



Evidence for dawsonite in Hanford high-level nuclear waste tanks

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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)₂CO₃] 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 Na₂CO₃·H₂O. 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.

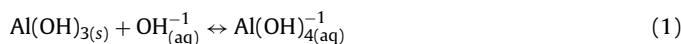
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1. Introduction

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, NaNO₂, NaNO₃, Na₂CO₃, Na₂SO₄, NaAl(OH)₄, Na₃PO₄, 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:



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

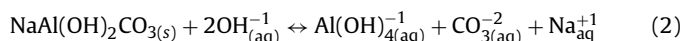
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streams. Aluminum is an important constituent in the manufacture of a stable, uniform glass product [17]. Its presence increases the durability, the viscosity and the melt temperature of high-sodium glasses. Excessive aluminum concentrations in the 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 [$\text{NaAl}(\text{OH})_2\text{CO}_3$] 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:



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).



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

Table 1
Weight data for AZ-102 caustic demand tests.

Cone label	A	B	C	D	E	F	G	H
Sludge weight (grams)	9.944	8.358	8.633	8.296	9.772	9.218	7.786	1.574
Supernatant liquid weight (grams)	6.690	7.197	6.921	7.058	7.094	6.589	7.187	11.715
Grams of 19.4 M NaOH added	0	0.295	0.397	0.688	0.912	0.975	1.306	0

SEM stub. The specimen preparation was then coated with conductive carbon via evaporative deposition. SEM analysis took place on an ASPEX PSEM (Model II) equipped with a Noran Light Element Energy Dispersive Spectrometer (EDS). The instrument was operated at an accelerating voltage of 20 Kv, and samples were examined at a working distance of 15–20 mm.

2.3. Caustic demand test for AZ-102

During the course of this eight year investigation, the Hanford tank farm personnel performed “Caustic Demand” tests on some waste samples. Caustic demand tests are used to determine how much NaOH must be added to Hanford sludge to bring the dissolved hydroxide concentration up to a targeted value. Given those tests were for production purposes rather than research purposes; they did not collect all of the data that a researcher would be interested in. Nonetheless, the data for the first sample from Tank AZ-102 is used here opportunistically because what is available is still useful. The AZ-102 sample does not contain a lot of phosphorus or dissolved organics to complicate the interpretation of the buffering data.

The AZ-102 caustic demand tests were performed in 15 mL centrifuged tubes. Each cone received six mL of sludge and supernatant mixture. The exact mass of sludge and supernatant liquid is shown in Table 1, determined by weight. NaOH (19.4 mol) was added to each tube, and the added weights are shown in Table 1. Each tube was mixed briefly in a vortex mixer, and then placed on an end-over-end tumbler for four days. Subsequently, the samples were centrifuged and liquid decanted. In the liquid phase, total aluminum was monitored by inductively coupled plasma atomic emissions spectroscopy (ICP-AES). Also, total inorganic carbon is measured by persulfate oxidation, and hydroxide was measured by a barium precipitation/acid titration technique.

3. Results and discussion

Dawsonite was suspected in samples from five of six tanks (see Table 2). Dawsonite was observed by XRD in four tanks. A sodium–aluminum bearing phase in the EDS spectra in the fifth tank (AN-102) is presumed to be dawsonite (see later discussion). No evidence of dawsonite was found in the sixth tank (C-103), but gibbsite was identified by XRD. Some tank samples that contained dawsonite also contained gibbsite or boehmite. Table 2 provides an overview of all of the minerals identified in these samples in this study. Below, the dawsonite identification is discussed in more detail. The XRD patterns can be found in the electronic appendix. In all cases, there were some minor reflections in the XRD spectrum that could not be identified.

The two AN farm tanks (AN-102, AN-107) have similar waste types and waste history. Therefore, they have similar waste mineralogy. They both contain high-chelate bearing waste known as complexed concentrate. Solid sodium oxalate ($\text{Na}_2\text{C}_2\text{O}_4$) was found in both tanks (Table 2). Oxalate, a breakdown product of more complex organics in the waste [20], is frequently observed in the solid phase in nuclear waste because of low solubility [22,23]. Being in large abundance, sodium oxalate was observed by XRD, SEM-EDS, and optical microscopy. Sodium fluoride phosphate ($\text{Na}_7\text{F}(\text{PO}_4)_2 \cdot 19\text{H}_2\text{O}$), was seen by optical microscopy in both tanks. There were few $\text{Na}_7\text{F}(\text{PO}_4)_2 \cdot 19\text{H}_2\text{O}$ particles in the samples from either tank, but the particles were large (more than 40 μm in diameter), making them easy to spot with the optical microscopy (data not shown). Both tank samples contained $\text{Na}_2\text{CO}_3 \cdot \text{H}_2\text{O}$, as observed with all three mineralogical analysis methods.

Dawsonite was the major difference between the two AN tanks. Dawsonite was clearly a major phase in the AN-107 samples, but not AN-102 samples. There was not sufficient dawsonite in Tank AN-102 to be observed by XRD. In Tank AN-102, there were some small particles that had sodium and aluminum, as observed by SEM-EDS on carbon coated samples (Fig. 1). Those particles, however, did not always have the same Na:Al mole ratio as dawsonite, being short sodium in some cases. Thus, the identification of dawsonite in tank AN-102 is not conclusive. Nonetheless, this sodium–aluminum bearing phase is likely dawsonite, given the similar waste chemistry to AN-107, and the fact that there are few other phases that contain only these two elements observable by EDS. True quantitative EDS analysis of these dawsonites is difficult because the particles are irregular shaped. The spot size employed varied from particle to particle depending on the particle size. Consequently the angle between the beam, particle, and detector vary from particle to particle. These factors may influence the relative intensity of characteristic X-rays.

Tanks AY-101 and AY-102 have similar waste types (a mixture of B plant high-level and low-level waste), and nearly identical mineralogy (Table 2). The mineralogy of both tanks was dominated by hematite (Fe_2O_3), $\text{Na}_2\text{CO}_3 \cdot \text{H}_2\text{O}$, and dawsonite. Dawsonite was the dominant aluminum-bearing mineral in both tanks, with a small amount of sodium aluminosilicates observed by SEM. One difference between the tanks, however, was the particle size and shape of the dawsonite. Dawsonite was too small to be identified by optical microscopy in Tank AY-102, but could easily be characterized by optical microscopy in Tank AY-101. Fig. 2 shows the SEM image of dawsonite from AY-101, and Fig. 3 shows the SEM image of dawsonite in AY-102. The dawsonite in AY-101 was typically between 10 and 25 μm in diameter (Fig. 2) whereas the dawsonite in AY-102 was typically acicular needles of 10 μm in length or less and 1 μm wide. Dawsonite was also identified by XRD in both tanks

Table 2
Minerals identified in the Hanford waste samples.

Tank	Dawsonite identified?	Other aluminum minerals	Other minerals
AN-102	Tentative	Boehmite, as well as an aluminosilicate	$\text{Na}_2\text{CO}_3 \cdot \text{H}_2\text{O}$, $\text{Na}_2\text{C}_2\text{O}_4$, $\text{Na}_7\text{F}(\text{PO}_4)_2 \cdot 19\text{H}_2\text{O}$
AN-107	Yes	None observed	$\text{Na}_2\text{CO}_3 \cdot \text{H}_2\text{O}$, $\text{Na}_2\text{C}_2\text{O}_4$, $\text{Na}_7\text{F}(\text{PO}_4)_2 \cdot 19\text{H}_2\text{O}$
AY-101	Yes	Trace amounts of aluminosilicates	$\text{Na}_2\text{CO}_3 \cdot \text{H}_2\text{O}$, Hematite, A particle rich in sodium and uranium
AY-102	Yes	Trace amounts of aluminosilicates	$\text{Na}_2\text{CO}_3 \cdot \text{H}_2\text{O}$, Hematite, Fe–Mn bearing solids
AZ-102	Yes in year 2002, no in year 2003	Gibbsite, Boehmite	Hematite, disodium diuranate
C-103	No	Gibbsite, a sodium aluminosilicate	Hematite, a Hg–Ag association, a ruthenium rich particle

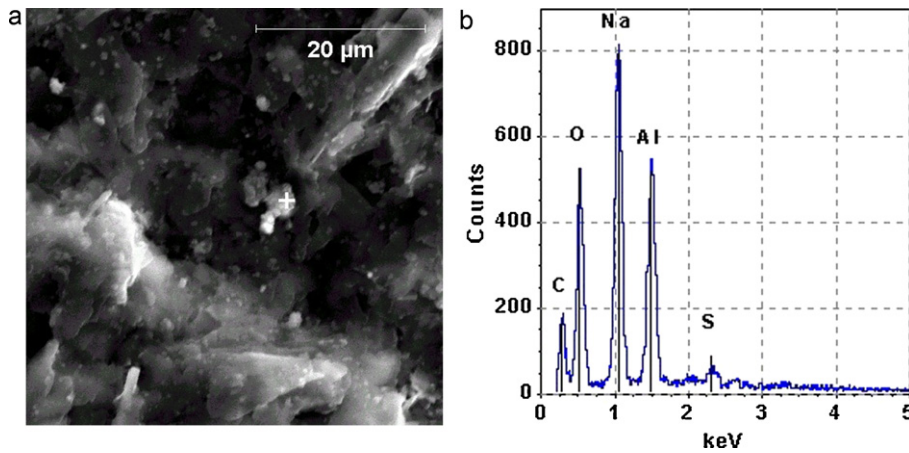


Fig. 1. (a) SEM image of suspected dawsonite particle in Tank AN-102. (b) EDS spectrum for suspected dawsonite particle in Tank AN-102.

(Fig. 4a and b). Krupka et al. [24] have previously reported the presence of dawsonite in Tank AY-101. They [24] also found dawsonite in samples from Tank C-106, and the C-106 waste has since been sluiced into Tank AY-101.

Solid NaNO_2 and NaNO_3 were observed in the AY-101 XRD spectrum, but not observed by optical microscopy. The optical microscopy samples were not dried prior to analysis whereas XRD samples are dried. Both NaNO_2 and NaNO_3 are much too soluble to be present at the native 5.5 M Na^+ concentration of this waste [25]. Thus, the NaNO_2 and NaNO_3 solids observed by XRD are likely artifacts of incomplete liquid removal prior to sample drying. The dawsonite in AY-101 could not have been a precipitation artifact of the sample drying because the quantity of aluminum in the liquid phase (0.86 g/L) was too small to account for the large amount of aluminum in the sludge (83 g/kg), given that dawsonite represents virtually all of the aluminum in the sludge.

Dawsonite was not observed in Tank C-103 by any of the three mineralogical methods used in this study. The dominant minerals found in the C-103 sludge were gibbsite and hematite (Table 2). Besides gibbsite, the only other aluminum-bearing phase in the Tank C-103 sample was trace amounts of a sodium aluminosilicate observed by SEM-EDS. The exact identity of this sodium aluminosilicate could not be determined, but it did have the “ball-of-twine” morphology that is common of nitrate cancrinite [26,27].

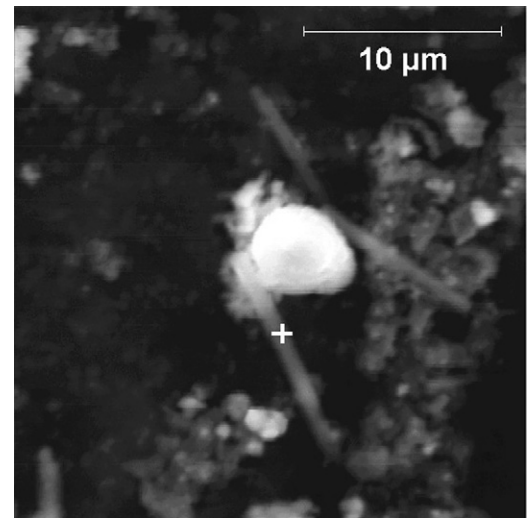


Fig. 3. SEM image of dawsonite in Tank AY-102, where dawsonite is the acicular mineral.

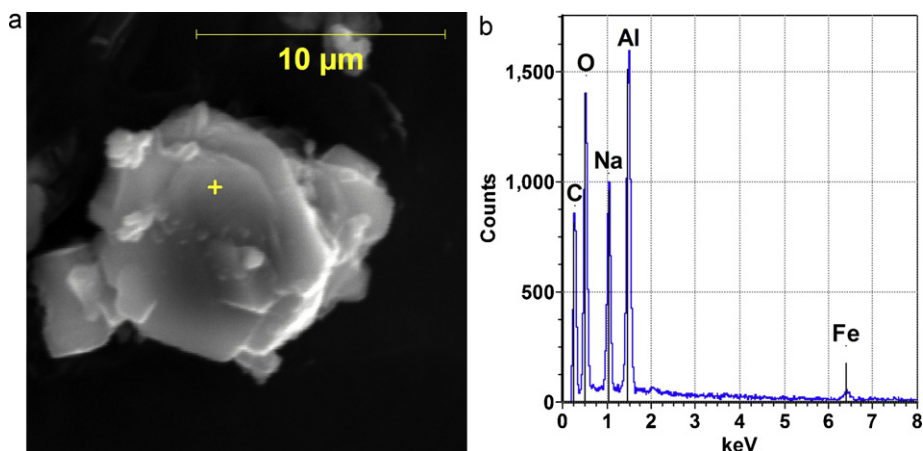


Fig. 2. (a) SEM image of dawsonite in Tank AY-101. (b) EDS spectra for the mineral in (a).

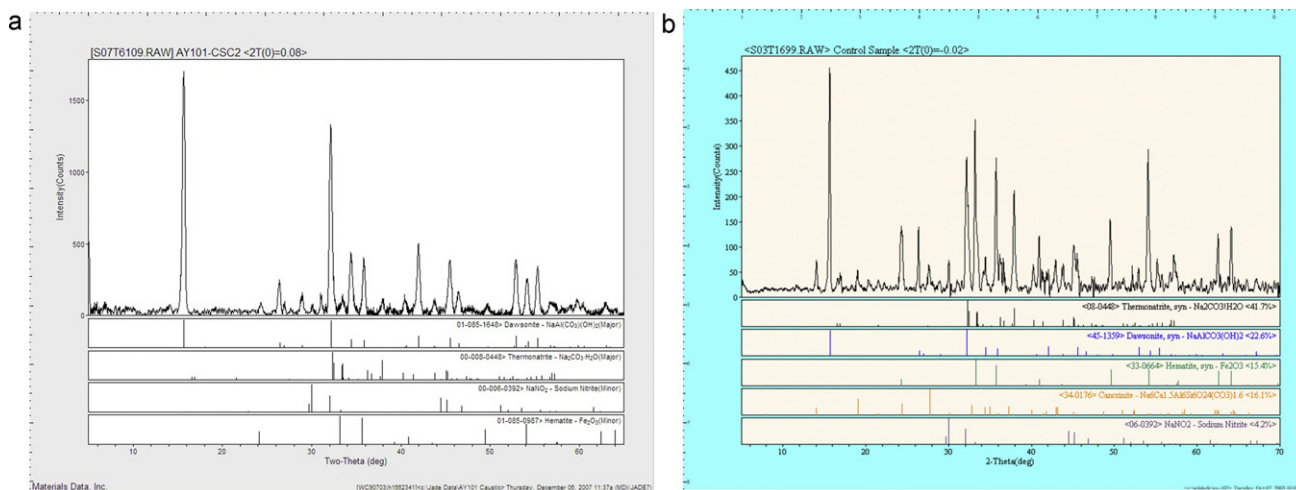


Fig. 4. (a) XRD spectrum for sample from Tank AY-101. (b) XRD spectrum for sample from Tank AY-102.

Table 3

Aluminum to silica and aluminum to total inorganic carbon mole ratios in the sludge samples.

Tank	Al:Si mol ratio	Al:TIC mole ratio
AY-101	37.5	1.0
AY-102	44.0	1.9
AZ-102 (first sample)	15.8	1.8
AZ-102 (second sample)	31.0	1.3
AN-102	68.2	0.5
AN-107	172.3	0.6
C-103	25.9	20.3

Gibbsite dominates the aluminum mineralogy of Tank C-103 instead of dawsonite because of the limited availability of inorganic carbon in the tank. Table 3 displays the mole ratio of aluminum to inorganic carbon in the tanks studied here. The five tank samples suspected to have dawsonite had Al:TIC mole ratios between 0.5 and 2. Tank C-103, however, contained more than 20 mol of aluminum per mole of inorganic carbon. Even if all of the inorganic carbon in the Tank C-103 sample had reacted with aluminum to form dawsonite, dawsonite would account for less than 5% of the aluminum. Therefore, the absence of observable dawsonite in Tank C-103 can be explained by insufficient quantities of inorganic carbon available to incorporate large amounts of aluminum into dawsonite.

Tank AZ-102 is interesting because the samples were taken after sodium hydroxide was added to the overlying tank supernatant liquid. The tank had a relatively shallow sludge layer (96 cm) at the time the samples were taken. Thirty four thousand liters of 50 weight% NaOH was added to the tank in May of year 2002. Two and 15 months later, the core samples probed for dawsonite here were taken from the tank. Dawsonite was found in the first core sample but not the second (Table 2), whereas gibbsite and boehmite were found in both core samples. There are two possible explanations for the presence of dawsonite in the first core sample but not the second. One possibility is that the hydroxide diffused into the sludge between 2 and 15 months and dissolved the dawsonite (Eq. (2)). Alternatively, there could be heterogeneity in the tank with respect to dawsonite.

The caustic demand tests (TIC, Al, and hydroxide were measured as a function of NaOH added) were also consistent with dawsonite presence in the first AZ-102 sludge sample. Given the 1:1 aluminum to carbonate molar ratio in dawsonite, the aluminum to inorganic carbon mole ratio in solution after NaOH addition can be used as an indicator of dawsonite dissolution; provided there

are no other significant sources or sinks for aluminum and TIC. If dawsonite dissolution were the only source of TIC and aluminum dissolved during NaOH addition, a plot of TIC versus aluminum molarity would produce a line with a slope of one. The intercept of this line would not be expected to be one because some TIC was in solution prior to the addition of NaOH. The molarity of dissolved inorganic carbon in solution as a function of aluminum molarity at different NaOH addition levels is shown in Fig. 5. Fig. 5 shows that the amount of aluminum dissolved when the NaOH was added is roughly equal to the amount of TIC dissolved. This is indicated by the data points laying near the 1:1 TIC to aluminum mole ratio line shown on the figure. Hence, the aluminum and TIC dissolution data from the AZ-102 caustic demand test are consistent with the presence of dawsonite in the sample. At the highest NaOH addition, the concentration of TIC in the liquid phase significantly decreases, presumably because of sodium carbonate precipitation. The single data point significantly off of the 1:1 line in Fig. 5 is the data point presumably affected by sodium carbonate precipitation. The intercept of this line does not equal zero because there was some inorganic carbon in solution before NaOH addition.

Hydroxide consumption by the AZ-102 sludge during caustic demand tests appeared to be controlled by dawsonite dissolution. The amount of free hydroxide consumed is defined as the difference between the free hydroxide measured in solution and the amount that would have been present had none been consumed. Fig. 6

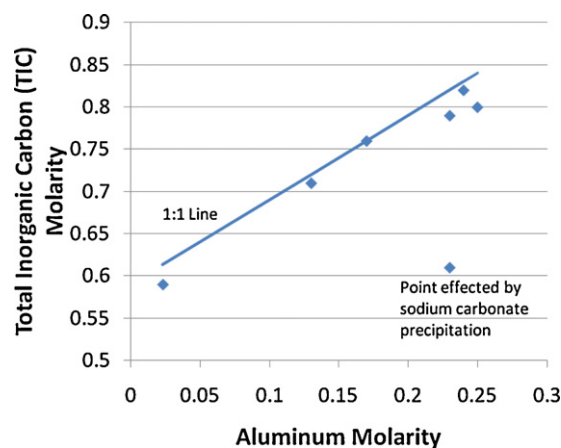


Fig. 5. TIC versus Al in Tank AZ-102 caustic demand tests. The 1:1 line represents one mole of TIC dissolved per mole of aluminum dissolved upon NaOH addition.

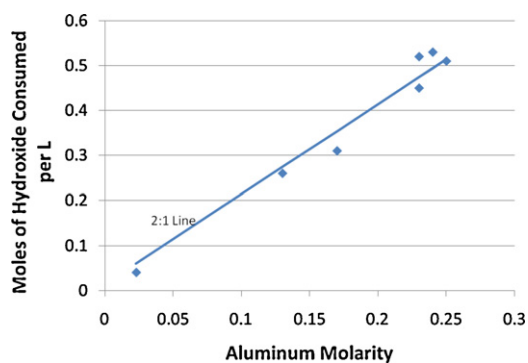


Fig. 6. Moles of hydroxide consumed as a function of aluminum molarity in AZ-102 caustic demand tests.

shows the quantity of hydroxide consumed by the sludge as a function of the concentration of aluminum dissolved into solution. If dawsonite dissolution is controlling the hydroxide concentration in the sludge, two moles of hydroxide would be consumed per mole of aluminum dissolved, per Eq. (2). This is represented by the 2:1 line in Fig. 6. As can be seen from Fig. 6, the points lay near this line, consistent with dawsonite consumption of the hydroxide. The actual slope of a line fitted to the data is 2.2 mol of hydroxide consumed per mole of aluminum dissolved. The extra 0.2 mol of hydroxide consumption may be due to the conversion of bicarbonate in the liquid phase to carbonate.

Goldbery and Loughnan [28] hypothesized that dawsonite would form in environments with high sodium and (bi)carbonate concentrations but low in silicates. These environments are consistent with most Hanford nuclear waste, and particularly relevant to the wastes investigated in this study. Yao et al. [29] have shown that even boehmite can be converted to dawsonite at low temperatures if carbonate is added to the system. The sodium molarity of Hanford waste is typically between one and 12 mol and the carbonate concentration is also usually very high [3,6], typically above 0.1 molar. In this study, four of the five tanks containing dawsonite also had solid-phase $\text{Na}_2\text{CO}_3 \cdot \text{H}_2\text{O}$, indicating ample carbonate was present in the system. The liquid phase TIC concentrations of the five tank samples containing dawsonite ranged from 0.59 mol/L to 1.60 mol/L. Tank C-103, which did not have dawsonite, had a TIC concentration of 0.58 mol/L and no observable solid-phase sodium carbonate. Thus, C-103 had the least (bi)carbonate of any of the six tanks studied here.

Goldbery and Loughnan [28] hypothesized that aluminosilicates would form instead of dawsonite in high silica environments. There is documented evidence that silica reacts with aluminate in solution to precipitate sodium aluminosilicates in Hanford waste [26,27,30]. Sodium aluminosilicates were found in several of the tanks in this study (Table 2). In all of these tank samples studied here, however, the amount of silica in the sludges was much less than the quantity of aluminum (Al:Si mole ratios between 16 and 173, see Table 3). Consequently, the quantity of silica available was too small to incorporate large amounts of aluminum into aluminosilicates. Thus, there was sufficient aluminum available for dawsonite formation. These results are consistent with Goldbery and Loughnan's [28] conclusion that dawsonite forms in low silica environments. Nonetheless, there may be some instances where dawsonite precipitates more rapidly than aluminosilicates. Thompson et al. [31] found a substantial amount of aluminum in a carbonate extract from silica-bearing soils contaminated by Hanford waste. They did not identify the aluminum-carbonate phase and their soil samples. Nonetheless, dawsonite could be a candidate for this carbonate form of aluminum found by Thompson et al.

[31], given that dawsonite is reported in tank waste in the present study.

4. Conclusion

This study concludes that dawsonite is a common aluminum-bearing phase in Hanford tank waste samples that were specifically selected for being (relatively) low in dissolved hydroxide and high in inorganic carbon. Dawsonite was identified in four of six tanks and is possibly present in a fifth tank. These results are consistent with Goldbery and Loughnan's [28] hypothesis that dawsonite will form in high sodium carbonate environments that have little silica. The amount of silicon in the waste was too small to convert much aluminum to aluminosilicates, leaving aluminum available to form dawsonite and other minerals. Most of the tanks with dawsonite also contained $\text{Na}_2\text{CO}_3 \cdot \text{H}_2\text{O}$. The tank without evidence of dawsonite (Tank C-103), had the lowest inorganic carbon concentration of the samples evaluated. Tank C-103 did not have enough (bi)carbonate to convert an appreciable amount of aluminum to dawsonite. Other aluminum-bearing solids in the samples included gibbsite, boehmite, and trace amounts of aluminosilicates.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jhazmat.2012.01.018.

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