

Uranium Oxide Elutriation Testing at Higher Flow Rates and Longer Times



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March 2022



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Nuclear Energy and Fuel Cycle Division

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ABBREVIATIONS

ID	inner diameter
INL	Idaho National Laboratory
MRPP	Material Recovery Pilot Plant
OD	outer diameter
ORNL	Oak Ridge National Laboratory

SUMMARY

This work supports the recovery of high-assay low-enriched uranium (i.e., U enriched in ^{235}U to >5% and <20%) from used nuclear fuel. One step includes elutriating triuranium octoxide (U_3O_8) from a fluidized bed of alumina (Al_2O_3) that fills the main reaction chamber. The experiments outlined in this report assessed the effects of the time and flow rate on the elutriation of U_3O_8 powder from the reaction vessel. Testing at Oak Ridge National Laboratory (ORNL) was performed in a one-fourth scale experimental apparatus based on a pilot-scale system, which is the Material Recovery Pilot Plant (MRPP) at Idaho National Laboratory (INL).

The experimental system comprises a supply of pressurized nitrogen (N_2), a gas heater, the reaction vessel, a knock-out pot, and a water trap where elutriated particles are collected for sampling. An Al_2O_3 fluidized bed is contained within the reaction vessel. A bed of Al_2O_3 with a nominal size of 180 μm and U_3O_8 with a nominal size of 7 μm was fluidized at 2 different flow rates so the U_3O_8 physically separated from the bed. The apparatus was simple and had no valves or sharp bends downstream from the reactor. The flow exited the reactor through a side port at the top. The flow passed through a knock-out vessel before the flow was passed through a bubbler to capture the U_3O_8 .

Seven tests were completed with U_3O_8 using an elutriating gas of N_2 heated to 200°C. Tests were performed with bed loadings that comprise 25.0 g of U_3O_8 , or 3.6 wt% of the bed mass. Except for one test performed at 12 SLPM, the gas flow rate through the bed for the other experiments was set at 10 SLPM as measured by the mass flow meter. Linear velocities through the bed were calculated as 28 and 34 cm/s, or 0.9 and 1.1 $\text{ft}\cdot\text{s}^{-1}$. The duration of the tests ranged from 20 to 180 min, and one test had a flow cycled between 0 and 5 SLPM every 5 min for 40 min.

The testing successfully demonstrated elutriation of U_3O_8 from the fluidized bed as up to a 100% of the U_3O_8 was transferred out of the bed. The removal of U_3O_8 had a logarithmic dependence on flow rate. The design changes made the apparatus easier to clean, and the mass balances were better than those used in previous studies. Some elutriated Al_2O_3 collected in the tubing that connected the reactor to the knock-out pot, but the amount of Al_2O_3 was minimal for 10 SLPM. The flow at 12 SLPM showed considerable transport of Al_2O_3 bed material into the reaction-vessel headspace and the transfer line to the knock-out pot.

1. INTRODUCTION

This report is the sixth in a series of ORNL reports that discusses parametric tests supporting the MRPP to process spent metal-clad metallic fuel (Wagner 2018) and the third to describe elutriation from a fluidized bed. The steps followed in the MRPP demonstration include (1) chemically removing Al via hydrochlorination, (2) oxidizing with NO_x to pulverize the fuel, and (3) removing the oxidized fuel from the reactor via elutriation. All steps were performed in the same fluidized bed (Monk et al. 1970). These head-end processes will remove the volatile fission products (McFarlane and Walker 2022), but others will be separated by the subsequent dissolution and solvent extraction. The goal of this work was to extend the range of operational parameters by working at consistently higher flow rates and for longer durations.

2. EXPERIMENTAL METHODS

2.1 FLUIDIZED BED APPARATUS

The fluidized bed comprises a scaled-down apparatus that was one-fourth the size of the MRPP reaction vessel that maintains the same ratios of bed length to free board length and bed inner diameter (ID) to length. The packed bed component of the elutriation vessel was 36 cm tall with an outer diameter (OD) of 3.8 cm and an ID of 3.6 cm. A 7.6 cm tall tapered midsection connected the bed to the freeboard zone, which was 16.5 cm long and 7.6 cm in diameter. A metal frit sat at the base of the elutriation vessel to prevent bed material from falling below the fluidization zone. The vessel top was capped with a removable #80 Ace Glass cap. Near the top of the vessel below the glass cap, an exit port with an OD of 1.27 cm was set perpendicularly to the freeboard zone axis. Perfluoroalkoxy alkane tubing with an OD of 0.635 cm was used to connect the exit port to the collection vessels.

Standard pressurized cylinders supplied dry N_2 , and the flow was regulated by a mass flow controller that could allow up to 30 SLPM. Pressure relief valves were used to prevent the system from over-pressurizing. The N_2 gas flowing into the fluidized bed was preheated in a resistive heater, and the gas was heated to 200°C as it passed through a heater before entering the bottom of the elutriation vessel. The gas heater comprised a heating jacket that surrounded a 46 cm long tube filled with alumina spheres that were 5 mm in diameter. The gas heater was set to be controlled at 200°C with a MicroMega controller. The bed was heated with heating tapes and insulated along the entire length to the bed outlet to achieve a homogeneous temperature profile.

The removable #80 Ace Glass cap had Teflon fittings and sealed the top of the elutriation vessel. It was removed to add bed material to the vessel at the beginning of an experiment and at the end of an experiment for cleaning. The Teflon top had a port for the 56 cm long alumina sheathed six-point Type-K thermocouple set. The bottom three thermocouples (numbered 1–3) recorded temperatures within the bed. The lowest thermocouple was located 1 cm from the bottom. The other three thermocouples (numbered 4–6) recorded temperatures in the freeboard zone. The thermocouple measurement points were spaced 10 cm apart. The thermocouple readings were recorded with an Omega OMB-DAC-56 data acquisition system and stored on a laptop computer. Output from the thermocouples was used to control upper and lower bed tape heaters to 200°C via two BriskHeat controllers.

Using a glass top on the elutriation apparatus and glass components downstream allowed the progress of the elutriation to be observed during the experiment. A 2 L aqueous scrubber was used at the exit of the test system to capture elutriated U_3O_8 powder released from the system so the U_3O_8 would not be released into the fume hood exhaust. A 46 cm long, 5 cm diameter gas tube was mounted in between the elutriation vessel and the scrubber to serve as a knock-out pot and prevent elutriated Al_2O_3 from

migrating through the apparatus. The test system had minimal pipe length and complexity in the collection zone downstream of the elutriation vessel to facilitate the recovery of elutriated solids. Figure 1 provides a diagram of the apparatus.

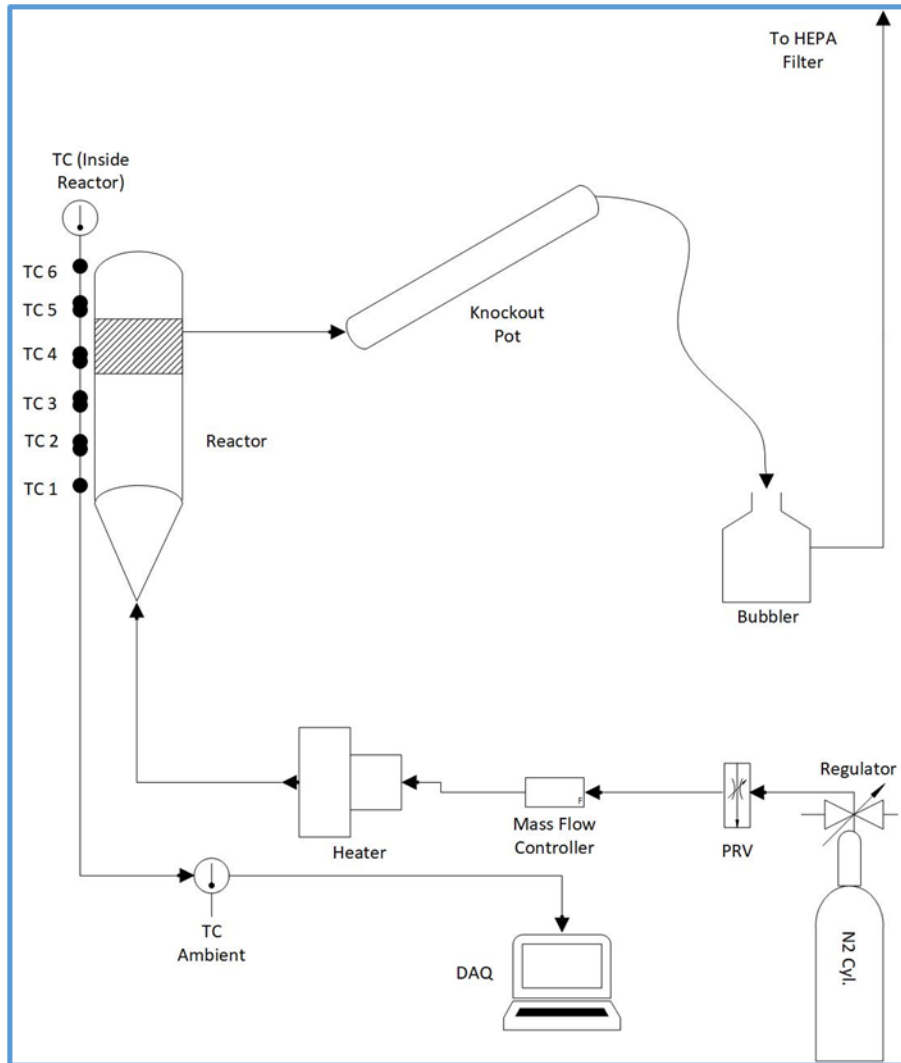


Figure 1. Piping and instrumentation diagram of the experimental system.

2.2 PREPARATION OF U_3O_8 POWDER

Uranium oxide powders for elutriation were prepared in advance of the elutriation experiments in a separate facility. Controlling the particle size distribution in the prepared material was important for testing elutriation accurately under the conditions expected at MRPP. A previous study (Iwasaki et al. 1968) demonstrated that the oxidation temperature of UO_2 pellets significantly affected the particle size distribution of the U_3O_8 powder produced. An oxidation temperature of $400^\circ C$ was selected to minimize the U_3O_8 particle size, and 87% of the U_3O_8 particles were expected to be less than $10 \mu m$. Approximately 250 g of depleted UO_2 pellets were transferred into an alumina crucible, which was placed in a muffle furnace. The furnace temperature was controlled by using a variable resistor power supply. Temperatures were monitored with a Type-K thermocouple. The oxidation continued for a minimum of 10 h during each day of operation. This oxidation process was repeated for several days until slightly more than 1 kg of U_3O_8 powder was collected. The starting U_3O_8 powder was characterized by scanning electron

microscopy. Image analysis was used to determine that the particle dimensions were $<10\ \mu\text{m}$ in diameter. This diameter is similar to that reported in Iwasaki et al. (1968). The mean and median were both $7\ \mu\text{m}$ and had a standard deviation of $3\ \mu\text{m}$.

Prior to each test, 675.0 g of Al_2O_3 was transferred into a weighed glass bottle, and 25.0 g of U_3O_8 powder was added to Al_2O_3 sample so the initial mass was 700.0 g. The sample bottle was closed, and powders were mixed until the color appeared to be uniform. The particle size of the Al_2O_3 bed material was to be $180\ \mu\text{m}$ by the manufacturer, and the reported particle size was confirmed by sieving. The mixture of U_3O_8 and Al_2O_3 was introduced into the fluidized bed apparatus at the beginning of each experiment. The weight of the empty sample bottle was measured so the mass of the Al_2O_3 and U_3O_8 in the reactor could be determined.

2.3 TEST MATRIX

The test matrix used for working with U_3O_8 was developed to investigate the effect of flow rate and time on the elutriation process. Tests were run at flow rates above those required for bed fluidization, which was calculated for $180\ \mu\text{m}$ of Al_2O_3 as $1.43\ \text{cm/s}$. The minimum fluidization velocity for $7\ \mu\text{m}$ of U_3O_8 is $8.49 \times 10^{-3}\ \text{cm/s}$. Table 1 provides the matrix for the elutriation tests with U_3O_8 , and the columns indicate the flow velocity through the bed.

Table 1. Matrix of elutriation tests.

Run number	Flow rate (SLPM)	Linear velocity through bed ($\text{cm}\cdot\text{s}^{-1}$)	Linear velocity through bed ($\text{ft}\cdot\text{s}^{-1}$)	Elutriation time (min)
1	10	28	0.9	60
2	10	28	0.9	120
3	10	28	0.9	20
4	20	34	1.1	120
5	10	28	0.9	90
6	10	28	0.9	180
7	10	28	0.9	$4 \times 5\ \text{min}$

2.4 METHODS

A low flow of N_2 gas (1 SLPM) was introduced to the bed, and the gas and bed were heated to 200°C . The preheating period was 1–1.5 h to establish the operating temperature through the heater and freeboard zone. To start an elutriation test, the flow rate was increased to a predetermined flow rate of 10 or 12 SLPM. The increase ramped up slowly over a couple minutes to the full operating flow rate. The test started when the target flow rate was stable. At the end of the test, the heaters were shut down, and the gas flow was reduced to 1 SLPM. The apparatus was allowed to cool to room temperature for 2 h before it was taken apart.

The test system was completely dismantled after each test, and powders were collected from each component. The powders and cleaning supplies were transferred to pre-weighed bags to enable a mass balance to be obtained on the elutriated and retained material.

Particles were collected from the elutriation vessel headspace, knock-out pot, and downstream lines. The powders were collected mechanically using Kimwipes, swabs, and weighing boats, all of which were tared before use. The boats, powder, and wipes were gathered inside pre-weighed bags. The filled bags

were reweighed, and the mass of the powder contained within was calculated by the mass change. The bubbler contents were filtered and dried to a constant mass. The vessel itself was unloaded by tipping the contents into a bag taped to the top of the vessel. In between tests, the apparatus was thoroughly cleaned with moistened Kimwipes.

3. RESULTS OF U₃O₈ TESTS

Table 2 shows the masses collected for each section of the apparatus during the tests. The masses listed refer to the combined Al₂O₃ and U₃O₈ mass. The material recovery from each run was almost complete.

Table 2. Results of U₃O₈ elutriation tests.

Location of Mass Recovery	Test 1	Test 2	Test 3	Test 4	Test 5	Test 6	Test 7
Initial mass (±0.1 g)	699.6	699.7	699.3	699.6	699.6	699.6	699.6
Mass in fluidized bed reactor after test (±0.1 g)	684.4	682.8	694	666.1	683.1	670.8	692.3
Mass in header (±0.01 g)	1.56	3.56	0.59	5.44	2.20	7.27	1.31
Mass in line from header to knock-out pot (±0.01 g)	5.35	N/A*	2.62	7.48	8.61	7.96	2.73
Knock-out pot (±0.01 g)	3.26	10.19	1.18	18.51	4.12	11.5	1.41
Tubing to water trap (±0.01 g)	0.46	2.07	0.33	0.30	0.94	1.00	0.66
Water trap (±0.1 g)	1.3	1.1	0.8	1.4	0.9	1.1	0.7
Mass balance (±0.1 g)	-3.3	0	0.3	-0.4	0.2	0	-0.5
Recovery (%)	99.5	100.0	100.0	99.9	100.0	100.0	99.9

* The mass in the line was combined with the mass removed from the knock-out pot.

Figure 2 shows the temperature profile of the run for tests 2–7. Thermocouples 1–3 are in the fluidized bed. Thermocouples 4–6 are in the freeboard zone. For test 1, the data were only collected manually, but they were comparable to the measurements in the other tests. During the heating phase at 1 SLPM, the temperatures tracked higher than when the flow was increased. A sharp drop in temperature was observed at the beginning of the elutriation phase. During the elutriation phase at the higher flow rates, the temperature recovered after a few minutes, and the system approached an isothermal condition. At the low flow rate during heating and cooling, the topmost part of the reactor, which was near the uninsulated header, was considerably cooler than the other reactor parts.

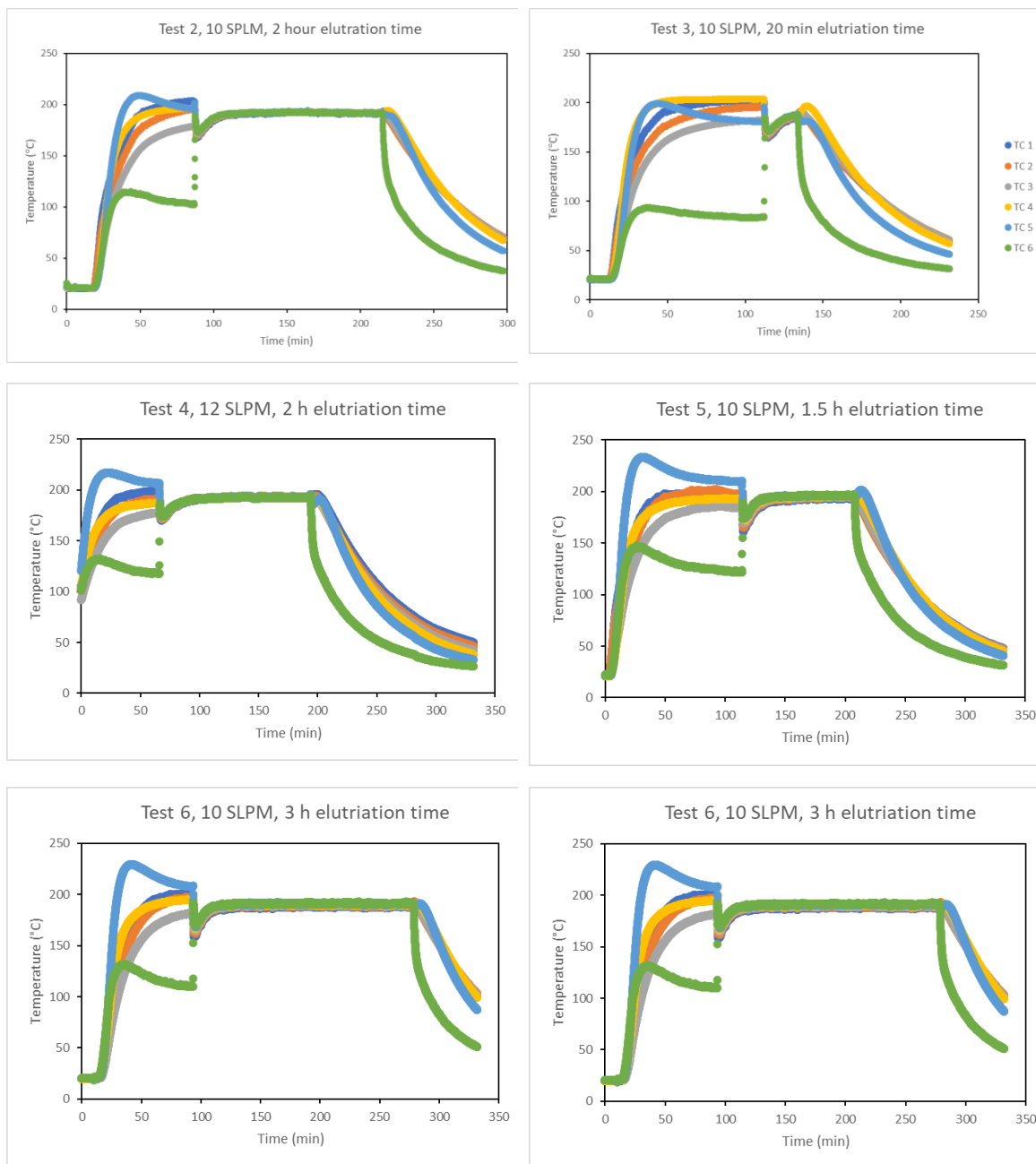


Figure 2. Temperature profile of reaction thermocouples for tests 2–7.

4. DISCUSSION

The elutriation results are plotted in Figure 3, and the mass elutriated is shown in blue. The mass elutriated appears to follow a logarithmic function as expected (Vögel et al. 1966). The results show that in a flow of 10 SLPM, the elutriation is nearly complete after 180 min. However, the mass elutriated was greater than the initial mass of U_3O_8 in the vessel. This suggests that at least 3 g of Al_2O_3 were elutriated along with the U_3O_8 . During the clean up of the apparatus, Al_2O_3 was observed in the line from the elutriation vessel to the knock-out pot when taking apart the apparatus. Aluminum oxide was not observed downstream through the knock-out pot and water trap. The value for the test run at 12 SLPM, which is shown in orange in Figure 3, indicates that over 8 g of Al_2O_3 were elutriated. In the 180 min test, Al_2O_3 also infiltrated the header, and a residue was found in the region of the lower O-ring seal. The amount of Al_2O_3 elutriated was estimated by assuming that the U_3O_8 was completely elutriated at 180 min, and the excess was all Al_2O_3 , or 3.83 g. Assuming a logarithmic function for Al_2O_3 elutriation (Vogel et al. 1966), the amount of Al_2O_3 was estimated. These values are shown as gray symbols in Figure 3. Subtracting the gray values from the overall amount elutriated results in the corrected U_3O_8 values, which are shown in yellow. The error bars indicate ± 3 g due to for mass losses during the experiment and the apparent Al_2O_3 elutriation.

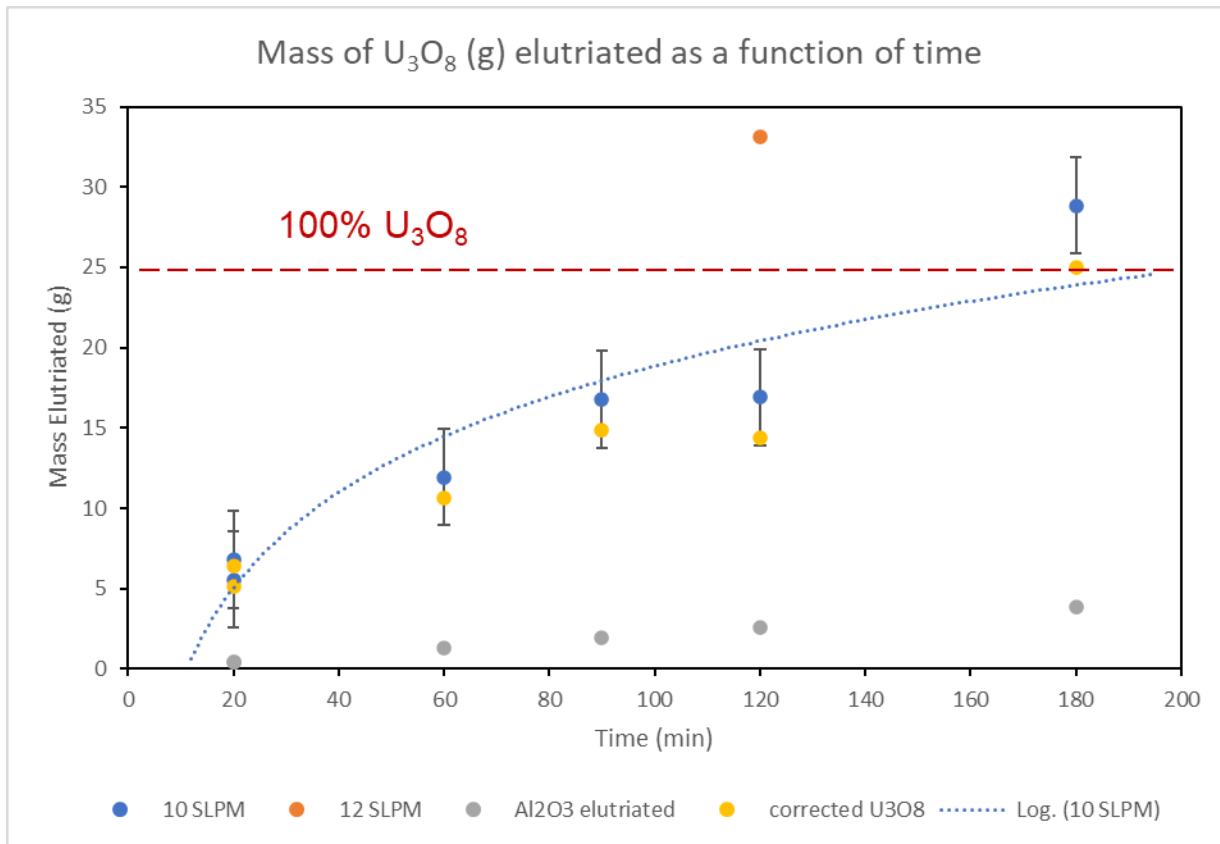


Figure 3. Apparent mass of U_3O_8 elutriated as a function of time at 10 SLPM (0.9 ft/s) (blue) and 12 SLPM (1.1 ft/s) (orange). Estimates of Al_2O_3 elutriated (gray) are subtracted from the overall mass elutriated to provide the corrected values for U_3O_8 removal (yellow).

The logarithmic fit was extrapolated to earlier times shorter than the duration of the shortest experiment (20 min). The extrapolation makes it appear as if the onset of elutriation was about 8 min into the experiment, which was not the case, as shown in the images taken during one of the 10 SLPM experiments for test 2 shown in Figure 4. Hence, the data were reevaluated, and the logarithms of both the corrected (blue) and uncorrected (orange) values for U_3O_8 were plotted. The resulting plot is provided in Figure 5 and clearly shows a reasonable linear fit to the logarithmic data. The correction slightly lowers the measured slope, but it does not affect the results significantly. The sharp increase in elutriation at early times may be an artefact of the how the experiment was conducted. A low flow of N_2 (1 SLPM) was used to promote heat transfer within the bed as it was heated to $200^\circ C$. Although elutriation was not observed in the header or downstream components during this time, a fraction of the U_3O_8 was likely brought to the upper surface of the fluidized bed. This fraction was readily released from the bed when the flow rate was abruptly increased to 10 SLPM.

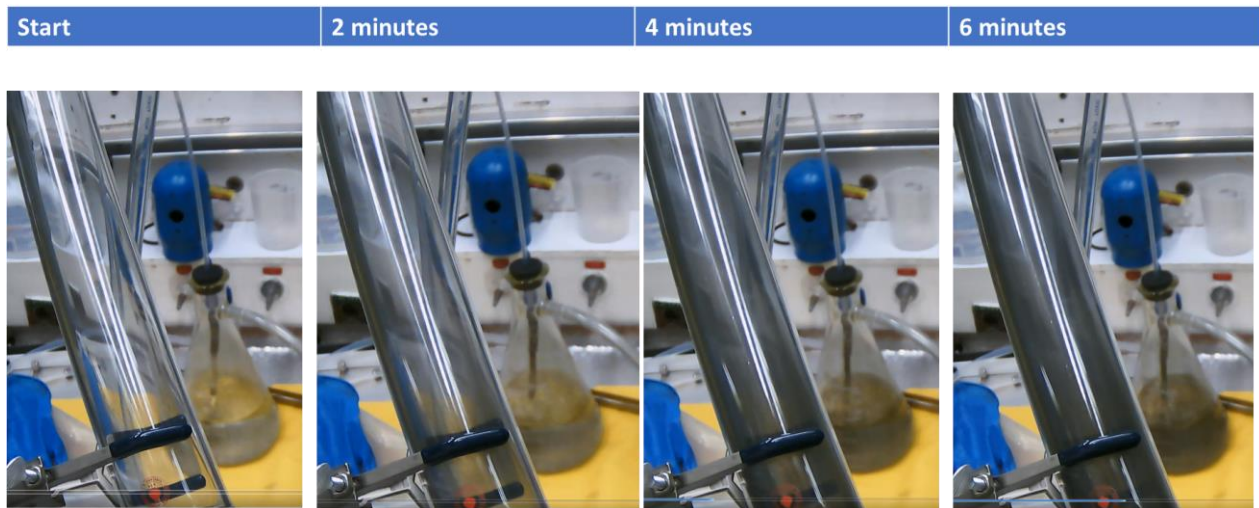


Figure 4. Screen capture from elutriation test at 10 SLPM (0.9 ft/s).

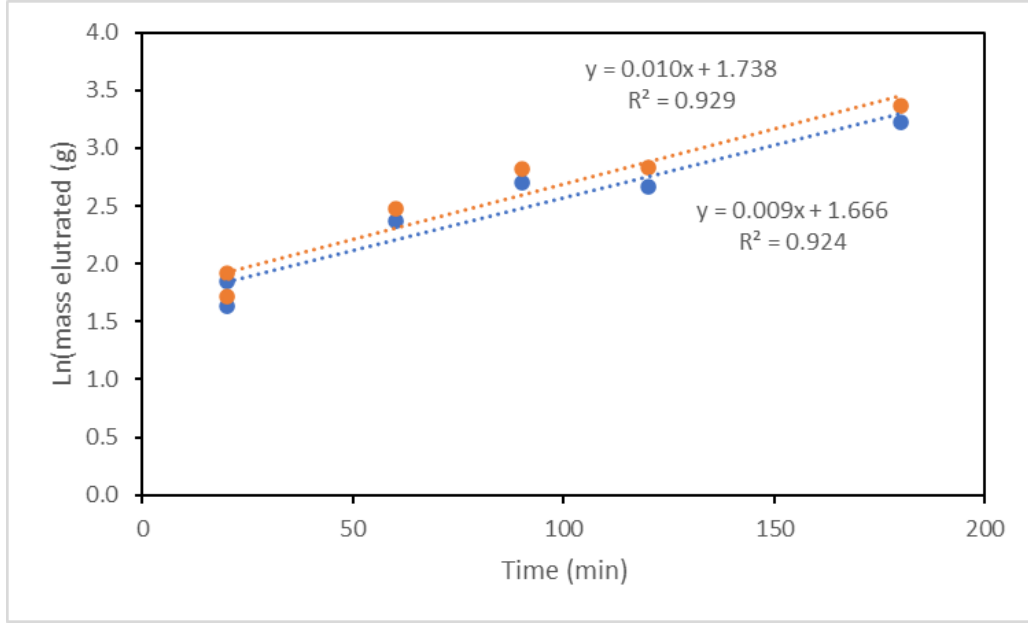


Figure 5. Semi-log plot of the elutriated mass of U_3O_8 at 10 SLPM (0.9 ft/s) uncorrected (orange) and corrected (blue) for concurrent Al_2O_3 elutriation.

The purpose of the elutriation test was to separate U_3O_8 from the Al_2O_3 bed material. Thus, the time-dependent average elutriation profiles of the two powders were calculated based on equation 1 with rate constants, k , determined from these tests. C is the concentration of the powder in the bed at the start, $C_{bed}(0)$, and at time, t , $C_{bed}(t)$.

$$\frac{C_{bed}(t)}{C_{bed}(0)} = \left(\frac{1}{kt}\right) [1 - e^{-kt}] \quad (1)$$

The time averaged percentage of U_3O_8 elutriated is shown in orange in Figure 6. The graph is similar to the plot in Figure 3 without the step change at the beginning of the experiment. The mass ratios of the amounts of elutriated material normalized to the starting amounts are plotted in Figure 6 in blue. The ratio decreases over time as the U_3O_8 elutriation levels off and the Al_2O_3 elutriation increases. Hence, the choice of elutriation time will be a trade-off between the amount elutriated and the purity of the elutriated product.

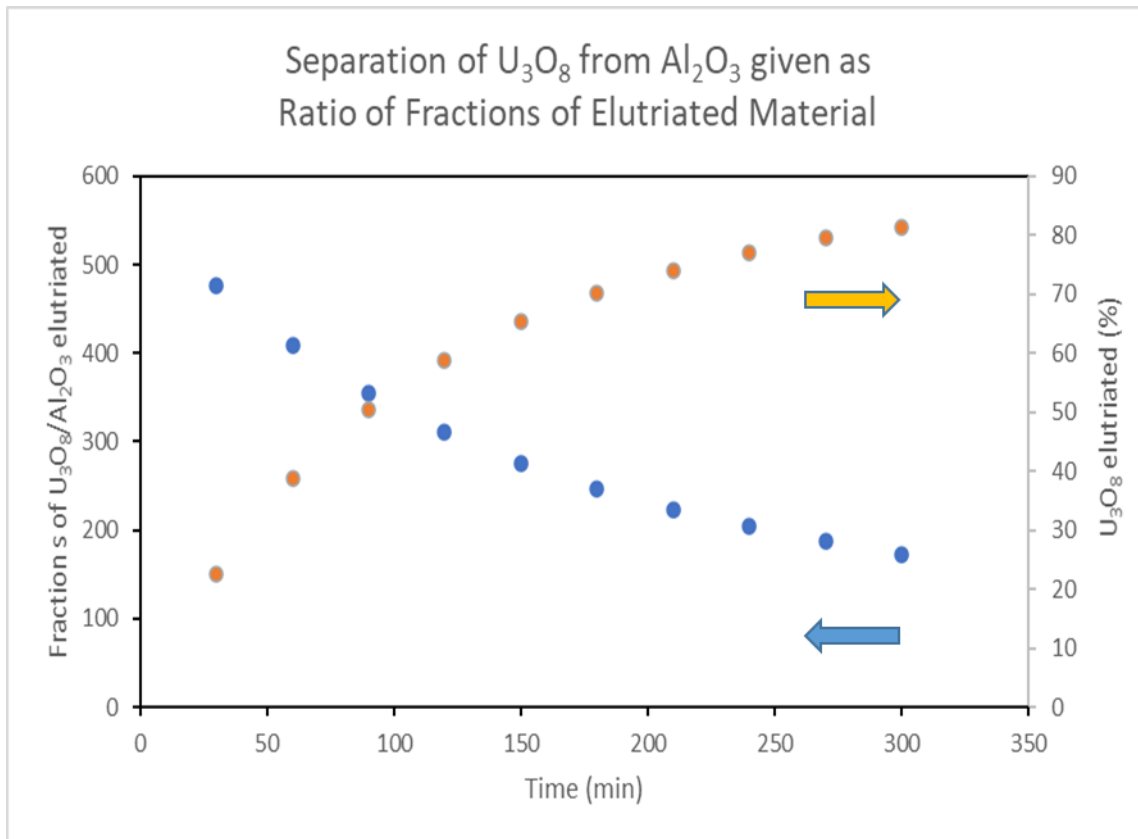


Figure 6. Ratio of the mass fraction of U_3O_8 divided by the mass fraction of Al_2O_3 (blue) and U_3O_8 elutriated (%) versus time (orange) in tests completed at 10 SLPM (0.9 ft/s).

5. CONCLUSIONS

In this study, U_3O_8 was elutriated from the fluidized bed at 10 SLPM (0.9 ft/s) at a temperature of 200°C, and the elutriation was complete at 180 min. The time profile of the elutriation followed a logarithmic curve.

The following experimental conditions and design changes are recommended for the MRPP:

Temperature: Temperatures were maintained at 200°C during all experiments presented in this report. A temperature gradient was observed in the reactor at low flow rates, but the temperatures leveled under the test conditions. Fluidization parameters are temperature-dependent because of the change in fluidizing gas properties. All recommendations herein pertain to a bed temperature of 200°C.

Flow Velocity: A velocity of 0.9 ft·s⁻¹ was optimal for the elutriation of ~7 μm U_3O_8 . Elutriation was more complete at 1.1 ft·s⁻¹, but Al_2O_3 particles were found to migrate from the fluidized bed.

Alumina Particle Size: The size of the Al_2O_3 powder in the pilot plant will be very important for separating materials. Even at 180 μm, which is much larger than the U_3O_8 , a small fraction of the Al_2O_3 elutriated under the test conditions.

System Design: Complex system design features, such as 90° elbows and valves in the piping, result in powder deposition. These types of features should be mitigated as much as possible in the MRPP. Although some elutriated U_3O_8 will deposit at the top of the elutriation vessel above the exit port, most of the elutriated U_3O_8 was transported through the side arm downstream of the vessel.

Powder Collection: A bubbler was used for this project because earlier work showed that cyclones did not effectively capture the U_3O_8 , and a candle membrane filter added backpressure to the system that prevented elutriation. As expected, the water-filled scrubbers captured elutriated material, but this design will likely not be scalable to a pilot plant.

6. ACKNOWLEDGMENTS

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7. REFERENCES

- Iwasaki, M., T. Sakurai, N. Ishikawa, and Y. Kobayashi. 1968. "Oxidation of UO_2 Pellets in Air: Effects of Heat-Treatment of Pellet on Particle Size Distribution of Powders Produced." *J Nucl Sci Technol* 5, no. 12: 652–653.
- Monk, T. H., J. H. Pashley, and R. B. Schappel. 1970. "Semiworks Fluid-Bed Studies of Volatility Process for Zircaloy-Clad Uranium Dioxide Power Reactor Fuels, Fluidization Fundamentals and Application." *Chemical Engineering Progress Symposium Series* 150, no. 105, vol. 66, AIChE.
- Wagner, J. C. 2018. *Using INL Capabilities to Support Meeting the Needs for HALEU*. INL/MIS-18-51704. Idaho Falls: Idaho National Laboratory.

Vögel, R. C., M. Levenson, J. H. Schraidt, and J. Royal. 1966. *Chemical Engineering Division Research Highlights, May 1965–April 1966*. ANL-7175. Lemont: Argonne National Laboratory.