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FY-13 Progress Report on the Cleanup of Irradiated 130 g-U/L Uranyl Sulfate SHINE Target Solutions

Chemical Science and Engineering Division

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July 3, 2013

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Introduction

Thus far during FY-13 Argonne has refined the cleanup process for irradiated Shine Target Solutions (STS). This includes:

1. Refinement of the sulfate to nitrate conversion step using a combination of both strontium and barium nitrate ($Sr(NO_3)_2$ and $Ba(NO_3)_2$, respectively) at 60°C.
2. Testing of the sulfate to nitrate conversion on large volumes of irradiated STS.
3. Testing of UREX on irradiated STS.

This report will present results from various experiments to determine the most suitable sulfate to nitrate conversion conditions, the results for a scale-up experiments with an STS and the results from a UREX experiment on an STS.

The baseline technology to cleanup a STS is the process shown in Figure 1. This has also been previously reported in the Final FY-12 Progress Report on the Cleanup of STS. The process has the following steps:

1. Addition of solid $Sr(NO_3)_2$ to the STS in appropriate reaction vessel accompanied with vigorous stirring; this is followed by the addition of solid, pulverized $Ba(NO_3)_2$ 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 either 1 M HNO_3 to ensure minimization of U loss.
3. The resulting filtrate solution then undergoes an adjustment to 1 M HNO_3. This is done to ensure that the filtrate is at the appropriate conditions for feeding 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 UO_3.
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.

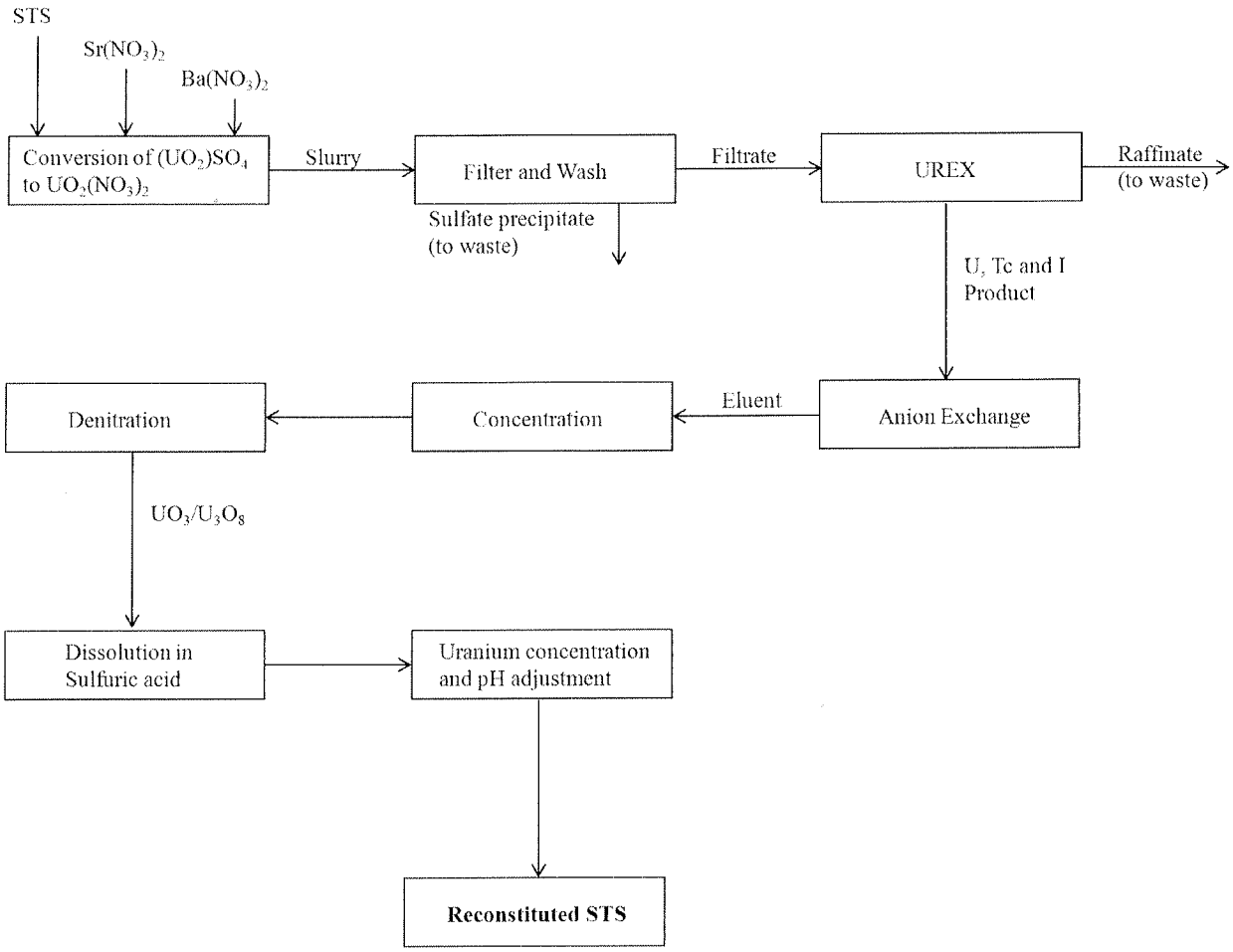

Figure 1. Flowsheet for cleanup of irradiated STS.

The majority of the cleanup steps are well understood and used commercially. The one area of uncertainty is the optimize conditions for the uranyl sulfate to nitrate conversion. This conversion step is vital to the decontamination of 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-2013]

Summary of Previous Results

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

1. 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. Addition of $Ba(NO_3)_2$, in 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 due to the 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 decreases the final sulfate concentration.
5. The addition of higher than 1.05 equivalents of strontium to sulfate did not result in 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.

Precipitation Results and Discussion – Condition Set 1

Based on 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 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. The $Ba(NO_3)_2$ was added to the reaction vessel and allowed to react for a certain amount of time. The results from these experiments can be seen in Table 1.

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 rxn time (hours)	Equiv. $Sr^{2+}:SO_4^{2-}$	Ba rxn 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

In order 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 that Ba^{2+} is below 0.0007 M, as this is the RCRA waste limit. It is useful to divide Table 1 into several smaller tables (Tables 2-5), which represent 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 lower 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 $SrSO_4$ 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-12 report on the STS cleanup process, further increasing the equivalents of Sr in the system will not reduce the concentration of sulfate in the system to below 0.01 M. Based on calculations and initial experiments in the same report it is believed that 1.05 equivalents of Sr with the addition of Ba should adequately reduce the sulfate concentration.

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 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-}
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

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, an assessment on the effect of temperature can be made. The results from these two samples indicate that 60 °C is a more effective temperature at reducing the sulfate concentration to below the desired concentration of 0.01 M. This is likely due to higher temperatures increasing the solubility of barium nitrate.
2. In addition to this result, if sample 12/06/12A is compared to 11/12/12B and 12/03/12B, this again indicates that even with long reaction times for the Ba precipitation step that 60 °C is the most effective temperature condition for reducing the sulfate concentration.
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 to 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.

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

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-} while keeping the total Sr+Ba:SO_4^{2-} = 1.10 - 1.15 was conducted, the results are shown in Table 4 and the conclusion reported below.

1. 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.

Table 4.

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-}
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

An issue of 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. It was believed that inconsistent placement of the temperature probe between the reaction vessel and the cotton insulator maybe the problem. In order to resolve this; the experimental apparatus was modified.

Table 5.

Sample	Temp.	Sr rxn time	Equiv.	Ba rxn time	Equiv.	Concentration (M) - Filtrate			
						Ba^{2+}	Sr^{2+}	NO_3^-	SO_4^{2-}

	(°C)	(hours)	$Sr^{2+}:SO_4^{2-}$	(hours)	$Ba^{2+}:SO_4^{2-}$				
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

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 have finer temperature control of the system, a water bath was brought up to the desired temperature, the reaction vessel containing 10 mL of a 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. The experimental conditions and results are shown in Table 6.

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 has allowed for the results to become self-consistent across multiple samples under nearly identical experimental conditions.

Table 6.

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-}
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

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 to some degree above ambient temperature. Based on 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 the Ba concentration is approximately equal to RCRA levels.

Table 7.

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-}
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

Precipitation Results and Discussion – Scale up with Irradiated U Spike

An STS simulant was processed with tracers supplied by a 1g depleted uranium (DU) foil that was irradiated at the Argonne LINAC. The DU was then dissolved in sulfuric acid and mixed into a uranyl sulfate system that resulted in 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 Precipitation Results and Discussion – Condition Set 2, without cooling between then 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 8), total U, Ba, Sr, NO_3^- and SO_4^{2-} concentrations have not yet been performed. In Table 8, the activities reported 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. Based on these results, presented in Table 8, 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 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 percentage of Sr and Ba is likely due to a large counting distance and non-point source like geometry in counting the filter apparatus and the reaction vessel. 2.51 % of ^{140}Ba in filtrate solution corresponds to 1.12 x 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 is 212 ppm in solution, nearly double the RCRA limit.

Table 8.

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.

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

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 ^{140}Ba present in the filtrate is nearly double the 100 ppm RCRA limits.

Conclusion and Future Work

A systematic study of the precipitation of sulfate using barium and strontium nitrate has been conducted. In small batch samples, it was found that the following conditions were the best:

- A water bath was brought up to the desired temperature, the reaction vessel containing 10 mL of a 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 the 30 minutes. The $Ba(NO_3)_2$ was then added to the reaction vessel and allowed to react for 60 minutes. The resulting solution was then filtered and analyzed.

When this was scaled up to 160 mL containing an irradiated DU, it was found that while the Ba content was low, it is still 212 ppm, which is twice the RCRA limit. Further treatment of the filtrate will need to be done in order to lower the Ba level.

Work will continue in a further scaled up experiment with a 1 L STS solution and processing of the resulting solutions with the UREX process will be done.

References

D. Bowers and G. F. Vandegrift; Final FY-12 Progress report on the Cleanup of Irradiated 130 g-U/L Uranyl Sulfate SHINE Target Solutions, September 29, 2012, ANL/CSE-13/12, in publishing.

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