ANL/CSE-13/47

FY 2013 Progress Report on the Cleanup of Irradiated 130 g-U/L Uranyl Sulfate SHINE Target Solutions Final

Chemical Science and Engineering Division

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FY 2013 PROGRESS REPORT ON THE CLEANUP OF IRRADIATED 130 g-U/L URANYL SULFATE SHINE TARGET SOLUTIONS FINAL

1 INTRODUCTION

In fiscal year (FY) 2012, Argonne National Laboratory (Argonne) developed a method for cleaning up uranium from a Subcritical Hybrid Intense Neutron Emitter (SHINE) Target Solution (STS) using a sulfate-to-nitrate conversion step (Bowers and Vandegrift 2013) followed by a UREX (uranium recovery by extraction) process flowsheet for purifying the uranium (Vandegrift et al. 2012a,b; Candido and Vandegrift 2012). In FY 2013, Argonne has refined the cleanup process for irradiated STS.

This report presents results from various experiments to determine the most suitable sulfate-to-nitrate conversion conditions, the results for scale-up experiments with an STS, and the results from a UREX experiment on a simulated STS. However, it does not include results on demonstration of UREX on an actual STS, nor denitration and dissolution of triuranium octoxide (U_3O_8) into an STS. The Laboratory's closure of Building 205 did not allow these steps to be demonstrated.

Figure 1 shows the baseline technology for the cleanup process for an STS. This was previously reported in Bowers and Vandegrift (2013). The process has the following steps:

1. Solid strontium nitrate ($Sr(NO_3)_2$) is added to the STS in an appropriate reaction vessel accompanied with vigorous stirring; this is followed by the addition of solid, pulverized barium nitrate ($Ba(NO_3)_2$) to the same reaction vessel.

2. The resulting slurry from Step 1 is then passed through a vacuum filtration system. The precipitate is washed with 1 M nitric acid (HNO_3) to ensure minimization of uranium loss.

3. The resulting filtrate solution then undergoes an adjustment to 1 M HNO_3. This is done to ensure that the filtrate is in an appropriate condition to be fed to the UREX process.

4. The UREX process produces a high-purity uranium product solution.

5. The resulting uranium product solution is then passed through an anion-exchange column to remove pertechnetate and iodide.

6. The resulting uranium solution is then concentrated and denitrated to form uranium trioxide (UO_3).

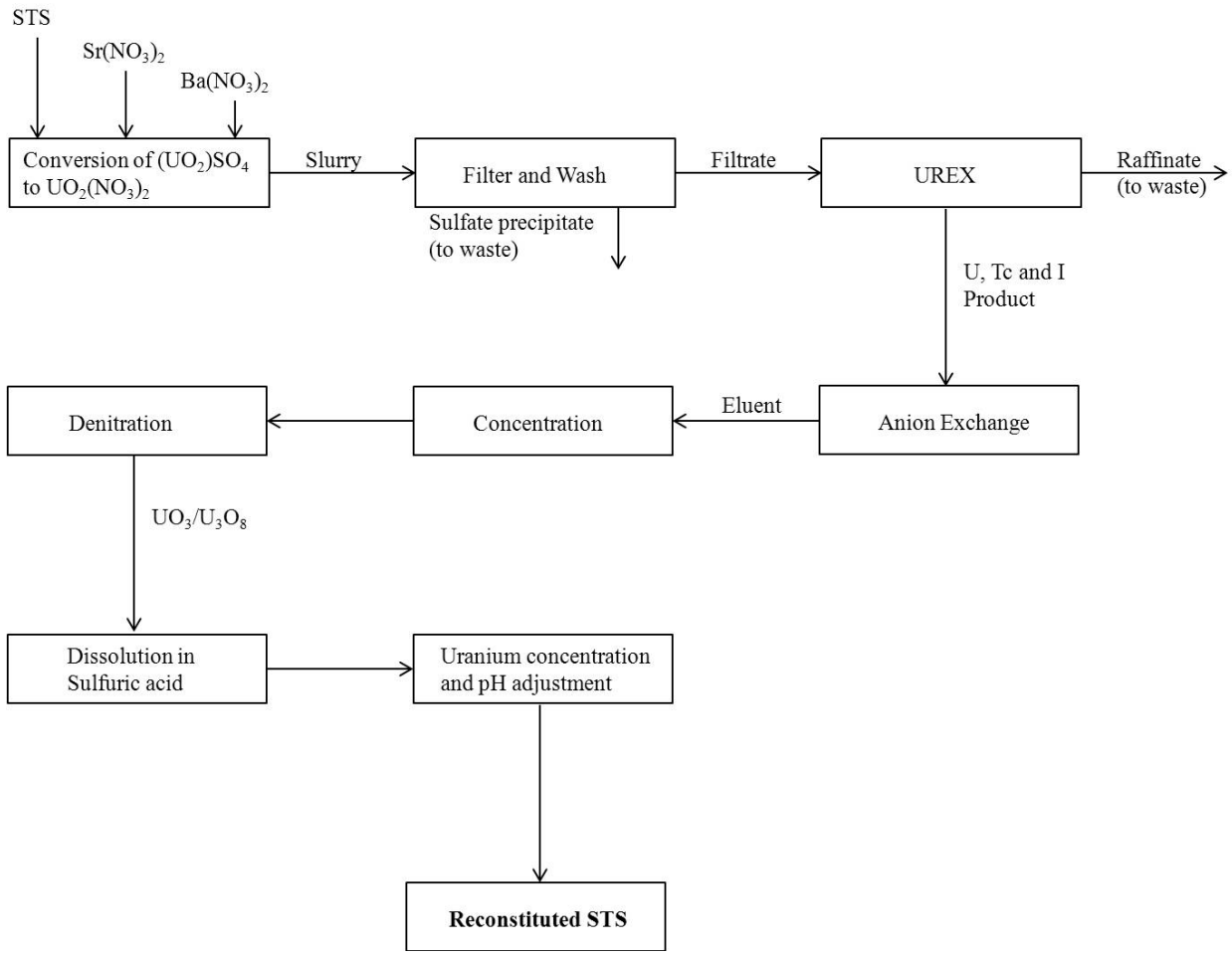

FIGURE 1 Flowsheet for Cleanup of Irradiated STS

7. The solid UO_3 product is then dissolved in sulfuric acid. If necessary, hydrogen peroxide (H_2O_2) will be added to oxidize any U_3O_8 to U(VI).

8. The resulting uranyl-sulfate solution will then be adjusted to the uranium concentration and pH necessary for the STS.

9. Finally, the generated waste streams will be treated for storage and final disposal.

The majority of the cleanup steps are well understood and used commercially. The one area of uncertainty is in optimizing conditions for the uranyl sulfate–to–nitrate conversion. This conversion step is vital to decontaminating the uranium from fission products during the UREX process. It has been previously established that sulfate concentrations above 0.01 M greatly increase the loss of uranium in the UREX process (Bowers and Vandegrift 2013).

2 SUMMARY OF PREVIOUS RESULTS

Previous experiments on optimization conditions for the sulfate-to-nitrate conversion have indicated several important factors:

1. The addition of just $Sr(NO_3)_2$ does not lower the sulfate concentration in the filtrate solution below 0.01 M, which is required for the UREX process to be successful.

2. The addition of $Ba(NO_3)_2$, following the addition to $Sr(NO_3)_2$, is necessary to lower the sulfate concentration to ~0.005 M. The addition of $Ba(NO_3)_2$ alone is not feasible because of its low solubility, and, thus, slow kinetics of its conversion to $BaSO_4$.

3. Stirring the system increases the kinetics of the system.

4. Pulverization of $Ba(NO_3)_2$ greatly increases the kinetics of the system, thus decreasing the final sulfate concentration.

5. The addition of higher than 1.05 equivalents of strontium to sulfate did not result in a lowered sulfate concentration.

6. Approximately 4% of the uranium remains in the precipitate upon filtration; however, this can be removed by washing the filter cake with 0.1 or 1 M HNO_3.

3 PRECIPITATION RESULTS AND DISCUSSION—CONDITION SET 1

On the basis of the previous results, it was determined that more data on variations of reaction time, temperature, and Sr^{2+}/Ba^{2+} to sulfate equivalence were needed. In the experiments discussed below, the reaction vessel was placed directly on a hot plate and insulated with cotton. The temperature probe was placed between the reaction vessel and the cotton. A condenser, with 15°C water flowing through it, was placed on top of the reaction vessel. First, $Sr(NO_3)_2$ was added to the reaction vessel containing 20 mL of the STS simulant and allowed to react for the desired amount of time. Then, the $Ba(NO_3)_2$ was added to the reaction vessel and allowed to react for a specified amount of time. Table 1 gives the results from these experiments.

For a sample series to be considered successful, the samples must be self-consistent, and sulfate concentration in the filtrate must be below 0.01 M. It is also preferable for Ba^{2+} to be below 0.0007 M, as this is the Resource Conservation and Recovery Act (RCRA) waste limit. It is useful to divide Table 1 into several smaller tables (Tables 2–5) representing similar experimental conditions.

In Table 2, only $Sr(NO_3)_2$ was used in the conversion of the uranyl-sulfate solution to a uranyl-nitrate solution; this was done to verify previous results. Several important conclusions can be garnered from Table 2:

1. None of the tested conditions lowered the sulfate concentration below 0.01 M.

2. Decreasing the reaction temperature by 20°C had little effect (15% increase) on the sulfate concentration, as indicated by comparing samples 10/09/12A–B and 10/11/12A.

3. The precipitation of strontium sulfate ($SrSO_4$) has fast kinetics, as indicated by the consistent concentration of strontium, nitrate, and sulfate in samples 10/25/12A–D.

4. Increasing the amount of strontium present in the system by 10% resulted in a decrease of sulfate concentration by ~50%; however, as reported in the final FY 2012 report on the STS cleanup process (Bowers and Vandegrift 2013), further increasing the equivalents of Sr in the system will not reduce the concentration of sulfate in the system to below 0.01 M. On the basis of calculations and initial experiments in the same report, it is

TABLE 1 Effects of Mixing Time, Temperature, Sr/SO_4^{2-}, and Ba/SO_4^{2-} on the Sulfate-to-Nitrate Conversion Process

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) in Filtrate			
						Ba^{2+}	Sr^{2+}	NO_3^-	SO_4^{2-}
10/09/12A	80	2	1.05:1	0	0	<3.6E-5	0.008	1.48	0.133
10/09/12B	80	2	1.05:1	0	0	<3.6E-5	0.009	1.50	0.123
10/11/12A	60	2	1.05:1	0	0	<3.6E-5	0.015	1.43	0.154
10/11/12B	60	1	1.05:1	1	0.05:1	<3.6E-5	0.005	1.07	0.305
10/13/12A	60	2	1.05:1	2	0.05:1	<3.6E-5	0.015	1.55	0.102
10/16/12A	25	2	1.05:1	2	0.05:1	<3.6E-5	0.014	1.41	0.161
10/25/12A	60	0.5	1.15:1	0	0	<3.6E-5	0.022	1.71	0.074
10/25/12B	60	1	1.15:1	0	0	<3.6E-5	0.022	1.77	0.071
10/25/12C	60	3	1.15:1	0	0	<3.6E-5	0.021	1.73	0.067
10/25/12D	60	18	1.15:1	0	0	<3.6E-5	0.024	1.73	0.072
11/12/12A	60	0.75	1.05:1	2	0.1:1	0.004	0.430	2.73	0.004
11/12/12B	60	1	1.05:1	1	0.1:1	0.003	0.408	2.61	0.005
11/12/12C	60	1	1.05:1	2	0.1:1	0.003	0.417	2.68	0.005
12/03/12A	80	1	1.05:1	0.5	0.1:1	<3.6E-5	0.025	1.74	0.073
12/03/12B	80	1	1.05:1	1	0.1:1	<3.6E-5	0.024	1.66	0.080
12/06/12A	33	1	1.05:1	3	0.1:1	<3.6E-5	0.015	1.63	0.073
01/03/12A	60	0.5	0.93:1	0.5	0.2:1	<3.6E-5	0.016	1.52	0.106
01/04/12A	60	0.5	1:1	1	0.2:1	<3.6E-5	0.009	1.41	0.136
01/04/12B	60	0.5	0.93:1	3	0.2:1	<3.6E-5	0.017	1.49	0.088
01/04/12C	60	0.5	0.83:1	1	0.3:1	<3.6E-5	0.011	1.44	0.139
01/04/12D	60	0.5	0.83:1	0.5	0.3:1	<3.6E-5	0.016	1.51	0.100
01/04/12E	60	0.5	0.83:1	3	0.3:1	<3.6E-5	0.018	1.49	0.092

TABLE 2 Effects of Mixing Time, Temperature, and Sr/SO_4^{2-} on the Sulfate-to-Nitrate Conversion Process—$Sr(NO_3)2$ Addition Only

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-}
10/09/12A	80	2	1.05:1	0	0	<3.6E-5	0.008	1.48	0.133
10/09/12B	80	2	1.05:1	0	0	<3.6E-5	0.009	1.50	0.123
10/11/12A	60	2	1.05:1	0	0	<3.6E-5	0.015	1.43	0.154
10/25/12A	60	0.5	1.15:1	0	0	<3.6E-5	0.022	1.71	0.074
10/25/12B	60	1	1.15:1	0	0	<3.6E-5	0.022	1.77	0.071
10/25/12C	60	3	1.15:1	0	0	<3.6E-5	0.021	1.73	0.067
10/25/12D	60	18	1.15:1	0	0	<3.6E-5	0.024	1.73	0.072

TABLE 3 Effects of Mixing Time and Temperature on the Sulfate-to-Nitrate Conversion Process

Sample	Temp. (°C)	Sr rxn Time (hours)	Equiv. $Sr^{2+}:SO_4^{2-}$	Ba rxn Time (hours)	Equiv. $Ba^{2+}:SO_4^{2-}$	Concentration (M) - Filtrate			
						Ba^{2+}	Sr^{2+}	NO_3^-	SO_4^{2-}
11/12/12A	60	0.75	1.05:1	2	0.1:1	0.004	0.430	2.73	0.004
11/12/12B	60	1	1.05:1	1	0.1:1	0.003	0.408	2.61	0.005
11/12/12C	60	1	1.05:1	2	0.1:1	0.003	0.417	2.68	0.005
12/03/12A	80	1	1.05:1	0.5	0.1:1	<3.6E-5	0.025	1.74	0.073
12/03/12B	80	1	1.05:1	1	0.1:1	<3.6E-5	0.024	1.66	0.080
12/06/12A	33	1	1.05:1	3	0.1:1	<3.6E-5	0.015	1.63	0.073

TABLE 4 Effects of Varying the $Sr^{2+}:SO_4^{2-}$ and $Ba^{2+}:SO_4^{2-}$ Ratios on the Sulfate-to-Nitrate Conversion

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-}
10/11/12B	60	1	1.05:1	1	0.05:1	<3.6E-5	0.005	1.07	0.305
11/12/12A	60	0.75	1.05:1	2	0.1:1	0.004	0.430	2.73	0.004
11/12/12B	60	1	1.05:1	1	0.1:1	0.003	0.408	2.61	0.005
11/12/12C	60	1	1.05:1	2	0.1:1	0.003	0.417	2.68	0.005
01/03/12A	60	0.5	0.93:1	0.5	0.2:1	<3.6E-5	0.016	1.52	0.106
01/04/12A	60	0.5	1.00:1	1	0.2:1	<3.6E-5	0.009	1.41	0.136
01/04/12B	60	0.5	0.93:1	3	0.2:1	<3.6E-5	0.017	1.49	0.088
01/04/12C	60	0.5	0.83:1	1	0.3:1	<3.6E-5	0.011	1.44	0.139
01/04/12D	60	0.5	0.83:1	0.5	0.3:1	<3.6E-5	0.016	1.51	0.100
01/04/12E	60	0.5	0.83:1	3	0.3:1	<3.6E-5	0.018	1.49	0.092

TABLE 5 Effects of Varying the Mixing Time for the $Ba(NO_3)_2$ Step—Inconsistent Results

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-}
01/04/12D	60	0.5	0.83:1	0.5	0.3:1	<3.6E-5	0.016	1.51	0.100
01/04/12C	60	0.5	0.83:1	1	0.3:1	<3.6E-5	0.011	1.44	0.139
01/04/12E	60	0.5	0.83:1	3	0.3:1	<3.6E-5	0.018	1.49	0.092

believed that 1.05 equivalents of Sr with the addition of Ba should adequately reduce the sulfate concentration.

In Table 3, both Sr and Ba were used for the precipitation of sulfate for the investigation of the effect of reaction temperature and time. Several conclusions can be drawn from the data presented in Table 3.

1. When Samples 11/12/12B and 12/03/12B are compared, the effect of temperature can be assessed. The results from these two samples indicate that 60°C is more effective at reducing the sulfate concentration below the desired concentration of 0.01 M. This is likely because higher temperatures increase the solubility of $Ba(NO_3)_2$.

2. In addition to this result, if sample 12/06/12A is compared with 11/12/12B and 12/03/12B, this again indicates that 60°C is the most effective temperature condition for reducing the sulfate concentration, even with long reaction times for the Ba precipitation step.

3. Comparing samples 11/12/12B and 11/12/12C, the Ba precipitation step reaches equilibrium in 1 hour, as indicated by the identical concentrations of Ba^{2+} and SO_4^{2-} present in the filtrate. If sample 11/12/12A is compared with the 11/12/12B and 11/12/12C samples, it can be concluded that the Sr reaction time has little effect on the Ba^{2+} and SO_4^{2-} concentrations.

During the precipitation procedure, it is important to keep the total number of equivalents of (Sr+Ba)/ SO_4^{2-} above 1.10 to ensure the precipitation of as much sulfate as possible. An investigation of the effect of Sr^{2+}: SO_4^{2-} and Ba^{2+}: SO_4^{2-} was conducted while keeping the total (Sr+Ba)/ SO_4^{2-} = 1.10–1.15; the results are shown in Table 4. It was concluded that decreasing the equivalents, from 1.05:1 of Sr^{2+}: SO_4^{2-} while increasing the equivalents of Ba^{2+}: SO_4^{2-} from 0.1:1, does not decrease the sulfate concentration below 0.01 M.

One concern was that the data did not appear to be self-consistent; an example of this can be seen in Table 5. One would expect that as reaction time increased the concentration of sulfate would decrease; however, this is not the case. Inconsistent placement of the temperature probe between the reaction vessel and the cotton insulator may be the problem. In order to resolve this, the experimental apparatus was modified.

4 PRECIPITATION RESULTS AND DISCUSSION—CONDITION SET 2

It was observed that the sulfate-to-nitrate conversion process was not self-consistent. It was therefore decided that (1) finer temperature control of the system was required, (2) samples should be repeated in triplicate, and (3) cooling to room temperature between removal from heat source and filtering was necessary. In order to achieve finer temperature control of the system, a water bath was brought up to the desired temperature, and the reaction vessel containing 10 mL of an STS simulant was then placed in the water bath and allowed to equilibrate for ~30 minutes. After equilibration, $Sr(NO_3)_2$ was added to the reaction vessel and allowed to react for 30 minutes. The $Ba(NO_3)_2$ was then added to the reaction vessel and allowed to react for 60 minutes. Vigorous stirring was applied in these experiments. Table 6 shows the experimental conditions and results.

Using the procedure described above, two major conclusions can be drawn (Sample 02/08/13B is omitted in this discussion):

1. Either set of sample conditions results in sulfate concentrations below 0.01 M and Ba concentrations below RCRA waste levels.

2. The addition of the water bath allowed the results to become self-consistent across multiple samples under nearly identical experimental conditions.

Despite the previous results being self-consistent and within the desired specifications for waste and UREX processes, the experiments were not truly representative of conditions in the STS. In the previous experiment, the filtrate was cooled to room temperature prior to filtering. Depending on how long this solution sits after irradiation, radioactive decay of fission products will keep the temperature of the solution above ambient temperature to some degree. On the basis of the results in the previous experiment, conditions were chosen for investigation without cooling between the end of the Ba precipitation step and filtering (everything else was kept as discussed in this section). The results from these experiments are shown in Table 7. The major conclusion that can be drawn from the data presented in Table 7 is that the current procedure decreases the sulfate to levels below 0.01 M, and that the Ba concentration is approximately equal to RCRA levels.

TABLE 6 Triplicate Results for Two Conversion Conditions with Improved Temperature Control

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-}
02/07/13A	60	0.5	1.05:1	1	0.05:1	0.0005	0.173	1.48	0.007
02/07/13B	60	0.5	1.05:1	1	0.05:1	0.0005	0.159	1.38	0.007
02/07/13C	60	0.5	1.05:1	1	0.05:1	0.0006	0.172	1.42	0.006
02/08/13A	60	0.5	1.05:1	1	0.10:1	0.0005	0.191	1.49	0.006
02/08/13B	60	0.5	1.05:1	1	0.10:1	0.0107	0.174	1.47	0.001
02/08/13C	60	0.5	1.05:1	1	0.10:1	0.0005	0.186	1.46	0.006

TABLE 7 Effects of Not Cooling the Slurry before Filtration

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-}
02/21/13A	60	0.5	1.05:1	1	0.05:1	0.0007	0.157	1.44	0.006
02/21/13B	60	0.5	1.05:1	1	0.05:1	0.0008	0.171	1.48	0.007
02/21/13C	60	0.5	1.05:1	1	0.05:1	0.0007	0.164	1.48	0.007

5 PRECIPITATION RESULTS AND DISCUSSION—SCALE-UP WITH IRRADIATED DU SPIKE

An STS simulant was processed with tracers supplied by a 1-g depleted uranium (DU) foil that was irradiated at the Argonne linear accelerator. Electrons hitting the target emit high-energy photons that cause fissioning in the ^{238}U. The irradiated DU was then dissolved in sulfuric acid and mixed into a uranyl-sulfate system that resulted in an STS solution of 0.65-M uranyl sulfate. This solution was fed to a molybdenum (Mo)-recovery column. The effluent of the column then underwent sulfate-to-nitrate conversion via the procedure described in Section 4, without cooling between the end of the Ba reaction time and filtration. Ratios of 1.05:1 equivalents of Sr^{2+}:SO_4^{2-} and 0.05:1 equivalents of Ba^{2+}:SO_4^{2-} were used. While these samples underwent γ-ray spectrometry analysis (Table 8), total U, Ba, Sr, NO_3^-, and SO_4^{2-} concentrations were not performed because of Argonne's shutdown of the Building 205 laboratories. The activities reported in Table 8 are the amount of activity present, back-calculated to that at the end of irradiation.

In Table 8, the feed solution is the effluent from the Mo-recovery column and serves as a reference of total activity. On the basis of the results presented in Table 8, it appears that ~50% of Ba, 40% of cerium (Ce), 73% of iodine (I), 72% of promethium (Pm), 91% of rhodium (Rh), 81% of ruthenium (Ru), 20% of Sr, and 93% of U is accounted for. In addition to the total amount accounted for, Table 9 shows the percentage of each nuclide recovered in each step. The low recovery percentages of Sr and Ba are likely due to a large counting distance and non–point source–like geometry in counting the filter apparatus and the reaction vessel. Finding 2.51% of ^{140}Ba in filtrate solution corresponds to 1.12×10^{-5} ppm, which is well below the RCRA limits. If it is assumed that the percentage of ^{140}Ba is indicative of all Ba in solution, which it is, then there are 212 ppm in solution, nearly double the RCRA limit.

Table 9 highlights several important results:

1. A large portion of rare-earth elements Rh, Ru, and I partition with the U to the filtrate. Because of this, the use of UREX to purify the U of such contaminates is critical to the reuse of STS.

2. The amount of Ba present in the filtrate is nearly double the 100-ppm RCRA limits.

TABLE 8 Partitioning of Gamma Emitters in the Sulfate-to-Nitrate Conversion Process

Nuclide	Feed µCi	Filtrate µCi	Wash 1 µCi	Wash 2 µCi	Wash 3 µCi	Filter Apparatus µCi	Reaction Vessel µCi
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 9 Partitioning of Gamma Emitters in the Sulfate-to-Nitrate Conversion Process: Percentage of Feed Concentration in Each Fraction

Nuclide	Filtrate	Wash 1	Wash 2	Wash 3	Filter Apparatus	Reaction Vessel
Ba-140	2.51	0.01	0.00	0.00	39.86	8.24
Ce-141	35.38	0.80	0.07	0.04	2.87	0.37
Ce-143	37.80	0.75	0.07	0.03	2.99	0.43
I-133	71.28	1.83	0.08	0.03	0.00	0.00
Pm-151	68.89	1.44	0.08	0.03	0.90	0.19
Rh-105	88.79	2.15	0.12	0.03	0.08	0.08
Ru-103	79.64	1.36	0.10	0.03	0.00	0.00
Sr-91	12.23	0.28	0.05	0.04	4.69	1.00
Te-131m	24.57	1.77	0.07	0.03	0.00	0.00
Te-132	82.79	1.56	0.09	0.03	0.00	0.00
U-237	90.00	3.46	0.10	0.03	0.01	0.03

6 PRECIPITATION RESULTS AND DISCUSSION—SCALE-UP WITH IRRADIATED U SPIKE

An STS simulant was processed with tracers supplied by a DU uranyl-sulfate solution that was spiked with 2 mL of an irradiated enriched-uranium micro-SHINE solution. This resulted in an STS solution containing 140 g-U/L (0.69 M uranyl-sulfate) at pH 1. This solution was fed to a Mo-recovery column (Stepinksi et al. 2013). The effluent of the column then underwent sulfate-to-nitrate conversion via the procedure described in Section 4, without cooling between the end of the Ba reaction time and filtration.

Ratios of 1.05:1 equivalents of Sr^{2+}:SO_4^{2-} and 0.05:1 equivalents of Ba^{2+}:SO_4^{2-} were used. While these samples have undergone γ-ray spectrometry analysis (Table 10), total U, Ba, Sr, NO_3^-, and SO_4^{2-} concentrations have not yet been performed because of the shutdown of Argonne's Building 205 laboratories. The activities reported in Table 10 are the amount of activity present, back-calculated to the time of the end of irradiation.

In Table 10, the feed solution is the effluent from the Mo-recovery column and serves as a reference of total activity. On the basis of the results presented in Table 10, it appears that ~60% of Ba, 75% of Ce, 90% of I, 621% of Pm, 91% of Rh, 100% of Ru, and 86% of Sr is accounted for. In addition to the total amount accounted for, Table 11 shows the percentage of each nuclide recovered in each step. The >100% recovery reported for some nuclides is likely due to poor counting statistics of the column effluent. Assuming isotopic equilibration of all barium in solution, 1.98% of ^{140}Ba in filtrate solution corresponds to 0.0270 ppm total Ba in solution, far below the RCRA limit.

Table 11 highlights several important results:

1. A large portion of rare-earth elements Rh, Ru, and I partition with the U to the filtrate. Because of this, the use of UREX to purify the uranium of such contaminates is critical to the reuse of STS.

2. The amount of Ba present in the filtrate is far below the RCRA limit.

TABLE 10 Partitioning of Gamma Emitters in the Sulfate-to-Nitrate Conversion Process

Nuclide	Feed (μCi)	Filtrate (μCi)	Filter Apparatus (μCi)
Sr-91	361.1	85.05	225.72
Ru-103	2.26	2.31	0.06
Rh-105	21.23	18.27	1.15
I-131	0.43	0.33	20.04
I-133	0.33	0.43	0.15
Ba-140	20.12	0.40	11.49
Ce-141	4.41	0.83	2.33
Ce-143	116.43	26.49	72.09
Pm-151	10.51	2.51	4.07

TABLE 11 Partitioning of Gamma Emitters in the Sulfate-to-Nitrate Conversion Process: Percentage of Feed Concentration in Each Fraction

Nuclide	Filtrate (%)	Filter Apparatus (%)
Sr-91	22.55	62.51
Ru-103	101.96	2.66
Rh-105	86.04	5.40
I-131	76.56	9.12
I-133	131.65	47.24
Ba-140	1.98	57.09
Ce-141	18.76	52.91
Ce-143	22.75	61.92
Pm-151	23.91	38.69

7 URANIUM SOLUTION CLEANUP

The UREX process separates uranium, technetium, and most of the iodine from the other components of the irradiated fuel in nitric acid solution. The time and equipment requirements were evaluated for treatment of 260-L batches of a solution containing 130 g-U/L using commercial annular centrifugal contactors from CINC Industries. The reference UREX flowsheet consists of four sections with a total of 32 stages. Two demonstrations of the UREX process were planned to be performed in FY 2013, but the closing of the Building 205 laboratories prevented them from being performed. The first demonstration would have used a 2-mL micro-SHINE solution as a tracer in a DU uranyl-nitrate solution (the product of the sulfate-to-nitrate conversion described in Section 3). The second would use ~500 mL of mini-SHINE target solution. Unfortunately, these demonstrations have not yet been funded for FY 2014.

The UREX work that was completed in FY 2013 was a report written to update the analysis of the use of CINC V-2 and V-5 centrifugal contactors for the 32-stage UREX flowsheet (Candido and Vandegrift 2013). The V-2 has a 2-in. (5-cm) rotor with a reported maximum total organic-plus-aqueous throughput of 1.9 L/min. We evaluated this version for a throughput of 1 L/min. The V-5 has a 5-in. (~12.5-cm) rotor with a reported maximum throughput of 19 L/min. Argonne's conclusion from this study is that the V-2 would take ~23 hours to process the STS and, therefore, has too low a throughput to be applicable to this application. The V-5 could process this solution in 4 to 6 hours; however, its large footprint (~12 m^2) and large hold-up volumes (39 L organic and 73 L aqueous) are problematic. Argonne is suggesting the use of an Argonne-designed 10-cm centrifugal contactor as an alternative (WARDLE-13). This contactor would have a throughput of 12 L/min and a footprint of 4 m^2; its hold-up volumes are approximately half of that of the V-5.

Following UREX processing and the removal of iodide and pertechnetate from the uranium product by anion exchange, the uranium product (uranyl nitrate in dilute nitric acid) will be concentrated and denitrated to produce UO_3 for reconstituting into the uranyl-sulfate STS. A report was written summarizing germane literature and describing how this process would be performed during the Argonne demonstrations (Bakel et al. 2013). However, because of the closing of the Building 205 laboratories, this work was not performed.

8 CONCLUSIONS AND FUTURE WORK

A systematic study of the precipitation of sulfate using barium and strontium nitrate has been conducted. In small-batch samples, the following conditions were found to be best. A water bath was brought up to the desired temperature; the reaction vessel containing 10 mL of an STS was then placed in the water bath and allowed to equilibrate for ~30 minutes. After equilibration, $Sr(NO_3)_2$ was added to the reaction vessel and allowed to react for 30 minutes. The $Ba(NO_3)_2$ was then added to the reaction vessel and allowed to react for 60 minutes. The system was stirred vigorously. The resulting solution was then filtered and analyzed.

If funding is provided in FY 2014, experiments will increase the scale of the sulfate-to-nitrate conversion to a 0.5–1-L STS simulant. The resulting solution will be processed using the UREX process; the uranium product will be treated by anion exchange to remove iodide and pertechnetate and denitrated to produce UO_3; and the STS will be reconstituted by dissolving the uranyl oxide in sulfuric acid.

Argonne will also assist SHINE in the design of its UREX processing facility.

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