Van de Graaff Experiments: Mo Redox Chemistry and Iodine Speciation

Chemical Science and Engineering Division

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by

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**VAN DE GRAAFF EXPERIMENTS:
Mo REDOX CHEMISTRY AND IODINE SPECIATION**

1 INTRODUCTION

Argonne National Laboratory (Argonne) is assisting Morgridge Institute for Research (MIR) in its efforts to develop SHINE, which is an accelerator-driven process that will use a uranyl-sulfate solution for the production of Mo-99. Mo will be separated from an irradiated uranyl-sulfate solution using a titania sorbent; however, the highly reducing environment may lead to Mo reduction. If Mo is reduced to Mo(IV) or Mo(V), its adsorption and/or recovery will decrease, and an oxidizing agent will be required to ensure that Mo is present as Mo(VI). Another concern for SHINE is related to the speciation of iodine during irradiation, cooling, column loading and stripping, and Mo-99 purification. Both Mo oxidation state and iodine speciation experiments were performed using a Van de Graaff generator as a source of radiation. Initial results indicate that Mo may be reduced during irradiation because low Mo recoveries were obtained for three separate column experiments performed using irradiated solutions. The results were complicated, however, because nearly 60 min passed between the end of irradiation and the initiation of column experiments, and high back pressures were observed for two out of the three experiments. This also made it difficult to determine what variable caused low Mo recovery. Radiation dose and starting iodine species had no effect on overall iodine speciation, and iodide was the predominant species for all tests.

2 EXPERIMENTS

2.1 Mo REDOX CHEMISTRY

Approximately 500 to 800 mL of uranyl-sulfate (125–150 g-U/L) solutions containing 10^{-6} M stable Mo and tracer Mo-99 were irradiated at the Van de Graff generator for 1 to 5 hours. The dose during irradiation was approximately 80 kRad/h. After irradiation, the solutions were transferred to Building 205 to perform direct downscale column experiments using an AKTA liquid chromatography system. Because of difficulties passing the irradiated uranyl-sulfate solution through two different types of columns, 10 ppm FeSO_4 was added to some of the solutions to destroy peroxide and prevent formation of uranyl peroxide.

2.2 IODINE SPECIATION

Two milliliters of uranyl-sulfate (125 g-U/L) and uranyl-nitrate (140 g-U/L) solutions containing 0.5 μM iodine added as potassium iodide, iodine, or potassium iodate and tracer I-131 were irradiated using the Van de Graaff generator. I-131 was received in a 0.2 M NaOH solution. An aliquot was taken and acidified using H_2SO_4 or HNO_3 to pH 1 before being added to the uranyl-sulfate or -nitrate solutions containing stable iodine. Doses ranged from 50 to 6,000 MRad. An aliquot of each irradiated and nonirradiated solution was taken, and a series of extractions was performed to separate the different iodine species. The extraction procedure is as follows:

1. Take an aliquot of irradiated and nonirradiated solution containing I-131 (0.25–0.5 mL).
2. Contact it with an equal volume of CHCl_3 and vortex it for 5 min to remove I_2 (repeat two times).
3. Contact the remaining aqueous phase with an equal volume of 0.1 M I_2 in CHCl_3 to establish isotopic equilibrium between the natural I_2 (at a far larger concentration) and the radioiodine present as I^- . The fraction of the radioiodine that was present in the aqueous solution as I^- will report to the organic phase with the I_2 due to isotopic exchange with the far larger mass of natural iodine. Vortex for 5 min (repeat three times).
4. The activity remaining in aqueous phase is IO_3^- .
5. Organic phases are contacted with an equal volume of 0.1 M $\text{Na}_2\text{S}_2\text{O}_3$ in 0.1 M NaOH to reduce any volatile I_2 to nonvolatile I^- prior to gamma counting.

2.3 COUNTING OF Mo-99 AND I-131

The amount of activity in the samples was determined using a germanium detector. Mo-99 was quantified by measurement of its 739-keV γ -ray, and I-131 was quantified by measurement of its 364-keV γ -ray. The activities of Mo-99 and I-131 in each sample were corrected for decay.

2.4 ICP-OES

Inductively coupled optical emission spectroscopy (ICP-OES) was used to determine the concentration of uranium; the error associated with these measurements is $\pm 5\%$.

3 RESULTS

3.1 Mo REDOX

Unfortunately, column experiments could not be performed under constant irradiation at the Van de Graaff generator. Figure 1 shows the setup for the Van-de-Graaff column experiments originally planned. Several problems were encountered with this set of experiments; however, many lessons were learned that will be useful for the mini-SHINE experiments. First, the metallic frit inside the stainless steel columns (planned for use at the linac as well) contains Teflon and has a pore size of only 2 microns. Second, uranyl-sulfate solution could not be pulled or pushed through the stainless steel columns using a 100-psi FMI pump. The back pressure for passing uranyl-sulfate solutions through the column was far greater than 100 psi even at a modest flow rate of 3 mL/min (0.6 cm ID $\times$ 10 cm L titania column). Third, a three-way solenoid valve failed during irradiation at the Van de Graaff. The valve failed mechanically because the piston did not actuate, and it appears that one of the internal components was not compatible with the pH 1 uranyl-sulfate solution. A solid brown material inside the valve was indicative of ferric oxide, which resulted from corrosion, and jammed the drive.

FIGURE 1 Setup for Column Experiments Planned at the Van de Graaff Generator

Therefore, it was decided to irradiate each solution for 1 to 5 hours and pass it through a column as quickly as possible after irradiation using the AKTA liquid chromatography system which can operate at pressures as high as 300 psi. This would prevent the solution from being under constant irradiation; however, the average amount of time elapsed between the end of irradiation and the start of column experiment was 60 min.

Glass columns with 30-micron frits were used with the AKTA liquid chromatography system, but the system could not withstand the back pressure generated by loading the first irradiated uranyl-sulfate solution onto the column. The system decreased the flow rate to 0.1 to 0.4 mL/min from a desired rate of 3 mL/min to keep the pressure below 300 psi, but it was still operating at 250 psi. Approximately 175 mL of solution was loaded onto the column over a period of 20 hours rather than the desired 360 mL of solution with a total loading time of 2 hours. Washes and strips had to be done in the down-flow direction to prevent exceeding the pressure limit of the system, which was reached after loading 175 mL of irradiated uranyl-sulfate solution onto the column. Table I shows the results for the first column experiment completed with a uranyl-sulfate solution irradiated at the Van de Graaff. Even with the pressure problems, only 1% Mo was observed in the effluent. However, the stripping results are low because only 5 CVs of 1 M NH_4OH was actually passed through the column due to the pressure constraints

developed during loading of the feed solution. In addition, ~13% was found in the washes; the column went dry overnight, however, due to the system overpressurizing and no liquid passing through the column for almost 6 hours. We cannot conclude whether or not Mo redox chemistry was affected by the radiation dose because there were too many extra variables. If Mo were reduced, the adsorption was not affected, only the recovery.

Looking more closely at the solution post-irradiation, a butter-like precipitate was observed, but it could not be centrifuged or filtered. This is most likely uranyl peroxide, which has been observed in higher dose irradiation tests at the Van de Graaff using uranyl-sulfate solutions. For the next experiment, 10 ppm FeSO_4 was added to the solution prior to irradiation to catalyze the destruction of peroxide and prevent precipitation of uranyl peroxide. In addition, higher-dose irradiation tests are planned to create a more strongly reducing environment that is closer to the expected dose for the SHINE target solution.

The next uranyl-sulfate (150 g-U/L) solution irradiated at the Van de Graaff contained 10 ppm FeSO_4 . Unfortunately, due to vacuum leaks at the generator, this solution was only irradiated for 1 hour. The total dose applied to the solution was about 80 kRad, and the solution

TABLE 1 Column Results for First Van de Graaff Irradiated Solution

Column Size (0.66 cm ID $\times$ 10 cm L)	
%Mo in effluent	1
%Mo in strip	26
%Mo in washes	13

was loaded onto a 1-cm ID $\times$ 3-cm L 1 hour after irradiation at a flow rate of 5.5 mL/min. The results shown in Table 2 show good adsorption of Mo (0.5% Mo found in the effluent) but poor recovery (72%) after 30 CVs of 1 M NH_4OH at 70°C was passed through the column at a flow rate of 2.8 mL/min. At this point, it is difficult to state whether or not a change in Mo oxidation state had an effect on Mo recovery. However, both column experiments using irradiated uranyl-sulfate solutions showed poor Mo recovery. By adding FeSO_4 to the solution prior to irradiation, no pressure problems were experienced when loading the irradiated uranyl-sulfate solution onto the column. The back pressure did not exceed 10 psi while being passed through a glass column with a 30-micron frit.

A third solution containing 125 g-U/L uranyl-sulfate, 10 ppm stable Mo, and 0.003 mM SO_4^{2-} was irradiated at the Van de Graaff for approximately 3 hours (250 kRad dose). The solution was transported to Building 205, and a column experiment was initiated 60 minutes after irradiation. A 0.66-cm ID $\times$ 5-cm L titania column was used, and despite having FeSO_4 in solution, the back pressure in the system was around 200 psi, while the uranyl-sulfate solution was loaded onto the column at a flow rate of 1.3 mL/min. Table 3 shows the results for the column experiment. A larger amount of Mo (2.5%) was found in the effluent, and the recovery was extremely low, at 13%, after 30 CVs of 1 M NH_4OH at 70°C was passed through the column. These results suggest that the Mo reduction is taking place because the recovery is so low.

Future experiments where the uranyl-sulfate solution is irradiated at the Van de Graaff and passed through a column while under constant irradiation are planned. Custom stainless steel columns with larger pore sized frits will be utilized to get a better handle on Mo redox chemistry. Initial experiments suggest that Mo may be changing the oxidation state because low Mo recoveries have been observed.

TABLE 2 Column Results for Second Van de Graaff Irradiated Solution

Column Size (1.0 cm ID $\times$ 3.0 cm L)	
%Mo in effluent	0.5
%Mo in strip	72
%Mo in washes	0.1

TABLE 3 Column Results for Third Van de Graaff Irradiated Solution

Column Size (0.66 cm ID $\times$ 5.0 cm L)	
%Mo in effluent	2.5
%Mo in strip	13
%Mo in washes	0.2

3.2 IODINE SPECIATION

3.2.1 Background

Jerden and Vandegrift (2008) utilized two modeling codes (OLI ESP Stream Analyzer and “The Geochemist’s Workbench[®]” Release 3.0) to determine the equilibrium state of a uranyl-nitrate (Jerden and Vandegrift 2008). The modeling results were used to create an Eh versus pH diagram for iodine speciation at 1.7×10^{-5} M (Figure 2). Iodate and uranyl iodate are predicted to be the dominant species; however, if the Eh decreases (due to hydrogen production and/or radiolysis), iodate may be reduced to iodine or even iodide (Jerden and Vandegrift 2008). This diagram will also be applicable to uranyl sulfate solutions; however, radiation will certainly affect the Eh of sulfate solutions differently than for nitrate solutions. The iodine speciation results from the samples irradiated at the Van de Graaff agree with the model results predicted by Jerden and Vandegrift (2008), where the predominant species found were iodide and iodine.

Iodine can exist in one of several oxidation states (-1 to +7) and may be present in aqueous solution as a number of different species (e.g., I^- , I_2 , I_3^- , HOI , IO_2^- , IO_3^- , and IO_4^-) (Wren et al. 2000). The reactivities of the different iodine species vary widely, and the speciation of iodine in aqueous solution and its partitioning into the gas phase is determined largely by reaction kinetics rather than equilibrium thermodynamics. The hydrolysis of molecular iodine to form hypoiodous acid (HOI) following rapid equilibrium involving intermediate species is an important reaction in the absence of radiation. The overall stoichiometry is shown in Equation 1. HOI disproportionates according to the stoichiometric reaction depicted by Equation 2 to form iodide and iodate. These two reactions combine to give the summary reaction depicted by Equation 3. Molecular iodine is significant under acidic and oxidizing conditions, since the equilibria are shifted to the left (Cripps et al. 2003).

FIGURE 2 Eh vs. pH Diagram for Iodine for the Reactor Solution (shown as yellow dot) (The dotted lines indicate the stability field of water [$\text{H}_2\text{O} \leftrightarrow \text{O}_2(\text{g})$ and $\text{H}_2\text{O} \leftrightarrow \text{H}_2(\text{g})$].)

In the presence of a radiation field, iodine speciation is dominated by reactions with radiolysis products of water ($\text{H}_2\text{O} \rightarrow \alpha \beta \gamma \rightarrow \text{e}^-_{(\text{aq})}, \bullet\text{H}, \bullet\text{OH}, \text{H}_2\text{O}_2, \text{HO}_2, \text{H}^+, \text{H}_2$) (Wren et al. 2000). For example, the rate of the oxidation reaction $2\text{I}^- \rightarrow \text{I}_2$ increases by orders of magnitude in the presence of the water radiolysis product $\bullet\text{OH}$. This oxidation involves a number of intermediate steps but the general reaction is:

Similarly, I_2 is readily reduced to I^- by the water radiolysis products H_2O_2 and O_2^- (e.g., $\text{I}_2 + \text{H}_2\text{O}_2 + 2\text{H}_2\text{O} \rightarrow 2\text{I}^- + 2\text{H}_3\text{O}^+ + \text{O}_2$). Under different conditions, H_2O_2 can actually oxidize I^- (e.g., $2\text{H}^+ + 2\text{I}^- + \text{H}_2\text{O}_2 \rightarrow \text{I}_2 + 2\text{H}_2\text{O}$); however, this reaction is believed to be of little importance because I^- would be more rapidly oxidized by highly reactive radicals such as $\bullet\text{OH}$ under radiolytic conditions (Wren et al. 2000). The reaction between I_2 and H_2O_2 , however, is important as it can strongly influence the relationship between pH and iodine volatility (Wren et al. 2000).

In a solution containing dissolved oxygen, the reactions with radiolytically produced electrons can form the radicals O_2^- and HO_2 , which are strong reductants for molecular iodine (Wren et al. 2000):

Under radiolytic conditions, the presence of oxidizable metal ions (e.g., Fe^{2+}) can strongly influence iodine speciation due to the catalytic consumption of the iodine reductants H_2O_2 and O_2^- by the metal (Sellers 1986):

Although the two primary controls on iodine speciation in acidic aqueous solutions are the pH and oxidation potential, the discussion above shows that radiolysis of water can play a key role in iodine speciation in a strong enough radiation field (Wren et al. 2000). Therefore, at sufficiently high dose rates, radiolysis in solution can strongly influence the speciation of iodine and result in formation of elemental and reduced forms of iodine (e.g., I₂, HI, and HOI) that may volatilize.

In this work, determination of iodine speciation in Van de Graaff-irradiated solutions was performed by utilizing solvent extraction techniques and differences in the chemical behavior of iodine species (Cripps et al. 2008; Mineo et al. 2003; Kahn and Kleinberg 1977; Kahn and Wahl 1953; Evans and Jervis 1992):

1. Molecular iodine, I₂, is nonpolar and can be extracted into a nonpolar organic solvent such as chloroform or toluene (Cripps et al. 2003; Mineo et al. 2003; Kahn and Kleinberg 1977; Kahn and Wahl 1953; Evans and Jervis 1992).
2. Iodide, I⁻, undergoes rapid isotopic exchange with I₂, and, therefore, tracer levels of radioactive iodide partition into an organic phase containing 0.1 M stable I₂ (Cripps et al. 2003).
3. Iodate, IO₃⁻, is highly polar and does not readily exchange with I₂, and, therefore, remains in the aqueous phase.
4. Periodate, IO₄⁻, is a strong oxidizer and is not expected to be present in the irradiated uranyl-nitrate solution.

To separate molecular iodine, the irradiated uranyl-sulfate or uranyl-nitrate solution (0.5 mL) was contacted with 0.5 mL of chloroform (Sigma-Aldrich) for 5 min, at room temperature, using a vortex mixer. Contact with the organic solvent was repeated twice to ensure full extraction of molecular iodine. Subsequently, and under the same conditions, the irradiated solution was contacted three times with 0.1 M I₂ in CHCl₃ or toluene. Due to the instantaneous isotopic exchange of I⁻/I₂, radioiodine that was in the form of iodide is expected to report in the organic phase (Cripps et al. 2003). The activity remaining in the aqueous phase is expected to be representative of IO₃⁻ species. The I-131 activity in each organic phase and in the remaining aqueous phase was determined by contacting 10 µL of each phase with 0.1 M Na₂S₂O₃ in 0.1 M NaOH (to reduce elemental iodine to nonvolatile iodide) and counting samples by gamma spectrometry using an Ortec HPGe well detector equipped with an Ortec DSpec Jr. 2.0 multichannel analyzer and Canberra 2002C preamp.

3.2.2 Results

Several uranyl-sulfate and uranyl-nitrate irradiations were performed at the Van de Graaff to examine the effects of dose and starting iodine species on overall speciation of iodine. Figure 3 shows the setup for the iodine speciation experiments, and Figure 4 shows the sample holder and the 1 M NaOH trap used to capture any volatile iodine.

Tables 4 and 5 show the distribution of the different iodine species pre- and post-irradiation for uranyl-sulfate and uranyl-nitrate solutions containing 0.5 μM stable iodine added as KI and tracer I-131. Solutions were irradiated at the Van de Graaff with doses ranging from 48 to 187 Mrad. Prior to irradiation, the predominant species in the uranyl-sulfate solution was iodine (64%), while iodine (48%) and iodide (48%) were the predominant species in the uranyl-nitrate solution. After irradiation at the Van de Graaff, the predominant species independent of radiation dose for both uranyl-sulfate and uranyl-nitrate solutions was iodide. In addition, a negligible amount of iodine was found in the NaOH trap, which suggests that the reducing environment created by the high radiation field may be enough to keep most of the iodine in solution.

Tables 6 and 7 show pH changes for uranyl-nitrate and uranyl-sulfate solutions irradiated at the Van de Graaff. The initial pH of the uranyl-nitrate solution was 0.96, and it only increased by 0.03 to 0.07 pH units, which implies not enough dose was applied to the solutions to see the large pH changes observed when sodium-nitrate solutions were irradiated at the Van de Graaff. During the sodium-nitrate irradiations, the pH of one of the solutions increased from 1 to 12. Small decreases in pH were observed with the sodium-sulfate irradiations at the Van de Graaff, so it is not surprising that the pH actually decreased by 0.06 to 0.10 pH units for the uranyl-sulfate solutions over the range of radiation doses shown here.

Table 8 shows the results obtained after 1,120 and 3,000 Mrad doses were applied to uranyl-sulfate solutions containing 0.5 mM KI and tracer I-131. Again, the predominant species post-irradiation was iodide (~96%), with 3 to 4% present as iodine. The solution pre-irradiation had a higher percentage of iodine (44%) compared to the uranyl-sulfate solution prepared for the first set of irradiations, which had ~21% present as iodine. This is most likely due to the fact that the first solution equilibrated for longer than 24 hours before extractions were performed. Over time, in a nonirradiated uranyl sulfate solution, iodine present in solution will reduce to iodide. These results suggest that even at higher doses, iodide is the predominant species and little to no iodine is found in the gaseous phase (NaOH trap).

Table 9 shows the iodine speciation results for uranyl-sulfate solutions containing stable iodine added as potassium iodide, potassium iodate, or iodine with tracer I-131 pre- and post-irradiation at the Van de Graaff. Isotopic equilibration between iodine or iodide and iodate is very slow, and adequate contact time was not given to ensure conversion of tracer I-131 to the iodate form. An approximately 6,000-Mrad dose was applied to the solutions, and the results suggest that the starting species has little effect on the overall iodine speciation because the predominant species for all cases post-irradiation is iodide (96–99%).

FIGURE 3 Setup for the Iodine Speciation Experiments

FIGURE 4 Sample Holder and 1 M NaOH for the Iodine Speciation Experiments

TABLE 4 Iodine Speciation as a Function of Radiation Dose for Uranyl-sulfate Solutions

135 g-U/L Uranyl Sulfate and 0.5 μ M KI					
Dose (Mrad)	Irradiation Time (min)	I ₂ gas	I ₂ solution	I ⁻	IO ₃ ⁻
0	0	—	63.8	21	15.2
49	12	0.06	2.5	96.8	0.6
66	18	0.08	1.8	97.5	0.6
93	25	0.09	2.3	97.3	0.3
152	37	0.07	1.3	98.2	0.4
187	50	0.16	1.4	98.3	0.1

TABLE 5 Iodine Speciation as a Function of Radiation Dose for Uranyl-nitrate Solutions

140 g-U/L Uranyl Nitrate and 0.5 μ M KI					
Dose (Mrad)	Irradiation Time (min)	I ₂ gas	I ₂ solution	I ⁻	IO ₃ ⁻
0	0	—	48	47.8	4.3
48	12	0.02	0.9	99.0	0.2
79	18	0	0.3	99.4	0.3
103	25	0.01	1.0	98.8	0.2
166	37	0.01	0.4	99.5	0.1
187	50	0.01	0.3	99.6	0.1

TABLE 6 pH Changes Observed for Uranyl-nitrate Solutions Irradiated at the Van de Graaff

Uranyl Nitrate (pH=0.96)		
Dose (Mrad)	Irradiation Time (min)	pH
48	12	0.99
79	18	1.03
103	25	1.02
166	37	1.02
187	50	0.99

**TABLE 7 pH Changes Observed
for Uranyl-sulfate Solutions
Irradiated at the Van de Graaff**

Uranyl Sulfate (pH – 1.18)		
Dose (Mrad)	Irradiation Time (min)	pH
49	12	1.12
66	18	1.10
93	25	1.09
152	37	1.08
187	50	1.08

**TABLE 8 Iodine Speciation Results after Exposure to 1,120 and
3,000 Mrad Doses**

135 g-U/L Uranyl Sulfate and 0.5 μ M KI						
Dose (Mrad)	Irradiation Time (min)	I ₂ gas	I ₂ solution	I ⁻	IO ₃ ⁻	pH
0	0	–	51	43.9	5.1	0.96
1120	30	0.01	3.8	95.9	0.2	0.95
3000	80	0.02	3.3	96.4	0.2	0.94

TABLE 9 Iodine Speciation Results after Exposure to 6,000 Mrad Dose

135 g-U/L Uranyl Sulfate and 0.5 μ M KI, I ₂ , or KIO ₃							
Dose (Mrad)	Irradiation Time (min)	Stable Species	I ₂ gas	I ₂ solution	I ⁻	IO ₃ ⁻	pH
0	0	I ₂	–	91	6.9	2.1	0.96
6,000	80	I ₂	0.1	3.8	95.7	0.3	0.97
0	0	KI	–	54.5	40.9	4.6	0.97
6,000	80	KI	0.1	2.1	97.7	0.5	1.03
0	0	KIO ₃ ^a	–	30.4	62	7.6	1.04
6,000	80	KIO ₃ ^a	0.1	0.9	98.8	0.2	0.95

^a Adequate contact time was not given to ensure full conversion of tracer I-131 to iodate.

4 CONCLUSIONS AND FUTURE WORK

We do not have a complete understanding of the effect of radiation on Mo redox chemistry because relatively low radiation doses were applied to the solutions, and column experiments could not be performed under constant irradiation. Still, results indicate that Mo reduction may be occurring in the solutions during irradiation because low Mo recoveries were obtained for all column experiments performed with irradiated solutions. Overall, these experiments provided us with a lot of information necessary for the success of the linac experiments. First, even if a precipitate cannot be seen, it does not mean that it is not forming. Uranyl-sulfate solutions post-irradiation generated extremely high back pressures even for our 300-psi AKTA liquid chromatography system. A catalyst such as Fe is needed to destroy peroxide to prevent formation of uranyl-peroxide. Second, the stainless steel columns cannot be used for the linac experiments because the frit is only 2 microns and contains Teflon. Third, the three-way solenoid valve failed due to mechanical failure of the piston from corrosion of one or more of the internal valve components after contact with uranyl-sulfate solution at pH 1. Column experiments will be optimized at the Van de Graaff prior to being conducted at the linac. If low Mo recoveries continue to be observed, oxidizing agents such as KMnO_4 will be used. New columns with larger pore frits and made without Teflon will be used. FeSO_4 was added to the second uranyl-sulfate solution irradiated at the Van de Graaff, and it was effective in destroying peroxide that formed during irradiation and made it difficult to pass the first irradiated uranyl-sulfate solution through a column with a 30-micron frit. Quartz or stainless steel frits and custom stainless steel columns will most likely be used.

For the iodine speciation experiments completed at the Van de Graaff, the predominant species was iodide, independent of radiation dose and starting species. No iodine was collected in the NaOH trap, but results from the mini-SHINE experiments will provide more conclusive results regarding the overall speciation of iodine in a uranyl-sulfate solution. In addition, samples will be collected to examine how it changes as a function of time and radiation dose.

5 REFERENCES

- Jerden, J.L., and G.F. Vandegrift, 2008, "Predictive Modeling of Solution Chemistry in an Aqueous Homogeneous Reactor Used for Mo-99 Production," presented at the RERTR International Conference, October 5–9, Washington, D.C.
- Wren, J.C., et al., 2000, "The Chemistry of Iodine in Containment," *Nuclear Technology* 129:297–325.
- Cripps, R., et al., 2003, "Quick Analytical Method for Determination of Iodide and Iodate Ions in Aqueous Solutions," *Journal of Radioanalytical and Nuclear Chemistry* 256: 357.
- Sellers, R.M., 1986, "A Database for the Reaction Kinetics of Iodine in Aqueous Solution," p. 91 in *Proceedings of Specialists' Workshop on Iodine Chemistry in Reactor Safety*. Harwell, United Kingdom, September 1985, AERE-R11974, A.M. Deane and P.E. Potter (Eds.), Atomic Energy Research Establishment.
- Mineo, H., et al., 2003, "Applicability of a Model Predicting Iodine-129 Profile in a Silver Nitrate Silica-Gel Column for Dissolver Off-Gas Treatment of Fuel Reprocessing," *Separation Science and Technology* 38:1981–2001.
- Kahn, M., and J. Kleinberg, 1977, *Radiochemistry of Iodine*, NAS-NS-306, National Academy of Sciences-National Research Council.
- Kahn, M., and A.C. Wahl, 1953, "Some Observations on the Chemical Behavior of Iodine at Low Concentrations," *Journal of Chemical Physics* 21:1185.
- Evans, G.J., and R.E. Jervis, 1992, "Radiochemical Studies of Iodine Behaviour under Conditions Relevant to Nuclear Reactor Accidents," *Journal of Radioanalytical and Nuclear Chemistry* 161:121.

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