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## Conversion of Uranyl Sulfate Solution to Uranyl Nitrate Solution for Processing in UREX

Megan E. Bennett, Delbert L. Bowers, Candido Pereira, George F. Vandegrift  
Chemical Sciences and Engineering Division  
Argonne National Laboratory, 9700 S. Cass Avenue, Argonne, IL 60439

### ABSTRACT

In 2016, the Canadian research reactor at Chalk River will no longer irradiate targets for  $^{99}\text{Mo}$  production, causing a worldwide shortage of  $^{99\text{m}}\text{Tc}$ , unless reliable, alternative production methods are developed. SHINE Medical Technologies is developing a production method using a deuterium-tritium (DT) neutron generator and a non-critical aqueous solution of low enriched uranium (LEU) in the form of uranyl sulfate solution. In this process, the recycling of uranium solution is necessary for the next irradiation. It has been proposed that the UREX purification process be used to recycle the uranyl sulfate solution; however, UREX requires a uranyl nitrate solution. Uranyl sulfate solutions do not perform well in UREX, because sulfate forms a strong complex with the uranyl ion and uranyl cannot be preferentially extracted; therefore, the uranyl sulfate solution must be converted to nitrate. A precipitation procedure for the conversion of uranyl sulfate solution to uranyl nitrate solution is discussed.

### 1. Introduction

The availability of metastable technetium-99 ( $^{99\text{m}}\text{Tc}$ ) is critical to the medical community; it is used in more than 80% of nuclear medicine diagnostic tests, or approximately 70,000 medical imaging procedures throughout the world daily [1]. In 2009, It was reported that Canada's Chalk River nuclear reactor and the Netherlands' High Flux reactor produce approximately 85% of Europe's and North America's  $^{99\text{m}}\text{Tc}$  supply [2]. It was recently announced that the Chalk River reactor will no longer irradiate targets for  $^{99}\text{Mo}$  production after 2016, creating a worldwide shortage of  $^{99\text{m}}\text{Tc}$  unless reliable, alternative production methods are developed.  $^{99\text{m}}\text{Tc}$  cannot be stockpiled because its parent isotope is molybdenum-99 ( $^{99}\text{Mo}$ ), which has a 66-hour half-life [3]. One possible production method is based on accelerator-driven fissioning of  $^{235}\text{U}$  in a non-critical (subcritical) solution.

Currently, most of the  $^{99}\text{Mo}$  is produced in a nuclear reactor by the neutron-induced fission of high-enriched uranium (HEU;  $\geq 20\%$   $^{235}\text{U}$ ). The  $^{99}\text{Mo}$  is isolated from the uranium and other fission products, purified, and loaded onto a generator. The  $^{99}\text{Mo}$  then decays to  $^{99\text{m}}\text{Tc}$ , which has a 6-hour half-life [4]. Production of  $^{99}\text{Mo}$  with HEU

is a nuclear proliferation concern, because HEU can be weaponized. It is far more desirable to produce  $^{99}\text{Mo}$  from either non-uranium-based sources, such as Mo irradiation, or using depleted uranium ( $\text{DU} < 0.7\% \text{ }^{235}\text{U}$ ), natural uranium ( $\text{NU} \approx 0.7\% \text{ }^{235}\text{U}$ ), or low enriched uranium ( $\text{LEU} \leq 20\% \text{ }^{235}\text{U}$ ) [4]. For systems designed to operate with HEU, the major downside of  $^{99}\text{Mo}$  production using LEU is that ~5 times more uranium is required to produce an equal amount of Mo as with HEU. Production using non-HEU methods, whether with a reactor or an accelerator, is greatly preferred because nuclear proliferation concerns are greatly reduced [5].

SHINE Medical Technologies is developing a production method that uses a deuterium-tritium (DT) neutron generator and a noncritical aqueous solution of LEU uranyl sulfate. After 5–7 days, the irradiated solution is given an 8–10 hour cooling period and then run through a Mo-recovery column. The effluent is then recycled for the next irradiation. Periodically after Mo recovery, the target solution will be processed to purify the uranium of unwanted fission and activation products.

During irradiation, a deuterium ( $^2\text{H}$ ) beam is accelerated toward a chamber containing tritium ( $^3\text{H}$ ) gas, generating high-energy neutrons when the  $^2\text{H}$  and  $^3\text{H}$  interact. These neutrons then impinge on the LEU solution, inducing fission of the  $^{235}\text{U}$ , and thus producing  $^{99}\text{Mo}$ . The vessel containing the LEU solution is subcritical by geometry to obviate concerns of a criticality accident (uncontrolled nuclear reaction) [5]. Two different LEU salts have been considered for use in SHINE, uranyl nitrate and uranyl sulfate. Currently, uranyl sulfate is preferred, because pH control is required when irradiating nitrate solutions due to generation of nitrate radiolysis products [6, 7].

Because sulfate stable to radiolysis, the use of uranyl-sulfate solution significantly reduces unwanted pH; however, uranyl-sulfate solutions do present a technical challenge to the periodic cleanup of the irradiated target solution from fission and activation products. Several methods for the purification of uranyl sulfate from fission and activation products were evaluated. They included: (1) Direct solvent extraction of uranyl sulfate; (2) Precipitation of the uranyl ion as uranyl peroxide; (3) Anion exchange of uranyl sulfate complexes; (4) Conversion of uranyl sulfate to nitrate followed by the UREX (URanium EXtraction) process.

The first option evaluated for the purification of uranium from fission and activation products was direct solvent extraction of uranyl sulfate. This is based on synergetic extraction of the uranyl disulfate anion using trioctyl ammonium sulfate (TOA) and trioctyl phosphate (TOPO), in a 2:1 ratio. A diluent of either an alkane or tetrachloroethylene is used. Extraction of this complex is easily achieved, but the stripping of uranium from the solvent becomes the technical challenge. In order for this system to be viable for the purification of uranium from fission and activation products, a complexing stripping agent is required. This complexant must have three important properties: (1) Forms strong complexes with uranyl ion; (2) Will not displace sulfate in the organic-phase trioctyl ammonium sulfate salt; (3) Can be destroyed in the aqueous uranyl-sulfate product solution without leaving residue in the solution. A literature survey and preliminary experimental work did not find a stripping agent that met the three criteria, and, therefore, direct extraction of uranyl sulfate was deemed not a viable system for the purification of uranium from fission and activation products.

The second option evaluated for the purification of uranium from fission and activation products was precipitation of the uranyl ion as uranyl peroxide. The solubility product ( $K_{sp} = [UO_2^{2+}] \times [O_2^{2-}]$ ) for uranyl peroxide is  $1.3 \times 10^{-36}$ . [8] However, there are many factors that influence the concentrations of free  $UO_2^{2+}$  ion and free  $O_2^{2-}$  ions, and therefore the completeness of the precipitation. For the uranyl ion, there are pH-dependent hydrolysis reactions that form the species  $UO_2OH^{1+}$ ,  $UO_2(OH)_2$ , and  $UO_2(OH)_3^{1-}$  and sulfate complexes  $UO_2SO_4$ ,  $UO_2(SO_4)_2^{2-}$ , and  $UO_2(SO_4)_3^{4-}$ . The formation of these species decreases the amount of free uranyl ion and thus the precipitation of uranyl peroxide. In addition to the formation of these complexes, the free peroxide-ion concentration is also effected by the pH, due to formation of the weak acids  $H_2O_2$  and  $HO_2^-$ . The relative concentrations of uranyl-sulfate complexes are also related to pH through the equilibria of sulfate ion with  $HSO_4^-$  and  $H_2SO_4$ . Further complications to the precipitation are that peroxide ion can also form complexes with uranyl ion  $UO_2(O_2)_2^{2-}$  and  $UO_2(O_2)_3^{4-}$ . Furthermore, low pH increases the uranyl-ion solubility by keeping the concentration of peroxide ion very low. As the pH is increased, the free uranyl ion concentration drops, due to an increase in the importance of hydrolysis reactions, complexation with sulfate, and eventually complexation with peroxide ion. Despite all of these potential complications, cursory experiments were performed to assess the viability of this system for the purification of uranium from fission and activation products. Based upon these it experiments it was concluded that this system is not viable, as it results in a colloidal suspension of uranyl peroxide that was nearly impossible to centrifuge or filter.

The third option evaluated for the purification of uranium from fission and activation products was anion exchange of uranyl sulfate complexes. Due to the high concentration of uranyl sulfate (~130-150g/L), and the low capacity of anion exchange resins, compared to those of solvent extraction, this process is not viable [9]. The fourth option evaluated for the purification of uranium from fission and activation products was the conversion of uranyl sulfate to uranyl nitrate followed by the UREX process. The first step in this process is to convert uranyl sulfate to uranyl nitrate. In order to do this, soluble alkaline earth nitrate salt(s) are introduced into the uranyl sulfate solution. The introduction of these salts causes the precipitation of alkaline-earth sulfate salts. If enough alkaline-earth cations are introduced into the sulfate media, all of the sulfate anion will be precipitated out (as alkaline-earth sulfate salt) thus leaving behind uranyl ion in a nitrate media. Initial experimental studies suggested that this conversion process could be performed easily, readily, and reliably. Because of this, this system was selected for further development.

Once the uranyl sulfate solution is converted to uranyl nitrate the UREX process can be performed. The UREX process is well-understood, so it was selected to purify uranium of fission products [10]. The UREX process selectively extracts uranium (with partial extraction of technetium and iodine) from nitric-acid solutions containing a mixture of actinides and fission products. Because uranyl sulfate does not extract into the UREX solvent, and sulfate is a strong complexation agent of uranyl ions, sulfate concentrations above 0.02 M impede the extraction of uranium [11]. Therefore, the irradiated LEU target solution must be converted from sulfate to the nitrate media prior to feeding into the UREX. A flowsheet for recovery of

uranium from the irradiated SHINE target solution was developed using the Argonne Model for Universal Solvent Extraction (AMUSE) code [12-14]

## 2. Experimental

American Chemical Society (ACS) reagent-grade strontium nitrate and barium nitrate from Merck were used in the conversion of uranyl sulfate to uranyl nitrate. The depleted uranium was obtained from Argonne National Laboratory (Argonne) stock. Dilute sulfuric acid was made using ACS reagent-grade concentrated sulfuric acid, available from Sigma-Aldrich, and 18-M $\Omega$  water. Dilute nitric acid was made using ACS reagent-grade concentrated nitric acid, available from Fisher, and 18-M $\Omega$  water. The depleted uranium was converted from the metal to U<sub>3</sub>O<sub>8</sub> in a furnace that was slowly ramped to between 300 and 900°C [15]. The resulting U<sub>3</sub>O<sub>8</sub> was then dissolved in sulfuric acid, resulting in a ~140 g-U/L solution at pH 1 that was ~0.7 M sulfate. This solution is in the composition range of the proposed SHINE LEU target solution (STS).

A flask containing 20 mL of simulated STS was immersed in a warm water bath for 30 minutes as the solution was stirred. The warm water bath was necessary because an elevated temperature of ~60°C is expected for the actual STS due to the presence of fission products. After the simulated STS was brought up to temperature, Sr(NO<sub>3</sub>)<sub>2</sub>, followed by Ba(NO<sub>3</sub>)<sub>2</sub>, was then added and allowed to react for 0.5 to 18 hours. The resulting precipitate was filtered by vacuum filtration. The resulting filtrate was then analyzed by inductively coupled plasma-optical emission spectrometry (ICP-OES) for U, Sr, and Ba content, and by ion chromatography for sulfate and nitrate content.

The AMUSE code simulates steady-state, multi-stage, counter-current solvent extraction processes. It was developed to design process flowsheets to recover radioactive species from solutions of dissolved spent nuclear fuel or radioactive waste. This code is an extension of the Generic TRUEX (TRansUranium EXtraction) Model (GTM) and can simulate a number of extraction processes including PUREX (Plutonium Uranium Extraction) and UREX with appropriate user-supplied process conditions (flow rates, number of stages, etc.). The Microsoft Excel version of the code was used to generate the flowsheets described in this work.

## 3. Results and Discussion

### 3.1 Determination of Effectiveness of Sr(NO<sub>3</sub>)<sub>2</sub> and Ba(NO<sub>3</sub>)<sub>2</sub> Addition for Sulfate Reduction

The addition of alkaline-earth nitrates to the STS generates insoluble alkaline sulfate species that precipitate while leaving the highly soluble uranyl nitrate in solution, as shown in Equation 1, where Ak is an alkaline-earth metal. The Geochemist's Workbench, Release 8.0, was used to calculate speciation for a series of alkaline-earth additions to the simulated STS [14]. Based on these calculations (shown in Table 1), it was determined that addition of Ca(NO<sub>3</sub>)<sub>2</sub> or Sr(NO<sub>3</sub>)<sub>2</sub> alone likely would not lower the [SO<sub>4</sub><sup>2-</sup>] sufficiently; therefore, addition of Pb(NO<sub>3</sub>)<sub>2</sub> or Ba(NO<sub>3</sub>)<sub>2</sub> would be necessary. A combination of Sr(NO<sub>3</sub>)<sub>2</sub> and Ba(NO<sub>3</sub>)<sub>2</sub> was chosen for further study. Ba(NO<sub>3</sub>)<sub>2</sub> was chosen because it lowers the sulfate concentration by 18,000 to 350,000 times and the allowable RCRA (Resource Conservation and

Recovery Act) concentration is 20 times higher than that of Pb. However, Ba(NO<sub>3</sub>)<sub>2</sub> has a limited aqueous solubility, so a second nitrate salt needs to be added to solution to precipitate the bulk of sulfate before a small quantity of Ba(NO<sub>3</sub>)<sub>2</sub> is added. Sr(NO<sub>3</sub>)<sub>2</sub> was chosen because SrSO<sub>4</sub> is much less soluble than CaSO<sub>4</sub> and would lower the sulfate concentrations by a factor of 12–55, while also reducing the amount of Ba that needed to be added:



**Table 1** Calculated compositions of solution and solid phases from the addition of solid alkaline nitrate salts to uranyl sulfate solutions

Additive ratio	Aqueous sulfate species (molal)							Solid species (moles)				
	Uranyl sulfates	Calcium Sulfates	Strontium sulfates	Lead sulfates	Barium sulfates	Free sulfates	Total	Calcium Sulfates	Strontium sulfates	Lead sulfates	Barium sulfates	Barium nitrate
No additive	5.58E-01	----	----	----	----	1.71E-01	7.29E-01	----	----	----	----	----
Ca/S = 1.0	1.30E-01	4.25E-03	----	----	----	5.55E-02	1.90E-01	0.54	----	----	----	----
Ca/S = 1.1	1.09E-01	4.25E-03	----	----	----	4.81E-02	1.61E-01	0.57	----	----	----	----
Ca/S = 1.25	8.42E-02	4.25E-03	----	----	----	3.91E-02	1.28E-01	0.61	----	----	----	----
Ca/S = 1.5	5.83E-02	4.25E-03	----	----	----	2.90E-02	9.16E-02	0.64	----	----	----	----
Sr/S = 1.0	3.66E-02	----	4.20E-04	----	----	1.68E-02	5.38E-02	----	0.68	----	----	----
Sr/S = 1.1	2.00E-02	----	4.20E-04	----	----	9.63E-03	3.01E-02	----	0.70	----	----	----
Sr/S = 1.25	1.05E-02	----	4.20E-04	----	----	5.28E-03	1.62E-02	----	0.71	----	----	----
Sr/S = 1.5	5.62E-03	----	4.20E-04	----	----	3.00E-03	9.04E-03	----	0.72	----	----	----
Pb/S = 1.0	4.14E-03	----	----	<1.0E-8	----	2.12E-03	6.26E-03	----	----	0.72	----	----
Pb/S = 1.1	3.78E-04	----	----	<1.0E-8	----	2.00E-04	5.77E-04	----	----	0.73	----	----
Pb/S = 1.25	1.53E-04	----	----	<1.0E-8	----	8.41E-05	2.38E-04	----	----	0.73	----	----
Pb/S = 1.5	7.91E-05	----	----	<1.0E-8	----	4.56E-05	1.25E-04	----	----	0.73	----	----
Ba/S = 1.0	2.75E-04	----	----	----	<1.0E-8	1.41E-04	4.16E-04	----	----	----	0.73	----
Ba/S = 1.1	1.66E-06	----	----	----	<1.0E-8	1.95E-07	1.86E-06	----	----	----	0.73	----
Ba/S = 1.25	1.37E-06	----	----	----	<1.0E-8	7.22E-07	2.09E-06	----	----	----	0.73	0.09

The initial solution was 0.55 M UO<sub>2</sub>SO<sub>4(aq)</sub> and a pH of 1 with H<sup>+</sup> balanced by SO<sub>4</sub><sup>2-</sup>. The speciation of the initial solution in molality was UO<sub>2</sub>SO<sub>4(aq)</sub> = 0.300, UO<sub>2</sub><sup>2+</sup> = 0.180, UO<sub>2</sub>(SO<sub>4</sub>)<sup>2-</sup> = 0.130, H<sup>+</sup> = 0.124, HSO<sub>4</sub><sup>-</sup> = 0.117, SO<sub>4</sub><sup>2-</sup> = 0.537.

After choosing Sr(NO<sub>3</sub>)<sub>2</sub> and Ba(NO<sub>3</sub>)<sub>2</sub> for further study based on the results shown in Table 1, several reaction conditions were chosen for investigation. Initially, only Sr(NO<sub>3</sub>)<sub>2</sub> was used, in slight excess; the results are presented in Table 2. It is immediately evident that the use of Sr(NO<sub>3</sub>) alone, to precipitate out the sulfate, does not lower the sulfate concentration sufficiently for further processing of the STS with the UREX process. It can also be seen that decreasing the temperature by 20°C has little effect in decreasing the residual sulfate concentration (a 15% increase is observed), as indicated by samples 1 through 3. Table 2 also shows that the precipitation of SrSO<sub>4</sub> is sufficiently fast, as indicated by the stable residual [SO<sub>4</sub><sup>2-</sup>] observed for samples 3 through 7. Increasing the amount of strontium present in the system by 10% resulted in a decrease in the sulfate concentration of ~50%; however, as reported in Table 1, further increasing the equivalents of Sr in the system will not reduce the concentration of residual sulfate in the system to below 0.01 M [11].

**Table 2** Effects of mixing time, temperature, and Sr<sup>2+</sup>/SO<sub>4</sub><sup>2-</sup> molar ratio on the sulfate-to-nitrate conversion process—Sr(NO<sub>3</sub>)<sub>2</sub> addition only

Concentration (M)—filtrate

Sample	Temp. (°C)	Sr reaction time (hours)	Equiv. Sr <sup>2+</sup> /SO <sub>4</sub> <sup>2-</sup>	Ba <sup>2+</sup>	Sr <sup>2+</sup>	NO <sub>3</sub> <sup>-</sup>	SO <sub>4</sub> <sup>2-</sup>
1	80	2	1.05:1	<3.6E-5	0.008	1.48	0.133
2	80	2	1.05:1	<3.6E-5	0.009	1.50	0.123
3	60	2	1.05:1	<3.6E-5	0.015	1.43	0.154
4	60	0.5	1.15:1	<3.6E-5	0.022	1.71	0.074
5	60	1	1.15:1	<3.6E-5	0.022	1.77	0.071
6	60	3	1.15:1	<3.6E-5	0.021	1.73	0.067
7	60	18	1.15:1	<3.6E-5	0.024	1.73	0.072

Using solely Ba(NO<sub>3</sub>)<sub>2</sub> to precipitate the sulfate is not an option due to the low solubility of barium nitrate. During the precipitation procedure, it is important to keep the total number of equivalents of (Sr<sup>2+</sup> + Ba<sup>2+</sup>)/SO<sub>4</sub><sup>2-</sup> above 1.10 to ensure the precipitation of as much sulfate as possible. An investigation of the effectiveness of different molar equivalent ratios of Sr<sup>2+</sup>/SO<sub>4</sub><sup>2-</sup> to Ba<sup>2+</sup>/SO<sub>4</sub><sup>2-</sup> was conducted while keeping the value of (Sr<sup>2+</sup> + Ba<sup>2+</sup>)/SO<sub>4</sub><sup>2-</sup> between 1.10 and 1.15; the results are shown in Table 3. Based on Table 3, it was concluded that a Sr<sup>2+</sup>/SO<sub>4</sub><sup>2-</sup> and Ba<sup>2+</sup>/SO<sub>4</sub><sup>2-</sup> ratios of 1.05/1 and ≥0.05/1, respectively, yielded [sulfate] below the desired 0.02 M. A minimal amount of Ba in the filtrate is desirable, because it is a RCRA metal. Sr<sup>2+</sup>/SO<sub>4</sub><sup>2-</sup> to Ba<sup>2+</sup>/SO<sub>4</sub><sup>2-</sup> ratios of 1.05:1 and 0.05:1, respectively, were chosen for further investigation.

**Table 3** Effects of varying the Sr<sup>2+</sup>:SO<sub>4</sub><sup>2-</sup> and Ba<sup>2+</sup>:SO<sub>4</sub><sup>2-</sup> molar ratios on sulfate-to-nitrate conversion

Sample	Temp. (°C)	Sr reaction time (hours)	Equiv. Sr <sup>2+</sup> /SO <sub>4</sub> <sup>2-</sup>	Ba reaction time (hours)	Equiv. Ba <sup>2+</sup> /SO <sub>4</sub> <sup>2-</sup>	Concentration (M)—Filtrate			
						Ba <sup>2+</sup>	Sr <sup>2+</sup>	NO <sub>3</sub> <sup>-</sup>	SO <sub>4</sub> <sup>2-</sup>
8	60	1	1.05:1	1	0.05:1	<3.6E-5	0.005	1.07	0.305
9	60	0.75	1.05:1	2	0.1:1	0.004	0.430	2.73	0.004
10	60	1	1.05:1	1	0.1:1	0.003	0.408	2.61	0.005
11	60	1	1.05:1	2	0.1:1	0.003	0.417	2.68	0.005
12	60	0.5	0.93:1	0.5	0.2:1	<3.6E-5	0.016	1.52	0.106
13	60	0.5	1.00:1	1	0.2:1	<3.6E-5	0.009	1.41	0.136
14	60	0.5	0.93:1	3	0.2:1	<3.6E-5	0.017	1.49	0.088
15	60	0.5	0.83:1	1	0.3:1	<3.6E-5	0.011	1.44	0.139
16	60	0.5	0.83:1	0.5	0.3:1	<3.6E-5	0.016	1.51	0.100
17	60	0.5	0.83:1	3	0.3:1	<3.6E-5	0.018	1.49	0.092

The optimal conditions chosen for further investigation were (1) a warm water bath used as a heating source at 60°C; (2) vigorous stirring of the suspension; (3) molar equivalents ratios of 1.05:1 for Sr<sup>2+</sup>/SO<sub>4</sub><sup>2-</sup>, followed by 0.05/1 for Ba<sup>2+</sup>/SO<sub>4</sub><sup>2-</sup>; and (4) reaction times of 0.5 and 1 hours. Results for these tests are presented in Table 4. Samples 18–22 demonstrate reproducible results that produce a [SO<sub>4</sub><sup>2-</sup>] below 0.02

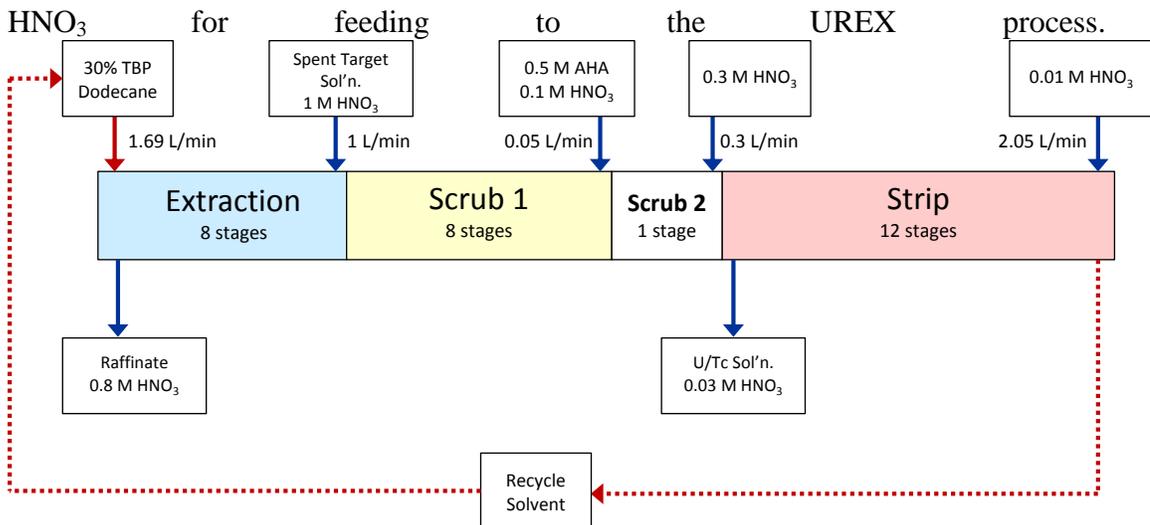
M, as is necessary for the UREX process and  $[Ba^{2+}]$  levels at or below RCRA limits for the filtrate.

**Table 4** Results sulfate precipitation using optimal conditions

Sample	Temp. (°C)	Sr reaction time (hours)	Equiv. $Sr^{2+}:SO_4^{2-}$	Ba reaction time (hours)	Equiv. $Ba^{2+}:SO_4^{2-}$	Concentration (M) - Filtrate			
						$Ba^{2+}$	$Sr^{2+}$	$NO_3^-$	$SO_4^{2-}$
18	60	0.5	1.05:1	1	0.05:1	0.0005	0.173	1.48	0.007
19	60	0.5	1.05:1	1	0.05:1	0.0005	0.159	1.38	0.007
20	60	0.5	1.05:1	1	0.05:1	0.0006	0.172	1.42	0.006
21	60	0.5	1.05:1	1	0.05:1	0.0007	0.157	1.44	0.006
22	60	0.5	1.05:1	1	0.05:1	0.0008	0.171	1.48	0.007
23	60	0.5	1.05:1	1	0.05:1	0.0007	0.164	1.48	0.007

### 3.2 AMUSE Flowsheet

Once a procedure resulting in acceptable  $[Ba^{2+}]$  and  $[SO_4^{2-}]$  levels in the STS was established, the next step in the SHINE procedure was purification of the uranium in solution using UREX. The AMUSE code was used to establish the UREX flowsheet to recover pure uranium from the STS after it had been converted to nitrate media. Figure 1 shows the flowsheet developed specifically to process the STS solution. (The flow rates in the flowsheet are relative to a feed of 1 L/min; the actual flow rates will be proportional feed flow rate.) In the simulations, all transuranic elements and fission products were assumed to be at  $10^{-4}$  M, while the barium and sulfate concentrations were derived for a 1/1 addition of barium nitrate. Since neither  $Sr^{2+}$  or  $Ba^{2+}$  are extracted by UREX solvent, their concentrations will have no effect on this flowsheet. The nitric-acid concentration in the filtrate was increased to 1 M  $HNO_3$  for feeding to the UREX process.



**Fig. 1** Schematic of the UREX flowsheet for 130 g-U/L uranyl nitrate derived from conversion from sulfate media by  $Ba(NO_3)_2$  addition

The flowsheet has four sections: extraction (8 stages), scrub 1 (9 stages), scrub 2 (1 stage), and strip (12 stages). In the extraction section, the uranium-containing feed

(the STS from sulfate/nitrate conversion and acidity modification) enters at stage 8; the clean solvent [30 vol% tributyl phosphate (TBP) in n-dodecane] enters at stage 1. The extraction section shifts all of the uranium present in the feed solution to the solvent; therefore, as the aqueous solution proceeds from stage 8 to stage 1, the uranium concentration is steadily lowered. The essentially “uranium-free” raffinate, which contains all feed components but the uranium and fractions of technetium and iodine, exits the contactor at stage 1.

The first scrub section removes from the U-loaded solvent the small amounts of other feed components that entered the organic phase in the extraction section. Acetohydroxamic acid (AHA) is introduced in the feed to this section. AHA is a strong complexant for Pu(IV) and many of the transition metals; it also reduces the extractable Np(VI) to un-extractable Np(V) and complexes Np(IV). The AHA complexes are far less extractable than the free metal ions; therefore, these ions partition to the aqueous phase. The AHA-feed solution is introduced at stage 17 and flows counter-currently to the U-loaded solvent continually scrubbing contaminants. It combines with the extraction-feed at stage 8 and passes out of the contactor at stage 1 as part of the raffinate. In the extraction section, AHA effectively limits the amount of non-uranium species that are extracted into the solvent.

The second scrub section is included to remove from the U-loaded solvent the residual AHA and AHA-metal species that remain in the organic solvent. The feed is a 0.3-M HNO<sub>3</sub> solution that enters the contactor at stage 18, flows counter-currently to the U-loaded solvent, mixing with the scrub 1 feed at stage 17, the STS feed at stage 8, and eventually exiting as part of the raffinate at stage 1.

Once the U-loaded solvent is purified, it moves into the U-strip section (stages 19–30), where the uranium is recovered as a uranyl nitrate solution. The aqueous feed to the strip section is 0.01-M HNO<sub>3</sub> that enters the contactor at stage 30, with a flow-rate ratio of 2.05 relative to that of the aqueous feed to the extraction section. The aqueous strip-feed flows counter-currently to solvent from stage 30 to stage 19. As the solvent moves from stage 19 to stage 30, uranium shifts to the aqueous phase so that the concentration in the solvent decreases steadily until the solvent leaving stage 30 is essentially free of extractible species and can be recycled to stage 1 for another pass through the contactor. The aqueous uranium product exits the contactor at stage 19 at a concentration that is 1/2.05 times that in the extraction feed.

Because of the potential for modification to the uranium concentration in the STS feed, ease in reconfiguring the flowsheet is an important factor in this design. As designed, the only parameter that would vary is the organic-to-aqueous (O/A) flow ratio in the extraction section; this would be varied by adjusting the flow rates of the feed solutions. This ratio should be kept high enough to minimize the extraction of impurities (to assure maximum decontamination of the uranium product), but low enough so that the organic phase will not segregate into a light and a heavy phase, thus forming a three-phase system that would cause significant hydraulic problems in the contactor. The O/A ratio is maintained to provide a maximum loading of the TBP in the solvent to a range of 70–72%. With the flowsheet of Figure 1, the contactor in the hot cell can be permanently plumbed into four sections, with the requisite number of stages in each section.

The final step in the purification of the uranium product is running through an anion-exchange column where pertechnetate and iodide will be removed from the uranium solution.

### 3.3 Conversion and Purification of a STS Simulant

An STS simulant containing tracers produced from irradiation of a 1-g depleted uranium (DU) foil at the Argonne linear accelerator was subjected to sulfate-to-nitrate conversions. Electrons hitting the target emitted high-energy photons that fissioned the  $^{238}\text{U}$ . The irradiated DU foil was then dissolved in sulfuric acid and added to a larger volume of uranyl-sulfate solution to produce a simulated STS solution of 0.65-M uranyl sulfate at pH 1. This solution was fed to the Mo-recovery column. The column effluent was converted from sulfate to nitrate by the optimized procedure described above. A  $\text{Sr}^{2+}/\text{SO}_4^{2-}$  ratio of 1.05/1 and a  $\text{Ba}^{2+}/\text{SO}_4^{2-}$  ratio of 0.05/1 were used. The resulting precipitate was rinsed with 1-M  $\text{HNO}_3$  to ensure the maximum amount of uranium is recovered. These samples were analyzed by  $\gamma$ -ray spectrometry. In Table 5, the gamma activities reported are the estimated activities at the end of irradiation (EOI), based on the amount of activity measured after processing.

In Table 5, the feed solution is the effluent from the Mo-recovery column and serves as a reference for the total activity fed to the sulfate-to-nitrate conversion process. Based on the results presented in Table 5, it appears that ~50% of Ba, 40% of Ce, 73% of I, 72% of Pm, 91% of Rh, 81% of Ru, 20% of Sr, and 93% of U are accounted for in the activity measured in the effluent. In addition to the total amount accounted for after processing, the low measured recovery percentages for Sr and Ba are likely due to the non-ideal counting configuration that arises from the large distance between the sample and the detector, as well as the large physical size and irregular shape of the filter apparatus and the reaction vessel. The total  $^{140}\text{Ba}$  that is present in the filtrate solution corresponds to  $1.12 \times 10^{-5}$  ppm. If the percentage of  $^{140}\text{Ba}$  is assumed to be proportional to the total Ba in solution, as it should be, then there is 212 ppm in solution; this is nearly double the RCRA limit, but it will likely be combined with other waste streams that arise during processing, thus decreasing the concentration of Ba to below RCRA levels. It is also likely that grouting this waste stream will act to retard leaching of Ba, thus alleviating any concerns about the waste form's acceptability.

**Table 5** Partitioning of gamma emitters in the sulfate-to-nitrate conversion process

Nuclide	Feed	Filtrate	Wash 1	Wash 2	Wash 3	Filter apparatus	Reaction vessel
	$\mu\text{Ci}$	$\mu\text{Ci}$	$\mu\text{Ci}$	$\mu\text{Ci}$	$\mu\text{Ci}$	$\mu\text{Ci}$	$\mu\text{Ci}$
Ba-140	6.60E+01	1.64E+00	< 2.30E-02	<1.28E-03	<1.88E-04	2.05E+01	2.46E+00
Ce-141	1.44E+01	5.10E+00	1.16E-01	1.02E-02	5.43E-03	2.59E+00	3.10E-01
Ce-143	3.94E+02	1.49E+02	2.95E+00	2.59E-01	1.37E-01	7.38E+01	8.86E+00
I-133	6.39E+00	4.56E+00	1.17E-01	5.22E-03	2.00E-03	<5.38E-02	<1.92E-02
Nd-147	<6.76E+00	<3.42E+00	3.64E-01	1.70E-02	5.93E-03	9.42E-01	1.13E-01
Pm-151	6.52E+01	4.49E+01	9.40E-01	5.37E-02	1.64E-02	3.67E+00	4.40E-01
Rh-105	1.87E+02	1.66E+02	4.01E+00	2.30E-01	4.95E-02	9.04E-01	1.50E-01

Ru-103	3.56E+00	2.83E+00	4.85E-02	3.55E-03	9.14E-04	<5.26E-02	<1.92E-02
Sb-127	<9.40E-01	1.49E+00	4.61E-02	<5.77E-04	8.18E-04	<1.02E-01	<5.29E-02
Sr-91	1.04E+03	1.28E+02	2.93E+00	4.90E-01	3.78E-01	3.06E+02	3.67E+01
Sr-92	<3.56E-01	<1.17E-01	<7.10E-03	<1.92E-04	<1.53E-04	1.18E+03	1.42E+02
Te-131m	1.21E+01	2.96E+00	2.13E-01	8.69E-03	4.06E-03	<2.08E-01	<4.95E-02
Te-132	6.46E+00	5.35E+00	1.01E-01	5.61E-03	1.66E-03	<3.31E-02	<1.30E-02
U-237	1.93E+03	1.74E+03	6.69E+01	2.01E+00	5.37E-01	1.62E+00	1.94E-01
Zr-95	<6.22E-01	3.20E-01	<1.48E-02	1.12E-03	8.23E-04	<7.46E-02	<2.61E-02

Table 6 shows the relative percentage of each nuclide found in each of the process fractions. It is evident from this table that a large portion of rare-earth elements, as well as Rh, Ru, and I, partition with the U to the filtrate. However, these components will easily be removed from the uranium in the UREX process.

**Table 6** Partitioning of gamma emitters in the sulfate-to-nitrate conversion process

Nuclide	Filtrate	Wash 1	Wash 2	Wash 3	Filter apparatus	Reaction vessel
Ba-140	4.96	0.02	0.00	0.00	78.74	16.28
Ce-141	89.50	2.02	0.18	0.10	7.26	0.94
Ce-143	89.85	1.78	0.17	0.07	7.11	1.02
I-133	97.35	2.50	0.11	0.04	0.00	0.00
Pm-151	96.31	2.01	0.11	0.04	1.26	0.27
Rh-105	97.30	2.36	0.13	0.03	0.09	0.09
Ru-103	98.16	1.68	0.12	0.04	0.00	0.00
Sr-91	66.87	1.53	0.27	0.22	25.64	5.47
Te-131m	92.93	6.69	0.26	0.11	0.00	0.00
Te-132	98.01	1.85	0.11	0.04	0.00	0.00
U-237	96.12	3.70	0.11	0.03	0.01	0.03

Following sulfate-to-nitrate conversion, the solution described as the filtrate in the Conversion and Purification of a STS Simulant section is to be treated using the flowsheet described above.

#### 4. Conclusions

A procedure for converting a uranyl-sulfate solution to a uranyl-nitrate solution has been established. A simulated STS was produced from irradiated depleted uranium for sulfate-to-nitrate conversion and purification using a UREX flowsheet generated with the AMUSE code. The optimal conditions for solution conversion were a two-step sulfate precipitation process, under vigorous stirring, using an initial precipitation with a molar ratio of 1.05/1 for  $\text{Sr}^{2+}/\text{SO}_4^{2-}$  followed by a 0.05/1 molar ratio addition of  $\text{Ba}^{2+}/\text{SO}_4^{2-}$ , with reaction times of 0.5 and 1 hours, respectively, at 60°C. This results in a solution that is <0.01-M sulfate, which is necessary for the UREX process, and  $\text{Ba}^{2+}$  levels at or below RCRA limits. A simulated STS solution

containing tracers from an irradiated DU target was processed using this method, which indicated that, after precipitation, the metals remaining in the filtrate can be removed using UREX.

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