ANL/CSE-13/12

Final FY-12 Progress Report on the Cleanup of Irradiated 130 g-U/L Uranyl Sulfate SHINE Target Solutions

Chemical Science and Engineering Division

About Argonne National Laboratory
Argonne is a U.S. Department of Energy laboratory managed by UChicago Argonne, LLC under contract DE-AC02-06CH11357. The Laboratory's main facility is outside Chicago, at 9700 South Cass Avenue, Argonne, Illinois 60439. For information about Argonne and its pioneering science and technology programs, see www.anl.gov.

DOCUMENT AVAILABILITY

Online Access: U.S. Department of Energy (DOE) reports produced after 1991 and a growing number of pre-1991 documents are available free via DOE's SciTech Connect (http://www.osti.gov/scitech/)

Reports not in digital format may be purchased by the public from the National Technical Information Service (NTIS):
U.S. Department of Commerce
National Technical Information Service
5301 Shawnee Rd
Alexandra, VA 22312
www.ntis.gov
Phone: (800) 553-NTIS (6847) or (703) 605-6000
Fax: (703) 605-6900
Email: **orders@ntis.gov**

Reports not in digital format are available to DOE and DOE contractors from the Office of Scientific and Technical Information (OSTI):
U.S. Department of Energy
Office of Scientific and Technical Information
P.O. Box 62
Oak Ridge, TN 37831-0062
www.osti.gov
Phone: (865) 576-8401
Fax: (865) 576-5728
Email: **reports@osti.gov**

Disclaimer
This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor UChicago Argonne, LLC, nor any of their employees or officers, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of document authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof, Argonne National Laboratory, or UChicago Argonne, LLC.

ANL/CSE-13/12

Final FY-12 Progress Report on the Cleanup of Irradiated 130 g-U/L Uranyl Sulfate SHINE Target Solutions

by
Delbert Bowers and George F. Vandegrift
Chemical Science and Engineering Division, Argonne National Laboratory

prepared for
U.S. Department of Energy, National Nuclear Security Administration,
Office of Defense Nuclear Nonproliferation

September 29, 2012

CONTENTS

1 INTRODUCTION 1

2 FIRST SET OF EXPERIMENTS 4

3 LARGER-SCALE EXPERIMENT 6

4 CONCLUSIONS AND FUTURE WORK 7

FIGURES

1 Flowsheet for Cleanup of Irradiated SHINE Target Solution 2

2 Effect on Uranium Loss to the Raffinate vs. Sulfate Concentration in the UREX Feed 3

3 Photograph of Ground and Out-of-the-Bottle $Ba(NO_3)_2$ Crystals 4

4 Photograph of the Sr/Ba Sulfate Precipitate from the Second Experiment before Washing 6

TABLES

1 Results for First Set of Experiments for Precipitation of Sulfate 5

2 Calculated Compositions of Solution and Solid Phases from the Addition of Solid Alkaline Nitrate Salts to Uranyl Sulfate Solution 7

FINAL FY-12 PROGRESS REPORT ON THE CLEANUP OF IRRADIATED 130 g-U/L URANYL SULFATE SHINE TARGET SOLUTIONS

1 INTRODUCTION

During Fiscal Year 2012 (FY-12), Argonne National Laboratory (Argonne) submitted a series of letter reports as the process for periodic cleanup of the SHINE target solution was first down-selected from a variety of options and then developed. These reports, in order of submission, were as follows:

- Use of Uranyl Peroxide Precipitation as a Means to Clean up Irradiated Uranyl Sulfate Target Solutions (February 28, 2012);
- UREX Flowsheet for Cleanup of a Spent 130 g-U/L Uranyl Sulfate SHINE Target Solution (March 29, 2012);
- Addendum to the Letter Report UREX Flowsheet for Cleanup of a Spent 130 g-U/L Uranyl Sulfate SHINE Target Solution of March 29, 2012 (May 18, 2012); and
- Centrifugal Contactor Operations for UREX Process Flowsheet (May 21, 2012).

Results on cleanup development were also presented at the SHINE technical meeting on August 23, 2012. This report will present results from two experiments; the results of the first experiment were presented at that meeting, and the second experiment was performed after the meeting.

The baseline technology to clean up irradiated SHINE target solution is the process depicted in Figure 1. The process has the following unit operations:

- Adding solid $Sr/Ba(NO_3)_2$ to the irradiated uranyl-sulfate solution in a stirred vessel; addition rate, stirring speed, and temperature must be set to optimize the morphology and size of the crystals formed, in order to allow facile filtration.
- Passing the slurry into a filtration system to collect and wash the precipitate (minimize uranium losses).
- Adding concentrated nitric acid to make the filtrate 1 M in HNO_3 and feeding the solution to the UREX (uranium extraction) process.

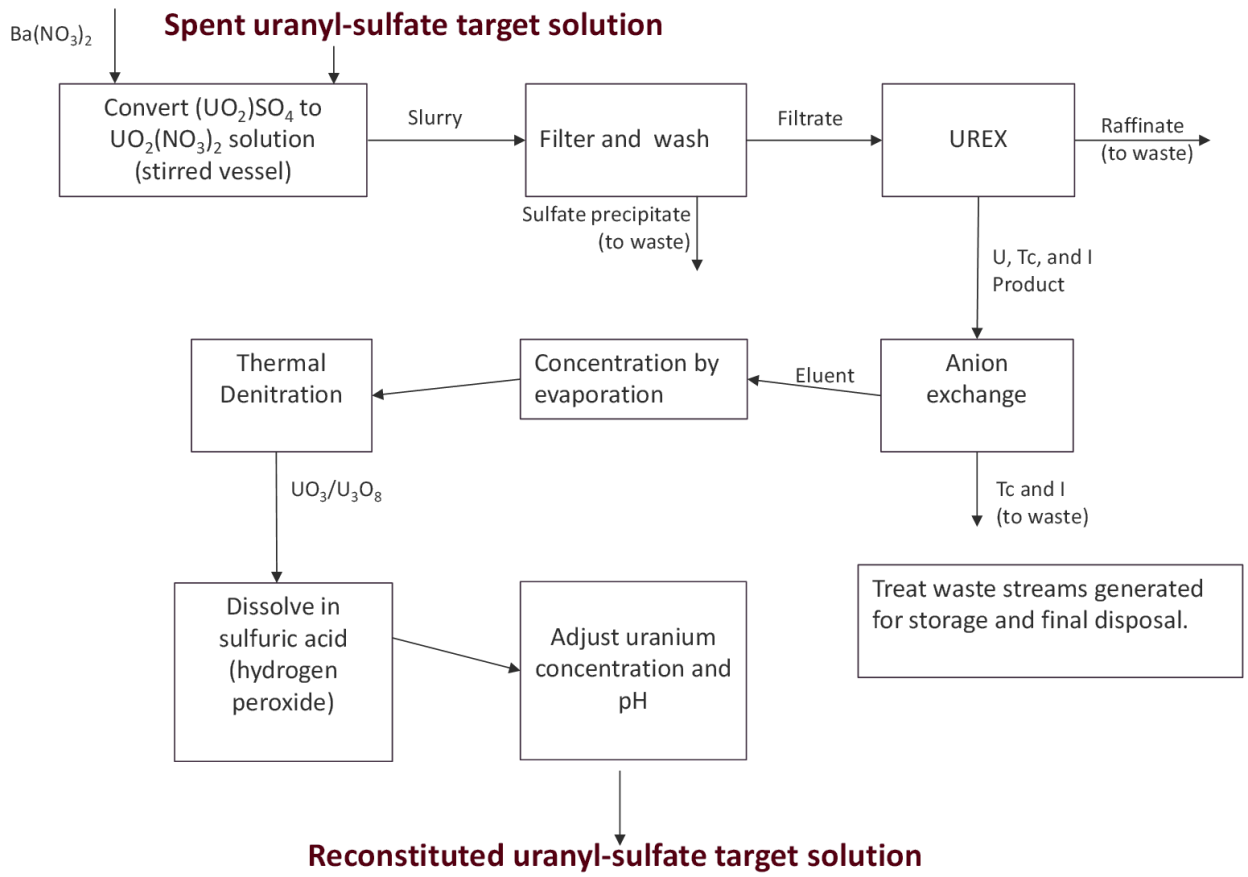

FIGURE 1 Flowsheet for Cleanup of Irradiated SHINE Target Solution

- Running the U-product solution through an anion-exchange column to remove pertechnetate and iodide.
- Concentrating and denitrating the solution to form UO_3.
- Dissolving UO_3 in sulfuric acid (some hydrogen peroxide may be required if all uranium is not in the VI oxidation state).
- Reconstituting the uranyl-sulfate/0.1 M-sulfuric-acid target solution.
- Treating of waste streams generated for storage and final disposal.

All of the processing steps are used commercially and are well understood. The one area of relative uncertainty is what the optimized conditions for the sulfate-to-nitrate conversion are. The addition of solid strontium- and/or barium-nitrate salts to precipitate sulfate and convert the solution to nitrate media is under development. Figure 2 presents calculations performed by AMUSE (Argonne Model for Universal Solvent Extraction) for the effects sulfate concentration has on the ability to extract uranium from the acidified filtrate of the sulfate-to-nitrate conversion step on the UREX process flowsheet developed for the target-solution cleanup operation

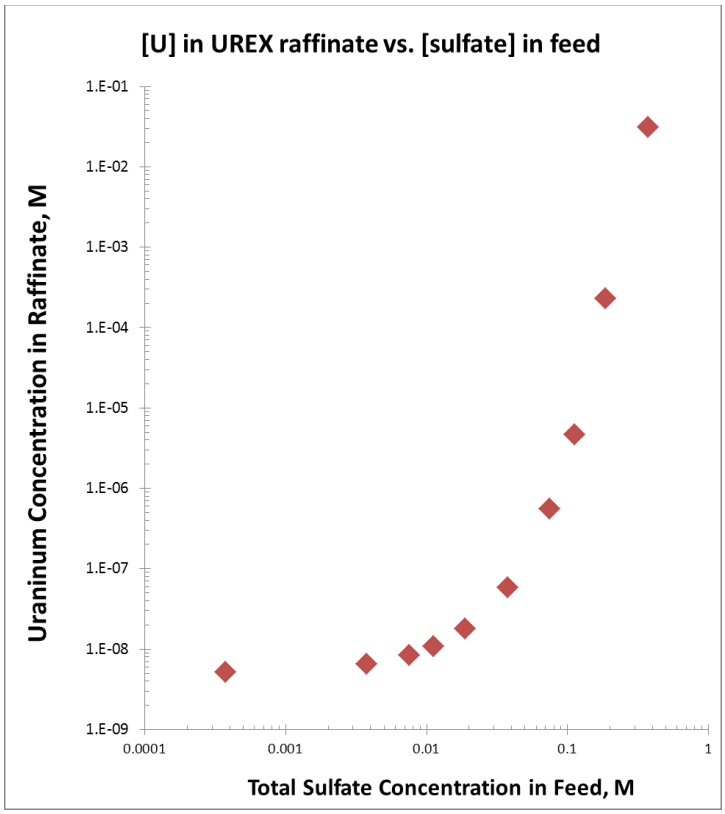

FIGURE 2 Effect on Uranium Loss to the Raffinate vs. Sulfate Concentration in the UREX Feed

(see *Addendum to the Letter Report UREX Flowsheet for Cleanup of a Spent 130 g-U/L Uranyl Sulfate SHINE Target Solution of March 29, 2012*). As can be seen from this figure, if the total sulfate concentration in the feed is kept below 0.02 M, uranium recovery will not be significantly affected. This report discusses the experiments performed during the latter half of FY-12 to verify the efficacy of this approach.

2 FIRST SET OF EXPERIMENTS

All experiments used 20 mL of a solution containing 136 g-U/L UO_2SO_4 with 0.68 M total sulfate, at a pH of 1.08. Two tests were performed by adding solid $Sr(NO_3)_2$ at 1.05 and 1.10 Sr^{2+}/SO_4^{2-} molar ratios. The slurries were heated to approximately 100°C and stirred for 45 minutes. They were then filtered using a glass frit (medium). Fifteen mL of each filtrate were heated and mixed with solid $Ba(NO_3)_2$ (equivalent to ~10% initial sulfate [1.05] and ~15% [1.10] of initial sulfate in solution) for 4 hours and then refiltered.

Two experiments were performed with only $Ba(NO_3)_2$ at 1.1 Ba^{2+}/SO_4^{2-} molar ratios. Both were heated and stirred for 1 hour before filtering. One experiment was run with out-of-the-bottle $Ba(NO_3)_2$ crystals and one was run with ground crystals. Figure 3 is a photograph of the out-of-the-bottle and ground crystals.

Results of these studies are presented in Table 1. The results clearly show that the addition of solid $Sr(NO_3)_2$ alone will lower the concentration of sulfate to a level below concern. Following up with a $Ba(NO_3)_2$ addition brings the concentration to a level far from that of concern. The 1-hour contact with large or fine crystals of $Ba(NO_3)_2$ was not sufficient to convert enough of the sulfate in solution to nitrate, although the finer crystals did show some improvement compared to the large crystals.

FIGURE 3 Photograph of Ground (left) and Out-of-the-Bottle (right) $Ba(NO_3)_2$ Crystals

TABLE 1 Results for First Set of Experiments for Precipitation of Sulfate

	M			
Sample	Ba^{2+}	Sr^{2+}	NO_3^-	SO_4^{2-}
Sr 1/1.05	0	0.09	1.6	0.018
Sr + Ba 1/1.05	0.07	0.10	2.1	<0.002
Sr 1/1.1	0	0.09	1.5	0.017
Sr + Ba 1/1.1	0.06	0.08	2.0	<0.002
Large-Ba 1/1.1	0.0004	–	1.2	0.12
Ground-Ba 1/1.1	0.006	–	1.2	0.087

3 LARGER-SCALE EXPERIMENT

The larger-scale experiment was performed using 100 mL of the same solution as used in the first set of experiments. The solution was placed in a 150-mL Erlenmeyer flask with 15.34 g of $Sr(NO_3)_2$ (~1/1 molar ratio of strontium to sulfate) and stirred and heated at ~100°C for 2 hours. At the time, 1.89 g of ground $Ba(NO_3)_2$ (~0.1/1 molar ratio of barium to sulfate) was added to the slurry, and the slurry was stirred and heated for an additional 2 hours. The slurry was allowed to cool and then filtered using a standard 47-mm Millipore apparatus with a Nuclepore 0.2-µm polycarbonate filter; Figure 4 is a photograph of the precipitate before washing. The filtration went very well, with the filtered material forming a nice cake. Three sequential 10-mL water washes were done on the filter cake; these were done with no stirring of the filter cake. The four solutions were analyzed for cation and anion concentrations.

After this treatment, the sulfate solution in the filtrate was only 0.0006 M. According to AMUSE calculations, this sulfate concentration is far below levels that would not interfere with the UREX process. The precipitate formed a highly crystalline filter cake that settled quickly and was easily filtered. Analysis of the rinses showed that approximately 4% of the uranium was held up in the filter cake, leading to the conclusion that the filter cake must be thoroughly rinsed. Because the filter cake was not stirred with the rinses, this experiment is the worst-case scenario for rinsing. The first rinse contained 3.5% of the original uranium; rinse two contained 0.6%; and rinse three contained 0.15%.

FIGURE 4 Photograph of the Sr/Ba Sulfate Precipitate from the Second Experiment before Washing

4 CONCLUSIONS AND FUTURE WORK

Conversion of uranyl-sulfate SHINE target solutions to nitrate solutions by adding solid strontium or strontium and barium nitrate to precipitate the sulfate from solutions appears to be practical. Thermodynamically, the process looks outstanding; however, it appears that the reaction limiting step is the rate of dissolution of the nitrate salts. The limited solubility of barium nitrate may also be limiting. Grinding the barium nitrate crystal into finer-sized crystals slightly improved sulfate removal from solution for a 1-hour contact, but the improvement was not sufficient. It appears from this initial work that at least 4 hours of stirring will be necessary.

Use of strontium nitrate alone appears to remove sulfate from solution to the extent necessary for complete recovery of uranium in the UREX process; further addition of barium nitrate assures that the sulfate concentration is well below that limit. However, because the process uses an excess of $Ba(NO_3)_2$, the filter cake must be treated with sulfuric acid after filtering to assure that all the barium is in the far less soluble form of $BaSO_4$.

Future development work is required to optimize this procedure. This work will be focused on understanding the kinetics of the dissolution/precipitation reaction. The rate of this reaction is very likely dependent on solid/liquid interfacial area, stirring, and temperature. Thermodynamics sets the minimum sulfate concentration in the solution. Table 2 shows thermodynamic calculations for the effects of the addition of alkaline-earth nitrate salts to uranyl sulfate solutions at pH 1; according to the calculations, Sr can only lower the sulfate concentrations by a multiple of 12–55, while Ba addition can lower it by a multiple of 18,000 to 350,000.

TABLE 2 Calculated Compositions of Solution and Solid Phases from the Addition of Solid Alkaline Nitrate Salts to Uranyl Sulfate Solution

	Aqueous sulfate species							Solid species				
Additive ratio	Uranyl sulfates (molal)	Calcium sulfates (molal)	Strontium sulfates (molal)	Lead sulfates (molal)	Barium sulfates (molal)	Free sulfates (molal)	Total: (molal)	Calcium sulfate (moles)	Strontium sulfate (moles)	Lead sulfate (moles)	Barium sulfate (moles)	Barium nitrate (moles)
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

At the beginning of Fiscal Year 2013 (FY-13), a series of experiments will be done to quantify the effects of solid/liquid interfacial area, stirring, and temperature on the reaction. The optimized conditions from these studies will be demonstrated cold, then with tracers, and finally with irradiated mini-SHINE solution.

If using $Ba(NO_3)_2$ alone or as a secondary step to $Sr(NO_3)_2$ addition is chosen as a baseline for SHINE, activities will be performed to assure that all Ba is in the form of the sulfate salt and, therefore, not leachable from the waste form.

Chemical Science and Engineering Division
Argonne National Laboratory
9700 South Cass Avenue, Bldg. 205
Argonne, IL 60439-4837

www.anl.gov

Argonne National Laboratory is a U.S. Department of Energy
laboratory managed by UChicago Argonne, LLC