

# **GADOLINIUM SOLUBILITY AND VOLATILITY DURING DWPF PROCESSING**

S. H. Reboul

January 2008

Process Science & Engineering Section  
Savannah River National Laboratory  
Aiken, SC 29808

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Prepared for the U.S. Department of Energy Under Contract Number  
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**SRNL**  
SAVANNAH RIVER NATIONAL LABORATORY

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## EXECUTIVE SUMMARY

Understanding of gadolinium behavior, as it relates to potential neutron poisoning applications at the DWPF, has increased over the past several years as process specific data have been generated. Of primary importance are phenomena related to gadolinium solubility and volatility, which introduce the potential for gadolinium to be separated from fissile materials during Chemical Process Cell (CPC) and Melter operations.

Existing data indicate that gadolinium solubilities under moderately low pH conditions can vary over several orders of magnitude, depending on the quantities of other constituents that are present. With respect to sludge batching processes, the gadolinium solubility appears to be highly affected by iron. In cases where the mass ratio of Fe:Gd is 300 or more, the gadolinium solubility has been observed to be low, one milligram per liter or less. In contrast, when the ratio of Fe:Gd is 20 or less, the gadolinium solubility has been found to be relatively high, several thousands of milligrams per liter. For gadolinium to serve as an effective neutron poison in CPC operations, the solubility needs to be limited to approximately 100 mg/L. Unfortunately, the Fe:Gd ratio that corresponds to this solubility limit has not been identified.

Existing data suggest gadolinium and plutonium are not volatile during melter operations. However, the data are subject to inherent uncertainties preventing definitive conclusions on this matter.

In order to determine if gadolinium offers a practical means of poisoning waste in DWPF operations, generation of additional data is recommended. This includes:

- Gd solubility testing under conditions where the Fe:Gd ratio varies from 50 to 150
- Gd and Pu volatility studies tailored to quantifying high temperature partitioning

Additional tests focusing on crystal aging of Gd/Pu precipitates should be pursued if receipt of gadolinium-poisoned waste into the Tank Farm becomes routine.

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## **LIST OF ACRONYMS**

DWPF	Defense Waste Processing Facility
FAVC	Formic Acid Vent Condenser
NCSE	Nuclear Criticality Safety Evaluation
SB3	Sludge Batch 3
SME	Slurry Mix Evaporator
SMECT	Slurry Mix Evaporator Condensate Tank
SRAT	Sludge Receipt & Adjustment Tank
SRS	Savannah River Site
WSRC	Washington Savannah River Company



## 1.0 INTRODUCTION

Washington Savannah River Company (WSRC) is currently evaluating use of gadolinium as a supplemental neutron poison for future potential receipts of fissile material into the Defense Waste Processing Facility (DWPF). The primary advantage of using gadolinium over other neutron poisons is associated with gadolinium's high thermal neutron absorption cross section, which has the potential for significantly lowering poison demand. Because the quantity of poison has a direct impact on the number of glass canisters produced at DWPF, use of gadolinium offers a potential means for reducing the number of glass canisters produced in the future. However, the practicality of using such an approach has not been fully demonstrated and will require a clear understanding of gadolinium partitioning during processing in the Sludge Receipt & Adjustment Tank (SRAT), the Slurry Mix Evaporator (SME), and the glass melter system. This understanding will be necessary to assure chemical conditions are sufficient to prevent segregation of gadolinium and fissile materials.

Over the past five years, several activities focusing on use of gadolinium as a neutron poison have been undertaken at WSRC. These activities have supported specific objectives, such as a) receiving additional fissile material into a DWPF sludge batch, b) adding relatively small quantities of gadolinium-poisoned fissile material to existing sludge waste stored in the Tank Farm, and c) possible dissolution of plutonium oxide material at H-Canyon. Now, with the expectation that several alternative fissile material streams may be dispositioned to DWPF, a more extensive evaluation of gadolinium as a neutron poison is warranted.

In this document, a literature search of gadolinium data pertaining to Savannah River Site (SRS) operations is addressed. The specific focus is gadolinium solubility during SRAT/SME processing and gadolinium/plutonium volatilization during the glass melting cycle. This literature search was performed at the request of the Waste Solidification Engineering group of the DWPF (Ray, 2007).

## 2.0 OBJECTIVES

- 1) Identify pertinent documentation addressing gadolinium solubility and volatility
- 2) Summarize R&D findings
- 3) Compile available data to illustrate data trends and gaps
- 4) Identify future studies that would be necessary to address data gaps

### 3.0 RESULTS AND DISCUSSION

Twenty-one formal reports addressing gadolinium poisoning of Savannah River Site (SRS) waste were identified. A summary of the pertinent information in each of these documents is given in Table 1. Nine of the reports provide fundamental data on solid-liquid phase partitioning of gadolinium, plutonium, and uranium under chemical conditions applicable to SRS waste storage and disposition processes. This includes the reports authored by Bronikowski et al. (2002 and 2004), Fellingner et al. (2002), Bibler et al. (2002), Herman et al. (2002a and 2002b), and Visser et al. (2003a, 2003b, and 2005). Four reports provide information focusing on general processing impacts associated with adding gadolinium to waste. This includes the reports authored by Peeler et al. (2002), Smith (2002b), Fellingner et al. (2002), and Herman et al. (2002a). Three reports contain information addressing volatility of gadolinium and plutonium during the SRAT/SME cycle and in the DWPF melter system. These are the reports authored by Herman et al. (2002a) and Smith (2002a and 2002b). Four of the reports address formation of gadolinium fluoride solids during acid dissolution of plutonium oxide at H-Canyon. These are the reports authored by Pierce et al. (2006, 2007a, 2007b, and 2007c). Five reports are Nuclear Criticality Safety Evaluations (NCSEs) which utilize the SRS data to draw conclusions regarding effective gadolinium poisoning.

Discussions of specific data applicable to gadolinium solubility during SRAT/SME processing and gadolinium/plutonium volatility during the SRAT/SME/melter cycle are presented below.

#### 3.1 Gadolinium Solubility at Negligible Fe:Gd Ratios

Test reports authored by Bronikowski et al. (2002 and 2004) and Visser et al. (2003a, 2003b, and 2005) provide fundamental data focusing on solid-liquid phase partitioning of gadolinium and fissile materials under acidic, neutral, and alkaline conditions. These data were generated to support specific waste campaigns originating from H-Canyon, under conditions where negligible iron was present to act as a neutron poison. For tests performed on actual canyon waste, the Fe:Gd mass ratio was nominally 0.10, while for tests performed on simulated waste, the iron content was zero. Initial waste solutions were highly acidic and contained gadolinium concentrations ranging from 1700 to 5700 mg/L, plutonium concentrations ranging from 0 to 3000 mg/L, and uranium concentrations ranging from 0 to 5000 mg/L. Solid-liquid phase partitioning was monitored as the pH of the waste was quickly raised to the following values: a) 3.0-4.5; b)  $\sim 7$ ; and c)  $\geq 14$ . Results indicated that significant phase separation of the gadolinium and fissile materials occurred at pH 3.0-4.5, where 70-90% of the gadolinium remained soluble, while  $<10\%$  of the plutonium and  $<50\%$  of the uranium remained soluble. In contrast, no significant phase separation occurred at the higher pH values ( $\sim 7$  and  $\geq 14$ ), where  $\leq 10\%$  of the gadolinium, plutonium, and uranium remained soluble.

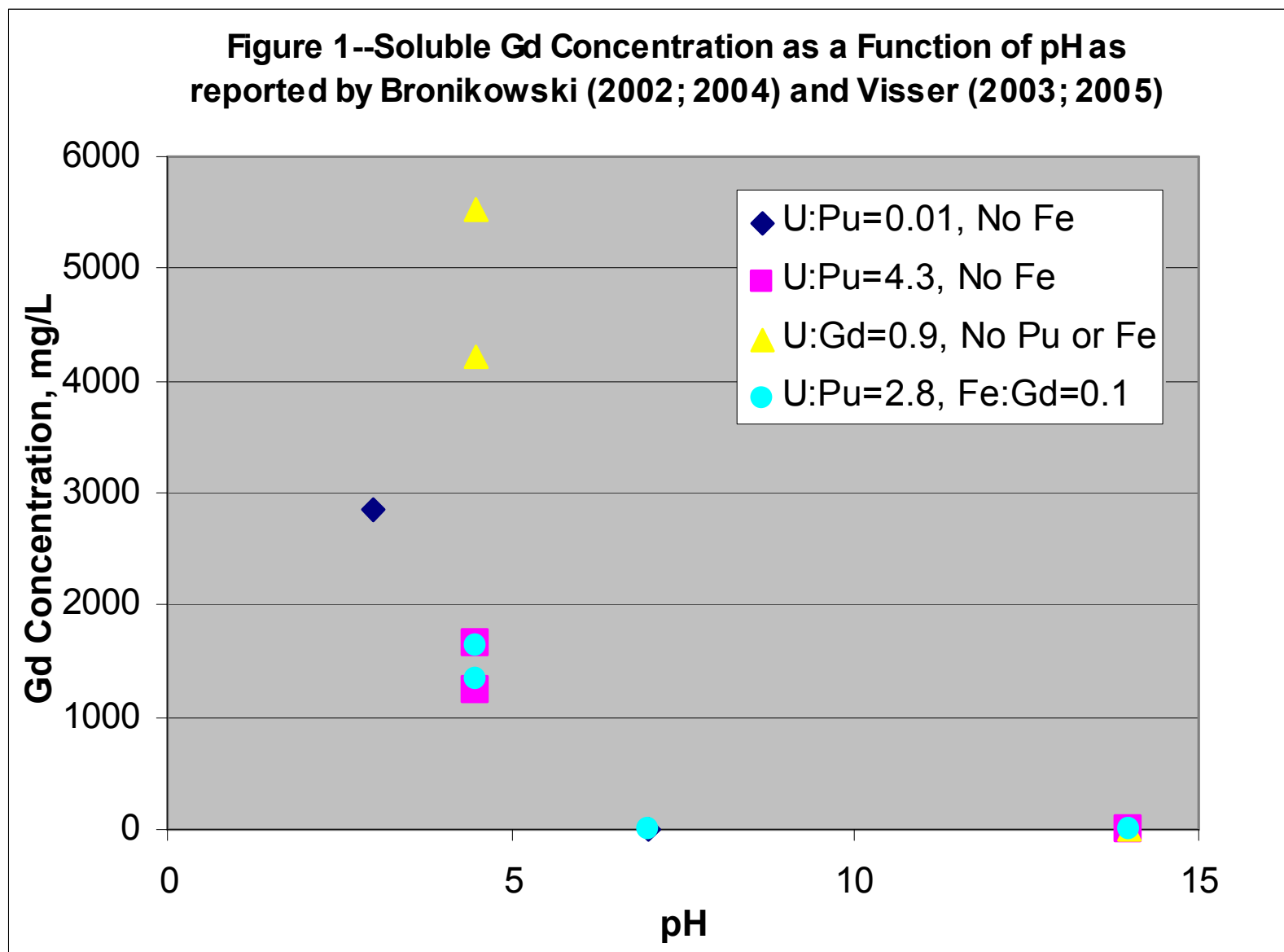
A plot of the soluble gadolinium concentrations as a function of pH (based on the Bronikowski and Visser data) is given in Figure 1. At pH 3.0 and 4.5, the concentrations range from a minimum of approximately 1000 mg/L to a maximum of approximately 5500 mg/L. At pH 7

**Table 1 (Cont'd on Next Page). Summary of Reports Addressing Gadolinium-Poisoning of SRS Waste**

Document Number	Lead Author	Summary of Pertinent Information
SRT-GPD-2002-00008	M. E. Smith	<ul style="list-style-type: none"> <li>No segregation of Ce (Pu surrogate), Fe, and Mn detected in DWPF melter off-gas samples</li> </ul>
WSRC-TR-2002-00145	D. K. Peeler	<ul style="list-style-type: none"> <li>Addition of 100 kg Pu and 150 kg Gd to SB3 will not impact glass quality, product performance, or processability</li> </ul>
WSRC-TR-2002-00198	M. G. Bronikowski	<ul style="list-style-type: none"> <li>Simulated waste contained no iron; U:Pu = ~ 0.01</li> <li>At pH 3, 95% of Gd was soluble, while only 5% of Pu was soluble, indicating separation</li> <li>As long as precipitated solids remain hydrated, the H:Pu:Gd ratio is adequate for criticality control</li> </ul>
WSRC-TR-2002-00199	M. E. Smith	<ul style="list-style-type: none"> <li>No Gd or Pu volatilization was observed during SRAT, SME, and melter cycles</li> <li>Gd did not impact DWPF glass quality</li> <li>More info needed on potential precipitation of Pu without Gd in SRAT</li> </ul>
WSRC-TR-2002-00208	T. L. Fellingner	<ul style="list-style-type: none"> <li>SB3 simulant with Fe:Gd = 300</li> <li>~1% of Gd was soluble and 0.2% Pu was soluble during Tank Farm washing</li> <li>3–5% of Gd was soluble and ~0.2% of Pu was soluble during the SRAT cycle</li> </ul>
N-NCS-H-00134, R1	K. J. McCoid	<ul style="list-style-type: none"> <li>NCSE for minimum safe Gd:Pu ratio in an infinite system</li> <li>1:1 mass ratio of Gd:Pu-239 equivalent is safe with H:Pu atomic ratio <math>\geq 30</math></li> </ul>
WSRC-TR-2002-00211	N. E. Bibler	<ul style="list-style-type: none"> <li>Tests performed in the absence of sludge (no iron) and with sludge (Fe:Gd = 19)</li> <li>In absence of sludge at pH 3.5, all of Gd was soluble, while only 10% of Pu was soluble</li> <li>With sludge at pH 3.5 and 4.0, about half of Gd was soluble, while &lt; 6% of Pu was soluble</li> <li>With sludge at pH 6, 13% of Gd was soluble, while 0.3% of Pu was soluble</li> </ul>
WSRC-TR-2002-00322	C. C. Herman	<ul style="list-style-type: none"> <li>Fe:Gd = 440 in simulant with no oxalate; Fe:Gd = 720 for simulant with 50% of projected oxalate</li> <li>Tests performed in absence of Pu</li> <li>In SRAT processing tests, Gd solubility increased with oxalate addition</li> <li>At pH 2.8, 13-22% of Gd was soluble as oxalate varied from 0-50% of Tk 7 projection</li> <li>At pH 2.2, 43-58% of Gd was soluble as oxalate varied from 0-50% of Tk 7 projection</li> <li>No volatility of Gd detected during SRAT cycle</li> </ul>
WSRC-TR-2002-00508	C. C. Herman	<ul style="list-style-type: none"> <li>Fe:Gd = 720 for simulants with 75% and 125% of projected oxalate</li> <li>Tests performed in absence of Pu</li> <li>At pH 2.5, 30-50% of Gd was soluble as oxalate varied from 75-125% of Tk 7 projection</li> <li>At pH 2.0, 50-100% of Gd was soluble as oxalate varied from 75-125% of Tk 7 projection</li> <li>At pH ~5 and 75% of Tk 7 oxalate projection, 2-3% of Gd was soluble</li> <li>At pH ~7 and 125% of Tk 7 oxalate projection, 80-100% of Gd was soluble</li> </ul>

**Table 1 (Cont'd from Previous Page). Summary of Reports Addressing Gadolinium-Poisoning of SRS Waste**

Document Number	Lead Author	Summary of Pertinent Information
WSRC-TR-2003-00193	A. E. Visser	<ul style="list-style-type: none"> <li>• Fe:Gd = 0.1 and U:Pu = 2.8</li> <li>• At pH 4.5, 91-94% of Gd was soluble, 40-47% of U was soluble, and 2-6% of Pu was soluble</li> <li>• At pH 7, up to 1% of Gd was soluble, up to 8% of U was soluble, and up to 5% of Pu was soluble</li> <li>• At pH 14, &lt; 1% of Gd, U, and Pu was soluble</li> </ul>
WSRC-MS-2003-00602	A. E. Visser	<ul style="list-style-type: none"> <li>• Version of WSRC-TR-2003-00193 prepared for Separation Science and Technology Conference</li> </ul>
WSRC-TR-2004-00053	M. G. Bronikowski	<ul style="list-style-type: none"> <li>• No iron; U:Pu:Gd ratio of 4.3:1:2.4 and U:Gd ratio of 1:1.1 (no Pu)</li> <li>• At pH 4.5, 72-74% of Gd was soluble, while 5-8% of U was soluble and 6% of Pu was soluble</li> </ul>
N-NCS-H-00172, R1	S. T. Gough	<ul style="list-style-type: none"> <li>• NCSE for minimum safe Gd to fissile mass ratio in an infinite system (addresses uranium additions)</li> </ul>
WSRC-MS-2005-00008	D. A. Eghbali	<ul style="list-style-type: none"> <li>• Discussion of how WSRC-TR-2002-00198, 00208, and 00211 were used to develop N-NCS-H-00134</li> </ul>
N-NCS-H-00185	L. M. Gundy	<ul style="list-style-type: none"> <li>• NCSE for Gd neutron poison in solution with Pu solids present</li> </ul>
WSRC-MS-2005-00086	A. E. Visser	<ul style="list-style-type: none"> <li>• More data for Fe:Gd = 0.1 and U:Pu = 2.8</li> <li>• At pH 4.5, 94-97% of Gd was soluble, while 8-47% of U was soluble and 6-10% of Pu was soluble</li> </ul>
N-NCS-H-00179, R2	L. A. Hedlund	<ul style="list-style-type: none"> <li>• NCSE for receipt, transfer, storage, and neutralization of HB-line Pu/U solutions poisoned with Gd</li> </ul>
WSRC-CP-2006-00001	R. A. Pierce	<ul style="list-style-type: none"> <li>• Flowsheet for Pu-Be dissolution, addressing use of Gd (instead of B) and KF (instead of CaF<sub>2</sub>)</li> <li>• GdF<sub>3</sub> solids formed with 4 M HNO<sub>3</sub>, 4.5 g Gd/L, and &gt; 0.10 M KF (no solids with ≤ 0.10 M KF)</li> <li>• No solids with 4 M HNO<sub>3</sub>, 2.2 g Pu/L, 0.22 g Be/L, 4.5 g Gd/L, 3.5 g Fe/L, and 0.05 – 0.15 M KF</li> <li>• Recommendation to dissolve Pu-Be with 4 M HNO<sub>3</sub>, 4.5 g Gd/L, and 0.05 M KF</li> </ul>
WSRC-ATS-2007-00048, R1	R. A. Pierce	<ul style="list-style-type: none"> <li>• Application of Pu-Be dissolution flowsheet to enriched U-Pu materials case</li> <li>• Initial solution of 4 – 6 M HNO<sub>3</sub> and 0.05 – 0.10 M fluoride can be used with 2 g Gd/L</li> <li>• Uncertainty of whether Gd will precipitate with U and Pu between pH 2 and 7</li> </ul>
SRNL-ATS-2007-00082	R. A. Pierce	<ul style="list-style-type: none"> <li>• Determination of whether Gd solids form when concentrating low assay Pu solutions to 4 g/L</li> <li>• Unconcentrated solutions contain 4 -5 M HNO<sub>3</sub>, 0.3 – 2.7 g Pu/L, plus Gd and KF</li> <li>• No Gd solids formed when concentrating HB-Line enriched U-Pu solutions with minor impurities</li> <li>• Gd solids did form when concentrating H-Canyon Pu-Be and enriched U-Pu solutions</li> </ul>
WSRC-STI-2007-00673	R. A. Pierce	<ul style="list-style-type: none"> <li>• Flowsheet studies to use Gd (instead of B) when dissolving high-fired plutonium oxide</li> <li>• In absence of Pu, some Gd solids formed in initial dissolving solution (8 - 12 M HNO<sub>3</sub>, 0.15 – 0.20 M KF, and 1 - 2 g Gd/L)</li> <li>• Gd solids dissolved as Pu was added and dissolved, due to fluoride complexation by Pu (this made less fluoride available to complex with Gd)</li> </ul>



and 14, the concentrations are orders of magnitude lower, ranging from <1 mg/L to a maximum of 6 mg/L. These data are consistent with solids analyses, which show little or no detectable gadolinium in precipitates formed at pH 3.0 and 4.5, but clearly detectable gadolinium in precipitates formed at pH ~7 and  $\geq 14$ . Analyses of solids formed at pH ~7 and  $\geq 14$  suggest that gadolinium and fissile materials are intimately mixed in the solids matrix. However, there is the possibility that aging of the solids will change the distribution of components when the solids become more crystalline. This potential aging effect is a concern for long term storage at the Tank Farm, not for the short term conditions of DWPF processing. To address this phenomenon, analyses of aged gadolinium/plutonium precipitates would be necessary.

### 3.2 Gadolinium Solubility at Low Fe:Gd Ratios

The test report authored by Bibler et al. (2002) provides data focusing on solid-liquid phase partitioning of gadolinium and plutonium under acidic conditions representative of the SRAT process. These data were generated to identify potential phase separation issues associated with adding gadolinium-poisoned plutonium to DWPF Sludge Batch 3 (SB3). The tests were performed in the absence and presence of a simulated sludge, at pH values of 3.5, 4.0, 4.5, and 6.0. In the presence of the simulated sludge, the Fe:Gd mass ratio was 19. Results indicated that phase separation of gadolinium and plutonium was significant at pH 3.5 and 4.0, and moderate at pH 4.5 and 6.0. In the absence of sludge at pH 3.5, virtually all of the gadolinium was soluble, while only about 10% of the plutonium was soluble. In contrast, in the presence of sludge at pH 3.5, about half of the gadolinium was soluble, while only 6% of the plutonium was soluble. At pH 4.0 the gadolinium solubility was only marginally lower. However, at pH 4.5 and 6.0, the solubilities were lower by factors of two and three, respectively.

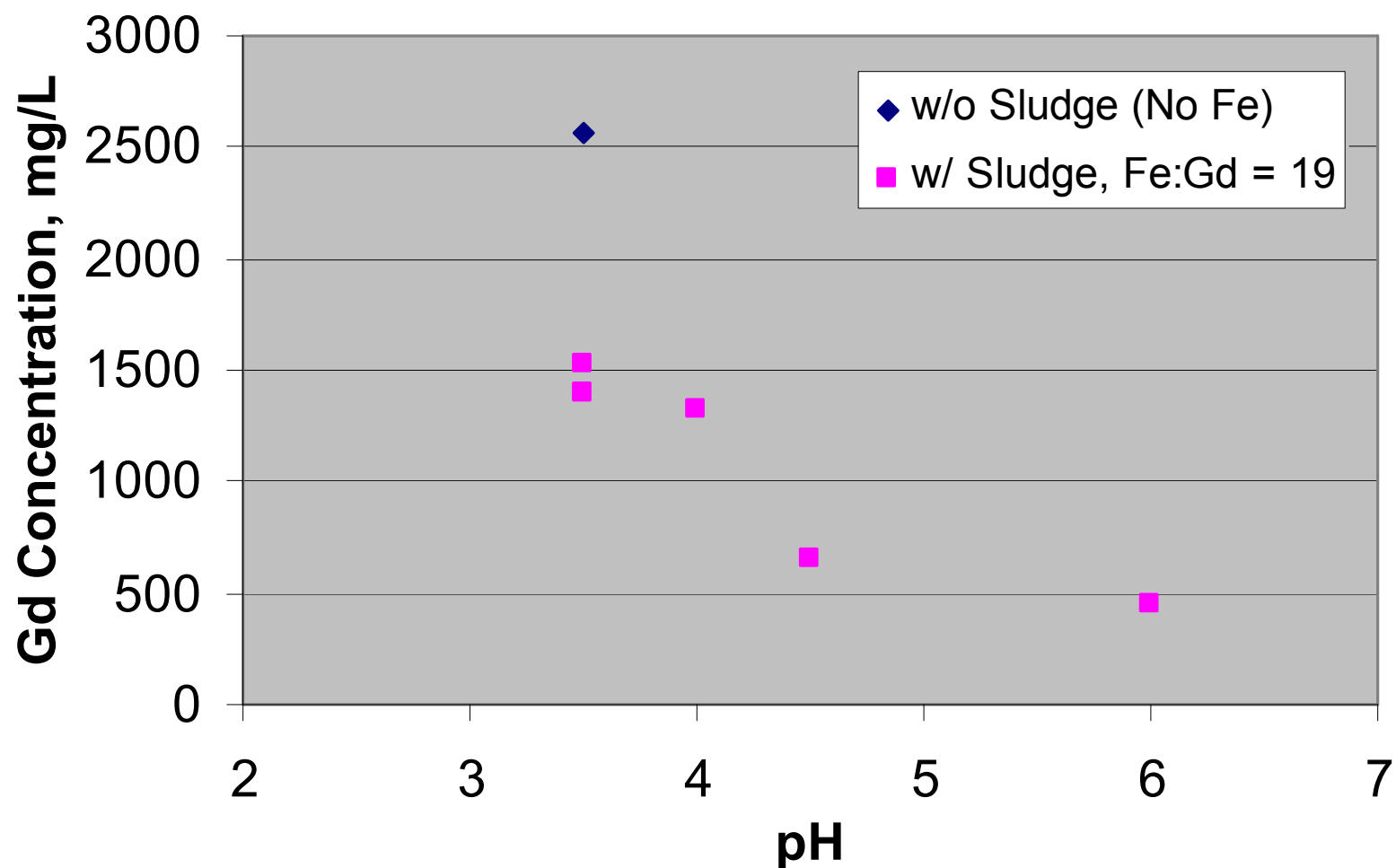
A plot of the soluble gadolinium concentrations as a function of pH (based on the Bibler data) is given in Figure 2. At pH 3.5, the gadolinium concentration was ~2600 mg/L in the absence of sludge and ~1500 mg/L in the presence of sludge. In contrast, at pH 4.5 and 6.0 in the presence of sludge, the gadolinium concentrations were ~700 and ~500 mg/L, respectively.

Note that in the absence of sludge, all available gadolinium was soluble. This suggests that the true gadolinium solubility in the absence of sludge is likely >2600 mg/L. Although additional data would be required to reach definitive conclusions regarding this solubility in the absence of sludge, the data set as a whole suggests that presence of sludge reduces gadolinium solubility. Although sludge contains many components that could impact gadolinium solubility, it is likely that iron, because of its dominance, is a major driver. Discussion of this phenomenon will be continued below, after presentation of other pertinent data.

### 3.3 Gadolinium Solubility at High Fe:Gd Conditions

Test reports authored by Fellingner et al. (2002) and Herman et al. (2002a and 2002b) provide data on solid-liquid phase partitioning of gadolinium when added to DWPF SB3. The Fellingner data were generated using SB3 simulant mixed with precipitated Gd/Pu material from H-Canyon Tank 18.3. In contrast, the Herman data were generated using SB3 simulant mixed with laboratory-prepared gadolinium, and hence, did not contain plutonium. The Herman data were

**Figure 2 -- Soluble Gd Concentration as a Function of pH  
as reported by Bibler (2002)**



generated over a range of oxalate concentrations, spanning from 0 to 125% of the projected SB3 value. (In units of concentration, this range is 0 to ~50,000 mg oxalate per kilogram sludge (Herman et al., 2003)). The Fe:Gd mass ratio associated with the Fellingner testing was 300. The Fe:Gd mass ratio for the Herman testing was 440 in the absence of oxalate and 720 for tests performed when oxalate was present. The Fellingner data were collected at pH values of ~3, ~4, and ~13, while the Herman data were collected for three SRAT processing scenarios (normal and off-normal scenarios) with a collective pH span of 2 to 6.

The Fellingner data suggested that minimal portions of the gadolinium and plutonium were soluble, regardless of whether the pH was 3, 4, or 12. A maximum of ~5% of the gadolinium and ~0.2% of the plutonium was found to be soluble under the most acidic condition (pH ~3). Consequently, separation of gadolinium and plutonium was assumed to be insignificant.

In contrast, larger portions of the gadolinium were found to be soluble, based on the Herman data. In the absence of oxalate, almost half of the gadolinium was soluble at pH 2, while about 10% of the gadolinium was soluble at pH 3. In the presence of the highest oxalate concentrations (75% and 125% of the projection), the gadolinium solubilities were typically higher – up to 100% of the gadolinium was soluble at pH 2, for example.

The disparity between the proportions of soluble gadolinium reported by Fellingner and Herman (low proportions in the Fellingner data and high proportions in the Herman data) is primarily due to the difference in quantities of gadolinium used in the respective tests. Significantly more gadolinium was used in the Fellingner tests, so the proportions that dissolved were commensurately lower. If significantly more gadolinium would have been used in the Herman tests, it is expected that the soluble portions would have been significantly lower.

A plot of the soluble gadolinium concentrations as a function of pH (based on the Fellingner and Herman data) is given in Figure 3. Between pH 2 and 7, the gadolinium concentrations ranged from <1 mg/L to ~20 mg/L. The highest gadolinium concentrations were seen at pH 2 when 75% of the projected oxalate was present and at pH 3-4 in the case where the Fe:Gd was 300. Also of note are the gadolinium concentrations occurring between pH 5 and 7 in the case where 125% of the projected oxalate was present (~50,000 mg/Kg sludge) – these Gd concentrations are relatively high (~10 mg/L) and attributed to the increased complexation with oxalate that occurs in this pH regime.

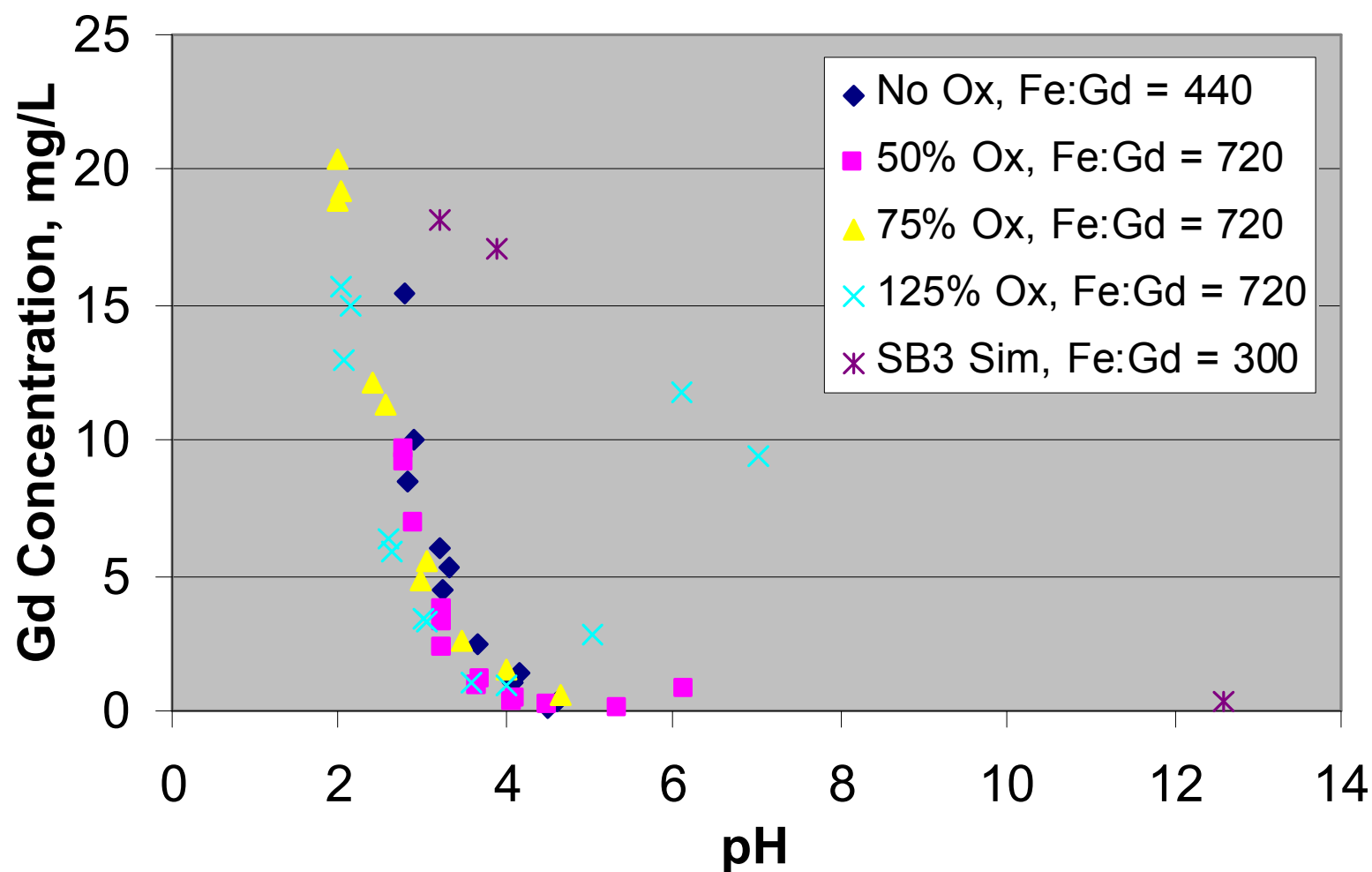
Although some of the gadolinium concentrations given in Figure 3 may underestimate the true gadolinium solubilities (for the reason stated above), they are thought to be of the appropriate order of magnitude, since only a small portion of the data suggest complete dissolution of available gadolinium.

### **3.4 Gadolinium Solubility as a Function of Fe:Gd Ratios**

As alluded to above, gadolinium solubilities under acidic conditions appear to be directly related to the quantity of iron that is present. This trend is demonstrated by the data applicable to the pH 2-6 regime – for Fe:Gd ratios of 0.1 or less, the solubility appears to be on the order of thousands



**Figure 3 -- Soluble Gd Concentration as a Function of pH  
as reported by Fellingner (2002) and Herman (2002)**



of mg/L; for Fe:Gd ratios of ~20, the solubility appears to be on the order of 1000 mg/L; and for Fe:Gd ratios ranging from 300-720, the solubility appears to be on the order of ten mg/L or less. To illustrate this relationship, a plot of soluble gadolinium concentrations as a function of Fe:Gd ratio is given in Figure 4. Note that Figure 4 is based on the data that were previously presented in Figures 1, 2, and 3. However, Figure 4 only contains the data pertaining to the pH 2-6 range and the data have been divided into two groups: 1) data pertaining to the pH 2.0-4.0 range and 2) data pertaining to the pH 4.1-6.0 range.

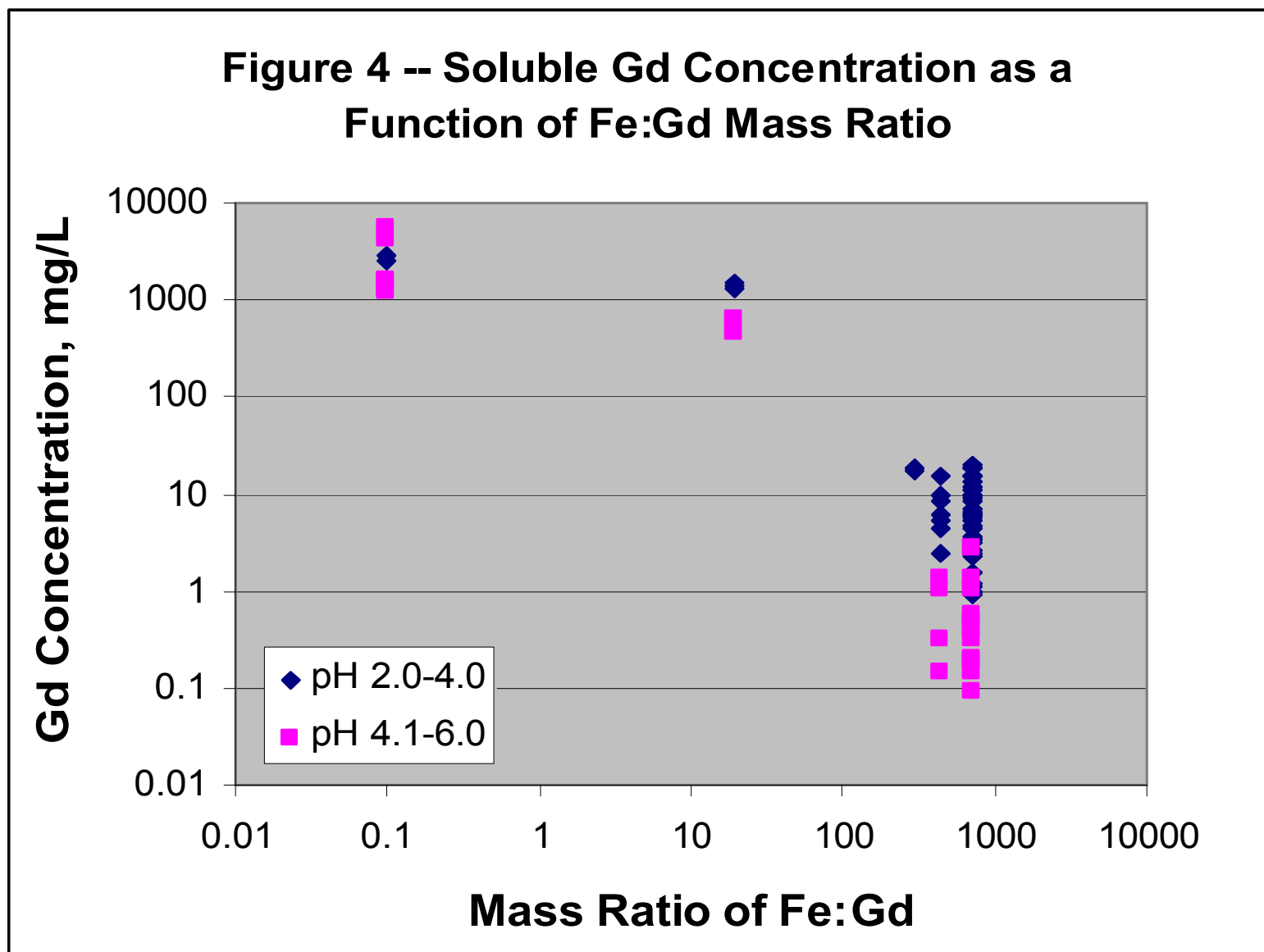
As shown in Figure 4, gadolinium solubilities decrease as the Fe:Gd ratio increases, and solubilities at pH 2-4 are typically somewhat higher than those at pH 4-6, although not in every case. For the purposes of this evaluation, it is important to recognize that conditions must support a gadolinium solubility sufficiently low that the vast majority of the gadolinium will remain integrated in the solid phase with the fissile materials. If one assumes that the initial concentration of gadolinium is on the order of thousands of milligrams per liter, a maximum solubility on the order of 100 mg/L would likely be acceptable. However, as shown in Figure 4, the Fe:Gd ratio that corresponds to such a solubility (~100 mg/L) is currently unknown, due to a lack of data.

A better understanding of the solubility behavior of gadolinium under conditions of moderate Fe:Gd ratios (~100) and mildly acidic conditions will be necessary to draw sound conclusions about the practicality of using gadolinium poisoning in the SRAT/SME. Opportunities for obtaining additional data supporting this objective include analysis of current and near-term process samples (aluminum dissolution and sludge batch qualification samples, for example), as well as independent gadolinium/iron laboratory testing. The expectation is that effective use of gadolinium will require sufficient iron to depress the gadolinium solubility and sufficient gadolinium to assure effective neutron poisoning. Of course, if the Fe:Gd ratio requirement is so high that the iron alone provides adequate neutron poisoning, use of gadolinium will be unnecessary.

### **3.5 Gadolinium and Plutonium Volatility**

Reports authored by Herman et al. (2002a) and Smith (2002a and 2002b) provide information pertaining to liquid-vapor phase partitioning of gadolinium and plutonium under elevated temperature conditions. This includes temperatures of around 100 °C during SRAT/SME processing and around 1200 °C during melter operations. The Herman document (2002a) addresses gadolinium volatility during SRAT/SME processing, based on gadolinium analyses of samples taken from the SRAT, the DWPF Slurry Mix Evaporator Condensate Tank (SMECT), and the Formic Acid Vent Condenser (FAVC). The primary conclusion was that gadolinium did not volatilize based on a) finding all of the original gadolinium in the SRAT product, and b) finding no detectable gadolinium in the SMECT and FAVC samples.

The first Smith document (2002a) contains analytical data from a pilot scale DWPF melter and plasma hearth test performed at the Argonne National Laboratory. Specifically, data are reported for cerium, which is considered an acceptable plutonium surrogate, and three dominant metals present in high level waste sludge (iron, manganese, and silicon). The primary conclusions were that there was no detectable separation of the plutonium surrogate (cerium) from the other metals



and that the metals were not volatile. The author identified the data in this report as being “somewhat limited.”

The second Smith document (2002b) addresses gadolinium volatility based on neodymium data generated during waste qualification runs at DWPF. Neodymium was assumed to be an acceptable surrogate for gadolinium, based on similarity of chemical and physical properties. The primary conclusion was that neodymium did not volatilize, because almost all of the original neodymium was found in the final glass form (after SRAT, SME, and melter processing).

Findings of these three reports provide no basis for identifying either gadolinium or plutonium as being volatile. However, because the data are limited and/or based on surrogate behavior, the technical bases are not considered definitive. One concern is that the uncertainty of the data may mask losses due to volatility. Additional data based on high sensitivity analyses of gadolinium and plutonium (not Gd and Pu surrogates) in off-gas samples would strengthen the technical basis.

## 4.0 CONCLUSIONS

- 1) Under mildly acidic conditions (pH 2–6), the solubility of gadolinium is dependent on the quantity of iron that is present. For Fe:Gd ratios  $\leq 0.1$ , the gadolinium solubility is on the order of thousands of mg/L. For Fe:Gd ratios  $\approx 20$ , the gadolinium solubility is on the order of 1000 mg/L. For Fe:Gd ratios ranging from 300–700, the gadolinium solubility is typically 10 mg/L or less.
- 2) Effective use of gadolinium as a neutron poison requires a gadolinium solubility that is small, on the order of 100 mg/L or less for most applications. This can probably be achieved through control of the Fe:Gd ratio, although the minimum Fe:Gd ratio necessary to assure the solubility requirement is currently unknown. If the Fe:Gd ratio requirement is too high, the advantage of using gadolinium is defeated. However, if the Fe:Gd ratio requirement is sufficiently low (on the order of 100 or less), use of gadolinium may prove practical.
- 3) Low pH gadolinium solubility data at Fe:Gd ratios between 20 and 300 will facilitate assessment of gadolinium poisoning practicality. In the absence of such data, a clear conclusion regarding practicality can not be drawn.
- 4) High concentrations of oxalate increase the gadolinium solubility at pH conditions typical of the normal SRAT cycle. This effect needs to be acknowledged when considering gadolinium poisoning of wastes with high oxalate content.
- 5) No evidence exists to support volatilization of gadolinium and plutonium during SRAT, SME, and glass melter cycles. However, the data that have been reviewed are limited and/or based on observations of surrogate materials that may not be representative. Additional data would provide a stronger basis for defining volatility behavior.

6) Understanding of Gd/Pu/U precipitate aging will become important if neutralized Gd-poisoned waste is stored for extended periods of time (such as is possible if acceptance of Gd-poisoned waste into the Tank Farm becomes routine). Existing data on Gd-containing precipitates are limited to fresh solids, in which Gd and fissile materials appear to be evenly distributed. A potential concern with aged solids is that crystallization effects could cause segregation of Gd and fissile materials. Although such effects are not directly related to SRAT/SME processing, they are pertinent to sludge awaiting disposition at DWPF and should be recognized.

## 5.0 RECOMMENDATIONS

- 1) Perform low pH gadolinium solubility tests under conditions of Fe:Gd ratios between 20 and 300. The goals of these tests would be a) to provide confirmation that gadolinium solubility is a function of the Fe:Gd ratio, and b) to identify the minimum Fe:Gd ratio needed to limit the gadolinium solubility to an acceptable level. Suggested conditions for the tests are:
  - Sufficient gadolinium present to assure <100% dissolution
  - Fe:Gd ratios of 50, 100, and 150
  - Soluble Gd and Fe concentrations measured over the pH 2-7 range
  - Two pH adjustment strategies – one where pH is adjusted after Gd and Fe are combined, and one where pH is adjusted prior to combining Gd and Fe
  - With and without oxalate, as appropriate
- 2) To strengthen the technical bases for defining Gd/Pu volatility behavior during DWPF processing, perform a) a detailed analysis, including assessment of data uncertainty impacts, of all existing process data relevant to Gd/Pu volatility; b) volatility tests designed for the specific purpose of quantifying Gd/Pu volatility during DWPF processing; and/or c) new DWPF process sampling and analysis tailored to quantifying Gd/Pu volatility.
- 3) If gadolinium-poisoning is expected to become routine and dominate over traditional poisoning practices, perform Gd/Pu/U precipitate aging tests to determine if gadolinium and fissile materials in hydroxide precipitate crystals will segregate over time. Although not a specific SRAT/SME processing concern, the effect of precipitate aging is a concern relevant to sludge storage at the Tank Farm (prior to transferring the waste to DWPF).

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