Fission Induced Radiolysis of Uranyl Sulfate Solutions

Chemical and Fuel Cycle Technologies Division

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1. INTRODUCTION

At Argonne National Laboratory, an experimental pilot facility is being tested for the production of the medical isotope molybdenum-99 (^{99}Mo). AMORE (Argonne Molybdenum Research Experiment) [1] is an experimental pilot facility in which a 40 MeV electron beam from the LINAC strikes a depleted uranium (DU) target. The target generates high energy neutrons, which are thermalized in an 18-liter uranyl sulfate solution of low enriched uranium (LEU). Thermalized neutrons fission the uranium-235 (^{235}U) to produce ^{99}Mo as well as many other fission products. The ^{99}Mo is recovered from the uranium solution and purified. The goal of our work is to reduce the use of highly enriched uranium (HEU) for the production of this isotope.

To better understand radiolytic gas generation in the AMORE pilot facility, a series of experiments called mini-AMORE were performed to ascertain accurate rates of hydrogen and oxygen generation that will occur due to the radiolysis of water during ^{99}Mo production. We also made observations of the solution for signs of uranyl peroxide precipitation; hydrogen peroxide is also a radiolysis product. The mechanism for the radiolysis of water will be discussed below.

For this series of experiments, a 2 mL uranyl-sulfate solution was placed inside a quartz vial. The vial was inserted into an aluminum capsule for secondary containment. The assembly was then inserted into the dry well of the AMORE target solution vessel (TSV) and irradiated. The solution experienced neutron/photon flux from the fissioning of LEU in the TSV and from the DU target that caused it to fission. This experiment is a continuation of similar experiments conducted in 2017 and 2018 in which 0.1 M sulfuric acid was present in the TSV [2].

In the current study, two uranyl-sulfate solutions were tested with different uranium enrichments: LEU at 19.8% ^{235}U and HEU at 92.6% ^{235}U . These solutions were irradiated with an LEU sulfate solution in the TSV, which created a higher neutron flux in the sample and more fissions than the earlier experiments. Approximately 200 ppm Fe, as FeSO_4 , was added to the solutions to prevent precipitation of uranyl peroxide [3]. We determined the hydrogen and oxygen composition of the radiolytically generated gases that evolved from these irradiated solutions, tested the pH change after irradiation, and examined them for the presence of uranyl peroxide precipitate after each irradiation.

Molecular hydrogen (H_2), hydrogen peroxide (H_2O_2), and oxygen (O_2) are generated by the radiolysis of water. The initial stage of the process begins with the formation of a solvated electron and the ionized and excited forms of the water molecule ($\text{e}^- (\text{aq})$, H_2O^+ , $\text{H}_2\text{O}^\bullet$) created by incident radiation. Radical fragments combine to generate the molecular species H_2 and H_2O_2 or to reform water [4]. The recombination of other radical fragments and the decomposition of H_2O_2 generate O_2 . In the mini-AMORE experiment, we have correlated the relationship of radiolytic gas generation and fission power.

Radiolytically produced H_2O_2 reacts with the uranyl ion to form uranyl peroxide, which has limited solubility and can precipitate, as shown in equation 1.1 [5]. Uranyl peroxide precipitation must be avoided during the proposed ^{99}Mo production process because it could create a high-concentration phase of ^{235}U that can lead to a criticality event. In addition, solid particles in solution transfer lines can lead to clogging and impair the extraction and separation process, and/or the precipitate could form an unequal distribution of uranium in the TSV solution and affect the efficiency of the ^{99}Mo production.

It should be noted that uranyl peroxide precipitate forms only in conditions where its concentration exceeds the solubility limit. Early experiments [6] and modeling of the ^{99}Mo process showed that the

conditions that affect the production and precipitation of uranyl peroxide are temperature, uranyl sulfate concentration, ferrous iron concentration, and H_2O_2 production rate. In those experiments, uranyl sulfate solutions were titrated with H_2O_2 until the peroxide of uranium precipitated. The precipitate was confirmed by x-ray diffraction (XRD) analysis to be meta-studite. Uranyl peroxide also decomposes from heat and energy. Two mechanisms have been proposed by Silverman et al. for the decomposition of uranyl peroxide back to the uranyl ion UO_2^{2+} . See Equations 1.2, 1.3 and 1.4 [0].

Later experiments performed at the 3MeV Van de Graff accelerator examined the radiolytic effects of low linear energy transfer (LET) particles on uranyl sulfate solutions. In these experiments, both solid and salt-based catalysts were tested for their effectiveness in preventing precipitation of uranyl peroxide. We saw that copper sulfate, potassium iodide, and ferric and ferrous sulfate salts were all effective at preventing precipitation. Even pieces of 304 stainless steel prevented it.

More recently, experiments showed that the addition of iron salts to the solution prevented the precipitation of uranyl peroxide in low LET irradiations [3]. In these experiments, uranyl sulfate solutions were irradiated in the presence and absence of iron salt $\text{Fe}_x(\text{SO}_4)_x$. Figure 1.1 shows two uranyl sulfate solutions irradiated under the same conditions at the Van de Graff accelerator with a 3 MeV electron beam [5]. The top solution in Figure 1.1 was spiked with $169 \mu\text{g/g Fe}^{2+}$ and shows no sign of a precipitate, while the bottom sample, which was not spiked, contains a uranyl peroxide precipitate. No visible precipitate was observed in solutions spiked with iron, while the un-spiked samples showed either immediate or delayed precipitate formation. The effectiveness of Fe^{2+} to decompose H_2O_2 may be reduced because its concentration is reduced by the oxidation to Fe^{3+} .

Those experiments showed that an active source of Fe^{2+} should be in solution. On average, a post-irradiated solution had a $\text{Fe}^{2+}/\text{Fe}^{3+}$ ratio of 0.74 to 1.

Figure 1.1. Two uranyl sulfate solutions irradiated under the same conditions at the Van de Graff accelerator with a 3 MeV electron beam [5]. The top solution was spiked with $169 \mu\text{g/g Fe}^{2+}$ and shows no precipitate. The bottom sample was not spiked, and a cloudy precipitate is evident.

2. MATERIALS AND METHODS

2.1 Experimental Setup

Drawings for the mini-AMORE capsule are shown in Figure 2.1. The mini-AMORE assembly consists of a threaded quartz vial that screws into an aluminum cap with fittings attached. The cap has a septum that seals the top of the vial. Two 1/16-in stainless steel tubes pierce the septum to allow a sweep gas in and out of the vial. The quartz tube–cap assembly screws into an aluminum capsule that provides secondary containment for the solution. The cap and capsule are sealed with an O-ring.

Figure 2.1 Drawings of the capsule for mini-AMORE irradiations.

A 2 mL solution containing uranyl sulfate, ferrous sulfate, and sulfuric acid (pH~1) is placed into the quartz vial, as shown in Figure 2.2. The vial is screwed onto the cap, and the aluminum capsule is affixed as shown in Figure 2.3.

The assembly was inserted into a dry well of the AMORE TSV shown in Figure 2.4. The assembly was positioned so the solution was located near the DU target at the center of the TSV, where the maximum neutron flux occurs. All irradiations were conducted at 40 MeV beam energy.

Figure 2.2. Quartz vial with 2mL of uranyl-sulfate solution.

Figure 2.3. Aluminum secondary container.

Figure 2.4. AMORE target solution vessel with dry wells and target sleeve.

Figure 2.5 shows the experimental setup with the mini-AMORE capsule positioned inside the dry well of the TSV and the sweep gas lines connected to the gas analyzer (RGA). The gas inlet side of the mini-AMORE assembly is connected to He/Xe sweep gas controlled with a calibrated OMEGA FMA 5400-ST mass flow controller. The gas outlet side of the assembly is connected to an RGA (Pfeiffer OMNI-STAR

GSD320) equipped with a 1-200 AMU PrismaPlus QMG220 mass spectrometer. The sweep gas flows in and out of the tube, carrying the radiolysis gases—hydrogen and oxygen—to the RGA analytical instrument, which samples approximately 5 mL/min. The gas finally enters the gas collection system where it is stored. The sweep gas cylinder and the RGA are located in a lab adjacent to the LINAC cell where the irradiations occur, because the radiation inside the cell causes damage to the sensitive equipment and unnecessarily activates the sweep gas cylinder.

Figure 2.5. Experimental setup showing the mini-AMORE capsule positioned inside the dry well of the TSV and the sweep gas flow path into and out of the capsule. The gas stream is sampled by the gas analyzer (RGA) and exhausts to the gas collection system.

2.2 Gas Data Calculations

A single-point calibration standard introduced at the sampling pressure was used to calibrate the RGA. Xenon at 1.044% was used as an internal standard. Primary calibration standards with an uncertainty of $\pm 2\%$ were purchased from Airgas. Working standards were made by diluting the primary standard with helium as the diluent. Calibration checks performed before the experiments were within $\pm 10\%$ of the expected values.

Equation 2.2.1 was used to calculate a response factor (RRF) for each analyte:

$$\text{RRF} = \text{IC}_{\text{analyte}} \times [\text{IS}] / \text{IC}_{\text{IS}} \times [\% \text{Analyte}] \quad (2.2.1)$$

where $\text{IC}_{\text{analyte}}$ and IC_{IS} are the ion current of the analyte and internal standard, respectively, and $[\% \text{Analyte}]$ and $[\text{IS}]$ are the concentration of the analyte and internal standard, respectively. The analyte concentration during the experiments was calculated using equation 2.2.2.

$$[\% \text{Analyte}] = \text{IC}_{\text{analyte}} \times [\text{IS}] / \text{IC}_{\text{IS}} \times \text{RRF} \quad (2.2.2)$$

Background levels of nitrogen, oxygen, and hydrogen were determined prior to the irradiation and subtracted from the data using equation 2.2.3. The oxygen values reported were corrected by subtracting a value based on the amount of nitrogen detected, which is related to the ratio of nitrogen to oxygen in air (0.2683):

$$[\% \text{Oxygen Corrected}] = [\% \text{Oxygen}] - [\% \text{Nitrogen}] \times 0.2683 \quad (2.2.3)$$

The system is a once-through system with a He/Xe sweep gas flowing at a constant rate by setting the mass flow controller. The RGA samples the sweep gas as it exits the system, scans the atomic mass unit for each analyte of interest, and generates a plot of concentration vs. time. After the concentration of each gas was determined, the micro-moles (μmoles) of the analyte were calculated from the concentration data using equation 2.2.4. The flow rate, corrected for the additional gas generated and analysis time, is used to determine the volume of gas at the sampling time:

$$\mu\text{mol} = [\text{PV}/\text{RT}] \times [\% \text{Analyte}/100] \times 10^6 \quad (2.2.4)$$

where μmol = micromoles, P (atm) = analysis pressure, V (L) = corrected gas flow rate $\times$ time, R (L atm/mol K) = gas constant, and T ($^{\circ}\text{K}$) = analysis temperature

2.3 Gamma Analysis and Fissions

Table 2.1. shows the isotopes used to determine the number of fissions, their half-life, gamma energy, and percent yield. Samples were counted on an ORTEC HpGe gamma detector and processed using GammaVision software. Count data were decay-corrected to the time the irradiation was stopped, the end of bombardment (EOB). From the gamma counting data of ^{95}Zr , ^{99}Mo , ^{103}Ru , ^{147}Nd and ^{140}Ba in the solution at EOB, the total number of fissions were calculated based on their percent yield. These isotopes were chosen for several reasons. They have relatively long half-lives, so the solution could be allowed to “cool down” for several days after an irradiation. This allowed the very short-lived and energetic isotopes time to decay before the sample was retrieved. Also, the relatively long half-lives of these isotopes allowed for neglecting their decay during irradiation, and their percent-yield per fission is relatively high, leading to a higher abundance and good counting statistics. In general, the energy chosen for analysis was based on highest percentage of gamma emissions per decay for that isotope. However, in the cases of ^{99}Mo and ^{140}Ba , other gamma energies were chosen because of interfering peaks from other fission products. It is assumed that the number of fissions is constant with beam energy (kWh), so fissions per experimental segments were determined by multiplying the total fissions by the ratio of the beam energy for the segment to the total beam energy of the entire experiment: kWh (segment)/kWh (total).

Table 2.1. Isotope, half-life, gamma energy and percent yield.

Isotope	Half-Life (Days)	Gamma Energy (keV)	Fission Yield (% per Fission)
Zr-95	64.02	756.73	6.50
Mo-99	2.75	181.06	6.13
Ru-103	39.26	496.95	3.10
Nd-147	10.98	91.17	2.23
Ba-140	12.752	423.72	6.31

2.4 pH Analysis

Sample pH was determined using an Accumet AB150 meter with a Thermo Fisher Scientific double junction pH electrode J9110DJWP calibrated between pH 1 and 4.

2.5 Temperature Data

The solution temperature could not be measured directly in this experiment. A thermocouple was affixed with Kapton[®] tape to the outside of the aluminum secondary containment capsule (Figure 2.3). Temperature data is thus comparative for the three experiments and the experimental segments.

3. EXPERIMENTAL DATA AND DISCUSSION

3.1 General Parameters

Table 3.1. shows the general parameters for the three sample irradiations: sample size, sample type, uranium concentration, ^{235}U enrichment, ferrous iron (Fe^{2+}) concentration, cumulative LINAC beam energy delivered to the target, and mass loss due to evaporation and, to a lesser extent, radiolysis. The intent was to irradiate only two solutions, the LEU and HEU. It was found that during the first irradiation on November 21, 2019, the solution vessel, which should have contained eighteen liters of uranium sulfate solution, was only 1/3 full. Understanding that this would cause a lower neutron flux than desired, the experiment was repeated. After the 11/21/19 irradiation, the catalyst pump used to circulate the headspace gas of the solution vessel and assist in the recombination of hydrogen and oxygen failed. It was replaced with a pump that had a lower volumetric flow rate. Since the rate of hydrogen production is directly proportional to beam power, and the rate of H_2 and O_2 recombination depends on flow rate through the catalyst, the lower flow meant limiting the maximum beam power for the next two experiments to 12.5 kW.

Table 3.1. General parameters for the three sample irradiations.

Irradiation Date	Sample Type	Sample Size (g)	Uranium Concentration (g-U/L)	U-235 Enrichment (% ^{235}U)	Fe^{2+} (mg/L)	Beam Energy (kWh)	Loss to Evaporation (g)
11/21/19	LEU, Fe^{2+} spiked	2.6719	240	19.7	229	71.7	0.3046
8/6/20	LEU, Fe^{2+} spiked	2.5136	240	19.7	233	54.9	0.2179
3/25/21	HEU, Fe^{2+} spiked	2.9677	175	92.6	199	46.3	0.2795

Table 3.2. shows the gamma counting data in μCi for the experiments, including the uncertainty ($\pm \mu\text{Ci}$) and duplicate (DUP) percent difference (% D). The samples were removed from the experimental setup three to four days after the EOB. The samples were weighed to determine mass loss. Aliquots were taken in duplicate a day or two after removal and counted on the gamma detector.

Table 3.2. Gamma counting data.

Isotope	Irradiation 11/21/19 (μCi)	Uncertainty (μCi)	DUP (% D)	Irradiation 11/21/19 (μCi)	Uncertainty (μCi)	DUP (% D)	Irradiation 11/21/19 (μCi)	Uncertainty (μCi)	DUP (% D)
Zr-95	33.5	$\pm$ (1.6)	4%	24.9	$\pm$ (0.4)	1%	58.9	$\pm$ (0.3)	0.2%
Mo-99	793	$\pm$ (143)	4%	535	$\pm$ (143)	0.1%	1305	$\pm$ (237)	0.6%
Ru-103	30.5	$\pm$ (1.8)	2%	18.6	$\pm$ (0.3)	1%	44.6	$\pm$ (0.2)	0.9%
Nd-147	67.2	$\pm$ (3.6)	4%	43.7	$\pm$ (1.9)	2%	104	$\pm$ (1.5)	0.7%
Ba-140	168	$\pm$ (43)	5%	108	$\pm$ (10)	2%	262	$\pm$ (27)	0.7%

Table 3.3 shows the number of fissions calculated from the gamma activity of the isotopes used and the relative standard of deviation (%RSD). The amount of each isotope is determined from the gamma activity, and, based on the percent yield per fission, the total fissions are calculated.

Table 3.3 Fissions calculated from the gamma activity each isotope.

Isotope	11/12/19 Irradiation Fission calculated from activity	8/6/20 Irradiation Fission calculated from activity	3/25/21 Irradiation Fission calculated from activity
Zr-95	1.56E+14	1.16E+14	2.74E+14
Mo-99	1.67E+14	1.13E+14	2.76E+14
Ru-103	1.79E+14	1.09E+14	2.62E+14
Nd-147	1.54E+14	1.00E+14	2.38E+14
Ba-140	1.56E+14	1.00E+14	2.45E+14
%RSD	6.6%	6.7%	6.6%

Table 3.4 shows the total gas production for H₂ and O₂, total fissions, and fission power for the three experiments. The total fissions were determined from the average calculated from the isotopes shown in Table 3.3.

Table 3.4. Total production of H₂ and O₂, total fissions, fission energy and average fission power.

Irradiation Date	Total H ₂ (μ mol)	Total O ₂ (μ mol)	Total Fissions	Fission Energy (Joule)	Average Fission Power (Watts)
11/21/19	482	145	1.63E+14	5.21E+03	2.30E-01
8/6/20	291	111	1.08E+14	3.45E+03	1.55E-01
3/25/21	706	323	2.59E+14	8.29E+03	3.84E-01

3.2 Irradiation November 21, 2019

Table 3.5 shows the three experimental segments for the 11/21/19 irradiation: the time spent at an average beam power, beam energy, fission power density, and gas production of H₂ and O₂. The plot in Figure 3.1 shows beam power and hydrogen and oxygen measurements for the three segments of the irradiation. The average beam power for the three segments was 4.84, 12.4 and 17.2 kW, respectively.

Segment one shows a 70-minute delay between the start of H₂ production and that of O₂. Previous experiments [5] with irradiating uranyl sulfate solutions show that hydrogen evolves before oxygen, and it is assumed that O₂ has a greater solubility in the solution than H₂, which would cause a slight delay until oxygen saturates the solution and is evolved. The initial production of peroxides prior to their decomposition adds to the delay, but these two factors cause a delay of only several minutes. Assuming that the primary source of oxygen evolution is the decomposition of H₂O₂ or uranyl peroxide in these solutions, the long delay seen in this experiment indicates that the H₂O₂ being generated is not decomposing to O₂ to a detectable level. Peroxide is increasing in concentration and reacting with the UO₂²⁺ ion to form uranyl peroxide, thus trapping oxygen in solution as peroxides. The overall H₂/O₂ ratio is 12:1 for this segment, far greater than the 2:1 which would be expected during water radiolysis. In uranyl sulfate solutions, it is expected that H₂O₂ is being generated by water radiolysis at a constant rate proportional to the power input. It would also decompose by heat and radiolysis. Similarly, the H₂O₂

would react with the UO_2^{2+} ion to form uranyl peroxide and would decompose due to heat and radiolysis. Balanced production and decomposition of the peroxides would be indicated by a constant rate of gas generation with a ratio of H_2 to O_2 near 2:1. This would be a nearly steady state condition. There is a spike in H_2 generation near the end of segment one, five minutes after O_2 is first detected, which cannot be explained by beam power fluctuations.

Segments two and three were run at an average beam power of 12.4 and 17.2 kW, respectively, and the H_2/O_2 ratios were 3.1 and 2.8, with a total of 3.3:1 over the entire experiment. As the experiment proceeded, the ratio got closer to the 2:1 ratio expected in water radiolysis.

No precipitation was observed in this solution after it was removed from the capsule, and two possible scenarios could account for this. In the first, uranyl peroxide does not precipitate, and its concentration stays below the solubility limit throughout the experiment. In the second scenario, a precipitate forms, but it ultimately decomposes due to heat and radiolysis. The initial solution pH was 1.01 and the final was 0.88. The final pH cannot be accounted for by the change in volume due to evaporation or radiolysis. The expected final pH due to evaporation was calculated to be 0.94, a difference of 7%. An amount of uranyl peroxide that formed and was present in solution would cause a drop in pH due to the formation of two hydronium ions $2\text{H}_3\text{O}^+$ (see equation 1.1).

Based on radiolysis of water, the total μmol oxygen generated should be half of H_2 or 241 μmol (based on total H_2 content of 482 μmol in Table 3.4). However, total oxygen content was 145 μmol , which represents 96 μmol of unaccountable O_2 . With the understanding that there is a 10% error in gas measurements, two known sources of oxygen trapped in solution can create disparities in total O_2 generation: the U-peroxide, indicated by the change in pH, and residual H_2O_2 in solution after data collection stopped. Residual peroxide has been seen in experiments where uranyl sulfate solution was irradiated in the Van de Graaff accelerator electron beam [3].

Table 3.5. Table parameters for the 11/21/19 irradiation.

Irradiation Time (minutes)	Beam Power (kW)	Beam Energy (kWh)	Fission Power (Watts/cc)	H_2 (μmol)	O_2 (μmol)	Temperature of Secondary Container ($^{\circ}\text{C}$)
155	4.84	12.5	4.82E-02	78.8	6.47	24
119	12.4	24.7	1.25E-01	168	54.6	42
120	17.2	34.5	1.57E-01	235	84.3	49

Figure 3.1. Plot of irradiation on 11/21/19 showing beam power and hydrogen and oxygen measurements for three experimental segments.

3.3 Irradiation August 6, 2020

Table 3.6 shows the two experimental segments for the 8/6/20 irradiation: time spent at an average beam power, beam energy, fission power density, and gas production of H_2 and O_2 . The plot shown in Figure 3.2 shows beam power and hydrogen and oxygen measurements for the two segments of the irradiation. Segment one was started at a higher beam power than intended, so a decision was made to run the experiment in two segments instead of three. The average beam power for the segments was 5.48 and 12.3 kW, respectively, and the H_2/O_2 ratios were 2.9:1 and 2.4:1, respectively, with a total of 2.6:1 over the entire experiment. There was a 22-minute delay between the initial onset of H_2 and that of O_2 , with a large spike of hydrogen in segment one. The delay was much shorter than the 70-minute delay seen in the 11/21/19 irradiation (Figure 3.1). The delay indicates that the H_2O_2 being generated is not decomposing to O_2 to a detectable level. It is increasing in concentration and reacting with the UO_2^{2+} ion to form uranyl peroxide. No precipitate was observed in this solution after it was removed from the capsule, and again there are two possible scenarios. In the first, uranyl peroxide does not precipitate, and its concentration stays below the solubility limit; in the second, U precipitation occurs, but it decomposes due to heat and radiolysis. As in the previous irradiation, pH dropped from 1.01 to 0.83, and this change could not be explained by a change in volume due to loss of water vapor. Based on the volume change, one would expect pH of 0.96 (14% lower). The much larger difference in pH is possibly due to formation of uranyl peroxide.

Based on radiolysis of water, the total μmol oxygen generated should be half of H_2 , or 145 μmol (From the total H_2 content of 291 μmol in Table 3.4). However, total oxygen content was 111 μmol , which represents a difference of 35 μmol O_2 . Oxygen not generated as a gas can be in the form of uranyl peroxide, as indicated by the change in pH and residual H_2O_2 .

Table 3.6. Table parameters for the two experimental segments for the 8/6/20 irradiation.

Irradiation Time (Minutes)	Beam Power (kW)	Beam Energy (kWh)	Fission Power (Watts/cc)	H₂ (μmol)	O₂ (μmol)	Temperature of Secondary Container (°C)
192	5.48	18.2	4.97E-02	92.8	30.4	32
180	12.3	36.7	1.07E-01	198	80.1	31

Figure 3.2. Plot of irradiation on 8/6/20 showing beam power and hydrogen and oxygen measurements for the two experimental segments.

3.4 Irradiation March 25, 2021

Table 3.7 shows the three experimental segments for the 3/25/21 irradiation: the time spent at an average beam power, beam energy, fission power density, and gas production of H₂ and O₂. The plot in Figure 3.3 shows beam power and hydrogen, and oxygen measurements for the three segments of the irradiation. The average beam power for the segments was 3.87, 8.19 and 11.1 kW, respectively, and the H₂/O₂ ratios 2.5:1, 2.2:1 and 2.1:1, with a total of 2.2:1 over the entire experiment. Unlike the previous two irradiations, there was only a 3-minute delay between the initial onset of H₂ and that of O₂, indicating that decomposition of peroxides was occurring early in the segment. This experiment showed near steady-state conditions throughout. No precipitate was observed in this solution after it was removed from the capsule. The initial solution pH was 1.07 and the final was 0.83. The final pH cannot be accounted for by the change in volume due to evaporation. The expected final pH due to evaporation was calculated to be 1.00 (17% drop). The pH drop can possibly be attributed to the formation of dissolved uranyl peroxide.

Based on radiolysis of water, the total μmol oxygen generated should be half of H₂ or 353 μmol (from the total H₂ content of 706 μmol in Table 3.4). However, total oxygen content was 323 μmol , which represents a difference of 30 μmol O₂. Oxygen not generated as a gas can be in the form of uranyl peroxide, as indicated by the change in pH and residual H₂O₂.

Table 3.7. Table parameters for the three experimental segments for the 3/25/21 irradiation.

Irradiation Time (Minutes)	Beam Power (kW)	Beam Energy (kWh)	Fission Power (Watts/cc)	H ₂ (μmol)	O ₂ (μmol)	Temperature of Secondary Container (°C)
120	3.87	7.73	9.62E-02	115	46.8	24
120	8.19	16.4	2.04E-01	270	124	42
120	11.1	22.1	2.75E-01	321	152	49

Figure 3.3. Plot of irradiation on 3/25/21 showing beam power and hydrogen and oxygen measurements for the three experimental segments.

3.5 Comparison of the Three Irradiations

The factors that drive the formation and precipitation of uranyl peroxide are temperature, uranium concentration, ferrous ion concentration, and H₂O₂ production rate. Table 3.8 compares the parameters in segment 1 of the three irradiations that can drive the precipitation of uranyl peroxide as well as the number of fissions per ng of ²³⁵U per beam power (Fission/ng-²³⁵U/kWh), which shows how efficiently the irradiation proceeded.

Ferrous ion concentration was similar in all irradiations. The H₂O₂ production rate is not known but can be inferred by power deposition, since it is directly driven by the radiolysis of water. The uranium concentration was the same for 11/21/19 and 8/6/20, but significantly lower for 3/25/21, and the temperature was the same for 11/21/19 and 3/25/21, but higher for 8/6/20.

The irradiations on 11/21/19 and 8/6/20 were similar with respect to the delay between the initial detection of H₂ and that of O₂, though the former was 48 minutes longer. The longer delay may be due to the lower temperature, since the production rate should be similar due to the similar power deposition. At lower temperatures, decomposition of H₂O₂ and uranyl peroxide is reduced, increasing the delay. The long delay indicates that the H₂O₂ being generated is not decomposing to O₂ to a detectable level. H₂O₂ is increasing in concentration and reacting with the UO₂²⁺ ion to form uranyl peroxide. That absence of

oxygen shows that it is trapped in solution as peroxides and dissolved gas. The delay for 3/25/21 was only 3 minutes, which was the shortest of all the experiments. In addition, the stoichiometric ratio of H₂ to O₂ was closer to the proportions indicative of the near steady-state condition expected in water radiolysis. Temperature does not seem to be the primary factor for the relative steady state of this experiment, since it is the same as in the 11/21/19 irradiation. The power deposition tied to the production rate of H₂O₂ is not causing the significant instability seen on 11/21/19, because 3/25/21 has the highest power deposition of all experiments. It appears that if the uranium concentration is lower, the system is driven closer to a steady state faster. It further indicates that at lower U concentration, solubility of uranyl peroxide is higher, which could explain the highest pH change, due to the formation of uranyl peroxide, for the last irradiation. Although it cannot be determined from these data sets, it may be beneficial to determine whether the addition of more iron to the solution could positively assist in driving the system to a steady state more rapidly.

The number of fissions per ng of ²³⁵U per beam power varies by 25% (last column in Table 3.8). This variation can be explained by the difference in beam placement on the target. Variations in the beam diameter, position relative to the center of the target and impact angle off the beam will all affect the rate of neutron production in the DU target and so the fission rate in the solution.

Table 3.8. Comparison of the experimental segment 1 parameters for the three irradiations on 11/21/19, 8/6/20 and 3/25/21. These parameters from previous tables are repeated here for comparison. These parameters—fission power density, Fe²⁺ concentration, uranium concentration and temperature—drive the formation and precipitation of uranyl peroxide. The table also includes the number of fissions per ng of ²³⁵U per beam power (Fission/ng-²³⁵U/kWh).

Date	Fission Power Density (watts/cc)	Fe ²⁺ (mg/L)	Uranium Concentration (g-U/L)	Temperature of Secondary Container (°C)	Fission/ng- ²³⁵ U/kWh
11/21/19	4.82E-02	229	240	24	2.26E+04
8/6/20	4.97E-02	233	240	32	2.11E+04
3/25/21	9.62E-02	197	175	24	1.70E+04

When comparing segments 2 and 3 of the three experiments, it can be seen that the oxygen-to-hydrogen ratio increases with time. This indicates that in all solutions, the generation of hydrogen and oxygen is driven toward stoichiometric proportions indicative of a steady-state condition, so the ratios of H₂ to O₂ become closer to 2:1. Since these experiments were performed over the relatively short time scale of several hours, we were not able to reach steady state. Loss of water due to evaporation and radiolysis increases both uranium and iron concentration, which would also affect how fast the solution reaches a steady state.

While all three experiments show an initial unbalanced H₂ to O₂ ratio, the 3/25/21 irradiation came closest to a stoichiometric hydrogen-to-oxygen ratio. This solution had the lowest uranium concentration, even though it had the highest fission power in solution (due to use of HEU).

3.6 Comparison of Fe²⁺ Spiked to Un-spiked Uranyl Sulfate Solutions

Table 3.9 compares the samples in this report with those run in 2017 and 2018. The table shows the date, sample type, fission per ng ²³⁵U per LINAC beam energy (Fission/ng-²³⁵U/kWh) and the presence or absence of LEU in the AMORE TSV for the three Fe²⁺ spiked samples in this report and the un-spiked samples run in 2017 and 2018 [2]. This shows the effect that uranyl sulfate in the TSV has on fission power in the mini-AMORE solutions. The Fission/ng-²³⁵U/kWh for the LEU solutions was 1.77 to 1.65 times higher, and the HEU solution was 1.28 times higher for the samples with uranium in the TSV. This shows how the TSV with uranium in it increased the neutron flux on the mini-AMORE samples.

Table 3.9. Comparison of Fe²⁺ spiked to un-spiked uranyl sulfate solutions. Experiment date, sample type and fissions per nanogram of ²³⁵U per LINAC beam energy (Fissions/ng-²³⁵U/kWh) for the three Fe²⁺ spiked samples in this report and un-spiked samples run in 2017 and 2018 [2].

Date	Sample Type	Fissions ng- ²³⁵ U ⁻¹ kWh ⁻¹	LEU Present in TSV
11/21/19	LEU, Fe ²⁺ Spiked	2.26E+04	YES
8/6/20	LEU, Fe ²⁺ Spiked	2.11E+04	YES
3/25/21	HEU, Fe ²⁺ Spiked	1.70E+04	YES
11/3/17	DU, Un-spiked	3.35E+04	NO
11/17/17	LEU, Un-spiked	1.28E+04	NO
1/11/18	HEU, Un-spiked	1.33E+04	NO

Figure 3.4 shows H₂ and O₂ production rate (μmole min⁻¹ cc⁻¹) vs fission power (watts cc⁻¹) for Fe²⁺ spiked and un-spiked uranyl sulfate solutions. The data for the un-spiked samples comes from mini-AMORE experiments that were run in 2017 and 2018 [2]. It can be seen that H₂ and O₂ each show decreased production with the addition of ferrous ion. The relative linearity in hydrogen and oxygen production is evident. The overall hydrogen production in the Fe²⁺ spiked sample is lower than the un-spiked. The production rates for hydrogen and oxygen in un-spiked solutions are 6.99 and 2.67 μmol min⁻¹ W⁻¹, respectively, while the spiked solutions are 5.29 and 2.24 μmol min⁻¹ W⁻¹, respectively.

Figure 3.4. Plot of hydrogen and oxygen production rate vs fission power density for Fe²⁺ spiked and un-spiked* uranyl sulfate solutions.

* Asterisk indicates previously recorded data from 2017 and 2018 [2].

4. CONCLUSIONS

- Hydrogen and oxygen production shows linearity with fission power. Total hydrogen and oxygen production is reduced with the addition of ferrous sulfate. The production rates for hydrogen and oxygen in Fe^{2+} un-spiked solutions are 6.99 and 2.67 $\mu\text{mol min}^{-1} \text{W}^{-1}$, respectively, and for spiked solution 5.29 and 2.24 $\mu\text{mol min}^{-1} \text{W}^{-1}$, respectively.
- Precipitation is avoided if the production and decomposition of H_2O_2 and uranyl peroxide are equal while keeping the latter below its solubility limit. Past experiments [6] and modeling show that the relevant conditions that affect the production and precipitation of uranyl peroxide are temperature, uranyl sulfate concentration, ferrous iron concentration, and H_2O_2 production rate. The rate of H_2O_2 production is directly proportional to power deposition. A delay in O_2 generation can indicate hydrogen peroxide and uranyl peroxide formation without any significant decomposition during an irradiation, because oxygen is trapped in solution as peroxides. An $\text{H}_2:\text{O}_2$ ratio significantly higher than 2:1 may strongly indicate this.
- Adding ferrous iron to the solution aids in preventing precipitation by reducing the H_2O_2 concentration. The concentration of Fe^{2+} should be high enough to overcome the H_2O_2 production rate, which depends on the power input. The effectiveness of adding the ferrous salt to decompose H_2O_2 may be reduced because it is oxidized to Fe^{3+} , and although Fe^{3+} decomposes H_2O_2 , the rate of oxidation is slower than the rate of reduction. It has been shown that Fe^{2+} should be in solution during an irradiation.
- At a higher temperature, the decomposition rate of peroxides increases. If the solution should not be allowed to boil, a temperature of 80°C would provide maximum peroxide decomposition while staying below the precipitation threshold [6].
- A decrease in solution pH can indicate the formation of uranyl peroxide in solution, due to formation of H_3O^+ by complexation reaction between UO_2^{2+} and H_2O_2 (eq. 1), but its concentration may be too low to form a precipitate.
- A deviation from the 2:1 ratio of hydrogen to oxygen over an entire irradiation, with oxygen being at a deficit, can indicate the presence of peroxides in solution.

Although it cannot be determined from these data sets, it may be beneficial to determine whether the addition of more iron into the solution could positively assist in rapidly driving the system closer to a steady state condition.

5. REFERENCES

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