

## **FY-15 Progress Report on Cleanup of Irradiated SHINE Target Solutions Containing 140 g-U/L Uranyl Sulfate**

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**Nuclear Engineering Division**

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by

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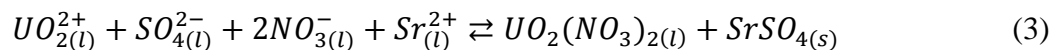
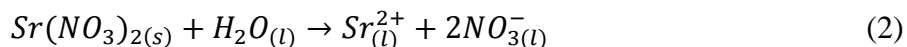
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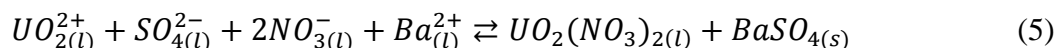
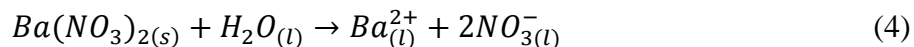
## 1 INTRODUCTION

During FY 2012 and 2013, a process was developed to convert the SHINE Target Solution (STS) of irradiated uranyl sulfate (140 g U/L) to uranyl nitrate [1, 2]. This process is necessary so that the uranium solution can be processed by the UREX (Uranium Extraction) separation process, which will remove impurities from the uranium so that it can be recycled. The uranyl sulfate solution must contain  $<0.02 \text{ M SO}_4^{2-}$  so that the uranium will be extractable into the UREX solvent [2]. In addition, it is desired that the barium content be below 0.0007 M, as this is the limit in the Resource Conservation and Recovery Act (RCRA). The developed process and rationale are outlined below:

1. The STS solution is heated, while stirring, to  $60^\circ\text{C}$ . It is expected that the solution temperature will be  $\sim 60^\circ\text{C}$  due to the heat from the fission products. The solution is stirred to ensure uniform heating.
2. A solution containing a 1.05:1 ratio of nitrate to sulfate is added to the STS in the form of  $\text{Sr}(\text{NO}_3)_{2(s)}$  and allowed to react for 30 minutes. The solution is continually heated (maintaining a  $\sim 60^\circ\text{C}$  temperature) and stirred to ensure uniform heating and contact with the  $\text{Sr}(\text{NO}_3)_{2(s)}$ . It was previously shown that  $>30$  minutes does not yield greater  $\text{SrSO}_{4(s)}$  precipitation [1]. The chemical reactions are as follows:



3. A solution containing a 0.05:1 equivalent of nitrate to sulfate is added to the STS in the form of  $\text{Ba}(\text{NO}_3)_{2(s)}$  and allowed to react for 60 minutes. The solution is continually heated (maintaining a  $\sim 60^\circ\text{C}$  temperature) and stirred to ensure uniform heating and contact with the  $\text{Ba}(\text{NO}_3)_{2(s)}$ . The addition of  $\text{Ba}(\text{NO}_3)_{2(s)}$  is necessary, as  $\text{SrSO}_{4(s)}$  is slightly soluble and does not cause all of the sulfate in the STS to precipitate. The chemical reactions are Equation 1 and the following:



4. The solution, while hot, is then filtered under vacuum to remove the precipitate from the uranyl-nitrate solution using a 0.45- $\mu\text{m}$  cellulose nitrate filter.



## 2 RESULTS

During FY 15, this procedure was scaled up from a volume of 160 mL to 1 L and repeated in triplicate. The feed for these experiments was a depleted-uranium solution irradiated in the bubble experiment [3]. The filtrate and subsequent washes were analyzed by inductively coupled plasma–optical emission spectrometry (ICP-OES) for Sr, Ba, and U and by ion chromatography (IC) for  $\text{NO}_3^-$  and  $\text{SO}_4^{2-}$ . The STS, filtrate 1, and precipitate 1 were also gamma counted. Three wash protocols were investigated during this experiment, as well.

### Precipitation Experiment #1

After completion of the precipitation procedure described above, the precipitate that remained in the reaction vessel was mixed with ~50 mL of 1 M  $\text{HNO}_3$  to ensure complete transfer of the precipitate to the filtration apparatus. This created a slight dilution of the uranium solution; for this reason, this step was not used in precipitation experiments 2 and 3. The precipitate was then washed eight times with 50 mL of 1 M  $\text{HNO}_3$ . The ICP-OES and IC results for the stock, filtrate, and washes are shown in Table 1.

The data in Table 1 indicate that the [Ba] is well below the required RCRA limit of 7.E-04 for the filtrate and all washes. The increase in [U] from wash 4 to wash 5 is likely due to the fact that the vacuum pump was allowed to dry the precipitate for longer than the previous washes. The  $[\text{SO}_4^{2-}]$  for the filtrate is slightly above the desired value [2.0E-02]. However, at sulfate concentration of 0.026 M, approximately the same amount of uranium as with 0.02 M will break through to the raffinate in the UREX process (1.35E-08 compared to 1.2E-08 M, or 12.5% higher) [2]. The weighted average of the  $\text{SO}_4^{2-}$  was calculated to be 2.36E-02 [2]. This would result in less U breaking through to the raffinate. Note that in wash 8 there is only 0.26% of the original uranium in the wash solution.

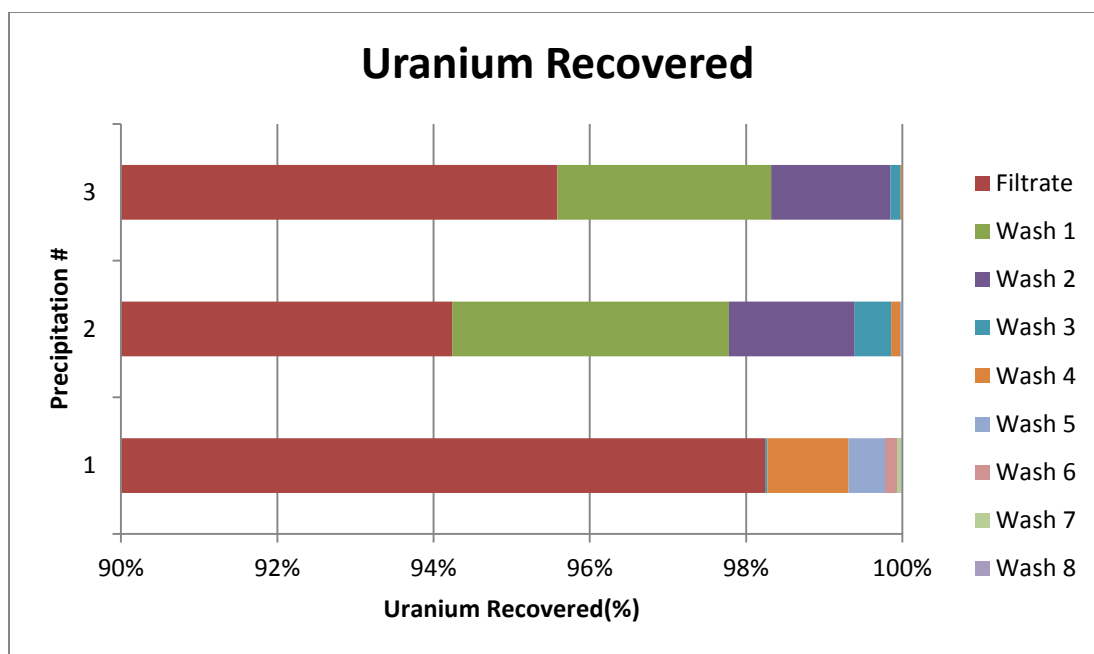
**TABLE 1 Concentrations of Feed Components in Stock, Filtrate, and Washes for First Conversion Experiment (M)**

	[Ba]	[Sr]	[U]	$[\text{NO}_3^-]$	$[\text{SO}_4^{2-}]$
Stock	<7.28E-05	4.78E-04	5.63E-01	8.39E-03	6.67E-01
Filtrate 1 + wash 1 & 2	1.49E-04	4.28E-02	5.17E-01	1.30E+00	2.58E-02
Wash 3	1.38E-05	1.35E-02	3.00E-03	1.02E+00	1.42E-02
Wash 4	1.41E-05	2.29E-02	1.18E-01	1.25E+00	1.81E-02
Wash 5	9.39E-06	1.63E-02	5.34E-02	1.07E+00	1.48E-02
Wash 6	1.26E-05	1.50E-02	1.65E-02	1.05E+00	1.55E-02
Wash 7	1.37E-05	1.38E-02	6.55E-03	1.01E+00	1.71E-02
Wash 8	1.41E-05	1.32E-02	1.48E-03	1.01E+00	1.44E-02

In addition to ICP-OES and IC analysis, the stock STS solution, filtrate, and precipitate cake were analyzed by gamma spectroscopy. Figure 1 shows the percent of uranium recovered in each step of the first precipitation experiment along with the other two. Some number of the wash solutions should be combined with the original filtrate to diminish uranium losses. The number of washes to combine in order to develop the most efficient process with the greatest uranium needs to be determined.

The gamma spectroscopy results can be seen in Table 2. Note that the reported results for the precipitate are only qualitative, as there is no geometric calibration source available. All data have been decay-corrected to a common point in time (September 1, 2015 at 12:00 PM), so that the results can be directly compared. The library used for analysis includes ~18 isotopes of interest and has been used in other SHINE analysis. For Table 2, the isotopes in this library with short half-lives were eliminated from consideration due to the long time elapsed since irradiation.

Because the precipitate data are qualitative, we can only conclude that Zr, Nb, Ru, Cs, and La partition, in part, to the precipitate cake. Comparing the stock and the filtrate data, it appears that the majority of the Zr, Nb, and Ru does not precipitate and pass through to the filtrate. Due to poor peak shapes and minimal detectable activity (MDA) values, we cannot reach any definitive conclusions for the other isotopes.



**FIGURE 1 The Percentage of Uranium Recovered in each Step for all Three Precipitations Relative to the Total Uranium in the Stock Solution. The data have been normalized to 100%. The error associated with the data is approximately 10%.**

**TABLE 2 Gamma Results for Isotope Partitioning in Feed, Filtrate, and Precipitate for Experiment 1**

Isotope	Line (keV)	Stock (μCi)	Filtrate (μCi)	Precipitate <sup>a</sup> (μCi)
Zr-95	757.40	5.21E-02	4.25E-02	1.80E-03
Nb-95	765.81	1.21E-01	1.14E-01	3.33E-02
Ru-103	497.08	1.12E-02	9.62E-03	2.63E-02
Cs-136	818.51	---	8.09e-6 <sup>b</sup>	2.53E-03
	1048.07	---	---	---
Ba-140	537.26	---	---	---
La-140	1596.21	3.41e-3 <sup>c</sup>	1.06e-1 <sup>c</sup>	6.79e-1 <sup>c</sup>
Sn-125	1088.9	1.34e-4 <sup>c</sup>	1.78e-4 <sup>b, c</sup>	---

<sup>a</sup> Qualitative measurement as there is no geometric standard.

<sup>b</sup> MDA value.

<sup>c</sup> Poor peak shape.

## Precipitation Experiment #2

Despite the success of precipitation #1, we decided that it would be beneficial to study the effect of reducing the precipitate wash volume. First, the small amount of precipitate remaining in the reaction vessel was not transferred from the vessel and into the filtration apparatus. This should result in minimal loss of uranium. The second step to reduce the wash volume was to allow the 50 mL added to wash the precipitate to interact with the precipitate cake for ~30 to 60 seconds prior to filtration. The analytical results for the stock, filtrate, and washes are shown in Table 3.

Table 3 indicates that [Ba] is well below the required RCRA limit of 7.E-04 for the filtrate and all washes. Again, [SO<sub>4</sub><sup>2-</sup>] for the filtrate is above the desired 2.0E-02 M. However, at a sulfate concentration of 0.033 M, approximately 42% more uranium as with 0.02 M will break through to the raffinate in the UREX process (1.7E-08 compared to 1.2E-08 M) [2]. The wash volume in this experiment was reduced from ~400 mL to 250 mL. As a result, the U concentration in wash 5 of this experiment is comparable to that in wash 8 of experiment 1, indicating that allowing the wash solution to interact with the precipitate cake for 30 to 60 seconds can decrease the wash volumes by 37.5%. The weighted average for [SO<sub>4</sub><sup>2-</sup>] was calculated to be 2.81E-02, which would result in ~1.6E-0.8 M U in the raffinate [2]. This is advantageous as the volume of the waste stream will be greatly reduced. Overall, this precipitation was a success and improved upon precipitation #1 with regard to waste volume.

**TABLE 3 Concentration of Feed Components in Stock and Filtrate and Washes for Second Conversion (M)**

	[Ba]	[Sr]	[U]	[NO <sub>3</sub> <sup>-</sup> ]	[SO <sub>4</sub> <sup>2-</sup> ]
Stock	<7.28E-05	4.78E-04	5.63E-01	8.39E-03	6.67E-01
Filtrate 2	1.33E-04	3.93E-02	5.76E-01	1.26E+00	3.30E-02
Wash 1	<7.28E-05	2.64E-02	4.33E-01	9.67E-01	2.35E-02
Wash 2	<7.28E-05	1.44E-02	1.97E-01	4.39E-01	1.15E-02
Wash 3	<7.28E-05	6.24E-03	5.71E-02	1.38E-01	5.14E-03
Wash 4	<7.28E-05	2.88E-03	1.42E-02	4.48E-02	2.23E-03
Wash 5	<7.28E-05	1.54E-03	3.50E-03	2.28E-02	1.21E-03

### Precipitation Experiment #3

A third washing protocol was investigated to determine if the wash volume could be further reduced. In this protocol the precipitate was rinsed with 50 mL of 1 M HNO<sub>3</sub>. During the rinsing the precipitate was stirred for ~ 60 seconds to create a slurry between the rinse solution and precipitate.

The data in Table 4 indicate that [Ba] is, again, well below the RCRA limit of 7.E-04 for the filtrate and washes. The sulfate concentration is slightly above the desired 0.02 M for UREX processing. A [SO<sub>4</sub><sup>2-</sup>] of 0.025 M results in ~1.35E-08 M U in the raffinate, compared to 1.2E-08 M U for 0.02 M SO<sub>4</sub><sup>2-</sup>, a 12.5% increase. The weighted average of [SO<sub>4</sub><sup>2-</sup>] is 2.23E-02, which results in less U in the raffinate [2]. In addition, the [U] is at a comparable value in wash 4 in precipitation #3, wash 8 in precipitation #1, and wash 5 in precipitation #2. This results in a total wash volume of 200 mL for precipitation #3, a 50% reduction compared to precipitation #1. Precipitation #3 is thus the recommended method due to the low [SO<sub>4</sub><sup>2-</sup>] and much reduced wash volume.

**TABLE 4 Concentration of Feed Components in Stock, Filtrate, and Washes for Third Conversion (M)**

	[Ba]	[Sr]	[U]	[NO <sub>3</sub> <sup>-</sup> ]	[SO <sub>4</sub> <sup>2-</sup> ]
Stock	<7.28E-05	4.78E-04	5.63E-01	8.39E-03	6.67E-01
Filtrate 3	2.72E-04	4.15E-02	5.71E-01	1.29E+00	2.53E-02
Wash 1	<7.28E-05	2.47E-02	3.27E-01	7.72E-01	1.41E-02
Wash 2	<7.28E-05	8.49E-03	8.57E-02	1.83E-01	4.88E-03
Wash 3	<7.28E-05	2.77E-03	1.56E-02	3.28E-02	1.05E-02
Wash 4	<7.28E-05	1.18E-03	2.34E-03	7.02E-03	7.84E-04

### 3 CONCLUSIONS

Conversion of uranyl sulfate STS to uranyl nitrate was successfully carried out on three 1-L samples, thus proving that the conversion method can be scaled up, and is within the desired parameters to successfully clean up the STS with a UREX process. The remaining waste is all well below RCRA limits. Three wash methods were tested to clean the precipitate. The most effective method was to mix the 1 M  $\text{HNO}_3$  wash solution and precipitate for ~ 60 seconds prior to filtration. This method yielded the lowest  $[\text{SO}_4^{2-}]$  (0.025 M) and the lowest wash volume (200 mL). While the desired  $[\text{SO}_4^{2-}]$  is 0.02 M, a  $[\text{SO}_4^{2-}]$  of 0.025 M yields only 12.5% more U in the raffinate ( $1.35\text{E-}08$  compared to  $1.2\text{E-}08$  M U). If lower  $[\text{SO}_4^{2-}]$  is needed, then additional  $\text{Sr}(\text{NO}_3)_2$  should be added. If this does not yield low enough  $[\text{SO}_4^{2-}]$ , then additional  $\text{Ba}(\text{NO}_3)_2$  can be added.

#### 4 REFERENCES

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