PNNL-27312
RPT-OSIF-002, Rev. 0

Pacific Northwest
NATIONAL LABORATORY

Proudly Operated by **Battelle** *Since 1965*

Precipitation Risk when Diluting DFLAW Feed Saturated in Aluminum Hydroxide

February 2018

CH Delegard
CI Pearce
MS Fountain

U.S. DEPARTMENT OF
ENERGY

Prepared for the U.S. Department of Energy
under Contract DE-AC05-76RL01830

PACIFIC NORTHWEST NATIONAL LABORATORY
operated by
BATTELLE
for the
UNITED STATES DEPARTMENT OF ENERGY
under Contract DE-AC05-76RL01830

Printed in the United States of America

Available to DOE and DOE contractors from the
Office of Scientific and Technical Information,
P.O. Box 62, Oak Ridge, TN 37831-0062;
ph: (865) 576-8401
fax: (865) 576-5728
email: reports@adonis.osti.gov

Available to the public from the National Technical Information Service
5301 Shawnee Rd., Alexandria, VA 22312
ph: (800) 553-NTIS (6847)
email: orders@ntis.gov <http://www.ntis.gov/about/form.aspx>
Online ordering: http://www.ntis.gov

PNNL-27312
RPT-OSIF-002, Rev. 0

Precipitation Risk when Diluting DFLAW Feed Saturated in Aluminum Hydroxide

February 2018

CH Delegard[1]　　MS Fountain
CI Pearce

Prepared for
the U.S. Department of Energy
under Contract DE-AC05-76RL01830

Pacific Northwest National Laboratory
Richland, Washington 99352

---

[1] TradeWind Services LLC

Abstract

The technical bases to support the One System River Protection Project Integrated Flowsheet assumption for diluting staged Direct Feed Low-Activity Waste (DFLAW) from the Hanford waste tanks with raw river water must be assessed in light of the risk of aluminum hydroxide (gibbsite) precipitation prior to the subsequent transfer of tank contents into the Low-Activity Waste Pretreatment System (LAWPS) from days to months after dilution. The operational and mission impacts of using other dilution fluids such as inhibited water, demineralized water, or a 2 M sodium hydroxide solution also must be assessed. As a first step to help inform this investigation, a survey was conducted of Hanford waste-related tests documenting the processing of tank waste materials (solutions, salt cakes, sludges) or their simulants for instances of gibbsite dissolution and precipitation. Experience from the aluminum industry, particularly the Bayer process, also was surveyed to gain insight into the precipitation and dissolution of gibbsite in sodium hydroxide solutions. The dependence of aluminum concentration on hydroxide concentration in analyses of actual tank waste solutions also was surveyed for tanks that have a long-term static inventory and tanks suspected of containing or known to contain substantial gibbsite solid phase in their sludge solids. Finally, an experimental program is outlined to aid prediction of the outcomes of DFLAW staged feed dilution with respect to significant variables that influence gibbsite dissolution and precipitation. The results of these investigations are summarized in this report.

Executive Summary

The technical bases to support the One System River Protection Project Integrated Flowsheet assumption for diluting staged Direct Feed Low-Activity Waste (DFLAW) from the Hanford waste tanks with raw river water must be assessed in light of the risk of aluminum hydroxide (gibbsite) precipitation prior to the subsequent transfer of tank contents into the Low-Activity Waste Pretreatment System (LAWPS) from days to months after dilution. The operational and mission impacts of using other dilution fluids such as inhibited water, demineralized water, or a 2 M sodium hydroxide solution also must be assessed. As a first step to help inform this investigation, a technical literature survey was conducted of Hanford waste-related tests documenting the processing of tank waste materials (solutions, salt cakes, sludges) or their simulants for instances of gibbsite dissolution and precipitation. Experience from the aluminum industry, particularly the Bayer process, also was surveyed to gain insight into the precipitation and dissolution of gibbsite in sodium hydroxide solutions. The dependence of aluminum concentration on hydroxide concentration in actual tank waste solutions also was surveyed for tanks that have a long-term static inventory and tanks suspected of containing or known to contain substantial gibbsite solid phase in their sludge solids. Finally, an experimental program is outlined to aid prediction of the outcomes of DFLAW staged feed dilution with respect to significant variables that influence gibbsite dissolution and precipitation. The results of these investigations are summarized in this report.

A number of different types of Hanford waste processing tests and analyses have been undertaken over the >40 years of reports examined for review. The technical literature from these Hanford tank waste studies was surveyed according to these specific waste processing alternatives and characterizations.

Testing of stepwise (or cascade) dissolution of tank waste salt cakes has been performed to understand the sequence of dissolution of the constituent salts when contacted with water or dilute “inhibited water.” Though observation of gibbsite precipitation was actively sought in these tests, it was implied or observed on only two occasions. In one instance gibbsite precipitation was suggested through the presence of excess hydroxide in solution from dissolution tests with BY-102 waste. However, gibbsite itself was not observed. In another test, saltcake dissolution from Tank SX-101 containing sodium aluminate solids produced gibbsite, as might be expected.

The “Clean Salt” process was investigated as a means of producing essentially nonradioactive sodium nitrate salt from tank waste by fractional crystallization. One “Clean Salt” test performed on the alkaline side was surmised to have produced a gibbsite precipitate upon cooling. Later, tests were undertaken to actively investigate gibbsite solubility in aluminum-fortified actual wastes. In one instance, apparent supersaturation with respect to gibbsite was maintained for about 2 months but gibbsite failed to precipitate. The presence of seed crystals caused other tests in this series, also of actual wastes, to attain equilibrium from both over- and undersaturation.

Caustic leaching was investigated for many actual tank waste sludges as a means of dissolving aluminum-bearing phases such as gibbsite and boehmite. In one test of caustic leaching performed at elevated temperature, the delayed appearance of a white precipitate, taken to be gibbsite, occurred upon leachate cooling and storage after 100 days, but no solids were present after 12 days. This was the only reported instance of post-precipitation (of gibbsite) in the numerous dedicated caustic leaching studies. However, some gibbsite was observed to form upon blending and concentrating solutions and rinses in subsequent integrated flowsheet testing of caustic and oxidative leaching and ion exchange processing. The genesis of these solids may have indicated transition through dawsonite.

Ion exchange testing has been performed to remove cesium-137 from alkaline tank wastes. One instance of gibbsite precipitation was observed after 1 week of waste solution aging in preparation of a candidate

feed (from AN-102 and C-104 wastes) for ion exchange for cesium removal testing. Uncharacterized white solids within the ion exchange column also have been observed in testing using simulant wastes, but the solids are unlikely to have been gibbsite based on feed-solution composition and generous rinses. A genuine waste from Tank AN-102 was characterized to have a composition well above that necessary to precipitate gibbsite, but no precipitation was observed.

Abundant technical literature exists from the aluminum industry about the dissolution of aluminum-bearing ores such as bauxite (which can contain gibbsite and boehmite) and the precipitation of purified gibbsite by dilution, cooling, and introduction of seed crystal. Accordingly, a number of studies of the solubility equilibria of gibbsite in $NaOH-NaAl(OH)_4$ solutions as a function of composition and temperature have been performed. The results of these studies have been surveyed and reduced to a useful published gibbsite solubility equation. The impact of additional salts (such as sodium nitrate) on gibbsite solubility has been studied and can be compared with solubilities expected in simple $NaOH-NaAl(OH)_4$ solutions as predicted by this equation. In four separate studies, gibbsite solubility was found to increase in the presence of added sodium nitrate (at a given sodium hydroxide concentration) and the effect is greater at higher temperature. Notably, however, the gibbsite solubility in one study was greater than that observed by another closely related study, likely because equilibrium or steady state was reached from oversaturation in the former case and the solutions remained at supersaturation, hampered by gibbsite’s slow crystallization, whereas the latter tests were run from undersaturation.

A more encompassing gibbsite solubility study was undertaken at Hanford in which the simulated waste solutions at 20, 40, 60, and 80°C and of varying sodium hydroxide concentration were saturated in sodium nitrate, sodium nitrite, sodium carbonate, sodium sulfate, and aluminum phases (gibbsite or sodium aluminate, depending on NaOH concentration). However, the gibbsite solubilities measured in these studies as outlined in the so-called “Barney Diagram” seem to be unusually high. Despite experimental techniques used to guarantee equilibrium, the observed high solubilities have been attributed in later reviews to the failure to allow sufficient time to reach equilibrium for this notoriously slow precipitation.

The compositions of waste solutions from tanks that have long quiescent times and from tanks known to contain high-aluminum content wastes in the sludge (REDOX/S-saltcake and aluminum cladding removal wastes) were surveyed in the historical Tank Waste Information Network System (TWINS) database. These data comprise about 160 separate tank waste measurements. A separate published survey of more than 300 tank waste solution analyses in TWINS and screened for solutions containing 3 to 7 molar total sodium also was identified.

Plots of aluminum concentration versus hydroxide concentration for these numerous tank waste solution analyses from TWINS show unit slope with respect to free hydroxide, as would be expected by the reaction stoichiometry. These plots also show an upper threshold of aluminum concentration that is approximately one-half to two-thirds of the free hydroxide concentration.[1] The presence of many data pairs below this upper threshold can be explained by the absence of gibbsite solid phase (and possibly the presence of sodium aluminosilicates) or dilution by later addition of buoyant solution. The relatively few data lying above this threshold might be explained by analytical variability and sampling error or by supersaturation attained by high temperatures within the tank wastes themselves. The aluminum

---

[1] This may be compared with aluminum molar concentrations of about one-third the free hydroxide concentration in Bayer process liquors at the gibbsite precipitation step run at ~42–62°C. The 50 to 100% greater aluminum concentration at a given hydroxide concentration in the Hanford tank waste liquors, which currently are no higher than 45°C, may be because the presence of high concentrations of other sodium salts (e.g., nitrate, nitrite, carbonate) in the Hanford solutions increases the hydroxide chemical activity, decreases the chemical activity of water, or increases cation-anion pairing.

concentration threshold observed in actual waste is about a factor of 5 to 8 greater than the gibbsite solubility line at 25°C provided by the Bayer process gibbsite solubility equation, but is nearer the concentrations predicted at higher temperature. Significantly, the observed gibbsite solubilities from tests of gibbsite precipitation and dissolution for wastes from Tanks AN-105 and AP-108 were studied and are near to and as much as a factor of 2 above the aluminum concentration threshold observed in the assembled TWINS data. However, the "Barney Diagram" findings do not accord with the observed actual waste aluminum concentration threshold, thereby lending credence to the hypothesis that the test solutions in these experiments had not reached equilibrium and remained supersaturated in gibbsite.

Dilution with raw water is already acknowledged to bring its own undesirable consequences by precipitating silicate and calcium phases. An engineering assessment of whether the quantities and types of these phases are so detrimental to justify the expense and complication of dilution with distilled or deionized water remains to be performed. The use of 2 M sodium hydroxide solution for dilution has its own downside because it introduces extraneous sodium burden to the pretreatment and vitrification processes, but it may be necessary if gibbsite post-precipitation risks cannot be foreclosed or ameliorated.

Accordingly, to establish a defensible technical basis for minimizing or avoiding aluminum hydroxide precipitation during DFLAW staged feed dilution, aluminum solubility must be predicted as a function of the significant variables that influence gibbsite dissolution and precipitation. These variables include temperature; equilibration time; other solution components that meaningfully affect the activity coefficient of either hydroxide or the aluminate ion, particularly nitrate, nitrite, and carbonate; the presence of gibbsite seed crystals; ionic strength, i.e., sodium concentration and the potential for ion pair formation; and the approach from above and below saturation.

Based on the present review of gibbsite solubility data and the impact of dilution on solution stabilities with specific focus on aluminum hydroxide, a "Task 2" work scope is proposed to study the impact of sodium nitrite on gibbsite solubility as a function of sodium nitrate and sodium hydroxide concentrations and a function of temperature. The relative hydroxide and aluminum levels will be above, at, and below the 2:1 molar threshold observed for actual tank waste solutions. Well-characterized synthetic aluminum hydroxide will be used as seed crystal and the time to attainment of equilibrium will be established in these tests to be conducted below saturation according to the approach outlined by most thermodynamic studies. Limited testing using sodium nitrate instead of sodium nitrite will be performed to tie with prior studies. The scope of this initial testing is further defined in the present report.

In addition, it is likely that further testing beyond the proposed "Task 2" work scope will be necessary to establish the key factors in gibbsite precipitation delay and rate. Among these avenues of testing are the following:

- establishment of the importance of dawsonite, $NaAlCO_3(OH)_2$, and carbonate on $Al(OH)_3$ dissolution and precipitation
- understanding the effect of gibbsite seed crystals as a means of inducing precipitation and mitigating the effects of unanticipated solids carryover into the LAWPS caused by delayed aluminum precipitation (e.g., fouling the LAWPS ion exchange operations and transfer line deposition)
- extension of the experimental timescale to encompass diluted DFLAW storage intervals, i.e., 1 to 9 months, to understand $Al(OH)_3$ precipitation kinetics
- definition of sodium counterion concentrations needed to stabilize polymeric aluminum solution species and limit precipitation.

Ultimately, this additional work would provide key information about (1) the mechanisms by which gibbsite becomes supersaturated; (2) $Al(OH)_3$ precipitation kinetics, including induction times to precipitation; and (3) potential blending strategies to minimize $Al(OH)_3$ precipitation or seeding strategies to manage precipitation.

Acknowledgments

The dissolution and precipitation behavior of gibbsite in alkaline Hanford Site tank wastes is of concern in forecasting process outcomes in storage, mixing, retrieval, and treatment and thus has been the subject of many laboratory and engineering studies. The authors gratefully acknowledge, in particular, the broad and essential contributions of Hanford (and other) scientists and engineers to the present understanding of gibbsite behavior in the Hanford tank wastes. Their names and affiliations are called out in the references. However, special mention must be made of three contributors. Chief among the chemists is Dan Herting, whose contributions span over 35 years and encompass nearly half of the references cited in this document. His manifold insights into Hanford tank waste chemistry are not limited to gibbsite and aluminum but encompass innovative process technologies including Clean Salt and salt cake leaching, elegant characterization methodologies including polarized light microscopy, and daily process support. The engineering and thermodynamic contributions into gibbsite behavior in the Hanford tank wastes have been led for the past 35 years by the Reynolds father and son team, Dan and Jacob. Their insightful and sophisticated interpretations of the laboratory and process findings have sharpened the state of the art while their championing of further and more detailed studies, including the present one, have improved the technical basis of the essential chemical and engineering factors.

We are also grateful to our technical reviewers – Courtney Bottenus and particularly Arich Fuher for their meticulous examinations of the various spreadsheets and calculations and Heather Colburn and Bill Dey for their review of the manuscripts. Finally, we thank our editor Susan Ennor for her graceful improvements to our technical English.

Acronyms and Abbreviations

DFLAW	Direct Feed Low-Activity Waste
DOE	U.S. Department of Energy
EFRC	Energy Frontier Research Center
FMP	flowsheet maturation plan
IDREAM	Interfacial Dynamics in Radiation Environments and Materials
LAWPS	Low-Activity Waste Pretreatment System
PNNL	Pacific Northwest National Laboratory
PUREX	Plutonium Uranium Extraction Plant
QA	quality assurance
R&D	research and development
REDOX	Reduction-Oxidation Plant
TWINS	Tank Waste Information Network System
WRPS	Washington River Protection Solutions LLC
WTP	Hanford Tank Waste Treatment and Immobilization Plant
WWFTP	WRPS Waste Form Testing Program

Contents

Figures

1.0 Introduction

Pacific Northwest National Laboratory (PNNL) provides Washington River Protection Solutions LLC (WRPS) with baseline technical support to the One System River Protection Project Integrated Flowsheet team by identifying and closing flowsheet model and operations gaps and realizing opportunities for reducing the waste treatment mission cost, schedule, and technical risk. These flowsheet gaps and opportunities are documented in the *One System River Protection Project Integrated Flowsheet Maturation Plan* (Reynolds et al. 2017). Approaches are proposed and declared in associated flowsheet maturation plans (FMPs) contained within the plan appendices. The present report fulfills Task 1 of the flowsheet maturation plan, FMP-WASTE-25, “Composition of Water for Diluting DFLAW [Direct Feed Low-Activity Waste] Feed Saturated in Aluminum Hydroxide” (found in Reynolds et al. 2017).

The current integrated flowsheet model, described and documented in the *One System River Protection Project Integrated Flowsheet* (Anderson et al. 2017), assumes raw filtered river water is used at all times to dilute the DFLAW staged feed tank prior to the subsequent transfer of tank contents into the Low-Activity Waste Pretreatment System (LAWPS). These transfers may occur from days to months after dilution. However, no technical basis has been identified and documented to support this flowsheet assumption while balancing the risk of aluminum hydroxide precipitation and the operational and mission impacts of using other dilution fluids such as inhibited water, demineralized water, or a 2-M NaOH solution. Aluminum hydroxide precipitation, primarily in the form of gibbsite, is a risk to tank farm operations by its accumulating as settled solids that occupy usable LAWPS feed tank space, unanticipated solids carryover to the LAWPS, possible delayed aluminum precipitation fouling of the LAWPS ion exchange operations, and/or transfer line deposition/plugging.

This report documents a review of PNNL and other U.S. Department of Energy (DOE) national laboratory test reports, Hanford’s 222-S Analytical Laboratory reports, and other WRPS reports identifying dilutions of supernatant tank waste or their simulants, resulting waste solubility data, and observations of precipitation or stable solution solubility during extended (days to months) periods and compares these findings with abundant related Bayer process solubility data from the aluminum industry.

These phenomenological observations are abstracted to discern trends. Plots of dissolved aluminum versus free hydroxide concentrations for some of these systems were prepared as an initial means to visualize the data and were compared with a published temperature-dependent gibbsite solubility model derived for simple sodium aluminate/hydroxide systems (after Misra 1970). Data from tank waste supernatant solution analyses also were gathered from the Tank Waste Information Network System (TWINS) and similarly plotted. Finally, a proposed “Task 2” work scope and schedule are provided to help close identified gaps in predicting gibbsite solubility as functions of solute concentrations and temperature.

2.0 Quality Assurance

This work was conducted with funding from WRPS under Project 67116, contract 36437-171, and under Project 71351, Contract 36437-239, both with the title "Tank Waste Disposition Integrated Flowsheet Support."

All research and development (R&D) work at PNNL is performed in accordance with PNNL's Laboratory-Level Quality Management Program, which is based on a graded application of NQA-1-2000, *Quality Assurance Requirements for Nuclear Facility Applications*, to R&D activities. To ensure that all client quality assurance (QA) expectations were addressed, the QA controls of the WRPS Waste Form Testing Program (WWFTP) QA program were also implemented for this work. The WWFTP QA program implements the requirements of NQA-1-2008, *Quality Assurance Requirements for Nuclear Facility Applications*, and NQA-1a-2009, *Addenda to ASME NQA-1-2008*, and consists of the WWFTP Quality Assurance Plan (QA-WWFTP-001) and associated procedures that provide detailed instructions for implementing NQA-1 requirements for R&D work.

Preparation of this report was assigned the technology level "Basic Research" and planned, performed, documented, and reported in accordance with procedure QA-NSLW-1101, *Scientific Investigation for Basic Research*. All staff members contributing to the work received appropriate technical and QA training prior to performing quality-affecting work. Note that the QA controls described above apply only to the compilation, review, analysis, and reporting of the information from the source documents cited in this report; the QA pedigree of the information in each source document is determined by the controls implemented by its author(s) and originating organization.

3.0 Background and Approach

Industrial experience in using the Bayer process for aluminum ore beneficiation to produce corundum (i.e., alpha alumina, α-Al_2O_3) has existed for well over a century. The initial step of this process includes the hydrothermal dissolution of aluminum from bauxite ores containing aluminum hydroxides and oxide hydroxides by the use of heated and concentrated sodium hydroxide (i.e., NaOH). The dissolution step is followed by crystallization of the purified aluminum trihydroxide phase gibbsite, γ-$Al(OH)_3$ from the pregnant (i.e., supersaturated) liquors. The gibbsite then is heated to produce corundum. For clear (solids-free) liquors, even those well above apparent saturation, the second (crystallization) step, however, is notoriously slow. The following excerpt from a well-known industrial monograph on aluminum oxides and hydroxides neatly summarizes the situation (Wefers and Misra 1987; *italicized text* added by the present authors):

> "In the Bayer process, bauxite is treated at temperatures between 415 and 560K *(i.e., 142-287°C)* with caustic solutions containing 140 to 350 g Na_2O per liter *(i.e., 4.5-11.3 M NaOH)*. Temperatures and sodium oxide concentrations are selected according to the aluminum hydroxide mineral prevailing in the bauxite and the type of pressure vessels (autoclaves) available.
>
> The digest reactions are
>
> $$Al(OH)_3 + NaOH \leftrightarrows Na^+ + Al(OH)_4^-$$
> $$AlOOH + H_2O + NaOH \leftrightarrows Na^+ + Al(OH)_4^-$$
>
> In the first step of the process sodium aluminate solutions are obtained having a molar ratio Na_2O:Al_2O_3 between 1.5 and 1.7 *(equivalent to a NaOH:NaAl(OH)$_4$ molar ratio of 0.5-0.7)*. To recover the dissolved aluminum hydroxide the liquor is diluted, if necessary, to 130 to 150 g Na_2O per liter *[i.e., 4.2-4.4 M total sodium, equivalent to 1.4-1.8 M free NaOH and 2.5-2.9 M sodium within NaAl(OH)$_4$]* and cooled to 315-335K *(i.e., 42-62°C)*. Large quantities of recirculated seed gibbsite (up to 400% of the amount dissolved) are added and the suspension is stirred. Gibbsite crystallizes out until a molar ratio of about 4 *(equivalent to a NaOH:NaAl(OH)$_4$ molar ratio of 3.0)* is reached. Above 375K *(i.e., 102°C)*, boehmite is the crystallization product.
>
> The behavior of aluminate solutions is remarkable in two ways: For one, they must be diluted for the precipitation of hydroxide to be initiated. Moreover, gibbsite crystallizes only after intensive seeding, even though the solutions are highly supersaturated at 315-335K *(i.e., 42-62°C)*."

As aluminum industry experience shows, sodium aluminate liquors have a marked propensity for supersaturation with respect to gibbsite precipitation. As is seen in the survey results documented herein, gibbsite supersaturation is also observed in Hanford tank waste laboratory studies, both for simulant and for actual wastes.

The size and shape of gibbsite crystals also are of importance in Hanford tank waste operations. Studies summarized by Herting et al. (2015) show gibbsite crystals present in Hanford tank wastes generally to be small – microns (μm) to tens of microns across – and to have hexagonal shapes. However, the gibbsite particles can grow to dimensions greater than 100 μm, some as aggregates (Figure 1). Herting and colleagues (2015) also maintain that although the $Al(OH)_3$ allomorphs bayerite and nordstrandite as well as amorphous $Al(OH)_3$ have been observed in Hanford tank wastes, the evidence of bayerite and nordstrandite is scant. Thus, the primary $Al(OH)_3$ phase of interest in Hanford tank waste is gibbsite.

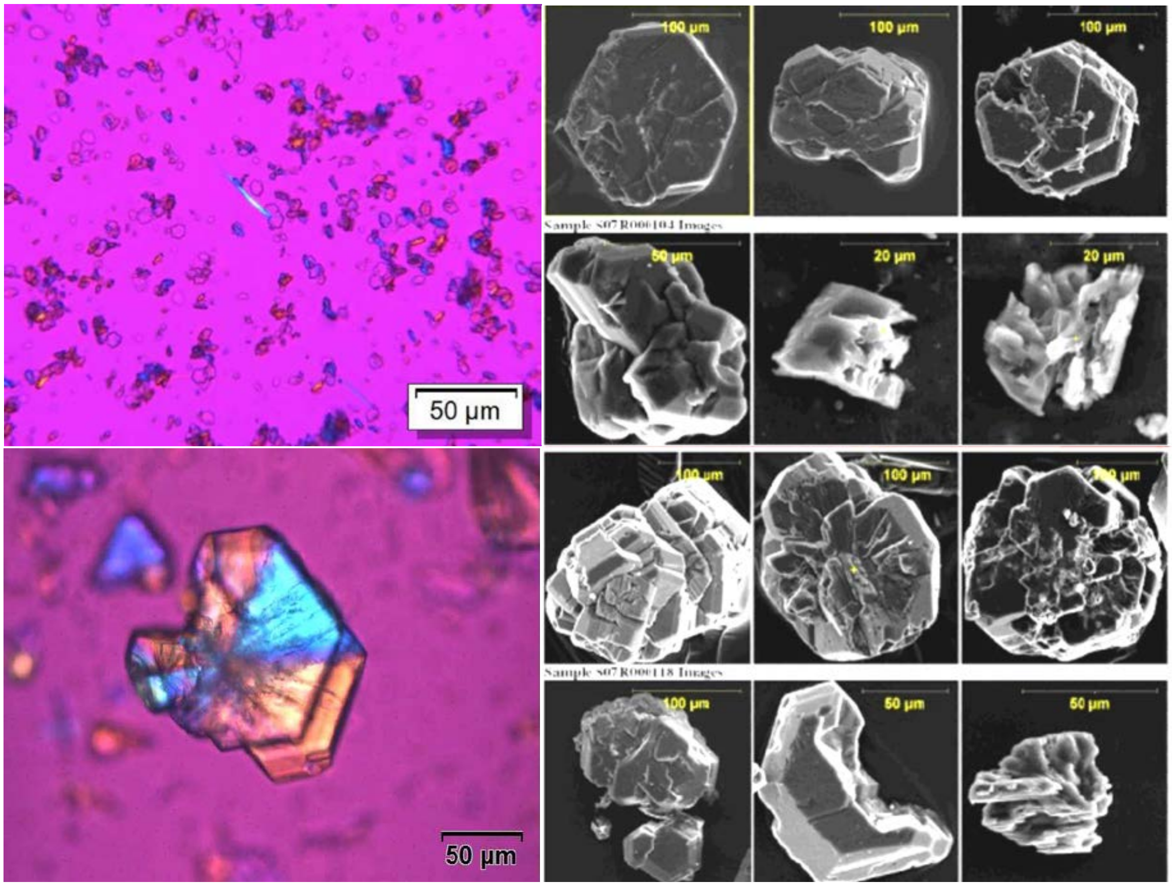

Figure 1. Microscope Images of Gibbsite from Hanford Tank Waste. Left: Polarized light microscope images of particles from Tanks 241-SX-101 (top) and -S-112 (bottom). Right: Scanning electron microscope images of particles from Tank 241-C-109. (Taken from Figures 3.1.2, 3.1.3, and 3.1.5, respectively, of Herting et al. 2015)

The potential for delayed gibbsite crystallization to occur following the dilution of aluminate-bearing tank waste solutions is of concern in the present study. Aluminum hydroxide precipitation, primarily in the form of gibbsite, is a risk to tank farm operations through the accumulation of settled solids occupying usable LAWPS staged feed tank space, the unanticipated carryover of the aluminum hydroxide solids into the LAWPS, possible delayed aluminum hydroxide precipitation fouling within the LAWPS ion exchange columns, and/or transfer line deposition/plugging. To this end, technical literature related to the dilution of actual Hanford tank wastes was surveyed to collect observations and define conditions leading to aluminum phase precipitation, turbidity, or other phenomena especially after extended aging periods. Results of studies of gibbsite solubility in systems simulating Hanford tank waste and Bayer process experience also were surveyed and the findings abstracted. Finally, aluminum and hydroxide concentrations in Hanford tank waste solutions were examined to determine apparent solubility thresholds.

4.0 Results and Discussion

Technical literature pertaining to aluminum phase solubility, especially with respect to gibbsite in Hanford tank waste solutions and in chemically analogous systems meant to model the Hanford tank wastes, is reviewed in this section. The literature generally describes experiments performed at Hanford Site's 222-S Laboratory and at national laboratories to understand aluminum solid-phase solubility and precipitation in Hanford tank waste. Related data obtained opportunistically to meet other waste processing goals also are examined. Many of the observations are interpreted in light of plots of dissolved aluminum versus free hydroxide concentrations as an initial means to visualize the data and compare them with a published temperature-dependent solubility model derived for simple sodium aluminate/hydroxide systems for the Bayer process (after Misra 1970). Aluminum-versus-hydroxide concentration data from tank waste supernatant solution analyses were also gathered from TWINS and are plotted here to suggest solubility thresholds and compare the data with observations from the controlled laboratory testing.

4.1 Observations of Actual Tank Waste

A number of types of laboratory studies have been performed to understand the behaviors of actual Hanford tank waste during proposed and implemented processes for its retrieval and treatment prior to immobilization. First among these are studies of stepwise or cascade dissolution of saltcakes by water or inhibited water (0.01 M NaOH / 0.01 M $NaNO_2$; note that the $NaNO_2$ concentration later was modified to 0.011 M). The objective of these studies was to understand characteristics of saltcake dissolution through modeling proposed retrieval operations in which the dissolvent is sprinkled over, and percolates through, the saltcake with the resulting salt-bearing solution collected at the bottom. These studies were performed during fiscal year (FY) 1998 through FY 2002 at the 222-S Laboratory by Daniel Herting and colleagues, and the results are summarized in annual reports. An early test of this concept also was reported in 1997. Other similar studies were undertaken by 222-S Laboratory scientists in 2002 and 2003. In addition, numerous tank waste treatment and characterization tests are in the Hanford technical literature related to 222-S Laboratory studies. Included in these are studies of the crystallization of purified sodium nitrate in the "Clean Salt" process, which uses fractional crystallization to separate practically nonradioactive sodium nitrate from Hanford tank waste.

A second type of study involved caustic leaching of gibbsite- and boehmite-bearing sludge, a treatment also known as "Enhanced Sludge Washing." These tests were performed primarily at PNNL but also at Los Alamos National Laboratory, Oak Ridge National Laboratory, and at the Savannah River Site. Many (but not all) of the results of the individual studies are collected in the publicly accessible Hanford Tank Waste Treatment and Immobilization Plant (WTP) report archive.[1] As will be seen, two summaries of these many studies prepared by key scientists in caustic leaching research provide encompassing overviews.

A third type of study, also found in the WTP report archive, investigates dilution of actual tank waste solution in preparation for reported testing of ion exchange removal of radiocesium. Dilution of aluminate-bearing solutions, as seen in the aluminum industry, can lead to gibbsite precipitation. All these data resources were surveyed to find additional information about delayed gibbsite precipitation from actual waste.

---

[1] http://www.pnl.gov/rpp-wtp/

4.1.1 Stepwise/Cascade Dissolution Tests and Other Tests at the 222-S Laboratory

As described by Herting and others, the stepwise (or cascade) dissolution test is a small-scale, batch-wise simulation of a continuous in-tank retrieval process that would be performed by sprinkling water (not otherwise specified whether distilled, filtered raw water, etc.) or perhaps inhibited water over the saltcake. In the laboratory, a single saltcake sample is contacted a number of times with fresh dissolvent, and the equilibrated liquid phase is removed after each contact before adding the next aliquot of fresh dissolvent. The progress made in dissolving the saltcake is monitored by taking mass and volume measurements of the solutions and undissolved heel and by conducting chemical analyses of the product solutions.

The observed dissolutions had the following general sequence. First, the fully dissolved salts present within the interstitial liquors of the saltcake were removed. Such salts included sodium hydroxide, chloride, and nitrite (NaOH, NaCl, and $NaNO_2$, respectively) and most potassium salts. Next, the highly soluble salts present not only in the liquors but as solids in the saltcake were removed. The most prominent of these salts was sodium nitrate ($NaNO_3$). Then, the salts that have multi-charged anions were dissolved. These included sodium carbonate (Na_2CO_3 and its hydrates), sodium sulfate (Na_2SO_4), sodium phosphate (e.g., $Na_3PO_4 \cdot 12H_2O \cdot \frac{1}{4}NaOH$), and their double salts [e.g., sodium fluoride phosphate; $Na_7F(PO_4)_2 \cdot 19H_2O$]). In many cases, sodium oxalate ($Na_2C_2O_4$) was among the last of the salts to be dissolved. Undissolved sludge heels then remained. Among the sludge constituents were iron and other transition metal hydroxides as well as aluminum-bearing solids such as sodium aluminosilicates (e.g., cancrinite), gibbsite, and boehmite.

The solutions from the initial contact would include sodium hydroxide and could include appreciable sodium aluminate. The dilution of sodium aluminate-rich interstitial liquors thus would be analogous to the gibbsite precipitation step in the Bayer process. Herting (1999b)[1] was aware of the possibility of gibbsite precipitation in the first study of stepwise saltcake dissolution, performed using waste from Tank 241-AN-105. The original solutions (i.e., with no dilution) at 25°C were 3.35 M hydroxide, 1.37 M aluminum, 3.00 M nitrate, 2.27 M nitrite, ~0.20 M carbonate, and 10.0 M total sodium. The maximum solution concentrations in the 25°C dilutions were 1.82 M hydroxide, 0.86 M aluminum, 1.94 M nitrate, 1.54 M nitrite, 0.41 M carbonate, and 7.09 M sodium. Other tests done with added 2 M NaOH (Herting 1999b) are of less interest relative to the present case because the added NaOH would favor keeping gibbsite in solution. As noted in the following direct quote, despite the high aluminate concentration, no post-precipitation was observed for any solution in this test series, whether the original supernatant or the diluted supernatant (which would have favored gibbsite precipitation) even after extended storage.

> "The supernatant liquid from each cone was divided into three containers. One portion was decanted into a 15 ml plastic centrifuge cone, which was stored in the water bath for at least 30 days to monitor for the slow precipitation of $Al(OH)_3$. (None formed in any of the test samples after storage for at least 4 weeks and up to 8 weeks.)"

The subsequent FY 1998 saltcake dissolution annual report (Herting and Edmonson 1998) did not mention gibbsite or aluminate (except for aluminate as a waste solution component) or precipitation from saltcake dissolution liquors.

Gibbsite precipitation was inferred in the FY 1999 annual report (Herting 1999a) by the observed presence of higher hydroxide concentrations than would have been provided by the native hydroxide in saltcake dissolution contacts of Tank 241-BY-102 waste (solutions in the duplicate tests averaged 0.67 M hydroxide, 0.42 M aluminum, and 8.39 M sodium). This additional hydroxide could have been caused by

---

[1] Initially released in 1997, updated and re-released in 1999.

the hydrolysis of aluminate ion upon contact with the inhibited water. However, because gibbsite was present in the solid phase of starting material and in the saltcake dissolution heels, actual gibbsite precipitation could not be observed. Nonetheless, the presence of gibbsite in the starting material provided good evidence that the initial interstitial solutions were at saturation.

FY 2000 studies examined stepwise dissolution of composite samples from Tanks 241-BY-106, -S-l02, and -A-101 to determine solid/liquid phase distribution during retrieval (Herting 2000). Gibbsite precipitation was predicted to occur for mixed 24-hour-aged saltcake dissolution samples according to modeling by researchers at Mississippi State University (Herting 2000). However, precipitation was not observed. According to Herting (2000), the lack of precipitation perhaps was because of the brief (24-hour) observation time and the notoriously slow gibbsite precipitation rate.

No mention was made in the FY 2001 report of gibbsite precipitation during saltcake dissolution tests (Herting 2001). However, preparation of gibbsite for solid-phase microscopy standards was described. Gibbsite was prepared by dissolving 14.2 g of technical grade sodium aluminate in 40 mL of hot water, adding 6.8 g of sodium nitrate and 5.5 g of sodium nitrite, both of reagent-grade, then filtering and cooling the solution. The desired $Al(OH)_3$ precipitated slowly after the solution had cooled.[1] The initial solution, as prepared and assuming the sodium aluminate had the composition $NaAl(OH)_4 \equiv NaAlO_2 \cdot 2H_2O$, would have contained no "free" NaOH, although NaOH would form with $Al(OH)_3$ precipitation.[2]

The FY 2002 report noted the presence of gibbsite in the heels from dissolution of 241-B-109 saltcake (Herting 2002). Sodium aluminate solids also were detected in the feed 241-SX-101 saltcake (i.e., the saltcake was a double-shell slurry[3]). Analogous to the gibbsite preparation process described in the FY 2001 testing (previous paragraph), solids formed after contact of 40 g of the SX-101 saltcake with 20 mL of water, heating to 50°C, and cooling to the 23°C hotcell temperature. In addition, about 30% of the initial aluminum in the SX-101 saltcake was soluble as shown by the cascade dissolution tests. Gibbsite solids were observed, upon cooling, from the precipitation of the 50°C water washing of the SX-101 saltcake (Herting et al. 2002). The composition of the solution from the first 50°C contact was 1.22 M aluminum, 1.26 M hydroxide, 10.4 M sodium, 6.2 M nitrate, 0.029 M phosphate, 0.41 M nitrite, 0.20 M carbonate, and others.

Stepwise or cascade dissolution tests of saltcakes from Tank 241-S-112 (Herting and Bechtold 2002) and Tank 241-S-102 (Callaway 2003) were reported but neither mentioned gibbsite in any way.

A number of additional letter reports about work conducted by Herting also were reviewed (Herting 2003a, 2003b, 2004a, 2005a, 2005b, 2006, and 2007). The Herting tests included caustic demand studies (determining if hydrolysable solids were present) and solids analyses/characterizations of actual wastes. In one of these studies (Herting 2004a), gibbsite dissolution was reportedly observed during a caustic demand test. In another caustic demand study (Herting 2003a), boehmite was present but did not dissolve and thus did not consume caustic. No other observations of gibbsite were reported. Herting (2004b) also

---

[1] The technical grade sodium aluminate solution may have been contaminated with gibbsite particles, which could have provided seed crystal for the observed product gibbsite.

[2] Related tests to produce gibbsite to emulate the gibbsite-bearing heel found in Tank 241-C-103 were reported 8 years later (Huber 2009). In one of the several reported methods, the gibbsite was synthesized by the dilution and cooling of a 5 M sodium aluminate solution (prepared by dissolving solid technical grade sodium aluminate in hot water) and holding it at 80°C for 4 days in the presence of gibbsite seed crystal.

[3] In tank waste evaporator campaigns in the late 1970s and early 1980s, tank waste that was intentionally evaporated beyond the sodium aluminate solubility limit to form sodium aluminate solids was referred to as "double-shell slurry," because it was disposed into double-shell tanks (Herting et al. 2015).

reported on analyses of a sample from Tank 241-S-112 and found aluminum in the solution. The aluminum was assumed to arise from aluminate ion in the interstitial liquid plus dissolution of solid-phase sodium aluminate. Despite the presence of (presumably) high aluminate concentrations in the solution, however, no gibbsite precipitation was observed or reported in the letter reports reviewed.

Other solids characterization test reports by Herting and others from the 222-S Laboratory were examined (Cooke 2002, 2015; Baker 2003; Herting et al. 2004; Callaway and Huber 2010; Herting et al. 2012; Mabrouki 2013). Although some reported the presence of gibbsite, none described post-precipitation even though dawsonite ($NaAlCO_3(OH)_2$) was present in at least one instance (Herting et al. 2012).[1] Dissolutions of gibbsite and boehmite from simulant sludge and sludge from three waste tanks were studied using 8 and 19 M NaOH (note that the effective NaOH concentrations were lower in the test items because of dilution by interstitial solution) and metathesis to sodium aluminate crystals was observed. However, no gibbsite post-precipitation was reported (Herting 2012). Tests of dissolution of simulant sludge containing both aluminum and iron hydroxide using oxalic acid also were performed but gave no germane information about gibbsite post-precipitation (Herting 2015).

Tests to establish the gibbsite precipitation equilibrium from aluminum-fortified actual waste solutions from Tanks 241-AN-105 and -AP-108 were performed (McCoskey et al. 2015). These tests formed the basis for a subsequent journal article reporting on the findings for Tank 241-AN-105 (Reynolds et al. 2016). In both tests, actual waste was contacted with supplemental commercial gibbsite. In half of the experiments, the gibbsite first was dissolved at 85°C and then the solutions were cooled to 40°C, aged, and gibbsite was allowed to precipitate. In the other half of the experiments, the gibbsite solids were added and the solutions were heated to 40°C. At each initial temperature, supplemental salts/solids from the respective tanks were added to half of the tests to act as "seed." The solutions were sampled and analyzed over a period of time ranging from about 47 to 93 days to establish equilibrium or steady state by approach from both oversaturation and undersaturation. The 80→40°C test with added tank waste solids for AP-108 was mishandled, so findings were not reported. In another test, AN-105 waste solution containing supplemental solids and cooled from 80 to 40°C failed to form additional solids (i.e., gibbsite) even after ~59 days. It was surmised that the failure to precipitate was caused by the observed absence of gibbsite crystals to act as seed. Because thermonatrite ($Na_2CO_3 \cdot H_2O$) was the dominant phase in the solids, it must not act as a nucleating agent for gibbsite. The solution thus remained supersaturated, even at this extended, nearly 2-month, aging time at 40°C. Gibbsite crystals were present in the residual solids for each of the other three tests run with AN-105 waste solution. The data from the AN-105 and AP-108 tests are considered in further detail later in this report.

A series of laboratory tests were conducted in the 1990s to investigate the feasibility of using fractional crystallization to separate practically nonradioactive sodium salts from Hanford tank waste (Herting 1996). Dubbed the "Clean Salt Process," most of the tests were conducted using tank wastes that first had been made acidic by addition of nitric acid (HNO_3). By acidification, the sodium hydroxide, sodium nitrite, and sodium carbonate present in the salt wastes were converted to sodium nitrate and, with the original sodium nitrate, could be crystallized, dissolved, re-crystallized, re-dissolved, and so on to obtain purified sodium nitrate containing undetectable radioactive contamination.[2] In an early series of tests, however, efforts were made to crystallize sodium nitrate and nitrite on the alkaline side (Herting 1993; see also Herting 1996). The test used a simulated Tank 241-SY-101waste supernatant solution containing

---

[1] An engineering laboratory study of gibbsite settling times and depths in apparatus corresponding to actual tank waste depths may be of interest in assessing sludge accumulation produced by precipitation of gibbsite. Ferric hydroxide and simulated neutralized current acid waste solids also were investigated. These results for simulated wastes were validated by comparison with findings observed elsewhere for actual wastes (MacLean 1999).

[2] The sodium nitrate product even became purified of potassium nitrate and its contained radioactive primordial potassium-40 ($t_{½} = 1.25 \times 10^9$ years).

2 M sodium hydroxide, 1.5 M sodium aluminate, 2.6 M sodium nitrate, 2.2 M sodium nitrite, 0.42 M sodium carbonate, and 0.20 M trisodium HEDTA (HEDTA is *N*-2-hydroxyethyl ethylenediamine triacetate). After removing 24 wt% water, some wet crystallized sodium carbonate was separated from the hot (70°C) slurry and, later, wet sodium nitrate and nitrite solids separated from the same solution cooled to room temperature. The remaining clear supernatant solution was then set aside at room temperature (unspecified; estimate 20–22°C). After a few days, the previously clear supernatant solution had solidified "to a face cream consistency, presumably due to precipitation of $Al(OH)_3$" (Herting 1993).[1] The approximate composition of the solution before this precipitation was 4.4 M sodium hydroxide, 3.3 M sodium aluminate, ~2.2 M sodium nitrate, 3.1 M sodium nitrite, and smaller concentrations of sodium carbonate and trisodium HEDTA.

Conclusions: Observations of gibbsite production within tests of stepwise (or cascade) dissolution of tank waste salt were actively sought but rarely witnessed. One instance of potential precipitation in tests with BY-102 waste was implied through the presence of excess hydroxide in solution although gibbsite itself was not observed (Herting 1999b). Another test of dissolution of a saltcake (SX-101) containing sodium aluminate solids produced gibbsite (Herting et al. 2002). The researchers were cognizant of the potential risk of gibbsite precipitation and were monitoring for it but did not observe it beyond these two occasions. A "Clean Salt" test performed on the alkaline side also was surmised to have produced gibbsite precipitate upon cooling (Herting 1993, 1996). Finally, some tests were undertaken to actively investigate gibbsite solubility in aluminum-fortified actual wastes. In one instance, apparent supersaturation was maintained for about 2 months but gibbsite failed to precipitate. The presence of seed crystals caused other tests in this series to attain equilibrium from both over- and undersaturation (McCoskey et al. 2015).

4.1.2 Studies Performed in Support of WTP

Several types of process development studies have been performed in support of pretreatment operations at the WTP. One study type relevant to gibbsite precipitation is caustic leaching. In caustic leaching (also known as Enhanced Sludge Washing), candidate waste sludges containing aluminum-rich solids such as gibbsite and boehmite are dissolved with NaOH solution to form soluble sodium aluminate according to the leach reactions outlined earlier for the first step of the Bayer process. Such solutions, especially if prepared at elevated temperatures and then cooled, could become supersaturated with respect to gibbsite and thus show delayed gibbsite precipitation. Another WTP pretreatment step is dilution of clear concentrated waste liquors to attain target 4 to 6 M (nominally 5 M) total sodium concentration in preparation for cesium-137 (^{137}Cs) removal by ion exchange. If rich in sodium aluminate, dilution of these concentrated liquors would correspond to the second step of the Bayer process wherein gibbsite precipitates. Findings of gibbsite post-precipitation from review of WTP publications and related studies pertaining to caustic leaching of genuine waste sludges and dilution of concentrated genuine waste liquors are presented in this report section.

---

[1] Herting (1996) went on to explain: "Precipitation of $Al(OH)_3$ occurred because its solubility is dramatically affected by the ionic strength of the solution – as the ionic strength is reduced by precipitating the sodium salts, the solubility of aluminum falls sharply. The kinetically slow $Al(OH)_3$ precipitation could lead to serious process upsets such as plugging of transfer pipes."

4.1.2.1 Caustic Leaching

Two summaries of the many caustic leaching studies have been written and both have been consulted (Lumetta et al. 1998).[1] These reviews were examined for observations of gibbsite post-precipitation. Both reviews identified an instance of post-precipitation in a study of the caustic leaching of Tank 241-S-111 waste sludge (Lumetta et al. 1997). In these tests, the liquors formed after 143 hours of 100°C leaching of the water-washed sludge were found to be clear for the first 12 days after cooling to room temperature, but they contained a white precipitate after 100 days (no intermediate observations were made). The aluminum concentration before precipitation was 1.38 M and the free hydroxide concentration was ~1.3 M (Lumetta et al. 1998). The solids were not analyzed but were postulated to be gibbsite based on the solution being ~5-fold in excess of the gibbsite solubility at 25°C measured by Felmy and colleagues (1994). Caustic leachates from digestions of washed sludges from Tanks 241-S-101 and -S-104 in the same set of experiments also were examined for post-precipitation after cooling to room temperature. No precipitation was observed even though one leachate, from Tank 241-S-104, contained 0.55 M aluminum and 2.3 M free hydroxide and was surmised (Lumetta et al. 1998) to be about twice the expected solubility based on gibbsite solubility studies reported by Felmy and colleagues (1994). Note that in all of these cases, because of prior sludge washing using water or inhibited water, the caustic leachate solutions were practically free of salts (e.g., sodium nitrate and nitrite) typically observed in abundance in Hanford tank waste liquors.

Modeling analyses of Tank 241-AZ-101 sludge/interstitial liquid, two sequential sludge washing steps, caustic leaching, and three subsequent rinsings of the leachates from the heels (performed by Geeting et al. 2002) indicated that aluminum concentrations were above expected solubility limits for gibbsite for all solution compositions except caustic leaching (Felmy and MacLean 2003). However, no gibbsite precipitation was reported in these or any other step in the laboratory studies themselves (Geeting et al. 2002).

Reports of studies of caustic leaching undertaken after the latter (2007) caustic leaching summary were also examined for instances of gibbsite post-precipitation. In one study, a composite of Reduction-Oxidation Plant (REDOX) waste and an S-Saltcake composite underwent sludge washing and caustic leaching (Fiskum et al. 2008). Each waste type contained both boehmite and gibbsite. The parametric testing evaluated the effects of free hydroxide concentration (1 to 5 M), temperature (80 to 100°C), and sodium nitrate concentration (1 to 5 M) on leaching. However, no instances of gibbsite post-precipitation were reported for either waste type. A similar study examined the caustic leaching behavior of Plutonium Uranium Extraction Plant (PUREX) and REDOX cladding waste sludges (Snow et al. 2009). Again, no post-precipitation from the wash or leach test solutions was reported.

Samples of the same REDOX waste and S-Saltcake composites examined by Fiskum et al. (2008) underwent caustic and oxidative leaching, crossflow filtration, solids washing using decreasing NaOH concentrations, further crossflow filtration, ion exchange processing for cesium removal, evaporative concentration for volume reduction, and the combination of the evaporated product with dissolved saltcake (Fiskum et al. 2009). Trace gibbsite was reported during evaporative concentration at 50°C of the combined ion exchange and caustic leach and rinse solutions. However, because the evaporative concentration occurred over several days with exposure to the hotcell air, the present authors speculate that atmospheric carbon dioxide could have been absorbed by the solution and could have formed dawsonite. If dawsonite were present, water wash of the solids in preparation for identification may have formed the observed gibbsite. However, no gibbsite was observed in the washed residual solids.

---

[1] The second summary document, titled *Review of Caustic Leaching Testing with Hanford Tank Waste Sludges*, is an unpublished internal PNNL report completed in 2007.

Conclusions: One test of caustic leaching using elevated temperature produced a delayed appearance of a white precipitate, taken to be gibbsite, upon cooling and storage with no solids after 12 days but with solids observed after 100 days (Lumetta et al. 1998). This was the only instance reported of post-precipitation in caustic leaching studies. Some gibbsite was observed to form upon blending and concentrating solutions and rinses in flowsheet testing of caustic and oxidative leaching and ion exchange processing (Fiskum et al. 2009). The genesis of these solids may indicate transition through dawsonite.

4.1.2.2 Ion Exchange

A number of cesium ion exchange studies have been performed since 2004 using simulated and actual tank waste solutions. For many of these studies (i.e., Fiskum et al. 2006a, 2006b, 2006c, and Nash and Duignan 2009), no gibbsite precipitation from solution or precipitates in the ion exchange media was reported. Based on the relatively low aluminum concentrations with respect to hydroxide concentration, this would be expected. A recent review of laboratory experience using spherical resorcinol-formaldehyde resin for cesium ion exchange did not note any instances of gibbsite precipitation in the feed solution, but the emphasis was more on ion exchange performance (Brown 2014).

A solution was prepared from a mix of Tank 241-AN-102 supernatant solution and Tank 241-C-104 saltcake leaches.[1] This solution was evaporated to an unknown final hydroxide concentration and contained 0.275 M aluminum and 4.44 M sodium. A gibbsite precipitate was found after 1 week of aging. Although the hydroxide concentration was not analyzed, it had to be $\leq$1.43 M according to the charge balance of the constituent ions. A subsequent ion exchange study used this same solution but did not report precipitate formation (Fiskum et al. 2004). The Tank 241-AN-102/C-104 waste mixture was analyzed to be 0.2 M hydroxide, 0.304 M aluminum, and 4.8 M sodium. The relatively high concentration of aluminum compared to hydroxide (based on Misra 1970, as will be seen) suggests that the solution was supersaturated with respect to gibbsite.

Recent ion exchange studies by Russell et al. (2012 and 2014) showed instances of precipitates forming. In the former study, a sodium aluminate precipitate (as determined by energy dispersive spectroscopy, which would only detect elements) formed in the column while processing a simulant waste solution containing 4 M hydroxide and 8 M sodium (Russell et al. 2012). In the latter study, conducted using a simulant waste containing 1.2 M hydroxide, 0.15 M aluminum, 0.017 M oxalate, and 5 M sodium (among other constituents), a white precipitate and a translucent precipitate were observed in the ion exchange column (Russell et al. 2014). Although neither precipitate was characterized (Russell et al. 2014), it seems unlikely that either precipitate was gibbsite given the feed-solution composition and the generous acid rinses used before and after cesium elution. Instead, the latter test may have precipitated sodium oxalate in the column because the effluent oxalate concentrations were lower than the target concentration.

In a tank waste analysis performed for WTP but not related to ion exchange processing, no additional precipitation was reported in the analysis of blends of waste solids and solutions from Tank 241-AN-102 (Urie et al. 2002). Specifically, the composites were prepared at the 31.5°C ambient hotcell temperature and, after mixing, were aliquoted into jars in which no additional precipitation or organic layer separation were observed. Although x-ray diffractometry was performed on the solids, only sodium nitrate and sodium nitrite were identified together with an amorphous background. The "dry" solids (i.e., drained of interstitial liquor) contained 11.3 wt% aluminum, indicating that aluminum in some form, likely gibbsite

---

[1] The reviewed work was summarized in an unpublished internal 2001 PNNL report titled *Evaporation of a Mixture of Tank AN-102 Low Activity Waste and C-104 Washing and Leaching Solutions.*

or boehmite, was present. Because the supernatant solution composition was unusually high in aluminum concentration (0.456 M) considering the hydroxide concentration (0.253 M) and the sodium concentration also was relatively high (8.00 M), the solution seems to be supersaturated with respect to gibbsite. The high sodium concentration may have acted to inhibit gibbsite precipitation.

Conclusions: One instance of gibbsite precipitation was observed after 1 week of aging in preparation of candidate feed (from AN-102 and C-104 wastes) for ion exchange (for cesium removal) testing.[1] *Uncharacterized white solids within the ion exchange column have been observed in ion exchange column testing using simulant wastes (Russell et al. 2014), but they are unlikely to be gibbsite based on feed-solution composition and generous rinses. A genuine waste (AN-102) was characterized to have a composition well above that necessary to precipitate gibbsite but no precipitation was observed (Urie et al. 2002).*

4.2 Testing of Aluminum Phase Solubilities in Alkaline Solution

Understanding the precipitation and dissolution behavior of aluminum-bearing phases in Hanford tank waste solutions has been a matter of concern in tank farm operations and in predicting aluminum disposition in WTP operations. The vast Bayer process experience is a fruitful starting point in understanding the dissolution/precipitation equilibria for the simple $NaAl(OH)_4$/NaOH system and more complex Bayer process liquors, which also contain dissolved sodium carbonate (Na_2CO_3), sodium chloride (NaCl), sodium oxalate ($Na_2C_2O_4$), and other minor salts. Using this information as a starting point, experiments have been conducted to understand the aluminum solid-phase equilibria with Hanford tank waste solutions, which contain not only those salts of interest to the aluminum industry but also dissolved salts including sodium nitrate ($NaNO_3$), nitrite ($NaNO_2$), sulfate (Na_2SO_4), phosphate (Na_3PO_4), fluoride (NaF), and others.

The aluminum solid phase examined in the present report is gibbsite, $Al(OH)_3$, but sodium aluminate, $NaAl(OH)_4$, also can form at high combined aluminum and sodium hydroxide concentrations. Sodium aluminate is of concern in prior Hanford tank waste operations in which this phase was crystallized in the final pass of tank waste liquors through the 242-S and 242-A vacuum evaporator-crystallizers (Reynolds and Herting 1984), where the product was known as double-shell slurry (Herting et al. 2015). Production of double-shell slurry ended in Hanford tank farm operations when it was realized that the flat and square sodium aluminate crystals adhered to gas bubbles evolved during chemical and radiolytic reactions in the tank waste. As such, the sodium aluminate particles were partly responsible for volume growth in these slurries because of their action in trapping small gas bubbles on their surfaces, thus not allowing the gas bubbles to coalesce and be released at low consistent rates as they were generated. Instead, the gas-inflated slurries increased in volume until a critical point in buoyancy occurred. At this point, the buoyant slurries began rising within the waste solution at rates accelerated by the decreasing hydrostatic pressure occasioned by their rising and by shear thinning. As the slurries reached the tank waste surface in these episodic rollover events, large volumes of the formerly trapped gas bubbled out and were released to the tank dome space.

In this section of the report, studies of the solubility of gibbsite in NaOH solution are reviewed and the results are summarized. The review begins with information from the simple $NaAl(OH)_4$-NaOH system as abstracted from numerous studies and continues with examination of a number of Hanford-related salt solubility studies.

---

[1] The reviewed work was summarized in an unpublished internal 2001 PNNL report titled *Evaporation of a Mixture of Tank AN-102 Low Activity Waste and C-104 Washing and Leaching Solutions.*

4.2.1 Gibbsite Solubility Equation after Misra

Studies of the solubility of gibbsite in solutions of $NaAl(OH)_4$-NaOH at a variety of temperatures have been examined and reviewed and the findings have been modeled by a solubility equation that, according to the author, fit 95% of the available data to ±15% (Misra 1970). Although the study is nearly 50 years old, the equation has great utility and still is cited in recent scientific technical literature (e.g., Li et al. 2005). Based on the parent data set, the equation is valid from 25 to 100°C and for caustic concentrations of 30 to 230 g Na_2O per liter, equivalent to ~1 to 7.4 M total sodium. The equation as originally presented is:

$$\ln\,(Al_2O_3/Na_2O\text{, at equilibrium, by weight}) =$$

$$6.2106 - 2486.7/(T,\ K) + 1.08753(Na_2O\text{ concentration, g/L})/(T,\ K) \qquad (1)$$

The original solubility equation may be algebraically rearranged to the following more useful form:

$$\ln\,([Al],\ M) = 5.7128 - 2486.7/(T,\ K) + 33.702([NaOH],\ M)/(T,\ K) + \ln\,([NaOH],\ M) \qquad (2)$$

where NaOH represents sodium present both as free NaOH and combined with aluminum as $NaAl(OH)_4$. Li and colleagues (2005) converted the Misra (1970) equation to the equation, below, which is nearly identical to the one derived here:

$$\ln(C^*) = 5.71 - 2486.70/T + 33.71[NaOH]/T + \ln[NaOH] \qquad (3)$$

where C* is the equilibrium molar aluminum concentration, [NaOH] is the total molar sodium concentration, and T is the absolute (K) temperature.

As noted earlier, NaOH is consumed on a one-to-one mole basis in dissolving $Al(OH)_3$ to make sodium aluminate according to the reaction:

$$Al(OH)_3 + NaOH \rightarrow NaAl(OH)_4. \qquad (4)$$

Thus, the free NaOH present in solution is the difference between the total sodium in solution and that present, on a 1:1 mole basis, in sodium aluminate.

According to the Misra (1970) equation, the solubility increases about a factor of 10 as NaOH concentration increases from 1 to 7 M at 25°C and increases about a factor of 8 (at 1 M NaOH) as temperature increases from 25 to 100°C (Figure 2). However, the temperature effect is markedly greater at higher NaOH concentrations, with aluminum concentration rising more steeply as NaOH concentration increases.

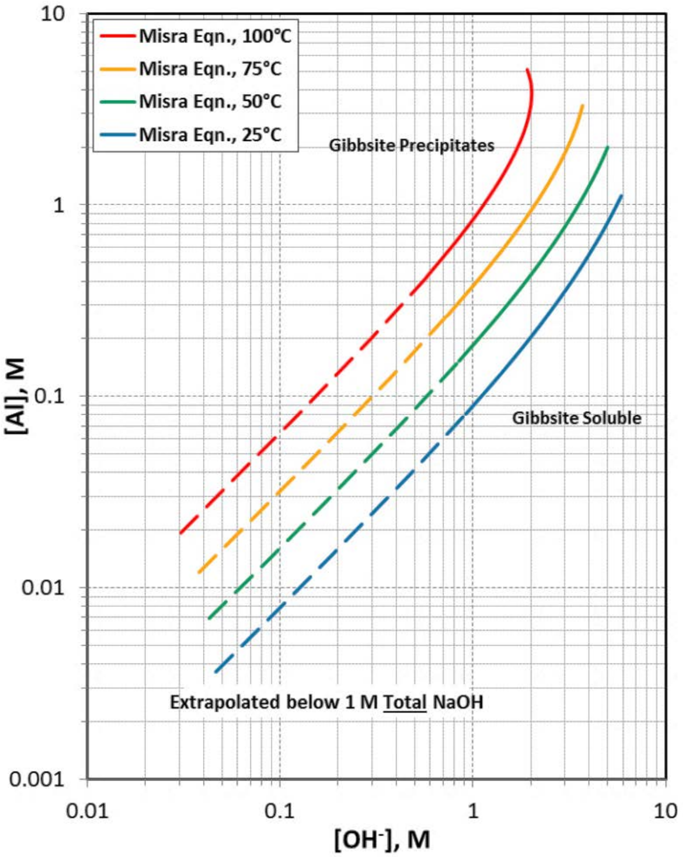

Figure 2. Gibbsite Solubility as Functions of NaOH Concentration and Temperature

Conclusions: The Misra (1970) equation summarizes gibbsite solubility observations from numerous studies and provides a useful gibbsite solubility relationship for NaOH-NaAl(OH)$_4$ solutions as a function of temperature.

4.2.2 Gibbsite Solubility in NaOH-NaAl(OH)$_4$-NaNO$_3$ Solutions

Two studies were undertaken to determine the solubility of gibbsite in NaOH-NaAl(OH)$_4$-NaNO$_3$ solutions. In the first study, solubility equilibrium was approached at 25°C from undersaturation by dissolution of excess water-washed, and otherwise undescribed, Al(OH)$_3$ (Felmy et al. 1994). Tests were run at 0.1, 0.5, 1, and 3 M initial NaOH. The testing showed gibbsite solubilities to be nearly independent of NaNO$_3$ concentration and the solubilities reached steady state (equilibrium) in less than 6 days for the lower NaOH concentrations but took over a year to equilibrate in the 3 M NaOH tests. This longer time was attributed to the extent of dissolution required for these more concentrated solutions. Solid-phase characterization at the end of testing confirmed the solid phase to be gibbsite.

The second study (Bénézeth et al. 2016) was similar to the first (Felmy et al. 1994); approaching equilibrium from undersaturation in the presence of excess Al(OH)$_3$, but run at 30, 63, and 89.8°C. The NaNO$_3$ concentrations ranged from 0 to ~4 M and the initial NaOH concentrations ranged up to ~4 M, but combinations of high (>1 M) concentrations in both were scarce. Equilibrium in all tests was reached within 20 days.

Concentrations were reported in molal (moles per kg water) in both data sets. To be consistent with other reported data (e.g., in TWINS), the concentrations were converted to molarity, at 30°C, by using a solution density prediction equation (Orme 2003) and iteration until convergence in molar concentrations was obtained for hydroxide, aluminate, and nitrate. The gibbsite solubilities obtained by these experiments are compared in Figure 3 with the solubilities predicted using the Misra (1970) equation at the same temperatures and NaOH molar concentrations. It is seen that, within the individual tests in the Felmy et al. (1994) and Bénézeth et al. (2016) studies, added nitrate had a small positive effect on gibbsite solubility in the 25°C and 30°C experiments. However, the observed concentrations are still very near those found in the Misra fit of the simple NaOH-NaAl(OH)$_4$ solutions. Even at the higher temperatures (63 and 89.8°C), only a small increase in aluminum concentration ensues as a result of the added NaNO$_3$ even though little difference is seen at higher temperatures between the observations of Bénézeth et al. (2016) and the predictions based on the Misra (1970) equation.

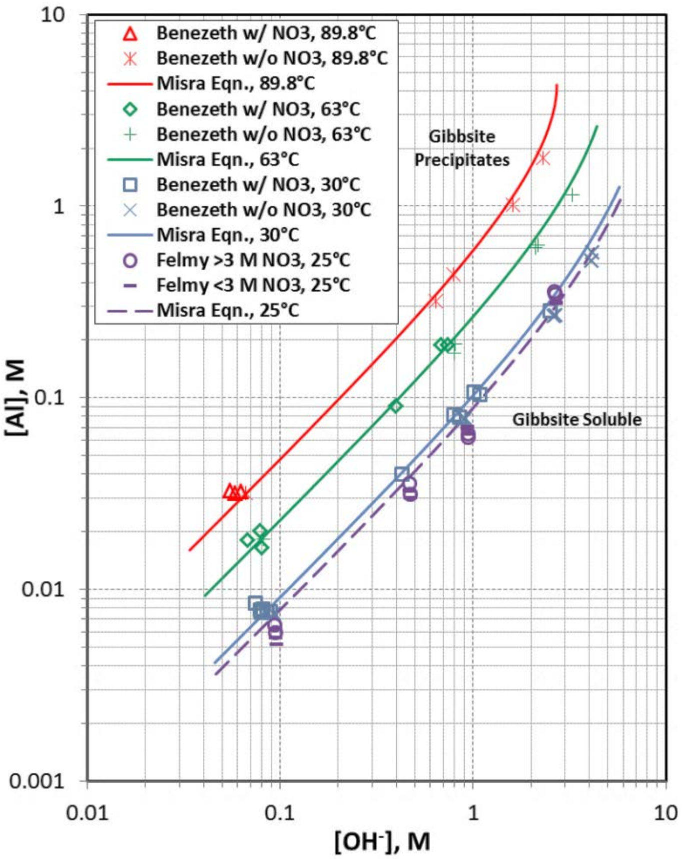

Figure 3. Gibbsite Solubility in the Presence of NaNO$_3$ (Felmy et al. 1994 and Bénézeth et al. 2016)

Conclusions: Addition of sodium nitrate to NaOH-NaAl(OH)$_4$ solution has relatively small positive effect on gibbsite solubility at ambient temperature to ~90°C.

4.2.3 Gibbsite Solubility in NaOH-NaAl(OH)$_4$-NaNO$_3$-NaF Solutions

The solubility of gibbsite in solutions of the system NaOH-NaAl(OH)$_4$-NaNO$_3$-NaF was determined in a parametric study in which the NaOH concentrations were varied at ~1, 1.5, and 2.5 M, the NaNO$_3$ concentrations were 0.4 and 4.0 M, and the NaF concentrations were 0.01 and 0.1 M (Herting et al. 1986). The tests took place at 40, 60, and 80°C with equilibration time being 2 to 4 weeks at 80°C in a shaker bath and 5 to 8 weeks at 80°C static (not shaken) conditions in an oven. The times to steady state for the experiments at the lower temperatures were not stated. Also unstated were details about the approach to equilibrium, i.e., whether excess Al(OH)$_3$ was present or the tests began supersaturated in gibbsite by the presence of excess dissolved sodium aluminate. The tests probably were run from supersaturation because polarized light microscopy was used to confirm the presence of gibbsite in the equilibrated solutions.[1] If this is the case, the precipitation of gibbsite within the stated 2- to 8-week test durations at 80°C gives some evidence of the stability of the aluminate solutions relative to supersaturation.

Fluoride concentration (at 0.01 and 0.1 M) was found to have no perceptible influence on gibbsite solubility. Increasing NaOH concentration and temperature, as expected, increased solubility as did increasing NaNO$_3$ concentration. The effect of higher NaNO$_3$ concentration was found to be more pronounced at 80°C than at the lower temperatures. The solubility data for these tests are compared in Figure 4 with the gibbsite solubilities in the NaOH-NaAl(OH)$_4$ system predicted by the Misra (1970) equation.

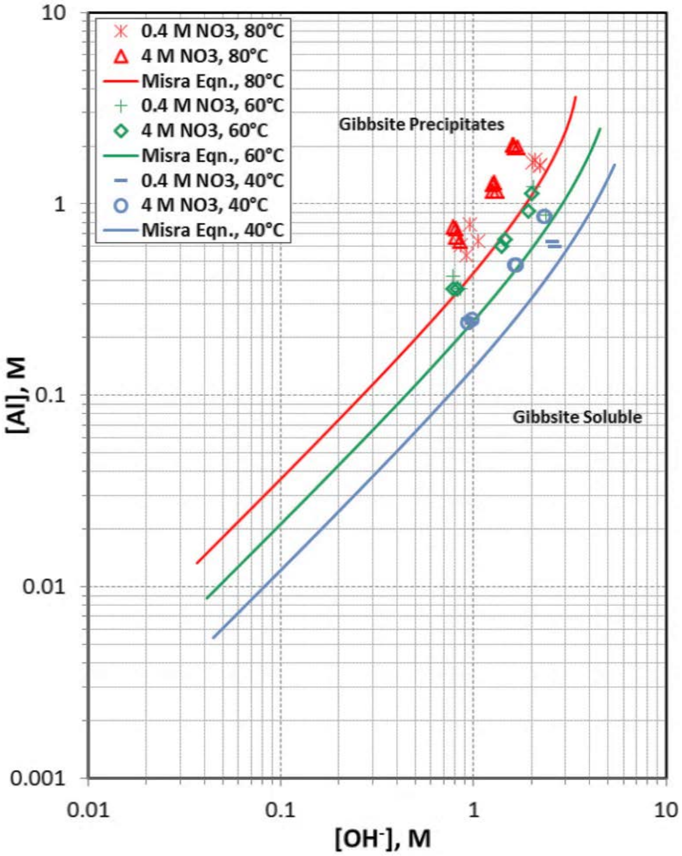

Figure 4. Gibbsite Solubility in the Presence of NaNO$_3$ (Herting et al. 1986)

Aside from the inclusion of NaF in the test solutions, the test temperatures, and the direction of approach to equilibrium, the experiments by Herting and colleagues (1986) were similar to those undertaken by Bénézeth et al. (2016). In the tests by Herting et al. (1986), however, positive deviations from the solubilities predicted by the Misra (1970) equation were observed even for tests involving low (0.4 M) supplemental NaNO$_3$. The deviations from the Misra (1970) equation also increased with increasing

---

[1] If the tests had been run from undersaturation with excess gibbsite present from the beginning, polarized light microscopy identification of the solids would have been meaningless.

temperature. The aluminum concentrations at 80°C for Herting et al. (1986) were about a factor of 4 higher than the Misra (1970) equation, whereas practically no difference from the Misra (1970) equation was found for Bénézeth et al. (2016) at 30 to 89.8°C. The approach to equilibrium from a condition of oversaturation (Herting et al. 1986) instead of a condition of undersaturation (Bénézeth et al. 2016) and the prolonged time needed to attain gibbsite crystallization from the oversaturated condition may explain this difference.

Conclusions: Nitrate seemingly increases gibbsite solubility for a given NaOH concentration and the effect is greater at higher temperatures (Herting et al. 1986; Bénézeth et al. 2016). The observed gibbsite solubilities may have been dependent on whether equilibrium or steady state was reached from oversaturation (Herting et al. 1986) or undersaturation (Bénézeth et al. 2016).

4.2.4 Gibbsite Solubility in $NaOH$-$NaAl(OH)_4$-$NaNO_3$-Na_3PO_4-$Na_7F(PO_4)_2$ Solutions

The solubility of gibbsite in $NaOH$-$NaAl(OH)_4$ solutions, with and without added nitrate, phosphate, or combined phosphate and fluoride, was determined in a more recent parametric study (Herting 2014). In Herting's tests, equilibrium was approached from undersaturation with gibbsite[1] dissolved at 22±1°C and at 40±1°C and the concentrations being measured as a function of time. Three NaOH concentrations, about ~1.2, 2.2, and 3.5 M, were used for each set of tests. The first set of tests had only gibbsite dissolved in NaOH (with no added salt). In the second set of tests, $NaNO_3$ also was present at about 3 M. In the third set of tests, phosphate was present at saturation with respect to sodium phosphate ($Na_3PO_4 \cdot 12H_2O$) solids. In the fourth set of tests, phosphate and fluoride were present together at saturation with respect to $Na_7F(PO_4)_2 \cdot 19H_2O$ solids. Most tests were performed in duplicate.

In the 22°C tests, the test durations were set to 5 or 10 weeks and the solutions were held in containers agitated by an end-over-end vessel tumbler. In the 40°C tests, test durations were set to 7 or 14 days and the vessels were agitated in a shaker bath. Five samples were taken over the selected time span for each test to determine the approach to equilibrium or steady-state concentration. Samples were analyzed for sodium, phosphorus, aluminum, and hydroxide concentrations. Nitrate was reasonably presumed to be fully dissolved for those tests containing nitrate and the fluoride concentration was taken to be half of the phosphorus concentration based on the dissolution stoichiometry of the $Na_7F(PO_4)_2 \cdot 19H_2O$ double salt.

The sample data showed that steady phosphate concentrations were reached well within the test durations. For the tests saturated with respect to $Na_3PO_4 \cdot 12H_2O$, the phosphate concentrations for the 22°C tests decreased from ~0.14 M to ~0.03 M as the NaOH concentration increased from ~1.2 to 3.6 M, while at 40°C the phosphate concentrations were higher than at 22°C, decreasing from ~0.42 to 0.13 M as the NaOH concentration increased from 1.2 to 3.4 M. Phosphate concentrations at 22°C with respect to $Na_7F(PO_4)_2 \cdot 19H_2O$ decreased from 0.11 to 0.03 M as NaOH concentration increased from 1.3 to 3.6 M. At 40°C, the phosphate concentrations with respect to $Na_7F(PO_4)_2 \cdot 19H_2O$ were higher than under otherwise comparable conditions at 22°C but again decreased from 0.19 to 0.07 M as NaOH concentration increased from 1.3 to 3.4 M. Phosphate concentrations with respect to $Na_7F(PO_4)_2 \cdot 19H_2O$ were generally lower than those found for the tests saturated with $Na_3PO_4 \cdot 12H_2O$ under similar temperature and NaOH concentration conditions.

However, the aluminum concentrations for most tests failed to reach steady aluminum concentration for gibbsite dissolution within the test durations. Therefore, the aluminum concentration data were fit, versus time, to an asymptotic function to project the equilibrium concentration. For the tests run at 22°C, the

---

[1] Almatis Premium Alumina; hydrated alumina C33.

aluminum concentrations at the final samplings at 5 or 10 weeks were from 68 to 97% of the projected equilibrium concentrations. For the 40°C tests, the concentrations in the final samplings at 7 or 14 days ranged from 86 to 100% of the projected equilibrium concentrations.

The projected gibbsite solubility, expressed as dissolved aluminum, with respect to final NaOH concentration[1] for each of these tests is compared in Figure 5 with the gibbsite solubility at the respective test temperature for the pure NaOH-$NaAl(OH)_4$ system predicted by the Misra (1970) equation. It is seen that the gibbsite solubility data in the tests by Herting (2014), irrespective of the presence or absence of the added salts, closely track the solubility predicted by the Misra (1970) equation for the simple NaOH-$NaAl(OH)_4$ system.

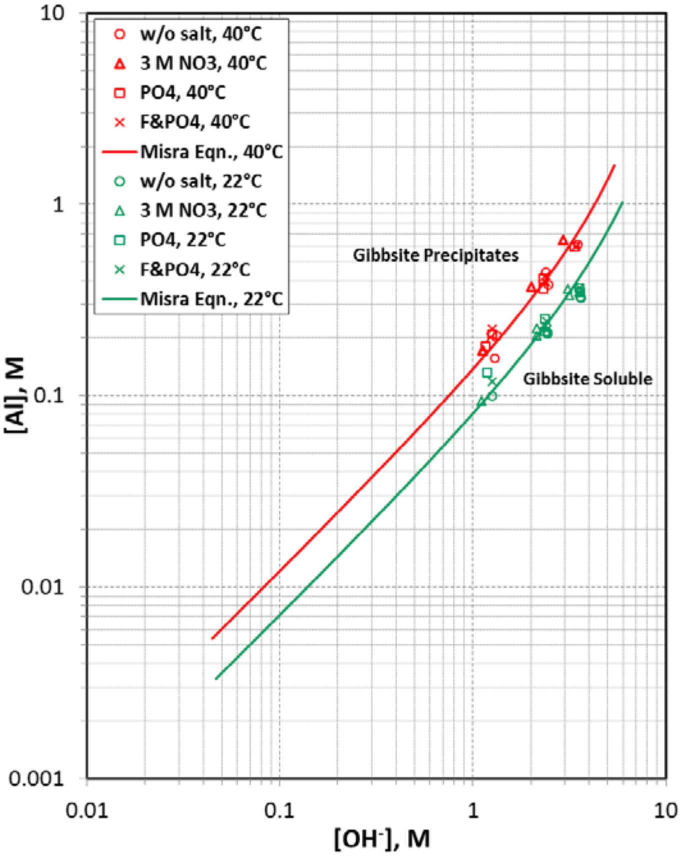

Figure 5. Gibbsite Solubility in the Absence/Presence of $NaNO_3$, $Na_3PO_4 \cdot 12H_2O$, and $Na_7F(PO_4)_2 \cdot 19H_2O$ (Herting 2014)

To better aid in visualizing the data, the differences between the projected equilibrium aluminum concentrations and those predicted by the Misra (1970) equation are plotted in Figure 6. The aluminum concentrations in the nominally duplicate tests vary about 0.01 to 0.04 M for total aluminum concentrations ranging from about 0.1 to 0.7 M. The measured aluminum concentrations in the gibbsite solubility systems with NaOH alone as well as with added phosphate or phosphate plus fluoride generally trend to lower values than those predicted by the Misra (1970) equation as the NaOH concentration increases. The effects of phosphate alone (at saturation in $Na_3PO_4 \cdot 12H_2O$) and phosphate plus fluoride (at

---

[1] The final NaOH concentration was adjusted to account for the hydroxide ion consumed between the final measured hydroxide concentration and that consumed by the reaction $Al(OH)_3 + OH^- \rightarrow Al(OH)_4^-$ in the projected continued gibbsite dissolution.

saturation in $Na_7F(PO_4)_2 \cdot 19H_2O$) on aluminum concentration are negligible compared to the salt-free NaOH system as measured by Herting (2014). This lack of significant effect is true for both the 22°C and 40°C tests. In contrast, the ~3 M added $NaNO_3$ increases gibbsite solubility, compared to the tests without added nitrate, with a distinct effect as the NaOH concentration exceeds 2 M. At ≥3 M NaOH, the aluminum concentration enhancement is about 0.08 M compared to the ~0.35 M aluminum for the nitrate-free solution in the 22°C tests and about 0.15 M compared to the ~0.7 M aluminum in the 40°C tests, relative solubility increases of ~20-25%.

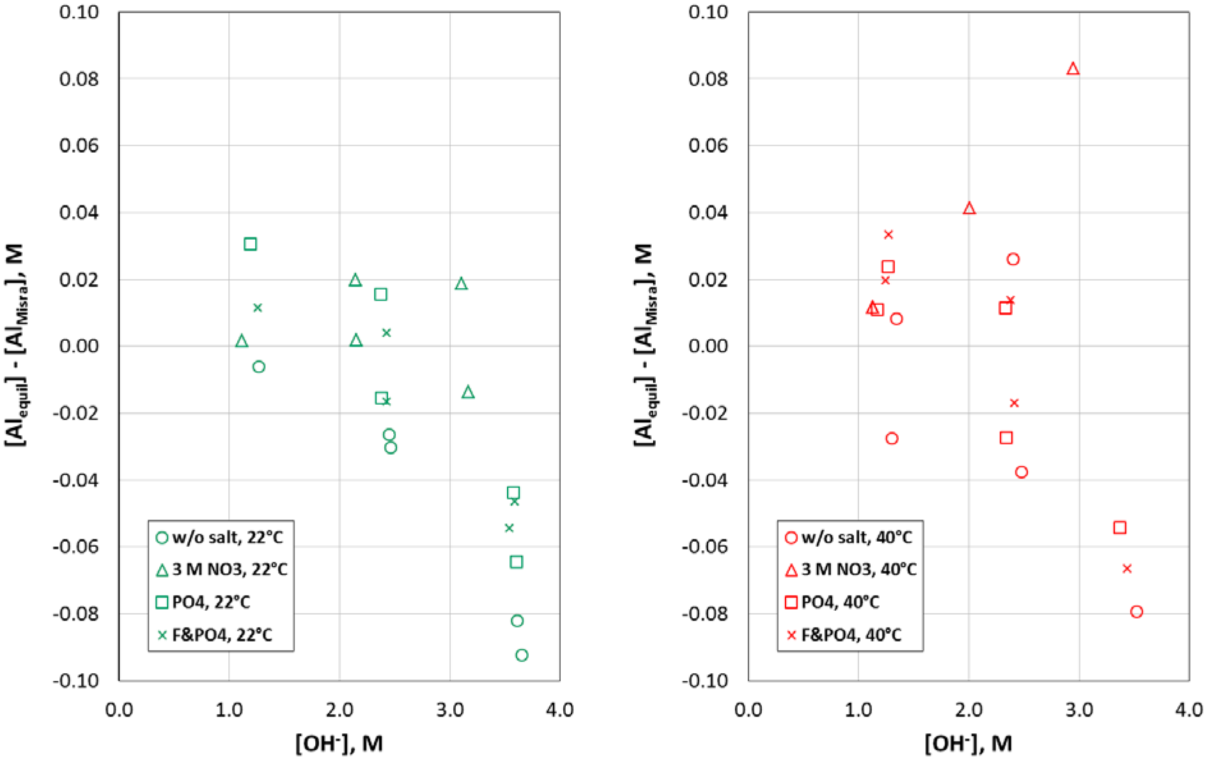

Figure 6. Difference between the Observed and Predicted (Misra 1970) Gibbsite Solubilities at 22°C (left) and 40°C (right) (Herting 2014)

Conclusions: The findings from these tests based on gibbsite dissolution, particularly at 22°C and to some extent at 40°C, are mildly suspect owing to their lack of demonstrated steady aluminum concentration and the use, instead, of "equilibrium" aluminum concentrations projected by asymptotic extrapolation of the dissolution rate data (Herting 2014). Nevertheless, based on these extrapolated values, and as seen in similar tests (Felmy et al. 1994; Bénézeth et al. 2016), high nitrate concentrations increase gibbsite solubility beyond that found in otherwise similar but nitrate-free solution. The effect is greater at higher temperatures and at higher NaOH concentrations. In contrast, phosphate, arising from saturation in $Na_3PO_4 \cdot 12H_2O$ *solid phase, and phosphate plus fluoride, from saturation in* $Na_7F(PO_4)_2 \cdot 19H_2O$ *solid phase, showed no observable impacts on gibbsite solubility. The lack of effect for the phosphate salts may be because of their relatively low concentrations.*

4.2.5 Gibbsite Solubility in NaOH-NaAl(OH)$_4$-NaNO$_3$-NaNO$_2$-Na$_2$SO$_4$-Na$_2$CO$_3$ Solutions

The solubilities of the aluminum solid phases of gibbsite and sodium aluminate and the salts sodium nitrate, nitrite, sulfate, and carbonate in simulated Hanford tank waste solutions containing sodium hydroxide were determined at 20, 40, 60, and 80°C (Barney 1976). Note that double salts and hydrates such as $Na_3NO_3SO_4 \cdot H_2O$ and $Na_2CO_3 \cdot H_2O$ also may have formed (Barney 1976; Herting et al. 2015), but the actual solid phases present in the individual tests were not directly identified. The tests were run from oversaturation in gibbsite (or in sodium aluminate, $NaAl(OH)_4$) using excess sodium aluminate, and were equilibrated for 3 to 7 days before filtration and analysis of the supernatant liquids. The attainment of equilibrium during the solubility tests was determined by following the compositions of paired synthetic waste mixtures. The composition of one member of the pair was measured after storage for an unspecified time at 80°C. The mixture then was cooled to 60°C and the composition was measured. This sequence was repeated at 40°C and then 20°C. The complementary identical mixture underwent a similar set of measurements but in the opposite order, beginning at 20°C and ending at 80°C. If the concentrations of the two mixtures run at decreasing and increasing temperature agreed at the common temperatures, the mixtures were judged to be at equilibrium and the concentration measurement valid.

The analyses began with rapid filtration at temperature and immediate dilution of the filtrates. Two media—distilled deionized water and 6 M sodium hydroxide—were used for dilution and aluminum concentrations were determined for both the water-diluted and NaOH-diluted samples. Significantly for the present study, gibbsite was observed to precipitate from most of the water-diluted samples. The differences in aluminum concentrations between the sodium hydroxide- and water-diluted (gibbsite-bearing) samples were found to equal the hydroxide concentration increase according to the reaction $Al(OH)_4^- \rightarrow Al(OH)_3 + OH^-$.

The solubilities of the added salts were found to decrease in the order sodium nitrite > sodium nitrate >> sodium carbonate > sodium sulfate and decrease with increasing sodium hydroxide concentration. The relative effects of sodium hydroxide concentration were greater, as expected, for salts of the divalent anions for which sodium ion concentration influences would be enhanced. The solubilities of each salt increased steeply below 2 M sodium hydroxide. This increase was attributed to the corresponding decrease in sodium aluminate concentration below 2 M sodium hydroxide caused by gibbsite precipitation. The salt solubilities (aside from sodium aluminate) increased with temperature but only at higher sodium hydroxide concentrations.

The solubilities of the aluminum phases are neatly summarized in Figure 7, referred to as the "Barney Diagram." The near vertical trace between 1 and 2 M sodium hydroxide defines the gibbsite solubility limit; the region to the left of the trace is oversaturated in gibbsite. Similarly, the region above the downward-right sloping curve above about 2 M NaOH was saturated with sodium aluminate. Surprisingly, and despite the measures taken to ensure equilibrium at 20, 40, 60, and 80°C, temperature had no appreciable effect on the observed solubilities.

Concerns have been expressed that the 3- to 7-day equilibration times were inadequate to crystallize gibbsite from supersaturated solutions that also contained high molar concentrations of sodium salts (Reynolds and Reynolds 2010). The objections are based on the 4-week equilibration times observed by Herting et al. (1986) for simpler and less concentrated solutions at 80°C and the high likelihood of ion pairing and aluminate dimerization in the concentrated liquors, both of which would inhibit nucleation and crystal growth.

Observations qualitatively similar to those of Reynolds and Reynolds (2010) exist in the aluminum industry's Bayer process wherein carbonate, chloride, fluoride, sulfate, and perhaps oxalate are seen to inhibit gibbsite precipitation (Hudson et al. 2012). It is reasonable to assume that nitrate and nitrite, both oxyanions as are carbonate, sulfate, and oxalate, also could inhibit gibbsite precipitation, perhaps through surface adsorption on incipient crystals. In industrial laboratory tests, precipitation from oversaturation reached apparent steady state within about a day at 85°C but was still above known saturation levels, while approach to equilibrium was much slower at lower digestion temperatures (Hudson et al. 2012).

The aluminum and hydroxide concentration data reported by Barney (1976) are compared with the Misra (1970) equation and findings from actual waste later in this report.

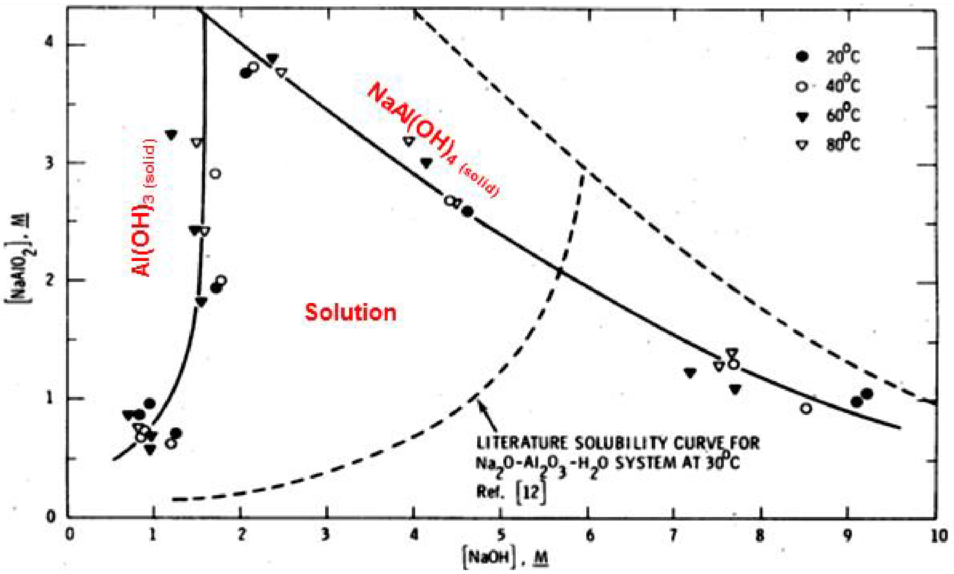

Figure 7. “Barney Diagram” for the Solubility of Gibbsite and Sodium Aluminate in Simulated Waste Solutions Saturated in Sodium Nitrate, Sodium Nitrite, Sodium Sulfate, and Sodium Carbonate (from Barney 1976; reference [12] in the figure is Volf and Kuznetsov 1955)

Conclusions: Gibbsite solubilities predicted by the “Barney Diagram” (Barney 1976) seem to be unusually high, as examined in greater detail later in this report. Despite experimental measures taken to guarantee equilibration, the observed high solubilities have been attributed to failure to reach equilibrium concentrations (Reynolds and Reynolds 2010).

4.2.6 Leaching of 241-AZ-101 Slurry

Treatment of actual waste slurry from Tank 241-AZ-101 through a series of wash, leach, and rinse steps was undertaken by Geeting and colleagues (2002). Thermodynamic analyses of the compositions of the product solutions showed that the aluminum concentrations in the initial solutions and in the two sludge wash solutions were oversaturated with respect to gibbsite (Felmy and MacLean 2003). The leaches were performed at 85°C starting with 3 M NaOH. Despite being at apparent oversaturation, no post-precipitation was observed. According to Felmy and MacLean (2003):

> “. . . the experimental Al concentrations in the initial solutions and in the two wash solutions (samples AZ-A, AZ-C, and AZ-E, Geeting et al. 2002) are higher than the model predictions. These higher aluminum concentrations indicate that the solutions are initially oversaturated with respect to the predicted stable phase, gibbsite. These results indicate that there is a potential for gibbsite precipitation from these solutions.”

Unfortunately, the concentration data, particularly for hydroxide, that were used in the thermodynamic evaluation (Tables A.1, A.2, and A.3 of Felmy and MacLean 2003) are not sufficiently identified to permit further interpretation.

4.3 Aluminum and Hydroxide Concentration Data for Actual Tank Wastes

One measure of the gibbsite solubility limit in actual tank wastes may be obtained by surveying the historical analytical data gathered and archived in the TWINS database. Although not all solutions are expected to be at saturation in gibbsite, the mass of analytical data might indicate solubility thresholds for aluminum concentration with respect to hydroxide concentration above which few data are observed.

With this in mind, three sets of TWINS data were gathered. One data set was of analyses of waste solutions from tanks that had remained undisturbed without additions or removals for periods ranging from 18 days to 17.2 years. The selection was made by this method to reflect solutions that may have had time to come to equilibrium with respect to gibbsite precipitation or dissolution. In addition to aluminum and hydroxide concentrations, the surveyed data were subdivided according to total sodium concentrations at >6 M, 2 to 6 M, and below 2 M to see if trends could be discerned. As is true of all examined TWINS data, the chemical analyses were performed at presumed ~25°C hotcell temperatures, but the temperatures of the tank wastes themselves were not logged. Therefore, some supersaturation caused by cooling from higher tank waste temperatures could have occurred.

The TWINS data selected by this process are plotted in Figure 8. In general and as expected, the solutions that have higher total sodium concentrations (which also would include NaOH) show higher aluminum concentrations. The aluminum concentrations for all wastes having >2 M sodium also were a factor of 3 to 10 greater than the concentrations predicted by the Misra (1970) equation at 25°C (laboratory hotcell temperature) but in the range of concentrations predicted by the Misra (1970) equation at 60°C, a nominal Hanford tank waste temperature. An apparent upper threshold in aluminum concentration versus hydroxide concentration is observed from these TWINS data and a dashed red line is traced in Figure 8 to mark this threshold. The line corresponds to a “free” hydroxide-to-aluminate mole ratio of 2:1. The 2:1 OH^-:$Al(OH)_4^-$ mole ratio is near the 3:1 ratio observed in cooled and diluted Bayer process liquors ready for gibbsite harvesting, as described in Section 2.0 (Wefers and Misra 1987). The unit slope of this line follows the expected stoichiometric requirement for one mole of hydroxide to produce one mole of aluminate by gibbsite dissolution. The lower 2:1 hydroxide:aluminate requirement in tank waste liquors compared with the 3:1 ratio in Bayer process liquors at similar temperatures (~50°C) is perhaps because of the effect of the high concentrations of other highly soluble tank waste salts (such as $NaNO_2$ and $NaNO_3$) that drive up the chemical activity of NaOH in the tank waste liquors.

Another set of analyses of actual waste solutions containing at least aluminum, hydroxide, and total sodium was selected from TWINS based on the tanks containing REDOX Sludge and S-Saltcake (Groups 5 and 6, respectively; see Fiskum et al. 2008). The REDOX Sludge is expected to contain high aluminum concentrations because of the use of aluminum ion as a salting agent in the REDOX solvent extraction process. Due to the heat evolved from the relatively high radionuclide concentrations in this waste, the gibbsite that would have precipitated upon making the acidic solvent extraction raffinates alkaline prior to discharge likely converted to boehmite in the waste tanks by radiolytic heating. Boehmite certainly is observed prominently in the REDOX Sludge, but gibbsite, too, is found (Fiskum et al. 2008) and thus would be the solubility-limiting aluminum-bearing phase. The S-Saltcake likewise arose from REDOX solvent extraction raffinates. For the S-Saltcake, gibbsite was the dominant solid phase remaining in the washed solids (Fiskum et al. 2008).

The surveyed tanks containing REDOX Sludge and S-Saltcake were those in the 241-S, -SX, -TX, and -U Tank Farms (Fiskum et al. 2008). Figure 9 illustrates the available TWINS data for these REDOX Sludge and S-Saltcake wastes. Most of the data come from Tank 241-S-102 but the hydroxide concentrations for that tank span a factor of 10. The same line of unit slope given in Figure 8, and corresponding to a “free” hydroxide:aluminate mole ratio of 2:1, is provided again in Figure 9. This ratio still seems to define a solubility threshold because few aluminum concentrations lie greatly above this line. For tank waste samples above ~0.5 M sodium hydroxide, the threshold line is about a factor of 5 to 8 greater than the gibbsite solubility line at 25°C provided by the Misra (1970) equation and generally even above the Misra (1970) equation gibbsite solubility line at 60°C. Hanford tank waste liquors currently are no higher than about 45°C (Reynolds et al. 2016).

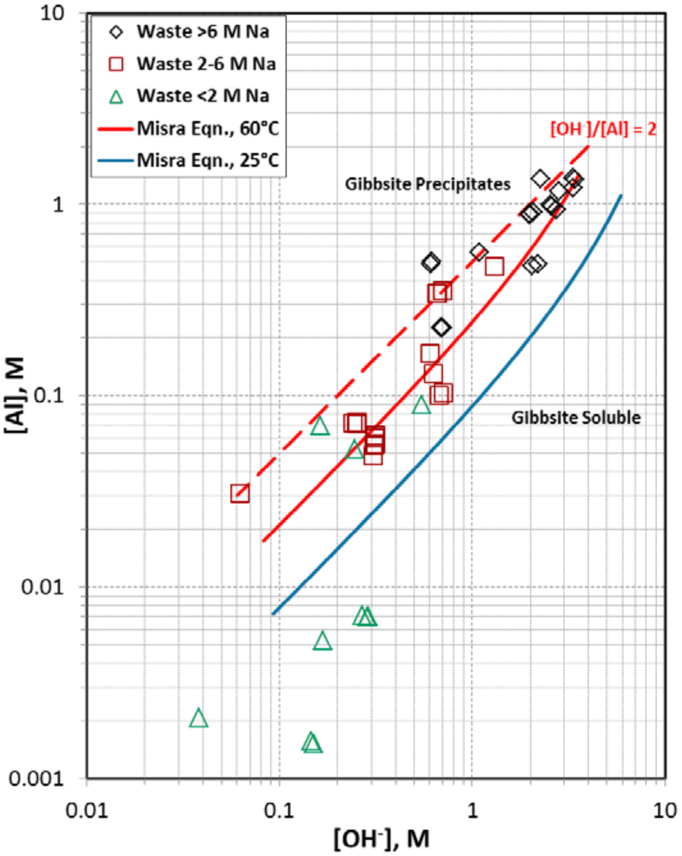

Figure 8. Waste Solution Analyses from TWINS for Undisturbed Tanks

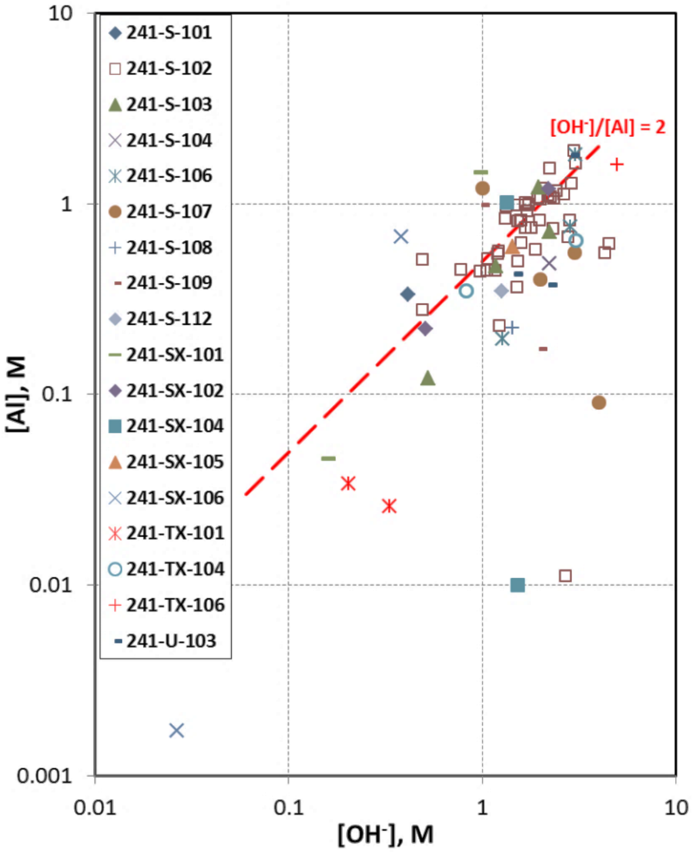

Figure 9. Solution Analyses from TWINS for REDOX Sludge and S-Saltcake Wastes

A third set of actual waste solution analytical data for aluminum and hydroxide concentration was taken from TWINS and selected from tanks containing high amounts of aluminum fuel cladding removal waste from PUREX and REDOX (Groups 3 and 4, respectively; see Snow et al. 2009). Gibbsite is found prominently in the sludges from these waste tanks (Snow et al. 2009) and would be the solubility-limiting aluminum-bearing phase. The tanks containing cladding removal wastes were identified by Snow et al. (2009) to be located in the 241-B, -BX, -C, -T, -U, and -U-200 Tank Farms. The individual tank data surveyed in TWINS for aluminum and hydroxide concentrations are presented in Figure 10. Again, the line of unit slope corresponding to a “free” hydroxide:aluminate mole ratio of 2:1 shown in Figure 8 is provided in Figure 10. Once again, this line seems to define a gibbsite solubility threshold but now for aluminum cladding removal waste solutions.

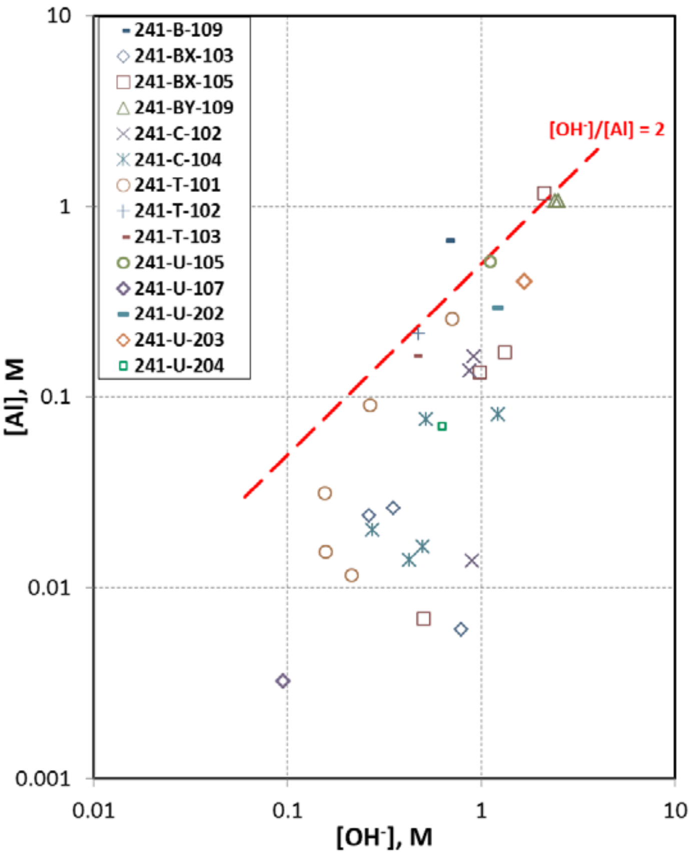

Figure 10. Solution Analyses from TWINS for Aluminum Cladding Removal Wastes

A separate fourth set of TWINS data, comprising more than 300 aluminum-versus-hydroxide concentration data pairs and selected because the solutions also contained from 3 to 7 molar total sodium, has been gathered (Agnew and Johnston 2013). The authors selected this total sodium concentration range because it brackets the target 5 molar sodium concentration for WTP feed-solution processing.

In Figure 11, the data from this fourth set (copied from Figure 1 in Agnew and Johnston 2013) are compared with the data collected for the undisturbed tank wastes (46 data pairs from Figure 8), with the REDOX Sludge and S-Saltcake waste data (82 data pairs from Figure 9), and with the aluminum cladding removal wastes data (32 data pairs from Figure 10). The data from Agnew and Johnston (2013) are clearly consistent with those of the other data sets and again show an apparent gibbsite solubility threshold corresponding to a "free" hydroxide:aluminate mole ratio of 2:1. A "free" hydroxide:aluminate mole ratio of 1.5:1, more encompassing of the data, also is plotted. At either ratio, aside from some rare "high-fliers" for aluminum concentration in the numerous data, a solubility threshold at a hydroxide:aluminate mole ratio of about 1.5:1 to 2:1 is apparent.

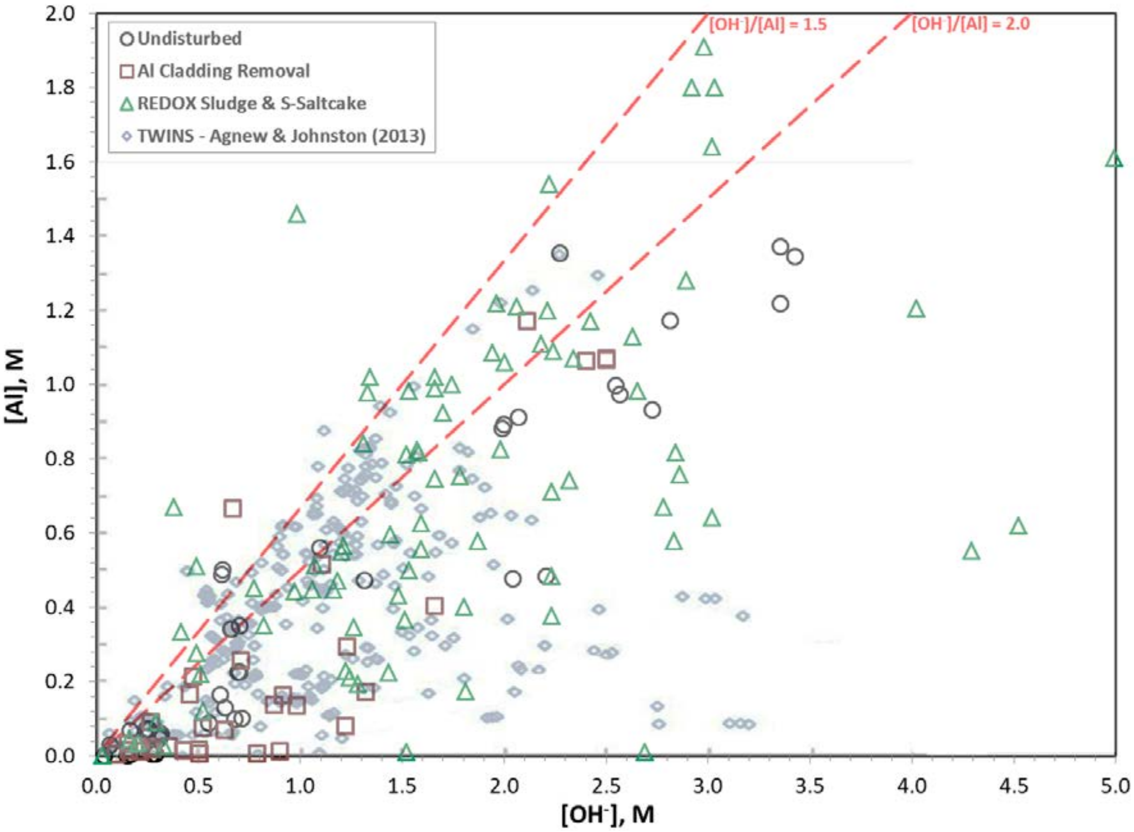

Figure 11. Solution Analyses for Undisturbed, REDOX Sludge and S-Saltcake, and Aluminum Cladding Removal Wastes from TWINS Compared with TWINS Values for Tank Wastes at 3 to 7 M Total Sodium (taken from Figure 1 of Agnew and Johnston 2013)

An alternative visualization of the same aluminum concentration threshold in comparison with hydroxide concentration was produced by Reynolds (2017). Also, using data gathered from TWINS, Reynolds (2017) confirmed that the lower "free" hydroxide:aluminate mole ratio threshold was 1.5:1 to 2:1 (Figure 12).

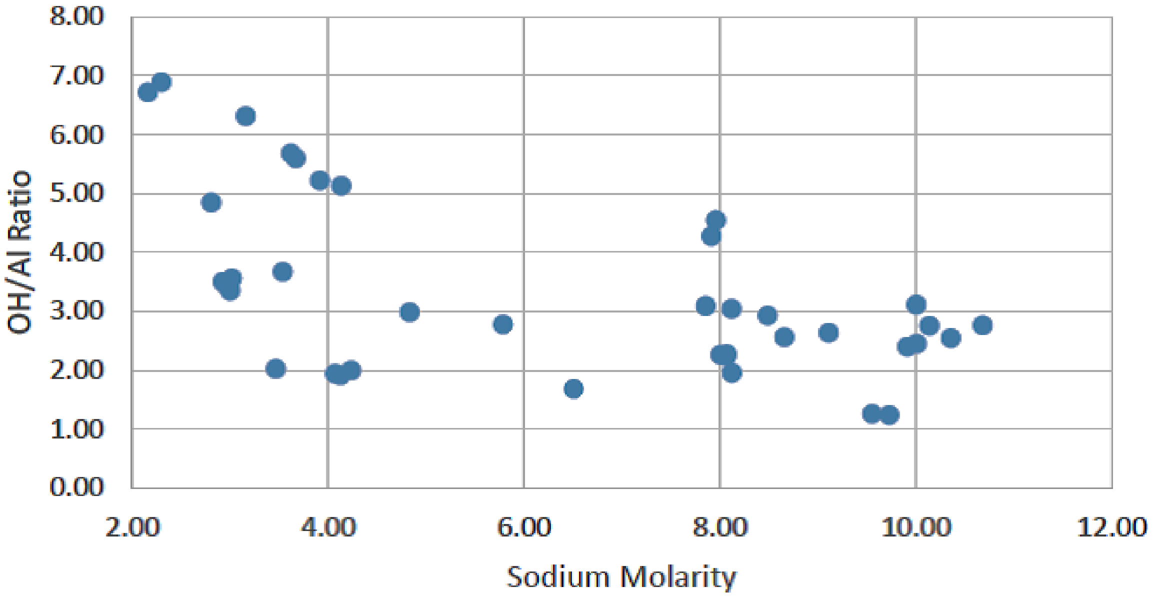

Figure 12. OH/Al Ratios in Actual Hanford Tank Waste Samples as a Function of Sodium Molarity (taken from Figure 2 of Reynolds 2017)

The tests to establish the gibbsite precipitation equilibrium at 40°C from aluminum-fortified actual waste solutions from Tanks 241-AN-105 and -AP-108 performed by McCoskey et al. (2015) are described earlier in this report. These tests also formed the basis for the subsequent journal article that reported only the findings for AN-105 (Reynolds et al. 2016). As noted previously, in one of the tests, solution from AN-105 with gibbsite added and heated to dissolution at 80°C failed to re-precipitate gibbsite even after addition of supplemental tank waste solids and ~59 days of aging. It was surmised that the failure to precipitate was due to the absence of gibbsite crystals to act as seed crystals (thermonatrite was the dominant phase in the tank waste solids). The apparent solubilities of gibbsite observed in these tests are illustrated in Figure 13, plotted in the same fashion as the actual tank waste data from TWINS shown in Figure 8, Figure 9, and Figure 10. It is seen that the observed gibbsite solubilities from the AN-105 and AP-108 tests are near to and as much as a factor of 2 above the aluminum concentration threshold observed for actual tank waste data from TWINS shown in Figure 8, Figure 9, and Figure 10. The test with no gibbsite solid phase present, however, was about a factor of 4 above the aluminum concentration threshold.

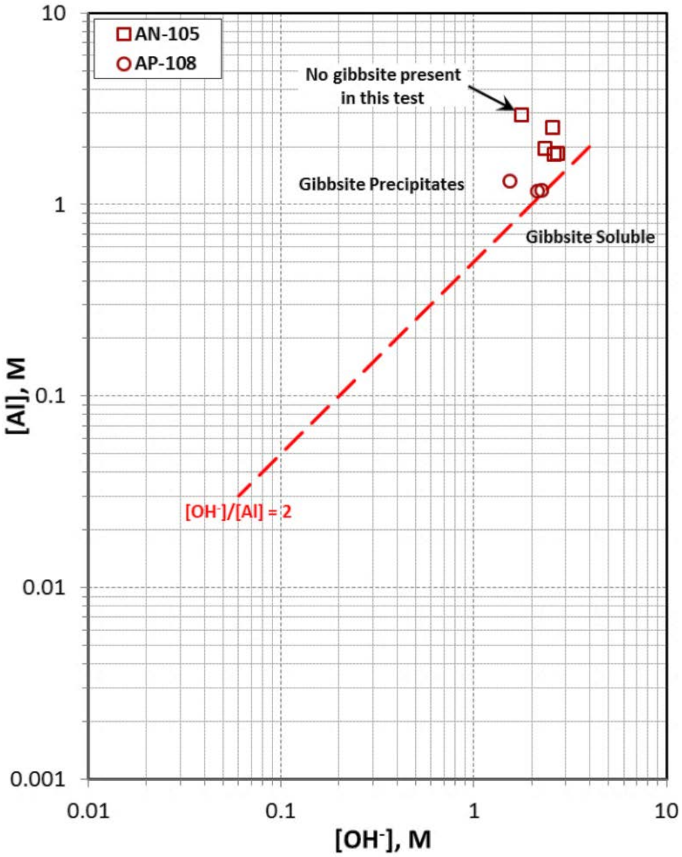

Figure 13. Gibbsite Solubility Test Results for Tank Wastes from Tanks 241-AN-105 and -AP-108 (data from McCoskey et al. 2015)

Barney (1976) reported the concentrations of dissolved aluminum from four 241-S tanks in his phase diagram study. These compositions are plotted in Figure 13 with the experimental gibbsite and sodium aluminate data found, at various temperatures, from the phase diagram work using simulated waste compositions (Barney 1976). The “Barney Diagram” solubility curve, redrawn in log-log coordinates, also is presented in Figure 14. It is seen that the four 241-S tank waste aluminum concentration data are consistent with observations made from TWINS values, as shown in Figure 8, Figure 9, and Figure 10. The aluminum phase solubility data from the tests saturated in sodium nitrate, nitrite, sulfate, and carbonate in the “Barney Diagram” curve, however, reach values markedly higher than the TWINS threshold between about 1 and 2.5 M sodium hydroxide and more closely align with the Misra (1970) equation prediction for the 100°C solution.

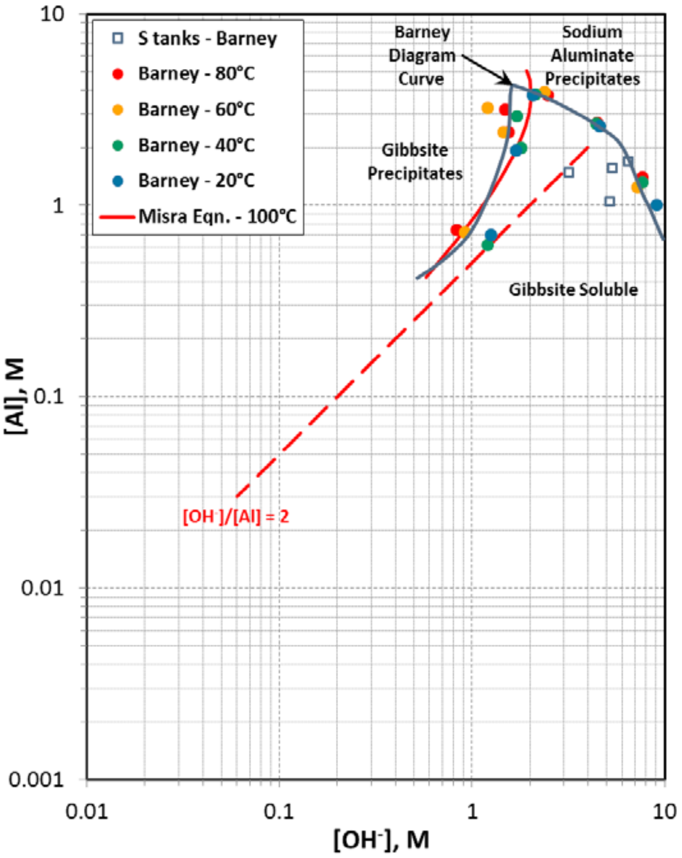

Figure 14. Aluminum Concentration Analyses for Four 241-S Tank Wastes and for High Salt Simulants (data from Barney 1976)

Conclusions: Plots of tank waste solution analyses show an aluminum molar concentration threshold that is approximately one-half to two-thirds of the free hydroxide concentration. The deviation of many data pairs below this upper limit can be explained by the absence of gibbsite solid phase. The relatively scarce data that lie above this threshold might be explained by analytical variability and sampling error or by supersaturation attained by high temperatures within the tank wastes themselves. The aluminum concentration threshold observed in actual waste is about a factor of 5 to 8 greater than the gibbsite solubility line at 25°C provided by the Misra (1970) equation. The observed gibbsite solubilities from the AN-105 and AP-108 tests (McCoskey et al. 2015) are near to and as much as a factor of 2 above the aluminum concentration threshold, while the "Barney Diagram" findings do not accord with the observed actual waste aluminum concentration threshold.

5.0 Conclusions and Recommendations

The chemistry of the Bayer process has been researched extensively over the last hundred years. The Bayer process involves dissolution of aluminum-containing minerals in hot, aqueous, concentrated sodium hydroxide solution followed by precipitation of purified gibbsite upon dilution, cooling, and, in process conditions, use of gibbsite seed crystals. Many of the synthetic Bayer liquors studied are concentrated alkaline aluminate solutions containing only the solutes Na^+, OH^-, and $Al(OH)_4^-$. These liquors are similar to, but not representative of, the complex DFLAW feed, which also contains varying proportions of nitrate, nitrite, carbonate, oxalate, phosphate, sulfate, fluoride, chloride, and chromate, in addition to aluminum, sodium, and hydroxide. Available industry, national laboratory, and Hanford contractor literature surveyed and discussed in Section 3, should be considered when establishing data gaps associated with the risk of precipitation upon dilution of DFLAW feed saturated in aluminum hydroxide. As described in Section 3, during the Bayer process aluminate solutions are diluted to initiate gibbsite precipitation. However, the effect of dilution is bounded by solution conditions, i.e., when the "free" hydroxide/aluminum mole ratio is much lower than the 2:1 ratio that seems to define the Al solubility threshold for actual tank wastes (above the dashed red line in Figure 8). Thus, at a simplistic level, it could be stated that if $[OH^-]/[Al] \geq 2$, dilution with raw filtered river water will not result in aluminum hydroxide precipitation. That said, the "free" hydroxide/aluminum 2:1 threshold represents a dissolved aluminum concentration that is considerably higher than expected based on current understanding of gibbsite solubility in high-pH systems, which, for this report, is represented by the Misra (1970) equation (Figure 2). The deviation of data below this upper threshold is likely due to the absence of gibbsite solid phase and the possible scavenging of dissolved aluminum by precipitation as low-solubility sodium aluminosilicates (e.g., cancrinite). Some deviation above and below the threshold for actual tank waste analyses can also be expected (1) given that the tank waste temperatures were not known, (2) because of analytical uncertainty, and (3) because of the unknown magnitude of effects from waste composition, such as ionic strength and concentrations of other sodium salts.

To establish a defensible technical basis for minimizing or avoiding aluminum hydroxide precipitation during DFLAW staged feed dilution, aluminum solubility must be predicted as a function of the significant variables that influence gibbsite dissolution and precipitation. These variables include (1) temperature (see Section 3.2.1); (2) equilibration time (see Section 3.2.3); (3) other solution components that meaningfully affect the activity coefficient of either hydroxide or the aluminate ion, particularly nitrate, nitrite, and carbonate (see Section 3.2.4); (4) the presence of gibbsite seed crystals (see Section 3.1.1); (5) ionic strength, i.e., sodium concentration (see Section 3.1.2.2) and the potential for ion pair formation; and (6) the approach from above and below saturation (see discrepancies between Herting et al. (1986) data and Bénézeth et al. (2016) data in Section 3.2.3).

5.1 Proposed Task 2 Work Scope

Based on this review of waste solubility data and the impact of dilution on solution stabilities with a specific focus on aluminum hydroxide (Task 1 of FMP-WASTE-25 [Reynolds et al. 2017]), a "Task 2" work scope is proposed. The proposed task will close the identified data gaps associated with the impact of temperature, equilibration time, other salts, seed crystals, ionic strength, and approach to equilibrium from above and below saturation on the prediction of aluminum hydroxide solubility in actual wastes. The proposed experiments build on those described by Barney (1976), Herting et al. (1986), Bénézeth et al. (2016), Herting (2014), Reynolds et al. (2016), and in the associated lab report by McCoskey et al. (2015). Key experimental conditions and limits are as follows:

- Aluminum hydroxide (i.e., $Al(OH)_3$) will be synthesized and characterized according to protocols developed through PNNL's Energy Frontier Research Center (EFRC) focused on interfacial dynamics in radiation environments and materials (IDREAM). This synthesis will provide a solid-phase starting material that does not contain any amorphous gel impurity and has controlled particle size with high surface area to provide faster dissolution kinetics.

- Solutions will be prepared using reagent NaOH, $NaNO_3$, and $NaNO_2$ and will be stored and experiments conducted in a glovebox under an argon atmosphere to minimize carbonate formation from atmospheric carbon dioxide.
- NaOH concentrations in the approximate range of 2 to 6 molal will be investigated.
- Experiments will focus on $Al(OH)_3$ solubility in NaOH solutions containing a range of $NaNO_2$ concentrations up to the solubility limit at a given temperature as described by Reynolds and Herting (1984). Analogous experiments with $NaNO_3$ will be carried out as well as experiments with both $NaNO_2$ and $NaNO_3$ in NaOH and with NaOH only.
- Experiments will be conducted at room temperature (~22°C), 45, and 80°C thus spanning the temperature in the tanks and up to the leaching temperature in the WTP but not exceeding the $Al(OH)_3$ to AlOOH transition temperature with agitation in sealed Teflon containers.
- Aliquots will be collected, filtered, and diluted with either 1 M HNO_3 or 5 M NaOH to prevent $Al(OH)_3$ precipitation or with H_2O to assess $Al(OH)_3$ precipitation by H_2O dilution.
- The weight of volumetric aliquots of the samples will be recorded to determine the solution density.
- The diluted solutions will be analyzed by inductively coupled plasma - atomic emission spectroscopy for aluminum, ion chromatography for nitrate and nitrite, for free hydroxide, and density.
- The analytical work will be performed in the PNNL Environmental Sciences Laboratory, which operates under Quality Assurance plans in compliance with DOE/RL-96-68, *Hanford Analytical Services Quality Assurance Requirements Document*, and the American Society of Mechanical Engineers quality assurance standard NQA-1-2012, *Quality Assurance Requirements for Nuclear Facility Applications*.
- According to Bénézeth et al. (2016), samples taken as a function of time should reach constant aluminum concentration in less than 20 days, but sampling will continue until aluminum concentrations of three consecutive samples form a horizontal asymptote as a function of time within experimental error.
- The solid phases will be characterized by x-ray diffractometry (to identify the crystalline phases), scanning electron microscopy (particle size and shape), and energy dispersive spectrometry (to establish the presence and absence of chemical elements).

The proposed experimental work outlined above, representing Task 2 work scope for FMP-DFLAW-25, will be planned, executed, and formally reported.

5.2 Recommendations for Follow-On Work

The work proposed here will close many identified gaps in predicting aluminum hydroxide solubility with dilution and temperature. The experiments will encompass effects of temperature, equilibration time, and specific solution components. However, the integrated flowsheet model and tank farm operations would further benefit from conducting additional experiments to accomplish the following:

- Include Na_2CO_3 in the solution composition matrix to determine the effects of $NaAlCO_3(OH)_2$ on $Al(OH)_3$ dissolution and precipitation.

- Understand the effect of seed crystals so that diluted tank waste solutions can potentially be seeded with $Al(OH)_3$ to induce precipitation and mitigate the effects of unanticipated solids carryover into the LAWPS, delayed aluminum precipitation fouling the LAWPS ion exchange operations, and transfer line deposition.

- Extend the timescale of the experiments to encompass kinetic effects on $Al(OH)_3$ precipitation over periods relevant to diluted DFLAW storage, i.e., 1 to 9 months.

- Define key counterion (Na^+) concentrations to stabilize polymeric aluminum solution species and limit precipitation.

Ultimately, this additional work would provide key information about (1) the mechanisms by which gibbsite becomes supersaturated; (2) $Al(OH)_3$ precipitation kinetics, including induction times to precipitation; and (3) potential blending strategies to minimize $Al(OH)_3$ precipitation.

This program of work is timely because it would leverage PNNL's current IDREAM EFRC and multi-million dollar investments in nuclear process science to develop a predictive understanding of concentrated alkaline aluminum-containing solutions of relevance to DFLAW.

6.0 References

Agnew SF and CT Johnston. 2013. *Aluminum Solubility in Complex Electrolytes*. Paper 13011 at WM2013 Conference, February 24-28, 2013, Phoenix, Arizona. http://www.wmsym.org/archives/2013/papers/13011.pdf

Anderson KA, MD Britton, JM Colby, LH Cree, MS Fountain, DW Nelson, VC Nguyen, and ME Stone. 2017. *One System River Protection Project Integrated Flowsheet*. RPP-RPT-57991, Rev. 2, 24590-WTP-RPT-MGT-14-023, Rev. 2, Washington River Protection Solutions LLC, Richland, Washington.

Baker HL. 2003. “Updated Tank 241-AN-107 Core 304 Analytical Results for the Final Report.” Letter report FH-0205877, Reissue 1, to GA Stanton. Fluor Hanford, Richland, Washington.

Barney GS. 1976. *Vapor-Liquid-Solid Phase Equilibria of Radioactive Sodium Salt Wastes at Hanford*. ARH-ST-133, Atlantic Richfield Hanford Company, Richland, Washington.

Bénézeth P, S Hilic, and DA Palmer. 2016. “The Solubilities of Gibbsite and Bayerite Below 100°C in Near Neutral to Basic Solutions.” *Journal of Solution Chemistry* 45:1288-1302.

Brown GN. 2014. *Literature Review of Spherical Resorcinol-Formaldehyde for Cesium Ion Exchange*. PNNL-23410, WTP-RPT-230, Rev. 0, Pacific Northwest National Laboratory, Richland, Washington.

Callaway WS. 2003. *Tank 241-S-102 Core Sample Dissolution Testing Report*. RPP-15940, Rev. 0, Fluor Hanford, Richland, Washington.

Callaway WS and HJ Huber. 2010. *Results of Physicochemical Characterization and Caustic Dissolution Test on Tank 241-C-108 Heel Solids*. LAB-RPT-10-00001, Rev. 0, Washington River Protection Solutions LLC, Richland, Washington.

Cooke GA. 2002. “Solid Phase Characterization of Tank 241-S-112 Dissolution Residues.” Letter report FH-0202771 to JN Appel. Fluor Hanford, Richland, Washington.

Cooke GA. 2015. “Solid Phase Characterization of Solids Recovered from Failed Sluicer Arm.” Letter report WRPS-1500668 to AM Templeton. Washington River Protection Solutions LLC, Richland, Washington.

Felmy AR and GT MacLean. 2003. *Thermodynamic Modeling of AZ-101 Slurry Leaching*. PNWD-3289, WTP-RPT-067, Rev. 0, Battelle–Pacific Northwest Division, Richland, Washington.

Felmy AR, JR Rustad, MJ Mason, and R de la Bretonne. 1994. *A Chemical Model for the Major Electrolyte Components of the Hanford Waste Tanks: The Binary Electrolytes in the System: Na-*NO_3-NO_2-SO_4-CO_3-*F*-PO_4-*OH*-$Al(OH)_4$-H_2O. PNL-SA-23952, Pacific Northwest Laboratory, Richland, Washington.

Fiskum SK, ST Arm, and DL Blanchard, Jr. 2004. *Small Column Ion Exchange Testing of SuperLig® 644 for Removing* ^{137}*Cs from Hanford Waste Tank 241-AN-102 Supernate (Envelope C) Mixed with Tank 241-C-104 Solids (Envelope D) Wash and Permeate Solutions*. PNWD-3240, Rev. 1, WTP-RPT-033, Rev. 1, Battelle–Pacific Northwest Division, Richland, Washington.

Fiskum SK, ST Arm, MS Fountain, MJ Steele, and DL Blanchard, Jr . 2006a. *Spherical Resorcinol-Formaldehyde Resin Testing for ^{137}Cs Removal from Simulated and Actual Hanford Waste Tank 241-AP-101 Diluted Feed (Envelope A) Using Small Column Ion Exchange*. PNWD-3697, WTP-RPT-134, Rev. 0, Battelle–Pacific Northwest Division, Richland, Washington.

Fiskum SK, JM Billing, EC Buck, RC Daniel, KE Draper, MK Edwards, ED Jenson, AE Kozelisky, PJ MacFarlan, RA Peterson, RW Shimskey, and LA Snow. 2009. *Laboratory Demonstration of the Pretreatment Process with Caustic and Oxidative Leaching Using Actual Hanford Tank Waste*. PNNL-18007, WTP-RPT-171, Rev. 0, Pacific Northwest National Laboratory, Richland, Washington.

Fiskum SK, EC Buck, RC Daniel, KE Draper, MK Edwards, TL Hubler, LK Jagoda, ED Jenson, AE Kozelisky, GJ Lumetta, PJ MacFarlan, K McNamara, RA Peterson, SI Sinkov, LA Snow, and RG Swoboda. 2008. *Characterization and Leach Testing for REDOX Sludge and S-Saltcake Actual Waste Sample Composites*. PNNL-17368, WTP-RPT-157, Rev. 0, Pacific Northwest National Laboratory, Richland, Washington.

Fiskum SK, IE Burgeson, OT Farmer, III, LR Greenwood, CZ Soderquist, MJ Steele, and MP Thomas. 2006c. *Spherical Resorcinol-Formaldehyde Resin Analysis Following Actual Hanford Tank Waste Processing*. PNWD-3752, WTP-RPT-144, Rev. 0, Battelle–Pacific Northwest Division, Richland, Washington.

Fiskum SK, MJ Steele, and DL Blanchard, Jr. 2006b. *Small Column Ion Exchange Testing of Spherical Resorcinol-Formaldehyde Resin for ^{137}Cs Removal from Pre-Treated Hanford Tank 241-AN-102 Waste (Envelope C)*. PNWD-3751, WTP-RPT-135, Rev. 1. Battelle–Pacific Northwest Division, Richland, Washington.

Geeting JGH, RT Hallen, LK Jagoda, AP Poloski, RD Scheele, and DR Weier. 2002. *Filtration, Washing, and Caustic Leaching of Hanford Tank AZ-101 Sludge*. PNWD-3206, Rev. 0, WTP-RPT-043, Battelle–Pacific Northwest Division, Richland, Washington.

Herting DL. 1993. *Clean Salt Process Applied to Double Shell Slurry (Tank 101-SY)*. WHC-SD-WM-DTR-029, Rev. 0, Westinghouse Hanford Company, Richland, Washington.

Herting DL. 1996. *Clean Salt Process Final Report*. WHC-EP-0915, Westinghouse Hanford Company, Richland, Washington.

Herting DL. 1999a. *Results of Dilution Studies with Waste from Tank 241-AN-105*. HNF-SD-WM-DTR-046, Rev. 0A, Numatec Hanford Corporation, Richland, Washington.

Herting DL. 1999b. *Saltcake Dissolution FY 1999 Status Report*. HNF-5193, Rev. 0, Numatec Hanford Corporation, Richland, Washington.

Herting DL. 2000. *Saltcake Dissolution FY 2000 Status Report*. HNF-7031, Rev. 0, Fluor Hanford, Richland, Washington.

Herting DL. 2001. *Saltcake Dissolution FY 2001 Status Report*. HNF-8849, Rev. 0, Fluor Hanford, Richland, Washington.

Herting DL. 2002. *Saltcake Dissolution FY 2002 Status Report*. HNF-12145, Rev. 0, Fluor Hanford, Richland, Washington.

Herting DL. 2003a. “Caustic Demand Test Results, Tank 241-AN-102 Sludge.” Letter report FH-0303343 to KG Carothers. Fluor Hanford, Richland, Washington.

Herting DL. 2003b. “Caustic Demand Test Results, Tank 241-AY-102 Sludge.” Letter report 7S110-DLH-03-007 to KG Carothers. CH2M Hill Hanford Group, Inc., Richland, Washington.

Herting DL. 2004a. “Caustic Demand Test Results, Tank 241-C-103 Sludge.” Letter report 7S110-DLH-04-015 to KG Carothers. CH2M Hill Hanford Group, Inc., Richland, Washington.

Herting DL. 2004b. “Characterization of Yellow Sample from Tank 241-S-112.” Letter report CH2M-0400924 to AR Felmy. CH2M Hill Hanford Group, Inc., Richland, Washington.

Herting DL. 2005a. “Tank 241-AN-102 Process Chemistry Test Results.” Letter report 7S110-DLH-05-028 to KG Carothers. CH2M Hill Hanford Group, Inc., Richland, Washington.

Herting DL. 2005b. “Tank AY-102 Centrifuged Solids Analysis Results.” Letter report 7S110-DLH-05-040 to KG Carothers. CH2M Hill Hanford Group, Inc., Richland, Washington.

Herting DL. 2006. “Tank 241-SY-102 Cooling Test Results.” Letter report 7S110-DLH-06-068 to KG Carothers. CH2M Hill Hanford Group, Inc., Richland, Washington.

Herting DL. 2007. “Characterization of Fines in Product Salt Samples.” Letter report 7S110-DLH-07-124 to DW Hamilton. CH2M Hill Hanford Group, Inc., Richland, Washington.

Herting DL. 2012. *Boehmite/Gibbsite Dissolution Rate Study Final Report*. WRPS-1201717, Washington River Protection Solutions LLC, Richland, Washington.

Herting, DL. 2014. *Effect of Phosphate, Fluoride, and Nitrate on Gibbsite Dissolution Rate and Solubility*. LAB-RPT-13-00011, Rev. 0, Washington River Protection Systems, Richland, Washington. http://www.iaea.org/inis/collection/NCLCollectionStore/_Public/45/068/45068209.pdf

Herting DL. 2015. *Test Results for Oxalic Acid Addition to Iron/Aluminum Sludge Simulant*. WRPS-1501657, Washington River Protection Solutions LLC, Richland, Washington.

Herting DL and DB Bechtold. 2002. *Tank 241-S-112 Saltcake Dissolution Laboratory Test Report*. RPP-10984, Rev. 0, Fluor Hanford, Richland, Washington.

Herting DL, GA Cooke, JS Page, and JL Valerio. 2015. *Hanford Tank Waste Particle Atlas*. LAB-RPT-15-00005 R0, Washington River Protection Solutions LLC, Richland, Washington.

Herting DL, GA Cooke, and JA Pestovich. 2012. *Characterization of Archive Sludge Samples from Tank 241-C-111*. RPP-RPT-53468, Rev. 0, Washington River Protection Solutions LLC, Richland, Washington.

Herting DL, GA Cooke, and RW Warrant. 2002. *Identification of Solid Phases in Saltcake from Hanford Site Waste Tanks*. HNF-11585, Rev. 0, Fluor Hanford, Richland, Washington.

Herting DL, GA Cooke, and RW Warrant. 2004. *Hanford Tank 241-AN-107 Solid Phase Characterization*. RPP-20018, Rev. 0, CH2M Hill Hanford Group, Inc., Richland, Washington.

Herting DL and DW Edmonson. 1998. *Saltcake Dissolution FY 1998 Status Report*. HNF-3437, Rev. 0, Numatec Hanford Corporation, Richland, Washington.

Herting D, T Welsh, and D Reynolds. 1986. Gibbsite Equilibrium in Simulated Liquid Waste. RHO-SD-WM-TI-211, Rev. 0, Rockwell Hanford Operations. Richland, Washington.

Huber HJ. 2009. *Report on Gibbsite Heel Formation Simulation and 241-C-103 Heel Analysis*. WRPS-0900975, Washington River Protection Solutions LLC, Richland, Washington.

Hudson LK, C Misra, AJ Perrotta, K Wefers, and FS Williams. 2012. "Aluminum Oxide." From *Ullmann's Encyclopedia of Industrial Chemistry*. Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim, Germany.

Li H, J Addai-Mensah, JC Thomas, and AR Gerson. 2005. "The influence of Al(III) supersaturation and NaOH concentration on the rate of crystallization of $Al(OH)_3$ precursor particles from sodium aluminate solutions." *Journal of Colloid and Interface Science* 286:511-519.

Lumetta GJ, IE Burgeson, MJ Wagner, J Liu, and YL Chen. 1997. *Washing and Caustic Leaching of Hanford Tank Sludge: Results of FY 1997 Studies*. PNNL-11636, Pacific Northwest National Laboratory, Richland, Washington.

Lumetta GJ, BM Rapko, J Liu, and DJ Temer. 1998. "Enhanced Sludge Washing for Pretreating Hanford Tank Sludges." Pages 203-218 in *Science and Technology for Disposal of Radioactive Tank Wastes*. WW Schulz and NJ Lombardo (eds.), Plenum Press, New York, NY. ISBN 0-306-45904-3. http://www.springer.com/us/book/9780306459047.

Mabrouki RB. 2013. *Final Report for the Solid Phase Characterization of Samples from the Boehmite/Gibbsite Dissolution Project*. RPP-RPT-52943, Rev. 0, Washington River Protection Solutions LLC, Richland, Washington.

MacLean GT. 1999. *The Settling and Compaction of Nuclear Waste Slurries*. HNF-5177, Rev. 0, Fluor Daniel Northwest, Richland, Washington.

McCoskey JK, GA Cooke, and DL Herting. 2015. *Chemical Equilibrium of Aluminate in Hanford Tank Waste Originating from Tanks 241-AN-105 and 241-AP-108*. LAB-RPT-14-00011 R0. Washington River Protection Solutions LLC, Richland, Washington.

Misra C. 1970. "Solubility of aluminium trihydroxide (hydrargillite) in sodium hydroxide solutions." *Chemistry and Industry* 19(5):619-623.

Nash CA and MR Duignan. 2009. *Real Waste Testing of Spherical Resorcinol-Formaldehyde Ion Exchange Resin*. SRNL-STI-2009-00594, Rev. 0, Savannah River National Laboratory, Aiken, SC.

NQA-1-2000, *Quality Assurance Requirements for Nuclear Facility Applications.* American Society of Mechanical Engineers, New York, NY.

NQA-1-2008, *Quality Assurance Requirements for Nuclear Facility Applications.* American Society of Mechanical Engineers, New York, NY.

NQA-1a-2009, *Addenda to ASME NQA-1–2008.* American Society of Mechanical Engineers, New York, NY.

Orme RM. 2003. *Hanford Tank Waste Operations Simulator Specific Gravity Model – Derivation of Coefficients and Validation*. RPP-14767, Rev. 0, Hanford Numatec Corporation. Richland, Washington.

Reynolds DA and DL Herting. 1984. *Solubilities of Sodium Nitrate, Sodium Nitrite, and Sodium Aluminate in Simulated Nuclear Waste*. RHO-RE-ST-14 P., Rockwell Hanford Operations, Richland, Washington.

Reynolds JG and DA Reynolds. 2010. “A Modern Interpretation of the Barney Diagram for Aluminum Solubility in Tank Waste – 10075.” WM2010 Conference, March 7-11, 2010, Phoenix, AZ. Washington River Protection Solutions LLC, Richland, Washington.

Reynolds JG, JK McCoskey, and DL Herting. 2016. “Gibbsite Solubility in Hanford Nuclear Waste Approached from above and below Saturation.” *Industrial and Engineering Chemistry Research* 55:5465-5473. http://dx.doi.org/10.1021/acs.iecr.6b00743.

Reynolds JG. 2017. “Potential Aluminum Precipitation during Water Additions to Tank 241-AP-107.” Letter report WRPS-1704198 to ST Arm. Washington River Protection Solutions LLC, Richland, Washington.

Reynolds JG, DR Reinemann, MS Fountain, ME Stone, and RB Wyrwas. 2017. *One System River Protection Project Integrated Flowsheet Maturation Plan*. RPP-PLAN-58003, Rev. 3, 24590-WTP-PL-MGT-15-0011, Rev. 2, Washington River Protection Solutions LLC. Richland Washington.

Russell RL, DE Rinehart, GN Brown, PP Schonewill, and RA Peterson. 2012. *Ion Exchange Kinetics Testing with SRF Resin*. PNNL-21109, WTP-RPT-214, Pacific Northwest National Laboratory, Richland, Washington.

Russell RL, DE Rinehart, and RA Peterson. 2014. *Ion Exchange Testing with SRF Resin FY 2012*. PNNL-21645, Rev. 1, WTP-RPT-223, Rev. 1, Pacific Northwest National Laboratory, Richland, Washington.

Snow LA, EC Buck, AJ Casella, JV Crum, RC Daniel, KE Draper, MK Edwards, SK Fiskum, LK Jagoda, ED Jenson, AE Kozelisky, PJ MacFarlan, RA Peterson, and RG Swoboda. 2009. *Characterization and Leach Testing for PUREX Cladding Waste Sludge (Group 3) and REDOX Cladding Waste Sludge (Group 4) Actual Waste Sample Composites*. PNNL-18054, WTP-RPT-167, Rev. 0, Pacific Northwest National Laboratory, Richland, Washington.

Urie MW, JA Campbell, OT Farmer, SK Fiskum, LR Greenwood, EW Hoppe, GM Mong, CZ Soderquist, RG Swoboda, MP Thomas, and JJ Wagner. 2002. *Chemical Analysis and Physical Property Testing of 241-AN-102 Tank Waste – Supernatant and Centrifuged Solids*. PNWD-3229, WTP-RPT-020, Rev. 1, Battelle–Pacific Northwest Laboratory, Richland, Washington.

Volf FF and SI Kuznetsov. 1955. “Polytherms in the Al_2O_3–Na_2O–H_2O System.” *Journal of Applied Chemistry (USSR)* 28:565-569.

Wefers K and C Misra. 1987. *Oxides and Hydroxides of Aluminum*. Alcoa Technical Paper No. 19, Revised. Alcoa Laboratories (no city or state provided).

Distribution*

TradeWind Services, LLC
CH Delegard

Washington River Protection Solutions LLC
ST Arm
MD Britton
JG Reynolds

Pacific Northwest National Laboratory

CLH Bottenus	K9-89
M Dembowski	K8-96
MS Fountain	K9-89
GJ Lumetta	P7-25
CI Pearce	P7-54
RA Peterson	P7-22
MMV Snyder	P7-54

* All distribution will be made electronically.

Pacific Northwest
NATIONAL LABORATORY

U.S. DEPARTMENT OF
ENERGY

Proudly Operated by **Battelle** *Since 1965*

902 Battelle Boulevard
P.O. Box 999
Richland, WA 99352
1-888-375-PNNL (7665)

www.pnnl.gov