Low LET Irradiations of Uranyl Sulfate Solutions in the Absence and Presence of Fe^{+2} and Fe^{+3} Ions

Chemical and Fuel Cycle Technologies Division

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1 INTRODUCTION

Argonne National Laboratory (Argonne) is assisting one of the potential domestic Mo-99 producers, SHINE Medical Technologies, as part of the National Nuclear Security Administration's (NNSA) Office of Material, Management, and Minimization (M³) program in the development of a domestic Mo-99 production pathway that does not use highly enriched uranium (HEU). The process proposed by SHINE would produce Mo-99 by neutron-induced fission of a low enriched uranium (LEU) solution as uranyl sulfate in a subcritical assembly.

One potential technical difficulty with using uranyl sulfate is possible precipitation of uranyl peroxide ($\text{UO}_2\text{O}_2 \cdot n\text{H}_2\text{O}$ or $\text{UO}_4 \cdot n\text{H}_2\text{O}$). Through a series of reactions, hydrogen peroxide is generated in solution by the radiolysis of water, which can react with the uranyl ion to form uranyl peroxide, thus forming a precipitate [1-5]. Uranyl-peroxide precipitation must be avoided for safe production of Mo-99 during the proposed process. Equation 1 shows the reaction of uranium and hydrogen peroxide in solution to form the precipitate:

Previous experiments [4] showed that uranyl peroxide was decomposed by high temperatures and radiolysis. Two mechanisms have been proposed by Silverman et al. for the destruction of uranyl peroxide, See Equations 2, 3, 4, and 5 [6].

These experiments also showed that precipitation could be prevented by the addition of a metal ion such as iron. A series of irradiation experiments were performed using a 3 MeV Van de Graaff accelerator to generate high radiation doses in 1 mL LEU uranyl-sulfate solutions at ~190 and 194 g/L (19.8% U-235). The purpose of these experiments was to examine whether Fe^{+2} or Fe^{+3} were equally effective at preventing precipitation of uranyl peroxide and determine the oxidation state of iron after an irradiation.

2 EXPERIMENTAL

2.1 PREPARATION OF URANYL SULFATE SOLUTIONS

Uranium metal was oxidized to U_3O_8 and dissolved in a mixture of hydrogen peroxide and sulfuric acid with heat [5].

2.2 PEROXIDE DETERMINATION

Although it was possible to identify the presence of peroxide using the peroxide indicator strips (QUANTOFIX[®] peroxide test strips), which in colorless solution turn into different shades of blue; in highly colored yellow uranium solution, the concentration range of peroxide is difficult to identify due to a change of the color of indicator strips to green. Two types of test strips were used in the test with concentration limits of 25 ppm and 100 ppm.

2.3 Fe^{+2} CONCENTRATION MEASUREMENTS

Samples were analyzed for Fe^{+2} content using the 1,10-phenanthroline method [7]. In this method, Fe^{+2} reacts with phenanthroline at a pH 3.2-3.3, where three molecules of phenanthroline chelate each atom of ferrous iron (Fe^{+2}), to form an orange-red complex with a peak absorbance at 510 nm. Color is independent in the pH range from 3-9, but pH=3 gives rapid color development in the presence of excess phenanthroline. Color solutions are stable for up to six months. An aliquot of the irradiated LEU solution (50-200 mg) was contacted with an excess of phenanthroline in the presence of ammonium acetate buffer. The colored solutions were measured on a Cary 5000 UV-Vis spectrophotometer. It is assumed that any iron not in the +2 oxidation state was present as +3. Samples were analyzed several days to weeks after irradiation. Figure 1 shows the standard calibration curve of the colorimetric method for detection of Fe^{+2} concentration.

FIGURE 1 Absorbance at 510 nm versus Fe^{+2} concentrations.

2.4 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. To determine the dependence of beam parameters and the dose delivered to the sample, an oxalic acid dosimeter was used. The dose was determined by comparing the concentration of oxalic acid prior to and after irradiation as the acid decomposed with irradiation [8].

Irradiated oxalic acid solution was titrated with NaOH to determine the amount of oxalic acid remaining. Once the concentration of acid was determined, the dose could be calculated from the following [8]:

$$\text{Log}(D) = a \log(C) + b \quad (10)$$

where D = absorbed dose in eV/mL; C = the number of oxalic acid molecules decomposed in 1 mL sample; and a and b are constants depending on the initial concentration of oxalic acid and the number of moles of oxalic acid decomposed [8].

Figure 2 shows oxalic acid dosimetry results obtained for this set of experiments using a 1 mL sample volume, where the y axis represents dose (Mrad) and the x axis the Van de Graaff current (μA). The dose delivered to sample is calculated using equation 11

$$\text{Mrad} = \text{Slope} \times \mu\text{A} \times \text{Time Interval (min)} \quad (11)$$

FIGURE 2 Dependence of dose vs. Van de Graaff irradiation parameters for a 1.0 mL sample.

The Van de Graaff beam can be used in pulse mode or direct current (DC) mode, with pulse widths of 5, 12, 25, 55, and 100 nanoseconds and a variable pulse-width feature. The frequency is adjustable from 1 to 720 Hz. A majority of experiments were performed in the pulse mode of operation; however, one sample was irradiated in the DC mode to see if the different beam mode could affect precipitation of uranium solution. Samples were irradiated in a sample holder mounted directly in front of the beam window.

2.5 TEMPERATURE MEASUREMENTS

The sample was temperature controlled using a water bath that circulates around the sample holder. Since sample temperatures varied as a function of beam current, temperature measurements were conducted for different Van de Graaff beam currents and water bath temperature settings. Figure 3 shows the difference in temperature of a 1 mL sample during the irradiation at different beam currents. Since the presence of the thermocouple could interfere with actual irradiation of the LEU solution, Equation 12 was used to determine the sample temperature for irradiation of LEU samples.

$$y = 2.269x + \text{Bath Temperature} \quad (12)$$

FIGURE 3 ΔT (°C) versus Van de Graaff current (μA).

2.6 EXPERIMENTAL DESIGN

Figure 4 shows a flow diagram of the experiment, and Figure 5 shows the enclosure with the experimental setup at the end of the Van de Graaff beamline. A helium/argon cylinder provided a sweep gas for the experiment. 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. Sweep gas was introduced via stainless steel tubing to the inlet of a quartz vial containing the uranyl sulfate solution. The vial was located inside a water-cooled stainless steel sample holder at the end of the Van de Graaff beamline. Stainless steel tubing was connected to the outlet of the vial to a Pfeiffer OmniStar[™] GSD320 gas analyzer equipped with a 1-200 amu PrismaPlus[™] QMG220 mass spectrometer.

FIGURE 4 Diagram of the irradiation setup.

Before each irradiation, a quartz tube containing 1 mL of uranyl sulfate solution was inserted into a water-cooled window located at the end of the Van de Graaff beamline. Headspace of the vial containing the LEU sample 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 predetermined length of time. The generated hydrogen and oxygen were monitored using the gas analyzer, which samples a small portion of the gas.

FIGURE 5 Photograph of the irradiation setup at the Van de Graaff accelerator facility.

2.7 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. A single-point calibration standard introduced at the sampling pressure was used to calibrate the analyzer. Argon at 0.499% was used as an internal standard. Calibration standards were purchased from the vendor with an uncertainty of $\pm 2\%$. Reported uncertainties for concentrations of hydrogen and oxygen were within 10%. Equation 13 was used to generate a response factor (RF) for each analyte. It is based on the ion current (IC_{analyte}) and concentration of the analyte and the ion current (IC_{is}) and concentration of the internal standard (IS). The analyte concentration during experiments was determined using Equation 14. Calibration by this method made the analysis independent of sample pressure and detector instability. Background levels of nitrogen, oxygen, and hydrogen were determined from the blank value and subtracted from the data. Oxygen values reported were corrected by subtracting a value based on the amount of nitrogen detected relative to the ratio of nitrogen to oxygen in air (0.2683) using Equation 15.

$$RF = IC_{\text{analyte}} \times [IS] / IC_{\text{is}} \times [\% \text{Analyte}] \quad (13)$$

$$[\% \text{Analyte}] = IC_{\text{analyte}} \times [IS] / IC_{\text{is}} \times RF \quad (14)$$

$$[\% \text{Oxygen Corrected}] = [\% \text{Oxygen}] - [\% \text{Nitrogen}] \times 0.2683 \quad (15)$$

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 and temperature at the analyzer were kept constant during the experiment. 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 16.

$$\mu m = [PV/RT] \times [\% \text{Analyte}/100] \times 10^6 \quad (16)$$

where: $\mu m = \mu\text{moles}$, $R = \text{gas constant}$, $T = \text{analysis temperature}$, $P = \text{analysis pressure}$, and $V = \text{gas flow} \times \text{time interval}$.

3 RESULTS AND DISCUSSION

3.1 Fe⁺² ANALYSIS

Initially, samples were taken for color development within 30 minutes after an irradiation. The samples would then be analyzed at a later date, since the method produces a colored solution that is stable for up to six months. This, however, proved to be problematic, as it was shown that due to presence of peroxide in the samples post irradiation, the redox reactions in the irradiated samples were affecting the concentration of Fe⁺²/Fe⁺³. Another potential analytical problem was seen during the analysis of unirradiated LEU samples spiked with Fe⁺³. It was determined that all Fe⁺³ added to an unirradiated sample of LEU solution turned to Fe⁺². This could be due to some presence of U⁺⁴ that could affect the oxidation state of Fe and interfere with the measurement of Fe⁺²/Fe⁺³ caused by irradiation. Equation 17 shows that uranium could donate an electron to the weakly bound 2Fe⁺³(Phen) complex, thus reducing it to the +2 state [9]. There are other metal ion interferences using this method.

While the Fe⁺² spike was primarily standard grade (99.99%) purity, the Fe⁺³ spiking solution had a purity of 96% and had other metal ion contaminants. Without better understanding of how the presence of U⁺⁴ or other impurities affects the distribution of Fe⁺²/Fe⁺³, we cannot assign the changes in Fe oxidation states solely to redox reactions caused by radiolysis during the irradiation.

Table 1 shows the impurities in LEU solution detected using ICP-MS (inductively coupled plasma mass spectrometry). Concentrations are reported with $\pm 10\%$ uncertainties. Concentration of Fe was analyzed using the 1,10-phenanthroline method after heating the sample in the presence of hydroxylamine hydrochloride to reduce Fe⁺³ to Fe⁺² state.

TABLE 1 LEU Solution ICP-MS analysis. *Fe analyzed using the phenanthroline method.

Uranium Concentration, gU/L solution	Cr mg/L	Mn mg/L	*Fe mg/L	Co mg/L	Ni mg/L	Cu mg/L	Zn mg/L	Cd mg/L	Pt mg/L
193.730	<1.57	<1.00	11	<0.19	<1.43	<0.79	<3.71	<0.19	<0.11

3.2 IRRADIATIONS TO DETERMINE THE EXPERIMENTAL PARAMETERS FOR PRECIPITATION

Table 2 shows the results of the irradiations of LEU solution at ~194 gU/L. The initial irradiations were performed to determine the base parameters of the accelerator current and temperature at which precipitation occurred. None of the samples showed signs of precipitate during or immediately after the irradiation. Uranium precipitate was observed only about 24 hours after the irradiation. Figure 6 shows a photograph of uranium samples with and without

precipitate. Samples at 2.5 and 5 μA current never showed signs of precipitation. Following the initial tests at lower current, irradiation using a current of 10 μA and a temperature of about 33°C was performed.

After testing all irradiated samples for peroxide, all samples tested positive immediately after irradiation; however, the exact concentration of peroxide could not be determined due to the change of indicator color from blue to green (i.e., the presence of uranium), as discussed previously.

The results listed below are from a re-analysis of the samples except for irradiation at 2.5 μA performed on 6/14. There was not enough sample to repeat the analysis, so the results reported are from a sampling immediately after the irradiation. No Fe^{+2} was detected immediately after the irradiation.

Another disagreement with the rest of the results is for the irradiation performed on 6/17 at a 10 μA current, where there was about a 50:50 split between the Fe^{+2} and Fe^{+3} distributions. When initially analyzed immediately after irradiating, the Fe^{+2} was at 2 $\mu\text{g/g}$. The analysis performed later showed 4.6 $\mu\text{g/g}$, with no appreciable pH changes.

Gas generation rates listed as $\mu\text{moles/min}$ were similar to those of irradiations performed in the past [5].

3.3 IRRADIATIONS OF Fe^{+2} SPIKED SAMPLES

Table 3 shows the data from unirradiated and irradiated samples of LEU spiked with Fe^{+2} at 169 $\mu\text{g/g}$. None of these LEU samples showed signs of precipitation during or after the irradiation. Comparing the samples irradiated for 240, 60, and 30 minutes, all tested positive for peroxide immediately after the irradiation. Figures 7 and 8 show pictures of the peroxide test strips immediately after irradiations. The photograph of the peroxide strip for sample irradiated on 7/2/19 without added Fe (Figure 7) indicates a higher concentration of peroxide than the sample with added Fe (Figure 8). This indicates that the presence of Fe affects the final concentration of peroxide that ultimately prevents precipitation of uranium. No appreciable pH changes were observed. The final Fe^{+2} concentrations were similar, showing no particular trend for different irradiation times between 30 and 240 minutes. The reporting limit for samples was about 5 $\mu\text{g/g}$, and the final concentration of Fe^{+2} was higher than that of Fe^{+3} .

FIGURE 6 Irradiated LEU sample containing U precipitate (bottom) and containing no U precipitate (top).

TABLE 2 Irradiation parameters and analysis data for LEU samples without added Fe spike

Description	Van de Graaff Mode	Date	LEU (gU/L)	Sample Temp. (°C)	Average Current (µA)	Irradiation Time (min)	Total Dose (Mrad)	O ₂ (µM/min)	H ₂ (µM/min)	Pre-irradiation Total Fe (µg/g)
LEU 194 gU/L	Not Irradiated		194							8.7
LEU_PPT Test 2.5 µA	Pulsed	6/14/19	194	26	2.5	229	1710	0.292	0.670	8.7
LEU_PPT Test 10 µA	Pulsed	6/17/19	194	31	9.9	240	7090	0.980	2.182	8.7
LEU_PPT Test 20 µA	Pulsed	6/19/19	194	58	21.0	147	9200	1.042	2.359	8.7
LEU_PPT Test 15 µA	Pulsed	6/25/19	194	42	14.6	240	10400	0.977	2.174	8.7
Re-Test of 20 µA	Pulsed	6/27/19	194	55	19.8	356	21000	1.136	2.622	8.7
DC vs Pulsed 10 µA	Direct Current	7/2/19	194	32	9.7	240	6920	0.852	1.967	8.7
PPT Test 5 µA	Pulsed	7/10/19	194	30	5.2	240	3710	0.666	1.522	8.7
<hr/>										
Description	Van de Graaff Mode	Date	FINAL Fe ⁺² (µg/g)	FINAL Fe ⁺³ (µg/g)	Final pH	Precipit. DURING Irradiation	Precipit. AFTER Irradiation	H ₂ O ₂ Test Strip	Precipit. Re-dissolved	
LEU 194 gU/L	Not Irradiated				1.05					
LEU_PPT Test 2.5 µA	Pulsed	6/14/19	<0.8	8.5	N.A.	No	NO	N.A.		
LEU_PPT Test 10 µA	Pulsed	6/17/19	4.6	4.1	1.01	No	Yes	N.A.	Yes	
LEU_PPT Test 20 µA	Pulsed	6/19/19	9.3	<0.8	1.06	No	Yes	N.A.	Yes	
LEU_PPT Test 15 µA	Pulsed	6/25/19	9.1	<0.8	1.07	No	Yes	Positive	Yes	
Re-Test of 20 µA	Pulsed	6/27/19	8.8	<0.8	1.00	No	Yes	Positive	Yes	
DC vs Pulsed 10 µA	Direct Current	7/2/19	9.3	<0.8	1.08	No	Yes	Positive	Yes	
PPT Test 5 µA	Pulsed	7/10/19	8.9	<0.8	1.05	No	No	Positive		

N.A. indicates sample was not analyzed.

TABLE 3 Irradiation parameters and analysis data for LEU samples with added Fe⁺² spike

Description	Van de Graaff Mode	Date	LEU (gU/L)	Sample Temp. (°C)	Average Current (μA)	Irradiation Time (min)	Total Dose (Mrad)	O ₂ (μM/min)	H ₂ (μM/min)
Fe ⁺² Spiked LEU	Not Irradiated		190						
Fe ⁺² Spiked LEU_PPT Test 10 μA	Pulsed	7/18/19	190	33	10	240	7110	0.430	0.997
Fe ⁺² Spiked LEU_Total Dose Effect 10μA_60min	Pulsed	7/19/19	190	33	10	60	1810	0.399	1.044
Fe ⁺² Spiked LEU_Total Dose Effect 10μA_30min	Pulsed	7/19/19	190	33	10	30	914	0.353	1.047
Fe ⁺² Spiked BLANK	Pulsed	7/23/19		33	10	63	1920	0.723	1.747
Description	Van de Graaff Mode	Date	Pre-irradiation Total Fe (μg/g)	FINAL Fe ⁺² (μg/g)	FINAL Fe ⁺³ (μg/g)	Final pH	Precipitation DURING Irradiation	Precipitation AFTER Irradiation	H ₂ O ₂ Test Strip
Fe ⁺² Spiked LEU	Not Irradiated		169			1.06			
Fe ⁺² Spiked LEU_PPT Test 10 μA	Pulsed	7/18/19	169	97	71	1.06	No	No	Positive
Fe ⁺² Spiked LEU_Total Dose Effect 10μA_60min	Pulsed	7/19/19	169	93	75	1.07	No	No	Positive
Fe ⁺² Spiked LEU_Total Dose Effect 10μA_30min	Pulsed	7/19/19	169	100	68	1.04	No	No	Positive
Fe ⁺² Spiked BLANK	Pulsed	7/23/19	205	42	164	N.A.	No	No	Positive

N.A. indicates sample was not analyzed.

FIGURE 7 Peroxide test of un-spiked sample from 7/2/19, 240 minute irradiation at 10 μ A direct current.

FIGURE 8 Peroxide test of Fe^{+2} spiked sample from 7/18/19, 240 minute irradiation at 10 μ A.

3.4 IRRADIATIONS OF Fe^{+3} SPIKED SAMPLES

Table 4 shows the data from un-irradiated and irradiated samples of LEU spiked with Fe^{+3} at 170 $\mu\text{g/g}$. None of these samples showed signs of precipitation during or after the irradiation. All irradiated samples tested positive for peroxide immediately after the irradiation. No appreciable pH changes were observed, and the gas generation rates were comparable to those of the Fe^{+2} spiked samples. The final Fe^{+2} concentrations were essentially the same, showing no particular trend between the different irradiation times. The reporting limit for samples was about 5 $\mu\text{g/g}$, and final concentration of Fe^{+3} was higher than that of Fe^{+2} .

TABLE 4 Irradiation parameters and analysis data for LEU samples with added Fe⁺³ spike

Description	Van de Graaff Mode	Date	LEU (gU/L)	Sample Temp. (°C)	Average Current (μA)	Irradiation Time (min)	Total Dose (Mrad)	O ₂ (μM/min)	H ₂ (μM/min)
Fe ⁺³ Spiked LEU	Not Irradiated		190						
Fe ⁺³ Spiked LEU_PPT Test 10 μA	Pulsed	7/25/19	190	33	10	241	7340	0.465	0.979
Fe ⁺³ Spiked LEU_Total Dose Effect 10μA_181min	Pulsed	7/29/19	190	33	10	181	5530	0.463	1.004
Fe ⁺³ Spiked LEU_Total Dose Effect 10μA_60min	Pulsed	7/30/19	190	33	10	60	1,800	0.341	0.713
Fe ⁺³ Spiked LEU_Total Dose Effect 10μA_30min	Pulsed	7/30/19	190	33	10	30	893	0.319	0.866
<hr/>									
Description	Van de Graaff Mode	Date	Pre-irradiation Total Fe (μg/g)	FINAL Fe ⁺² (μg/g)	FINAL Fe ⁺³ (μg/g)	Final pH	Precipitation DURING Irradiation	Precipitation AFTER Irradiation	Hydrogen Peroxide Test Strip
Fe ⁺³ Spiked LEU	Not Irradiated		170			1.06			
Fe ⁺³ Spiked LEU_PPT Test 10 μA	Pulsed	7/25/19	170	70	100	1.04	No	No	Positive
Fe ⁺³ Spiked LEU_Total Dose Effect 10μA_181min	Pulsed	7/29/19	170	70	100	1.02	No	No	Positive
Fe ⁺³ Spiked LEU_Total Dose Effect 10μA_60min	Pulsed	7/30/19	170	74	96	1.03	No	No	Positive
Fe ⁺³ Spiked LEU_Total Dose Effect 10μA_30min	Pulsed	7/30/19	170	74	96	1.04	No	No	Positive

N.A. indicates sample was not analyzed.

3.5 SUMMARY OF RATIOS OF IRON OXIDATION STATES

Table 5 shows a summary of the final ratios of $\text{Fe}^{+3}/\text{Fe}^{+2}$ for the Fe^{+2} and Fe^{+3} spiked LEU solutions. When the solution was spiked with Fe^{+2} or Fe^{+3} , the preponderance of the final oxidation state favored the original oxidation state for these experiments. Although the irradiation times were limited to 240 minutes, the experiments indicate that the presence of Fe^{+3} oxidation state predominates after longer irradiation times.

TABLE 5 Final $\text{Fe}^{+2}/\text{Fe}^{+3}$ ratios for samples initially spiked with Fe^{+2} and Fe^{+3}

Test Solution	Total Dose (Mrad)	$\text{Fe}^{3+}/\text{Fe}^{2+}$	Test Solution	Total Dose (Mrad)	$\text{Fe}^{2+}/\text{Fe}^{3+}$
	7110	0.74		7340	0.69
Fe^{2+} Spiked	1810	0.81	Fe^{3+} Spiked	5530	0.70
LEU	914	0.68	LEU	1800	0.78
				893	0.77

4 CONCLUSION

Uranyl peroxide precipitates from a uranyl sulfate solution after bombardment with low LET particles (electron, gamma, x-rays). The precipitation process is a delayed phenomenon occurring within about 24 hours after bombardment. Hydrogen peroxide is detectable immediately after irradiation. Iron ions spiked into the solution prevent precipitation. When iron is spiked, there is reduced gas production (H_2 and O_2) and hydrogen peroxide concentrations are reduced. The +2 or +3 oxidation states of iron appear to be equally effective at preventing precipitation, limiting gas production and reducing the post-irradiation hydrogen peroxide concentration. For these experiments, samples spiked with Fe^{+2} had more Fe^{+2} post-irradiation. Similarly, samples spiked with Fe^{+3} had more Fe^{+3} post irradiation. The data does indicate that with a longer irradiation time, the +3 oxidation state would be favored.

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