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PLUTONIUM-238 RECOVERY FROM IRRADIATED NEPTUNIUM TARGETS USING SOLVENT EXTRACTION

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1. Introduction

The United States Department of Energy proposes to re-establish a domestic capability for producing plutonium-238 (²³⁸Pu) to fuel radioisotope power systems primarily in support of future space missions. A conceptual design report is currently being prepared for a new ²³⁸Pu, and neptunium-237 (²³⁷Np) target fabrication and processing facility tentatively to be built at the Idaho National Laboratory (INL) in the USA. The facility would be capable of producing at least 5 kg of ²³⁸Pu-oxide powder per year. Production of ²³⁸Pu requires fabrication of ²³⁷Np targets with subsequent irradiation in the existing Advanced Test Reactor (ATR) located at the INL. The targets are ²³⁷Np oxide dispersed in a compact of powdered aluminum and clad with aluminum metal. The ²³⁸Pu product is separated and purified from the residual ²³⁷Np, aluminum matrix, and fission products. The unconverted ²³⁷Np is also a valuable starting material and is separated, purified and recycled to the target fabrication process. The proposed baseline method for separating and purifying ²³⁸Pu and unconverted ²³⁷Np post irradiation is by anion exchange (IX). Separation of Pu from Np by IX was chosen as the baseline method because of the method's proven ability to produce a quality Pu product and because it is amenable to the relatively small scale, batch type production methods used (small batches of ~200g ²³⁸Pu are processed at a time). Multiple IX cycles are required involving substantial volumes of nitric acid and other process solutions which must be cleaned and recycled or disposed of as waste. Acid recycle requires rather large evaporator systems, including one contained in a hot cell for remote operation. Finally, the organic based anion exchange resins are rapidly degraded due to the high α -dose and associated heat production from ²³⁸Pu decay, and must be regularly replaced (and disposed of as waste). In summary, IX is time consuming, cumbersome, and requires substantial tankage to accommodate the process. The primary purpose of the preliminary study discussed here is to develop an alternative process flowsheet using well-known solvent extraction (SX) techniques based on decades of experience with PUREX processing of nuclear materials. Ultimately, this initial study will be used to determine if an SX approach would offer any significant processing advantages relative to the currently proposed anion exchange process.

2. Process Summary

The currently proposed baseline process is adapted from that used historically for several decades at the Savannah River Site for the production of ²³⁸Pu from irradiated ²³⁷Np targets using anion exchange separation [1]. A generalized process flow diagram is indicated in Figure 1. Irradiated targets are first cooled for an appropriate amount of time to allow decay of the shorter lived fission and activation products. The next processing step involves caustic dissolution in NaOH and NaNO₃ to separate the aluminum clad and matrix material from the heavy metal (HM) oxides, predominately Np and Pu (note that henceforth Pu and Np will imply the isotopes ²³⁸Pu and ²³⁷Np, respectively). The caustic Al containing solutions are sent to the waste treatment facilities. The solid HM oxides and residual fission, activation, and other impurities are recovered by filtration and dissolved in ~8M HNO₃ with small amounts fluoride ion; the resulting acidic stream is the primary feed material sent through the multiple cycles of anion exchange to separate, purify and concentrate the Np and Pu products from one another and from other impurities. The acidic Np product solution is recycled to the upfront target fabrication process where the Np is ultimately converted to the oxide form and fabricated into additional targets for irradiation in ATR. In a similar manner, the Pu product is precipitated as the oxalate, calcined to the oxide, and subsequently used to fabricate heat sources.

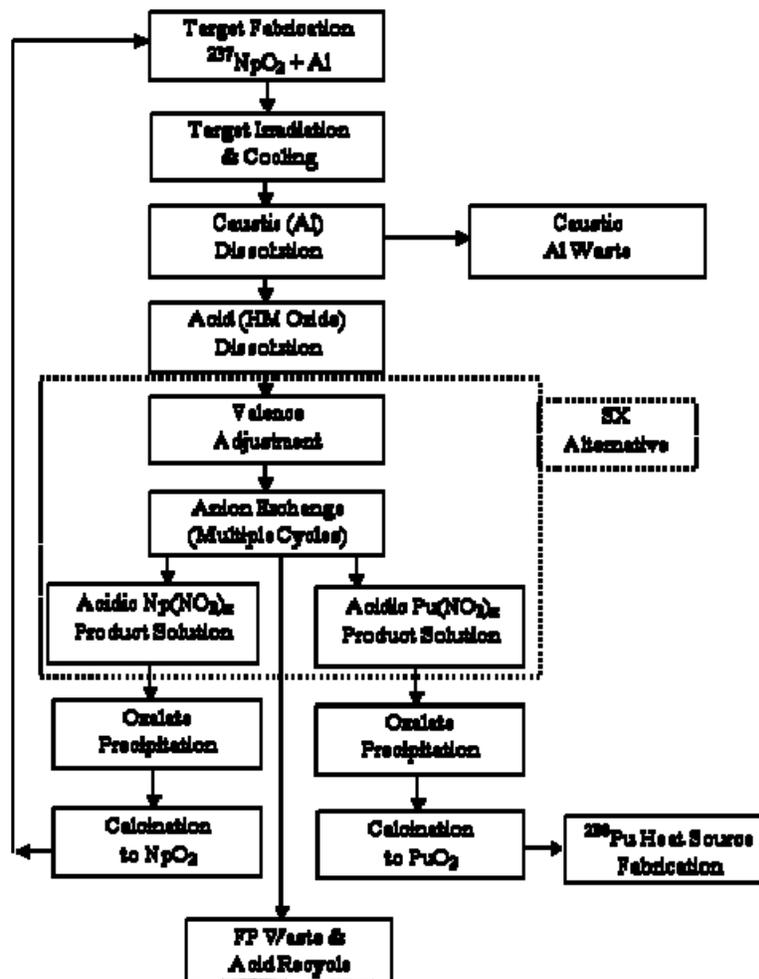


Figure 1 Simplified ^{238}Pu process schematic indicating location of the solvent extraction alternative

2.1 Anion Exchange

The IX process chemistry is based on controlling nitric acid concentration in the process solutions and the Np and Pu valence before, during, and after loading onto the IX columns. A batch of the acidic solution from dissolving the HM oxides is first adjusted by adding nitric acid, ferrous sulfamate ($\text{Fe}(\text{NH}_2\text{SO}_3)_2$ or FS), and hydrazine mononitrate. Nitric acid is added to bring the total concentration to $\sim 8\text{ M HNO}_3$. The Np and Pu valences are adjusted by the addition of FS, which reduces Np(V) and (VI) to Np(IV). Plutonium (VI) is simultaneously reduced to Pu(III). Hydrazine mononitrate solution is then added to the solution to reduce gassing in the anion exchange column and to retard oxidation of Np and Pu to the (V) and (VI) valence states, respectively. A “heat kill” step (heating the solution to $\sim 55^\circ\text{C}$) is used to oxidize Pu(III) to Pu(IV), giving both Pu and Np in the (IV) oxidation states (Np(IV) oxidizes at a much slower rate than does Pu(III)). Typical concentrations in the adjusted feed are 6 g/L Np and 0.6 g/L Pu.

Multiple cycles (6-7) of IX are required. The first cycle separates the Np and Pu from the Al and fission products. The second cycle partitions the Np from Pu and provides additional decontamination from fission products. Pu then undergoes two successive anion exchange cycles to accomplish the necessary purification and concentration. Np also receives as many as 2 additional cycles for final decontamination and concentration. An additional IX cycle is used to recover Pu and Np losses from a variety of process streams in order to minimize overall losses. Several different columns are used, differing in size (10 to 100 L bed volumes) to accommodate different volumes and concentrations of the various process solutions.

A typical IX cycle consists of a sequence of processing steps. Before loading the adjusted feed solution onto the column, it is reconditioned to remove the storage (elution) solution from the previous cycle and re-acidified by flushing with several bed volumes of 8M nitric acid reconditioning solution through the column. After reconditioning, the adjusted feed solution is transferred to the column. Np and/or Pu in the (IV) valence state are sorbed by the anion resin, while the fission products and other impurities pass through the column. The column, loaded with Np and/or Pu, is washed with several bed volumes of 8M HNO₃ to flush impurities from the column. The wash solutions are either sent to acid recycle or processed through an additional IX cycle to minimize any actinide losses. In a typical partition cycle, Pu is selectively eluted from the column using several bed volumes of 4.8M HNO₃ containing 0.08M FS and 0.10M hydrazine mononitrate. Finally, Np is eluted with a solution of 0.05M hydrazine nitrate in 0.17M HNO₃. The Np is typically concentrated during the elution step by allowing the initial fraction of eluant or the “head cut”, which contains very little Np, to be discharged to a separate tank. When Np(IV) is observed in the column effluent, the “heart cut” is collected until the green color of Np(IV) is no longer visible in the effluent. No “tail cut” is made during the Np elution and the column is placed in standby mode and stored containing the hydrazine mononitrate and nitric acid solution until the next cycle.

The Pu and Np purities in the product streams are determined and additional cycles of IX exchange may be required to enhance FP decontamination and remove actinide cross contamination from the respective product streams. The additional cycles are performed in much the same manner as previously described: acidity and valence of the feed solution is adjusted; columns are conditioned, loaded, and eluted.

2.2 Solvent Extraction

Decades of process knowledge is available with regard to actinide separation and purification based on the SX chemistry of tributylphosphate (TBP) in a hydrocarbon (e.g., kerosene or dodecane) diluent (PUREX processing) [2]. The Argonne Model for Universal Solvent Extraction (AMUSE) code [3] was used to establish the detailed conditions to be used in the proposed SX flowsheet. AMUSE was developed to design multistage countercurrent flowsheets for SX processes and designed to give accurate predictions of chemical behavior by calculating distribution ratios using established chemical equilibria and thermodynamic parameters for the major components, including HM, FP, hydrogen ion, nitrate, and water. Furthermore, the counter-current mass balance algorithm contains terms for stage efficiency and other-phase-carryover for both the aqueous and organic phases. The proposed Np and Pu process cycles discussed herein were designed using the AMUSE code. The only constraints used in the analysis were Np and Pu extraction efficiencies of 99.99+% (to minimize process losses) and to provide Pu and Np concentrations in the respective products that were similar to those in the IX produced streams.

The SX process flowsheet is based on the use of commercially available annular centrifugal contactors (CC) as the processing equipment. A series of 5-cm diameter CC stages, each with a total throughput of 1.25 L/min, is anticipated to provide ample capacity to meet the annual Pu production goal in a series of short processing campaigns. This size of centrifugal contactors offer a number of significant advantages, some particularly relevant to the Pu processing. These advantages include low stage volumes (~200 mL/stage, with interstage connections), which minimizes the required volume of organic phase. Furthermore, the short residence times (~3-4 sec/stage) minimizes the amount of time the Pu is in contact with the organic phase. Another advantage of CCs is that they “tolerate” gas evolution well.

2.2.1 Dissolution and Feed Adjustment

For the preliminary SX flowsheet, the caustic dissolution cycle for the irradiated targets remains identical to that used in the proposed IX process. The acidic HM oxide dissolution cycle can be slightly altered for SX. The HM concentration can be increased from the ~6-7 g/L HM metal concentration desired for IX. In this analysis, the HM concentration was increased by a factor of ~2 by using a smaller volume of 8M HNO₃ in the dissolution process. These conditions are by no means optimized and additional work is required to determine optimal conditions in the acid dissolution cycle for the SX alternative.

The SX flowsheet is also based on controlling actinide oxidation state. The Np is selectively extracted as Np(IV) in the first cycle while Pu(III) is rejected to the raffinate along with the FP and matrix components. To this end, the SX feed is adjusted with FS solution in the amount needed to give a molar

ratio of Fe:Np of 4; sulfamic acid is also present to aid in stabilizing the FS. The FS is added to reduce all Pu to Pu(III) and all Np to Np(IV). Concentrated HNO₃ is added to re-adjust the feed solution to 8M HNO₃. It is important to note that this oxidation state control for the SX process is much more certain than that for the IX process, which depends on control of reaction time and redox conditions such that oxidation of all the Pu(III) is complete before appreciable oxidation of Np(IV) occurs. Furthermore, the notable lack of hydrazine in the SX flowsheet mitigates at least one safety concern (formation of hydrazoic acid) associated with the IX process.

2.2.2 Np Cycle

The solvent extraction flowsheet developed for the Np cycle is shown in Figure 1 and the concentrations and relative flow rates for the feed stream and the major outputs streams are given in Table 1. The adjusted feed solution is processed in the first or Np cycle of the SX flowsheet. This cycle uses an organic phase composed of 30 vol % TBP in hydrocarbon diluent (standard PUREX solvent). In the extraction section, Np and minor quantities of other metals are transferred to the organic phase. The section requires 7 CC stages to effect the required extraction efficiency. The loaded organic phase is next scrubbed in 3 CC stages with 1.5M HNO₃ and 0.02M FS aqueous phase to remove trace quantities of Pu, FP and matrix metals extracted into the organic phase. The FS is added to this scrub solution to reduce any Pu(IV) that might have formed in the extraction section. Two additional stages of scrub using 1.5M HNO₃ are employed, primarily to increase Fe (from FS) decontamination in the Np product.

The purified Np in the organic phase is back extracted in the stripping section of the flowsheet. A total of 6 CC stages are employed for the Np stripping operation in this flowsheet. A dilute solution of 0.01M HNO₃ is used in the strip section to effectively back-extract Np (and nitric acid) from the loaded solvent. By using a high organic-to-aqueous flow ratio (O:A), the Np is concentrated in the aqueous phase. Note that the final Np product stream exits at >15 g/L in 1.3 M HNO₃.

The predicted Np recovery is >99.99% in this cycle while >99.98% of the Pu is rejected to the raffinate. The relatively pure Np solution would be recycled to the target fabrication portion of the process without any additional cleanup. The raffinate from this Np cycle is treated to adjust the Pu valence state and then goes to a Pu cycle where it is processed to recover and purify the Pu product. Note that in the actual process, the clean organic phase exiting the strip section would be washed in a single CC stage (with

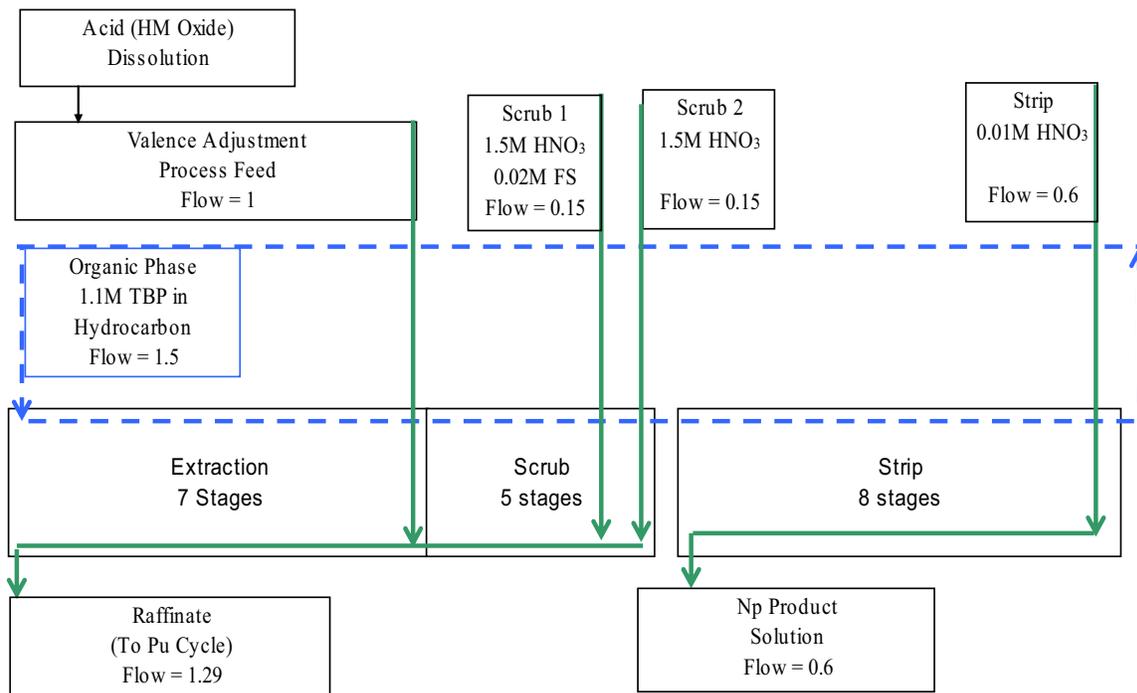


Figure 2 Process schematic for the proposed ²³⁷Np separation cycle using solvent extraction

Table 1 Process parameters for the Np cycle

Stream ID:	Feed	Raffinate	Np Product	Organic
Component	Concentration			
H ⁺ (M)	8.00	5.944	1.273	6.63E-05
Al (g/l)	0.944	0.731	5.7E-08	1.7E-16
Fe (g/L)	8.82	6.96	5.8E-05	1.4E-13
Np (g/L)	9.39	5.17E-04	15.5	7.69E-05
Pu (g/L)	1.16	0.897	2.83E-04	6.37E-12
F ⁻ (g/L)	0.165	0.128	9.9E-09	3.1E-17
Relative Flow Rate	1.0	1.3	0.6	1.5

dilute Na₂CO₃) and re-acidified in another stage (with dilute HNO₃) to remove any degradation products from radiolysis and hydrolysis before recycle of the organic to the extraction section.

2.2.3 Intercycle Adjustment

To facilitate recovery in the Pu cycle, the Pu must all be oxidized from Pu(III) to the Pu(IV) state. An established method to carry out this oxidation step is to sparge nitrogen dioxide (as N₂O₄ gas) through the solution with slight heating. This approach to Pu oxidation, which is documented for several operating PUREX plants [3], adds neither volume nor mass to the raffinate stream, but does convert sulfamate to sulfate, which impacts the extraction of Pu(IV). The raffinate from the Np cycle is collected in an intercycle collection tank and valence adjustment could be done either “in tank” or “in line”.

2.2.4 Pu Cycle

The solvent extraction flowsheet designed for the Pu cycle is shown in Figure 3 and the concentrations and relative flow rates for the feed, raffinate, Pu product and organic recycle streams are given in Table 2. Following intercycle adjustment, the Pu(IV) feed solution is fed to the extraction section of the Pu cycle. Again, a 30 vol % TBP solution in hydrocarbon diluent is the organic process solvent. The extraction section contains 6 CC stages and the scrub section contains 4 CC stages. In a manner similar to the Np cycle, Pu is preferentially extracted into the organic and small quantities of FP and other matrix components are back-extracted in the scrub section. The purified Pu in the organic phase is back extracted in the stripping section of the flowsheet using a total of 6 CC stages. A dilute solution of 0.1M HNO₃ with 0.05M oxalic acid (H₂C₂O₄) is used in the strip section to effectively back-extract Pu from the loaded solvent. The oxalate anion effectively complexes Pu and enhances stripping. Oxalate in the Pu product stream also has the potential to facilitate the subsequent oxalate precipitation step in the overall Pu processing scheme. By adjusting the organic-to-aqueous flow ratios (O:A), Pu is effectively concentrated in the organic phase of the extraction section and is then concentrated even more in the aqueous phase of the stripping section. Note that the final Pu product stream exits at ~6 g/L in 0.48M HNO₃. The predicted recovery of Pu in this cycle is >99.99%; only 0.007% of the Pu is lost into the raffinate. Nearly all of the Fe is rejected to the raffinate, with the Pu product stream estimated to contain only 0.32 µg Fe/ g Pu. Sulfate anion is also rejected to the raffinate and the final Pu product solution contains 1.1 µg SO₄²⁻/ g Pu. The relatively pure Pu solution would subsequently be processed through the oxalate precipitation and heat source fabrication steps of the process (refer to Figure 1).

3. Conclusions

A preliminary flowsheet for the separation and purification of ²³⁸Pu and ²³⁷Np by solvent extraction has been designed based on the AMUSE code. The flowsheet appears to be a viable alternative to the baseline anion exchange process currently being considered for a new processing facility. Several potential advantages are anticipated with SX processing, including: simplified operations, faster processing times, and reductions in waste volumes. It is conceptually possible that a single bank of centrifugal contactors will provide sufficient throughput to be used for both the Np and Pu cycles as well as for potentially separation of Pa (protactinium) from Np prior to the target fabrication process. Future efforts must ultimately rely on validating concepts of the proposed flowsheet with laboratory and engineering scale experiments.

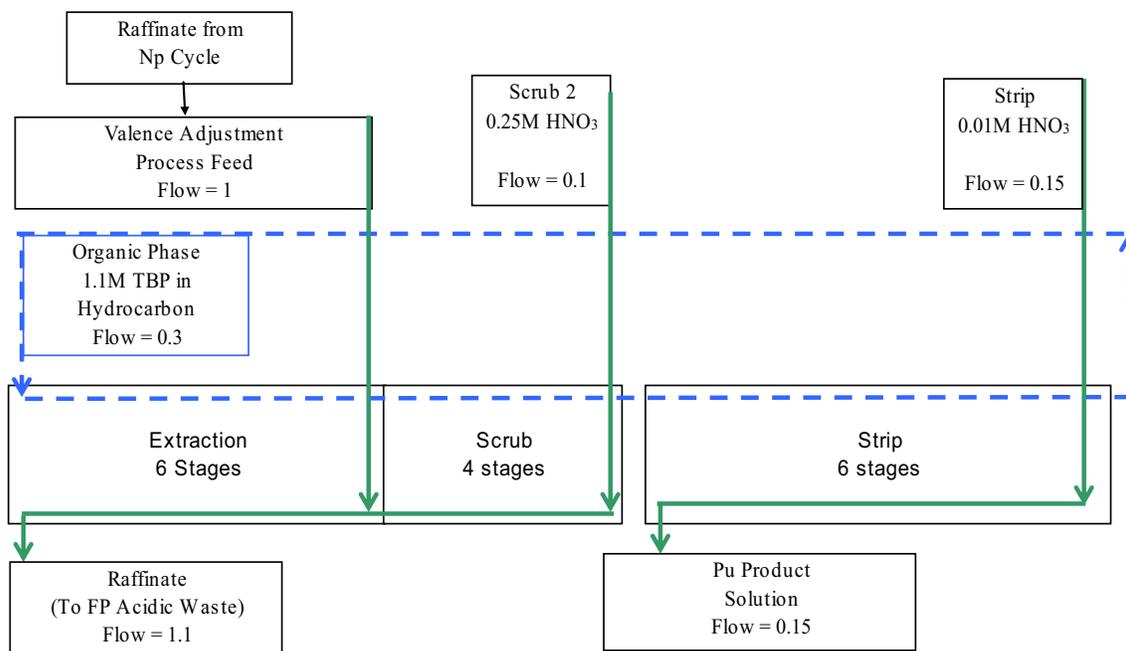


Figure 3 Process schematic for the proposed ^{238}Pu separation cycle using solvent extraction

Table 2 Process parameters for the Pu cycle

Stream ID:	Feed	Raffinate	Pu Product	Organic
Component	Concentration			
H ⁺ (M)	5.94	5.39	0.48	3.8E-03
Al (g/L)	0.731	0.666	2.0E-07	9.7E-14
Fe (g/L)	6.98	6.35	1.9E-06	9.3E-13
Pu (g/L)	0.897	6.47E-05	5.92	3.3E-06
C ₂ O ₄ (M)	0	0	4.94E-02	5.0E-05
SO ₄ (M)	0.249	0.227	6.77E-08	3.3E-14
F (g/L)	0.128	0.116	3.5E-08	1.7E-14
Flow Rate	1.0	1.1	0.2	0.3

4. Acknowledgements

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