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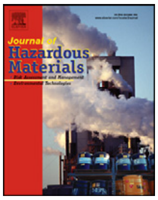

Evidence for dawsonite in Hanford high-level nuclear waste tanks

Jacob G. Reynolds*, Gary A. Cooke, Daniel L. Herting, R. Wade Warrant

Washington River Protection Solutions, LLC, A Contractor to the U.S. Department of Energy, P.O. Box 850, Richland, WA, 99352, USA

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ABSTRACT

Gibbsite [$Al(OH)_3$] and boehmite (AlOOH) have long been assumed to be the most prevalent aluminum-bearing minerals in Hanford high-level nuclear waste sludge. The present study shows that dawsonite [$NaAl(OH)_2CO_3$] is also a common aluminum-bearing phase in tanks containing high total inorganic carbon (TIC) concentrations and (relatively) low dissolved free hydroxide concentrations. Tank samples were probed for dawsonite by X-ray Diffraction (XRD), Scanning Electron Microscopy with Energy Dispersive Spectrometry (SEM-EDS) and Polarized Light Optical Microscopy. Dawsonite was conclusively identified in four of six tanks studied. In a fifth tank (AN-102), the dawsonite identification was less conclusive because it was only observed as a Na–Al bearing phase with SEM-EDS. Four of the five tank samples with dawsonite also had solid phase $Na_2CO_3{\cdot}H_2O$. The one tank without observable dawsonite (Tank C-103) had the lowest TIC content of any of the six tanks. The amount of TIC in Tank C-103 was insufficient to convert most of the aluminum to dawsonite (Al:TIC mol ratio of 20:1). The rest of the tank samples had much lower Al:TIC ratios (between 2:1 and 0.5:1) than Tank C-103. One tank (AZ-102) initially had dawsonite, but dawsonite was not observed in samples taken 15 months after NaOH was added to the tank surface. When NaOH was added to a laboratory sample of waste from Tank AZ-102, the ratio of aluminum to TIC in solution was consistent with the dissolution of dawsonite. The presence of dawsonite in these tanks is of significance because of the large amount of OH^- consumed by dawsonite dissolution, an effect confirmed with AZ-102 samples.

1. Introduction

Hanford radioactive high level waste consists of 56 million gallons left over from plutonium production. The waste is currently stored in 177 large underground steel tanks at a site near Richland, WA, U.S.A. [1]. Aluminum-bearing minerals make up a large portion of the Hanford Site nuclear waste sludge [2]. The solubility of these aluminum-bearing minerals is important to a number of current and proposed waste treatment options. The liquids of these tanks consist of concentrated aqueous solutions of NaOH, $NaNO_2$, $NaNO_3$, Na_2CO_3, Na_2SO_4, $NaAl(OH)_4$, Na_3PO_4, NaF and organic anions [3–6]. Many other less prevalent electrolytes may influence the solubility of minerals in the waste. The total sodium molarity generally ranges between 1 and 12 mol/L. The relative proportions of all electrolytes vary widely across the 177 tanks. The dominant form of aluminum in the liquid phase is the aluminate ion, $Al(OH)_4{}^-$, because of the large hydroxide concentration [3,5]. Less prevalent dissolved aluminum species are also likely present [5–7].

Gibbsite [$Al(OH)_3$] and boehmite (AlOOH) have been assumed to be the most prevalent aluminum-bearing solids in Hanford waste [2]. Boehmite is slow to dissolve and precipitate at the current tank temperatures, which are between 20 and 40 °C [8,9]. Consequently, boehmite has been assumed to play a negligible role in controlling the liquid phase concentration of aluminum in the tank waste. Boehmite likely formed at a time when the tanks were much hotter than they are currently [10,11]. Thus, most previous modelers have assumed that gibbsite solubility played the dominant role in limiting the liquid phase aluminum concentration [12–15].

Aluminum solubility influences tank corrosion control measures because aluminum dissolution and precipitation buffers the pH. Gibbsite buffers the pH through the reaction:

$$Al(OH)_{3(s)} + OH^{-1}_{(aq)} \leftrightarrow Al(OH)^{-1}_{4(aq)} \qquad (1)$$

where one mol of hydroxide is consumed per mol of aluminum dissolved. Understanding the chemistry of pH buffers, such as gibbsite, is important for determining the quantity of sodium hydroxide that must be added to raise the pH for corrosion control [16].

The current plan for stabilization and long-term storage of the Hanford tank waste calls for the majority of it to be incorporated in a glass matrix. The Hanford Waste Treatment Plant (WTP), currently under construction, will split the waste into high level and low level radionuclide fractions and manufacture from both waste

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* Corresponding author. Tel.: +1 509 373 5999.
E-mail addresses: Jacob_G_Reynolds@rl.gov, reynoldsjacob@hotmail.com (J.G. Reynolds).

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streams. Aluminum is an important constituent in the manufacture of a stable, uniform glass product [17]. Its presence increases the durability, the viscosity and the melt temperature of high-sodium glasses. Excessive aluminum concentrations in the glass can result in undesirable crystallization of aluminosilicates in the melt [17]. These can impact the uniformity and durability of the glass and cause processing problems.

The present paper documents the results of a long-term study of the mineralogy of Hanford sludges with (relatively) low dissolved hydroxide concentrations and high carbonate concentrations. In particular, this study sought to document that dawsonite [$NaAl(OH)_2CO_3$] is present in some of these tanks. The tank samples were probed for dawsonite whenever tank samples that met this criterion were available. This study was started because pH buffering experiments performed by the Hanford tank farm laboratory in the 1990s indicated that the buffering by aluminum-bearing minerals was consistent with the presence of dawsonite [18,19].

The chemical reaction for dawsonite dissolution and precipitation in caustic solutions is:

$$NaAl(OH)_2CO_{3(s)} + 2OH^{-1}_{(aq)} \leftrightarrow Al(OH)^{-1}_{4(aq)} + CO^{-2}_{3(aq)} + Na^{+1}_{aq} \quad (2)$$

As is evidenced by this reaction stoichiometry, 2 mol of dissolved hydroxide are consumed per mol of aluminum dissolved, as opposed to gibbsite where only one mol of hydroxide is consumed. The relative amount of hydroxide consumed by dawsonite and gibbsite dissolution can be seen more readily by making gibbsite the reaction product rather than aluminate, as in Eq. (3).

$$NaAl(OH)_2CO_{3(s)} + OH^{-1}_{(aq)} \leftrightarrow Al(OH)_{3(s)} + CO^{-2}_{3(aq)} + Na^{+1}_{aq} \quad (3)$$

Note that some hydroxide is consumed just to transform the dawsonite to gibbsite, at least when the pH is high enough for carbonate (rather than bicarbonate) to be a product. Thus, dawsonite dissolution lowers the pH of the solution more strongly than gibbsite dissolution. Over time, the hydroxide concentration of the Hanford tanks decreases and the carbonate concentration increases. This is because of degradation of organics [20] and CO_2 infiltration into the caustic waste from the atmosphere. The pH buffering from aluminum dissolution and precipitation must be taken into account to determine the rate of hydroxide depletion and the amount of NaOH needed for corrosion control [16]. Hanford staff use models to predict when tanks will leave the desired waste composition range for corrosion control. The minimum pH target depends on the waste composition. Nonetheless, the pH is always deemed acceptable when it is above pH 13.5. NaOH is added to the tanks that are below the waste specific pH target to raise the pH. Any NaOH that is added to the waste must subsequently be treated as waste, so the solubility of aluminum has a noted impact on the treatment costs. Given the effect of dawsonite dissolution/precipitation, dawsonite will impact the pH regardless of what pH is targeted.

2. Materials and methods

2.1. Sampling

Hanford staff maintains a model that conservatively predicts when tanks may go outside of the acceptable pH range. Such tanks are termed “hydroxide depleted”. Potentially hydroxide depleted tanks are sampled, and NaOH is added to the tanks if the sample results confirm the model prediction. The tanks investigated in the present study were all predicted to be hydroxide depleted [19]. The tanks sampled for this program were probed for dawsonite because they were thought to be the tanks most likely to contain dawsonite. All of the samples studied here had a pH between 10 and 12.5. Sludge samples were taken from Hanford tanks AN-102, AN-107, AY-101, AY-102, AZ-102, and C-103. The samples were taken and analyzed over an eight year period. Tank AZ-102 was sampled twice, once in two months and a second time 15 months after NaOH was added the supernatant liquid overlying the sludge. The samples were taken by push mode core method. The core segment samples were stored in a cast-iron holder for shielding prior to being transferred to the hot cell at the 222-S Laboratory at the Hanford site. Hot-cell temperatures are typically around 30 °C. In the hot-cells, the core samples were extruded and segmented, and sludge samples were composited. Sub-samples of the sludges were digested in water and acid to determine the concentration of major anions and metals in the samples. To dissolve the sample in acid, a sample is immersed in a 50 weight-% HNO_3 and water mixture, refluxed at 90 °C, and then cooled. Subsequently, 5 mL of concentrated HNO_3 is added per gram of sludge, and this addition is repeated until no brown fumes are given off by the sample. Next, 30% hydrogen peroxide is added until effervescence subsides.

2.2. Mineralogical analysis

The sample preparation for X-ray diffraction analysis must consist of a fine-grained, dry, aggregate of solid particulate. For many tank samples, consisting of highly soluble salts in contact with solutions that are saturated with dissolved solids, the separation of solid from aqueous phases was difficult and likely remained incomplete. Simply drying the original sample will result in the dilution of the original solids with precipitates. Thus, liquids were removed from the solids by vacuum filtration. The samples were then placed in an agate mortar and pestle and ground to a fine crystal size. Each sample was then transferred to a shallow depression in a zero background quartz sample holder, air dried, and a drop of collodion binder was used to fix the sample in place. The sample holder was then transferred to the diffraction instrument for analysis.

The Rigaku Miniflex X-ray diffractometer used in this study was operated with a tube voltage of 40 kilovolts (kv) and filament current of 30 mA. Data were collected from 5° 2θ to >60° with a step size of 0.02° 2θ and from 2 h to overnight runs using copper radiation. Data were interpreted with the aid of the Jade search/match program (Materials Data, Inc) using the International Centre for Diffraction Data (PDF-4).

Optical microscopy analysis requires the sample particulate matter be dispersed in a medium with a refractive index only moderately different from that of the particulate. This minimizes the contrast between particles and the surrounding medium. The native Hanford waste supernatant liquids meet this criterion for the salt phases evaluated here. Refractive index for the supernatant liquids used here were not measured, but the author’s experience is that Hanford liquids have refractive indexes around 1.38, whereas most of the salt crystals in Hanford waste have a refractive index between 1.3 and 1.55. Using the native supernatant liquid as the dispersing medium eliminates any precipitation/dissolution artifacts that could occur if the particulate is suspended in a different medium. The mineral standards [21] and waste samples were prepared for optical microscopy analysis by suspending the particulate in the supernatant liquid using a plastic disposable pipette. The pipette tip was touched to a glass slide, allowing a portion of the drop to be transferred to the glass surface, and a cover slip was pressed onto the surface to disperse the particulate. The optical microscopy analysis was conducted using a Nikon Eclipse E600 polarizing light microscope. Optical microscopy analysis could not be performed on the AZ-102 samples because of excessive radioactivity. A more detailed description of the optical microscopy method is found in reference [21].

The Scanning Electron Microscopy (SEM) analysis was performed by vacuum filtering a portion (about 0.2 mL) of the sludge onto a 0.4 μm pore-sized polycarbonate filter and then transferring the particulate to an adhesive carbon tab attached to an aluminum