Role of Aluminum Dimer and Carbonate in the Aluminum Solubility for Hanford Wastes

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Abstract

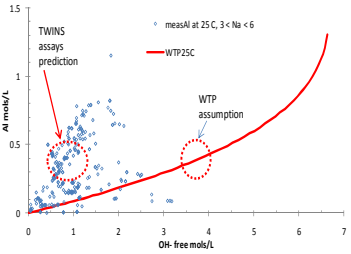
The chemistry of concentrated sodium aluminate solutions stored in many of the large, underground storage tanks containing high-level waste (HLW) at the Hanford and Savannah River Nuclear Reservations is an area of continued research interest. The total amount of aluminum observed in a large number of Hanford Tank Waste Information System (TWINS) assays is frequently above the WTP criteria (Figure 1). In this study, we examined a suite of tank waste surrogate solutions based on actual waste assays. All of the solutions were supersaturated relative to the WTP solubility curve. We employed Raman and FTIR spectroscopy in order to determine aluminum speciation as a function of time (0 to 127 days) and temperature (25, 45 and 85 C). In addition, macroscopic properties (solution density and water activities) of these solutions were also determined.

Objectives

1. Determine the extent of the aluminate dimer formation in tank waste surrogate solutions
2. Examine the role of carbonate as a potential 'stabilizing' constituent
3. Identify / characterize precipitates using Raman, FTIR and XRD
4. Explore the geochemical conditions where the mineral dawsonite forms

Introduction

- Understanding the nature of both solid and solution aluminum oxy-hydroxides is important for waste storage and pretreatment in order to prevent unwanted precipitation.
- Due to the complexity of waste, little is known about the speciation of Al.
- The Waste Treatment Plant aluminum solubility criteria (shown below by the solid red line) is based on thermodynamic equilibrium models of aluminum solubility where gibbsite, bayerite and boehmite are solid phases controlling solubility.
- The total amount of aluminum observed in a large number of Hanford Tank Waste Information System (TWINS) assays is frequently above the WTP criteria.



Possible explanations to account for this discrepancy between TWINS assays and the WTP solubility curve include:
(1) Some other solid phase may be controlling aluminum solubility
(2) Slow kinetics / equilibrium has not been achieved
(3) Some other constituent present in Hanford waste (e.g., CO_3^{2-}, NO_3^{1-}, NO_2^{1-}, PO_4^{3-}, SO_4^{2-}, oxalate, citrate and EDTA) may interfere with aluminum precipitation observed in clean systems

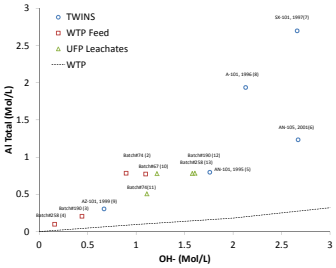
Solid Phase Characterization

Approach

- The focus of the current effort was on studying aluminum solution and solid phase chemistry in tank waste surrogate solutions based on actual waste
- Waste solutions were modeled after WTP feed solutions, TWINS, and UFP leachates (see Table 1 below):

WTP feed	Na+	Al(OH)4-	free OH-	CO3-2	NO2-	NO3-	PO4-3	SO4-2	TOC
Batch#67	6.405	0.809	0.925	0.391	1.533	1.652	0.097	0.061	0.218
Batch#74	9.03	0.81	1.15	0.81	2.01	3.33	0.020	0.057	0.22
Batch#190	4.64	0.21	0.45	0.16	0.76	2.48	0.064	0.030	0.016
Batch#258	3.53	0.10	0.16	0.17	0.50	1.50	0.23	3.53	0.026
twins									
AN-101, 1995	5.38	0.82	1.81	0.21	1.05	1.56	0.015	0.016	0.31
AN-105, 2001	10.11	1.32	2.86	0.24	2.95	3.37	0.032	0.016	0.22
SX-101, 1997	10.34	2.91	2.87	0.15	1.62	1.74	0.027	0.015	0.027
A-101, 1996	10.7	2.11	2.32	0.38	3.44	2.66	0.033	0.014	0.30
AZ-101, 1999x	5.00	0.31	0.68	0.56	1.54	1.16	0.028	0.26	0.030
UFP leachates									
Batch#67	5.67	0.80	1.25	0.42	0.82	1.65	0.058	0.034	0.12
Batch#74	6.00	0.52	1.14	0.50	1.23	2.06	0.012	0.035	0.14
Batch#190	5.88	0.80	1.64	0.42	0.54	1.80	0.046	0.022	0.011
Batch#258	5.42	0.80	1.62	0.42	0.50	1.58	0.032	0.043	0.034

- A set of 13 tank waste surrogate solutions based on the table above were prepared.
- The composition of these solutions is shown below in Figure 2 which plots the amount of aluminum in solution against the free OH^- concentration.
- All of these solutions are above the WTP aluminum solubility curve derived from gibbsite – H_2O – NaOH (Apps and Neil, 1990; Wesolowski, 1992).



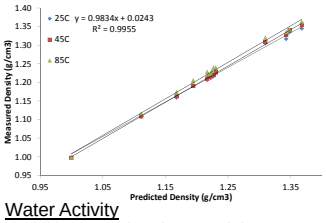
Experimental

- 13 tank waste surrogate solutions (Table 1)
- Macroscopic properties of each solution were measured (density and water activity).
- Solutions were equilibrated at three temperatures (25, 45 and 85 C) for 4 months.
- Raman and FTIR spectra were collected
- Aluminum speciation determined
- Precipitated solids characterized using Raman, FTIR and XRD
- Constant pH precipitation experiments were conducted to identify the solid phases that precipitate at lower pH values.

Macroscopic Properties

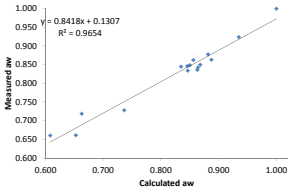
Density

Good agreement was obtained between the measured densities and the predicted densities as shown below.



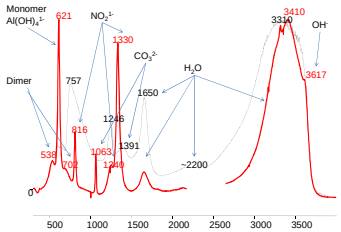
Water Activity

The activity of water above the 25 ºC solutions was measured at room temperature between days 35 and 40 after solution preparation.
The slope between the measured versus predicted values was 0.84 indicating that the measured water activities were greater than what was predicted.



Molecular Properties

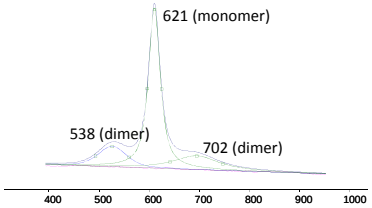
Why use spectroscopy to study tank waste?



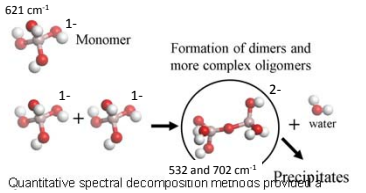
Raman spectrum of Solution 7 (modeled after SX-101, 1997 assay) shown above in red. The corresponding FTIR spectrum is represented by the dashed line. All of the solution constituents with the exception of Na^+ have 'Raman signatures' including the speciation of aluminate monomer / dimer. FTIR spectroscopy is less diagnostic here but useful because it is sensitive to the activity of water.

Speciation of aluminum: the aluminate dimer

The aluminate monomer and dimer bands are shown below (Solution 7)

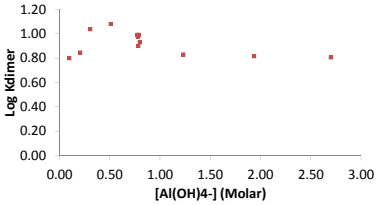


- The formation of the dimeric species are shown below.
- Raman spectra are characterized by a strong band at 621 cm^{-1} that has been assigned as the symmetric Al-O stretching mode of the monomer $Al(OH)_4^-$).
- With increasing Al concentration, two Raman bands appear and increase in intensity at 538 and 702 cm^{-1} at the expense of the 621 cm^{-1} band.

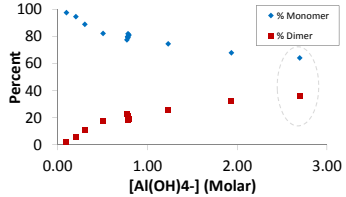


Quantitative spectral decomposition methods provided a means to determine the apparent dimer formation constant, K', defined as:

$$K' = \frac{[(Al(OH)_4)_2^{2-}][H_2O]}{[Al(OH)_4^-]^2}$$

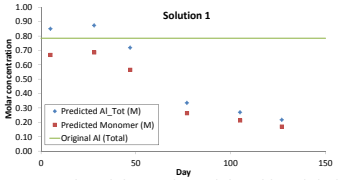


Aluminum distribution coefficient shown below. For the highest solution examined in this study (Solution 7), for example, approximately 40% of the aluminum is present in the dimeric form.

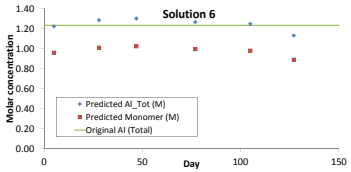


Stability of Aluminate Solutions

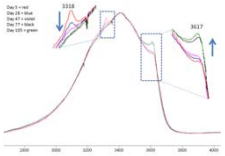
- Raman-based method used to determine the total aluminum concentration and speciation for each of the 13 solutions as a function of time and temperature.
- All of the solutions were supersaturated with respect to the WTP solubility curve.
- Some of the solutions resulted in significant precipitation early on (~40 days) as shown below for Solution 1 (see Table 1).



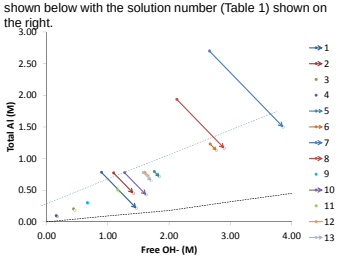
However, other solutions, such as Solution 6 (shown below) was stable over the 127 days despite the fact that its concentration of aluminate was higher than that of Solution 1 (shown above).



- When precipitation occurred, the aluminate concentration was decreased and the corresponding free OH^- concentration was increased.
- This is shown in the figure below for Solution 7 where the intensity of the free OH^- band at 3617 cm^{-1} increases upon precipitation.
- Also shown in the figure below is a band at 3318 cm^{-1} that is present as a type of 'precursor to precipitation' band.

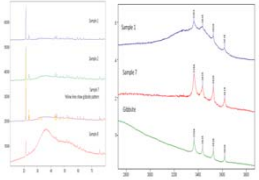


The initial and final concentrations of the solutions are shown below with the solution number (Table 1) shown on the right.



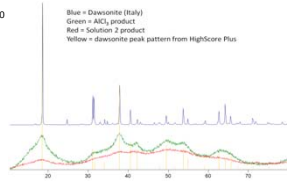
Analysis of Precipitates

XRD & Raman of the precipitates - revealed the presence of gibbsite. It was the only crystalline solid phase identified in the precipitates.



Constant pH precipitation

Dawsonite is a sodium-aluminum carbonate ($NaAl(CO_3)(OH_2)$) that has been identified in a number of Hanford tanks. Based on earlier work (Felmy 2005; Scholtz 1984) we conducted a constant pH precipitation experiment at pH 8.5 using several of the solutions in this study. We identified dawsonite using both XRD (shown below) and FTIR spectroscopy (not shown)



Next Steps

- Explore the basis of the linear relationship observed in the aging experiment which is ~ 3X to WTP curve
- Follow the solution composition and mass balance of these solutions over time using ICP and related techniques.
- Follow the morphology of the crystals during aging and in the presence of other constituents using micro-Raman, micro-FTIR and X-ray diffraction.
- Link this information to real waste (e.g., 222-S).
- Better define evaporation conditions for dawsonite precipitation. Dawsonite is a known precipitate in Hanford waste and was observed in this study. We need to identify the chemical conditions where dawsonite is likely to form.
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