{238}Pu.

A separate study by the Idaho National Engineering and Environmental Laboratory evaluated the potential production of ^{238}Pu in the ATR (Schnitzler 1998). The amount of ^{238}Pu produced and its quality are a function of the target loading, geometry, irradiation location, reactor power, cycle length, and the number of cycles. This study evaluated the effect of reasonable variations in these parameters on production. Calculations were performed for a minimal number of cycles in the reactor. Based on the results of this study, it is clear that a large fraction of the available reflector positions would have to be used. For targets containing 30 vol % NpO_2, about 75% of the reflector positions would be required for a yield of 4 kg/year. A similar yield could be achieved for 10 vol % targets, but the use of more irradiation positions would be required. To reduce the number of positions used, the number of cycles or neptunium loading could be increased; however, there is a trade-off in product quality (i.e., lower ^{238}Pu as a fraction of total plutonium and increased ^{236}Pu production) that would have to be evaluated. Another approach to achieve the desired production rate would be to build up a backlog of irradiated targets for processing. Finally, production can be supplemented by irradiation of targets in the HFIR.

The irradiation experiments performed by ORNL at the ATR (Icenhour et al. 2003) are being used to evaluate cross-section sets for modeling ^{238}Pu and ^{236}Pu production. Recent modeling efforts show good agreement between predicted and measured results. Additional experiments will further validate the models, which can then be used to develop optimized irradiation plans.

3. TARGET PROCESSING

After irradiation and cooling, the targets will be processed to extract the product material and to recycle the residual neptunium back into target production. The targets are first dissolved, and the resulting solutions are then sent through a series of separations processes. The plutonium product could be packaged for shipment, or alternatively, it could be pressed into pellets for use as heat sources.

3.1 DISSOLUTION

Dissolution of the aluminum-clad irradiated targets will be accomplished using a two-step process. A caustic nitrate solution will be used to dissolve the aluminum cladding, which will separate the bulk of the aluminum and caustic soluble fission products from the actinide products. An acid dissolution of the actinide products and remaining fission products will follow to prepare the feed for the first mainline separation process. Prior to adjustment, the feed will be filtered to remove solids—a procedure that produces a solids-free acid-product solution suitable for additional chemical adjustment for subsequent separation and purification steps. The steps used for the dissolution flowsheet have been demonstrated during the post-irradiation examination of targets irradiated at the ATR by ORNL (Icenhour et al 2003).

3.1.1 Caustic Dejacketing

The caustic dejacketing (Fig. 3.1) is accomplished by submerging the irradiated targets in 2.3 *M* $NaNO_3$ solution, heating to 90–95ºC, and then metering in 10 *M* NaOH solution at a controlled rate to sustain the dissolution reaction. The overall chemical reaction occurring during this caustic–nitrate dejacketing step is given as follows:

$$Al + 0.63NaOH + 0.38NaNO_3 + 0.26H_2O \rightarrow NaAlO_2 + 0.37NH_3 + 0.01NaNO_2 + 0.02H_2 \ . \qquad (3.1)$$

The use of the sodium nitrate solution significantly reduces the formation of hydrogen gas during the dissolution when compared with dissolution in sodium hydroxide alone. The aluminum-bearing caustic solution is then pumped through sintered stainless steel filters and discarded as waste. The filter is backflushed to the dissolver tank. The remaining solids are then dissolved in the acid dissolution process.

3.1.2 Acid Dissolution

Acid dissolution of the residual solids may be performed by either fluoride-promoted dissolution (i.e., HNO_3 plus a small amount of fluoride) or catalyzed electrolytic plutonium oxide dissolution (CEPOD).

3.1.2.1 Fluoride-promoted acid dissolution

After the caustic dissolution the remaining neptunium and plutonium oxides will be dissolved using 8 *M* HNO_3 with 0.02 *M* NaF (Fig. 3.2). A small amount of $Al(NO_3)_3$ will be added to react with any excess fluorides. The solution will be continuously agitated and heated to gentle reflux with the temperature maintained between 106 and108ºC. After cooling, the acid-product solution will be pumped from the dissolver to a storage vessel through a 2-µm filter to remove any remaining solids. A series of acid flushes will be performed to wash the dissolver tank and any residual product or solids using 8 *M* HNO_3 –0.02 *M* NaF. The product will then be stored for analytical evaluation and feed adjustments for separation operations.

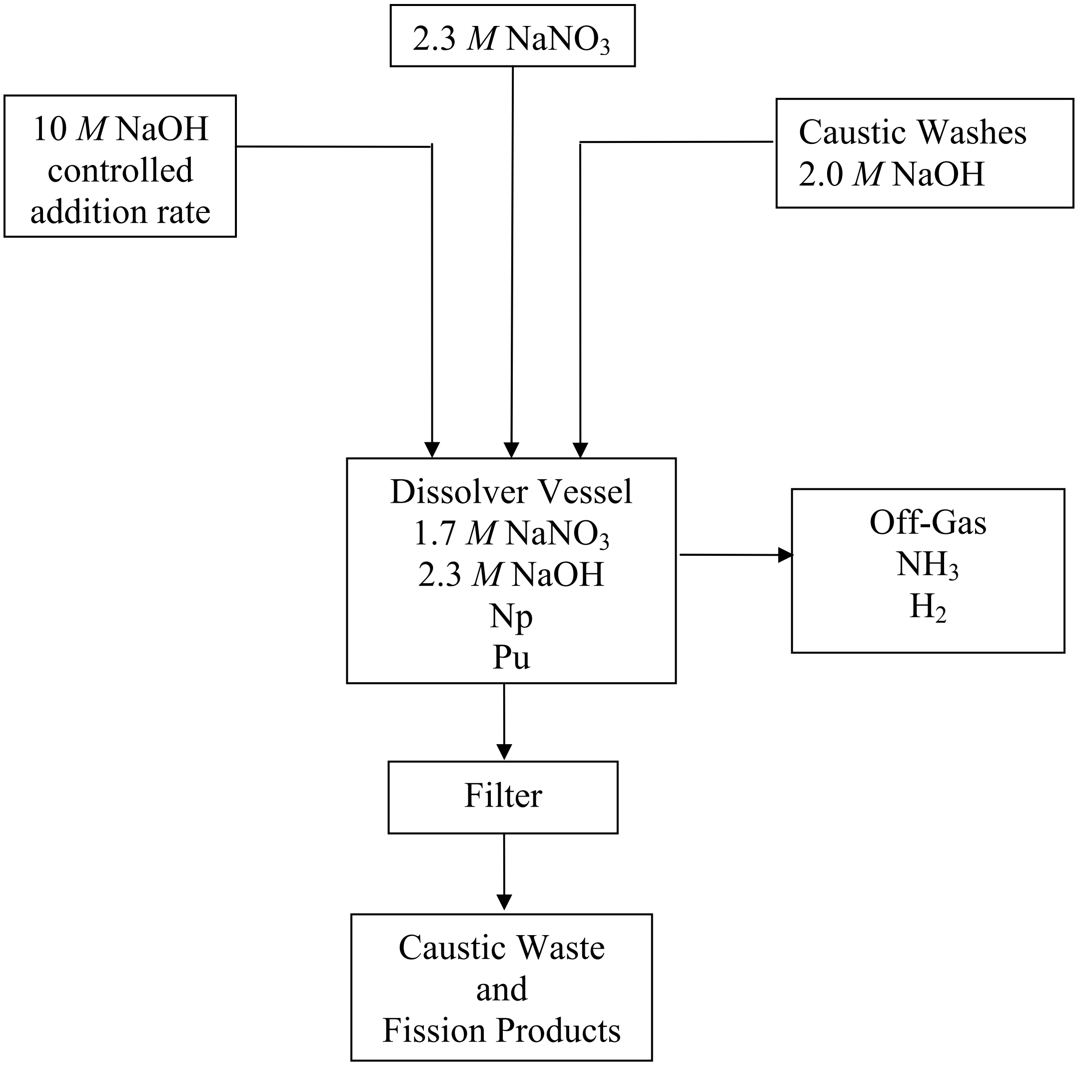


Fig. 3.1. Overview of caustic dejacketing flowsheet.

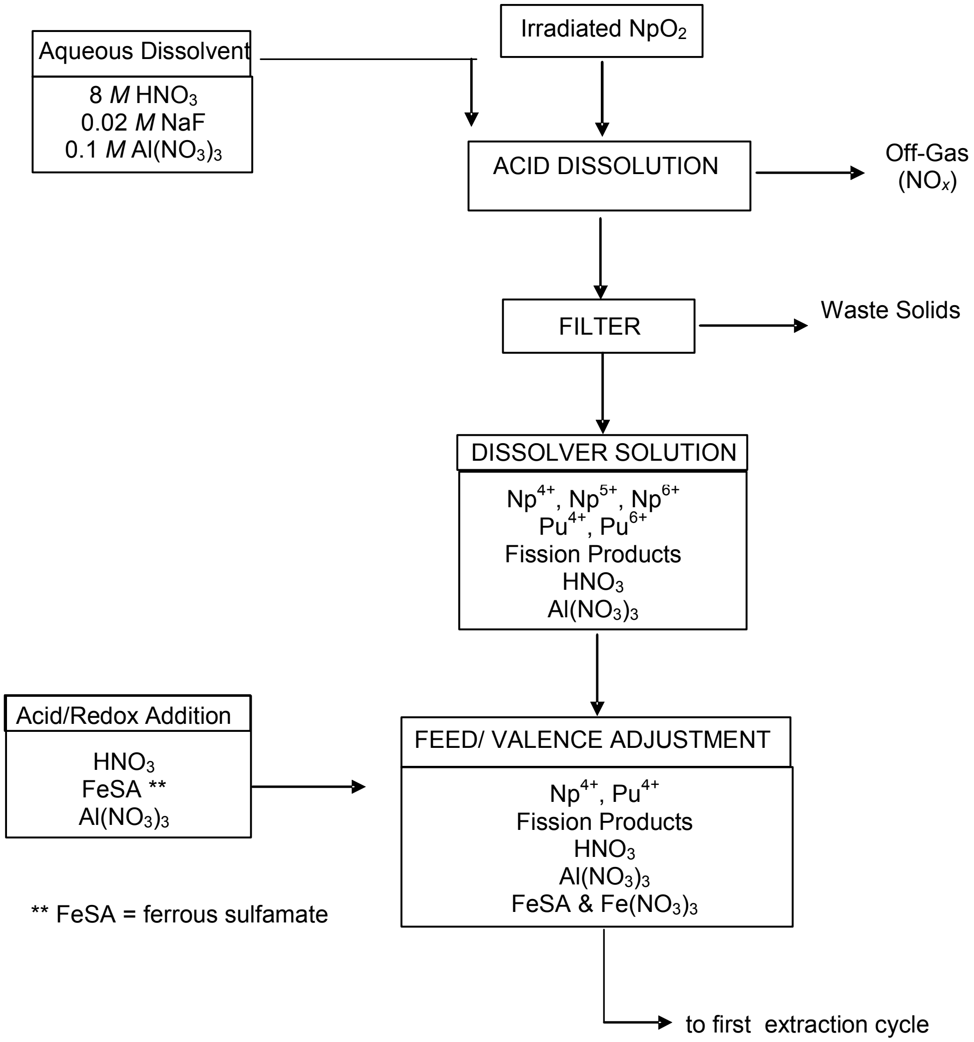


Fig. 3.2. Overview of fluoride-promoted acid-dissolution flowsheet.

3.1.2.2 CEPOD dissolution

Another target dissolution method CEPOD, which eliminates the use of fluorides in the dissolution process, was investigated. CEPOD is an electrolytic process that has been used to dissolve PuO_2 in an anolyte containing small catalytic amounts of Ce(IV) that forms kinetically fast, strongly oxidizing ions. The oxidizing ions are regenerated at the anode and act in a catalytic manner, carrying electrons from the solid PuO_2 surface to the anode of the electrochemical cell. A more detailed description of the theory of operation is provided in Hylton et al. (2004).

A laboratory-scale CEPOD cell was fabricated and tested at REDC to dissolve PuO_2 in a glove box. Based on the glove-box model, a CEPOD cell was developed to dissolve irradiated NpO_2 targets in a hot cell.

Three irradiated, aluminum-clad NpO_2 pellets were processed in the hot cell using the previously described aluminum caustic dissolution to dissolve the aluminum cladding and pellet matrix. On completion of the aluminum dissolution, the caustic solution was transferred out of the CEPOD cell. The remaining solids were washed several times with caustic solution. The electrolytic dissolution of the solids was carried out using 4 *M* HNO_3–0.15 *M* Ce in the dissolution vessel. Direct current was applied to the electrodes at ~3 A. The solution was continuously agitated and heated to ~60–80ºC. The pellets were dissolved within ~1–2 h, and analysis indicated that the process was comparable to the fluoride-promoted dissolution previously described. This dissolution test is further described in Hylton et al. (2004).

3.2 SEPARATIONS

The plutonium and neptunium in the dissolver solution will be processed through a separations cycle to yield the final plutonium product and the neptunium for recycle. The chemistry of these solutions greatly affects the separations. Aqueous chemicals are traditionally used for chemistry control in such separations systems. However, electrochemical methods, combined with spectrophotometric analytical techniques, may also be effective. A two-cycle solvent-extraction system is used to provide separated plutonium and neptunium streams. These streams may then be further purified before preparation of the final products.

3.2.1 Chemistry of Plutonium and Neptunium Solutions

Valence control and stability are a critical part of the solvent extraction separations envisioned for plutonium purification. The key to development of appropriate valence-adjustment steps is to first review the fundamental chemistry underlying the determination of plutonium and neptunium valences.

3.2.1.1 Valence control and stability

The flowsheets for recovery and separation of neptunium and plutonium described here are based on coextracting these two transuranics in their quadrivalent (extractable) states and then partitioning the plutonium by reducing it to inextractable Pu(III). Maintaining the valence states both in the feed stream and in the extraction banks is necessary to prevent losses of neptunium or plutonium. Solutions containing excess ferrous ion or hydroxylamine nitrate (HAN) can be employed to reduce hexavalent or pentavalent neptunium to the quadrivalent form and to reduce quadrivalent plutonium to the trivalent form.

The stability of inextractable pentavalent neptunium in 0.5 to 4 *M* HNO_3 solutions makes it difficult to maintain the extractable tetravalent or hexavalent species in highly radioactive solutions (Drake 1990). This is mainly a result of the radiolytic generation of nitrous acid (HNO_2). When the neptunium solutions contain macro (grams-per-liter) quantities of ^{238}Pu (0.55 W/g), the radiolytic species are generated at rates too rapid to maintain 99.9% of the neptunium/plutonium in the extractable valence states for practical processing times (Thompson and Thompson, 1977a). Nevertheless, results of continuous-countercurrent extraction tests at the SRS (Thompson and Thompson, 1977b) indicated that the judicious use of aqueous backscrub streams containing reducing agents may make it possible to eliminate losses caused by radiolytic products forming NpO_2^+ from Np(IV) or NpO_2^{2+}. The location of the reductive backscrub stream within the coextraction bank is critical because reductants that reduce inextractable Np(V) to extractable Np(IV) also reduce extractable Pu(IV) to inextractable Pu(III). Therefore, the backscrub stream must be inserted at a location where the more-extractable Pu(IV) has already been removed and only neptunium species are present in the organic and aqueous phases.

Nitrous acid does not lead to plutonium inextractability because it oxidizes the trivalent form to extractable Pu(IV) and reduces the extractable hexavalent form to extractable Pu(IV) by the following irreversible reactions:

$$Pu^{3+} + HNO_2 + H^+ \rightarrow Pu^{4+} + NO + H_2O \qquad (3.2)$$

and

$$PuO_2^{2+} + HNO_2 + H^+ \rightarrow Pu^{4+} + NO_3^- + H_2O \,. \qquad (3.3)$$

The neptunium reactions are quite different with HNO_2. Extractable Np(IV) is oxidized to inextractable NpO_2^+ [Eq. (3.4)]. The NpO_2^+, in turn, may be either completely or partially oxidized by HNO_3 to extractable NpO_2^{2+}, depending on the HNO_2 concentration, according to the reversible reaction [Eq. (3.5)]:

$$Np^{4+} + HNO_2 + H_2O \rightarrow NpO_2^+ + NO + 3H^+ \tag{3.4}$$

and

$$2NpO_2^+ + NO_3^- + 3H^+ \rightleftharpoons 2NpO_2^{2+} + HNO_2 + H_2O\,. \tag{3.5}$$

When HNO_2 concentrations are maintained below 0.001 *M* in HNO_3 solutions, NpO_2^+ is completely oxidized to NpO_2^{2+}; above that value, reduction of NpO_2^{2+} begins and increases rapidly with increasing HNO_2 concentration (Shulz and Benedict 1972). The reactions shown in Eqs. (3.2) and (3.4) are autocatalytic, or self-accelerating, because the NO formed in each case generates additional HNO_2, according to

$$2NO + H_2O + HNO_3 \rightarrow 3HNO_2\,. \tag{3.6}$$

Once initiated, the reactions shown in Eqs. (3.2) and (3.4) proceed very rapidly. Similar to Pu(IV), Np(IV) is very stable at high HNO_3 concentrations (6 *M*) because of NpO_2^+ disproportionation and almost complete complexation of Np(IV) by nitrate ions (Thompson and Thompson 1977b):

$$2NpO_2^+ + 4H^+ \rightarrow Np^{4+} + NpO_2^{2+} + 2H_2O \tag{3.7}$$

and

$$Np^{4+} + 6NO_3^- \rightarrow Np(NO_3)_6^{2-} \tag{3.8}$$

Equations (3.7) and (3.8) provide the principal basis for recovery and separation of neptunium by anion-exchange methods such as those previously employed at SRS for ^{237}Np–^{238}Pu recovery and separation (Groh and Schlea, 1970). Agents such as HNO_2 are added to reduce the NpO_2^{2+} formed in Eq. (3.7) to NpO_2^+ and thus produce only Np(IV).

Nitrous acid scavengers have been used extensively in processing irradiated targets and spent nuclear fuels for recovery and separation of uranium, neptunium, and plutonium (Groh and Schlea 1970; Bond 1981). The function of the scavenger is to react with HNO_2 as it is formed and thereby prevent its reactions with plutonium and neptunium. Typical scavengers that have been employed include sulfamic acid (NH_2SO_3H), hydrazine nitrate ($N_2H_5NO_3$), and urea (NH_2CONH_2). These scavengers react to give soluble products and gases. The reaction for sulfamic acid is

$$NH_2SO_3H + HNO_2 \rightarrow H_2SO_4 + N_2 + H_2O\,. \tag{3.9}$$

The specific gases involved in the hydrazine–HNO_2 reaction depend on the relative amounts of HNO_2 and hydrazine present. With stoichiometric or excess amounts of hydrazine, azoic acid is formed [Eq. (3.10)], whereas excess HNO_2 leads to the formation of N_2 and N_2O [Eq. (3.11)]:

$$N_2H_5NO_3 + HNO_2 \rightarrow HN_3 + 2H_2O + HNO_3 \tag{3.10}$$

and

$$HN_3 + HNO_2 \rightarrow N_2 + N_2O + H_2O\,. \tag{3.11}$$

In contrast with hydrazine, urea reacts to form only N_2 and CO_2 gases:

$$NH_2CONH_2 + 2HNO_2 \rightarrow 2N_2 + CO_2 + 3H_2O\,. \tag{3.12}$$

Sulfamic acid has been the scavenger used most extensively in PUREX processing. However, it has the disadvantage of adding sulfate to the aqueous waste. Although hydrazine has also been used, it results in the generation of azoic acid and raises potential safety concerns. Urea reacts more slowly than either sulfamic acid or hydrazine and finds its principal application in removing HNO_2 from feed streams to solvent extraction or ion-exchange processes. Because of its slow reaction rate, HAN requires high concentrations when used for HNO_2 scavenging. Therefore, it has not normally been employed.

3.2.1.2 Reduction kinetics

Because of its successful use in valence adjustment of plutonium and neptunium, ferrous ion in combination with a suitable scavenging agent, such as sulfamic acid, has been selected as the reductant of choice for use in the first cycle. The reduction reactions for the neptunium and the plutonium are

$$NpO_2^+ + Fe^{2+} + 4H^+ \rightarrow Np^{4+} + Fe^{3+} + 2H_2O \tag{3.13}$$

and

$$Pu^{4+} + Fe^{2+} \rightarrow Pu^{3+} + Fe^{3+}\,. \tag{3.14}$$

The reaction half-time for reduction of NpO_2^+ with ferrous ion [Eq. (3.13)] is on the order of minutes. The reaction rate is first-power dependent on the Fe(II) and NpO_2^+ concentrations and varies with the

1.38-power dependence on H^+ concentration (Orth et al. 1984). The reduction of Pu(IV) [Eq. (3.14)] is much faster. The reaction is first-power dependent on the Fe(II) and Pu(IV) concentrations but is inverse first-power dependent on the H^+ concentration.

For first-cycle coextraction, the Pu(III) is oxidized back to the tetravalent state with the HNO_2 that is generated by heating the solution or that is added as nitrite. Potentiometric titration may be required to ensure that only the plutonium is oxidized.

The use of HAN as the reductant in the second- and third-cycle separations is preferred because it does not lead to additional processing of plutonium products or add to the waste volumes as does the use of ferrous ion. However, it appears that reaction with HAN is too slow to accomplish the reduction of NpO_2^+ to Np(IV) when it is used as backscrub stream or when the neptunium is in continuous-countercurrent extraction banks. Nevertheless, it may be advantageous to use HAN in the primary reduction of the feed solutions. Excess HAN reduces NpO_2^+ to Np(IV) according to Eq. (3.15) and Pu(IV) to Pu(III) via Eq. (3.16):

$$NpO_2^+ + NH_3OH^+ + 2H^+ \rightarrow Np^{4+} + \tfrac{1}{2}N_2 + 3H_2O \qquad (3.15)$$

and

$$Pu^{4+} + NH_3OH^+ \rightarrow Pu^{3+} + \tfrac{1}{2}N_2 + H_2O + 2H^+ . \qquad (3.16)$$

The reduction of Pu(IV) occurs much more rapidly than does that of NpO_2^+, and thus HAN has been used with success in plutonium partitioning and purification cycles where low acidity (0.3 to 0.5 *M*) may be utilized (Bond 1981). The reaction-rate dependence on H^+ is complex and varies as $[H^+]^n$. Reported values of *n* vary from 4 to 6 (Bond 1981; Orth et al.1984), which indicates a very strong dependence on H^+. The rate of reduction of NpO_2^+ is insignificant at room temperature, but reduction at elevated temperature occurs within a few hours (Orth et al. 1984) The H^+ dependence of the reaction rate for Eq. (3.15) is $[H^+]^{1.65}$. When Pu(IV) is present in NpO_2^+ solutions, it catalyzes the reaction shown in Eq. (3.15). The reaction half-times may be as short as 1 to 3 h for HNO_3 concentrations of 1 to 3 *M* at 35ºC. Therefore, HAN may well have application in primary feed adjustment, but such use would require verification in experimental tests.

3.2.1.3 Effects of HNO_3 and neutral-salt concentrations on neptunium and plutonium extraction

Nitric acid is extracted into tributyl phosphate (TBP), whereas neutral salts such as aluminum or calcium nitrates are virtually inextractable. Because of the moderate extractability of solvates of HNO_3 (e.g., HNO_3• TBP), HNO_3 is extracted in significant amounts at high acidity and serves to limit the capacities of TBP solvents. This phenomenon is illustrated in Fig. 3.3 (Bond 1981). Increasing the HNO_3 concentration increases actinide extractability because of the mass-action effect that drives the formation

ORNL DWG 99C-348

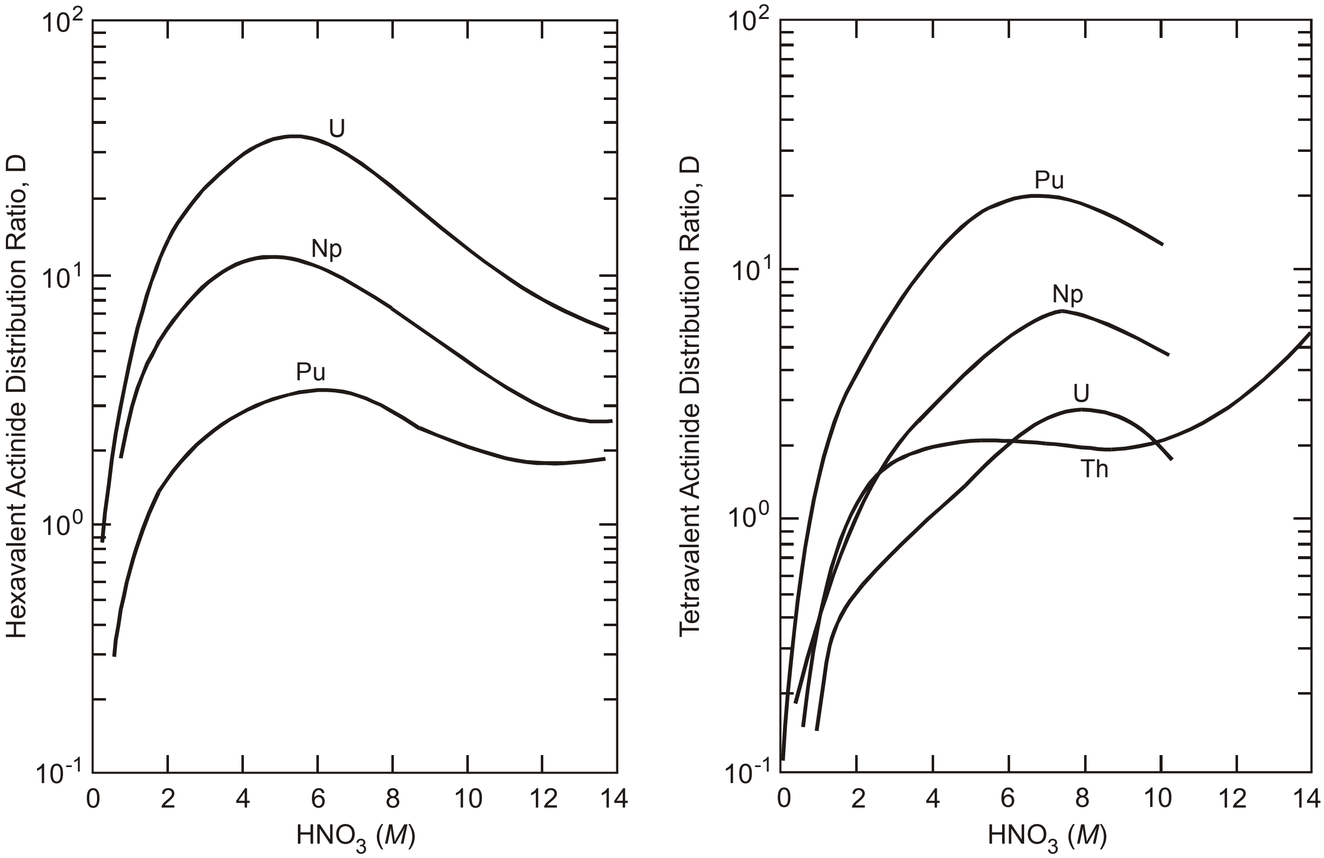


Fig. 3.3. Extraction of tracer concentrations of hexavalent and tetravalent actinides by 19% TBP as a function of HNO_3 concentration of the equilibrium aqueous phase at 25°C (kerosene diluent).

of organic-soluble TBP solvates of the actinide nitrates [e.g., $Pu(NO_3)_4 \bullet 2TBP$] from Pu(IV) ions. However, the extractability reaches a maximum and then decreases because the loading of HNO_3 solvates into the TBP phase offsets the mass-action effect on actinides. Neutral nitrate salts of the monovalent, divalent, and trivalent elements enhance actinide extractability because the extractability of these salts is almost negligible (Orth et al. 1984).

Although the extraction coefficient of quadrivalent neptunium is much lower than that of hexavalent neptunium, for solvent extraction flowsheets, we chose to extract the former from 1–2 *M* HNO_3 solutions. Previous studies at Savannah River (Thompson and Thompson 1977b) had indicated that at significant radioactivity levels, the quadrivalent state was more maintainable throughout the multistage solvent extraction operations than the hexavalent state. To offset the disadvantage of lower extraction coefficients of Np(IV), aluminum nitrate was added to feed solutions to a 1 *M* Al(III) (3 *M* NO_3^-) concentration.

3.2.1.4 Effect of temperature on neptunium and plutonium extraction

The enthalpy change for the extraction of actinides is very small, and modest changes in temperature do not greatly enhance or inhibit extraction by TBP. Enthalpy changes for the extraction of the nitrates of quadrivalent neptunium and plutonium are positive (2–3 kcal/mol), whereas such changes for the hexavalent state are negative (3–5 kcal/mol).

3.2.1.5 Effect of radiation on process solutions

Because of the intense radiation from ^{238}Pu ($t_{1/2}$ = 87.7 years , 0.55 W/g), significant quantities of radiolytically generated species are present in both aqueous and organic solutions containing this isotope. In the aqueous phase, the principal species produced is nitrous acid, which undergoes redox reactions with both plutonium and neptunium. Thus, valence control is difficult throughout the processing sequence of extraction cycles. Hydrogen peroxide is also produced. However, it is destroyed by nitrous acid and will not accumulate in solutions that are >0.5 *M* HNO_3 (Savel'ev et al. 1967):

$$HNO_2 + H_2O_2 \rightarrow HNO_3 + H_2O \,. \qquad (3.17)$$

Hydrogen peroxide and nitrous acid are also produced in the organic phase because of the presence of extracted nitric acid and water.

Dibutyl phosphoric acid (DBP) and monobutyl phosphoric acid (MBP) are formed from the radiolysis of the TBP extractant. These alkyl phosphoric acids are powerful extractants for both Pu(IV) and Np(IV), rendering them virtually unstrippable with aqueous acid solutions. Also, many cations extracted by DBP and MBP result in the formation of compounds that have very limited solubility (Davis 1961) in organic and aqueous phases and cause operational difficulties. Therefore, the concentration of ^{238}Pu in feed solutions and/or residence time of extraction cascades must be selected so that excessive quantities are not produced and result in excessive losses. The solvent must be purified if it is to be recycled (see Sect. 3.2.1.6).

Mixer–settlers are reported (Warner et al. 1974) to produce about 40-fold more DBP than centrifugal contactors. The choice of extraction contactors will depend on the feed concentrations and the throughput desired. Savannah River researchers (Thompson and Thompson 1977b) reported no difficulties from DBP/MBP when using mixer–settlers in the processing of irradiated neptunium targets at feed concentrations of 0.4–1.0 g/L plutonium.

Because of the high specific activity of ^{238}Pu, it will be important to remove the entrained TBP from plutonium product streams in solvent extraction cycles. If solutions are allowed to stand in holdup for appreciable periods of time, solid compounds will form from plutonium and degradation products of TBP (Thompson and Thompson 1977b). A normal paraffin hydrocarbon (NPH) diluent wash of product solutions is used to remove the TBP.

Phosphoric acid is rapidly produced from TBP in thermal evaporation of aqueous solutions; thus, its presence is to be avoided in intercycle evaporators. Phosphoric acid inhibits the reextraction of plutonium in the subsequent cycle (Bond 1981).

3.2.1.6 Solvent purification and recycle

In addition to radiolytic reactions, TBP also undergoes both thermal and chemical hydrolysis via the following reactions:

$$(C_4H_9O)_3PO \quad + \quad HOH \quad \rightarrow \quad (C_4H_9O)_2\,POOH \quad + \quad C_4H_9OH\ , \qquad (3.18)$$

$$(C_4H_9O)_2\,POOH \quad + \quad HOH \quad \rightarrow \quad (C_4H_9O)_2\,PO(OH)_2 \quad + \quad C_4H_9OH\ , \qquad (3.19)$$

and

$$(C_4H_9O)_2\,PO(OH)_2 \quad + \quad HOH \quad \rightarrow \quad H_3PO_4 \quad + \quad C_4H_9OH\ . \qquad (3.20)$$

Therefore, it must be purified of alkyl phosphoric acids before its reuse in solvent extraction (Bond 1981). The TBP is purified by a single-stage batch contact with an aqueous sodium carbonate solution, in which the aqueous-soluble sodium salts of DBP and MBP transfer to the aqueous phase:

$$2(C_4H_9O)_2\,POOH \quad + \quad Na_2CO_3 \quad \rightarrow \quad 2(C_4H_9O)_2\,POONa \quad + \quad 2NaHCO_3\ . \qquad (3.21)$$

The spent solvent from the solvent extraction cycle also contains solvates of TBP •HNO_3, and the nitric acid is removed as aqueous soluble $NaNO_3$:

$$TBP \bullet HNO_3 \quad + \quad Na_2CO_3 \quad \rightarrow \quad TBP \quad + \quad NaNO_3 \quad + \quad NaHCO_3 \qquad (3.22)$$

After scrubbing with the sodium carbonate solution, the solvent is contacted with dilute nitric acid to remove any entrained carbonate and to reacidify it before it is returned to the solvent extraction cycle. In addition to removal of DBP and MBP, the solvent purification after each cycle inhibits the buildup of secondary degradation products such as butyl lauryl phosphoric acid (Maya and Bopp 1978). Secondary degradation products result from irradiation-produced free radicals from the diluent combining with those produced from the TBP extractant (Bond 1980).

3.2.1.7 Solvent extraction modeling

The conceptual solvent extraction processing flowsheets for the separation of neptunium and plutonium were evaluated using the Solvent Extraction Processes Having Interacting Solutes (SEPHIS) computational model (Watson and Ramey 1975, Mills 1990) This model predicts the extraction behavior of U(VI), Pu(III and IV), and nitric acid. The model accounts for the effects of nonextracting nitrates on the partitioning of these solutes and also has the capability to calculate the effect of reductant addition on plutonium distribution.

In the application of SEPHIS to neptunium extractions, it was assumed that the neptunium extraction coefficients could be predicted on the basis of equations previously developed for the recovery and separation of uranium and plutonium by TBP extraction. The data for uranium and plutonium extraction are extensive, and the SEPHIS code accurately predicts their distribution throughout multistage countercurrent extraction systems. The variation of neptunium distribution with solution parameters such as the organic- and aqueous-phase concentrations of metal nitrate salts and HNO_3 has not been investigated extensively. Nevertheless, it is sufficient to make reasonable estimates of the stages required to achieve desired recoveries of neptunium and plutonium. It is also assumed that valence control can be achieved primarily in the feed-adjustment operations, with additional or secondary controls provided by judicious introduction of reductants at certain stage positions of the countercurrent solvent extraction bank.

Since no algorithms specifically describe the partitioning behavior of Np(IV), the SEPHIS code was modified by adding a distribution prediction capability for neptunium. Equilibrium distribution data for Np(IV) indicate that its distribution coefficients are approximately one-third those for Pu(IV) over the range of conditions applicable to this process. Therefore, the Np(IV) distribution coefficients used in the revised SEPHIS code were calculated using a modified form of the Pu(IV) distribution coefficient algorithm. The validity of the model was evaluated by performing a simulation using parameters applied in flowsheet tests performed at SRS and comparing predicted and experimental results. The SEPHIS program does not take into account either (a) the redox kinetics of neptunium and plutonium or (b) the effects of radiolytic degradation products on process recoveries and losses. It was assumed that chemical and physical process conditions can be selected to control recoveries and losses of neptunium and plutonium at acceptable levels. Development work will be required to demonstrate that such process conditions can be met.

3.2.2 Electrochemistry

As an alternative to process control through chemical additions, electrochemical control of the actinide oxidation states has been shown to be possible under laboratory conditions (Cohen 1961, Hindman et al. 1956). If it is at all practical for process control, it could significantly reduce (or eliminate) the amount of redox agent that must be added. The addition of some holding reductants might still be necessary, but any minimization of these additions could be a significant process simplification that deserves further consideration. Especially desirable would be the elimination of the ferrous sulfamate reductant, because of its spectral interference with the analytical determination of the on-line actinide determinations and the ultimate disposal nuisance that its presence adds to the waste solutions.

It is envisioned that a simple electrochemical potential might be applied in the feed-adjustment tanks and then even downstream, as deemed necessary to hold the desired oxidation states in solution. Of course, the need for the addition of either chemical or electrochemical control in the process would be established by on-line analytical measurements such as those described in the following section.

3.2.3 Spectrophotometric Process Control

The need for redox control of the aqueous feed lies in the fact that only a few of the oxidation states of neptunium and plutonium are extractable. Therefore, in order to achieve efficient separation and purification of these actinides, it is necessary that the oxidation states be set and held at specific values. However, radiolytic products from the intense ^{238}Pu alpha/aqueous solution interaction compromise this redox control by reacting with the actinide species to produce other oxidation states that cannot be separated by the process. The remedy for these competing reactions and the resulting kinetic instability is to adjust the oxidation states of the actinides as necessary and to separate them before they have a chance to reactively change. In order to achieve such control, some analytical means of identifying the oxidation states is required, as well as a means to follow the stability of these actinide species prior to their decomposition. It is best that these species be observed on-line, because off-line determinations on such kinetically unstable solutions usually cannot be made fast enough to accurately characterize the chemical conditions at the time of sampling.

Absorption spectrophotometry is perhaps the only means of achieving this direct on-line measurement with the quantitative detail required for the separation process. It is particularly attractive for the actinides since the various oxidation states of neptunium and plutonium have distinct characteristic spectra that permit the determination of both the species and its concentration. For example, Figs. 3.4–3.11 illustrate calibration spectra for the various oxidation states of these actinides at 22ºC in

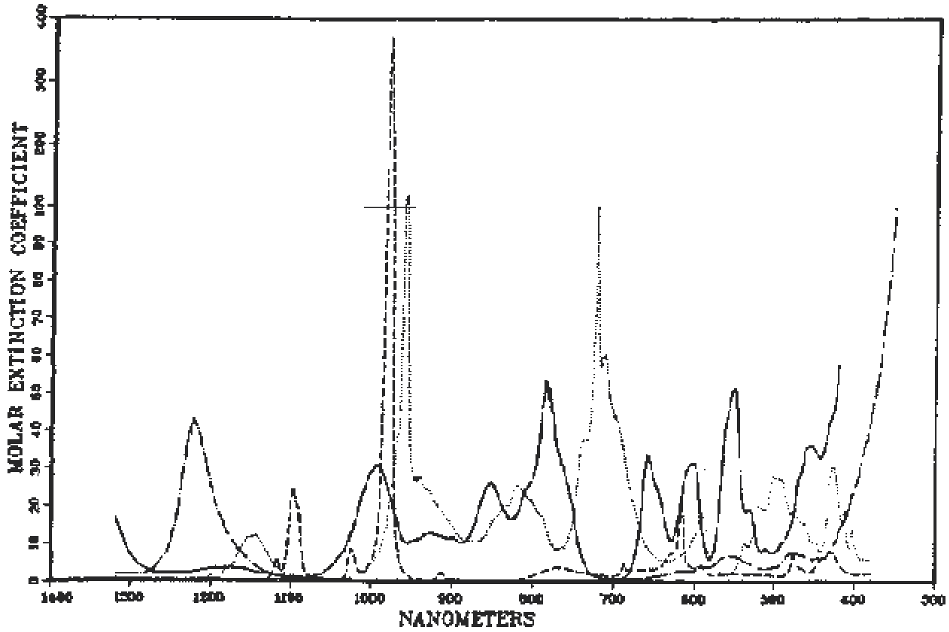


Fig. 3.4. Absorption spectrum of neptunium ions in 0.1 *M* HNO_3 at 22ºC. ----, Np(III); …., Np(IV); _ _ _ _, Np(V); -.-.-.-., Np(VI).

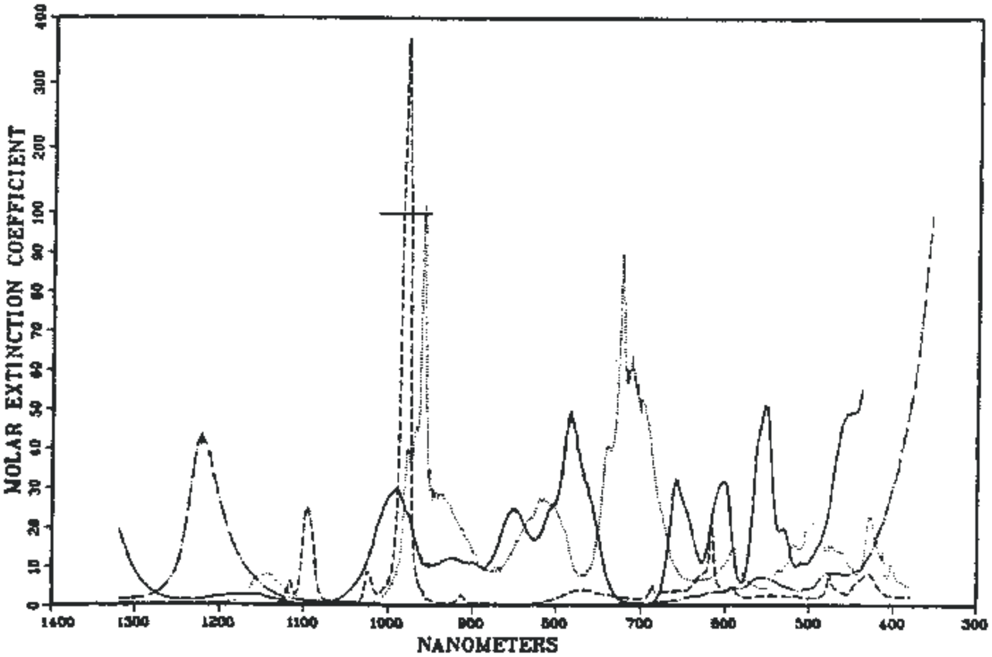


Fig. 3.5. Absorption spectrum of neptunium ions in 0.5 *M* HNO_3 at 22ºC. ----, Np(III); …., Np(IV); _ _ _ _, Np(V); -.-.-.-., Np(VI).

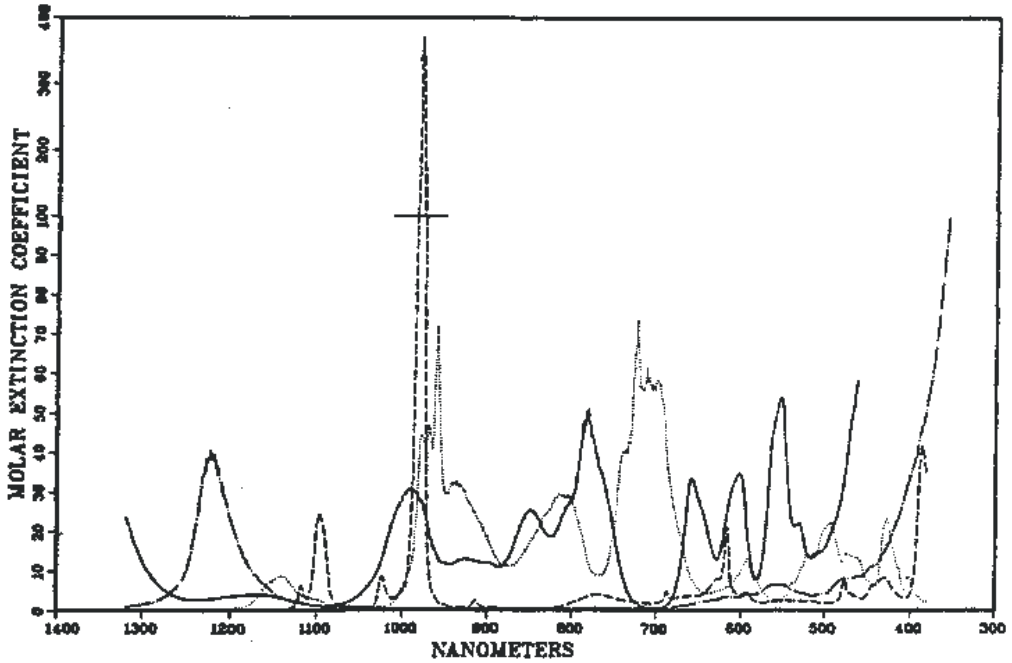


Fig. 3.6. Absorption spectrum of neptunium ions in 1.0 *M* HNO_3 at 22ºC. ----, Np(III); …., Np(IV); _ _ _ _, Np(V); -.-.-.-., Np(VI).

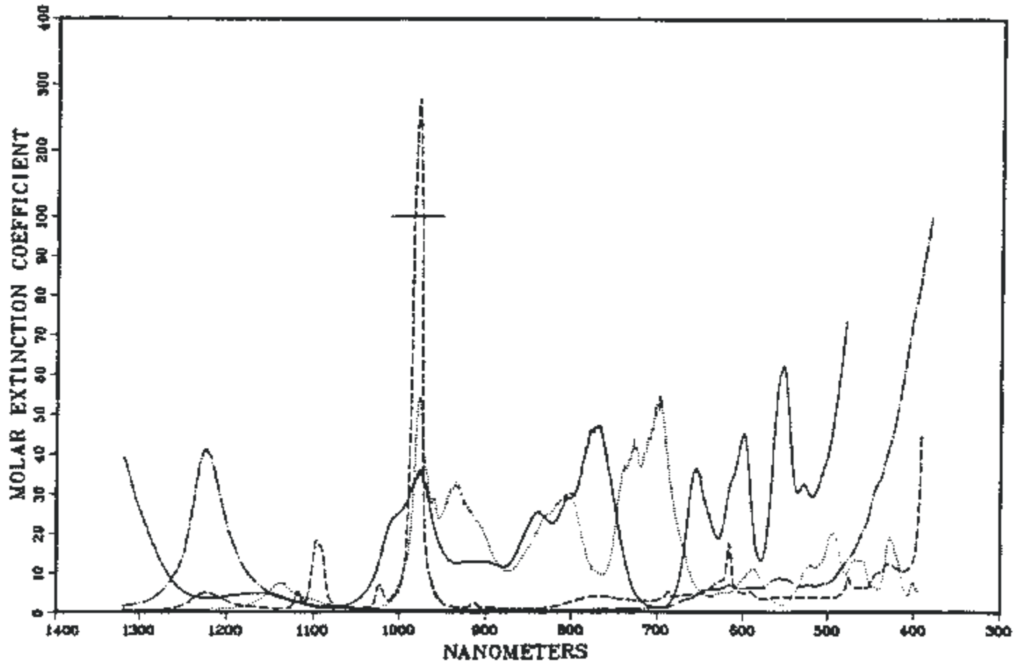


Fig. 3.7. Absorption spectrum of neptunium ions in 4.0 *M* HNO_3 at 22ºC. ----, Np(III); …., Np(IV); _ _ _ _, Np(V); -.-.-.-., Np(VI).

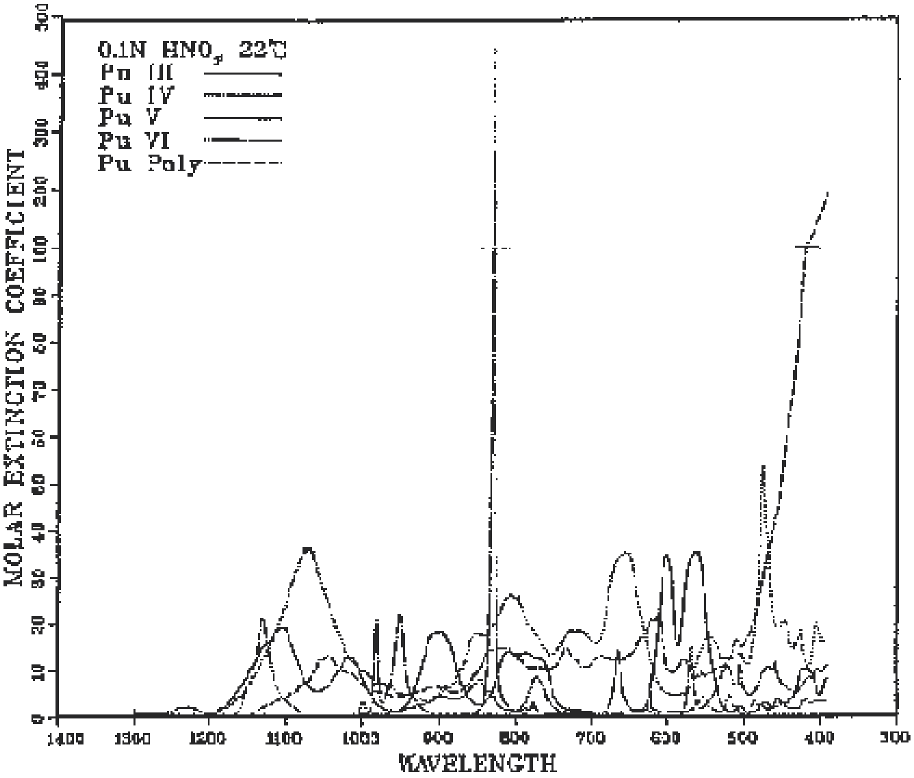


Fig. 3.8. Absorption spectrum of plutonium ions in 0.1 *M* HNO$_3$.

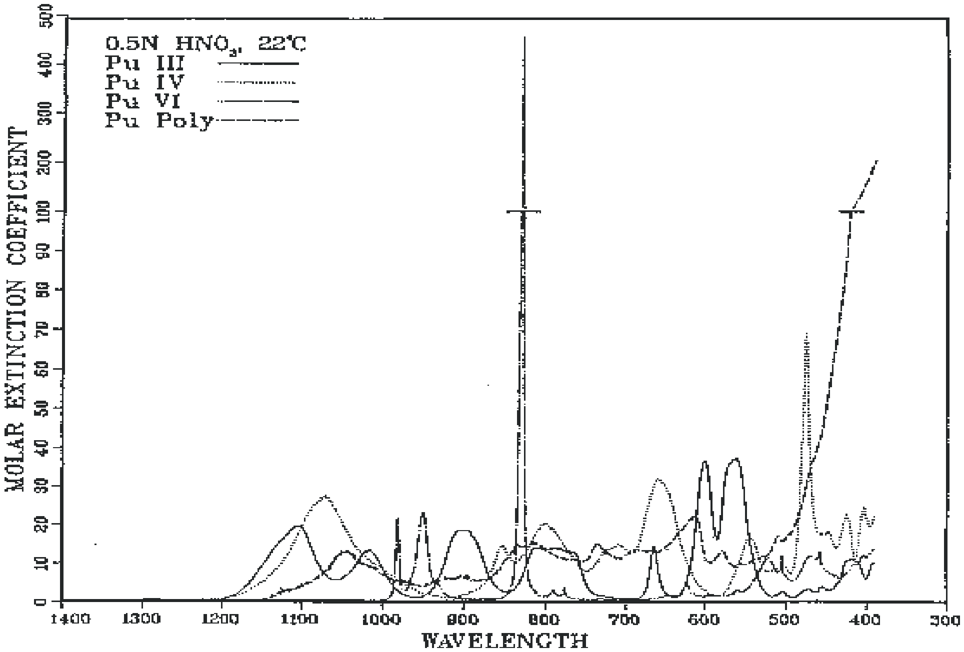


Fig. 3.9. Absorption spectrum of plutonium ions in 0.5 *M* HNO$_3$.

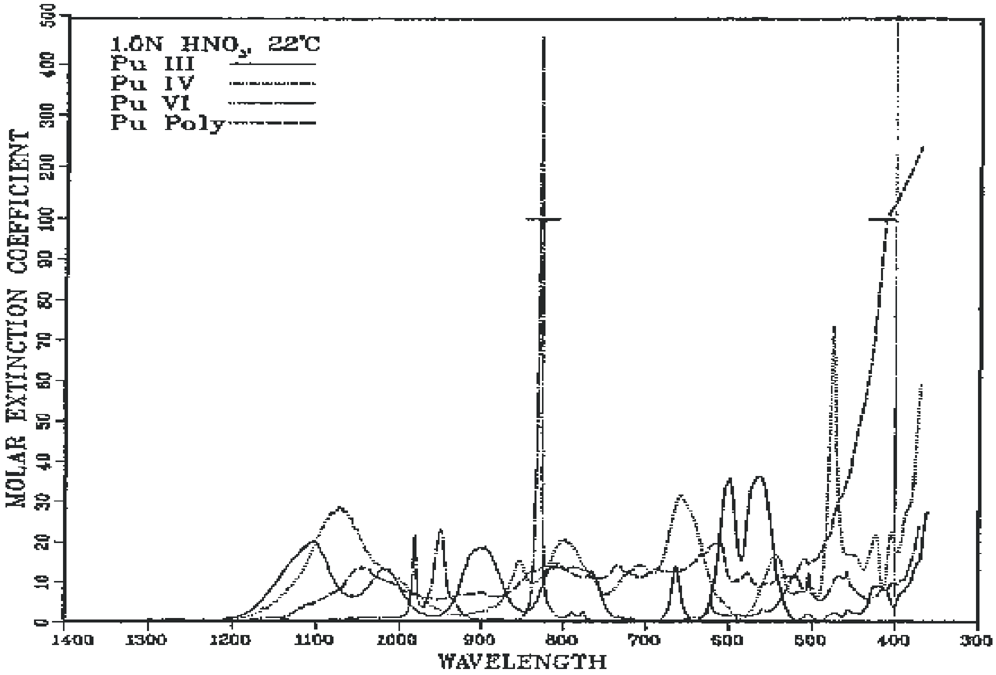


Fig. 3.10. Absorption spectrum of plutonium ions in 1.0 *M* HNO_3.

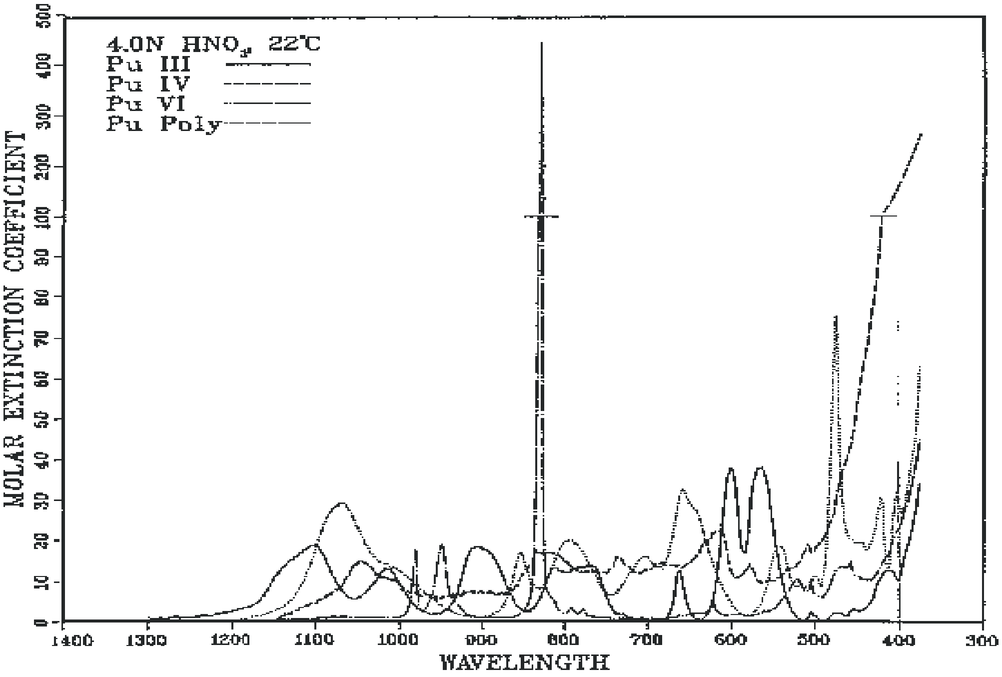


Fig. 3.11. Absorption spectrum of plutonium ions in 4.0 *M* HNO_3.

nitric acid concentrations of 0.1– 4.0 N. Significantly, much of the valuable characteristic spectral "fingerprint" lies in the wavelength region greater than 700 nm—which is especially important for Np(VI) at 1220 nm, Np(IV) and (V) between 900 and 1000 nm, and Pu(VI) at 830 nm. Without the ability to measure and *resolve* the spectra in these regions, the spectral measurement would be adversely compromised. [Note that the very narrow band of Pu(VI) would require an instrument of great resolution since its bandwidth is extremely narrow. Few absorption spectrometers are available with such capabilities in this region, and care should be taken in selecting proper instrumentation for quantitative measurements.]

The use of fiber optics to carry the analytical light beam from the spectrometer to the process system where it can pass through the aqueous solution at a defined optical pathlength and back to the spectrometer is an available technology that enables the practical application of absorption spectrometry to the remote processing of these actinide solutions. Through multiplexing of the fiber-optic cables, many points in the process can be monitored for optimal process control. Light losses through such a fiber-optic system have been shown to be acceptable—and necessary spectral resolution maintained—if the proper integration of the spectrometer/fiber-optic/solvent medium are taken into account.

Spectral measurements over the 400–1300-nm range in nitric acid solutions of these actinides have been shown to produce composite spectra consisting of contributions from their various oxidation states. The nitric acid component does not interfere, because its strong absorbance lies in the ultraviolet region below 400 nm. However, process additives such as ferrous sulfamate could obscure these actinide spectra with absorbances in this region of interest. Thus, if spectrophotometry is chosen as the analytical means, the use of such additives should be taken into account when contemplating the overall chemical composition of the process.

In order to obtain individual species concentrations from composite absorption spectra, simple use of Beer's law permits the determination of the concentration of each species by measurement of the absorbance at a given wavelength. According to Beer's law, A = , cl, where *A* is the measured optical absorbance; , is the molar absorbtivity of that species, as given in the calibration spectra shown in the figures; *c* is the concentration of that species; and ***l*** is the optical pathlength through the solution medium. If several species absorb at the same wavelength, Beer's law further states that the net absorbance at a particular wavelength is the sum of the individual absorbances for each species present, $A_{net} = A_i + A_j + ...$, etc. Therefore, by selecting key wavelength positions at which one chemical species absorbs the strongest relative to the others and then making measurements at each of these positions, a set of simultaneous absorbance equations can be generated, which will yield the individual concentrations of each species.

Qualitatively, however, chemical adjustments could be made until a characteristic peak of an unwanted species just disappears and the operator is left with only the desired oxidation states. Initial operational experience is expected to follow such a qualitative approach until proper process control is understood.

3.2.4 First-Cycle Solvent Extraction

In the first cycle, decontamination of the neptunium and plutonium from fission products is accomplished by coextraction of Np(IV) and Pu(IV) into an organic phase that consists of the extractant TBP (30 vol %) dissolved in an NPH diluent (Fig. 3.12). Fission products and other contaminants (NaF and aluminum salts) remain in the aqueous phase. Flowsheet simulations were performed with and without the addition of aluminum nitrate to the feed stream to enhance extraction. Results of the simulations indicate that addition of the nonextracting nitrate to the feed solution is required for extraction enhancement, due to the relatively low nitric acid concentration in the feed stream. The neptunium and plutonium are costripped into the aqueous phase using a dilute stripping solution of nitric acid containing the reductant HAN and are then routed to the second cycle.

A key feature of the first cycle is the introduction of an aqueous scrub stream of ferrous sulfamate solution (1A-Fe) at an intermediate stage of the multistage extraction cascade to maintain neptunium in its extractable quadrivalent state. The scrub stream enters the extraction cascade at a stage at which all of the more extractable plutonium has been extracted from the aqueous phase. Nitric acid scrub streams 1AIS and 1AS are used to scrub fission products ruthenium and zirconium from the organic. A more detailed flowsheet is given in Appendix A.

3.2.5 Second-Cycle Solvent Extraction

For the second cycle, plutonium is partitioned by selective extraction of Np(IV), leaving inextractable Pu(III) in the aqueous phase. The control of the valence state is accomplished by the presence of HAN in the feed solution to establish the Np(IV) and Pu(III) valence states and the use of an aqueous ferrous sulfamate scrub stream (2AIFe) to maintain the proper reducing conditions and reductant profile within the solvent extraction contactor (Fig. 3.12). Scrub stream 2AS is used to backscrub any Pu(IV) that resulted from reoxidation in the extraction bank.

Neptunium is stripped from the organic phase using a dilute solution of nitric acid and HAN. After acid adjustment, the aqueous neptunium product is routed to a third solvent extraction cycle, where the neptunium is purified by scavenging the trace plutonium (see Sect. 3.2.6). The plutonium product is routed to oxide conversion, where it can, if necessary, undergo further purification by anion exchange or solvent extraction (see Sect. 3.2.7). A more detailed flowsheet including material balance is given in Appendix A.

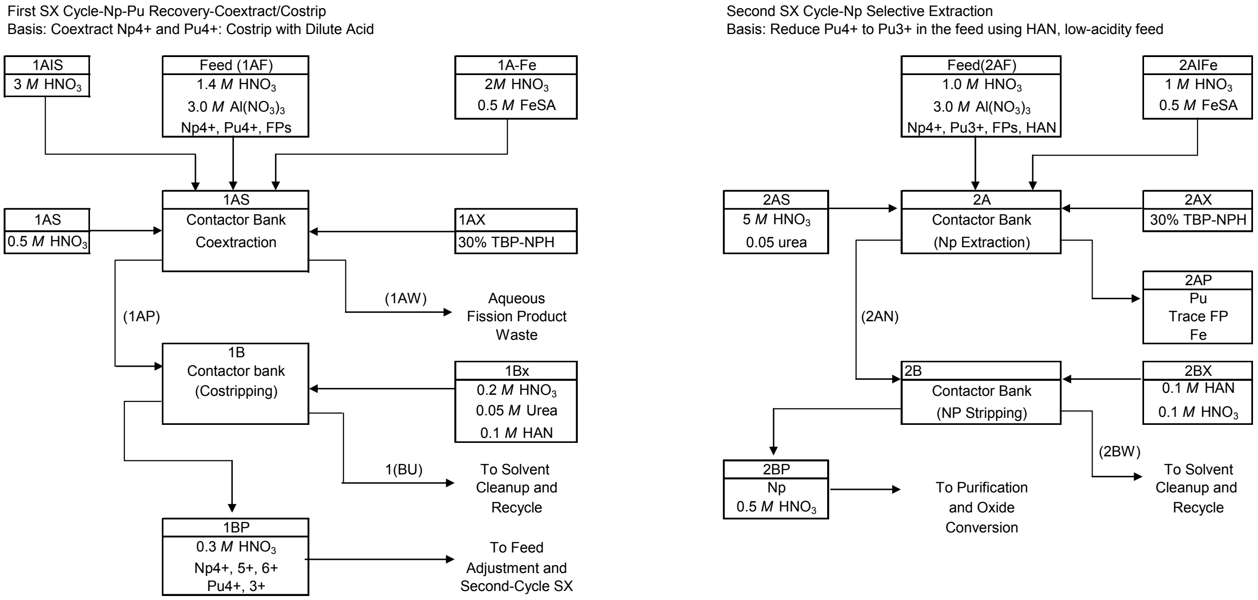


Fig. 3.12. Overview of first- and second-cycle solvent-extraction flowsheets.
SX = solvent extraction; FPs = fission products.

3.2.6 Neptunium Processing

3.2.6.1 Third-Cycle Solvent Extraction

Results from simulations of the second-cycle extraction system indicate that the concentration of plutonium present in the neptunium product stream is negligible. However, an optional third neptunium cycle (Fig. 3.13) may be desired for the final cleanup of the aqueous product stream from second-cycle solvent extraction. As in the case of first- and second-cycle processes, the feed to the third neptunium cycle will require solution adjustment to ensure that Np(IV) is maintained, in order to maximize neptunium extraction by TBP.

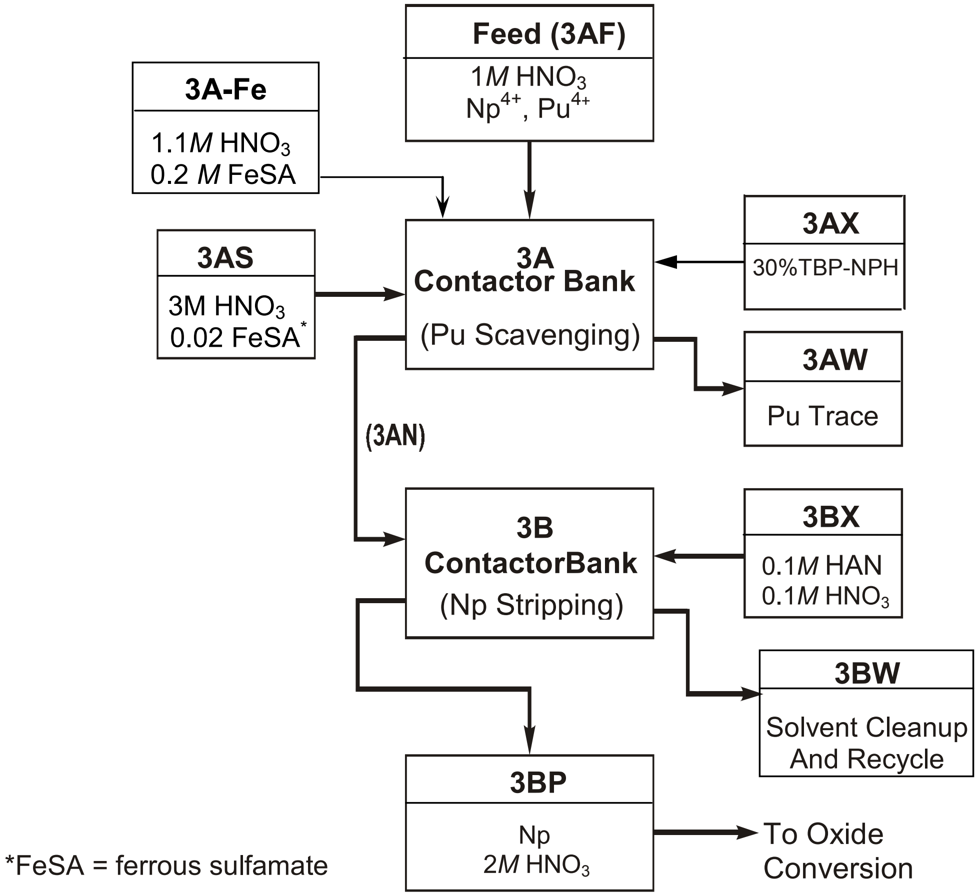


Fig. 3.13. Third-cycle neptunium purification.

Consistent with the second-cycle concept, a single acid scrub is used in the third cycle, because the neptunium should be essentially free of contaminants (other than aluminum). Scrubbing serves to remove trace impurities other than aluminum, which is not extracted to any significant extent by TBP.

Although fewer stages are required in the third neptunium extraction cycle than in the first and second cycles to achieve the same level of decontamination, the basic stage configuration from the earlier cycles has been retained for ease of operation. This ensures that a single process system will be used to accomplish all extraction cycles. To minimize system reconfiguration between cycles, feed solution entry points in the third neptunium cycle are similar to those used in the earlier cycles. In the third-cycle extraction system, aqueous neptunium feed solution (3AF) enters stage 12, the single aqueous scrub stream (3AS) enters stage 8, and the product (3BP) exits stage 7. The solvent (3AX) and aqueous strip

(3BX) solutions enter at opposite ends of the cascade (stages 20 and 1, respectively). A reductant stream (3A-Fe) is introduced at stage 10 to strip Pu(IV) from the solvent and to maintain Np(IV).

The composition of the feed stream to the third extraction cycle is based on concentration of the second cycle with aluminum nitrate and ferrous sulfamate addition during the feed adjustment. The concentrations of the third-cycle feed have been limited to values that fall safely below the solubility limits for the aqueous aluminum nitrate and ferrous sulfamate solutions.

3.2.6.2 Neptunium Product

The neptunium product solution from solvent extraction is converted to neptunium dioxide powder using an oxalate precipitation process (Porter 1964), and the oxide is then routed to target fabrication. In certain cases it may be desirable or necessary to hold the oxide powder (or the neptunium solution) in interim storage to better stage with target-fabrication operations.

Oxalate precipitation was used for preparing neptunium oxide for target production at SRS and has also been used at the REDC for a number of years. The process has been used with a variety of solutions, and the experience base is broad. Most recently, the process has been demonstrated at ORNL in glove-box operations in preparing neptunium oxide for a variety of studies. SRS demonstrated that both the oxalate precipitation and peroxide precipitation methods could be successfully applied on a plant scale. Oxalate precipitation was selected for plant operation because of its superior performance.

Using this oxalate precipitation process, SRS produced neptunium dioxide with consistently high quality suitable for fabrication into target elements to be irradiated to produce ^{238}Pu. The oxide usually contained less than 0.3 wt % metallic impurities. The process was adapted to plant-scale operation without difficulty and proved highly satisfactory in 2 years of operation. The oxalate precipitation process is illustrated in Fig. 3.14.

3.2.7 Plutonium Purification and Oxidation

The plutonium product from the separation process will be purified and converted to an oxide.

3.2.7.1 Plutonium purification

If the plutonium-product solution from the second-cycle solvent extraction process does not meet desired specifications, additional processing will be performed using an either anion-exchange (AIX) process or a third-cycle solvent extraction process. Both options have been evaluated and considered in the process design.

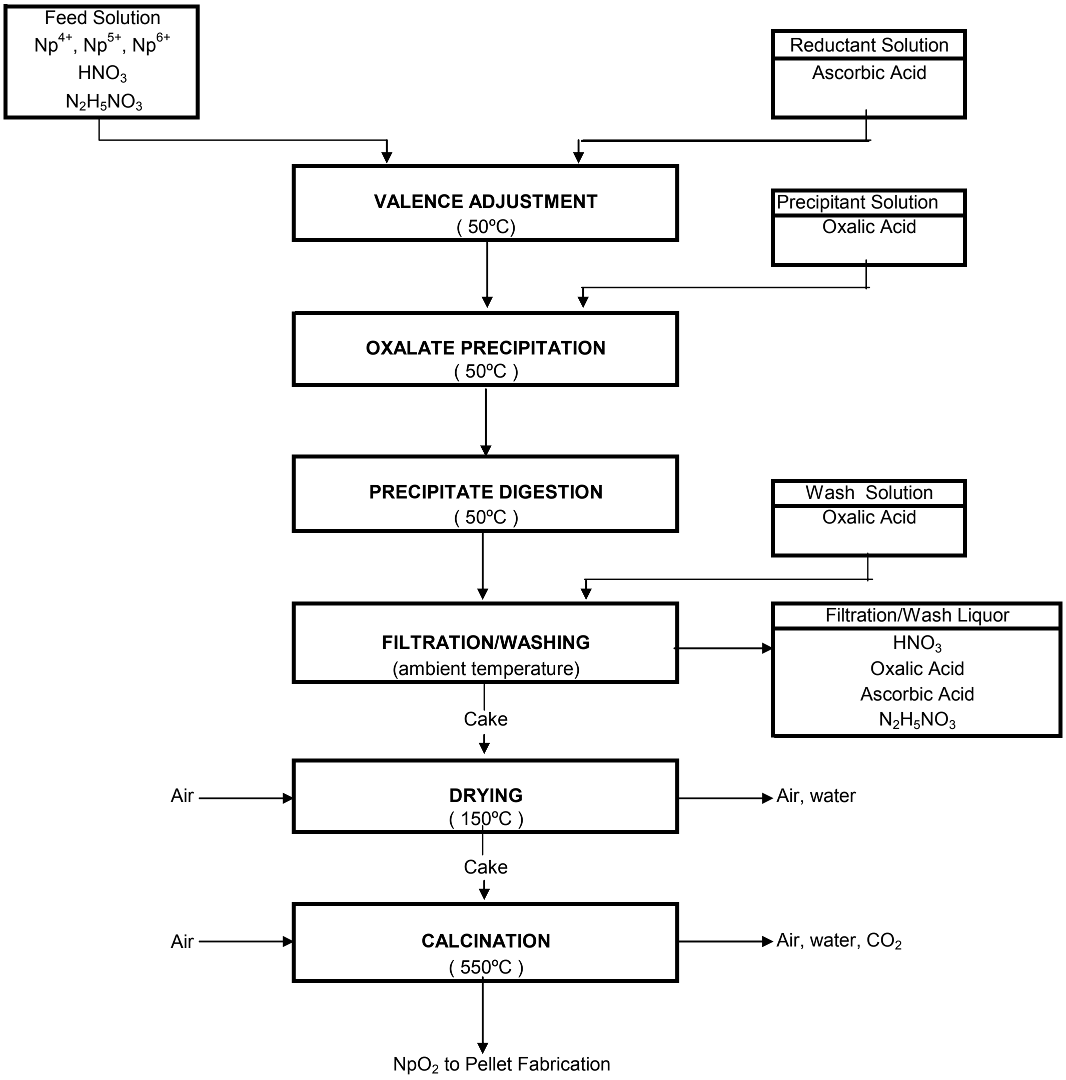


Fig. 3.14. Oxalate precipitation of neptunium for production of NpO_2.

3.2.7.1.1 Anion-exchange purification

Anion exchange (Fig. 3.15) has been used for a number of years at the REDC to purify plutonium products in preparation for precipitation and calcination to an oxide product. New resins with greater radiation resistance have been developed over the years, and a number of processing and equipment improvements have been implemented to reduce the safety concerns associated with this process. The need for anion exchange in the processing of the irradiated materials has not been fully determined; however, it is included in the processing scheme both to allow for flexibility in processing and to make it possible to process small batches of rework material or off-spec products. In this process, the feed is typically adjusted to a high nitric acid concentration (7.5 *M* HNO_3) and the plutonium valence is adjusted to Pu(IV) in order to form the hexanitrato complex, $Pu(NO_3)_6^{-2}$, which loads tightly on the anion resin.

Several compounds have been used for the valence adjustments, with ferrous [Fe(II)] ion as the sulfate or sulfamate being the most widely used. The column is washed with 7.5 *M* HNO_3 to flush the residual feed solution through the column. This allows the sorption of plutonium from the last column volume of feed solution while also flushing the nonsorbable species (added process chemicals and trace fission products) from the column. The plutonium is then eluted from the column with dilute (0.3 *M*) HNO_3. The anionic hexanitrato complex dissociates in dilute acid to form neutral and cationic plutonium species which are not retained by the resin.

There are two concerns with the use of the anion-exchange process. The first concern is the volume of waste generated in the column loading and washing sequence due to the feed adjustments and volumes of wash solution needed to achieve good impurity removal. The second is the safety concern associated with the use of nitrated resin columns. Waste-processing equipment can be used to help minimize the waste generation. Additionally, a number of equipment modifications have been developed over the years to significantly improve the safety aspects of the use of anion-exchange resin columns. Such improvements include column designs that maintain an adequate liquid level and a constant vent on the columns. These improvements will be incorporated in the design of this equipment.

3.2.7.1.2 Third-cycle plutonium solvent extraction

Any third-cycle extraction process will require that the plutonium-bearing raffinate from the second cycle be valence adjusted so that the plutonium is oxidized from inextractable Pu(III) to Pu(IV) (Fig. 3.16). The processing objective of the third extraction cycle is the selective recovery of plutonium from the second-cycle raffinate stream. Since Pu(IV) is more readily extracted by TBP than Np(IV), fewer extraction stages are required in the third plutonium cycle than in the first or second cycles, and the

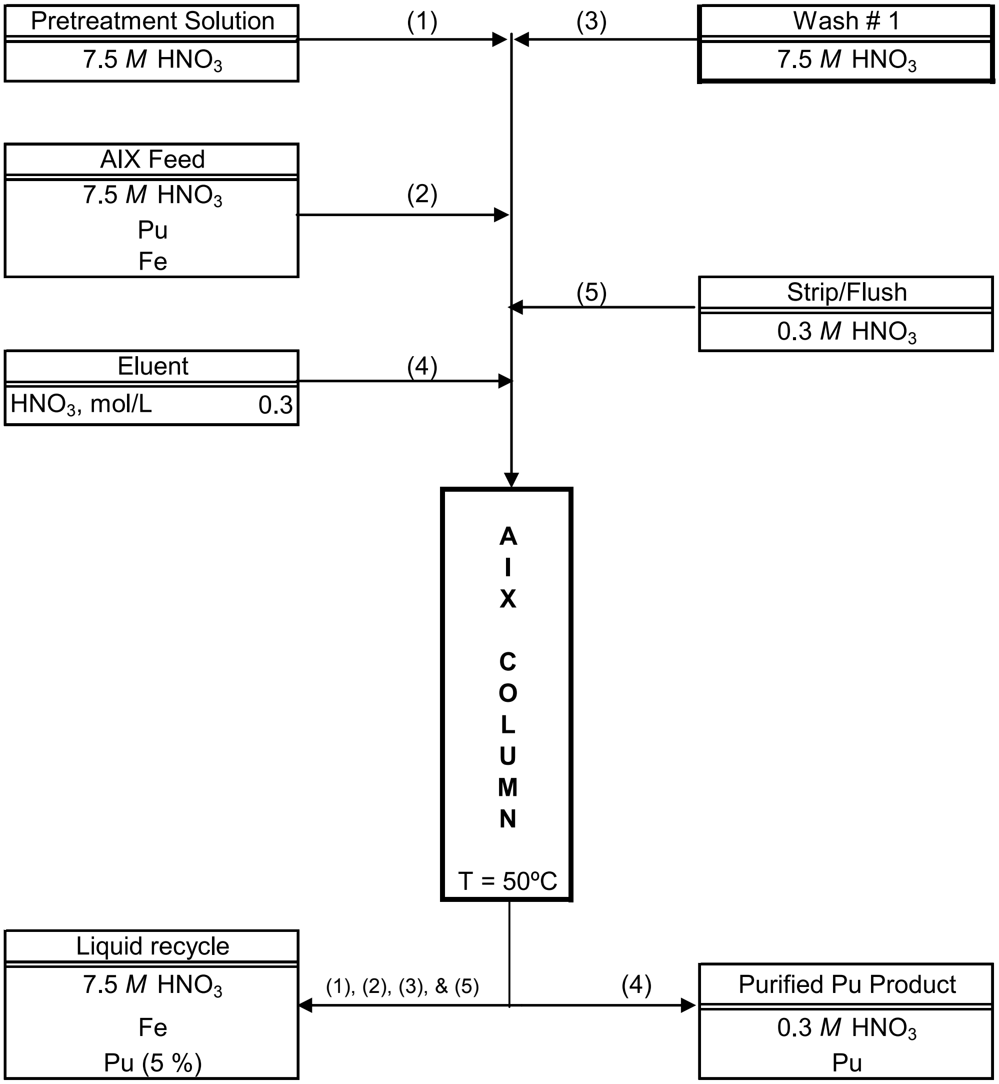


Fig. 3.15. Purification of plutonium by anion exchange.

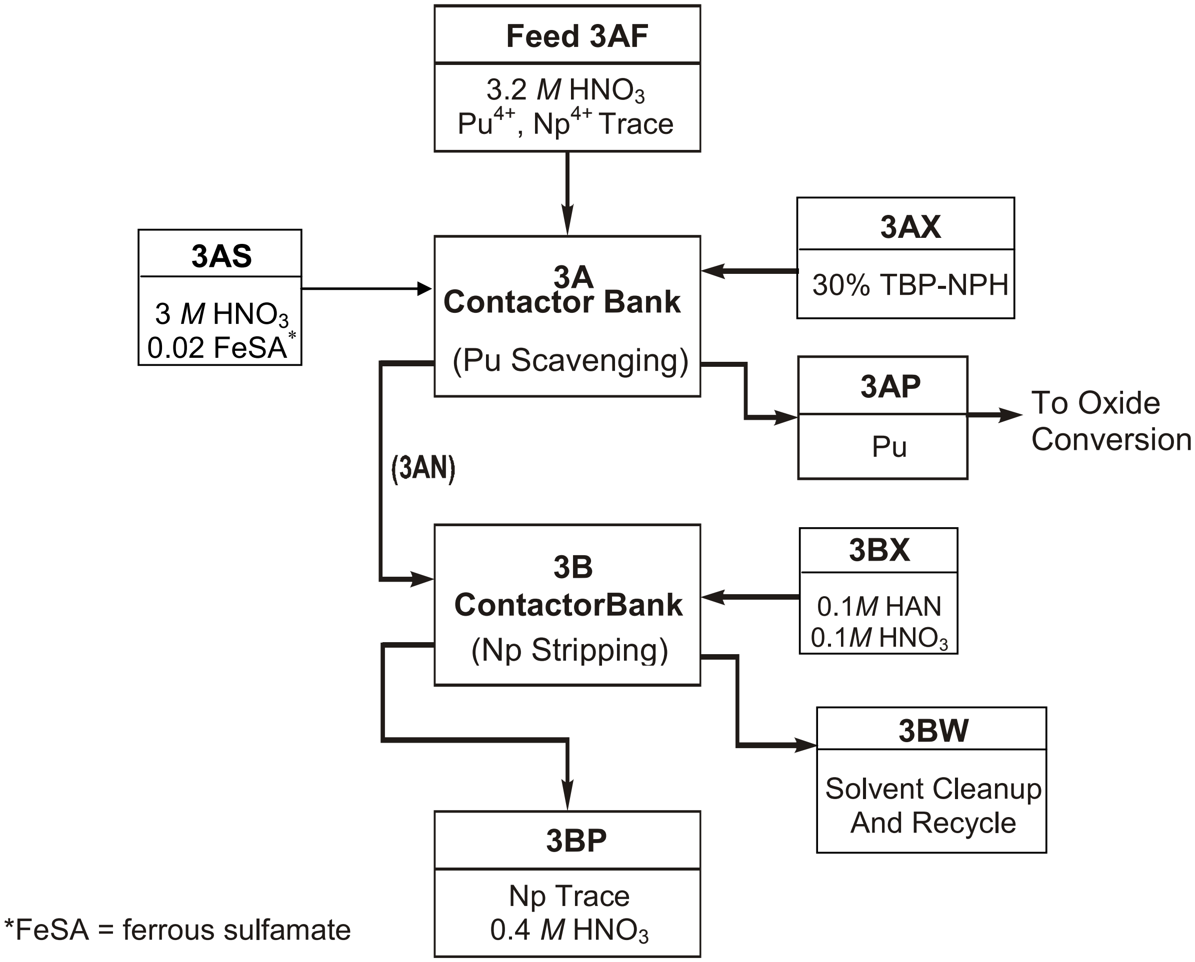


Fig. 3.16. Third-cycle plutonium purification.

number of stages required for solvent stripping increases. However, the same number of stages is included in the third-cycle flowsheet since the same processing equipment will be used to perform all extraction cycles. As in the second-cycle flowsheet, a single acid scrub stream is used in the third cycle since the plutonium should be essentially free of contaminants (other than aluminum).

In the third-cycle plutonium extraction system, the aqueous plutonium feed solution (3AF) enters stage 10, the single aqueous scrub stream (3AS) enters stage 8, and the product (3AP) exits stage 7. The solvent (3AX) and aqueous strip (3BX) solutions enter at opposite ends of the cascade (stages 20 and 1, respectively).

The composition of the feed stream to the third extraction cycle is based on concentration of the second-cycle raffinate only—no chemical additions have been considered. Therefore, the feed composition is an approximation, because oxidation of the plutonium in the second-cycle raffinate is required prior to third-cycle processing. The concentrations of the third-cycle feed have been limited to values that fall safely below the solubility limits for aqueous aluminum nitrate solution.

3.2.7.2 PuO_2 production

The purified plutonium solution will be transferred into an enclosed cubicle for preparation of the oxide. The solution may be precipitated as an oxalate or loaded on a cation resin. After conversion to an oxide, it will then be packaged for shipment.

3.2.7.2.1 Oxalate precipitation of plutonium product

The oxalate precipitation process has also been used at the REDC for a number of years. The process has been used with a variety of solutions, and the experience base is broad. A flowsheet depicting oxalate precipitation is shown in Fig. 3.17. The plutonium product solution will be adjusted to give a final solution concentration of 1.0 M HNO_3 with the plutonium as Pu(IV). Ascorbic acid was selected as the reductant to adjust the plutonium valence, because it will not add extraneous ions to the final product upon conversion to the oxide. Two oxalic acid additions (1.0 M oxalic acid) are made to the plutonium solution to quantitatively precipitate the plutonium as the oxalate. The solution is then filtered, and the precipitate is collected on a sintered platinum/Inconel filter for calcination to the oxide. The use of the platinum/Inconel filter eliminates the need to transfer the precipitate to another container for calcination. The precipitated plutonium product is transferred to a furnace and calcined in air at 735ºC for 2 h. When the calcination is completed, the plutonium oxide product remains in the filter for the oxygen-exchange process (depicted in Fig. 3.18).

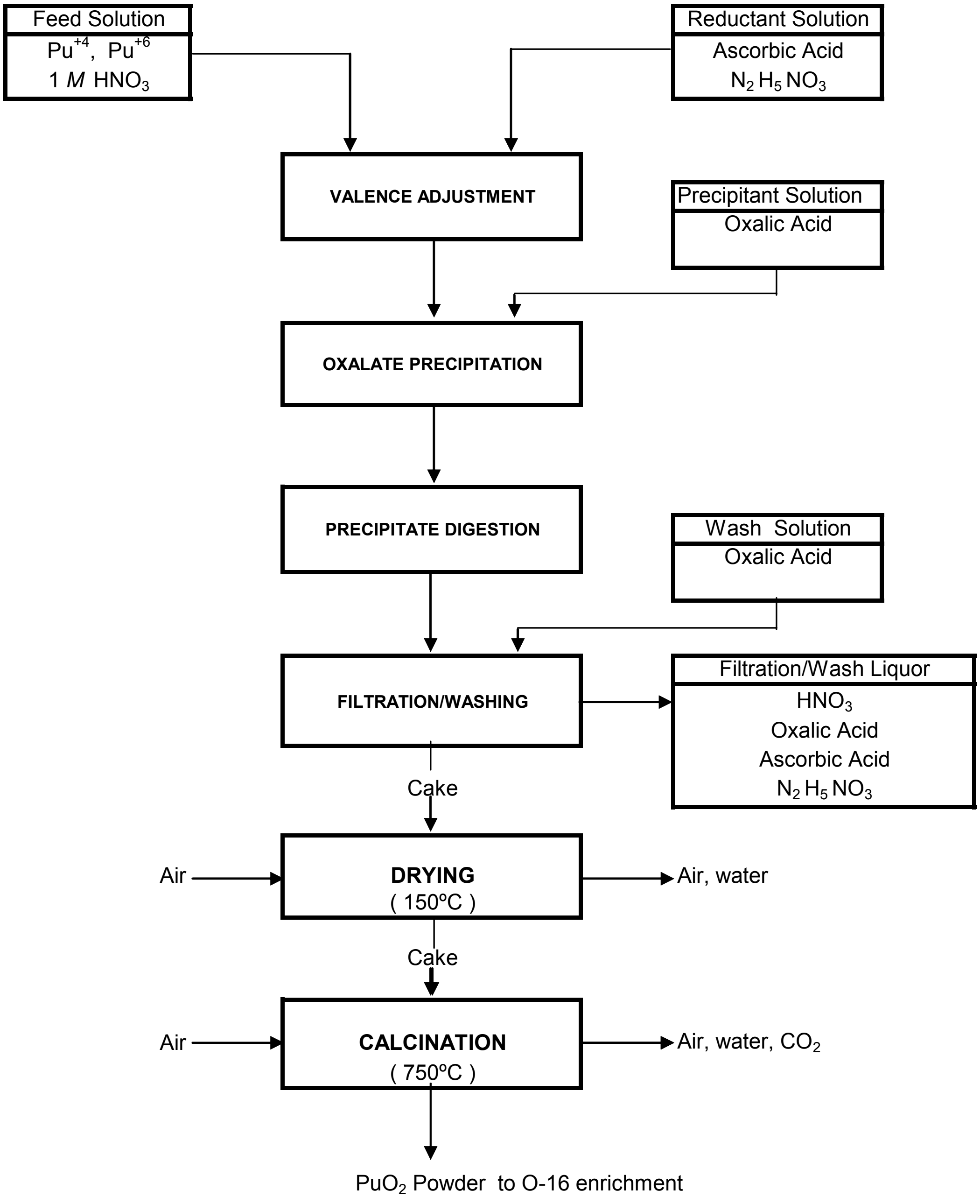


Fig. 3.17. Production of PuO_2 by oxalate precipitation.

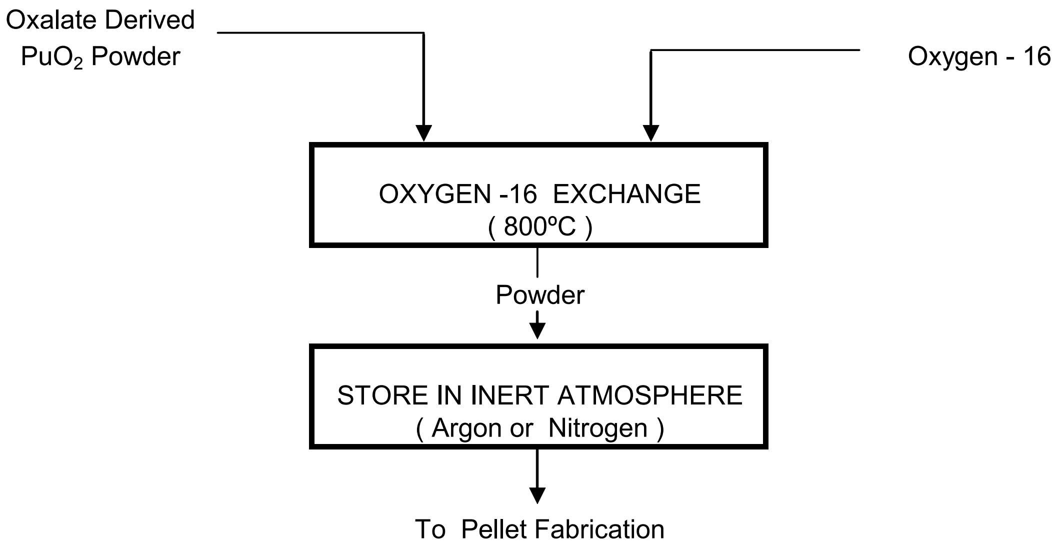


Fig. 3.18. Oxygen exchange of PuO_2.

3.2.7.2.2 Cation-resin loading

Cation-resin-loading and calcination techniques have been developed and used at REDC to produce uniform particles of curium–americium oxide in the size range desired for the fabrication of targets for irradiation in the HFIR. Although SRS used oxalate precipitation and calcination exclusively, these techniques could possibly be developed as an alternative to oxalate precipitation and calcination for the production of ^{238}Pu oxide.

For curium target production, Dowex 50W-X8, a sulfonic acid cation-exchange resin, is loaded to saturation from a dilute HNO_3 solution of curium–americium. The resin bed is then rinsed with water and calcined to destroy the resin and form dense actinide oxide microspheres. Since 1971, the curium–americium oxide for HFIR targets has been produced exclusively by this process.

The process variables that affect the oxide production are the acid concentration of the feed and the drying/calcination steps. The acid concentration determines the amount of actinides that are sorbed on the resin. An acid concentration in the range of 0.01–0.70 *M* resulted in curium being sufficiently sorbed on the resin to produce oxide products; however, a reduced actinide capacity of the resin was noticeable at higher acidities. Production runs were generally carried out using an acid concentration from 0.2 to 0.35 *M*.

The sequence of drying and calcining is important to produce an acceptable product. Initially drying is performed at 150ºC to remove the moisture and prevent the resin from shattering from internal generation of steam at higher temperatures. Calcinations at 800ºC with air and with 4% H_2–Ar remove the carbon and sulfur, which results in a higher-tap-density oxide. The higher-density oxide is more desirable since it is a more robust particle that will not easily break when handled. Low-density oxides have a low crushing strength and will contain fines created from excessive particle breakage.
Another variable is the size of the resin bead. Tests indicated that curium oxide particles formed from large resin beads, 200–300 µm, show acceptable tap densities but have large internal voids. These voids, which decrease with decreasing diameter, make the particles more fragile. Resin beads ranging from 60–80 µm in diameter are now used in processing to eliminate the internal voids and produce sintered oxide spheres of ~20 µm in diameter.

3.2.7.3 Oxygen exchange

The need for oxygen exchange on the plutonium product is driven by the goal of reducing the dose to workers who will handle the material in subsequent processing. The (α,n) reaction of the ^{238}Pu on naturally occurring oxygen produces a significant number of neutrons. To reduce the dose, an oxygen-exchange process is incorporated to replace the higher-cross-section oxygen isotopes with ^{16}O, which has a very small cross section for the (α,n) reaction. This process would follow the conversion of the oxalate product to the oxide in a fritted platinum filter. This filter prevents the need for a material transfer and can be incorporated into the design of the oxide conversion equipment. To accomplish the exchange, oxygen gas (^{16}O enriched) is passed through the plutonium oxide product at 800ºC for approximately 4 h. A neutron detector located adjacent to the plutonium oxide can provide constant monitoring of the exchange efficiency. The plutonium oxide is then cooled in an inert atmosphere and immediately transferred to an EP-60 container, preferably under an inert atmosphere, for final packaging. Any exposure to naturally occurring oxygen on cooling and packaging will allow for back-exchange of the naturally occurring oxygen with the ^{16}O. Therefore, an inert atmosphere will be used to prevent oxygen back-exchange.

3.3 PLUTONIUM PRODUCT

Once the plutonium has been converted to an oxide, it could either be pressed into pellets or packaged for shipment to another facility.

3.3.1 Pellet Fabrication

The plutonium oxide could be pressed into pellets for use in radioisotope thermoelectric generators (RTG). In the following discussion a general approach to pellet production is outlined. The major goal of the activity would be to use processes that are less dusty than that which is currently used.

3.3.1.1 Background

The approach to pellet fabrication at ORNL is to eliminate the PuO_2 milling operations required by the General Purpose Heat Source (GPHS) flowsheet developed at Los Alamos National Laboratory. The GPHS process was subsequently used at Savannah River for manufacture of $^{238}PuO_2$ pellets for use in space applications of RTGs (Burney and Congdon 1982). The GPHS process is complex and includes precipitation of small Pu(III) oxalate crystals (Maraman 1956), calcination to PuO_2, ball milling, granulation, and granule sintering prior to hot pressing to form the fuel pellet. In addition, the PuO_2 powders (or granules) are treated with $H_2{}^{16}O$ to convert them to $^{238}Pu^{16}O_2$, which reduces the neutron shielding requirements in space mission (Porter and Thompson 1968).

During the production at Savannah River, it was recognized that a direct process for particle preparation was desirable to eliminate the airborne particles and dusting that resulted from the ball milling and mechanical granulation operations (Burney and Congdon 1982). Initial laboratory-scale studies at Savannah River indicated that oxalate precipitation conditions could be changed to produce large agglomerates (40–100 µm) of small crystals (2–3 µm) directly and thus eliminate the need for mechanical milling/granulation. The synthesis of the large agglomerates was achieved mainly by changing from the traditional GPHS flowsheet process of "reverse strike" precipitation of Pu(III) oxalate to "direct strike" precipitation.*

Although the results in a few limited tests were encouraging, a significant amount of work remains before a direct fabrication process can be implemented. A number of process parameters require further investigation to determine optimum conditions for oxalate precipitation and subsequent direct pellet fabrication.

3.3.1.2 ORNL approach for direct fabrication

In our flowsheet development for plutonium pellet pressing, we will follow a direct fabrication approach (Fig. 3.19) to avoid the need for milling of powders. Two methods will be evaluated for powder production. Controlled oxalate precipitation of Pu(III) (Burney and Congdon 1982) is chosen as the

---

* "Direct strike" involves adding oxalic acid solution to the plutonium solution, whereas "reverse strike" involves the opposite—adding the plutonium solution to oxalic acid solution.

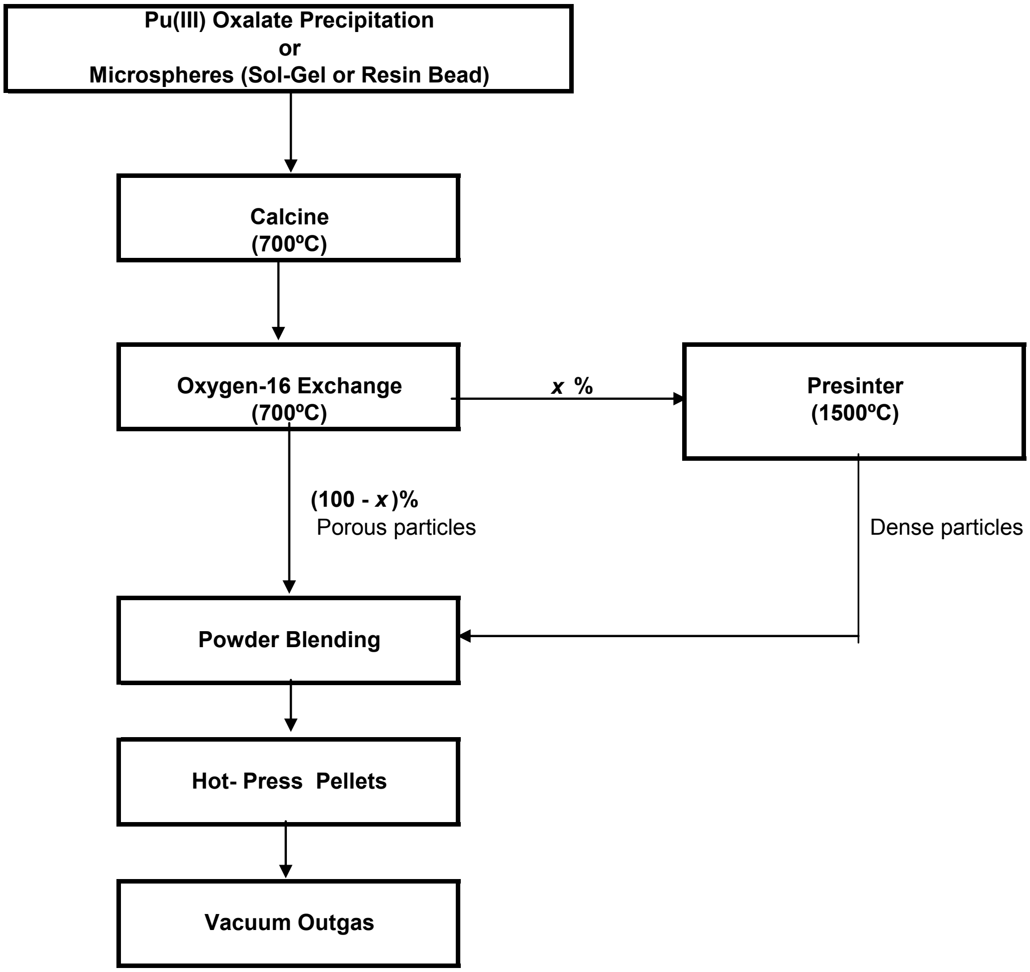


Fig 3.19. Conceptual approach to direct fabrication flowsheet.

mainline process. Oxide preparation from the calcination of Pu(IV)-loaded cation resin (Chattin et al. 1981) is chosen as the backup process. We will continue the past approach (Burney and Congdon 1982) of blending dense (higher-temperature-sintered) particles with more porous (lower-temperature-sintered) particles to obtain a powder suitable for fabrication of crack-free, dense (85% theoretical) pellets by hot pressing. A blend of high- and low-density powders avoids excessive shrinkage in pellet pressing and the resultant pellet cracking.

Sol-gel preparation of PuO_2 spherical particles was examined as an alternative to the resin precursor approach because of recent developments in particle size control using the internal gelation process

(Collins 2004) and also because highly sinterable particles (Kitts et al. 1971) are produced. The cation resin process was selected as the backup method because of its more advanced state of development and the significant operational experience.

3.3.1.2.1 Oxide powder preparation

Oxalate Precipitation: Plutonium oxalate precipitation conditions must be carefully controlled to produce particles that can be calcined to prepare PuO_2 powders that have the properties acceptable for pellet fabrication. The nature of the precipitate depends on a host of process variables, which include the valence of the plutonium, solution acidity, method used for addition and mixing of the oxalic acid solution with the plutonium feed solution, excess of oxalic acid used, temperature, and precipitate digestion or aging.

Oxalate precipitation of either tetravalent or trivalent plutonium has been employed to prepare nuclear-fuel-grade PuO_2 for fast-reactor applications (Lerch and Norman, 1984). However, only the precipitation of trivalent plutonium oxalate is considered here. Burney and Congden (1982) have shown that precipitation from Pu(III) solutions can produce large agglomerates (60–100 µm) of small crystals (2–3 µm), whereas precipitation from Pu(IV) solutions produces only 15–20 µm aggregates. Direct preparation of large agglomerates from Pu(III) solutions thus avoids the necessity of forming large aggregates mechanically. Although the precipitation conditions were not optimized, pellet-fabrication tests with certain of the oxides prepared showed good potential. It is believed that additional optimization work on the oxalate precipitation/oxide conversion and the hot-pressing conditions will show that PuO_2 powders derived from Pu(III) oxalate can be used for routine preparation of PuO_2 pellets of GPHS quality. The optimization work is discussed further in Sect. 3.3.1.3.

Pu(IV)-Loaded Cation Resin: Cation resin (sulfonic acid type) loaded with Pu(IV) appears to be an ideal precursor for PuO_2 preparation. Ease of adaptability of loaded resin to remote operations has been demonstrated for the preparation of americium and curium oxides (Chattin et al. 1981). However, fabrication of dense pellets from oxides synthesized from resin precursors has not been demonstrated. Development of a flowsheet for GPHS pellet production that is based on resin particle feeds is most desirable because of its adaptability to remote operations. Recent developments in the preparation of a conceptual process flowsheet are shown in Fig. 3.20. In this process, oxide particle size is controlled by the size of the resin particles that are loaded with plutonium. The desired resin particle size is obtained by hydraulically classifying bulk commercial resin to obtain the desired size fraction, for example, 60–80-µm diameter. The plutonium-loaded particles (11 mL resin/g ^{238}Pu) are prepared by passing a nitric acid solution of Pu(IV) through a fixed bed of the cation resin spheres. The loaded resin is then

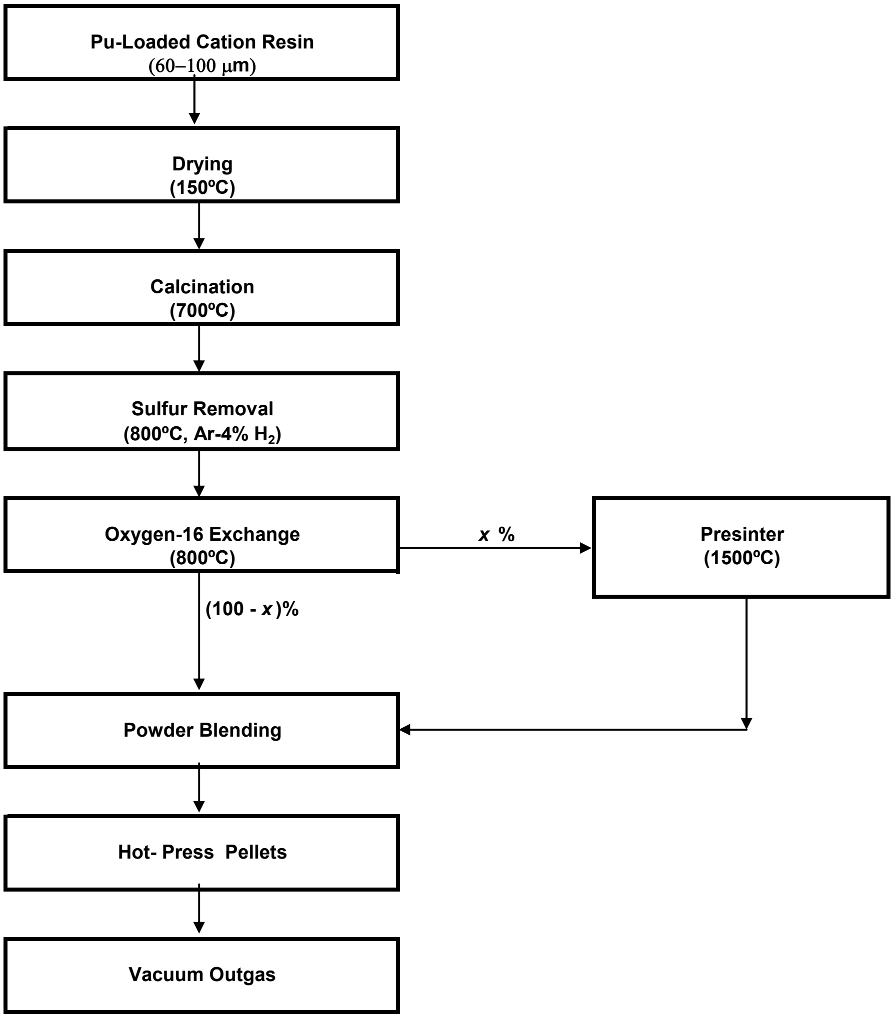


Fig. 3.20. Conceptual process for conversion of plutonium-loaded cation resin to oxide.

water washed, dried at 150ºC, and calcined in air at 800ºC. The calcination removes the organic resin matrix and converts the plutonium to PuO_2. Subsequently, sulfur is removed at 800ºC with a stream of 4% H_2–Ar. After sulfur removal, ^{16}O exchange is conducted in an atmosphere of $H_2{}^{16}O$ at 800ºC.

Prior to pellet pressing, the oxide is divided into two portions in relative amounts that are presently unknown and must be determined experimentally. One portion undergoes additional sintering and densification at a higher temperature than the other. The two portions are then blended together for hot pressing.

3.3.1.3 Experimental needs

To fully develop the pellet-fabrication capability outlined above, a number of process parameters and techniques need to be established. Most of the experiments would be conducted with ^{239}Pu rather than ^{238}Pu because it is much less radioactive and reduces the dose to workers. A "stand-in" stable element that is very similar to plutonium in both aqueous solution chemistry and solid-state chemistry would be even more desirable than ^{239}Pu. Unfortunately, such an element does not exist. When successful pellet fabrication is achieved with a particular powder, final confirmation would then be made with ^{238}Pu. The following subsections outline needed experimental investigations to develop and demonstrate the pellet production techniques.

3.3.1.3.1 Oxide powder preparation and characterization

The permissible impurities and their levels of contamination are given in Table 3.1. Experimental studies on oxygen exchange would not be needed because it has already been well demonstrated in ^{238}Pu^{16}O$_2$ production (Burney and Congdon 1982, Porter and Thompson 1968).

Oxalate Precipitation: Only "direct strike" precipitation of Pu(III) would be investigated since this technique is known to produce particle sizes in the range of interest (50–100 μm). Control of particle size of precipitates by appropriate choice of process conditions would be emphasized. Scanning electron microscopy would be employed to assess the size and shape of oxalate particles before and after calcination. The effects of temperature, rate of addition of oxalic acid, quantity of excess oxalic acid, precipitate aging time, initial plutonium concentration of feeds, and solution acidity would be evaluated. Finally, calcination temperature, atmosphere and powder sintering times would be investigated, and the final particle density and shape would be determined.

Pu(IV)-Loaded Cation Resin: The effect of initial resin bead size is the only variable that needs to be explored. The conditions for removal of the carbonaceous resin matrix and its attendant sulfur have been previously determined (Chattin et al. 1981) for Am–Cm and should apply equally to plutonium.

The plutonium-loaded particles (11 mL resin/g ^{238}Pu) would be prepared by passing a nitric acid solution of Pu(IV) through a fixed bed of the cation resin spheres. Two particle size ranges of resin could be explored: (1) 50–100 μm and (2) 40–60 μm. Oxide particles produced would be evaluated with regard to particle size, shape, density, and resistance to crushing. Chemical analysis would be performed to determine residual sulfur, carbon, and other elemental impurities.

Table 3.1. Impurities in ^{238}Pu fuel

Impurity	Concentration (μG/G)
Actinides[a]	
Am-241	5000
Np-237	5000
Pu-236	2
U-234	5000
Th	5000
Sum of actinides (not to exceed)	10000
Nonactinides	
Al	500
B	5
Be	5
Ca	300
Cd	50
Cr	500
Cu	200
Fe	800
Mg	100
Mn	50
Mo	250
Na	250
Ni	500
Pb	100
P	25
Si	750
Sn	50
Zn	50

[a] *Source*: Adapted from GPHS Rev. A (26Y-318180), Los Alamos National Laboratory

3.3.1.3.2 Hot pressing

Hot-pressing conditions for fabricating GPHS pellets from the oxide powders require experimental determination of appropriate parameters. The powders produced either by oxalate precipitation or resin loading would be utilized in the hot-pressing tests. The effects of the mix of particles in the feed material, pressing load, load ramping, temperature, and time at temperature would be evaluated with respect to their influence on pellet quality.

3.3.2 Packaging

If the PuO_2 powder is to be packaged for shipment, then it is envisioned that the powder will be prepared by firing the oxalate in a simple thin-wall stainless steel tube that has a metallic frit in the bottom held in place by a perforated disk. This tube then serves as the precipitation and calcination vessel, as well as the final inner package. The frit allows gas to flow through the container during the oxygen exchange and inert-gas backfill processing steps. Upon completion of those processes, caps would be pressed into either end of the container. This package then serves as the inner container for the PuO_2, which is then placed inside an outer container consisting of a stainless steel tube with a welded bottom cap. The outer container is then plugged, welded, and the top severed using the bagless transfer technique developed at Savannah River. The outer container is then a welded package that has had essentially no exposure to the glove-box atmosphere, thereby providing a clean package to be loaded into an EP-61 container. A cation-resin-derived powder could be prepared in a similar manner.

4. WASTE STREAMS AND PROCESSING

Under a separate program, new waste processing capabilities that are based on future processing requirements will be installed at ORNL (van Hoesen and Robinson 2003). A detailed study of waste processing needs and requirements was recently completed, and future processing capabilities for various waste streams have been identified. Waste generators will pretreat their liquid waste to remove high-gamma-emitting radionuclides (e.g., cesium and strontium) and to remove organic liquids (e.g., solvent extractants) prior to discharge into the ORNL liquid waste system. Because of similarities in the waste streams, the methods used to preprocess the waste would be identical to those used to treat liquid wastes in Building 7920. Trace transuranics will be removed by a solvent extraction process. These transuranics may either be recycled to the main process or solidified for disposal. Cesium and strontium will be removed by an ion-exchange process using crystalline silicotitanate. Organics will either be destroyed or solidified.

The remaining aqueous stream would be sent to the ORNL low-level liquid waste processing system, which consist~~s~~ of ion-exchange columns and evaporation, resulting finally in the production of a grouted product. This grouted product would be sent to the Nevada Test Site for final disposition.

5.   SUMMARY

This report describes the overall flowsheet for the production of ^{238}Pu. The facilities available at ORNL have been described in previous reports (Wham et al. 2004a, 2004b, 2004c). The flowsheet has been updated based on results from post-irradiation examination of irradiated test targets. The solutions from these targets are currently being used for further studies related to flowsheet development. Separations experiments, combined with ongoing spectrophotometric and electrochemical studies at ORNL, will be used to finalize the flowsheet and to validate selected parameters.

REFERENCES

Bond, W. D. 1981. "Purex Solvent Extraction Chemistry," in *Light Water Reactor Nuclear Fuel Cycle*, ed. R. G. Wymer and B. L. Vondra, CRC Press, Boca Raton, Fla.

Burney, G. A., and J. W. Congdon. 1982. *Direct Fabrication of* $^{238}PuO_2$ *Fuel Forms*, DP-1621, DuPont Savannah River Plant, Aiken, S.C. (July).

Chattin, F. R., D. E. Benker, M. H. Lloyd, P. B. Orr, R. G. Ross, and J. T. Wiggins. 1981. "Preparation of Curium-Americium Oxide Microspheres by Resin Bead Loading," in *Transuranium Elements—Production and Recovery*, ACS Symposium Series No. 161, ed. J. D. Navratil and W. W. Schulz, American Chemical Society, Washington, D.C.

Cohen, D. 1961. "Electrochemical Studies of Plutonium Ions in Perchloric Acid Solution," *J. Inorg. Nucl. Chem.* **18**, 207–210.

Collins, J. L. (Oak Ridge National Laboratory). 2004. Personal communication (August 13).

Davis, W. 1961. *The Solubilities of Uranyl and Iron(III) Dibutyl and Monobutyl Phosphates in TBP Solvent Extraction Solutions*, ORNL-3084, Oak Ridge National Laboratory, Oak Ridge, Tenn.

Drake, V. A. 1990. "Extraction Chemistry of Neptunium," p. 123 in *Science and Technology of Tributyl Phosphate*, Vol. III, ed. W. W. Schulz, J. D. Navratil, L. L. Burger, and K. P. Bender, CRC Press, Boca Raton, Fla.

Federal Register. 2001. "Record of Decision for the Programmatic Environmental Impact Statement for Accomplishing Expanded Civilian Nuclear Energy Research and Development and Isotope Production Missions in the United States, Including the Role of the Fast Flux Test Facility," *Fed. Regist.* **66**(18) (January 26).

Groh, H. J., and C. S. Schlea. 1970. "The Recovery of Np-237 and Pu-238," *Prog. Nucl. Energy*, *Ser. 3: Process Chem.* **4**, 507.

Hindman, J. C., D. Cohen, and J. C. Sullivan. 1955. p. 345 in *International Conference on the Peaceful Uses of Atomic Energy* [Geneva], Vol. 7, United Nations, New York.

Hylton, T. D., R. R. Brunson, A. S. Icenhour, L. M. Toth, and R. M. Wham. 2004. *Dissolution of Neptunium and Plutonium Oxides Using a Catalyzed Electrolytic Process,* ORNL/TM-2004-211, Oak Ridge National Laboratory, Oak Ridge, Tenn.

Icenhour, A. S., R. M. Wham, R. R. Brunson, and R. R. McMahon. 2003. *Post-Irradiation Examination of Array Targets—Part I*, ORNL/TM-2003/220, Oak Ridge National Laboratory, Oak Ridge, Tenn. (December).

Kitts, F. G., R. E. Brooksbank, R. G. Haire, and M. H. Lloyd. 1971. *Mound Assistance Program: Development of a Sol-Gel Process and Equipment for the Production of Dense* $^{238}PuO_2$ *Microspheres*, ORNL-4565, Oak Ridge National Laboratory, Oak Ridge, Tenn. (March).

Lerch, R. E., and R. E. Norman. 1984. “Nuclear Fuel Conversion and Fabrication Chemistry,” *Radiochim. Acta* **36**, 75–88.

Maraman, W. J. 1956. *Purification and Concentration of Solvent Extraction Plutonium by Oxalate Precipitation*, LA 1991, Los Alamos National Laboratory, Los Alamos, N.M.

Maya, L., and C. D. Bopp. 1978. “Extraction of Zirconium from Nitric Acid by Butyl Lauryl Phosphoric Acid in Dodecane,” *J. Inorg. Nucl. Chem.* **40**, 1147.

Mills, A. L. 1990. “Computation and Modeling,” p. 181 in *Science and Technology of Tributyl Phosphate,* Vol. III, ed. W. W. Schulz, J. D. Navratil, L. L. Burger, and K. P. Bender, CRC Press, Boca Raton, Fla.

Orth, D. A., R. M. Wallace, and D. G. Karraker. 1984. “Solvent Extraction Reactions and Mechanisms,” p.161 *in Science and Technology of Tributyl Phosphate*, Vol. I, ed. W. W. Shulz, J. D. Navratil, and A. E. Talbot, CRC Press, Boca Raton, Fla.

Porter, J. A. 1964. “Production of Neptunium Dioxide,” *Ind. Eng. Chem. Process Des. Dev.* **3**, 289–282.

Porter, J. A., and M. C. Thompson. 1968. *Preparation of* $^{238}Pu^{16}O_2$, DP-1153, DuPont Savannah River Plant, Aiken, S.C. (November).

Savel’ev, Yu. I., Z. V Ershova, and M. V. Vladimirova. 1967. “Alpha Radiolysis of Aqueous Solutions of Nitric Acid,” *Soviet Radiochemistry* **9**, 221.

Schulz, W. W., and G. E. Benedict. 1972. *Neptunium-237 Production and Recovery*, AEC Critical Review Series, TID-25955, U.S. Atomic Energy Commission, Washington, D.C.

Schnitzler, B. G. 1998. *Advanced Test Reactor Plutonium-238 Production Feasibility Assessment* [Draft CD-0 report on waste processing at ORNL], Idaho National Engineering and Environmental Laboratory, Idaho Falls, Idaho (April 30).

Thompson, G. H., and M. H. Thompson. 1977. *Solvent Extraction of Irradiated Neptunium Targets. I. Valence Stabilization*, DP-1452, DuPont Savannah River Plant, Aiken, S.C. (January).

Thompson, G. H., and M. H. Thompson. 1977. *Solvent Extraction of Irradiated Neptunium Targets. II. Flowsheet Development*, DP-1480, DuPont Savannah River Plant, Aiken, S.C. (July).

van Hoesen, S. D., and S. M. Robinson. 2003. *Oak Ridge National Laboratory Liquid and Gaseous Waste Treatment System Strategic Plan,* ORNL/TM-2003/197, Oak Ridge National Laboratory, Oak Ridge, Tenn. (August).

Warner, B. F., A. Naylor, A. Duncan, and P. D. Wilson. 1974. “A Review of the Suitability of Solvent Extraction for the Reprocessing of Fast Reactor Fuels,” p. 1481 in *Proc. Int. Solvent Extraction Conf.*, Vol. 2, ed. G. V. Jeffreys, Society of Chemical Industry, London.

Watson, S. B., and R. H. Rainey. 1975. *Modifications of the SEPHIS Computer Code for Calculating the Purex Solvent Extraction System*, ORNL/TM-5123, Oak Ridge National Laboratory, Oak Ridge, Tenn.

Wham, R. M., et al. 2004a. *Development and Evaluation Study of the Separation of* ^{237}*Np and* ^{238}*Pu Using a Three-Cycle Solvent Extraction Method with Multistage Contactors*, ORNL/TM-2004/168, Oak Ridge National Laboratory, Oak Ridge, Tenn.

Wham, R. M., et al. 2004b. *Preconceptual Design Planning for Chemical Processing to Support* ^{238}*Pu Production*, ORNL/TM-2004/213*,*Oak Ridge National Laboratory, Oak Ridge, Tenn.

Wham, R. M., et al. 2004c. *Preliminary Program Management Plan for Reestablishing Plutonium-238 Production Capability*, ORNL/TM-2004/105, Oak Ridge National Laboratory, Oak Ridge, Tenn.

Wham, R. M., et al. 2004d. *Summary Report of Pellet Target Fabrication and Irradiation in the High Flux Isotope Reactor (HFIR) and Advanced Test Reactor (ATR)*, ORNL/TM-2004/170, Oak Ridge National Laboratory, Oak Ridge, Tenn.

Wham, R. M., et al. 2004e. *Test Target Experimental Plan, Part I: Data Analysis and Test Target Design Consideration,* ORNL/TM-2004/165, Oak Ridge National Laboratory, Oak Ridge, Tenn.

APPENDIX A

PROCESS FLOWSHEETS

APPENDIX A
PROCESS FLOWSHEETS

This appendix contains the process flowsheets for the production of 5 kg of ^{238}Pu per year at REDC. The flowsheets describe requirements for processing aluminum-clad targets containing pellets of neptunium oxide in an aluminum powder matrix. The flowsheets include a two-stage target dissolution process, a two-cycle neptunium and plutonium solvent extraction process, and neptunium and plutonium purification using solvent extraction and ion-exchange processing. The conversion of neptunium to an oxide for target fabrication is shown using both cation resin loading and oxalate precipitation, each followed by calcination. A similar oxide conversion process is shown that converts purified plutonium solutions to the final oxide powder product using oxalate precipitation and calcination, which is followed by an ^{16}O exchange process to reduce neutron activity.

The conceptual solvent extraction processing flowsheets for the separation of neptunium and plutonium were evaluated using the SEPHIS (Solvent Extraction Processes Having Interacting Solutes) computational model. This model predicts the extraction behavior of U(VI), Pu(III and IV), and nitric acid. The model accounts for the effects of nonextracting nitrates on the partitioning of these solutes and also has the capability to calculate the effect of reductant addition on plutonium distribution. Since no algorithms specifically describe the partitioning behavior of Np(IV), the SEPHIS code was modified by adding a distribution prediction capability for neptunium. Equilibrium distribution data for Np(IV) indicate that its distribution coefficients are approximately one-third those for Pu(IV) over the range of conditions applicable to this process. Therefore, Np(IV) distribution coefficients used in the revised SEPHIS code were calculated using a modified form of the Pu(IV) distribution coefficient algorithm. The validity of the model was evaluated by performing a simulation using parameters applied in flowsheet tests performed at SRS and comparing predicted and experimental results. The SEPHIS program does not take into account either (a) the redox kinetics of Np and Pu or (b) the effects of radiolytic degradation products on process recoveries and losses. It was assumed that chemical and physical process conditions can be selected to maintain recoveries and losses of neptunium and plutonium at acceptable levels. Development work will be required to demonstrate that such process conditions can be met.

The anion- and cation-exchange processes were based on previous neptunium and plutonium processing at SRS and ORNL. To some degree the neptunium oxide conversion flowsheet has been verified at REDC with the production of neptunium oxide that was used in the fabrication of targets that were irradiated at ATR and processed at ORNL. REDC also produced neptunium oxide for radiolysis studies using oxalate precipitation and calcination methods.

These conceptual flowsheets were developed for use as a guideline to identify areas that require more chemical and engineering development and to estimate equipment sizing. These flowsheets are shown in Figs. A.1–A.10.

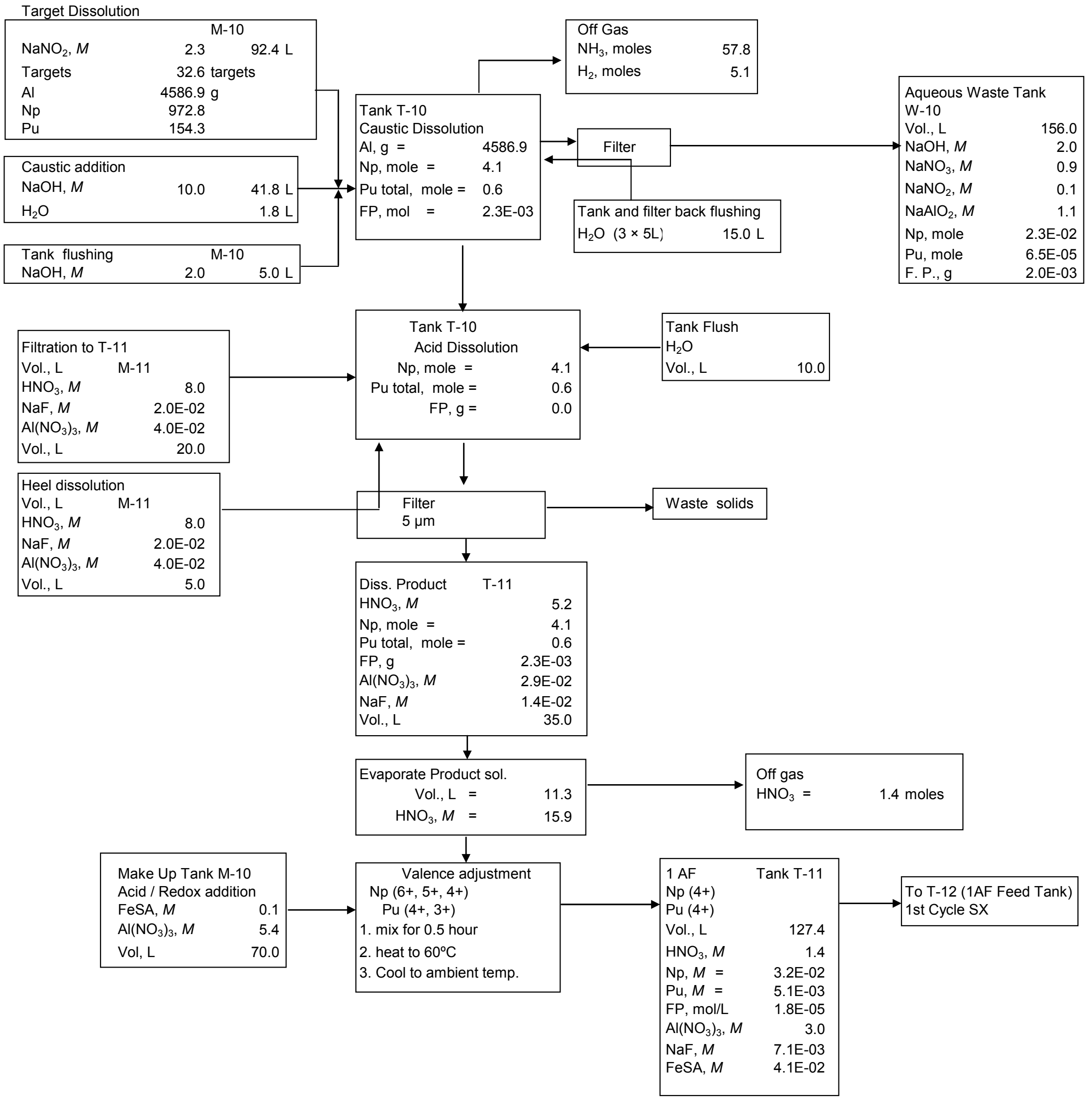


Fig. A.1. Target dissolution.

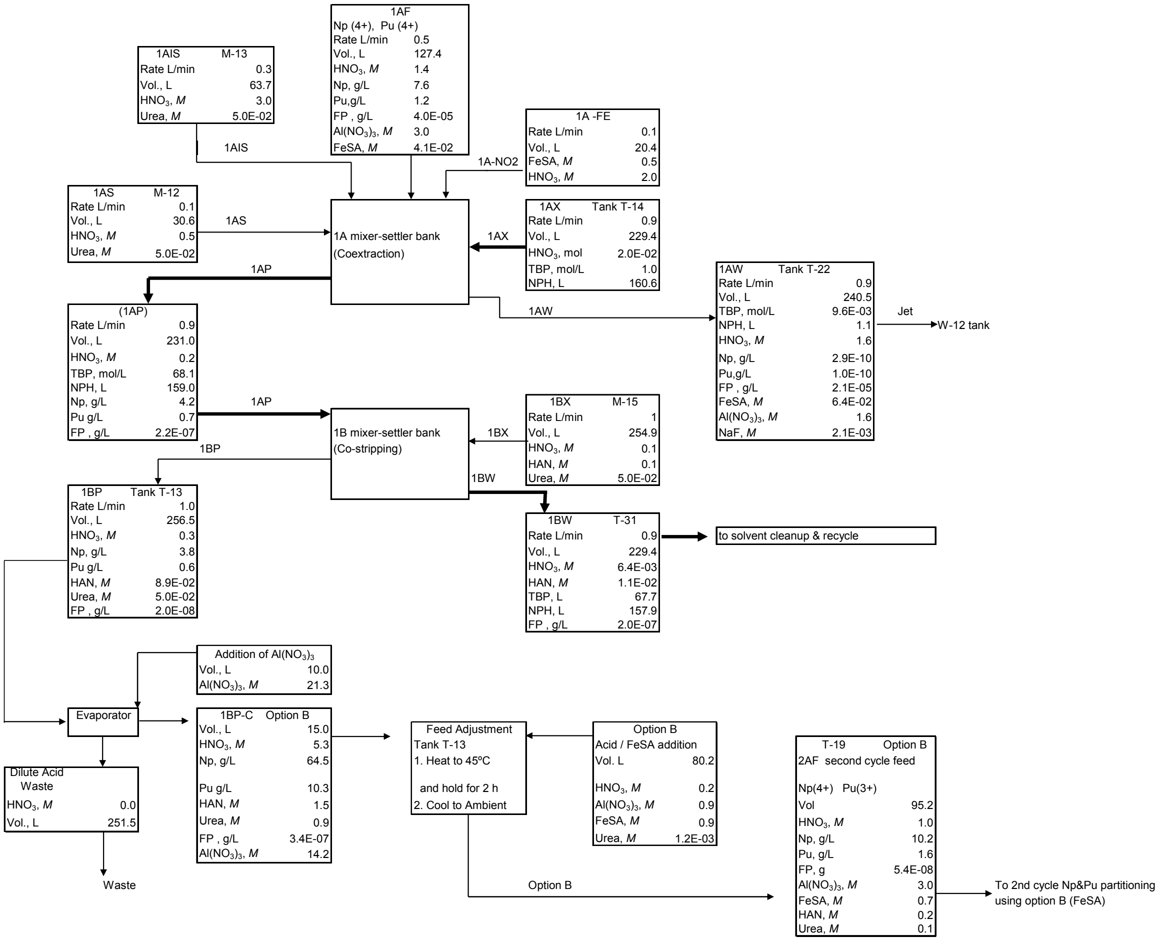


Fig. A.2. First-cycle solvent extraction.

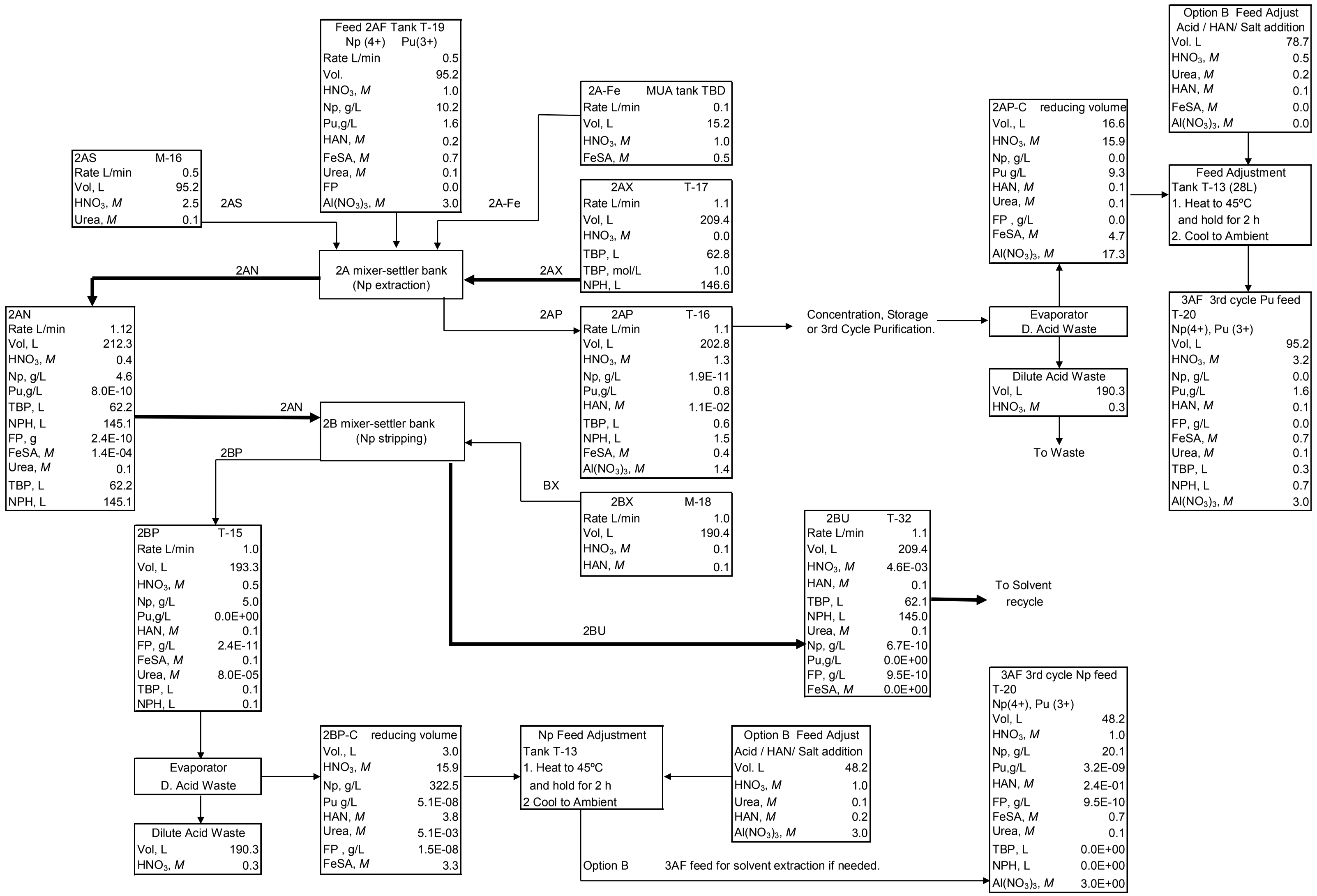
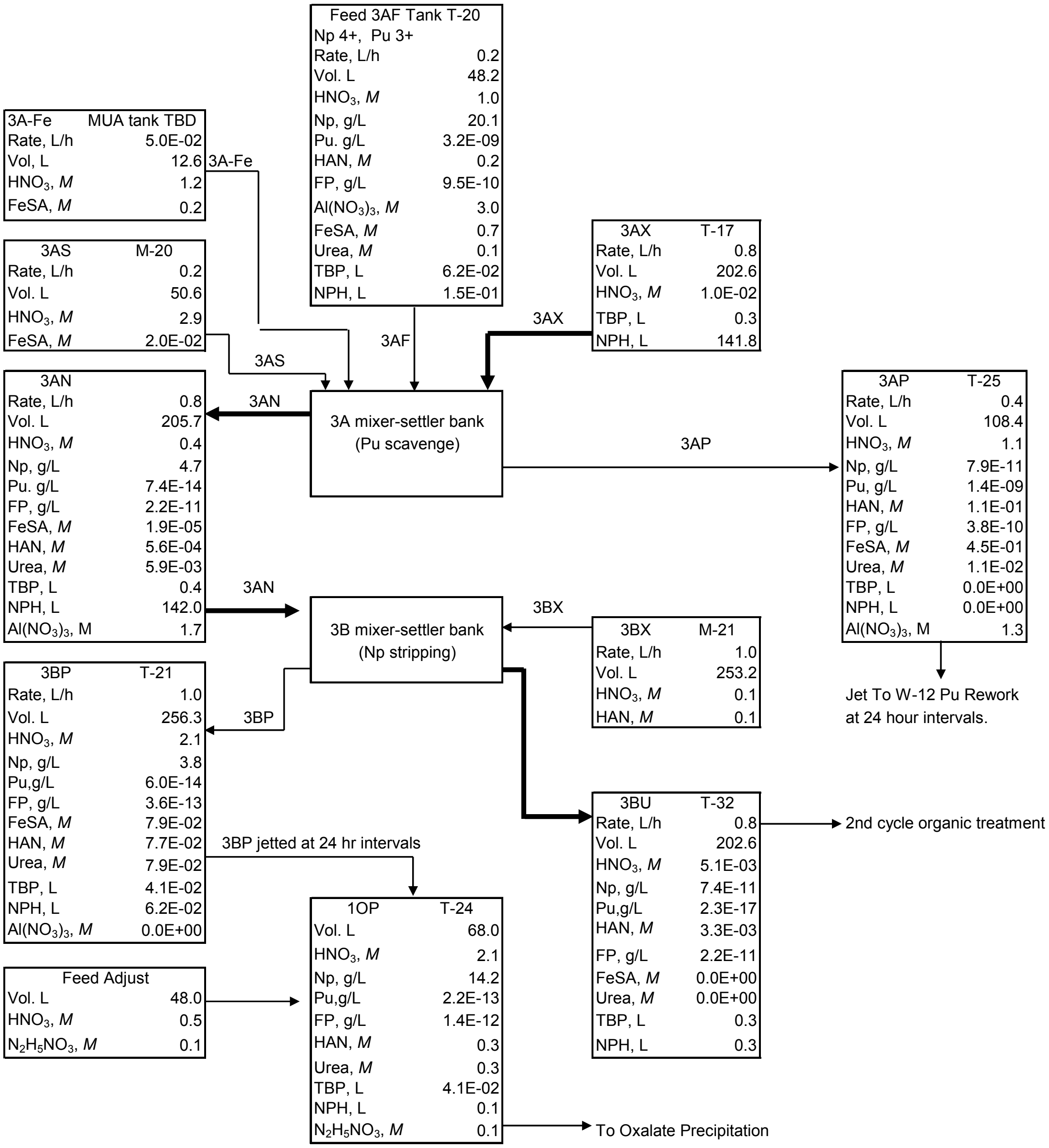


Fig. A.3. Second-cycle solvent extraction.



Feed 3AF Tank T-20	
Np 4+, Pu 3+	
Rate, L/h	0.2
Vol. L	48.2
HNO_3, *M*	1.0
Np, g/L	20.1
Pu. g/L	3.2E-09
HAN, *M*	0.2
FP, g/L	9.5E-10
$Al(NO_3)_3$, *M*	3.0
FeSA, *M*	0.7
Urea, *M*	0.1
TBP, L	6.2E-02
NPH, L	1.5E-01

3A-Fe	MUA tank TBD
Rate, L/h	5.0E-02
Vol, L	12.6
HNO_3, *M*	1.2
FeSA, *M*	0.2

3AS	M-20
Rate, L/h	0.2
Vol. L	50.6
HNO_3, *M*	2.9
FeSA, *M*	2.0E-02

3AX	T-17
Rate, L/h	0.8
Vol. L	202.6
HNO_3, *M*	1.0E-02
TBP, L	0.3
NPH, L	141.8

3AN	
Rate, L/h	0.8
Vol. L	205.7
HNO_3, *M*	0.4
Np, g/L	4.7
Pu. g/L	7.4E-14
FP, g/L	2.2E-11
FeSA, *M*	1.9E-05
HAN, *M*	5.6E-04
Urea, *M*	5.9E-03
TBP, L	0.4
NPH, L	142.0
$Al(NO_3)_3$, M	1.7

3AP	T-25
Rate, L/h	0.4
Vol. L	108.4
HNO_3, *M*	1.1
Np, g/L	7.9E-11
Pu, g/L	1.4E-09
HAN, *M*	1.1E-01
FP, g/L	3.8E-10
FeSA, *M*	4.5E-01
Urea, *M*	1.1E-02
TBP, L	0.0E+00
NPH, L	0.0E+00
$Al(NO_3)_3$, M	1.3

3BX	M-21
Rate, L/h	1.0
Vol. L	253.2
HNO_3, *M*	0.1
HAN, *M*	0.1

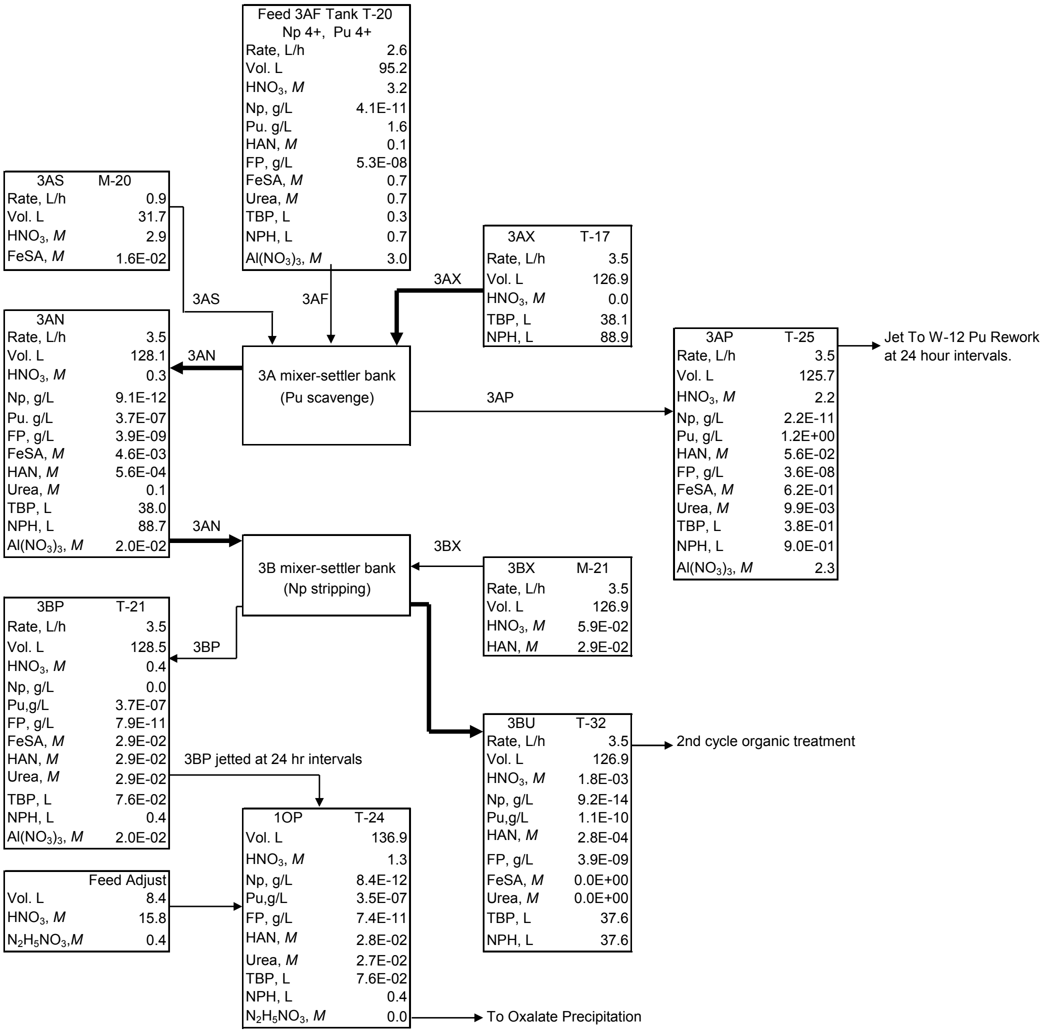
3BP	T-21
Rate, L/h	1.0
Vol. L	256.3
HNO_3, *M*	2.1
Np, g/L	3.8
Pu,g/L	6.0E-14
FP, g/L	3.6E-13
FeSA, *M*	7.9E-02
HAN, *M*	7.7E-02
Urea, *M*	7.9E-02
TBP, L	4.1E-02
NPH, L	6.2E-02
$Al(NO_3)_3$, *M*	0.0E+00

3BU	T-32
Rate, L/h	0.8
Vol. L	202.6
HNO_3, *M*	5.1E-03
Np, g/L	7.4E-11
Pu,g/L	2.3E-17
HAN, *M*	3.3E-03
FP, g/L	2.2E-11
FeSA, *M*	0.0E+00
Urea, *M*	0.0E+00
TBP, L	0.3
NPH, L	0.3

Feed Adjust	
Vol. L	48.0
HNO_3, *M*	0.5
$N_2H_5NO_3$, *M*	0.1

1OP	T-24
Vol. L	68.0
HNO_3, *M*	2.1
Np, g/L	14.2
Pu,g/L	2.2E-13
FP, g/L	1.4E-12
HAN, *M*	0.3
Urea, *M*	0.3
TBP, L	4.1E-02
NPH, L	0.1
$N_2H_5NO_3$, *M*	0.1

Fig. A.4. Third-cycle solvent extraction, neptunium purification.



Feed 3AF Tank T-20 Np 4+, Pu 4+	
Rate, L/h	2.6
Vol. L	95.2
HNO_3, *M*	3.2
Np, g/L	4.1E-11
Pu. g/L	1.6
HAN, *M*	0.1
FP, g/L	5.3E-08
FeSA, *M*	0.7
Urea, *M*	0.7
TBP, L	0.3
NPH, L	0.7
$Al(NO_3)_3$, *M*	3.0

3AS	M-20
Rate, L/h	0.9
Vol. L	31.7
HNO_3, *M*	2.9
FeSA, *M*	1.6E-02

3AX	T-17
Rate, L/h	3.5
Vol. L	126.9
HNO_3, *M*	0.0
TBP, L	38.1
NPH, L	88.9

3AN	
Rate, L/h	3.5
Vol. L	128.1
HNO_3, *M*	0.3
Np, g/L	9.1E-12
Pu. g/L	3.7E-07
FP, g/L	3.9E-09
FeSA, *M*	4.6E-03
HAN, *M*	5.6E-04
Urea, *M*	0.1
TBP, L	38.0
NPH, L	88.7
$Al(NO_3)_3$, *M*	2.0E-02

3AP	T-25
Rate, L/h	3.5
Vol. L	125.7
HNO_3, *M*	2.2
Np, g/L	2.2E-11
Pu, g/L	1.2E+00
HAN, *M*	5.6E-02
FP, g/L	3.6E-08
FeSA, *M*	6.2E-01
Urea, *M*	9.9E-03
TBP, L	3.8E-01
NPH, L	9.0E-01
$Al(NO_3)_3$, *M*	2.3

3BX	M-21
Rate, L/h	3.5
Vol. L	126.9
HNO_3, *M*	5.9E-02
HAN, *M*	2.9E-02

3BP	T-21
Rate, L/h	3.5
Vol. L	128.5
HNO_3, *M*	0.4
Np, g/L	0.0
Pu,g/L	3.7E-07
FP, g/L	7.9E-11
FeSA, *M*	2.9E-02
HAN, *M*	2.9E-02
Urea, *M*	2.9E-02
TBP, L	7.6E-02
NPH, L	0.4
$Al(NO_3)_3$, *M*	2.0E-02

3BU	T-32
Rate, L/h	3.5
Vol. L	126.9
HNO_3, *M*	1.8E-03
Np, g/L	9.2E-14
Pu,g/L	1.1E-10
HAN, *M*	2.8E-04
FP, g/L	3.9E-09
FeSA, *M*	0.0E+00
Urea, *M*	0.0E+00
TBP, L	37.6
NPH, L	37.6

	Feed Adjust
Vol. L	8.4
HNO_3, *M*	15.8
$N_2H_5NO_3$,*M*	0.4

1OP	T-24
Vol. L	136.9
HNO_3, *M*	1.3
Np, g/L	8.4E-12
Pu,g/L	3.5E-07
FP, g/L	7.4E-11
HAN, *M*	2.8E-02
Urea, *M*	2.7E-02
TBP, L	7.6E-02
NPH, L	0.4
$N_2H_5NO_3$, *M*	0.0

Fig. A.5. Third-cycle solvent extraction, plutonium purification.

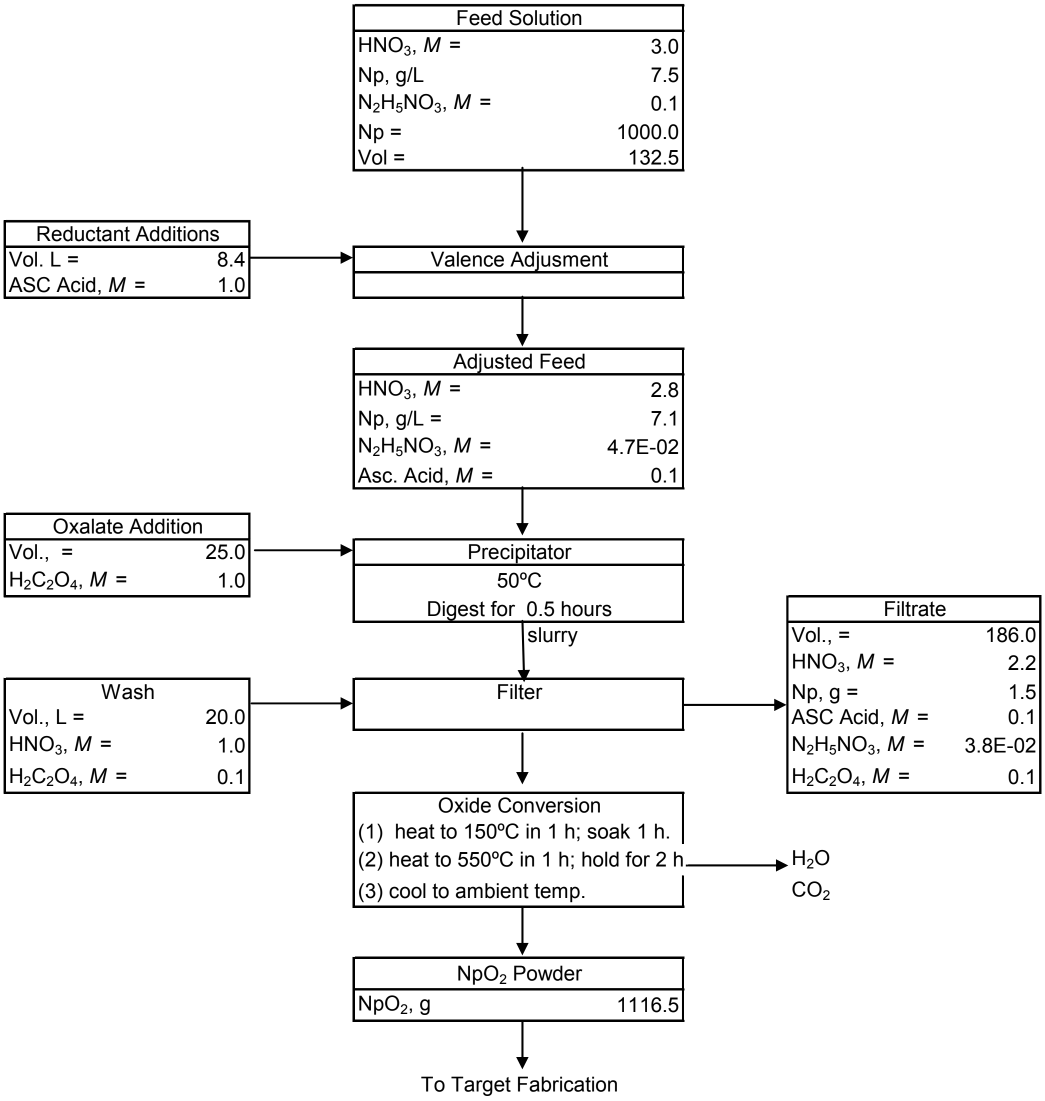


Fig. A.6. Neptunium oxalate precipitation and oxide conversion.

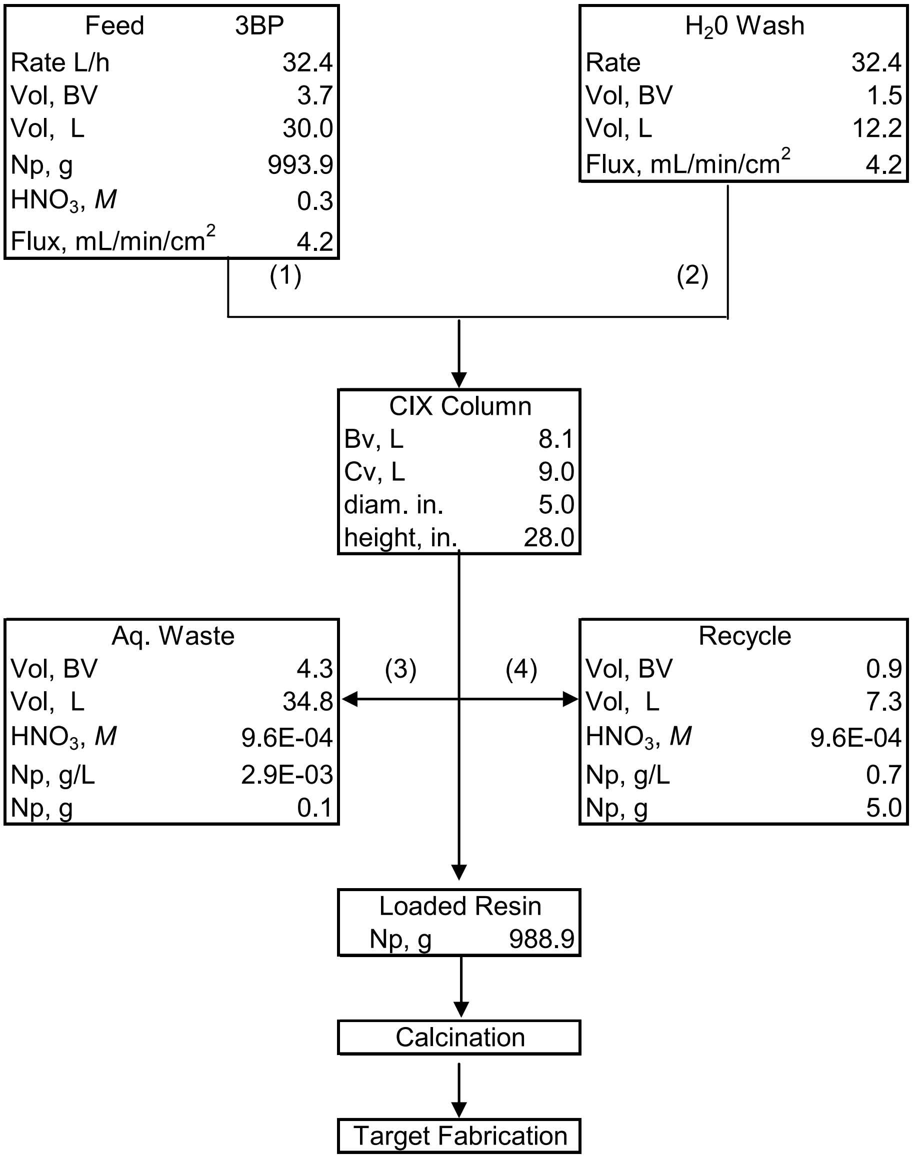


Fig. A.7. NpO_2 particle preparation: cation-exchange-resin loading.

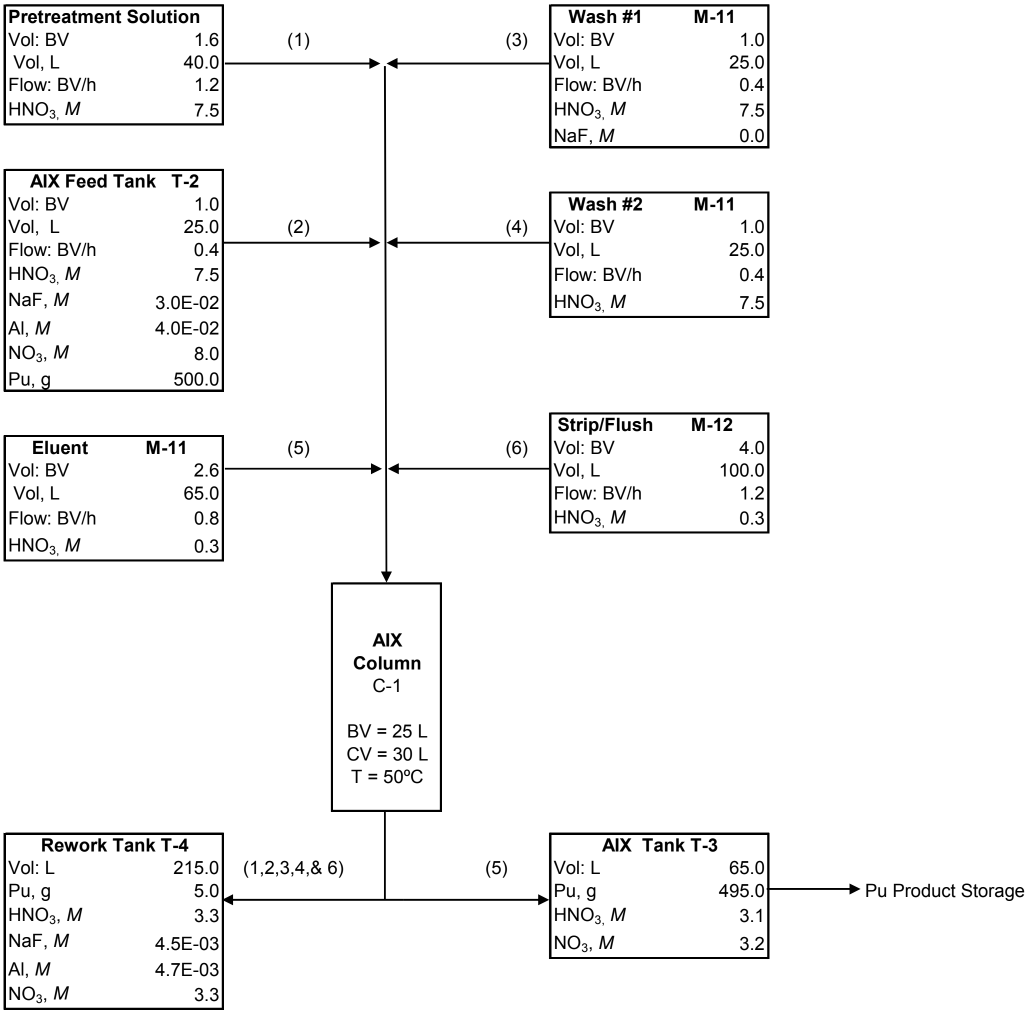


Fig. A.8. Ion-exchange purification of plutonium.

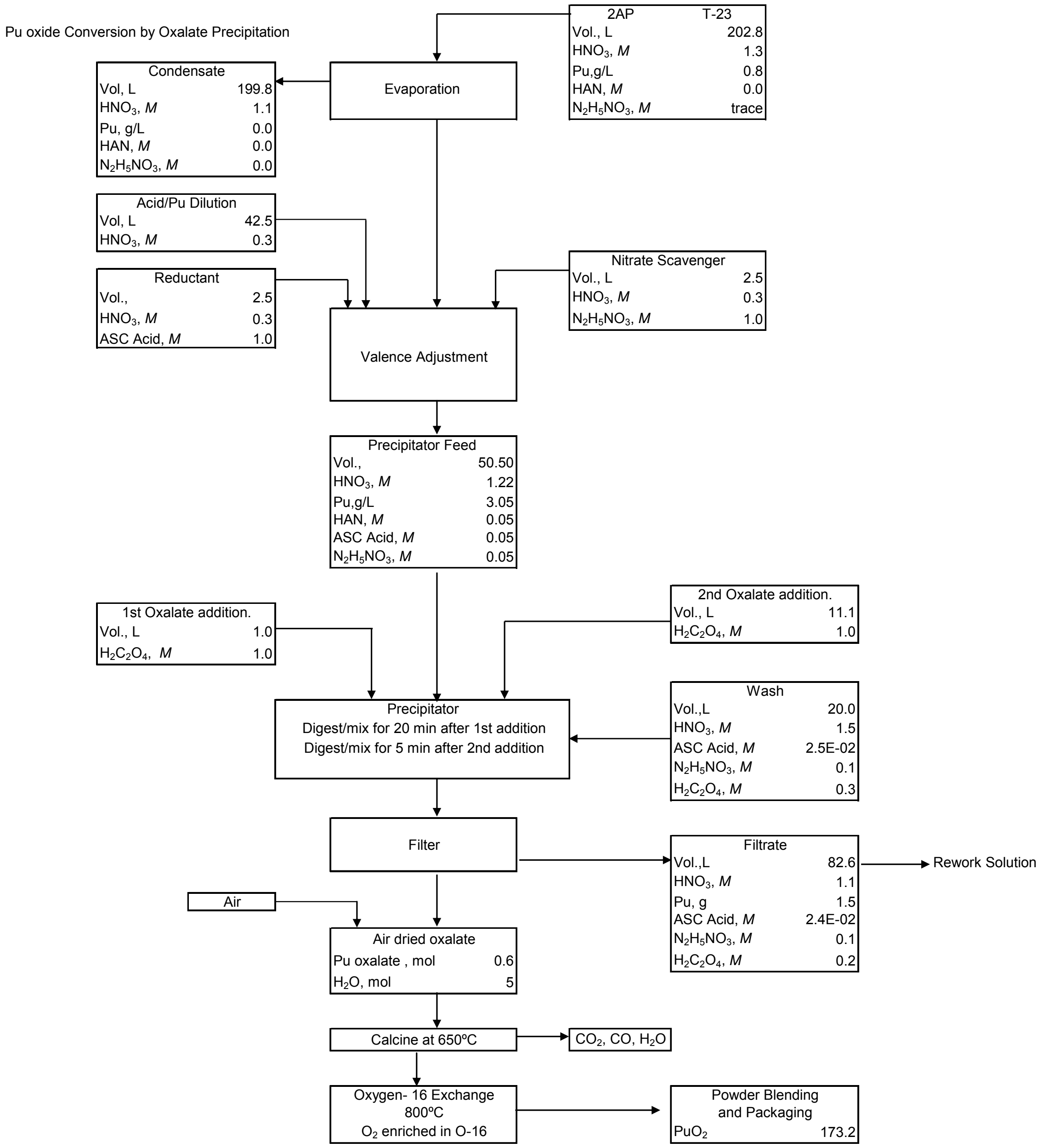


Fig. A.9. Oxalate precipitation of $Pu_2(C_2O_4)_3$ by the two-stage method of SRS.

ORNL/TM-2004/174

INTERNAL DISTRIBUTION

1. C. W. Alexander
2. J. F. Birdwell
3. W. D. Bond
4–5. R. R. Brunson
6. E. D. Collins
7. G. D. Del Cul
8. L. K. Felker
9. M. A. Green
10. D. J. Hill
11. T. D. Hylton
12–13. A. S. Icenhour
14. R. T. Jubin
15. J. M. Keller
16. B. E. Lewis
17. S. C. Marschman
18. B. D. Patton
19. S. M. Robinson
20. J. E. Rushton
21. C. M. Simmons
22. D. W. Simmons
23. B. B. Spencer
24. L. M. Toth
25. L. D. Trowbridge
26–28. R. M. Wham
29. D. F. Williams
30. NSTD DMC
31. OTIC–RC, OSTI, CRL

EXTERNAL DISTRIBUTION

32. L. W. Boyd, DOE-ORO, U.S. Department of Energy, P.O. Box 2008 MS-6269, Oak Ridge, TN 37831
33. W. P. Carroll, DOE-HQ, NE-40/Germantown Building, U.S. Department of Energy, 1000 Independence Ave., S.W., Washington, DC 20585-1290
34. E. Kendall, NNSA, U.S. Department of Energy, P.O. Box 2001 MS-8139, Oak Ridge, TN 37831
35. S. R. Martin, Jr., DOE-ORO, U.S. Department of Energy, P.O. Box 2008 MS-6269, Oak Ridge, TN 37831
36. K. H. Reynolds, DOE-ORO, U.S. Department of Energy, P.O. Box 2008 MS-6269, Oak Ridge, TN 37831
37. B. G. Schnitzler, Idaho National Engineering and Environmental Laboratory, P.O. Box 1625, Idaho Falls, ID 83415