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Experimental Results for Potential Precipitates in SHINE Target Solution

Chemical Sciences and Engineering Division

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EXPERIMENTAL RESULTS FOR POTENTIAL PRECIPITATES IN SHINE TARGET SOLUTION

1 INTRODUCTION

Argonne National Laboratory is assisting SHINE Medical Technologies in developing recovery and purification processes for molybdenum-99 (Mo-99) from an accelerator-driven, subcritical target consisting of an aqueous uranyl sulfate solution. Use of low-enriched as opposed to high-enriched uranium reduces proliferation concerns.

SHINE Medical Technologies needs data to assure themselves and the Nuclear Regulatory Commission (NRC) that precipitate formation will not occur in their 140 g-U/L uranyl-sulfate target solution. Potential sources of precipitation include uranyl peroxide, fission products, and corrosion products. Formation of uranyl peroxide can be mitigated by adding 1 ppm $FeSO_4$ prior to irradiation to catalyze the destruction of peroxide before it can build up enough to cause precipitation. This observation has been verified with irradiation tests performed at the Van de Graaff and phase-1 micro-SHINE irradiation tests performed using the linac [1,2]. Chemical modeling of the SHINE target solution showed that certain phases could form, but their precipitation kinetics are unknown [3]. As a result, the potential for precipitation of ZrO_2, SnO_2, $BaSO_4$, $CoWO_4$, and RuO_2 in a uranyl sulfate solution at room temperature and 60°C has been examined experimentally. Small-scale corrosion tests were performed at Argonne using Types 304 and 316 stainless steel disks in contact with uranyl sulfate at room temperature, 60°C, and 80°C. No precipitation of any potential corrosion products (Fe, Co, Cr, and Ni) was observed during these tests, which had incubation times of 6 hours to 30 days. Analysis by inductively coupled plasma mass spectrometry (ICP-MS) indicated that corrosion rates are high at first, but once a passivation layer forms, they become negligible. This report discusses the experimental results for the potential precipitation of ZrO_2, SnO_2, $BaSO_4$, $CoWO_4$, and RuO_2 in a 140 g-U/L uranyl sulfate solution at room temperature and 60°C after one week.

2 MATERIALS AND METHODS

An Excel spreadsheet, entitled Solution Composition_101813, was issued to Argonne by SHINE and used for the chemical modeling [3]. For the values used in this spreadsheet we assumed the highest concentration of each element in the target solution, which also includes the upper limit of impurities present in the low-enriched uranium (LEU) metal. The highest concentrations of each metal species present in the target solution at any time are as follows: Zr - 0.35 mM, Sn - 0.11 mM, Ba - 0.0056 mM, Co - 0.011 mM, W - 0.069 mM, and Ru - 0.0076 mM. The solids utilized for the precipitation tests were dissolved in water and included $Zr(SO_4)_2 \cdot 4H_2O$, $SnCl_4 \cdot 5H_2O$, $Ba(NO_3)_2$, $CoSO_4 \cdot 7H_2O$, $Na_2WO_4 \cdot 2H_2O$, and K_2RuCl_6. Precipitation experiments were performed by adding known quantities of each salt to a concentrated uranyl sulfate solution to make the final concentration 140 g-U/L. Stock solutions of 100 mM of each metal salt were prepared except for K_2RuCl_6, which had a stock concentration of 1 mM due to limited solubility. Precipitation experiments done at 60°C were performed using a thermostated shaker bath.

3 RESULTS

The experimental results are as follows:

- Zr, added as $Zr(SO_4)_2 \cdot 4H_2O$, did not precipitate in the presence of a 140 g-U/L uranyl sulfate solution with pH 1 at concentrations as high as 30 mM at room temperature and 60°C. Precipitation was not observed in solutions containing 30 mM Zr after being left for one week at room temperature and 60°C. Solutions will be monitored for up to one month every few days to ensure precipitation has not occurred.

- Sn, added as $SnCl_4 \cdot 5H_2O$, showed no signs of precipitation when the final Sn concentration was 0.01 mM, 0.1 mM, 1 mM, 3 mM, 10 mM, or 20 mM; however, when the final Sn concentration reached 30 mM in the presence of a 140 g-U/L uranyl sulfate solution with pH 1, instantaneous precipitation occurred at room temperature and 60°C. All remaining solutions (0.01–20 mM Sn) will be monitored for up to one month every few days at room temperature and 60°C to ensure precipitation does not occur at a lower concentration over time. After one week, solutions containing 0.01–20 mM Sn at room temperature and 60°C showed no signs of precipitation after one week.

- Ba, added as $Ba(NO_3)_2$, was soluble in the presence of a 140 g-U/L uranyl sulfate solution with pH 1 at concentrations of 0.01 mM and 0.1 mM, but when the concentration reached 1 mM Ba at room temperature and 60°C, a precipitate formed immediately. After one week, precipitates did not form in solutions containing 0.01 mM and 0.1 mM Ba at room temperature and 60°C, but they will be monitored for one month.

- $CoWO_4$, added as two separate metal salts, $CoSO_4 \cdot 7H_2O$ and $Na_2WO_4 \cdot 2H_2O$, was soluble when 0.01 mM of each salt was added to a 140 g-U/L uranyl sulfate solution with pH 1 at room temperature. When the final concentrations of $CoSO_4 \cdot 7H_2O$ and $Na_2WO_4 \cdot 2H_2O$ were 0.1 mM in the presence of a 140 g-U/L uranyl sulfate solution with pH 1 at room temperature, a flaky precipitate formed within 2 minutes, but precipitation at 60°C did not occur until the concentration of each salt was equal to 10 mM, and this precipitate formed immediately. Samples containing 0.01 mM of each salt at room temperature will be monitored for up to one month, but precipitation did not occur after one week. Samples containing 0.01, 0.1, 1, and 3 mM of each salt will be kept at 60°C for one month, but no precipitation was seen after one week in any of these samples.

- Lastly, due to the limited solubility of K_2RuCl_6, precipitation did not occur when the concentration of Ru reached a maximum of 0.5 mM tested in the presence of a 140 g-U/L uranyl sulfate solution at room temperature and

60°C. Samples will be kept at room temperature and 60°C for up to one month, but no precipitates formed in either sample after one week.

4 DISCUSSION

The potential precipitation of Zr was tested at a concentration about 85 times higher than what is the highest concentration of Zr expected to be present in the SHINE target solution at any point. Even with a very conservative estimate based on data from batch and tracer column studies, at least half of the Zr should remain adsorbed on the titania column. Tin did precipitate when the concentration reached 30 mM at room temperature and 60°C, but that is greater than 200 times the highest expected concentration of Sn. The tin did not precipitate at a concentration of 20 mM, which is well over 100 times its highest expected concentration. Barium precipitated when the concentration reached 1 mM independent of temperature, and this is nearly 200 times higher than the highest expected Ba concentration in the target solution. In addition, $CoWO_4$, added as two separate metal salts, precipitated at a concentration of 0.1 mM at room temperature, which is only about 10 times higher than the highest Co concentration expected and 1.4 times greater than the highest W concentration expected. Increasing the temperature to 60°C allowed the solids to remain in solution up to a concentration of 10 mM, which is about 900 times higher than the highest concentration expected for Co and about 140 times higher than the highest concentration of W. Precipitation tests using Co and W salts independently showed that both are soluble up to 30 mM at room temperature and 60°C. Ruthenium did not precipitate when the concentration was 0.5 mM, which is about 65 times higher than the highest expected concentration of Ru in the target solution.

The finding of most concern here is the potential precipitation of $CoWO_4$, which occurs at relatively low concentrations compared to what is expected in the SHINE target solution. Mini-SHINE solutions should provide data more representative of what will be expected in the real SHINE target solution, where the effects of a high radiation field will be present.

5 CONCLUSIONS AND FUTURE WORK

The effects of a radiation field will dramatically affect the redox chemistry and possibly the pH of the solution slightly. The solubilities of the different elements will change as the redox chemistry and pH of the solution change. For example, the small-scale laboratory tests showed that Zr precipitation is not a huge concern, but fission product precipitation is a possibility when the pH reaches around 1.7-1.8. A more complete understanding of what will have the greatest potential for precipitation will be identified after the mini-SHINE experiments have been completed using a LEU solution as uranyl sulfate.

The addendum to this report discusses the results from samples left at room temperature and 60°C for one month to determine if kinetics plays a role in precipitation formation for the metals predicted to potentially lead to precipitation based on Jerden's chemical models.

6 REFERENCES

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[3] James Jerden, 2014, *SHINE Target-Solution Chemistry: Thermodynamic Modeling of Speciation, Precipitate Formation, and the Chemical Effects of Stainless Steel Corrosion*, Argonne National Laboratory Report ANL/CSE-14/11.

ADDENDUM TO EXPERIMENTAL RESULTS FOR POTENTIAL PRECIPITATES IN SHINE TARGET SOLUTION

Results observed over a period of 30 days are shown in Table 1. At concentrations as high as 30 mM, ZrO_2 did not precipitate at room temperature or 60°C. At a concentration of 20 mM, SnO_2 precipitated at room temperature and 60°C after 2 weeks. When the concentration reached 1 mM, $BaSO_4$ precipitated instantaneously at room temperature and 60°C. The precipitation of cobalt tungstate was the most concerning because it precipitated at room temperature after 2 minutes when the concentration was only 0.1 mM. After 3 weeks, $CoWO_4$ precipitated at a concentration of 1 mM at 60°C. Precipitation was not observed for RuO_2 after 30 days at room temperature (RT) or 60°C when the concentration was 0.1 mM.

Table 1. Precipitation results observed from 0-30 days.

Precipitate	RT Concentration	60°C Concentration
ZrO_2	No precipitation	No precipitation
SnO_2	30 mM – instant	30 mM – instant
	20 mM – 2 weeks	20 mM – 2 weeks
$BaSO_4$	1 mM – instant	1 mM – instant
$CoWO_4$	0.1 mM – 2 min	10 mM – instant
		3 mM – 1.5 weeks
		1 mM – 3 weeks
RuO_2	No precipitation	No precipitation

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