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Progress Toward Mitigating Uranyl Peroxide Precipitation and Controlling Pu Behavior on Titania

A.J. Youker, M. Kalensky, K. J. Quigley, T. Brossard,
M. A. Brown, S.D. Chemerisov, and G.F. Vandegrift

Nuclear Chemical Engineering
Argonne National Laboratory, 9700 S. Cass Ave., 60439 Argonne – United States

ABSTRACT

Two concerns for the production of Mo-99 from a fissioning LEU uranyl sulfate solution are the precipitation of uranyl peroxide and the generation of greater-than-class-C (GTCC) waste. Argonne performed a series of irradiation experiments using a 3 MeV Van de Graaff accelerator in an effort to better understand uranyl peroxide formation and precipitation and develop a means to combat it. Conditions were found to prevent uranyl peroxide precipitation at the Van de Graaff, and more experiments will continue at the linac. Additionally, Pu-239 is the main driver for GTCC waste and with no known disposal path, controlling its behavior in the Mo-99 separation is crucial. Argonne found that temperature and post-load acid wash concentration were key parameters to controlling Pu behavior on titania. Results from Van de Graaff experiments and Pu batch and column experiments will be discussed.

1. Introduction

Argonne National Laboratory (Argonne) is providing technical assistance to help accelerate the US production of Mo-99 using a non-highly enriched uranium (non-HEU) source. A potential Mo-99 production pathway uses a fissioning low enriched uranium (LEU) solution as uranyl sulfate. There are two possible issues that must be addressed related to (1) the use of a uranyl sulfate solution and (2) increased Pu-239 generation due to the higher U-238 concentration in LEU compared to HEU. Hydrogen peroxide, generated along with hydrogen from the radiolysis of water, will form in a fissioning uranyl sulfate solution, and it can build up in solution and cause precipitation of uranyl peroxide if not mitigated properly. Argonne has performed a series of irradiation experiments using a 3-MeV Van de Graaff (VDG) accelerator, which can generate high doses without producing fission and activation products, making samples easy to handle post-irradiation. Small volumes of different uranium sources as uranyl sulfate were irradiated at various temperatures, dose rates, and concentrations in the presence and absence of several different metal ions, which are known to catalyze the destruction of hydrogen peroxide. Results from the VDG experiments and plans for experiments to be performed using a 55-MeV electron linear accelerator, where fission and activation products will form, will be discussed.

The second potential issue for a Mo-99 producer using LEU is related to the use of LEU over HEU, where about 30 times more Pu-239 will form [1]. The larger amount of Pu-239 produced can affect how the waste is handled and packaged, where generation of greater-than-class-C (GTCC) should be avoided. In the United States, a radioactive waste having a Pu-239 concentration of $\geq$1 nCi/g is classified as GTCC, and no current disposal path exists [2]. One of the first steps toward preventing formation of GTCC waste is understanding Pu-239 behavior during the Mo-99 separation, recovery, and purification processes. Argonne performed a series of batch and column experiments to gain a more thorough understanding of Pu's behavior on titania, which is used to separate and recover Mo-99. Results from these experiments will be discussed in detail as well as plans to look at the effect of Pu-239 buildup in a recycled uranyl sulfate solution as part of the AMORE (Argonne Molybdenum Research and development Experiment).

2. Experimental

2.1 Preparation of uranyl sulfate solutions

Two different methods were used for the preparation of uranyl sulfate. For the depleted uranium (DU) solutions, uranium metal was dissolved in 8 M HNO_3 to form uranyl nitrate, heat and sulfuric acid were used to drive off nitrate and convert it to uranyl sulfate [3]. For the natural uranium (NU) and LEU solutions, uranium metal was oxidized to U_3O_8 and dissolved in a mixture of hydrogen peroxide and sulfuric acid with heat [3]. The LEU samples used are from the batch that will soon be added to the 20-L AMORE experiment.

2.2 Peroxide concentration measurements

Samples were analyzed for peroxide approximately 20 minutes post-irradiation using an indirect means of analysis that measures the decrease in absorbance at 628 nm for toluidine blue [4]. An aliquot of the irradiated solution (10-200 μL) was contacted with an excess of potassium iodide in the presence of hydrochloric acid, toluidine blue, and sodium acetate. When hydrogen peroxide is present in solution, it oxidizes the iodide to iodine, while bleaching the toluidine blue in acidic solution. The amount of free iodine is directly proportional to the peroxide concentration in solution. For some of the samples containing metal catalysts, sodium fluoride was added because certain metal ions, such as Fe, can interfere with the analysis [4].

2.3 Van de Graaff operation and oxalic acid dosimetry

The low energy (3 MeV) Van de Graaff accelerator provides the capability of delivering high levels of electron/photon dose rates without creating activation and handling hazards for the irradiated materials. Dose rates were determined using oxalic acid dosimetry for the direct electron beam irradiations performed to study peroxide formation in uranyl sulfate solutions [5]. Figure 1 shows oxalic acid dosimetry results obtained for this set of experiments using a 2 mL sample volume. Oxalic acid dosimetry measurements were repeated for the 0.5 mL samples.

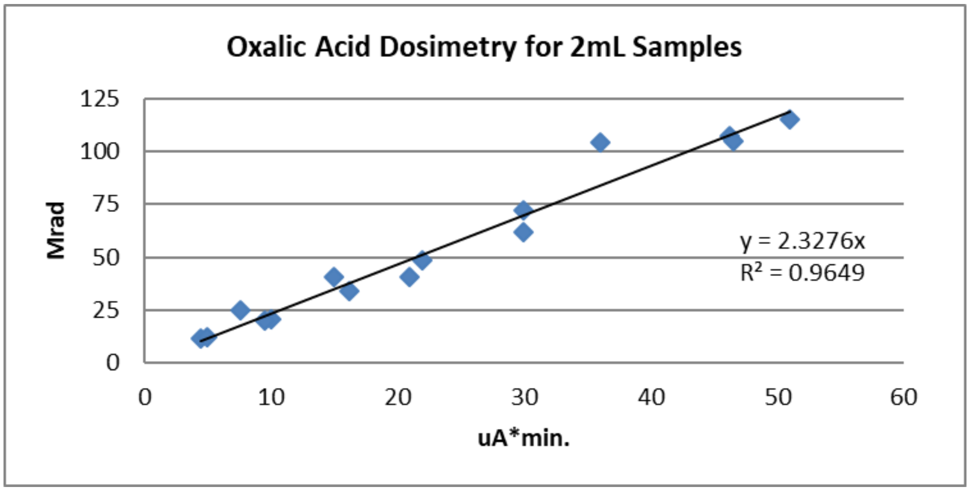

Figure 1. Dose on a 2.0 mL sample shown as Mrad versus μA*min.

The Van de Graaff beam can be used in pulse mode or direct current (DC) mode, with pulse widths of 5, 12, 25, 55, 100 nanoseconds and a variable pulse-width feature. The frequency is adjustable from 1 - 720 Hz. These experiments were all performed in the DC mode of operation in order to keep the dose rates uniform throughout the samples. Samples were irradiated by the electron beam in a sample holder mounted directly in front of the beam window. The sample was temperature controlled by water from a bath that circulates around the holder. The temperature was varied in this series of experiments in an effort to find a correlation between temperature and precipitation. Figure 2 shows an example of a sample where precipitation occurred. Prior to analysis, the sample was centrifuged, and the supernatant was used for peroxide analysis measurements.

Figure 2. A typical LEU sample where precipitation occurred during irradiation.

2.4 Gas analysis setup

Figure 3 shows a flow diagram of the experiment. A helium/argon cylinder provided a sweep gas for the experiment: Argon, at 0.5%, was added as an internal calibration source. A calibrated OMEGA FMA 5400-ST Mass Flow controller was used to control the flow of the sweep gas. A calibrated OMEGA MMA030V10H4C0T3A5CE pressure transducer was used to monitor the pressure at the outlet of the sweep gas, which was connected with stainless steel tubing to the inlet of a quartz vial containing the uranyl sulfate solution. The vial was located inside a water-cooled sample holder at the end of the Van de Graaff beamline. Stainless steel tubing connected the outlet of the vial to a Residual Gas Analyzer (RGA) (Pfeiffer OMNI-STAR GSD320) equipped with a 1-200 AMU PrismaPlus QMG220 mass spectrometer. A calibrated OMEGA MMA030V10H4C0T3A5CE pressure transducer monitored the analytical pressure of the sweep gas.

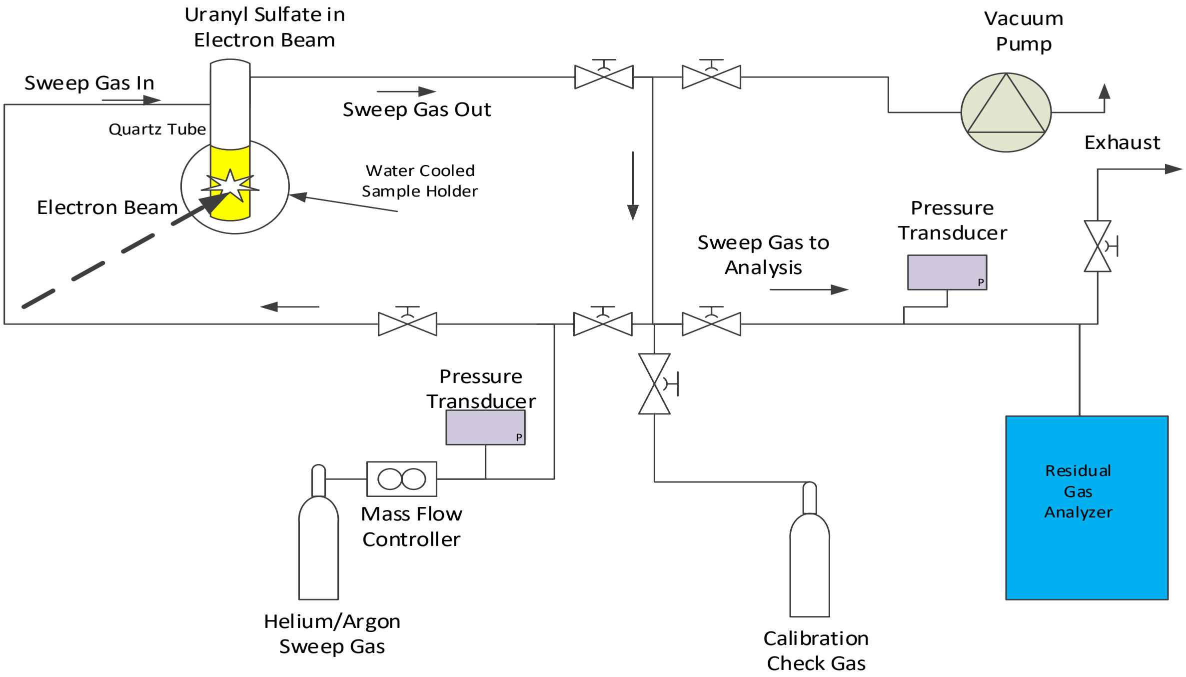

Figure 3. Experimental design for the Van de Graaff irradiations.

2.5 Calculations and Gas Data Analysis

Gases that were dissolved in solution were not analyzed. The solution was not continuously purged during irradiation to release the dissolved gases. single-point calibration standard introduced at the sampling pressure was used to calibrate the RGA. Argon at 0.5% was used as an internal standard. Equation 1 was used to generate a response factor (RF) for each analyte. It is based on the ion current ($IC_{analyte}$) and the concentration ([Analyte]) of the analyte, and the ion current (IC_{is}) and concentration ([IS]) of the internal standard. The analyte concentration during experiments was found using Equation 2. Calibration by this method made the analysis independent of sample pressure and detector instability. A calibration check was performed prior to each analysis and reproducible within +/- 10% of the true value. Background levels of nitrogen, oxygen and hydrogen were determined from the blank value and subtracted from the data. During some of the irradiations, a small amount of nitrogen was detected. The source of the nitrogen was most likely due to leaks, outgassing from the stainless steel components of the system, or dissolved gas that liberated from solution during irradiation. The oxygen values reported are corrected by subtracting a value based on the amount of nitrogen detected related to the ratio of nitrogen to oxygen in air (0.2683) using Equation 3.

$$RF = IC_{analyte} \times [IS] / IC_{IS} \times [\%Analyte] \qquad \text{Equation 1}$$

$$[\%Analyte] = IC_{analyte} \times [IS] / IC_{IS} \times RF \qquad \text{Equation 2}$$

$$[\%Oxygen\ Corrected] = [\%Oxygen] - [\%Nitrogen] \times 0.2683 \qquad \text{Equation 3}$$

After the concentration of each gas was determined, the total μmoles of each analyte was calculated using the concentration data. The system was a once through system with the He/Ar sweep gas flowing at a constant rate set by the mass flow controller. The pressure at the analyzer RGA was kept constant during the experiment. Temperature at the analyzer “room temperature” was constant during the experiments. The RGA sampled the sweep gas as it exited the system. The data generated by the RGA was set by the scan time per atomic mass unit (AMU) of the analyte of interest, so as it scanned through the AMU’s it generated a data point for that analyte at a time during the analysis. The relationship between the volume of gas flowing through the system and the analysis time was used to determine the µmoles of gas generated throughout the experiment and the total generated. The ideal gas law equation was used to find the µmoles of gas detected, which was summed over the entire experiment for the total using Equation 4,

$$\mu m=[PV/RT] \times [\%Analyte/100] \times 10^{6} \qquad \text{Equation 4}$$

where: µm=µmoles, R=gas constant, T=analysis temperature, P=analysis pressure, and V=gas flow × time interval. Gas generation data is the represented in the tables as µmole/Mrad. This done by dividing the Total umoles of gas by the Total Dose (Mrad). All gas analysis figures shown give mole % of each gas that the RGA analyzed for during irradiation.

A quartz tube containing 0.5 to 2 mL of uranyl-sulfate solution was inserted into a water-cooled window located at the end of the Van de Graaff beamline. Connections were made to the set-up, and the system was purged with the He/Ar sweep gas. The chiller was set to the desired temperature, and the 3-MeV electron beam was set to the desired current. The sample was irradiated with the electron beam for a pre-determined length of time. The electron beam impinged on the cooling water and quartz tube. Electrons and X-rays interacted with the uranyl-sulfate solution causing radiolysis of water. This generated hydrogen, hydrogen peroxide, and oxygen in the sample vial; sulfate appeared to be stable to radiolysis. The sweep gas flows in and out of the tube carrying the radiolytic gases, hydrogen and oxygen, to the RGA analytical instrument. The RGA sampled a small portion of the gas, which exited the system through the exhaust.

2.6 Apparent Steady State Determination for Peroxide Experiments

The time to reach an apparent steady state is based on observations of gas data when the ratio of hydrogen to oxygen appeared to stabilize within about three tenths of the total final ratio. This apparent steady state is with respect to gas concentration and is subjective. Only gas data at that time are being considered and should not be thought of as a true steady state equilibrium, but it may give an indication as to when the solution has achieved some stability with respect to radical diffusion and reactions. It may indicate that the forces driving the solution to one state or another have slowed enough to be observed in the gas data. When precipitation is actively occurring, there could not be a steady state in the solution. In the experiments where delayed precipitation occurred, decreasing temperatures and cessation of radiolysis disrupted that stability.

2.7Materials for Pu Experiments

A pure titania sorbent (TiO_2, 110 µm, 60 Å, Sachtopore) was received from ZirChrom Separations, Inc. (Anoka, MN). The sorbent was washed with pH 1 sulfuric acid and pre-equilibrated with pH 1 sulfuric acid prior to use in batch and column studies. Sodium molybdate dihydrate ($Na_2MoO_4\cdot 2H_2O$) was purchased from Sigma-Aldrich (St. Louis, MO) and was dissolved in pH 1 sulfuric acid for use in column experiments. Molybdenum-99 was obtained by stripping a 1 Ci Tc-99m generator (Lantheus, N. Billerica, MA) with 1.0 M NH_4OH, bringing the solution to dryness, and re-dissolving it in pH 1 sulfuric acid. Pu-239 and Pu-242 were obtained from Argonne stocks, which were purified of Am-241 using a process described previously [6].

2.8 Pu-242 Batch Studies

The uptake of Pu-242 was determined by contacting 1 mL of a Pu-242 acidic solution with a known amount (~10 mg) of titania sorbent. The sorbent was kept in contact with a Pu solution (Pu concentrations varied from trace to ~12 ppm) for 24 hours using a thermostated shaker bath. After equilibration, the solution was withdrawn and filtered using a syringe fitted with a polyvinylidene fluoride (PVDF) membrane filter (Millipore, 0.22 µm pore size). Blank experiments showed that the filter does not uptake Pu-242. The distribution coefficient (K_d) of Pu for a given initial $[H_2SO_4]_i$ was quantified as:

$$K_{di} = ([\mathrm{Pu}]_0 / [\mathrm{Pu}]_i - 1)\mathrm{mLg}^{-1}$$

where $[\mathrm{Pu}]_0$ represents the blank concentration in the absence of sorbent.

2.9 AKTA Column Experiments

The method for packing the titania columns has been described elsewhere [7]. A freshly packed 0.66 cm ID (inner diameter) × 10 cm L (length) titania column was use for all column experiments, which is a direct down-scale of the plant-scale design [8-9]. The columns were equilibrated with 12 CVs of pH 1 sulfuric acid, and the feed solution was loaded in the up-flow direction. The feed solution used for the column experiments was a pH 1 sulfuric acid solution containing stable Mo, Mo-99, and/or Pu-239. After the feed solution was loaded, the column was washed with 10-30 CVs of sulfuric acid (concentrations varied) and 10 CVs of water also in the up-flow direction. Mo was removed from the column using 20 CVs of 1 M NaOH in the down-flow direction, and the column was washed with 10 CVs of water. An additional 15-30 CVs of 1 M sulfuric acid was passed through the column in an effort to remove any additional Pu for some of the column experiments. After each column experiment, the sorbent was removed from the column casing and left in contact with 1 M sulfuric acid overnight.

2.10 Radiometric Measurements

Pu-242 and Pu-239 results were quantified by measuring their α-emissions on a liquid scintillation counter (PerkinElmer TriCarb, α/β discrimination) using an UltimaGold scintillation cocktail. Mo-99 activities were determined using a Perkin Elmer 1480 Wizard 3-inch NaI Gamma Counter with a window range of 700-900 keV.

2. Results and Discussion

Van de Graaff Experiments

A brief discussion of the Van de Graaff results is given here, but a full discussion of the results will be available as part of an ANL technical report (ANL/NE-17/17). Uranyl sulfate solutions prepared from NU, DU, and LEU were irradiated at the Van de Graaff accelerator to find conditions where precipitation of uranyl peroxide occurs and determine how to prevent it from occurring. Table 1 shows the impurities that are known to catalyze peroxide destruction present in the various solutions. The data presented in Table 1 show that impurity levels vary dramatically in uranium samples that have gone through different processing methods.

Table 1. Solutions that were irradiated at the Van de Graff. BDL means below detection limit.

Solution	Cr (ppm)	Fe (ppm)	Ni (ppm)	Cu (ppm)	Pt (ppm)	NO_3^- (mM)
NU - 140 g-U/L	<0.25	<0.1	<0.05	0.41	0.54	0
DU - 185 g-U/L	9.6	81	6.3	4.2	0.02	500
LEU - 148 g-U/L	1.1	18	2.7	1.3	<0.01	0

Table 2 shows results obtained from irradiating NU and DU solutions; in some cases, hydrogen peroxide was added to the solutions prior to irradiation to see how radiolysis affects hydrogen peroxide and uranyl peroxide destruction. Some solutions were irradiated with enough hydrogen peroxide prior to irradiation to cause precipitation of uranyl peroxide. The irradiations on 11/21/16 and 11/22/16, had hydrogen peroxide added at a concentration above the solubility limit of 1 mM with pre-irradiation concentrations of 2.3 and 4.3 mM. Dose rates were comparable, but the sample irradiated on 11/22/16 had a total dose of 13,330 Mrad compared to 10,300 Mrad for the sample irradiated on 11/21/16. A precipitate was observed pre- and post-irradiation in both of these samples; however, the precipitate appeared to be less than what was in solution before irradiation in both samples. Observations from a camera showed the disappearance of the precipitate as the experiments progressed. The gas generation values for hydrogen and oxygen for these two experiments are suspect because flow from the experiment was higher than what could be measured due to the excessive generation of oxygen. The data are presented for comparison purposes only. The high gas generation values for oxygen observed in the 11/21/16 and 11/22/16 samples as compared to the other samples are indicative of uranyl peroxide decomposition. Once a solid has formed, decomposition occurs at a faster rate than formation because significantly more oxygen is observed in the samples that already had a solid before irradiation. All other NU samples with the exception of the pre-precipitated samples had H_2:O_2 ratios greater than 2 and precipitation either did not occur or was observed several days post-irradiation. Delayed onset of precipitation occurred in two of the samples (11/29/16 and 12/01/16) even though the final concentration of free peroxide measured in solution was less than the solubility limit of 1 mM [10]. The hydrogen and oxygen generation values were the lowest for the NU samples that had no hydrogen peroxide added before irradiation.

For the DU samples, gas production rates and measured peroxide concentrations were low due to the presence of 0.5 M nitrate remaining in solution from the method of preparation. Nitrate radiolysis products such as nitrous acid are known to catalyze the destruction of hydrogen peroxide [11]. It took 25-140 minutes to reach an apparent steady state.

Table 2. NU and DU samples irradiated at the Van de Graaff accelerator.

Date	Sample Type	U-Sulfate (g-U/L)	Sample Size (mL)	Sample Temp (°C)	Average Current (μA)	Total Dose (Mrad)	Dose Rate (Mrad/min)	Measured H_2O_2 (μM)	Precipitation	Gas Generation H2 (μmoles/Mrad)	Gas Generation O2 (μmoles/Mrad)	Overall H to O Ratio	Apparent Steady State Time (min)	Measured H:O Ratio @ Steady State
12/12/16	NU	140	2	62	19	13,550	44	130	NO	0.045	0.019	2.4	60	2.0
11/29/16	NU - 30μM/L H2O2 added	140	2	64	20	15,788	47	390	Delayed[1]	0.079	0.036	2.2	45	2.2
11/30/16	NU - 17μM/L H2O2 added	140	2	80	20	16,043	48	60	NO	0.089	0.043	2.1	60	2.0
11/17/16	NU - 170μM/L H2O2 added	140	2	60	18	17,317	42	610	NO	0.065	0.031	2.1	83	2.1
11/21/16	NU - 4300μM/L H2O2 added	140	2	60	18	10,283	41	540	YES	0.075	0.049	1.5	140	2.1
11/22/16	NU - 2300μM/L H2O2 added	260	2	60	17	13,329	41	60	YES	0.122	0.087	1.4	140	2.0
12/01/16	NU - 50μM/L H2O2 added	90	2	63	20	15,820	46	800	Delayed[2]	0.101	0.046	2.2	42	2.1
12/08/16	NU - 240μM/L H2O2 added	90	2	63	20	15,015	47	840	NO	0.104	0.047	2.2	50	2.1
12/13/16	NU - 130μM/L H2O2 added	90	2	60	18	15,085	41	880	NO	0.100	0.043	2.4	130	2.2
12/06/16	DU - 50μM/L H2O2 added	140	2	63	19	12,179	48	100	NO	0.011	0.005	2.2	25	2.2
12/07/16	DU - 55μM/L H2O2 added	90	2	63	20	14,892	46	6	NO	0.011	0.005	2.5	30	2.5

[1] Sample was cloudy on 12/07/16, and precipitate was observed on 12/22/16. [2] Precipitate was observed on 12/06/16. *Gas data estimated. Excessive oxygen production caused a high flow that could only be estimated.

Figure 4 shows typical gas generation data where hydrogen is generated first from the solution, and oxygen follows later. The mole percent is equal to the percent by volume and is determined from the ideal gas law where 1 mole of an ideal gas occupies 22.4 L at 0°C and 1 atm. In this NU sample, no hydrogen peroxide was added prior to irradiation, the solution temperature was kept at 62°C, and precipitation did not occur. The overall H_2/O_2 ratio was 2.4 but after an apparent steady state was reached, the ratio averaged 2.0.

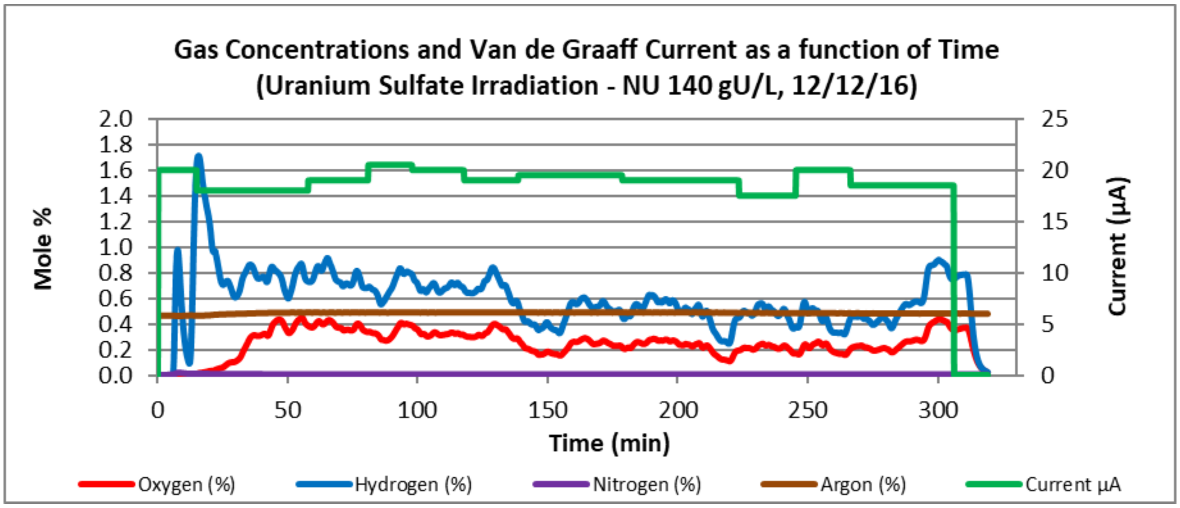

Figure 4. Gas generation and Van de Graaff current as a function of time for NU sample irradiated without additional hydrogen peroxide before irradiation (12/12/16).

Table 3 shows the LEU solutions irradiated at the Van de Graaff accelerator; the table also includes results for irradiation of pH 1 sulfuric acid for comparison. The solution volume was the same (2 mL) for all samples. The uranium concentration was approximately the same for all samples shown in Table 3. The LEU sample irradiated without an additional catalyst before irradiation had a 5% higher concentration, which was due to the slight dilution from the addition of a catalyst to all other samples. LEU solutions irradiated on 12/15/16 & 12/20/16 did not contain an additional catalyst and were irradiated under similar conditions. They are replicates of each other and serve as the base to compare to the other LEU samples irradiated with catalysts and also shown in Table 3. The remaining LEU samples shown in Table 3 had various catalysts added to them prior to irradiation to prevent the precipitation of uranyl peroxide. Tests were performed with different catalyst concentrations to determine the lowest amount required to prevent precipitation. The effect of different dose rates was examined as well, which was done by changing the current of the accelerator. All catalysts were effective at catalyzing the destruction of peroxide to the extent of preventing precipitation except for the sample irradiated on 03/09/17 where 500 ppm of Cu^{2+} was added as $CuSO_4$ to the solution. Metal ions present in solution such as Fe^{2+}, Fe^{3+}, or Cu^{2+} interfere with the spectrophotometric method used to measure peroxide concentration, so NaF was added to the solution prior to peroxide measurements being done to complex the metal ions and prevent interference in samples where a catalyst was added and shown in Table 3 [4].

LEU-only samples irradiated on 12/15/16 & 12/20/16 showed signs of precipitation within 20 minutes of irradiation based on camera images during irradiation. The differences in temperature and dose rate are due to the slight difference in the average current. The measured H_2O_2 concentration for both samples was less than the solubility limit of 1 mM. This is due to free peroxide reacting to form the precipitate, which leaves little free peroxide left in solution. The ratio of hydrogen to oxygen is also >2, which is not surprising because the precipitation of uranyl peroxide causes oxygen atoms to bind leaving two atoms of hydrogen as acid in solution.

Samples irradiated on 3/2/17 & 3/6/17 both had 1000 ppm Fe^{+2}, which was effective at preventing uranyl peroxide precipitation in both samples. When compared to the samples without an additional catalyst, the major difference was lower gas generation for hydrogen and oxygen in samples with 1000 ppm Fe^{2+}. The other parameter being tested was the effect of dose rate. The 3/6/17 sample was run at a lower dose rate (12 vs 50 Mrad/min). The differences were related to the time it took to reach an apparent steady state and the generation of H_2 and O_2. Generation values were lower at a lower dose rate, and the time it took to reach an apparent steady state was longer at a lower dose rate.

Experiments performed on 3/8/17, 3/7/17 & 3/16/17 were run to test a lower concentration of Fe^{2+} and to see if it was effective at preventing precipitation a lower temperature. Fe^{+2} added at 200 ppm was effective at preventing precipitation of uranyl peroxide even at a temperature of 19°C. The dose rate was lower for this sample, but it has already been shown that precipitation will occur at the lower dose rate without a catalyst.

In the samples that had a low final free peroxide concentration, a significant amount of precipitate had formed during irradiation reducing the amount of free peroxide available for the measurements. The overall hydrogen-to-oxygen ratios were higher than 2 for all of the LEU samples irradiated without the addition of a catalyst.

The next 8 LEU samples shown in Table 3 were irradiated with a metal catalyst such as $FeSO_4$, $CuSO_4$, or $Fe_2(SO_4)_3$. At least 200 ppm Fe^{2+} or 250 ppm Fe^{3+} were required to prevent precipitation or a combination of 100 ppm Fe^{2+} as $FeSO_4$ and 100 ppm Cu^{2+} as $CuSO_4$. All samples irradiated showed hydrogen to oxygen ratios greater than 2, and the sample irradiated with 250 ppm Fe^{3+} as $Fe_3(SO_4)_2$ had an overall H_2:O_2 ratio of 3.

The apparent steady-state time for all Table 3 samples that reached a steady state, took approximately 50-250 minutes to reach it. Both samples irradiated on 03/22/17 were not irradiated long enough for an apparent steady state to be reached. Catalysts tested except 500 ppm Cu^{2+} catalyzed the destruction of peroxide at a rate fast enough to prevent accumulation of peroxide to cause precipitation. Total gas production represented by generation values shows a trend when Fe^{2+} peroxide catalyst is added to the uranium solution. Fe^{2+} causes a significant decrease in hydrogen and oxygen generation. The more catalyst was added, the less gas was generated.

Table 3. LEU samples irradiated at the Van de Graaff accelerator.

Date	Sample Type	U-Sulfate (g-U/L)	Sample Size (mL)	Sample Temp (°C)	Irradiation Time (min)	Average Current (μA)	Total Dose (Mrad)	Dose Rate (Mrad/min)	Measured H_2O_2 (μM)	Precipitation	H_2 (μmoles/Mrad)	O_2 (μmoles/Mrad)	Overall H to O Ratio	Apparent Steady State Time (min)	Measured H:O Ratio @ Steady State
12/15/16	LEU	148	2	64	360	20	16,728	46	100	YES	0.135	0.054	2.5	60	2.3
12/20/16	LEU	148	2	62	329	19	13,990	43	17	YES	0.146	0.060	2.4	60	2.3
03/02/17	LEU - Fe^{+2} @1000ppm	140	2	66	360	21	17,994	50	1300*	NO	0.025	0.010	2.4	55	2.4
03/06/17	LEU - Fe^{+2} @1000ppm	140	2	32	360	5	4,150	12	2100*	NO	0.011	0.002	5.4	252	3.1
03/08/17	LEU - Fe^{+2} @500ppm	140	2	66	366	22	18,519	51	16*	NO	0.039	0.017	2.3	50	2.3
03/07/17	LEU - Fe^{+2} @500ppm	140	2	29	360	4	3,295	9	440*	NO	0.057	0.023	2.5	107	2.3
03/16/17	LEU - Fe^{+2} @200ppm	140	2	30	360	4	3,575	10	2600*	NO	0.048	0.019	2.5	173	2.4
03/09/17	LEU - Cu^{+2} @500ppm	140	2	34	366	5	4,541	12	1600*	YES	0.066	0.027	2.5	N/A	N/A
03/22/17	LEU - Fe^{+2} & Cu^{+2} @100ppm	140	2	28	120	4	1,112	9	860*	NO	0.032	0.011	2.6	N/A	N/A
03/22/17	LEU - Fe^{+3} @250ppm	140	2	30	120	4	1,336	11	1600*	NO	0.030	0.009	3.0	N/A	N/A
03/09/17	pH-1 Sulfuric Acid	N/A	2	63	331	20	15,146	46	1400	NO	0.018	0.008	2.3	60	2.4

*NaF was added as a complexant.

Figure 5 (12/20/16 LEU) shows the sample where uranyl peroxide precipitated during irradiation. Hydrogen was evolved from solution first followed by oxygen. The overall H_2/ O_2 ratio was 2.4 due to the lower production of oxygen through the precipitation of uranyl peroxide, and the apparent steady state ratio did not change that much--decreasing to only to 2.3, which again is due to precipitation of uranyl peroxide during irradiation.

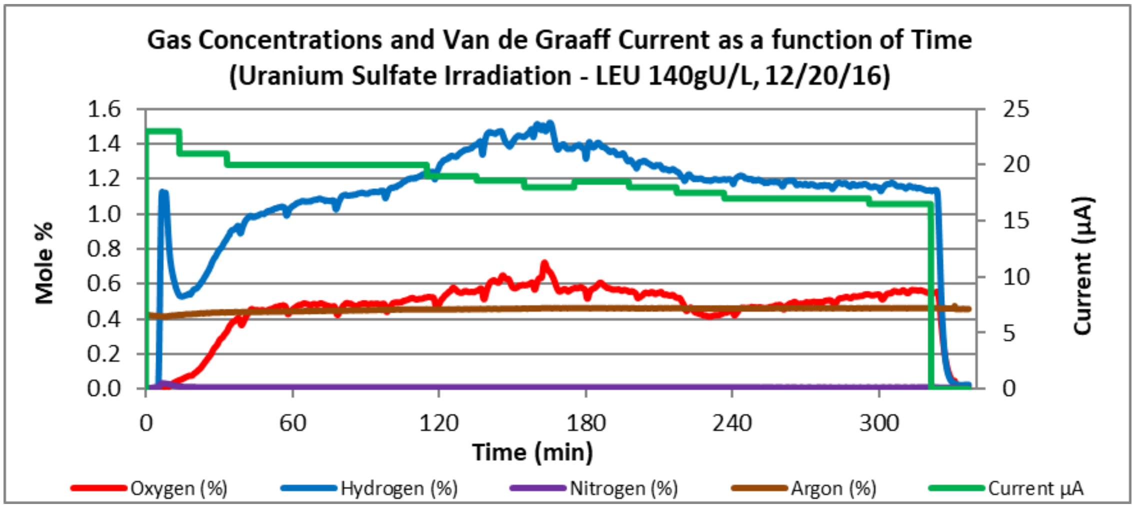

Figure. 5 (12/20/16 LEU) gas generation and Van de Graaff current as a function of time.

Figure 6 shows typical gas behavior for a sample irradiated with a catalyst (500 ppm Fe^{2+}) that was effective at preventing uranyl peroxide precipitation during and post-irradiation. The overall H_2/O_2 ratio and apparent steady state ratio was 2.3. It was very high during the beginning of the irradiation due to O_2 being consumed as peroxide.

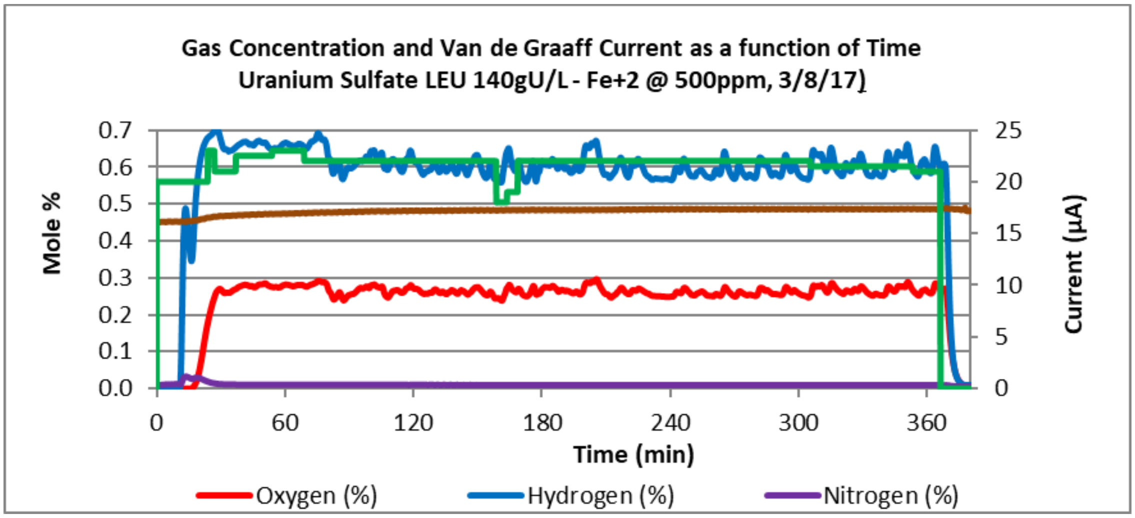

Figure 5. (3/8/17 140 g-U/L 500 ppm Fe^{2+}) gas generation and Van de Graaff current as a function of time.

Pu Batch and Column Results

Batch study data indicate that Pu adsorption on titania is unaffected by the amount of time 1-10 ppm Pu solutions were left in pH 1 sulfuric acid solutions before contact was made with titania. K_d values for Pu-242 of ~360 mL/g titania sorbent were obtained for solutions that were left sitting at room temperature for 1 hour to 3 weeks, which suggests the speciation and/or oxidation state does not change over that period of time to the extent of changing Pu adsorption behavior on titania [12].

Additional batch studies using tracer Pu-242 examined the effect of temperature and H^+ concentration on Pu adsorption on titania. Results indicate that Pu adsorbs on titania more effectively when the H+ concentration is lower, so for example, higher K_d values are obtained in 0.1 M H_2SO_4 compared to 1 M H_2SO_4. Additionally, less Pu is adsorbed on titania at 25°C compared to 80°C, which is the optimum temperature for Mo adsorption and elution in base. Temperature and acid wash concentration were varied during the column experiments to help control Pu behavior on titania [12].

Direct down-scale column experiments were completed using a pH 1 sulfuric acid solution containing Pu-239 to gain a better understanding of Pu-239 behavior on titania. The plant-scale operation, which has been optimized for Mo is performed at 80°C. Additionally, the post-feed acid wash is pH 1 sulfuric acid with a volume equivalent to 10 column volumes (CVs). Decreasing the temperature to 25°C was effective at decreasing Pu adsorption on titania where about three times more Pu-239 was found in the column effluent at 25°C compared to what was found at 80°C. The post-feed acid wash and post-processing acid wash were also more effective at 25°C. Increasing the amount and concentration of the post-feed acid wash to 0.5 M and 1 M compared to 0.085 M and passing 30 CVs through the column increased the amount of Pu-239 removed from the titania column. For experiments done at 80°C, less than 1% Pu-239 was found in a 10 CV 0.085 M H_2SO_4 wash, 36% Pu-239 was found in a 30 CV 0.5 M H_2SO_4 wash, and 23% Pu-239 was found in a 30 CV 1 M H_2SO_4 wash [12].

4. Conclusions

Uranyl peroxide precipitation was observed in the NU and LEU samples irradiated at the Van de Graaff accelerator. Precipitation was not observed in irradiated DU samples due to the presence of nitrate in solution whose radiolysis products are known to catalyze the destruction of peroxide [11]. It was determined that at least 200 ppm Fe^{2+}, 250 ppm Fe^{3+} or 100 ppm Fe^{2+} with 100 ppm Cu^{2+} was needed to prevent precipitation from occurring under the given conditions. Depending on how much corrosion takes place in the Mo-99 production system, additional metal catalysts may be necessary to prevent precipitation. Peroxide destruction increases with increasing temperature, but due to the significant temperature gradient expected in the target vessel and the fact that the solution will be stored at room temperature while not being irradiated prevent using temperature as a means to combat precipitation. The effectiveness of 200 ppm of a metal ion will be tested as part of the upcoming mini-AMORE experiments.

Results from the Pu experimental study suggest that Pu behavior can be controlled to a certain extent using acid wash concentration and volume as well as temperature (not recommended due to Mo losses). However, a more comprehensive examination of Pu behavior on titania in the presence of uranium and fission products as well as a high radiation field needs to be investigated. Argonne's phase-2 AMORE will look at Pu-behavior throughout the process. Changing the acid concentration to control Pu behavior on titania will most likely affect fission product partitioning on titania, which will be investigated as well [12].

5. Acknowlegement

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