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Gadolinium Oxalate Solubility Measurements in Nitric Acid Solutions

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EXECUTIVE SUMMARY

HB-Line will begin processing Pu solutions during FY2012 that will involve the recovery of Pu using oxalate precipitation and filtration. After the precipitation and filtration processes, the filtrate solution will be transferred from HB-Line to H-Canyon. The presence of excess oxalate and unfiltered Pu oxalate solids in these solutions create a criticality safety issue if they are sent to H-Canyon without controls in H-Canyon. One approach involves H-Canyon receiving the filtrate solution into a tank that is poisoned with soluble gadolinium (Gd). Decomposition of the oxalate will occur within a subsequent H-Canyon vessel.

The receipt of excess oxalate into the H-Canyon receipt tanks has the potential to precipitate a portion of the Gd poison in the receipt tanks. Because the amount of Gd in solution determines the maximum amount of Pu solids that H-Canyon can receive, H-Canyon Engineering requested that SRNL determine the solubility of Gd in aqueous solutions of 4-10 M nitric acid (HNO_3), 4-12 g/L Gd, and 0.15-0.25 M oxalic acid ($H_2C_2O_4$) at 25 °C. The target soluble Gd concentration is 6 g/L. The data indicate that the target can be achieved above 6 M HNO_3 and below 0.25 M $H_2C_2O_4$.

For 6 M HNO_3, 10.5 g/L and 7 g/L Gd are soluble in 0.15 M and 0.25 M $H_2C_2O_4$, respectively. In 4 M HNO_3, the Gd solubility drops significantly to 2 g/L and 0.25 g/L in 0.15 M and 0.25 M $H_2C_2O_4$, respectively. The solubility of Gd at 8-10 M HNO_3 exceeds the solubility at 6 M HNO_3. The data for 4 M HNO_3 showed good agreement with data in the literature. To achieve a target of 6 g/L soluble Gd in solution in the presence of 0.15-0.25 M oxalate, the HNO_3 concentration must be maintained at or above 6 M HNO_3.

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LIST OF ABBREVIATIONS

AD	Analytical Development
DI	de-ionized
GdNH	gadolinium nitrate hexahydrate
IC	ion chromatography
ICPES	inductively coupled plasma emission spectroscopy
NP>11	no precipitate after 11 days
NM	not measured
SRNL	Savannah River National Laboratory

1.0 Introduction

HB-Line will begin processing Pu solutions during FY2012 that will involve the recovery of Pu using oxalate precipitation and filtration. After the precipitation and filtration processes, the presence of excess oxalate and unfiltered Pu oxalate solids pose a criticality safety issue downstream of HB-Line. In previous campaigns, HB-Line performed an oxalate decomposition (or oxalate "kill") step to prevent the transfer of excess oxalate and Pu oxalate solids to the non-geometrically favorable tanks within H-Canyon. The current flowsheet has H-Canyon receiving the filtrate solution with possible Pu solids into a tank that is poisoned with Gd in solution; decomposition of the oxalate will occur within a subsequent H-Canyon vessel.

The receipt of excess oxalate into the H-Canyon receipt tank has the potential to precipitate a portion of the Gd poison in the receipt tanks.[1] The amount of Gd in solution determines the maximum amount of Pu solids that H-Canyon can receive. The current H-Canyon target is a minimum of 6 g/L Gd in solution at nitric acid (HNO_3) concentrations of 6-10 M. H-Canyon Engineering requested that SRNL determine the solubility of Gd in aqueous solutions of HNO_3 and oxalic acid ($H_2C_2O_4$) at 25 °C.[2]

2.0 Background

The precipitation of lanthanides, such as Gd, has been studied at SRNL[3] and solubility data are available in the literature.[1,4] The research by Sarver and Brinton[1] is of particular interest because it was conducted in 2-4 M HNO_3 and 0-0.25 M $H_2C_2O_4$. Figure 2-1 contains the data pertinent to this study. The SRNL data were collected at 4-10 M HNO_3 and 0.15-0.25 M $H_2C_2O_4$ to address the operating range for H-Canyon. Although the data at 4 M HNO_3 and 0.25 M $H_2C_2O_4$ do not meet the H-Canyon objectives, the trends as functions of HNO_3 and $H_2C_2O_4$ concentrations indicate that adequate solubility of Gd may occur at higher HNO_3 concentrations and lower $H_2C_2O_4$ concentrations.

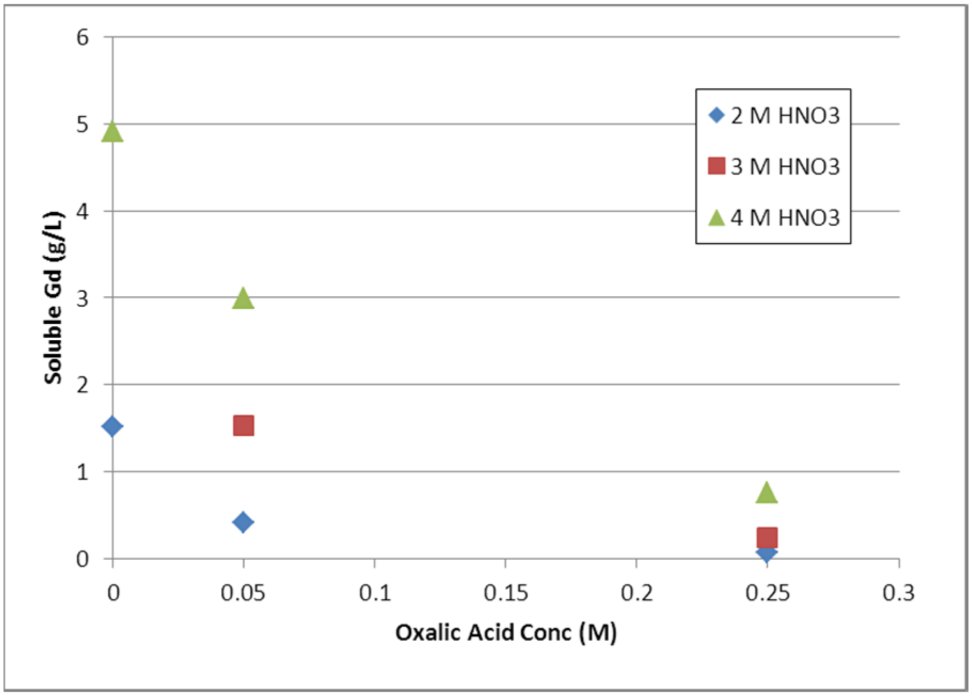

Figure 2-1. Gadolinium Oxalate Solubility in Nitric Acid[1]

3.0 Experimental Procedure

A solubility test matrix was established that varied the HNO_3 (4-10 M), $H_2C_2O_4$ (0.15-0.25 M), and Gd (4-12 g/L) concentrations. The target concentrations are listed in Table 3-1. Samples were prepared by adding the chemicals of Table 3-1 into 60-mL polyethylene bottles and diluting with de-ionized (DI) water to 25 mL. The 1 M $H_2C_2O_4$ was prepared by combining 55.046 g of DI water with 7.4427 g of $H_2C_2O_4$-$2H_2O$ in a polyethylene bottle, adding a Teflon^{TM}-coated stir bar, and stirring at ambient temperature for 24 h (the final volume was 59 mL).

The bottles were capped and placed into a controlled-temperature water bath with a shaker table. The samples were maintained at 25±1 °C for the duration of the test and shaken periodically. The samples were regularly inspected for the formation of a precipitate.

After 30 h at temperature, only Sample 2 formed a precipitate. Consequently, 0.287 g of gadolinium nitrate hexahydrate (the equivalent of 4 g/L Gd) were added to the remaining nine samples. Therefore, Samples 1, 3, and 4 contained ~0.574 g of $Gd(NO_3)_3$-$6H_2O$ (~8 g/L Gd), and Samples 5-10 contained ~0.861 g of $Gd(NO_3)_3$-$6H_2O$ (~12 g/L Gd). The final $Gd(NO_3)_3$-$6H_2O$ additions and Gd concentrations are shown in Table 3-1.

Table 3-1. Test Matrix Final Target Concentrations and Preparation Masses

	Target Concentrations			Added and Diluted to 25 mL		
Sample	HNO_3 (M)	$H_2C_2O_4$ (M)	Gd (g/L)	15.7 M HNO_3 (mL)	1 M $H_2C_2O_4$ (mL)	GdNH* (g)
1	4	0.15	8	6.37	3.75	0.574$^{\#}$
2	4	0.25	4	6.37	6.25	0.287
3	6	0.15	8	9.55	3.75	0.574$^{\#}$
4	6	0.25	8	9.55	6.25	0.574$^{\#}$
5	6	0.15	12	9.55	3.75	0.861$^{\#}$
6	6	0.25	12	9.55	6.25	0.861$^{\#}$
7	8	0.15	12	12.74	3.75	0.861$^{\#}$
8	8	0.25	12	12.74	6.25	0.861$^{\#}$
9	10	0.15	12	15.92	3.75	0.861$^{\#}$
10	10	0.25	12	15.92	6.25	0.861$^{\#}$

* GdNH = gadolinium nitrate hexahydrate [$Gd(NO_3)_3$-$6H_2O$]
$^{\#}$ An addition of 0.287 g of GdNH (~4 g/L Gd) occurred after 30 h

After 5 days, liquid subsamples were submitted to Analytical Development (AD) from Samples 1, 2, 4, 6, and 8 for analysis by inductively coupled plasma emission spectroscopy (ICPES) and ion chromatography (IC). After 7 days, a few crystals of $H_2C_2O_4$-$2H_2O$ were added to Samples 3, 5, 7, and 9 to facilitate precipitation. After 11 days, liquid subsamples were withdrawn from Samples 3, 5, 7, 9, and 10 for analysis by ICPES and IC. The samples for each analysis contained ~1.8 mL.

4.0 Results and Discussion

Of the ten samples prepared, only seven precipitated (determined by visual observation) with the presence of precipitate in Sample 5 considered questionable. The supernatant liquids were analyzed for Gd concentration by ICPES. Those data are listed in Table 4-1. Based on the Gd data, the initial $H_2C_2O_4$ concentration, and the stoichiometry for the formation of gadolinium oxalate [$Gd_2(C_2O_4)_3$], the soluble concentrations of $C_2O_4^{2-}$ were calculated and are provided in Table 4-1. The soluble Gd and the calculated $C_2O_4^{2-}$ concentrations for 4-8 M HNO_3 are graphed along with the 1927 data from Sarver and Brinton[1] in Figure 4-1.

Table 4-1. Soluble Gadolinium and Oxalate Concentrations in 4-10 M HNO_3

Sample	HNO_3 (M)	$H_2C_2O_4$ (M)	Gd (g/L)	Days to Precipitate	Soluble Gd (g/L)*	Soluble $C_2O_4^{2-}$ (M)* [Calc / Measure]
1	4	0.15	8	4	3.47	0.107 / 0.109
2	4	0.25	4	1	1.03	0.222 / NM
3	6	0.15	8	NP>11	8.05	0.150 / 0.151
4	6	0.25	8	4	7.18	0.242 / 0.232
5	6	0.15	12	11	11.5	0.144 / 0.131
6	6	0.25	12	4	7.86	0.211 / 0.207
7	8	0.15	12	NP>11	12.0	0.150 / NM
8	8	0.25	12	4	11.5	0.245 / NM
9	10	0.15	12	NP>11	11.9	0.150 / NM
10	10	0.25	12	5	12.2	0.252 / 0.144

* measurement uncertainty for ICPES and IC was 10%
NP>11 = no precipitate after 11 d
NM = not measured

The 4 M HNO_3 data for the current study exhibit good agreement with the data from the literature. The trend for the 6 M HNO_3 samples appears to follow that of the 2-4 M HNO_3 samples. Consequently, the formation of precipitate in Sample 5 would be borderline because it is near the projected solubility limit. Similarly, precipitates in Samples 3, 7, and 9 would not be expected. Analyses of the oxalate concentrations (Table 4-1) agree with the calculated values within analytical uncertainty for all samples except Sample 10.

For Sample 10, the Gd measurement of 12.2 g/L does not agree with the observation that a precipitate formed after five days. If the measured value for $C_2O_4^{2-}$ was used to calculate the corresponding Gd concentration, the calculated Gd concentration would be 1.0 g/L, which is also not consistent with the observed precipitation behavior. It is not known if the high HNO_3 concentration is having a negative impact on the sample (i.e., decomposition of $H_2C_2O_4$).

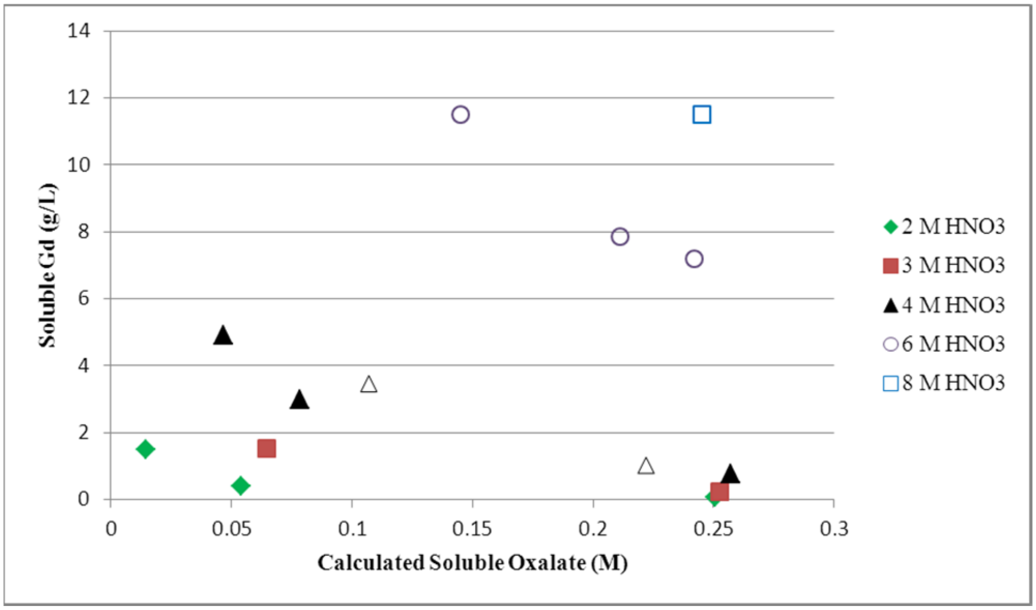

Figure 4-1. Gadolinium Solubility as Functions of HNO_3 and Oxalate

Interpolation of the 4 M HNO_3 data in Figure 4-1 indicates that, for the system containing only Gd, $H_2C_2O_4$, and HNO_3, 2 g/L and 0.8 g/L Gd are soluble in 0.15 M and 0.25 M oxalate, respectively. Similarly, at 6 M HNO_3, 10.5 g/L and 7 g/L Gd are soluble in 0.15 M and 0.25 M oxalate, respectively. The increase in solubility from 4 M to 6 M HNO_3 was expected, but the magnitude of the increase was not anticipated. The solubility of Gd at 8-10 M HNO_3 is greater than the solubility at 6 M HNO_3. It should be noted that the addition of other cations, such as iron, would create competition with Gd for oxalate and would thus likely increase Gd solubility.[5] Plutonium(III) shows similar behavior to that of Gd, but the data are too few to draw direct comparisons.[6]

5.0 Conclusions

SRNL measured gadolinium oxalate solubility at 4-10 M HNO_3, 4-12 g/L Gd, and 0.15-0.25 M oxalate. Solubility data for 4 M HNO_3 show good agreement with data in the literature. The data indicate that the target of 6 g/L soluble Gd can be achieved above 6 M HNO_3 and below 0.25 M $H_2C_2O_4$. For 0.15 M oxalate, 2 g/L and 10.5 g/L Gd are soluble in 4 M and 6 M HNO_3, respectively. For 0.25 M oxalate, 0.25 g/L and 7 g/L Gd are soluble in 4 M and 6 M HNO_3, respectively. The increase in Gd solubility from 4 M to 6 M HNO_3 was expected, but the magnitude of the increase in solubility was greater than expected. The solubility of Gd at 8-10 M HNO_3 exceeds the solubility at 6 M HNO_3.

6.0 References

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