ANL/CSE-13/10

Letter Report: UREX Flowsheet for Cleanup of a Spent 130 g-U/L Uranyl Sulfate SHINE Target Solution

Chemical Science and Engineering Division

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by
George F. Vandegrift, Laura Maggos, Candido Pereira, James Jerden, and Delbert Bowers
Chemical Science and Engineering Division, Argonne National Laboratory

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

March 29, 2012

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1 THE COMPLETE SOLUTION-CLEANUP PROCESS

The process for cleaning up a uranyl-sulfate solution has the following steps:

1. Addition of $Ba(NO_3)_2$ 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 and to allow facile filtration.

2. Passing the slurry into a filtration system to collect and wash the precipitate (minimize uranium losses).

3. UREX processing of the filtrate.

4. Anion exchange step to remove pertechnetate and iodine from uranium product.

5. Precipitation of uranium as ammonium diuranate and its filtration.

6. Conversion of uranium to UO_3/U_3O_8.

7. Dissolution of uranium oxide in sulfuric acid.

8. Reconstituting the uranyl-sulfate/0.1-M-sulfuric-acid target solution.

9. Potential recycle of uranium from ammonium diuranate filtrate.

10. Treatment of waste streams generated for storage and final disposal.

The processing begins with the conversion of the sulfate solution to a nitrate solution as a result of adding barium nitrate, which will precipitate much of the sulfate as the barium salt. If $Ba(NO_3)_2$ is added at a 1/1 molar ratio with the total sulfate in the solution, it will precipitate almost all sulfate as $BaSO_4$, there will be a solution of uranyl nitrate and almost all of the accompanying fission and activation products, and there will be a very much reduced amount of soluble sulfate. The $BaSO_4$ precipitate should be quite low in radioactivity. Of course, the ^{140}Ba sulfate will precipitate, but the radio-Sr may not, since strontium sulfate has a solubility of approximately 0.1 g/L; however, Sr may be pulled down with $BaSO_4$. The lanthanide sulfates will remain in solution (e.g., lanthanum sulfate has a solubility of ~30g/L). A few minor fission products may precipitate. The precipitation operation would likely be a batch type with a removable reservoir/filter apparatus.

Table 1 and Figures 1 and 2 show the effects of adding both calcium and barium nitrate. Our first instinct was to use the calcium salt because soluble barium compounds are toxic. However, it is clear from the modeling results in Table 1 and Figure 1 that the solubility of $CaSO_4$ is too high to effectively remove sulfate from the solution. On the other hand, the very low solubility of $BaSO_4$ allows for very effective removal of sulfate (Table 1 and Figure 2). Even though barium is considered toxic, $BaSO_4$ is not (e.g., it is used as a radiocontrast agent for X-ray imaging of the digestive system). Because of the extremely low solubility of barium sulfate, the radioactive waste will not be considered mixed waste, and will readily pass the Toxicity Characteristic Leaching Procedure (TCLP).

Once most of the sulfate is replaced by nitrate, the uranium solution can be purified using the UREX process. Pertechnetate and iodide that extract with uranium will be removed from the uranium product by an anion-exchange column.

The resulting uranyl-nitrate product in 0.01-M HNO_3 would be ideally suited for uranium precipitation using the ammonium hydroxide (or ammonia) to produce ammonium diuranate. The technique is well understood and, with pH control, produces a quantitative and filterable precipitate. The ammonium-diuranate solid would subsequently be placed in a furnace and heated to approximately 400°C (Sato and Shiota 1985) (optimum temperature needs to be found in the literature) to form UO_3. This process typically produces U_3O_8, but UO_3 is better for our purposes. The liquid waste from the uranium precipitation would be very low in radioactivity and could be either evaporated or solidified using Acid Bond© or another acceptable solidification process. The UO_3 is then dissolved in H_2SO_4 for reuse; this step may need some development. The uranium will dissolve without much difficulty, but we need to have a solution of pH 1, so there cannot be any excess of H_2SO_4. Unlike the uranyl nitrate system, where we could just use heat to drive off HNO_3, excess H_2SO_4 is more problematic.

TABLE 1 Model Calculations for the Effects of Calcium and Barium Nitrate Additions to a Solution of 130 g-U/L Uranyl Sulfate in pH 1 Sulfuric Acid

Additive Ratio	No Additive	Ca/S = 1.0	Ca/S = 1.1	Ca/S = 1.25	Ca/S = 1.5	Ba/S = 1.0	Ba/S = 1.1	Ba/S = 1.25
Aqueous Species	molal	molal	molal	molal	molal	molal	molal	molal
Uranyl sulfates	5.58×10^{-1}	1.30×10^{-1}	1.09×10^{-1}	8.42×10^{-2}	5.83×10^{-2}	2.75×10^{-4}	1.66×10^{-6}	1.37×10^{-6}
Calcium sulfates	—	4.25×10^{-3}	4.25×10^{-3}	4.25×10^{-3}	4.25×10^{-3}	—	—	—
Barium sulfates	—	—	—	—	—	$<1.0 \times 10^{-8}$	$<1.0 \times 10^{-8}$	$<1.0 \times 10^{-8}$
Free sulfates	1.71×10^{-1}	5.55×10^{-2}	4.81×10^{-2}	3.91×10^{-2}	2.90×10^{-2}	1.41×10^{-4}	1.95×10^{-7}	7.22×10^{-7}
Total	7.29×10^{-1}	1.90×10^{-1}	1.61×10^{-1}	1.28×10^{-1}	9.16×10^{-2}	4.16×10^{-4}	1.86×10^{-6}	2.09×10^{-6}
Soldis species	moles	moles	moles	moles	moles	moles	moles	moles
Calcium sulfate	—	0.54	0.57	0.61	0.64	—	—	—
Barium sulfate	—	—	—	—	—	0.73	0.73	0.73
Barium nitrate	—	—	—	—	—	0.00	0.00	0.09

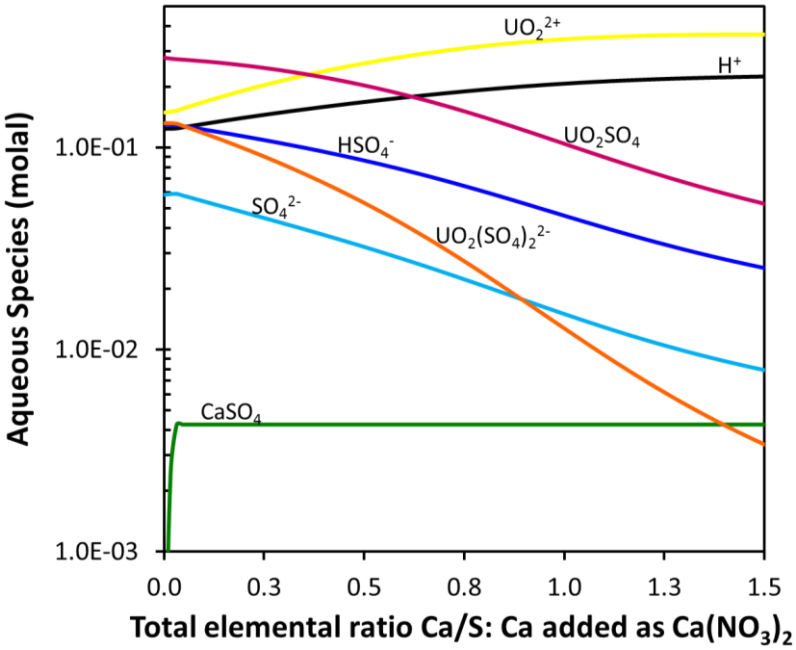

FIGURE 1 Solution Speciation vs. Addition of $Ca(NO_3)_2$

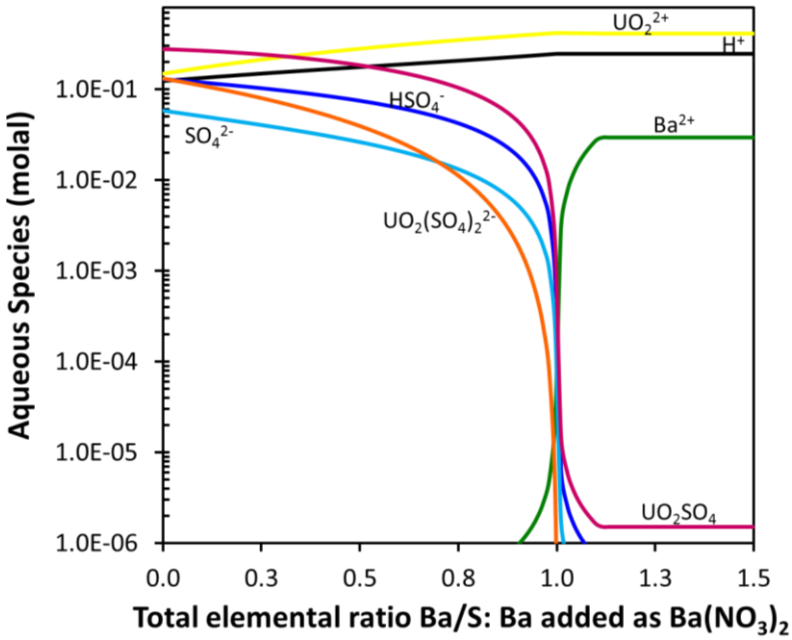

FIGURE 2 Solution Speciation vs. Addition of $Ba(NO_3)_2$

2 THE UREX FLOWSHEET FOR 130 g-U/L URANYL NITRATE (CONTAINING MINOR AMOUNTS OF SULFATE)

2.1 BACKGROUND

On July 6, 2011, Argonne sent two UREX flowsheets to Morgridge Institute for Research (MIR) for processing a 150 and 300 g-U/L solution of uranyl nitrate. Argonne was tasked by the National Nuclear Security Agency (NNSA) in Fiscal Year 2012 (FY-12) to develop a method to clean up a spent SHINE target solution prepared with uranyl sulfate. This process is described above. Discussions between Argonne and SHINE led to us look at a solution of 130 g-U/L solution of uranyl sulfate in sulfuric acid at pH 1.

Briefly described below is the UREX flowsheet that was designed using the Argonne Model for Universal Solvent Extraction (AMUSE) for recovering pure uranium from that solution after it has been converted to nitrate media. The barium precipitation of sulfate is so effective that the number of stages developed for treating this solution is exactly the same as for the two earlier flowsheets. The only parameter that needed to be changed is the organic-to-aqueous (O/A) flow ratio in the extraction section. This ratio is maintained to provide a maximum loading of the tributyl phosphate (TBP) in the solvent to a range of 70–72%. This ratio should be kept high enough to minimize the extraction of other species into the solvent (to assure maximum decontamination of the uranium product), but low enough so that the organic phase will not divide into a light and heavy phase (third-phase formation) that would cause significant hydraulic problems for the contactor.

As it was initially designed, an important feature of this flowsheet is the ease developing a new flowsheet if the concentration of uranium is modified. This means that the contactor in the hot cell can be permanently plumbed into four sections, with the requisite number of stages in each section. The only variable to be changed if the uranium concentration is modified is the flow rate of feed solutions.

Figure 3 shows the flowsheet for processing this solution. For this exercise, we assumed all transuranic elements (TRU) and fission products were at 10^{-4} M; barium and sulfate concentrations were derived from the model results for a 1/1 addition of barium nitrate.

The major features in this workbook are as follows:

- The first sheet is the run status, which shows whether the sheet converged and (if applicable) how long it took to converge.

- The next sheet is the full report, which shows the composition of each feed (in) and effluent (out) stream and the temperature of the section. Note that the extraction and scrub sections are at 25°C and the strip section is at 50°C. Concentrations listed below 10^{-12} M are essentially zero (i.e., undetectable; the plots cut off at 10^{-19} M).

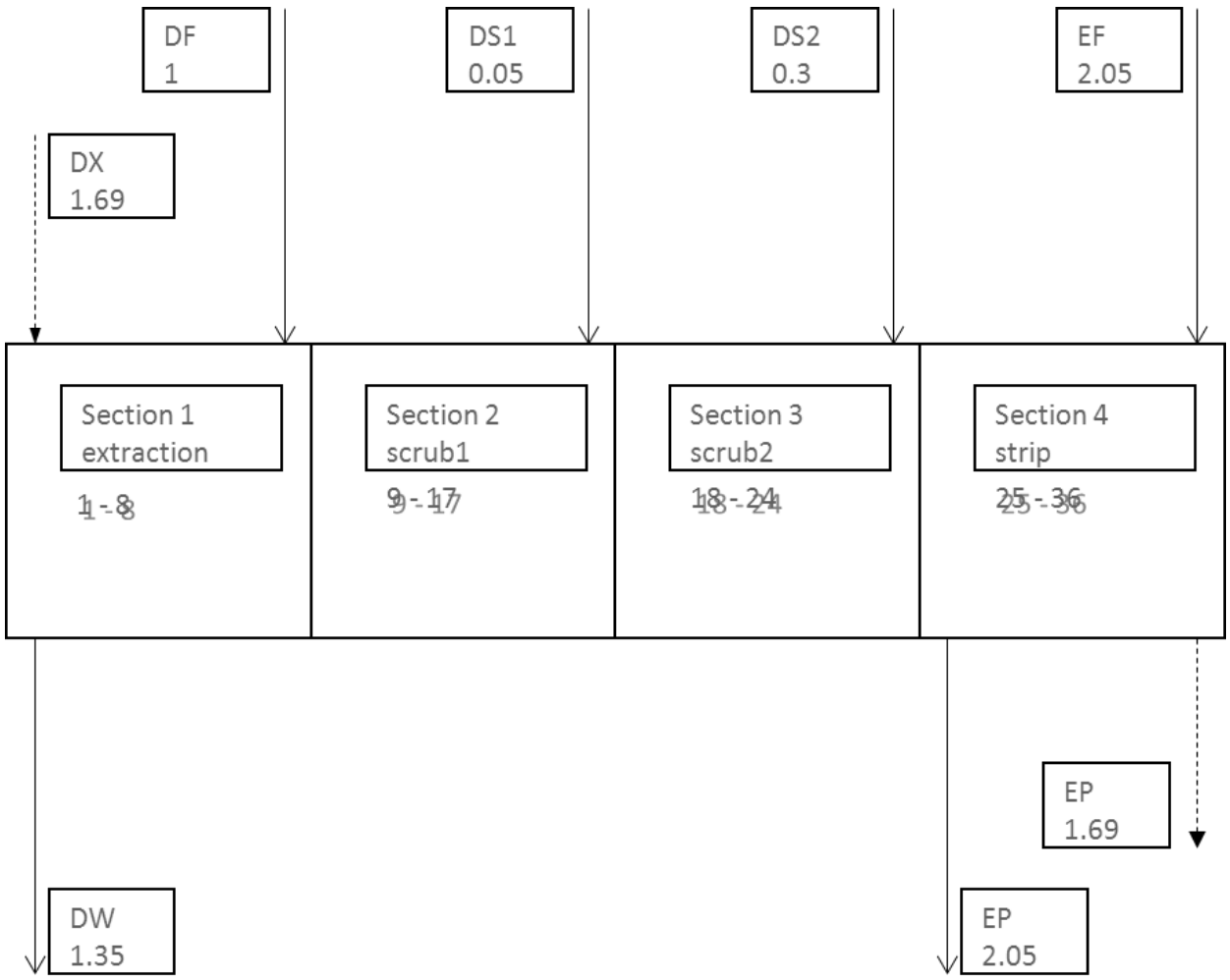

FIGURE 3 Schematic of the UREX Flowsheet for 130 g-U/L Uranyl Nitrate Derived from Conversion from Sulfate Media by $Ba(NO_3)_2$ Addition

- The next section is the flowsheet display. It is not beautiful, but it does show the stages in each section and the flow rates of all streams. The stream names are arbitrary.

- The next sheets are the stagewise concentration profiles of each component in the feeds.

- The last sheet displays the data used to generate the charts.

2.2 FLOWSHEET DESCRIPTION

The flowsheet has four sections—Extraction (8 stages), scrub 1 (9 stages), scrub 2 (7 stages), and strip (12 stages). In the extraction section, the uranium-containing feed (the spent

target solution from sulfate/nitrate conversion in 1 M HNO_3) enters at stage 8; the clean solvent (30 vol% tributyl phosphate in n-dodecane) enters at stage 1. As the aqueous solution moves from stage 8 to stage 1, its uranium concentration is lowered. The "uranium-free" raffinate exits the contactor at stage 1. The flow-rate ratio of the organic and aqueous feeds entering the contactor in the extraction section is 1.69.

The primary goal of the first scrub section is to remove from the U-loaded solvent the small amounts of other feed components that entered the organic phase in the extraction section. Acetohydroxamic acid (AHA) enters the contactor 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 formed are far less extractable than the free metal ions and, therefore, their extractability is greatly reduced. The AHA-feed solution to the first scrub enters the contactor at stage 17. As it flows countercurrently to the U-loaded solvent (which is moving through the first scrub section from stage 9 to 17), it scrubs contaminants from the U-loaded solvent. The aqueous phase flows from the first scrub section to the extraction-feed stage (stage 8), where it mixes with the extraction feed solution and passes out of the contactor with the raffinate at stage 1. In the extraction section, AHA will continue to act as a complexing and reducing agent, limiting the amount of non-uranium species that are extracted into the solvent. The composition of the feed to the first scrub section is 0.5-M AHA dissolved in 0.1-M HNO_3. It has a flow-rate ratio to that the aqueous feed entering the extraction section of 0.05.

The primary goal of the second scrub section is to remove from the U-loaded solvent the small amount of AHA and AHA-metal species that have extracted into the organic solvent. The feed composition is 0.3-M HNO_3. It has a flow-rate ratio to that the aqueous feed entering the extraction section of 0.3. This feed solution enters the contactor at stage 24, where it flows countercurrent to the U-loaded solvent that enters this section at stage 18. As the U-loaded solvent moves from stage 18 to stage 24, its concentrations of AHA and other contaminants drop. The U-loaded solvent moves from the second scrub section to the strip section, where pure uranium is stripped from the solvent. The aqueous phase leaving the second scrub section mixes with the aqueous feed into the first scrub section, where it travels from the first scrub section into the feed stage to the extraction section and eventually leaves the contactor in the raffinate exiting at stage 1. The relative flow rate of the raffinate to that of the extraction-section feed is, therefore, the sum of the three feed rates (1 + 0.05 + 0.3 = 1.35).

Once the U-loaded solvent is purified, it moves into the U-strip section (stages 25–36), where the uranium is recovered as a uranyl nitrate solution in 0.01-M HNO_3. The aqueous feed to the strip section is 0.01-M HNO_3 and enters the contactor at stage 36. Its relative flow rate to that of the aqueous feed to the extraction section is 2.05. The aqueous feed moves countercurrent to the flow of the solvent (which flows from stage 25 to stage 36). As the solvent moves from stage 25 to stage 36, its uranium concentration decreases; conversely, as the aqueous feed moves from stage 36 to stage 25, its U concentration increases. Due to the relative flow ratios and the fact that, at steady-state, $mass_{in}$ must equal $mass_{out}$, the concentration of uranium in the product stream leaving stage 25 is 1/2.05 of that in the extraction feed. The solvent leaving stage 36 is now essentially free of extractible species and can be recycled to stage 1 for another pass through the contactor.

3 ANCILLARY FLOWSHEET SECTIONS

Two other sections are not specified in this flowsheet, but they should be included in a full UREX process (which would include diluent-wash and solvent-cleanup sections).

3.1 DILUENT WASH

In the diluent wash step, the U-product is washed with dodecane to remove TBP that is dissolved or entrained in the aqueous product. The best design we have come up with is a three-stage centrifugal contactor section, in which a continuous recycle loop of dodecane is moving through each stage. The distribution ratio for TBP in the dodecane/aqueous-product stream is in the range of 300–400. Therefore, its concentration in the U-product will drop by about 100 if the organic-to-aqueous flow rate is set at 3/1 in each stage (1,000,000 overall drop).

The total volume of the dodecane in each of the three recycle steams would need to be about 10 times the holdup volume in a contactor stage—at most a few liters. Most of the TBP will end up in the first recycle tank, with a lesser amount in the second recycle tank, and a very small amount in the third. After a number of uses (to be determined), the first recycle tank will be wasted, the second tank will be piped into the first stage, and the third into the second; fresh dodecane will then be used in the third stage.

This step can either be used in the hot cell, if convenient, or outside. The product solution could be pumped out of the cell, and this operation could be performed before or after the Tc/I-removal column. The dose rate of the U-product should be relatively low, depending on the amount of radioiodine in the feed solution.

3.2 SOLVENT CLEANUP

It is possible that a periodic solvent cleanup to remove degradation products from the recycled solvent might be necessary. Because of the relatively low burnup of the solution, it is uncertain how often this will be needed. It is not necessary or desirable to put this in the overall process in the hot cell. Because of the low radioactivity that will be present in the solvent, it could be performed in a glovebox or a chemical hood with a smaller contactor. This would be accomplished by removing the solvent from the hot cell and using a four-stage 2- or 4-cm centrifugal contactor for the operation. The solvent volume should be fairly low.

It may be just as easy, and likely more economical, to periodically just replace the solvent and dispose of the spent solvent as low-level waste. There is a material much like Aquaset for organic materials that could produce a solid for low-level waste disposal.

4 PROCEDURE FOR RUNNING THE UREX PROCESS

A draft procedure for running the UREX process and the estimated process times in a 5-cm contactor was developed. This procedure was modified from what Argonne used in our hot-cell demonstrations of the UREX processing of spent fuel in a 2-cm centrifugal contactor. Once the target solution composition and volume are finalized, the UREX flowsheet is defined for that target solution, and a contactor size is specified, the final procedure can be written.

5 REFERENCE

Sato, T., and S. Shiota, 1985, "Thermal Decomposition of Ammonium Uranates," *Journal of Thermal Analysis* 30: 107–120.

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

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