ANL/CSE-13/21

Means to Eliminate Uranyl Peroxide Precipitation in SHINE Target Solution

Chemical Science and Engineering Division

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MEANS TO ELIMINATE URANYL PEROXIDE PRECIPITATION IN SHINE TARGET SOLUTION

1 INTRODUCTION

Argonne National Laboratory (Argonne) is assisting the potential domestic producer, Morgridge Institute for Research (MIR), as part of the National Nuclear Security Administration (NNSA) Global Threat Reduction Initiative's (GTRI) program in the development of a Mo-99 production pathway that does not use high enriched uranium (HEU). In cooperation with its corporate partners, MIR is developing SHINE, which produces Mo-99 by neutron-induced fission of low enriched uranium (LEU) in a subcritical aqueous solution. MIR is considering aqueous uranyl sulfate at pH 1as the target solution.

One potential technical difficulty in the uranium-sulfate target-solution system is the precipitation of uranium peroxide from solution. Hydrogen peroxide is generated in solution by the radiolysis of water; the peroxide generated can form uranyl peroxide, which precipitates. Precipitation of uranium from the solutions must be avoided for safe and reliable SHINE operation. The following equation shows the reaction of uranium and hydrogen peroxide in solution to form the precipitate:

$$UO_2^{2+} + H_2O_2 + 2H_2O \leftrightarrow UO_2O_2 \cdot 2H_2O(s) + 2H^+$$

The purpose of this project was to determine whether the addition of a catalyst could enhance the rate of autodestruction of peroxide to oxygen and water, thus limiting the buildup of hydrogen peroxide in solution and preventing the precipitation of uranium peroxide. The composition of radiolytically generated gases evolved as a result of low linear energy transfer (LET) bombardment of uranium sulfate solutions was also analyzed.

Experiments were performed at the Van de Graaff accelerator facility to determine whether the precipitation of uranium peroxide could be prevented by the addition of various materials known to catalyze autodestruction of hydrogen peroxide. The experiments were designed to simulate conditions inside the subcritical target solution of the SHINE Mo-99 production system.

2 EXPERIMENTAL SETUP

The setup (see Figure 1) was designed with two interconnected systems, the process loop and the sampling manifold. The process loop is a closed loop of stainless steel tubing that consists of the target sample, the electron beam, and a peristaltic pump. The target sample is inserted into a holder directly in the accelerator electron-beam path. The holder is attached to a recirculating pump and water bath to provide continuous cooling to the sample. The electron beam impinges on the cooling water and quartz tube in the setup. Mostly electrons and some x-rays interact with the test solution causing radiolysis of water. Hydrogen peroxide, oxygen, and hydrogen are generated in the sample tube; sulfate appears to be stable to radiolysis. The sample tube has an inlet and outlet through which headspace gases can be continuously recirculated throughout the process loop. Recirculation of gas is achieved using a peristaltic pump. The Van de Graaff accelerator has a 2.5-MeV direct current (DC) electron beam.

The sampling manifold is connected to the process loop by a bellows valve. The sampling manifold consists of a capacitance monometer, vacuum pump, and two analytical instruments connected by stainless steel tubing and a series of valves used to either evacuate, measure pressure, or analyze the gaseous constituents in the manifold. The gases are analyzed using a SRI-8610C gas chromatograph with a thermal conductivity detector (TCD) and a helium ionization detector (HID). Separation is achieved with a molecular sieve and Haysep-d columns.

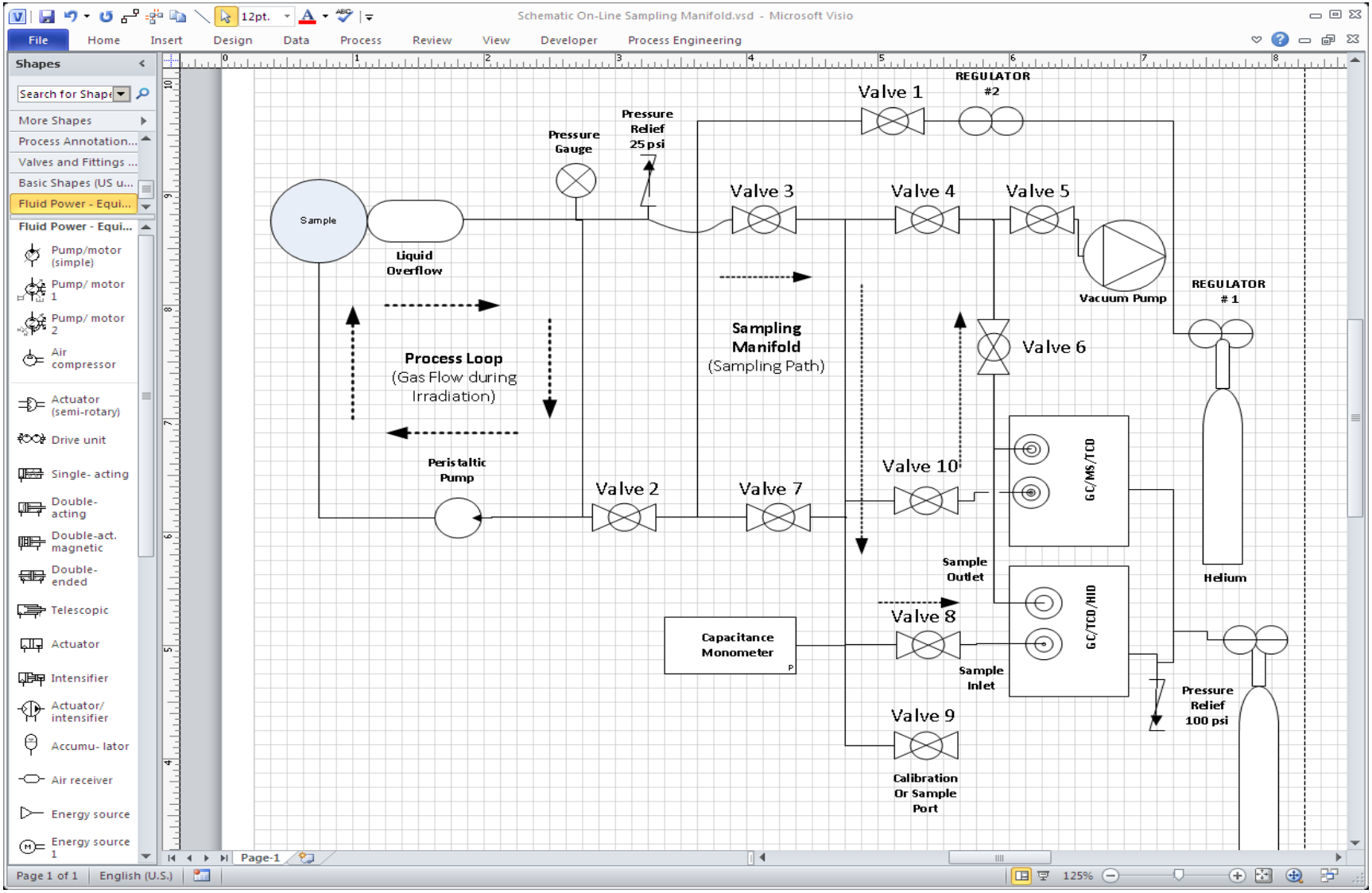

FIGURE 1 Schematic of Experimental Setup

3 PROCEDURE

A 2-mL test solution is placed into a quartz sample tube. The sample tube is connected to the process loop in the beam path. The system is then evacuated and purged with helium several times to remove atmospheric gases. The process loop is pressurized to 800 torr with ultra-high purity (UHP) helium.

The 2.5-MeV electron beam is set to 20 µA, and the sample is irradiated for approximately 5 hours. At 30-minute intervals, a sample of the headspace gas is withdrawn into the evacuated "Sampling Manifold" for analysis. The gas removed is replaced with helium to keep a constant pressure in the system. Prior to these experiments, oxalic-acid dosimetry was performed to determine the dose deposited into the sample.

Uranyl-sulfate solutions were tested at various concentrations. Several known hydrogen peroxide catalysts were tested.

4 GENERAL DISCUSSION OF THE DATA

No attempt was made to analyze the gases dissolved in solution. The solution was not continuously purged during irradiation to release dissolved gasses. It was assumed that gasses would dissolve in solution, react, or undergo radiolysis during the experiment. Each data point in the graphs represents the accumulated gasses in the headspace of the system at sampling time.

Small amounts of nitrogen were detected and increased slightly throughout the test, but within the scope and design of this test, it could not be determined whether the N_2 was being generated, entering through leaks, or from outgassing of the system. A baseline "leak rate" was determined while no experiments were being run, so the nitrogen detected was either a leak or outgassing from the stainless steel components. The amounts detected were comparable to those detected during the experiments. Therefore, the assumption was made that nitrogen was an interfering species and that the nitrogen detected was not from radiolysis. In the same test, small amounts of oxygen were detected as a contaminant. 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.

The results tables show final accumulated value at the end of the experiment. Hydrogen and oxygen values are reported as total µmoles produced during the entire run. Energy deposited in Greys (Gy) is the accumulated dose. Hydrogen-to-oxygen ratios are calculated from the final concentration at the end of the experiment.

5 URANYL SULFATE SOLUTIONS SUMMARY—NO CATALYST ADDED

Table 1 and Figures 2, 3, and 4 provide experimental data for the irradiation of uranyl sulfate solutions without a peroxide catalyst added. Figures 2 and 3 show total µmoles of analyte (either hydrogen or oxygen) versus accumulated Dose (Gy) during the 5-hour experiment. Each data point is at the sampling time for the analyte. Each figure is displayed for the analyte at the various uranyl sulfate concentrations. These data follow the tabular data such that the final point on the graph is the value listed in Table 1. Figure 4 presents the hydrogen-to-oxygen ratios versus dose. The following is a summary of that data.

5.1 PRECIPITATION OF URANYL PEROXIDE

Uranyl peroxide precipitated from solution for each of the uranyl sulfate experiments performed. It was assumed to be the peroxide because of previous experiments on uranyl-sulfate solutions. It was also indicated by the fact that the uranium went back in solution after being heated in a hot water bath (due to thermal destruction of peroxide). Density measurements were performed on the post-irradiated solutions after the precipitate was filtered to determine the final resulting uranyl-sulfate concentration. Those data are listed in Table 1. The percentage of uranium that precipitated decreased as the concentration of uranium increased. At 88 g-U/L, 28% or 24.5 g-U/L precipitated to a final concentration of 63.5 g-U/L. At 138 g-U/L, 16% or 22 g-U/L precipitated to a final concentration of 116 g-U/L. Finally, at 298 g-U/L, 12% or 36 g-U/L precipitated to a final concentration of 262 g-U/L. Hydrogen peroxide formation during irradiation is assumed to be the culprit causing the precipitation. Experiments performed and listed in the next section show that this can be avoided using a catalyst for hydrogen peroxide destruction.

5.2 PH CHANGES

Consistently, the pH of all solutions decreased with dose. This was likely due to the formation of uranium peroxide precipitate, which follows the equation $UO_2^{+2} + H_2O_2 + 2H_2O \leftrightarrow UO_2O_2 \cdot 2H_2O + 2H^+$.

5.3 HYDROGEN AND OXYGEN EVOLUTION

The production of hydrogen and oxygen was quite high for all the experiments. There was a definite trend showing that as the uranyl-sulfate concentration increased, the production of H_2 and O_2 decreased. The ratio of H_2:O_2 was at or slightly above 2:1, favoring hydrogen in the headspace. This is most likely due to incomplete degradation of hydrogen peroxide.

TABLE 1 Data from the Irradiation of Uranyl Sulfate Solutions (Precipitation occurred during these experiments.)

UO_2SO_4 (g-U/L)	Energy Deposited (Gy)	Final $[UO_2(SO_4)]$ (g-U/L)	pH Initial	pH Final	µmoles H_2 Total Produced	µmoles O_2 Total Produced	H_2-to-O_2 Ratio	% Uranium Remaining
88	1.71×10^8	63.5	1.0	0.64	2972	1446	2.05	72.2%
138	2.29×10^8	116	1.0	0.63	1320	634	2.08	84.1%
298	2.03×10^8	262	1.0	0.58	1092	459	2.38	87.9%

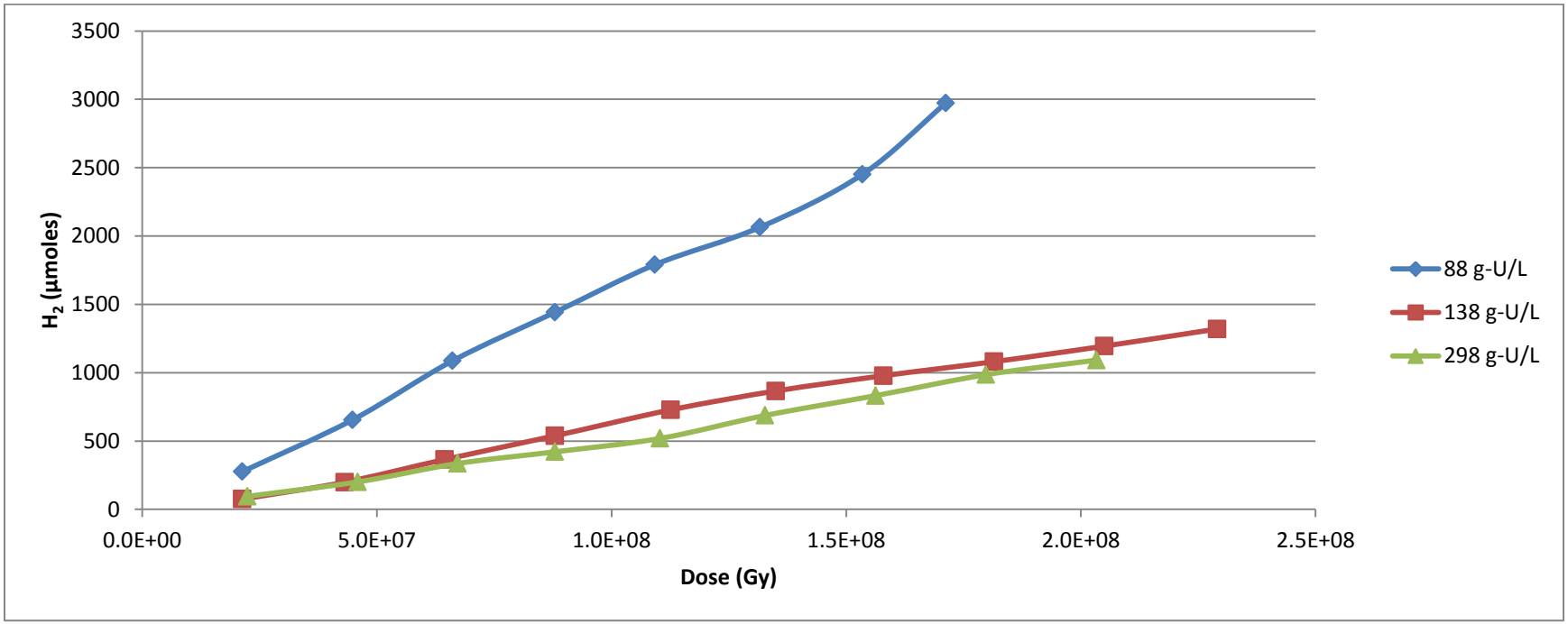

FIGURE 2 Hydrogen Evolution from UO_2SO_4 Solutions (Precipitation occurred during these experiments.)

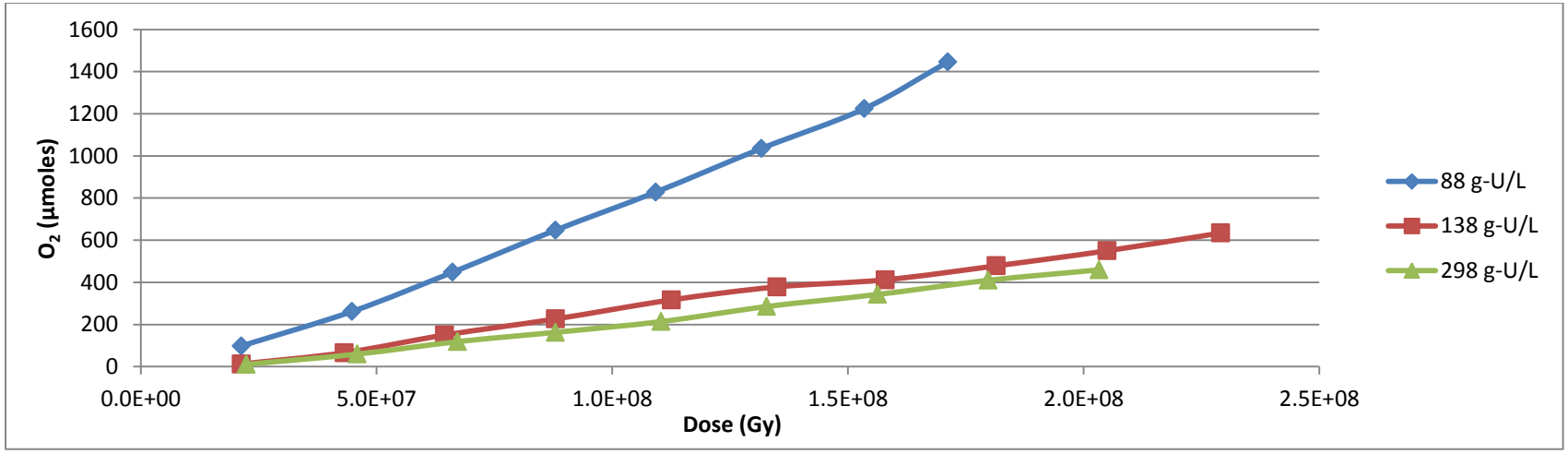

FIGURE 3 Oxygen Evolution from UO_2SO_4 Solutions (Precipitation occurred during these experiments.)

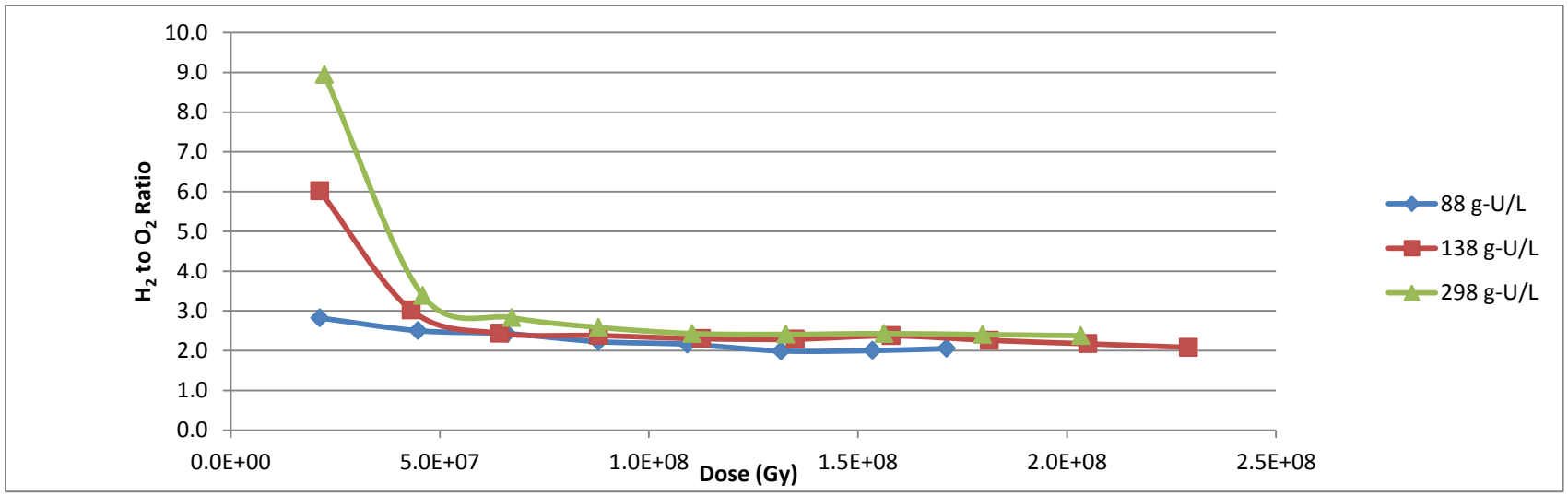

FIGURE 4 Hydrogen-to-Oxygen Ratio versus Dose and UO_2SO_4 Concentration

6 PREVENTING PEROXIDE PRECIPITATION IN URANYL SULFATE SOULUTIONS USING Fe(II) AS A CATALYST

The data in Section 5 show that uranyl peroxide precipitates during irradiation. This is caused by the reaction of UO_2^{2+} ions with hydrogen peroxide. Since hydrogen peroxide is continuously produced by the radiolysis of water, a method for destroying hydrogen peroxide (H_2O_2) as it forms in solution is needed. We pursued the route of having an ion in solution to make close contact with molecules of H_2O_2 as they are produced during irradiation. Ferrous ion (Fe^{+2}) was examined because it is known to react catalytically with H_2O_2 through the following equations:

$$Fe^{+2} + H_2O_2 \rightarrow Fe^{+3} + OH^- + OH\cdot$$
$$Fe^{+3} + H_2O_2 \rightarrow Fe^{+2} + \cdot HO_2 + H^+$$

6.1 VARYING THE URANIUM CONCENTRATION

Table 2 and Figures 5, 6, and 7 provide experimental data for the irradiation of uranyl-sulfate solutions at various concentrations. The samples each contain $FeSO_4$ at 0.99 mg/L. The figures show total µmoles of analyte (either hydrogen or oxygen) versus accumulated dose (Gy) during the 5-hour experiment. Each data point is at sampling time for the analyte. Each figure is displayed for the analyte at the various uranium sulfate concentrations. These data follow the tabular data such that the final point on the figure is the value listed in Table 2. Figure 7 presents the hydrogen-to-oxygen ratios versus dose for the data. The following is a summary of that data.

6.1.1 Precipitation of Uranyl Peroxide

None of the solutions to which Fe(II) was added formed the uranyl-peroxide precipitate.

6.1.2 Hydrogen and Oxygen Evolution

When ferrous sulfate was added as a catalyst, the total production of hydrogen and oxygen was significantly lower. As with the untreated sample, the lowest uranium concentration produced the largest amount of hydrogen and oxygen. The ratio of hydrogen to oxygen was greater than 2:1. As with untreated solutions, the higher concentration of uranyl sulfate generated lower amounts of gases.

6.2 VARYING THE $FeSO_4$ CONCENTRATION

Table 3 and Figures 8, 9, and 10 provide experimental data for the irradiation of uranyl sulfate solutions at 126 g-U/L at a pH of 1. Each sample contains varying amounts of $FeSO_4$ (0.99, 9.9, and 99 mg/L). Figures 8 and 9 show total µmoles of analyte (either hydrogen or

TABLE 2 Data from the Irradiation Uranyl Sulfate Solutions with Fe(II) Added $FeSO_4$ at 0.99 mg/L

UO_2SO_4 (g-U/L)	Energy Deposited (Gy)	Final (UO_2SO_4) (g-U/L)	pH Initial	pH Final	µmoles H_2 Total Produced	µmoles O_2 Total Produced	H_2-to-O_2 Ratio
90	2.16×10^8	No precipitation	1.0	NA[a]	529	327	1.62
130	2.32×10^8	No precipitation	1.0	NA	36	43	0.84
300	2.34×10^8	No precipitation	1.0	NA	118	88	1.16

[a] NA = "not analyzed."

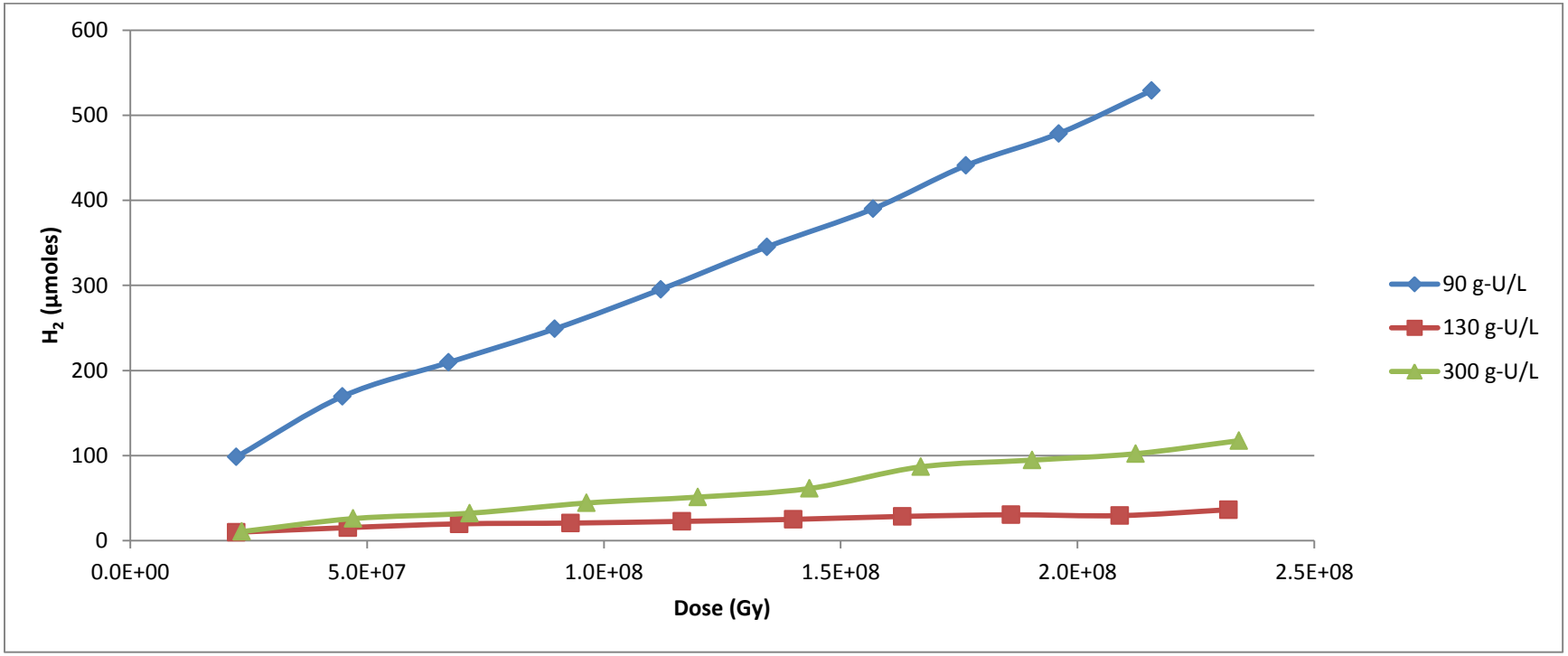

FIGURE 5 Hydrogen Evolution from UO_2SO_4 Solutions with Fe(II)SO_4 at 0.99mg/L

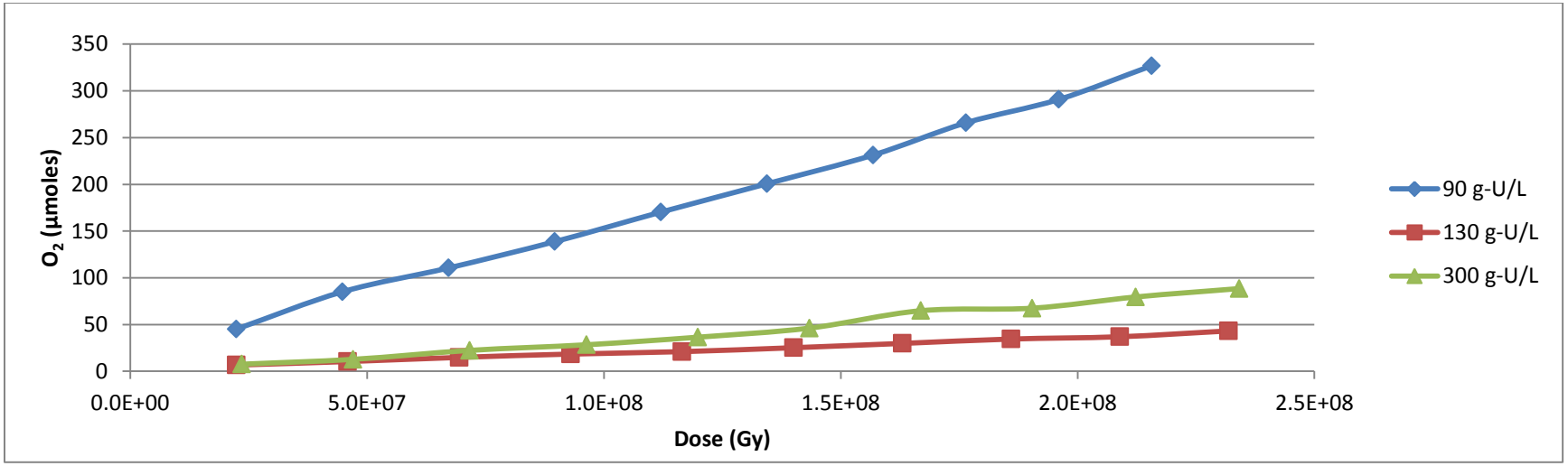

FIGURE 6 Oxygen Evolution from UO_2SO_4 Solutions with $Fe(II)SO_4$ at 0.99mg/L

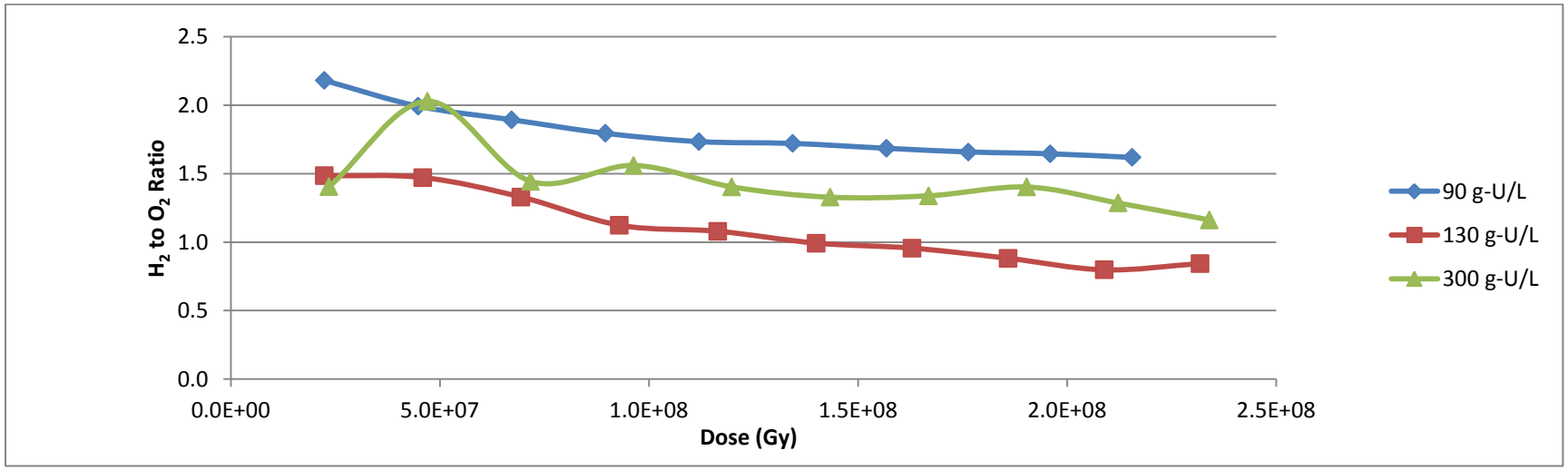

FIGURE 7 Hydrogen-to-Oxygen Ratio from UO_2SO_4 Solutions with $Fe(II)SO_4$ at 0.99mg/L

TABLE 3 Data from the Irradiation Uranyl Sulfate Solutions with $FeSO_4$ Added at Varying Concentrations

Peroxide Catalyst (mg/L $FeSO_4$)	Energy Deposited (Gy)	Initial $UO_2(SO_4)$ (g-U/L)	Final $UO_2(SO_4)$ (g-U/L)	pH Initial	pH Final	H_2 µmoles Total Produced	O_2 µmoles Total Produced	H_2-to-O_2 Ratio
0.99	2.31×10^8	123.5	No precipitation	1.42	NA	239	163	1.47
9.9	2.31×10^8	123.5	No precipitation	1.42	1.44	540	343	1.57
99	2.20×10^8	123.5	No precipitation	1.42	1.37	462	302	1.53

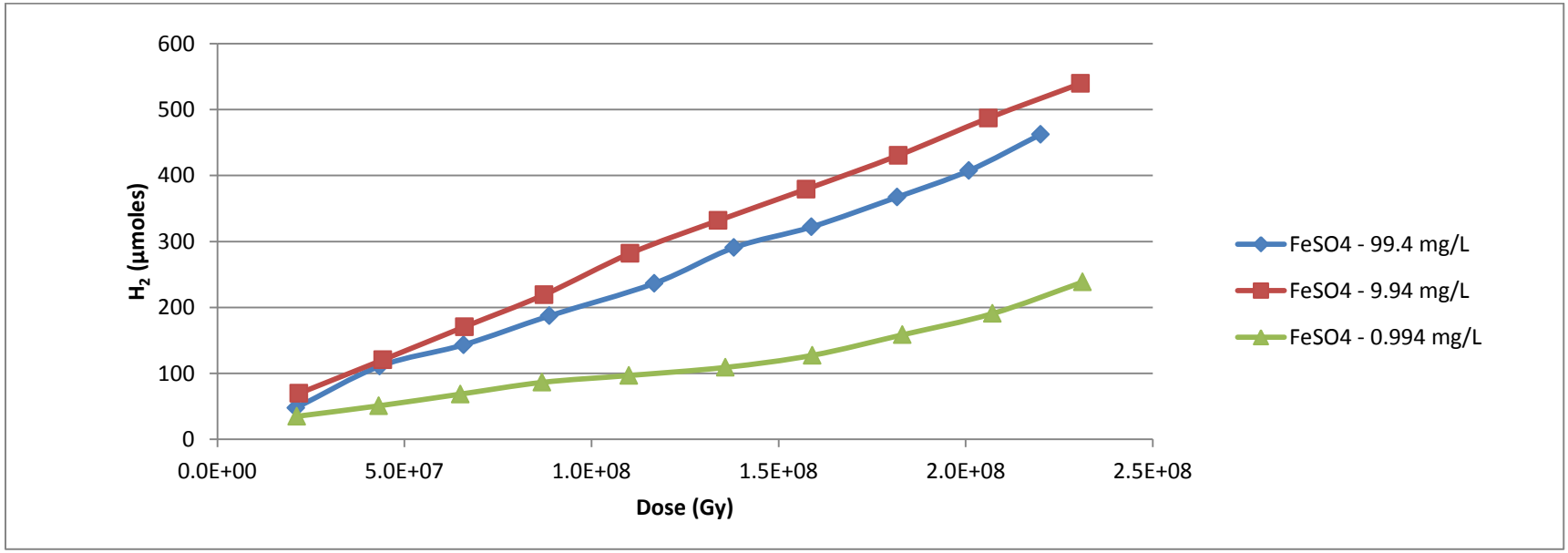

FIGURE 8 Hydrogen Evolution from 126 g-U/L UO_2SO_4 Solutions with Varying $Fe(II)SO_4$ Concentrations

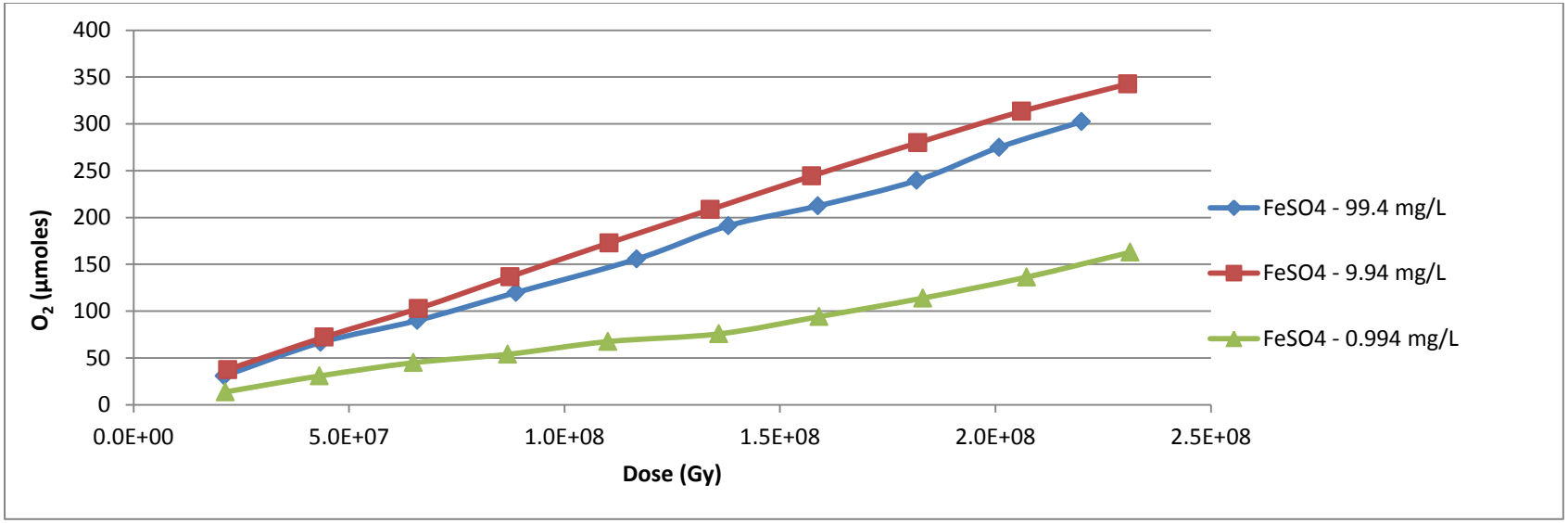

FIGURE 9 Oxygen Evolution from 126 g-U/L UO_2SO_4 Solutions with Varying $Fe(II)SO_4$ Concentrations

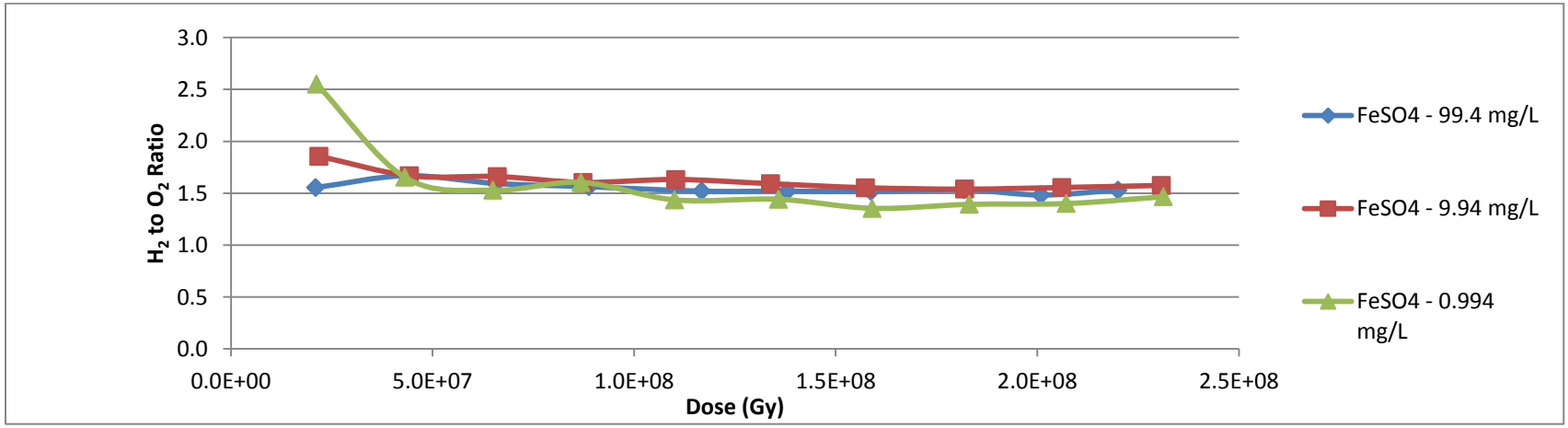

FIGURE 10 Hydrogen-to-Oxygen Ratio for 126 g-U/L UO_2SO_4 Solutions with Varying $Fe(II)SO_4$ Concentrations

oxygen) versus accumulated dose (Gy) during the 5-hour experiment. Each data point is at the sampling time for the analyte. Each figure is displayed for the analyte at the various ferrous sulfate concentrations. These data follow the tabular data such that the final point on the figure is the value listed in Table 3. Figure 10 presents the hydrogen-to-oxygen ratios versus dose for the data. The following is a summary of that data.

6.2.1 Precipitation of Uranyl Peroxide

None of the solutions to which Fe(II) was added formed the uranyl-peroxide precipitate.

6.2.2 Hydrogen and Oxygen Evolution

When ferrous sulfate was added as a catalyst, the total production of hydrogen and oxygen was significantly lower. As with the untreated sample, the lowest uranium concentration produced the largest amount of hydrogen and oxygen. The ratio of hydrogen to oxygen was greater than 2:1.

7 PREVENTING PEROXIDE PRECIPITATION IN URANYL SULFATE SOLUTIONS USING VARIOUS CATALYSTS

In order to prevent precipitation of uranium peroxide, a catalyst must be added to the solution of the reactor vessel to inhibit the production of radiolytically generated hydrogen peroxide. Fe(II) was added because $FeSO_4$ has been shown to accomplish this. In order to expand the available options for use in the SHINE reactor system, other salts were tested because of their known catalytic activity with H_2O_2. Experiments were performed using copper sulfate, potassium iodide, and iron (III) sulfate [$Fe_2(SO4)_3$] in solution. Also tested were materials that the target and holding vessels would possibly be fabricated from: 304 stainless steel and zirconium American Society of Mechanical Engineers (ASME) 658.

Table 4 and Figures 11, 12, and 13 provide experimental data for the irradiation of uranyl-sulfate solutions. Each sample contained a different catalyst at the concentration shown. Figures 11 and 12 show total µmoles of analyte (either hydrogen or oxygen) versus accumulated dose (Gy) at the sampling time during the 5-hour experiment. Each plot is displayed for the various catalysts tested. These data follow the tabular data such that the final point on the graph is the value listed in Table 4. Figure 13 presents the hydrogen-to-oxygen ratios versus dose for the data.

Zirconium experimental data is only presented in tabular form and has been omitted from the graphs because precipitation occurred.

The following is a summary of that data.

7.1 PRECIPITATION OF URANYL PEROXIDE

Only the zirconium test formed the uranyl-peroxide precipitate. A zirconium vessel requires the addition of a catalyst for peroxide destruction. The solution with 304 stainless steel turnings showed no uranyl-peroxide precipitation. This may be due to the chromium or iron acting as a peroxide catalyst. Whether the catalytic effect is a surface effect or occurs through dissolution of reactive ions is unknown.

Irradiations with the salt catalysts (copper sulfate, potassium iodide, and ferric sulfate) showed no precipitation.

7.2 HYDROGEN AND OXYGEN EVOLUTION

Zirconium metal exhibited the behavior of an untreated uranyl-sulfate solution with high volumes of both hydrogen and oxygen generated with hydrogen-to-oxygen ratios greater than two. The 304 stainless steel test showed low overall gas production and a low H_2:O_2 ratio.

All of the salt catalysts reduced the overall gas production and reduced the hydrogen-to-oxygen ratios below two.

TABLE 4 Data from the Irradiation Uranyl Sulfate Solutions with Various Catalysts Added

Catalyst	UO_2SO_4 (g-U/L)	Energy Deposited (Gy)	Did Sample Precipitate?	pH Initial	pH Final	µmoles H_2 Total Produced	µmoles O_2 Total Produced	H_2-to-O_2 Ratio
Cu(II), 62.5 mg-Cu/L	126	2.20×10^8	No	1.4	NA[a]	406	286	1.42
KI, 9.94 mg-I^-/L	126	2.28×10^8	No	1.4	NA	206	147	1.40
Fe(III) 0.96 mg/L	126	2.28×10^8	No	1.4	NA	566	369	1.53
304 Stainless Steel	126	2.24×10^8	No	1.4	NA	261	223	1.17
Zirconium	298	2.32×10^8	Yes	1.0	NA	1112	460	2.42

[a] NA = "not analyzed."

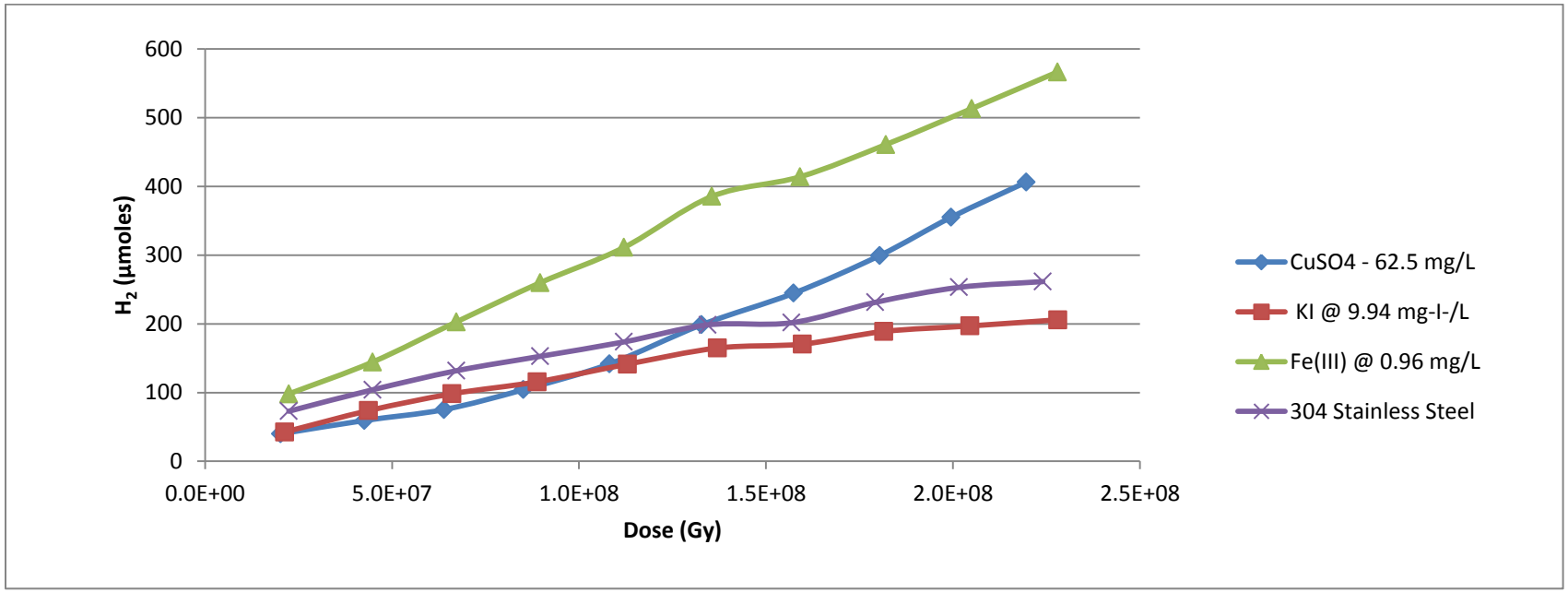

FIGURE 11 Hydrogen Evolution from 126 g-U/L UO_2SO_4 Solutions with Various Peroxide Catalysts Added

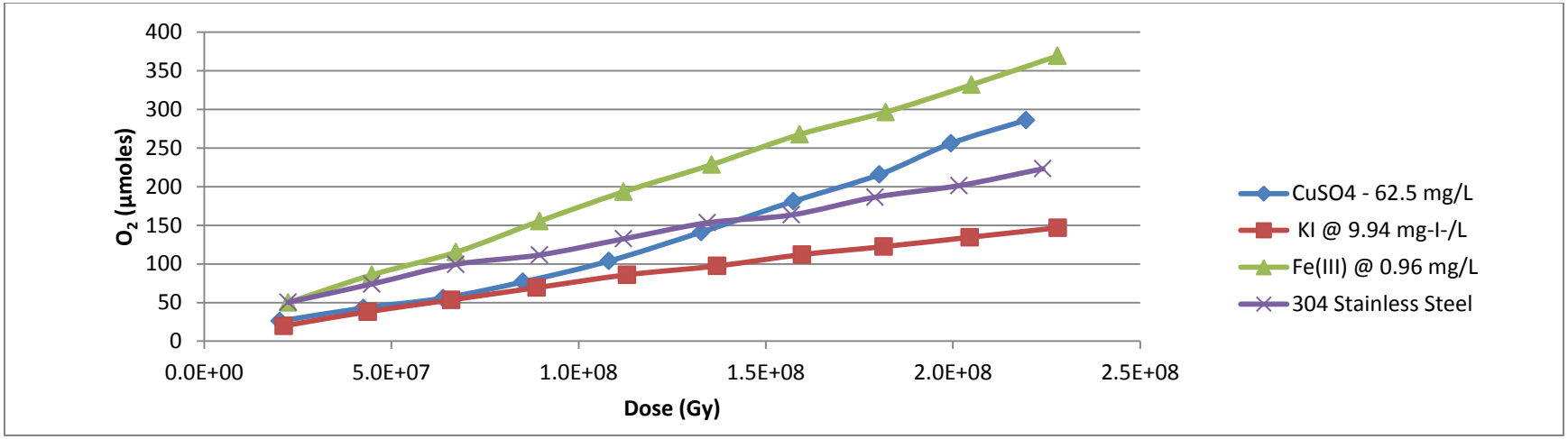

FIGURE 12 Oxygen Evolution from 126 g-U/L UO_2SO_4 Solutions with Various Peroxide Catalysts Added

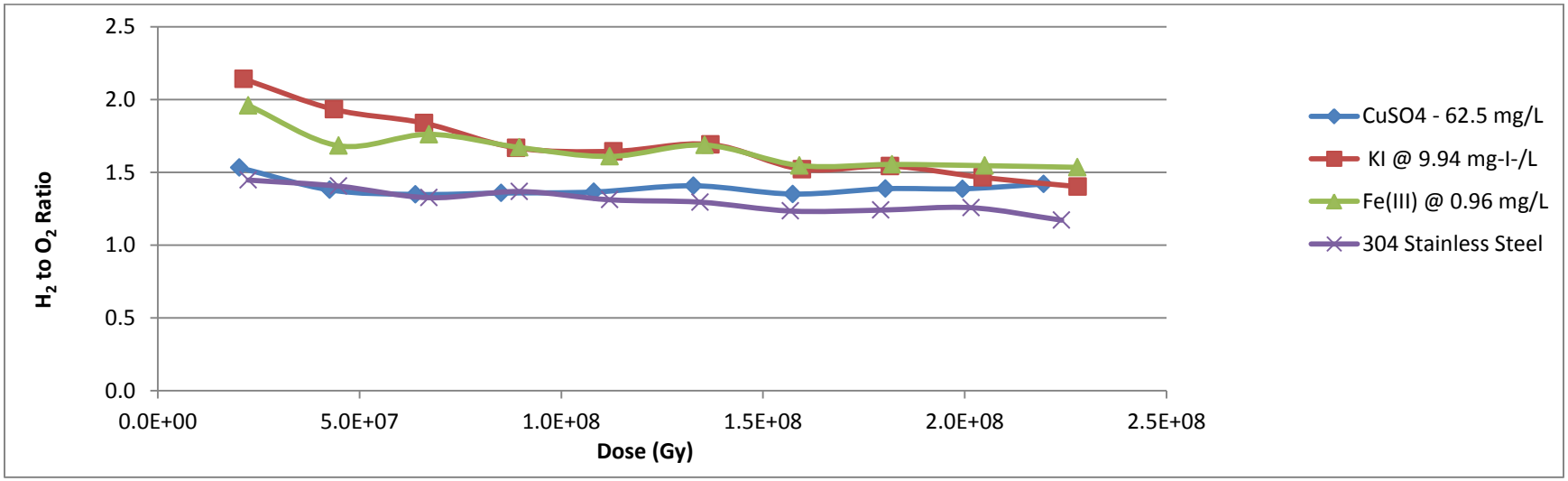

FIGURE 13 Hydrogen-to-Oxygen Ratios versus Dose for 126 g-U/L UO_2SO_4 Solutions with Various Peroxide Catalysts Added

8 CONCLUSIONS

The addition of a catalyst will effectively prevent the precipitation of uranium peroxide in the SHINE uranyl-sulfate target solution. Addition of a catalyst will have the added benefit of reducing the overall radiolytic production of hydrogen and oxygen. There is also the benefit of keeping the ratio of hydrogen to oxygen under 2:1; having more than a stoichiometric ratio of oxygen means that hydrogen will not accumulate in the headspace during catalytic recombination of the two gasses to water.

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