Micro-SHINE Uranyl Sulfate Irradiations at the Linac

Nuclear Engineering Division

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by

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MICRO-SHINE URANYL SULFATE IRRADIATIONS AT THE LINAC

ABSTRACT

Peroxide formation due to water radiolysis in a uranyl sulfate solution is a concern for the SHINE Medical Technologies process in which Mo-99 is generated from the fission of dissolved low enriched uranium. To investigate the effects of power density and fission on peroxide formation and uranyl-peroxide precipitation, uranyl sulfate solutions were irradiated using a 50 MeV electron linac as part of the micro-SHINE experimental setup. Results are given for uranyl sulfate solutions with both high and low enriched uranium irradiated at different linac powers.

1 INTRODUCTION

Work is in progress to evaluate the SHINE Medical Technologies process for producing Mo-99 for medical use from the fission of dissolved low enriched uranium (LEU). Because it can lead to precipitation of uranyl peroxide, peroxide formation due to water radiolysis in a uranyl sulfate solution is a concern for the SHINE process [1-3]. Several samples containing 2 mL of enriched uranium solution (19.8 or 93% U-235) as uranyl sulfate were irradiated at a 50 MeV electron linac as part of the micro-SHINE experimental setup. The purpose of this set of experiments was to study the effects of power density and fission on peroxide formation and uranyl-peroxide precipitation. In 2012, a set of experiments was performed with a 3 MeV Van de Graaff (VDG) accelerator, where precipitation of uranyl peroxide occurred in an irradiated uranyl-sulfate solution; however, adding a catalyst such as Fe prevented precipitation of uranyl peroxide [1]. Similar experiments were performed in 2014 and 2015 with uranyl-sulfate solutions containing 0-70 ppm Fe, and precipitation was not observed during any of the irradiations [4]. Because precipitation was not observed after irradiating samples at the VDG in 2014-2015 at doses as high as 35,000 Mrad, irradiations continued at the linac, but precipitation did not occur during the linac experiments either.

Argonne's 50-MeV electron linac was used to irradiate enriched uranyl-sulfate solutions in an effort to generate enough peroxide through the radiolysis of water to induce precipitation of uranyl peroxide. Irradiation of samples was performed in dry wells in the Argonne mini-SHINE experiment [5] by impinging the linac electron beam on a tantalum target, which was located in a dry well of the target vessel holding ~5 L of solution. Neutrons and high-energy x-rays were produced, which led to the radiolysis of water. Radiolysis produced many radicals in the water, which ultimately led to the formation of peroxide, hydrogen, and oxygen. Quartz vials containing 2 mL of enriched uranyl sulfate solution (pH 1 using sulfuric acid) were placed in the two dry wells located in the tank lid of the target solution vessel. The target solution vessel contained ~5 L of 140 g-U/L LEU uranyl sulfate solution, and sample vials were either connected to an RGA (residual gas analyzer) to measure hydrogen and oxygen with a helium cover gas or kept in

a closed quartz vial with a Pt/Pd on alumina catalyst above the solution, which recombined hydrogen and oxygen to water. A 157 g-U/L low enriched uranium (LEU, 19.8% U-235) uranyl sulfate solution was irradiated at 3, 5, and 10 kW, and a 105 g-U/L high enriched uranium (HEU, 93% U-235) uranyl sulfate solution was irradiated at 1, 3, 5, and 10 kW. The LEU and HEU solutions did not contain Fe (below detection limits for inductively coupled plasma-mass spectrometry analysis), but the HEU stock solution contained peroxide that was not fully removed during preparation of the uranyl sulfate.

The primary products from water radiolysis are hydrogen and hydrogen peroxide, and oxygen is a decomposition product of hydrogen peroxide. The initial interaction of an electron with a water molecule generates the following byproducts: ionized water (H_2O^+), excited water (H_2O^*), and an electron (e^-) [6,7]. It has been shown that the electron quickly (10^{-12} sec) becomes solvated (e^-_{aq}) [6,7]. Reactions involved in the radiolysis of water are given below [6,7].

Interactions with electron

Radicals dissociate to further form radical and ionic species

Production of hydrogen

Production of hydrogen peroxide and decomposition to oxygen

Back reactions and the formation of water

2 EXPERIMENTAL

Micro-SHINE experiments were performed in two ways. In the first way, the uranyl sulfate solution was placed in a closed tube with catalyst contained above the solution to recombine the hydrogen and oxygen generated by radiolysis during irradiation. This method has the advantage of allowing longer high-power irradiations without the concern of drying out the sample solution through radiolysis and evaporation of water, but does not allow the collection of data on hydrogen and oxygen generation rate. In the second method, a He stream runs through the tube, passing the gas into a gas analysis system for measuring hydrogen and oxygen generation.

Figure 1 shows this micro-SHINE experimental setup. It consists of capsules containing 2 mL of aqueous uranyl-sulfate solution. Each capsule is positioned in a dry well near the center of the mini-SHINE target solution vessel. The solution experiences a neutron flux, which causes uranium to fission. Helium flows into the micro-SHINE capsule, sweeping the headspace gas from the capsule. Flow is controlled by an OMEGA FMA 5502 Mass Flow Controller. The gas is analyzed by a Pfeiffer Omni-Star Prisma Plus QMG220 Residual Gas Analyzer (RGA), shown in Figure 2. The gas stream flows into the gas collection system.

FIGURE 1 Micro-SHINE experimental setup

FIGURE 2 RGAs used in the micro-SHINE and mini-SHINE experiments

The RGA was calibrated by means of standards prepared from a primary standard procured from a vendor and certified with an accuracy of $\pm 5\%$. The instrument was calibrated at the pressures produced during the experiment. Calibration of hydrogen, oxygen, nitrogen, and argon was performed by the internal standard method. Xenon was added as a spike in the helium purge gas and served as the internal standard. A response factor (RF) was generated using

$$RF = \frac{A_x \cdot C_{is}}{A_{is} \cdot C_x} \quad (1)$$

and the concentration of the analyte (X) was determined from

$$X = \frac{A_x}{RF} \cdot \frac{C_{is}}{A_{is}} \quad (2)$$

where C_x is the concentration of the calibration standard, A_x is the area response of the calibration standard in %, C_{is} is the concentration of the internal standard, and A_{is} is the area response of the internal standard.

The calibration was verified with a check standard and was acceptable within $\pm 10\%$ of the true value. Hydrogen has a detection limit of 50 ppm, and oxygen has a detection limit of 30 ppm. The equation to determine the micromoles of gas was based on the volumetric flow through the capsule multiplied by the time for an analytical measurement:

$$n(\text{moles}) = \frac{P \cdot V}{R \cdot T} \quad (3)$$

where P is the measured pressure (atm), V (L) is volume calculated from flow rate times time interval, R (0.08205 L atm/mol K) is the universal gas constant, and T (K) is the temperature.

3 RESULTS AND DISCUSSION

Table 1 provides the experimental conditions and gas production rates for irradiations performed using the LEU and HEU uranyl-sulfate solutions. The LEU results show a delayed release of oxygen due to the formation of peroxide and slow decomposition to oxygen and water and/or the higher solubility in solution compared to hydrogen; however, once steady state was reached, the H₂-to-O₂ ratio remained at 3.6 but quickly decreased to 3.2 once the linac power was increased from 5 to 10 kW. For the HEU solution, more O₂ was observed initially, creating a H₂-to-O₂ ratio less than 1. The HEU results are consistent with the fact that peroxide was still present in the HEU solution prior to being irradiated. The peroxide was not completely removed during solution preparation. Nonetheless, the results from the final HEU irradiation at 10 kW indicate that all of the excess peroxide had been destroyed because the H₂-to-O₂ ratio increased to 3.

TABLE 1 Conditions and results from micro-SHINE linac irradiations

Date	Enrichment	Concentration (g-U/L)	LINAC		Total H ₂ (μmoles)	Total O ₂ (μmoles)	H ₂ - to-O ₂ Ratio	Irradiation Time (min)	H ₂ Rate (μmoles/min)	O ₂ Rate (μmoles/min)
			Power (kW)							
12/02/15	LEU	157	3.2		20	4	5.6	71	0.28	0.05
12/14/15	LEU	157	3.2		38	10	3.6	120	0.31	0.09
12/14/15	LEU	157	5		35	10	3.6	59	0.32	0.16
12/14/15	LEU	157	10		13	3.9	3.2	13	0.95	0.30
12/04/15	HEU	105	1		12	72	0.2	75	0.15	0.96
12/04/15	HEU	105	3		13	77	0.2	24	0.53	3.2
12/16/15	HEU	105	3		56	310	0.2	89	0.63	3.4
12/16/15	HEU	105	5		110	130	0.9	90	1.2	1.4
12/16/15	HEU	105	10		34	11	3.0	14	2.4	0.77

To calculate the fission power in solution, we used the following method. The number of fissions for the duration of the experiment was calculated from the gamma counting results for several fission products. We found that Zr-95, Mo-99, Ru-103, Ba-140, and Te-132 provided consistent and reliable signals for fission rate and fission power calculations. The number of atoms for a particular isotope (N) was calculated from the formula:

$$N = \frac{A \times T_{1/2}}{\ln(2)} \quad (4)$$

where A is activity of a particular isotope at the end of bombardment (EOB) in disintegrations per second, and T_{1/2} is the half-life of the isotope in seconds. From Eq. 4, using the fission yield for a particular isotope, we can calculate the total number of fissions. Because each fission produces ~200 MeV of energy, we can calculate the total fission energy deposited in

the solution by multiplying the number of fissions by 200 MeV (3.2×10^{-11} J). Results of the calculations are presented in the tables below.

Figures 3 and 4 show the gas concentration results for the first LEU micro-SHINE irradiation performed at 3.2 kW linac power. There was an air leak during this experiment, but the oxygen present in the system from the air leak was subtracted from the total micromoles of oxygen measured (based on the nitrogen content in the gas stream). As was observed during the phase 1 mini-SHINE experiments, there was a delay in oxygen exiting the system, which is why the final H₂:O₂ ratio was above 2 [5]. This sample was irradiated twice at ~3.2 kW power, but the hydrogen-to-oxygen ratio never decreased to 2. Table 2 shows the gamma counting results for the two LEU samples irradiated with and without a catalyst. Also presented in the table is the calculated fission power in solution based on isotopes with clean gamma peaks and decay behavior.

FIGURE 3 Gas concentration and linac power as a function of time for LEU micro-SHINE irradiation

FIGURE 4 Total μmoles of O₂ and H₂ as a function of time for LEU micro-SHINE irradiation

TABLE 2 Gamma counting results for two LEU samples irradiated on 12/02/15 with and without catalyst. Counting 1-sigma errors are $\pm 5\%$. Also shown in the table is the fission power calculated from the activities of five isotopes (Zr-95, Mo-99, Ru-103, Ba-140, and Te-132). For a variety of reasons, other isotopes did not provide consistent fission energies; for example, iodine isotopes were not used to draw any conclusions due to the volatility of iodine in acidic solution and the elapsed time between EOB and gamma counting.

Nuclide	EOB Total Activity (μCi) of LEU with Catalyst	EOB Total Activity (μCi) of LEU without Catalyst	Yield (%)	Half-life of Isotope (s)	Fission Energy (J) for LEU with Catalyst	Fission Energy (J) for LEU without Catalyst
Zr-95	1.2	1.3	6.5	5.53E+06	174	189
U-237	4	8.4				
Np-239	56	69				
Mo-99	26	30	6.13	2.38E+05	172	199
Ru-103	0.9	1	3.10	3.39E+06	168	187
I-132	16	18				
Te-131m	4.6	5.5				
I-131	4.1	4.7				
I-133	98	110	6.59			
Ba-140	6	6.9	6.31	1.10E+06	179	206
Ce-143	51	57				
Zr-97	87	99				
Tc-99m	27	31				
Te-132	19	22	4.28	2.77E+05	210	243
Rh-105	10	12				
Sn-125	0.1	0.3	0.03			
Sb-127	0.4	0.5				
Nd-147	3	2.6				
Pm-151	3.1	4	0.42			

Figures 5–8 show the gas concentration results for the LEU micro-SHINE irradiation performed at 3, 5, and 10 kW linac power. As before, an air leak occurred during this set of irradiations, so the oxygen present in the system from the air leak was subtracted from the total micromoles measured (based on the nitrogen content in the gas stream). As was observed during the mini-SHINE experiments, a delay in oxygen exiting the system kept the H_2/O_2 ratio 2 or above [5]. The hydrogen-to-oxygen ratio at 3 kW was 3.6 after 122 min, and it reached a steady state at 5 kW with a ratio of 2. When the linac power was increased to 10 kW, the ratio increased to 3.2. The hydrogen and oxygen production rates increased as the linac power was increased, and the rates also indicated that steady state was reached in going from 3 to 5 kW linac power for oxygen while hydrogen had already reached steady state. The hydrogen production rate only increased from 0.31 $\mu\text{mol}/\text{min}$ to 0.32 $\mu\text{mol}/\text{min}$ in going from 3 to 5 kW linac power, whereas the oxygen production rate increased from 0.09 $\mu\text{mol}/\text{min}$ to 0.16 $\mu\text{mol}/\text{min}$ under the same condition. Table 3 shows the gamma counting results for the two LEU samples irradiated with and without a catalyst. Also presented in the table is the calculated fission power in solution

based on isotopes with clean gamma peaks and decay behavior. Activities are higher for the LEU sample with a catalyst because the sample was also irradiated on 12/16/15.

FIGURE 5 Gas concentration and linac power as a function of time for later LEU micro-SHINE irradiation

FIGURE 6 Total μmoles of O₂ and H₂ as a function of time at 3 kW linac power for later LEU micro-SHINE irradiation

FIGURE 7 Total μmoles of O_2 and H_2 as a function of time at 5 kW linac power for later LEU micro-SHINE irradiation

FIGURE 8 Total μmoles of O_2 and H_2 as a function of time at 10 kW linac power for later LEU micro-SHINE irradiation

TABLE 3 Gamma counting results for two LEU samples irradiated on 12/14/15 with and without catalyst. Counting 1-sigma errors are $\pm 5\%$. Also shown in the table is fission power calculated from the activities of five isotopes (Zr-95, Mo-99, Ru-103, Ba-140, and Te-132). For a variety of reasons, other isotopes did not provide consistent fission energies; for example, iodine isotopes were not used to draw any conclusions due to the volatility of iodine in acidic solution and the elapsed time between EOB and gamma counting.

Nuclide	EOB Total Activity (μCi) of LEU with Catalyst ^a	EOB Total Activity (μCi) of LEU without Catalyst	Yield (%)	Half-life of Isotope (s)	Fission Energy (J) for LEU with Catalyst ^a	Fission Energy (J) for LEU without Catalyst
Zr-95	6.5	3	6.5	5.53E+06	950	440
U-237	17	10				
Np-239	230	150				
Mo-99	120	66	6.132	2.38E+05	800	440
Ru-103	4.8	2.3	3.103	3.39E+06	900	430
I-132	72	40				
Te-131m	16	13				
I-131	21	11				
I-133	300	260				
Ba-140	33	15	6.314	1.10E+06	980	450
Ce-143	190	120				
Zr-97	260	210				
Tc-99m	120	65				
Te-132	76	42	4.276	2.77E+05	840	460
Rh-105	38	27				
Sn-125	0.9	0.4				
Sb-127	1.9	1				
Nd-147	12	7.6				
Pm-151	11	6.3				

^a This sample was irradiated once on 12/14 and again on 12/16/2015. The activities were measured after the second irradiation.

Figures 9-11 show the gas concentration results for the HEU micro-SHINE irradiations performed on 12/04/2015 at 1 and 3 kW linac power. The hydrogen-to-oxygen ratio at 1 and 3 kW was only 0.2, which suggests that peroxide was present in solution before irradiation. Additionally, after sitting on the benchtop for several weeks, a solid formed in the non-irradiated stock solution, most likely uranyl peroxide. Oxygen production rates were extremely high for the irradiations performed at 1 and 3 kW linac power. The hydrogen production rates at 3 kW were about 65% higher for the HEU solution compared to the LEU solution. Table 4 shows the gamma counting results for the two HEU samples irradiated with and without a catalyst. Also presented in the table is the calculated fission power in solution based on isotopes with clean gamma peaks and decay behavior.

FIGURE 9 Gas concentration and linac power as a function of time for HEU micro-SHINE irradiation

FIGURE 10 Total μmoles of O_2 and H_2 as a function of time at 1 kW linac power for HEU micro-SHINE irradiation

FIGURE 11 Total μmoles of O_2 and H_2 as a function of time at 3 kW linac power for HEU micro-SHINE irradiation

TABLE 4 Gamma counting results for two HEU samples irradiated on 12/04/15 with and without catalyst. Counting 1-sigma errors are $\pm 5\%$. Also shown in table is fission power calculated from the activities of five isotopes (Zr-95, Mo-99, Ru-103, Ba-140, and Te-132). For a variety of reasons, other isotopes did not provide consistent fission energies; for example, iodine isotopes were not used to draw any conclusions due to the volatility of iodine in acidic solution and the elapsed time between EOB and gamma counting.

Nuclide	EOB Total Activity (μCi) of HEU with Catalyst	EOB Total Activity (μCi) of HEU without Catalyst	Yield (%)	Half-life of Isotope (s)	Fission Energy (J) for HEU with Catalyst	Fission Energy (J) for HEU without Catalyst
Zr-95	1.3	1.3	6.5	5.53E+06	190	190
U-237	0.2	0.2				
Np-239	1.5	2.4				
Mo-99	29	28	6.1	2.38E+05	190	190
Ru-103	1	1	3.1	3.39E+06	190	190
I-132	16	17				
Te-131m	4.6	4.8				
I-131	2	3.1				
I-133	45	64				
Ba-140	7.3	7.1	6.3	1.10E+06	220	210
Ce-143	58	55				
Zr-97	100	97				
Tc-99m	30	30				
Te-132	19	18	4.3	2.77E+05	210	200
Rh-105	10	9.8				
Sb-127	0.4	0.4				
Nd-147	2.7	2.5				
Pm-151	3.6	3.4				

Figures 12–15 show the gas concentration results for the HEU micro-SHINE irradiations performed on 12/16/2015 at 3, 5, and 10 kW linac power. The hydrogen-to-oxygen ratio at 3 and 5 kW was still below 2 at 0.2 $\mu\text{mol}/\text{min}$ and 0.9 $\mu\text{mol}/\text{min}$, which again suggests that peroxide was present in solution before irradiation. At 10 kW linac power, the excess peroxide in solution was destroyed because the hydrogen-to-oxygen ratio reached 3.0. Oxygen production decreased over the series of three continuous irradiations decreasing from 3.45 $\mu\text{mol}/\text{min}$ at 3 kW to 1.43 $\mu\text{mol}/\text{min}$ at 5 kW and eventually reaching a production rate of 0.77 $\mu\text{mol}/\text{min}$ at 10 kW. The hydrogen production rates almost doubled each time the power was increased, increasing from 0.63 $\mu\text{mol}/\text{min}$ to 1.24 $\mu\text{mol}/\text{min}$ when the power was increased from 3 kW to 5 kW, and from 1.24 $\mu\text{mol}/\text{min}$ to 2.36 $\mu\text{mol}/\text{min}$ when power was increased from 5 kW to 10 kW. Table 5 shows the gamma counting results for a single HEU sample irradiated without a catalyst. Also presented in the table is the calculated fission power in solution based on isotopes with clean gamma peaks and decay behavior.

FIGURE 12 Gas concentration and linac power as a function of time for later HEU micro-SHINE irradiation

FIGURE 13 Total μmoles of O_2 and H_2 as a function of time at 3 kW linac power for later HEU micro-SHINE irradiation

FIGURE 14 Total μmoles of O_2 and H_2 as a function of time at 5 kW linac power for later HEU micro-SHINE irradiation

FIGURE 15 Total μmoles of O_2 and H_2 as a function of time at 10 kW linac power for later HEU micro-SHINE irradiation

TABLE 5 Gamma counting results for a single HEU sample irradiated on 12/16/15 without a catalyst. Counting 1-sigma errors are $\pm 5\%$. Also shown in table is fission power calculated from the activities of five isotopes (Zr-95, Mo-99, Ru-103, Ba-140, and Te-132). For a variety of reasons, other isotopes did not provide consistent fission energies; for example, iodine isotopes were not used to draw any conclusions due to the volatility of iodine in acidic solution and the elapsed time between EOB and gamma counting.

Nuclide	EOB Total		Half-life of Isotope (s)	Fission Energy (J)
	Activity (μCi)	Yield (%)		
Zr-95	8.4	6.5	5.53E+06	1200
U-237	1.2			
Np-239	16			
Mo-99	180			
Ru-103	6.4			
I-132	110	6.3	1.10E+06	1300
Te-131m	32			
I-131	25			
I-133	530			
Ba-140	43			
Ce-143	350	4.3	2.77E+05	1200
Zr-97	590			
Tc-99m	190			
Te-132	110			
Rh-105	63			
Sb-127	3.1	17		
Nd-147	17			
Pm-151	23			

TABLE 6 Summary of gas generation and yields for the experiments described above. Zr-95, Mo-99, Ru-103, Ba-140, and Te-132 fission energies were averaged to determine the fission energy for each micro-SHINE sample.

Sample	Fission Energy (J)	Hydrogen Produced (μ mole)	Oxygen Produced (μ mole)	Hydrogen Yield (ml/W•s)	Oxygen Yield (ml/W•s)	Hydrogen Yield (mol/kWh)	Oxygen Yield (mol/kWh)
120215 LEU no catalyst	200	41	8.2	0.0045	0.00090	0.72	0.14
121415 LEU no catalyst	440	92	27	0.0046	0.0013	0.75	0.22
121415 HEU no catalyst	200	25	150	0.0028	0.017	0.45	2.8
121615 HEU no catalyst	1200	200	450	0.0037	0.0082	0.59	1.3

Hydrogen yields measured in this work can be compared with the literature data for the hydrogen yield measured from a uranyl nitrate solution in an aqueous homogeneous reactor, which generated a yield of 0.55 mol/kWh [8]. For the LEU irradiations, we measured hydrogen yields of 0.72 and 0.75 mol/kWh, which are higher than that for the fissioning uranyl nitrate solution [8]. The higher value can be explained by the presence of X-ray radiolysis. In our experiment, neutrons were produced in the Ta target from the (γ ,n) reaction. A large portion of the bremsstrahlung X-rays entered the solution and generated radiolysis products in addition to fission fragment-induced radiolysis. This explanation is also supported by the lower gas generation yields for the HEU samples where fission fragment-induced radiolysis is dominant.

4 CONCLUSION

Unfortunately for a scientific study but encouraging for the SHINE system, we could not induce precipitation of uranyl peroxide under the conditions discussed above using our electron linac. We were also unable to make comparisons on peroxide formation as a function of fission or power density. The plan for FY 2017 is to perform similar micro-SHINE irradiations in quartz vessels and Zircaloy vessels using an internal catalyst to allow for much longer irradiation times without drying out the sample. To achieve power densities in solution equal to and significantly higher than those envisioned for the SHINE target solution, we will vary the enrichment of the U-235. The uranium will also have low amounts of iron impurities. If we can induce precipitation, we will examine the effects of temperature, fission, power density, Fe concentration, and time on formation of a uranyl peroxide precipitate.

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