Conversion of Uranium Metal to Uranyl Sulfate Solution

Chemical & Fuel Cycle Technologies Division

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ABSTRACT

Experiments involving conversion of uranium (U) metal to U_3O_8 , followed by dissolution to form uranyl sulfate solution, were performed with batches of up to 300 g of U metal. The focus was to identify major U species formed during the oxidation process, determine the particle size distribution of the uranium oxide product, and identify the size of the dissolution vessel needed to accommodate the exothermic reaction during the conversion of U_3O_8 to uranyl sulfate using 30% hydrogen peroxide and H_2SO_4 . The information obtained in this study will be used for designing full-scale processes to convert kilogram quantities of U metal to uranyl sulfate solution with a concentration of 300 g U/L.

1 INTRODUCTION

Argonne National Laboratory, with support from DOE's National Nuclear Security Administration Office of Material Management & Minimization, is helping SHINE Medical Technologies in developing domestic production of Mo-99. SHINE is planning to produce Mo-99 by fission of low-enriched uranium-235 (LEU) in a subcritical aqueous solution using accelerator-based neutron generation.¹ SHINE's subcritical system can contain ~250 L of LEU solution, and several units may be implemented. In order to prepare a large volume of uranyl sulfate solution, the process of conversion of U metal to oxide and uranyl sulfate solution needs to be well understood and optimized. The full-scale dissolution setup should be able to process up to ~600 g of U per batch, and have sufficient head space to contain the reaction. Here we report results on conversion of 50-g and 300-g U batches to uranyl sulfate.

2 EXPERIMENTAL

2.1 MATERIALS AND REAGENTS

All reagents listed were used as received unless specified in the text.

Nitric Acid - TraceMetal Grade was purchased from Fisher Chemical (Part # A509-P212). Sulfuric acid was purchased from Sigma-Aldrich (Part # 320501-2.5L).

¹ S. Chmerisov, G.F. Vandegrift, "Mini-SHINE/MIPS Experiment," Argonne National Laboratory Report ANL/CSE-14/2, September 2011.

30% hydrogen peroxide solutions from three suppliers were tested:

- Hydrogen Peroxide Certified ACS, Fisher (Part # H325-500)
- Hydrogen Peroxide GR ACS, Millipore (Part # HX0635-2)
- Hydrogen Peroxide ACS reagent, Acros Organics (Part # 41188-5000)

These hydrogen peroxides were chosen because they were described on their certificates of analysis as 30% high-purity hydrogen peroxide with no chemical stabilizers present, and were readily available in large quantities.

If needed, 18.2 M Ω ·cm deionized water was used for all washing and dilution steps.

2.2 EXPERIMENTS

Multiple oxidation experiments were performed using depleted uranium (DU) at scales of ~50 and ~300 g, and are summarized in Table 1.

TABLE 1 Amounts of uranium, hydrogen peroxide and sulfuric acid used for conversion of U-metal to uranyl sulfate.

Batch	Initial Mass	Final Mass	Volume Added	
	Uranium (g)	U ₃ O ₈ (g)	H ₂ O ₂ (mL)	H ₂ SO ₄ (mL)
1	41.3	48.6	252.0	10.3
2	41.5	50.3	222.0	10.4
3	36.9	44.9	201.0	9.2
4	42.8	50.4	282.0	10.7
5	42.1	51.2	255.0	10.0
6	37.1	44.5	228.0	10.0
A	309.2	364.2	1712.0	77.3
B	286.6	337.4	1580.0	71.7
C	289.9	347.3	1673.0	72.5

These dissolution experiments were performed in a vessel that was custom-made in the Argonne glass shop with parts obtained from ChemGlass. The dissolution vessel was assembled by joining a reaction vessel (CG-1920-02) to a section of 10-cm-ID glass pipe. This assembly rested in a heating mantle (CG-10007-10) and was closed at the top with a 4-neck reaction vessel lid (CG-1941-02). The lid was secured with a clamp (CG-141-02) and three of the ports in the reaction lid were occupied. The first held a high-efficiency condenser (CG-1215-01), while two others were used for SS thermocouples that measured 1/8" wide and 40" long (Omega part # CASS-18U-40-DUAL) with specially adapted stoppers with pass-through openings (CG-1042-E-01). The final port was sealed with a normal glass stopper and used for additions and rinsing the

walls of the vessel when necessary. One thermocouple was attached to a J-KEM controller for temperature control and over-temperature protection, while the second was connected to a data logger to record temperature profiles during the experiments.

Uranium metal was oxidized into uranium oxides by heating in the presence of oxygen. The muffle furnace was set to a starting temperature of 450°C and kept at this temperature for approximately 2 hours. After that, the temperature was increased each hour incrementally from 450°C to 600°C to 720°C and then to 820°C. The U baked at 820°C for approximately 4 hours to complete the oxidation. The muffle furnace was then turned off and the material was allowed to cool overnight. The final stage of heating ensured that other uranium oxides such as UO_3 and UO_2 decomposed or were converted to U_3O_8 . Any oxygen lost from heating U_3O_8 above 800°C was rapidly replaced upon cooling.

The final uranium oxide product identity was confirmed by analysis with a Siemens D5000 X-Ray Diffractometer (XRD). The XRD program ran from 5 to 70 degrees with a step size of 0.01 and a dwell time of 10 seconds at each step while both axes were scanned with a sample spin rate of 30 RPM. The diffraction patterns were compared to the instrument database and literature to positively identify each sample.

First, 50-g batches of U were processed using DU and LEU metal material. These tests were focused on determining the particle size distribution of U_3O_8 particles obtained after oxidation of U metal from different materials. DU metal was in the form of metal foil, while LEU material was in the form of U-metal pellets (Figure 1).

FIGURE 1 DU plates (left) and LEU pellets (right) used for the oxidation experiments.

Particle sizes of the oxidized U were determined by using sieves with various mesh sizes in a Meinzer II sieve shaker (VWR, Part # 47732-822). Each sample was shaken in the sieve for 40 min and the amount of material that passed through the sieve was weighed after each step. Mesh sizes of 40, 140 and 230 were used for the sorting, corresponding to 400 μm , 105 μm , and 63 μm , respectively. Dissolution of 50-g U batches converted to U_3O_8 was performed in a 1-L beaker by addition of 30% hydrogen peroxide followed by addition of sulfuric acid (Table 1).

For large-scale tests using 300-g batches of DU, the dissolution was performed by adding the amount of 30% hydrogen peroxide found in Table 1 to the oxidized DU (U_3O_8). Next, approximately 70 mL of concentrated sulfuric acid was added to the dissolution vessel. The

temperature was measured and recorded during the experiment with a temperature logger and a temperature controller was used when the heating mantle was needed to keep the reaction vessel at 95°C. Once the reaction was completed, the solution was allowed to cool before collection.

3 RESULTS AND DISCUSSION

3.1 OXIDATION OF U METAL

Six 50-g batches of DU metal plates and one 50-g batch of LEU metal pellets (Figure 1) were converted to U_3O_8 by heating. The U was placed in a custom quartz beaker with a handle and baked at ramping temperatures until 820°C was reached, and the material was allowed to bake for 4 hours. It was noted during the baking of the material that the initial phase was exothermic. This was noted because the temperature of the muffle furnace reached over 500°C during the initial setting at 450°C and remained there for approximately 30 minutes. The muffle furnace used for the experiments and one of the completed oxidations can be seen in Figure 2.

FIGURE 2 Muffle furnace used for the oxidation of uranium (left) and a batch of uranium post-oxidation (right) in the custom quartz beaker.

Another observation noted while baking the U during the oxidation experiments was that sufficient volume is necessary for the U to expand during the process. The plates shown in Figure 1 expand to the oxidized uranium powder depicted in Figure 3. If the container is too small, there is potential for the DU powder to be spread while removing the container from the muffle furnace, or to spill over into the furnace during oxidation.

After the oxidation of the DU plates or LEU pellets, the particle size distribution was analyzed. The results from these experiments are listed in Table 2. The results showed that the particle size distribution varied only slightly between trials when the experiments were performed identically. The particle size distributions obtained after oxidation of the DU metal plates and LEU metal pellets (Table 2) are very similar, indicating that the particle size does not vary much when the starting point is U metal. Samples were taken from each batch and analyzed by X-ray diffraction (XRD); the results are shown in Figure 4.

FIGURE 3 A 300-g batch of uranium mid-oxidation (left) and the completely oxidized batch (right).

TABLE 2 Particle size results from the batches of oxidized DU with a comparison to a batch of oxidized LEU.

Experimental Batch	Particle Size (μm)			
	> 400	> 105	> 63	< 63
4 - DU 50 g	3.1	16.1	12.1	18.7
5 - DU 50 g	5.5	18.9	13.7	17.6
6 - DU 50 g	3.4	18.5	9.2	13.2
A - DU 300 g	7.6	95.0	86.0	173.9
B - DU 300 g	5.0	73.4	81.1	177.2
C - DU 300 g	15.7	113.1	66.6	150.4
DU Average (g)	6.7	55.8	44.8	91.8
DU Percent (%)	3.4	28.0	22.5	46.1
LEU 50 g Weight (g)	3.2	17	15.1	24.7
LEU 50 g Percent (%)	5.3	28.3	25.2	41.2

FIGURE 4 Powder X-ray diffraction analysis for the 300-g batches after oxidation.

The resulting spectra were verified to be U_3O_8 by matching to the program's internal library and the literature. This analysis revealed that we were getting complete conversion to U_3O_8 for each of the experiments, with no other major signals present in the spectra.

3.2 DISSOLUTION OF U_3O_8

After oxidation of U metal to U_3O_8 and determination of particle size distribution, dissolution using H_2O_2 and H_2SO_4 was performed. The oxidized material from the 300-g batches was added to the digester system shown in Figure 5, while the 50-g batches were dissolved in 1-L beakers to test the different types of hydrogen peroxide.

First, 50-g U batches were used to test the effect of hydrogen peroxide. The Acros Organic, Fisher Chemical, and Millipore certificates of analysis were all nearly identical and they did not have any stabilizers listed on their product page. As expected, there was no noticeable difference among the three with respect to U dissolution. The reactions of all three showed nearly identical times for each stage of the dissolution. Because there was no detectable difference among the three manufacturers, the same lot of hydrogen peroxide (Fisher Chemical) was used for all 300-g-scale experiments. The reaction times of the dissolution experiments were also very consistent once we settled on a specific hydrogen peroxide manufacturer, as seen in Table 3.

FIGURE 5 Bottom of the dissolution apparatus (left); top of the apparatus (right), with the thermocouple connections and condenser.

TABLE 3 Reaction times for the dissolution of U_3O_8 in hydrogen peroxide after the addition of sulfuric acid to the vessel.

Experimental Batch	H_2O_2 Manufacturer	Reaction Time (min.)	Turned to Precipitate (min.)	Turned to Sulfate (min.)
1	Fisher	3	12	29
2	Acros	3	12	29
3	Millipore	3	11	29

Before the dissolution, a water chiller connected to the condenser on top of the dissolution vessel was set to 5°C and a thermocouple was placed in the vessel to monitor the temperature during the reaction. When the setup was ready, hydrogen peroxide was added to the vessel containing U_3O_8 . After a short wait time, concentrated sulfuric acid was added, and the reaction started immediately thereafter, as seen in Figure 6.

FIGURE 6 The beginning of the dissolution of uranium immediately after sulfuric acid was added to the hydrogen peroxide and uranium. The temperature quickly reached 99°C, and the reaction at this stage was extremely vigorous.

The temperature ramped very quickly from room temperature up to nearly 100°C and the solution turned to a charcoal black, with vigorous bubbling. The primary dissolution took between 15 and 20 min and the total processing time was 1–1.5 hours. The temperature profile of a typical dissolution experiment is shown in Figure 7.

FIGURE 7 A typical temperature profile of a dissolution experiment.

In Figure 7, the peroxide was added at 3.5 min; the sulfuric acid was added at approximately the 6-min mark. The temperature quickly rose when the concentrated sulfuric acid was added to the reaction vessel, and the initial reaction lasted for 15 min (from 6 to 21 min in Figure 7). When the temperature started to drop at 21 min, heat was added by turning on the heating mantle. The temperature in the vessel was controlled to stay between 95°C and 99°C for the remainder of the experiment, starting at ~30 minutes in Figure 7.

The solution bubbled and continued self-heating for approximately 15 minutes, as mentioned above and depicted in Figure 7, before it started to thicken and turn to a grey/green color as seen in Figure 8.

FIGURE 8 The transition from charcoal black to a gray/green color and a thickening of the solution, starting at ~21 min, is shown above. The temperature of the reaction also started dropping at this point, and heat was applied.

During this transition, the temperature of the reaction began to drop to ~95°C; therefore, heat was applied, with the thermostat adjusted to 99°C. The solution volume also increased significantly during this phase; with a beginning volume of around 1.7 L, the solution expanded as much as up to the 5-L mark of the reaction vessel. The reaction also burped frequently during this phase and coated the sides of the vessel with an occasional projection, making it to the lid of the reaction vessel near the condenser and thermocouple attachments. This phase continued for approximately 15 minutes before the reaction started to slow and the solution continued

thickening while turning from the gray-green shown in Figure 8 to a light yellow color (Figure 9).

FIGURE 9 Approximately 35 minutes into the experiment, the reaction settled down from the vigorous stage, the solution turned more yellow, took on a foamy consistency, and started to “breathe.”

After the color change to light yellow, the nature of the reaction changed from constant bubbling and burping to a more controlled “breathing,” with the volume of the solution varying from about 2 to 3.5 L. The thick solution also began to take on a more foamy consistency. With the vigorous reaction slowing down, we took this opportunity to rinse down the sides of the reaction vessel with water in an attempt to get the remaining residue on the sides of the vessel into solution for a complete dissolution. Within 5 to 10 minutes, the foamy solution mixture switched to a liquid consistency with a deeper yellow color and looked more like orange juice, as depicted in Figure 10.

FIGURE 10 The foamy mixture transitioned to a more traditional liquid 40 to 45 minutes into the experiment and began to clear.

Upon the transition to a deeper yellow, the foam continued to clear and the solution volume dropped back to about 1.7 L. It was also at this point that the solution started to go from completely opaque to a more translucent state. Within 5–10 minutes, the solution became transparent and a deep gold color, as shown in Figure 11. Heating continued until fizzing of the solution stopped, which indicated complete destruction of excess peroxide.

FIGURE 11 The solution turned completely clear and became the desired uranyl sulfate solution after reacting for approximately an hour.

The resulting uranyl sulfate solution was allowed to cool to room temperature before being transferred to another vessel. The dissolution apparatus was inspected after each run and little residue was found left behind in the reaction vessel. A small amount of residue, which is typically less than a few grams for a 300-g batch of U, can be seen in Figure 12.

FIGURE 12 A small amount of residue left behind from the dissolution process.

On visual inspection, no black powder remained in the residue, indicating that the conversion to U_3O_8 was complete. This supposition was confirmed via XRD: a sample of the residue was analyzed, and only U_3O_8 was observed in the spectrum. The weight of the residue was estimated to be < 5 grams.

4 CONCLUSION

30% hydrogen peroxide solutions from three different manufacturers were tested, and no significant difference in the dissolution behavior of U_3O_8 was observed. Since the reaction times were nearly identical, price or availability of the hydrogen peroxide could be the basis for determining which manufacturer should be used. For consistency, the Fisher brand was used for all additional experiments. Furthermore, we determined that the particle size distribution of U_3O_8 obtained after oxidation of all U metal batches was very consistent, regardless of the starting U metal form (plates vs. pellets). It was also observed that the time for each phase of the dissolution process was consistent for all 300-g U batches, with a total processing time between 1 and 1.5 hr when Fisher Chemical 30% hydrogen peroxide was used. The results showed near-complete dissolution of the U_3O_8 , and the small amount of residue left behind was confirmed to be U_3O_8 that was not completely dissolved and converted to uranyl sulfate. The residue could be added to future batches to prevent loss of material in large-scale operations.

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