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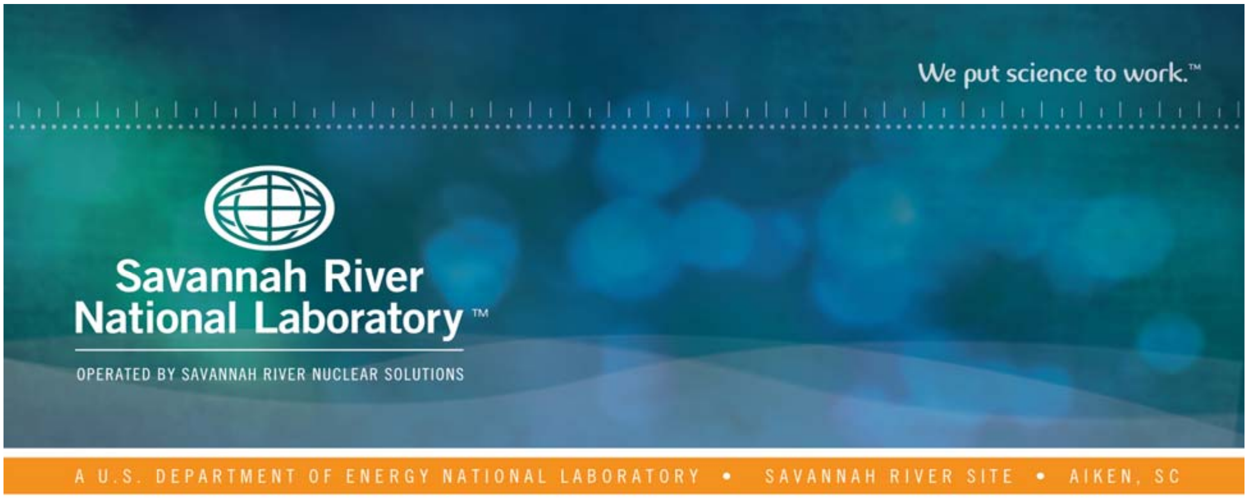

Determination of Filter Pore Size for Use in HB Line Phase II Production of Plutonium Oxide

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EXECUTIVE SUMMARY

H-Canyon and HB-Line are tasked with the production of plutonium oxide (PuO_2) from a feed of plutonium (Pu) metal. The PuO_2 will provide feed material for the Mixed Oxide (MOX) Fuel Fabrication Facility. After dissolution of the Pu metal in H-Canyon, plans are to transfer the solution to HB-Line for purification by anion exchange. Anion exchange will be followed by plutonium(IV) oxalate precipitation, filtration, and calcination to form PuO_2. The filtrate solutions, remaining after precipitation, contain low levels of Pu ions, oxalate ions, and may include solids. These solutions are transferred to H-Canyon for disposition. To mitigate the criticality concern of Pu solids in a Canyon tank, past processes have used oxalate destruction or have pre-filled the Canyon tank with a neutron poison.

The installation of a filter on the process lines from the HB-Line filtrate tanks to H-Canyon Tank 9.6 is proposed to remove plutonium oxalate solids. This report describes SRNL's efforts to determine the appropriate pore size for the filters needed to perform this function. Information provided in this report aids in developing the control strategies for solids in the process. The tests performed during this effort report the following results.

- Percent losses to the filtrate were < 1% for four of five tests and 1.5% for one test.
- Sub-micron particle sizes are retained by initial filtration using a 10 µm filter. The filter cake aids in the filtration of the smaller particles.
- The mean particle size increases with an increase in the initial acid concentration.
- Larger mean particle sizes were observed when changing from a nitric acid/oxalic acid flush to nitric acid alone.
- The size of Pu oxalate particles in HB-Line filtrate solutions averages 2.0 ± 0.4 µm in range of precipitation conditions tested.

Further development of the "filter the filtrate" strategy must be geared to retain particles of the 2 µm size range.

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FAFOF	flush after flush on the fly
FOF	flush on the fly
IC	ion chromatography
MOX	Mixed Oxide
PHA	pulse height analysis
PSA	particle size analysis
PSD	particle size distribution
SRNL	Savannah River National Laboratory
SEM	scanning electron microscope
XRD	x-ray diffraction

1.0 Introduction

H-Canyon and HB-Line are tasked with the production of plutonium oxide (PuO_2) from a feed of plutonium (Pu) metal. The PuO_2 will provide feed material for the Mixed Oxide (MOX) Fuel Fabrication Facility. After dissolution of the Pu metal in H-Canyon, plans are to transfer the solution to HB-Line for purification by anion exchange, followed by plutonium (IV) oxalate precipitation, filtration and calcination to form PuO_2. The filtrate solutions, remaining after precipitation, contain low levels of Pu ions, oxalate ions, and may include solids. These solutions are transferred to H-Canyon for disposition. To mitigate the criticality concern of Pu solids in a Canyon tank, past processes have used oxalate destruction[1-2] or have pre-filled the Canyon tank with a neutron poison.

A new strategy for making precipitator filtrate drops from HB-Line to H-Canyon has been proposed. This strategy is designed to enhance the production throughput of HB-Line Phase II in producing PuO_2 and to significantly reduce the liquid waste generated in H-Canyon from handling/processing the filtrate solutions. The installation of filters between the HB-Line filtrate tanks and H-Canyon Tank 9.6 is proposed to remove plutonium oxalate solids. This report describes SRNL's efforts to determine the appropriate pore size for the filters needed to perform this function. Plutonium oxalate solids may get into the HB-Line Phase II filtrate tanks either by being small enough to navigate through the 10 micron filter boats or via post precipitation in the filtrate tanks themselves as the solution cools from 50 °C to ambient. Information that is needed to fully develop the control strategy is as follows:

I. Determine the particle size distribution of plutonium oxalate solids that may either navigate through the 10 micron filter boats into the HB-Line Phase II filtrate tanks or post precipitate in the filtrate tanks after cooling from 50 °C to ambient (about 25 °C).[3]

II. Determine the concentration of plutonium ions, oxalate ions, and nitric acid remaining in solution after filtration and cooling.[3]

2.0 Experimental Procedure

Purified Pu(IV) was produced by anion exchange using conditions similar to expected HB-Line process conditions. The resulting purified Pu, in a solution of 1.5 to 4 M HNO_3, was precipitated by oxalic acid addition using conditions expected for the HB-Line process (i.e., 0.9 ± 0.1 M oxalic acid is added until a 0.1 M oxalic acid excess is attained). Demonstrations of the precipitation process planned for HB-Line was demonstrated and documented in SRNL-STI-2012-00338 and SRNL-STI-2012-00422.[4-5]

In this study, filtration testing was performed using plutonium oxalate prepared in nominally 3 g batches using Pu purified by anion exchange. Conditions for the precipitation targeted the oxalate addition time and digestion time expected in HB-Line. The oxalate precipitate preparation was performed in a glass beaker at 50 °C over 30 minutes as used by HB-Line.[6]

As part of this work, a variable considered in the experiments is the removal of the oxalic acid from the "Flush on the Fly" (FOF) and "Flush after Flush on the Fly" (FAFOF) operations. Simulated FOF and FAFOF were performed with 1.4 M HNO_3/0.1 M oxalic acid or with 1.4 M HNO_3 without added oxalic acid. The flush volume targeted HB-Line conditions with each flush used to rinse the beaker containing Pu oxalate slurry.[3]

Oxalate batches were filtered through 10-µm woven stainless steel wire filters provided by HB-Line Engineering. These were cut from a filter screen made for use in HB-Line. For each batch, a small volume filtrate sample was collected and analyzed for total Pu. The bulk of the filtrate was cooled and allowed to stand for 24 hours, half of which was filtered through a fine (0.1 µm) filter, sampled, diluted with concentrated nitric acid, and analyzed to assess post-precipitation of Pu oxalate. After four days, the remaining filtrate was filtered through a fine (0.1 µm) filter, sampled, diluted, and analyzed to assess post-precipitation of Pu oxalate. The precipitation of plutonium oxalate was demonstrated to begin within 24 hours and reach a maximum precipitation in five days.[7] After this time, the oxalate precipitate begins to dissolve. The previous study sampled the test solutions at 1, 5, 10 and 21 days.

2.1 General experimental steps

- Perform oxalate precipitation followed by filtration
- Simulate FOF and FAFOF by washing vessel used to precipitate the oxalate into filter
- Sample initial filtrate for Pu analysis and take sample of precipitate for particle size analysis
- Allow remaining solution to cool and filter with finer filter. The filtrate was analyzed by ion chromatography for anions (IC Anions), free acid, and alpha pulse height analysis (PHA) for Pu analysis. The fine solids were sent for analysis of particle size by scanning electron microscopy (SEM).

Table 2-1. Description of samples for each experiment

Sample description	Analysis
Initial filtrate from 10 µm filter	Alpha PHA
Initial precipitate slurried in 1.4 M HNO_3 / 0.1 M oxalate	PSA
1-day sample filtrate	Alpha PHA, IC Anions, Free Acid
1-day sample filtered solid	SEM
4-day sample filtrate	Alpha PHA
4- day sample filtered solid	SEM

2.2 Purification of Pu Working Stock

2.2.1 Plutonium Feed Solutions

Feed material for this work was in the form of a low-fired oxide. A peroxide fusion was performed on the Pu oxide material to make dissolution with nitric acid easier. This process in general uses sodium peroxide mixed with PuO_2 in a crucible that is heated to 700 °C for 2 hours in a muffle furnace. After cooling overnight, the material dissolved quickly in concentrated nitric acid and was sampled in preparation for purification by anion exchange. Due to the uncertainty associated with the solution, the solution was treated with ferrous sulfamate (FS) to convert Pu^{6+} to Pu^{3+}, heated to 50 °C for 60 min to convert Pu^{3+} to Pu^{4+}, and acidified with 15.7 M HNO_3 to a final volume of 250 mL (~7.5 M HNO_3)..

2.2.2 Column Description

To perform Pu(IV) oxalate precipitation tests, researchers prepared a purified Pu solution by anion exchange. The ion exchange column was fabricated from 38-mm borosilicate glass tubing (1.5-mm wall thickness) by the SRNL Glass Shop. A coarse frit was sealed into the bottom of the column to hold the resin. Approximately 1.0 L of Reillex™ HPQ anion exchange resin was loaded into the column for a bed height of ~44 cm. Solutions were fed to the column from the top and effluent was withdrawn from the bottom. Solutions were fed to the column using a FMI QG-50 piston pump. Polyethylene tubing (6.35-mm outside diameter) linked feed bottles, effluent collection bottles, and the pump to the column.

2.2.3 Column Operation

The ion exchange resin was conditioned, loaded, washed, and eluted with downward flow. Prior to loading Pu onto the resin, the column was conditioned with 0.9 L of 8 M HNO_3 at 20 mL/min. Feed loaded onto the column at 10 mL/min. After feeding was complete, the Pu on the column was washed with 2 L of 8 M HNO_3 at 15 mL/min. The Pu was eluted with 0.35 M HNO_3. The heads cut (0.23 L) was collected at a flow rate of 5 mL/min. The hearts cut (0.6 L) was obtained at 5 mL/min with a targeted Pu concentration of ~50 g/L.

2.2.4 Characterization

The feed, product and other effluent solutions from the anion exchange column experiment were characterized by: alpha pulse height analysis (PHA), ion chromatography (IC) for anions, and free acid.

2.3 Precipitation and Filtration of Plutonium Oxalate

The precipitation process used in these experiments followed the process demonstrated by SRNL which is documented in SRNL-STI-2012-00338 and SRNL-STI-2012-00422.[4-5] All precipitations occurred at 50 °C ± 3 °C with continuous stirring at 350 RPM. A 100-mL volume of the purified Pu stock solution was used in each precipitation. Concentrated nitric acid was added to each batch to adjust the initial acidity for the experiments from 1.5 M to 2.5 M HNO_3 (Table 2-2). Oxalic acid (0.9 M) was added using a low flow FMI pump until 0.1 M excess was attained. The oxalic acid was added at ~0.5 mL/min, which achieved a total addition time for the oxalic acid of 30 minutes. The solution was left stirring at temperature for an additional 10 minutes digestion time. Following the digestion time period, the solution/slurry was filtered through a 10 µm filter made of woven stainless steel wire provided by HB-Line Engineering (Figure 2-1).

Table 2-2. Precipitation conditions

Test	29.4 g/L Pu (mL)	Oxalic Acid 0.9 M (mL)	Conc HNO_3 (mL)	Addition time for oxalic acid (min)	Target Initial Acidity (M)	Total volume (mL)
A	100	44	10.6	30.8	1.5	154.6
B	100	44	10.6	30.8	1.5	154.6
C	100	45.1	16.6	31.6	2	161.8
D	100	46.2	23.3	32.3	2.5	169.5
E	100	46.2	23.3	32.3	2.5	169.5
–Stirring speed set to 350 RPM –Target temperature = 50 °C (actual temperature = 51 ± 2 °C) –Flush on the Fly = 60 mL –Flush after Flush on the Fly = 30 mL –Test A, C, and D used 1.4 M HNO_3 / 0.1 M oxalic acid flush –Test B and E used 1.4 M HNO_3 flush only –Vacuum drying time = 30 min – Note: In all batches the Pu oxalate cake was kept open overnight, allowing additional drying						

Figure 2-1. Woven stainless steel wire 10 µm filter

To simulate the FOF and FAFOF methods used in HB-Line[6] to flush the precipitator, the filtrate was washed with aliquots of either 1.4 M HNO_3/0.1 M oxalic acid or 1.4 M HNO_3 alone. An aliquot of the filtrate was collected after the final flush and diluted 2x with concentrated HNO_3 for analysis for total Pu by alpha PHA. Approximately 0.15 g of the precipitate was slurried into a 1.4 M HNO_3 / 0.1 M oxalic acid solution for particle size analysis.

The remaining filtrate was allowed to sit for 24 hours before filtering half of the filtrate through a 0.1 µm filter. An aliquot from this second filtrate was diluted by a factor of two with concentrated HNO_3 and submitted for analysis by alpha PHA. Another aliquot from this second filtrate was submitted undiluted for analysis by IC anion, and free acid. The plutonium oxalate was collected from the filter and submitted for SEM analysis to determine particle size. This set of steps, including sampling, was repeated after four days using the second portion of the initial filtrate.

2.4 Quality Assurance

Requirements for performing reviews of technical reports and the extent of review are established in manual E7 2.60. SRNL documents the extent and type of review using the SRNL Technical Report Design Checklist contained in WSRC-IM-2002-00011, Rev. 2.

3.0 Results and Discussion

3.1 Plutonium Purification by Anion Exchange

Analysis of the hearts cut by gamma spectroscopy measured the total Pu concentration to be 29.4 g/L. Free acid analysis measured 0.57 M H^+. The acidity of the hearts cut was raised on a per batch basis as shown in Table 2-2 to bound the expected process acidity found in HB-Line's plans for acid addition.

3.2 Precipitation

On inspection, the five precipitations produced the same quality/quantity of solids at all initial acid concentrations. No visible changes were observed upon changing from a 1.4 M HNO_3 / 0.1 M oxalic acid mixture to 1.4 M HNO_3 alone for performing the simulated FOF and FAFOF operations. Figure 3-1 shows the precipitated solid before filtration and after filtration, respectively, for Test A. The precipitate formed was an easily-filterable tan solid that was free flowing, as observed upon transferring the sample to a suitable storage container after drying overnight in air. Analysis of the initial filtrate solutions for all five tests shows minimal Pu losses to the filtrate (Table 3-1). This is in good agreement with the observed quantity of plutonium oxalate solids after filtration on the 0.1 µm filters at the 1- and 4-day sampling events. Samples were taken from both the 1- and 4-day filtrates and analyzed by alpha PHA to determine Pu concentration. Analysis of the 1- and 4-day filtrate samples shows a decrease in the [Pu] in the order T = 0 > T = 1 d > T = 4 d, as shown in Table 3-2. This decrease can be attributed to both the filtration with a finer 0.1 µm filter and additional precipitation where the particles passing through the filter act as seeds for subsequent plutonium oxalate precipitation.

Figure 3-1. Freshly precipitated plutonium oxalate (L) and Plutonium oxalate collected using a 10 µm stainless steel filter (R) from Test "A"

Table 3-1. Pu Losses during filtration using a 10 µm filter

Test	Pu (g) (100 mL stock)	Pu in Filtrate (g)	% Pu Losses to Filtrate
A	2.94	4.42 x 10^{-2}	1.50
B	2.94	2.54 x 10^{-2}	0.86
C	2.94	2.12 x 10^{-2}	0.72
D	2.94	2.16 x 10^{-2}	0.74
E	2.94	2.00 x 10^{-2}	0.68

Table 3-2. Pu in filtrate after 0-, 1-, and 4-day filtrations

Test	Initial Filtrate (g)	1-Day Filtrate (g)	4-Day Filtrate (g)
A	4.42E-02	1.48E-02	1.30E-02
B	2.54E-02	9.81E-03	9.56E-03
C	2.12E-02	9.70E-03	6.10E-03
D	2.16E-02	5.99E-03	3.60E-03
E	2.00E-02	7.14E-03	4.36E-03

Samples from the 1-day filtrate were submitted for analysis for free acid, nitrate, and oxalate concentrations. Table 3-3 shows the results from the free acid and IC anions analysis. Results for free acid and nitrate concentration are in good agreement with each other and are within 1-2 standard deviations of the targeted initial acidity. Oxalic acid concentrations for all tests were lower than the targeted 0.1M excess target. The lower values can be accounted for by the 20% uncertainty in the analytical measurements and in the case of B or E through dilution of the oxalic acid by the nitric acid only wash. Additional precipitation was observed in a comparison of 1- to 4- day filtrate samples.

Table 3-3. Free acid, [NO_3^-], and [$C_2O_4^=$] in the 1-day filtrate samples

Test	Free acid (M)	[NO_3^-] (M)	[$C_2O_4^=$] (M)
A	1.71	1.71	0.07
B	1.58	1.69	0.03
C	2.24	2.32	0.03
D	2.54	2.63	0.07
E	2.50	2.66	0.04

3.3 Characterization

3.3.1 Particle Size Analysis

The particle size distribution (PSD) was determined using the Microtrac X-100. The Microtrac X-100 particle size analyzer uses a wet sample delivery controller (recirculator) to disperse the sample uniformly in a fluid and deliver the sample to the analyzer. This wet sample delivery controller in its basic form consists of a reservoir where the sample is introduced, a fluid pump, a valve to the drain system, and the necessary tubing connections to the analyzer. The flow through the analyzer sample cell is always from the bottom to the top. A laser beam is projected through a transparent quartz cell containing a stream of moving particles suspended in solution. Light from the laser strikes the particles and is scattered through various angles. The scattering angles and intensities of the scattered light are measured by two photodiode arrays producing electronic signals proportional to the measured light flux. The Microtrac proprietary mathematical software processes the signals to obtain a particle size distribution. Upon completion of the analysis, the Microtrac generates a report containing the tabular data, a histogram plot of the data, and lists various instrument parameters.

A sample of the precipitate collected during the initial filtration was slurried into a 1.4 M HNO_3 / 0.1 M oxalic acid solution for introducing the solid into the Microtrac analyzer. The volumetric particle size distribution is reported in Table 3-4. The first precipitation provided the smallest average particle size with nearly 40% of particles smaller than 5.5 µm. The largest average particle size was observed in the 5th precipitation which had only 3.6% of the particles smaller than 5.5 µm. It appears that the change in initial acidity does have an effect on the particle size during precipitation. When comparing only the mean particle sizes, the particle size increases linearly with an increase in initial acid concentration. The maximum particle sizes in the tests where HNO_3 and oxalic acid are used do not change linearly. The largest individual particle size was observed with an initial 2 M HNO_3 concentration but the largest average particle size was observed with the 2.5 M HNO_3 using 1.4 M HNO_3 without oxalic acid for the flushes. This set of tests had conditions similar to the AFS-2 "Demo".[4] Table 3-4 includes the particle size for Demo 1 and 2 for comparison. The acid concentration used in the Demo study was 1.5 M where the mean particle size was between 13 – 17 µm. In the current work, the mean particle size varied from 7.9 – 19.4 µm which is in line with the earlier work. The larger particle size at higher initial acid concentration suggests that a higher acid concentration promotes a larger average particle size in a plutonium oxalate precipitation. In general, the best case in terms of average particle size and percent of particles less than 5.50 µm is Test E. Test E exhibited the largest mean particle size and had the lowest percent of particles measuring less than 5.50 µm. This would directly relate to lower loss of Pu to the filtrate. An increase in particle size with increasing nitric acid concentration during Pu(III) oxalate precipitation has been previously reported.[8-9] In the earlier of the two reports, analysis of 44 precipitations with ^{239}Pu and ^{238}Pu was reported to show the mass mode size of the calcined PuO_2 depended on the variables affecting final solubility of Pu(III) oxalate.[8] The particle size was observed to increase with increasing precipitation temperature, increasing nitric acid concentration in the feed, decreasing Pu concentration in the feed, and decreasing oxalic acid concentration.[8]

Table 3-4. Particle size analysis of Pu oxalate samples

Test	Particle Size Range (µm)	Mean Particle Size* (µm)	Standard Deviation (µm)	% of Particles <5.50 µm
A	0.172 – 52.33	7.89	5.53	39.80
B	0.486 – 104.7	19.37	10.33	7.36
C	0.578 – 248.9	25.35	15.33	7.20
D	0.486 – 176.0	27.51	16.48	7.56
E	4.625 – 176.0	35.33	18.39	3.62
Demo 1[5]	0.344 – 124.5	13.2	NA	16.8
Demo 2[5]	0.409 – 124.5	17.1	NA	10.3
*Mean Particle Size determined on a volumetric basis.				

3.3.2 SEM

SEM images were taken for solids collected by filtration of the initial filtrate using a 0.1 µm filter after 1- and 4-day time intervals. Solids present in the solutions represent those solids that passed through the initial filtration step using the 10 µm filter or precipitated from solution after the initial filtration. Figure 3-2 to Figure 3-11 are all images taken at 1000x magnification and correspond to tests described in Table 2-2. As can be observed in the figures, the changes in particle size do occur with the slight changes in the preparation method for each test. Note that despite the change in size, the general morphology for each test at both the 1- and 4-day sampling events are the same cubic form. On closer inspection, Figure 3-12 shows at a 3000x magnification that each cube is layered, as observed in previous work.[4-5]

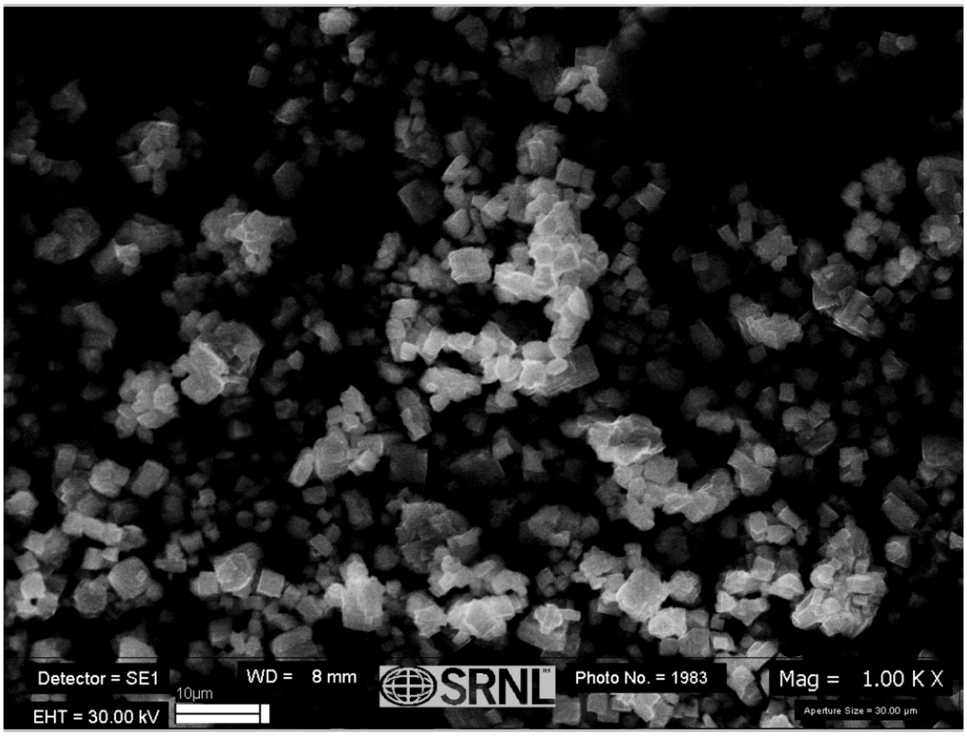

Figure 3-2. Test A (1.5 M HNO_3 with HNO_3/oxalic acid flush) 1-Day Sample at 1000x magnification

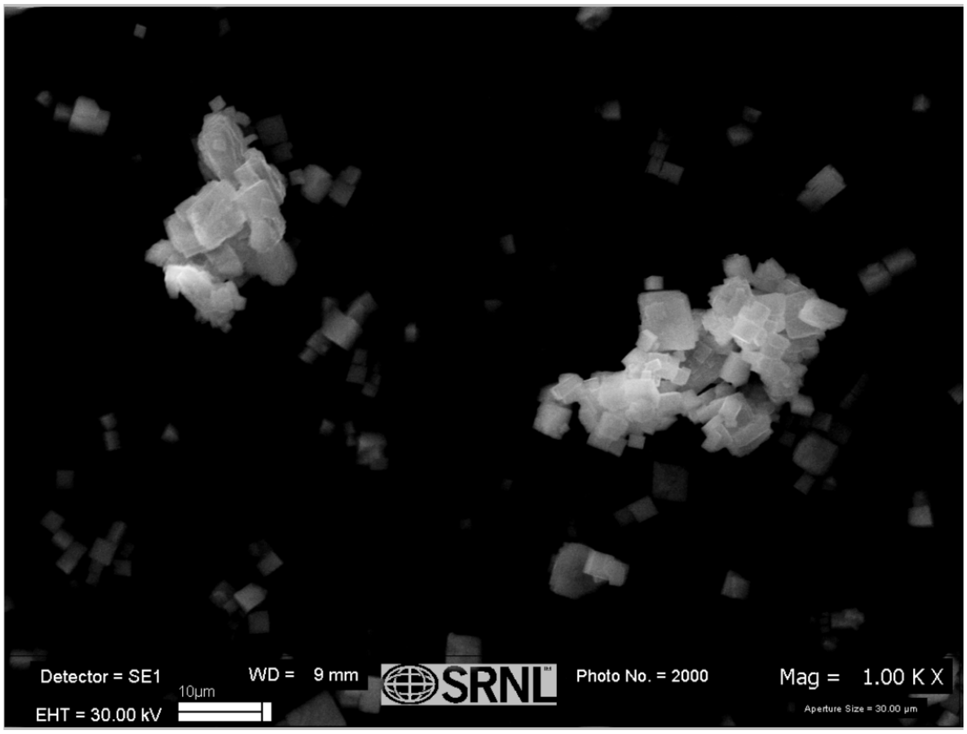

Figure 3-3. Test B (1.5 M HNO_3 with HNO_3 flush) 1-Day at 1000x magnification

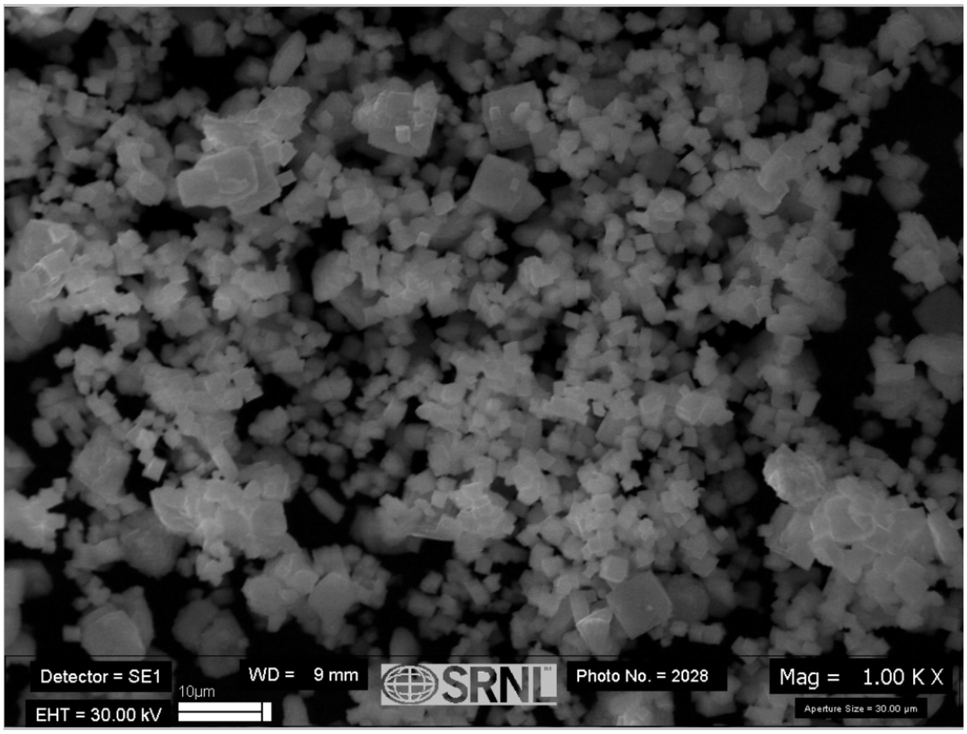

Figure 3-4. Test C (2 M HNO_3 with HNO_3/oxalic acid flush) 1-Day at 1000x magnification

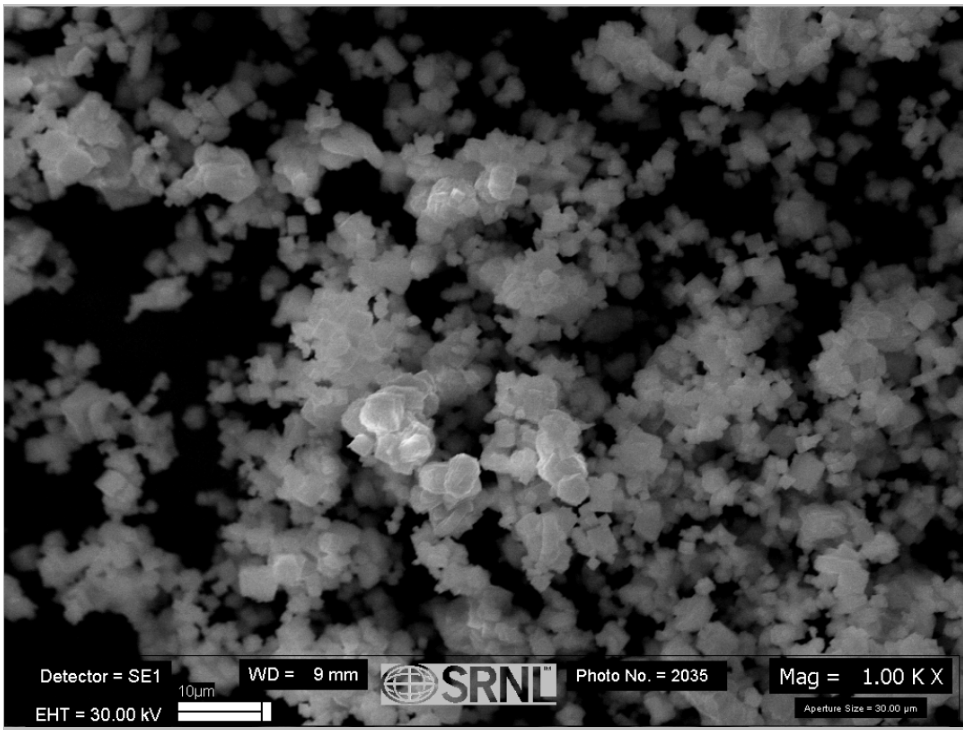

Figure 3-5. Test D (2.5 M HNO_3 with HNO_3/oxalic acid flush) 1-Day at 1000x magnification

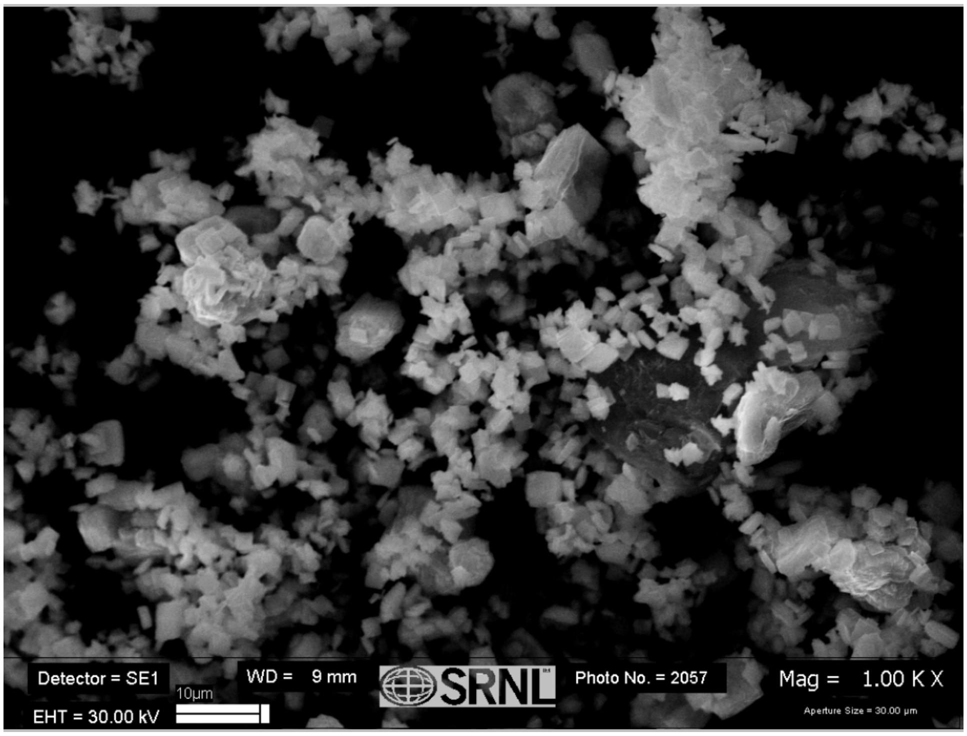

Figure 3-6. Test E (2.5 M HNO_3 with HNO_3 flush) 1-Day at 1000x magnification

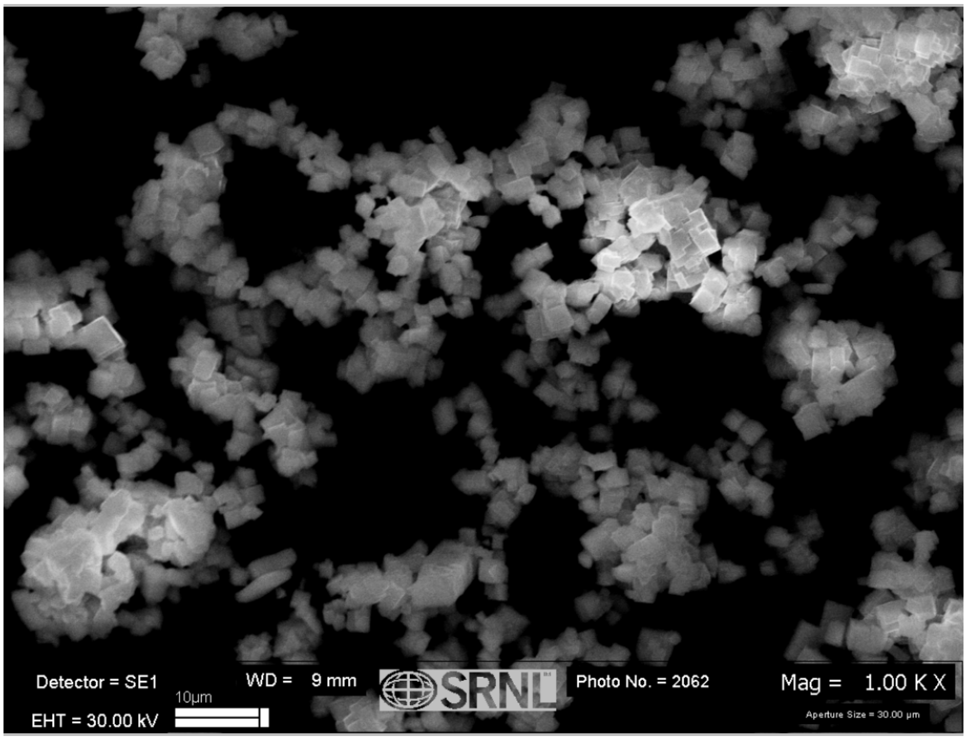

Figure 3-7. Test A (1.5 M HNO_3 with HNO_3/oxalic acid flush) 4-Day Sample at 1000x magnification

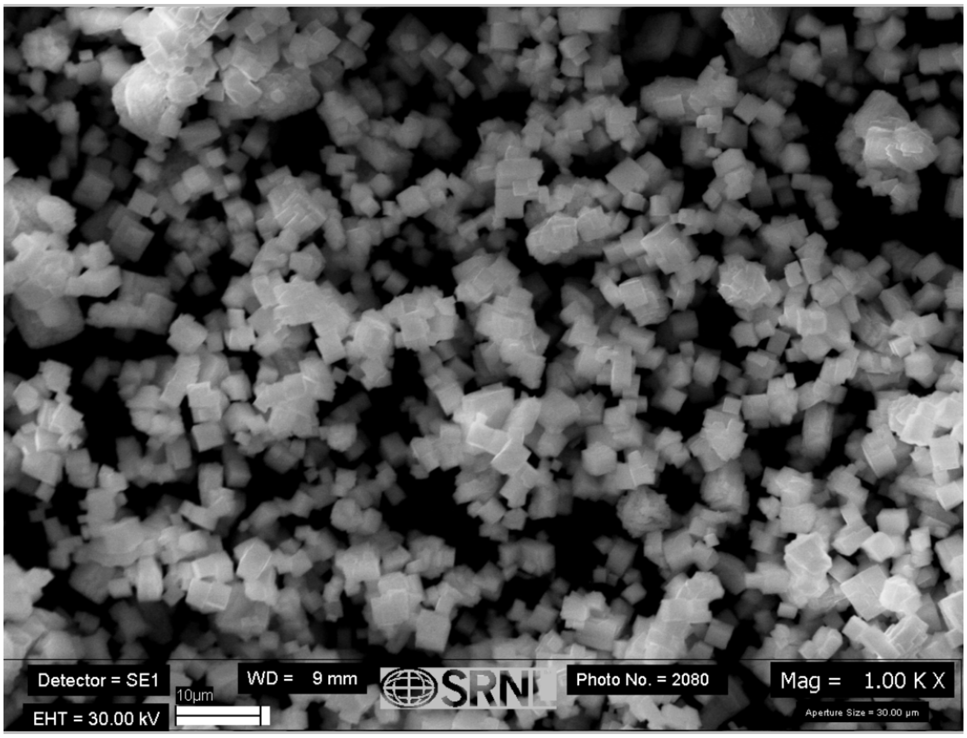

Figure 3-8. Test B (1.5 M HNO_3 with HNO_3 flush) 4-Day at 1000x magnification

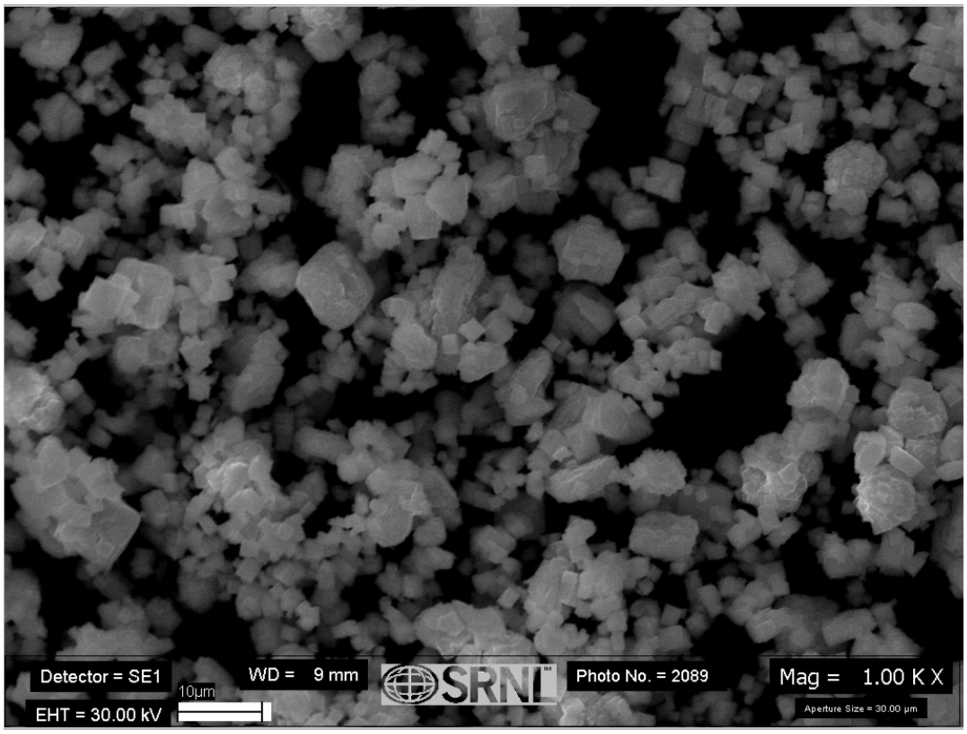

Figure 3-9. Test C (2 M HNO_3 with HNO_3/oxalic acid flush) 4-Day 1000x magnification

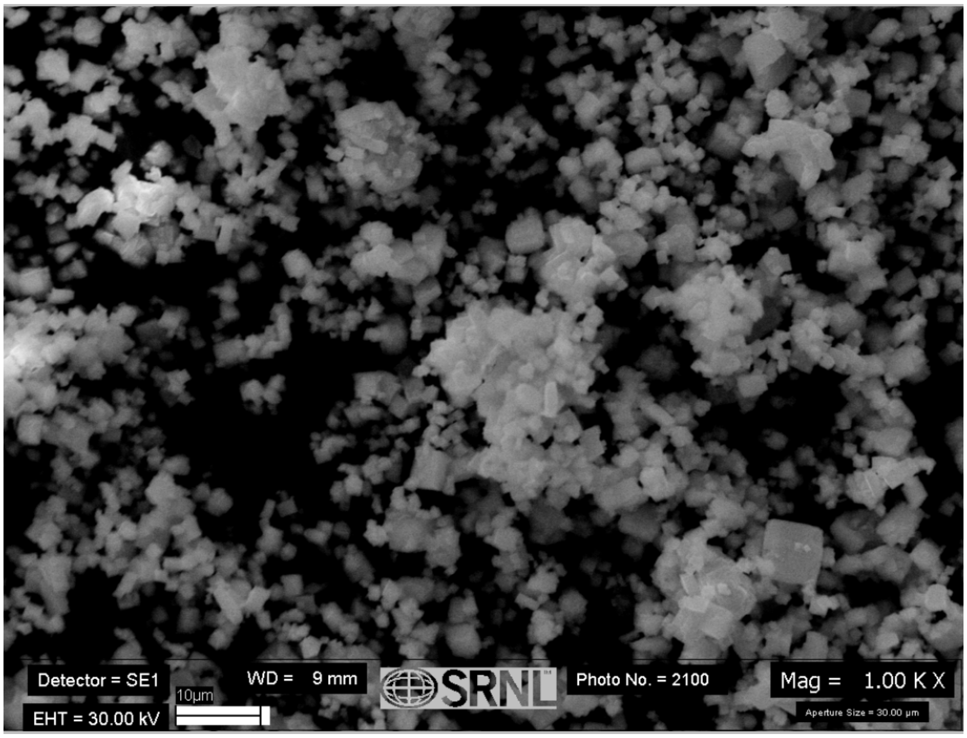

Figure 3-10. Test D (2.5 M HNO_3 with HNO_3/oxalic acid flush) 4-Day at 1000x magnification

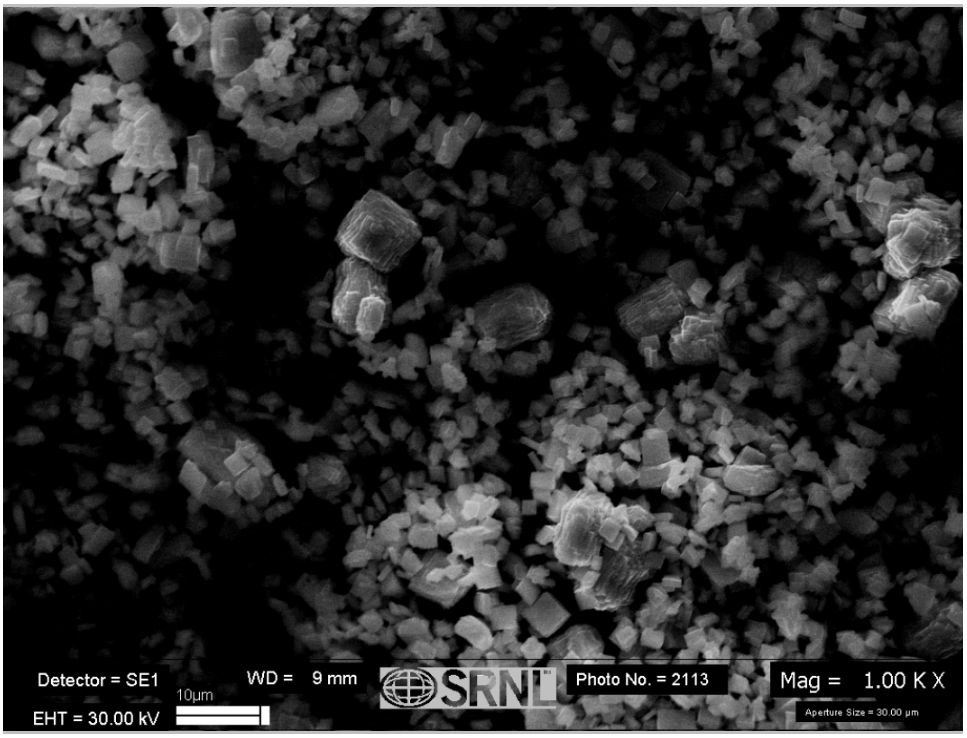

Figure 3-11. Test E (2.5 M HNO_3 with HNO_3 flush) 1-Day at 1000x magnification

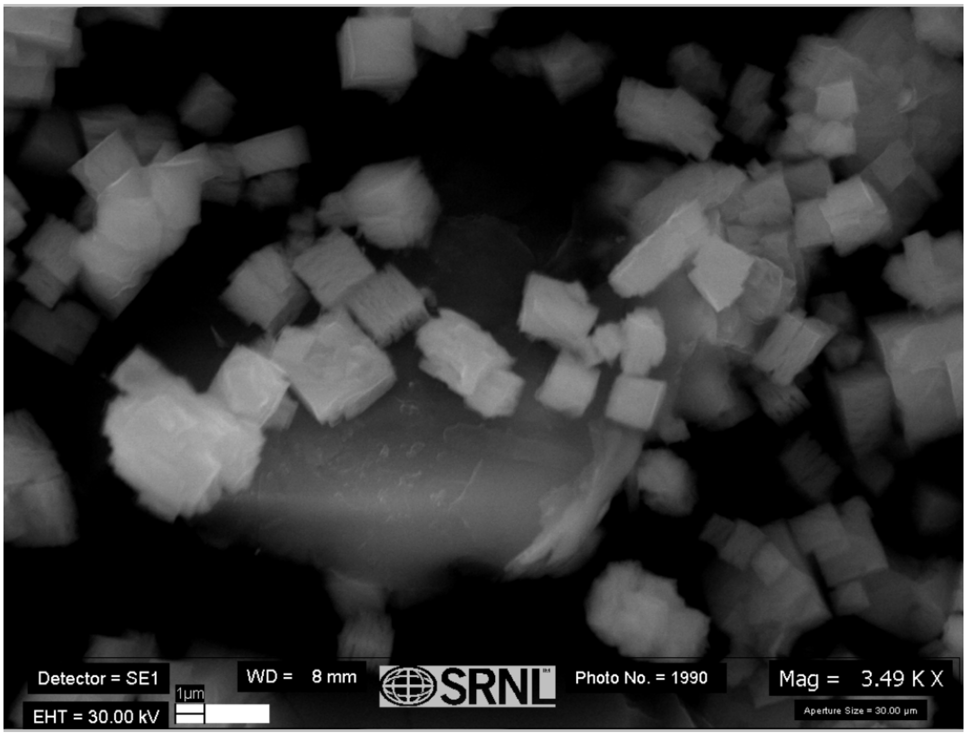

Figure 3-12. Test A (1.5 M HNO_3 with HNO_3/oxalic acid flush) 1-Day Sample at 3000x magnification

The average particle size for the solids collected on the 0.1 µm filter for both the 1- and 4- day aged initial filtrate solution has been determined by applying the program Pixcavator 1A, version 6.0. The results from the Pixcavator program are shown in Table 3-5. The sample IDs labeled 45.4X are for the 1-day aged filtrates and the sample IDs labeled 45.6X are the 4-day aged filtrates. The particle sizes were placed in “bins” where a bin is a range of particle sizes (Table A-1, Table A-2). The range of these bins can be changed smaller or larger depending on the needs of the experiment or the observed dataset. Frequency is the number of particles within a particular size. The primary particle size reflects one side of a "cube". If the particles were more disconnected from each other, then the perimeter and the area would have been provided. Also, using the SEM image for 45.4B, it was possible to capture the "aggregated" PSD which includes particles that grew by annexing other primary particles (i.e. secondary nucleation). Omitting results of 45.4B, the average particle size for all the other 4 tests at both 1 and 4 days is 2.0 ± 0.4 µm. All 1- and 4- day precipitate samples have an average particle size (except 45.4B and 45.6D) within 1 standard deviation of each other. No clear pattern emerges from changes to initial acidity and changes to the FOF/FAFOF.

Table 3-5. Particle size analysis of Pu oxalate samples collected with a 0.1 µm filter

1-Day Sample ID	Particle Size Range (µm)	Mean Particle Size* (µm)	Standard Deviation (µm)
NB00009-45.4A	0.38 – 10.84	2.82	2.58
NB00009-45.4B	1.33 – 55.43	6.71	6.89
NB00009-45.4C	0.94 – 3.46	1.71	0.62
NB00009-45.4D	0.75 – 4.13	2.13	0.96
NB00009-45.4E	0.62 – 8.73	2.13	1.57
4-Day Sample ID	**Particle Size Range (µm)**	**Mean Particle Size* (µm)**	**Standard Deviation (µm)**
NB00009-45.6A	0.57 – 3.99	1.59	0.70
NB00009-45.6B	1.05 – 4.92	2.16	0.78
NB00009-45.6C	0.48 – 8.62	2.29	1.56
NB00009-45.6D	0.57 – 3.73	1.41	0.76
NB00009-45.6E	0.62 – 3.61	1.66	0.86

4.0 Conclusions

For all tests, the precipitation conditions were similar with only a change in the initial acidity, which varied from 1.5 to 2.5 M HNO_3. Simulated flushes of either a 1.4 M HNO_3 / 0.1 M oxalic acid at 1.5, 2.0, and 2.5 M HNO_3 or 1.4 M HNO_3 alone at 1.5 and 2.5 M HNO_3 were applied to all tests. General conclusions for these tests are listed below.

- Percent loses to the filtrate were < 1% for tests B through D and 1.5% for test A. With a single test being performed under a given set of conditions, it is unknown whether the increase in Pu in solution is statistically significant based on the limited number of precipitation experiments.
- Sub-micron particle sizes are retained by initial filtration using a 10 µm filter. The filter cake aids in the filtration of the smaller particles.
- Variations in the largest particle size from 52 µm to 250 µm have been observed. This variation was not directly related to the initial acid concentration.
- The mean particle size increases with an increase in the initial acid concentration.
- Larger mean particle sizes were also found when changing from a nitric acid/oxalic acid flush to nitric acid alone.
- Mean particle size of samples filtered with the 0.1 µm filter were less than 10 µm with an average size of 2.0 ± 0.4 µm (omitting only Sample 45.4B).
- Secondary nucleation is attributed to the larger maximum particle size in sample 45.4B. This secondary nucleation along with the decreased Pu concentration in the filtrate indicates additional precipitation does occur between the 1- and 4-day sampling times.

5.0 Recommendations

As this study showed Pu oxalate particle sizes of 2.0 ± 0.4 µm in four cases and larger in one case, a secondary filter used for HB-Line filtrate solutions must capture particles that are 2.0 ± 0.4 µm. An evaluation of the appropriate filter geometry (cross flow, tubular, dead end, etc.), filter materials, and the appropriate filter positions in the HB-Line facility is required. As samples become available from the

HB-Line filtrate tanks, those samples should be characterized for solids quantity and particle size distribution, as well as plutonium, oxalate and nitric acid concentrations.

6.0 References

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Appendix A. Particle Distribution for 1- and 4-Day Samples

Table A-1. Frequency of particle sizes for primary particles identified at 1 and 4 days.

Bin (µm)	45.4A	45.4B	45.4C	45.4D	45.4E	45.6A	45.6B	45.6C	45.6D	45.6E
0.5		0			0	0	1	1	0	0
1	0	1	2	3	3	6	4	4	10	9
1.5	10	10	12	4	8	16	17	7	7	5
2	6	5	7	3	4	8	21	9	6	7
2.5	5	4	6	2	5	4	22	11	2	5
3	2	2	2	5	3	3	14	5	0	1
3.5	0	0	1	1	1	0	6	2	1	1
4	1	2	0	1	2	1	2	2	1	2
4.5	0			1	0	0	1	1	0	0
5	1				0	0	1	0	0	0
5.5	0						0	0		
6							0	0		
6.5							0	0		
7							0	0		
7.5							0	0		
8							1	1		

Table A-2. Frequency of particle sizes in the 1-day sample exhibiting aggregation

45.4A			45.4B	
Bin (µm)	**Frequency**		**Bin (µm)**	**Frequency**
0.9	3		**1.3**	126
1.4	4		**5.2**	45
1.9	4		**9.1**	23
2.5	5		**12.9**	9
3.0	0		**16.8**	8
3.5	0		**20.6**	1
4.0	2		**24.5**	1
4.6	0		**28.4**	2
5.1	0		**32.2**	1
5.6	1		**36.1**	0
6.1	1		**40.0**	1
6.7	0		**43.8**	0
7.2	1		**47.7**	0
7.7	0		**51.6**	1
8.2	1			
8.7	0			
9.3	0			
9.8	0			
10.3	1			

Distribution:

S. L. Marra, 773-A
T. B. Brown, 773-A
D. H. McGuire, 999-W
S. D. Fink, 773-A
C. C. Herman, 773-A
E. N. Hoffman, 999-W
F. M. Pennebaker, 773-42A
W. R. Wilmarth, 773-A
Records Administration (EDWS)

T. C. Shehee, 773-A
M. L. Crowder, 773-A
T. S. Rudisill, 773-A
R. A. Pierce, 773-A
F. F. Fondeur, 773-A
P. M. Almond, 773-A
E. A. Kyser, 773A

P. R. Jackson, DOE-SR, 703-46A

K. P. Burrows, 704-2H
W. E. Harris, 704-2H
J. B. Schaade, 704-2H
K. J. Gallahue, 221-H
J. E. Therrell, 704-2H
K. D. Scaggs, 704-2H
T. E. Worth, 221-H
J. M. Jordan, 704-2H
R, M, Mobley, 704-2H

D. E. Welliver, 704-2H
J. R. Lint, 704-2H

P, M, Palmer, 704-2H
K. J. Usher, 704-2H
W. G. Dyer, 704-2H
R. R. Livingston, 730-2B