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Precipitation and Deposition of Aluminum-Containing Phases in Tank Wastes DE-FG07-98ER14929

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Summary

Aluminum-containing phases compose the bulk of solids precipitating during the processing of radioactive tank wastes.^{1,2} Processes designed to minimize the volume of high-level waste through conversion to glassy phases require transporting waste solutions near-saturated with aluminum-containing species from holding tank to processing center. The uncontrolled precipitation within transfer lines results in clogged pipes and lines and fouled ion exchangers, with the potential to shut down processing operations.² The principal focus of our research was to maintain the fluidity of aluminum- or silicon-containing suspensions and solutions during transport, whether by preventing particle formation, stabilizing colloidal particles in suspension, or by combining partial dissolution with particle stabilization. We have found that all of these can be effected in aluminum-containing solutions using the simple organic, citric acid. Silicon-containing solutions were found to be less tractable, but we have strong indications that chemistries similar to the citric acid/aluminum suspensions can be effective in maintaining silicon suspensions at high alkalinities.

In the first phase of our study,³ we focused on the use of simple organics to raise the solubility of aluminum oxyhydroxides in high alkaline aqueous solvents. In a limited survey of common organic acids, we determined that citric acid had the highest potential to achieve our goal. However, our subsequent investigation revealed that the citric acid appeared to play two roles in the solutions: first, raising the concentration of aluminum in highly alkaline solutions by breaking up or inhibiting “seed” polycations and thereby delaying the nucleation and growth of particles; and second, stabilizing nanometer-sized particles in suspension when nucleation did occur. The second phase of our work involved the solvation of silicon, again in solutions of high alkalinity. Here, the use of polyols was determined to be effective in maintaining silicon-containing particles under high pH conditions but at smaller size with respect to standard suspensions of silicon-containing particles.

Aluminum in Alkaline Solution

We began with control solutions of aluminum-containing species under near-saturated conditions, determined by varying the OH/Al ratio (molar), with no citric acid added. Based on literature values, near-saturation was achieved in aqueous solutions composed of NaOH (aq) and AlCl₃ (aq) mixed to attain OH/Al ratios ~2.47 (mol/mol), a condition under which the polycation Al₁₃O₄(OH)₂₄(H₂O)⁷⁺ is stable. Increasing the OH/Al ratio beyond 2.47 generated aluminum-containing particles whose persistence in suspension was determined by the solution conditions. It was thought that the large 13-aluminum polycation would act as a seed for the nucleation and growth of larger particles in suspension; its presence at near-saturation presaged nucleation and growth of insoluble particles. We have determined that the polycation is absent in solutions containing citric acid and particle precipitation is thereby delayed to higher hydrolysis levels (i.e., higher OH/Al ratios).

The progressive effect of adding NaOH (aq) to solutions of AlCl₃ (aq) is shown in Fig. 1. photon correlation spectroscopy (PCS)⁴ measurements were made initially on solutions in which

the amount of added NaOH resulted in a solution of OH/Al ratio of 2.47. The principal limitation in the use of PCS in solutions of this type was low particle content (<0.2% by volume) necessary to avoid extensive diffuse reflection within the suspension. As a result, the OH/Al ratio in solution was the variable determining the formation and stability of particles. Studies on simulated tank wastes near saturation and under basic conditions found that the solubility of aluminum first increased and then decreased with increasing hydroxide concentrations.² The kinetics of both precipitation and dissolution of Al-containing phases were shown to depend on the nature and solubility of the aluminum-containing species present in the system. In the determination of overall aluminum solubility under conditions of near saturation and high pH, several soluble monomeric and polymeric species were found to be present in solution.¹ The prevalent form of the cation in solution of increasing pH follows the series $\text{Al}(\text{H}_2\text{O})_6^{3+}$, $\text{Al}(\text{OH})(\text{H}_2\text{O})_5^{2+}$, $\text{Al}(\text{OH})_2(\text{H}_2\text{O})_4^{+}$, $\text{Al}_{13}\text{O}_4(\text{OH})_{24}(\text{H}_2\text{O})^{7+}$, and $\text{Al}(\text{OH})_4^{-}$.¹

As seen in Fig. 1, particles quickly formed upon adding NaOH (aq) due to the transient high and localized OH^- concentration at the addition site. Depending on the overall OH/Al ratio, particle sizes were observed to decrease quickly, falling below the detection limits (~3nm diameter) of the PCS instrument in solutions where $\text{OH/Al} < 2.6$. The time necessary for the particles to disappear depended on the overall OH/Al ratio. The behavior of sequential additions of NaOH (aq) to solutions of AlCl_3 (aq) (Fig. 1) repeated this initial behavior. The first aliquot raised the OH/Al ratio in solution to 2.469, forming particles that disappeared from suspension in less than an hour following addition. The next addition of NaOH (aq) raised the OH/Al ratio to 2.535 and again resulted in the formation of transient particles. The subsequent behavior of these particles was distinguished only by a longer time needed to shrink below the detection limit, more than 90 min. Solutions of similar composition (OH/Al set to 2.47 and 2.54 respectively) remained free of detectable particles for long periods when stored at room temperature and sealed against solvent loss.

Three mechanisms are suggested by the above observations: first, that the initial large particles were soluble under the solution conditions and so quickly dissolved. Alternatively, large aggregates of small clusters or primary particles formed quickly, then fragmented into smaller particles under the action of the OH^- ions in solution, particles that were smaller than the detection limit of the PCS instrumentation. A third mechanism combines fragmentation with dissolution: the fragmentation into smaller particles or clusters increases surface area and thereby favors dissolution, which may or may not be complete. No distinction could be made between complete dissolution or aggregate fragmentation using PCS measurements.

The third and final addition of NaOH (aq) brought the overall solution composition to OH/Al = 2.600 (Fig. 1). After the characteristic rapid reduction in diameter, detectable particles (~30 nm diameter) remained in suspension for several weeks, showing no appreciable change in the measured diameter over that time. Subsequent additions of NaOH (pushing OH/Al over 2.6)

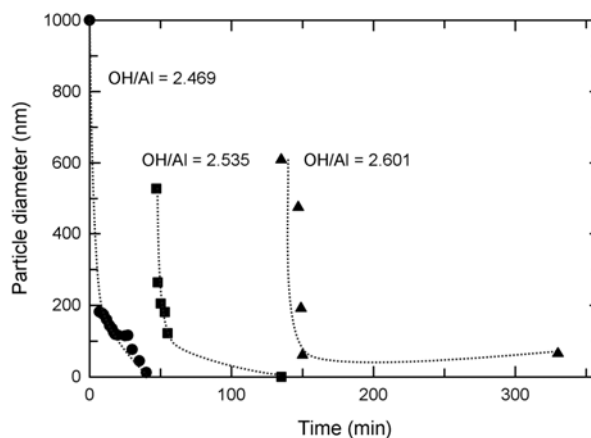


Figure 1: Successive additions of NaOH (aq) result in a standard profile: large particles form quickly, then shrink. At sufficiently high OH/Al ratios (2.601 in the above chart), particles do not completely disappear and stable suspensions are formed.

resulted in rapid aggregation and precipitation from suspension.

^{27}Al nmr measurements on similar solutions clearly show the formation of the polycation $\text{Al}_{13}\text{O}_4(\text{OH})_{24}(\text{H}_2\text{O})^{7+}$ at $\text{OH}/\text{Al} = 2.46$ (Fig. 2), indicated by the signature tetrahedrally coordinated Al center prominent at $\delta = 63$ ppm and octahedrally coordinated, oligomeric Al centers indicated by the broad band centered at $\delta = 10$ ppm.⁵ The concentration of monomeric octahedrally coordinated Al ($\text{Al}(\text{H}_2\text{O})_6^{3+}$, $\text{Al}(\text{OH})(\text{H}_2\text{O})_5^{2+}$) at $\delta = 0$ ppm is seen to decrease in solutions containing the polycation. The nmr spectra of solutions at $\text{OH}/\text{Al} = 2.00$ resembles that of the standard solution with an intense peak at $\delta = 0$ ppm, and small quantities of oligomeric species indicated by the small, broad peak at $\delta = 4$ ppm.

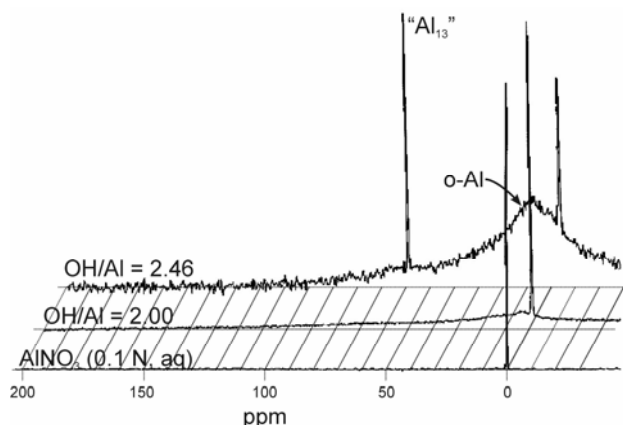


Figure 2: ^{27}Al nmr scans on aluminum standard (AlNO_3 , aq), and aqueous solutions containing NaOH and AlCl_3 . The primary soluble species at lower OH/Al ratio are the monomeric aluminum species, $\text{Al}(\text{H}_2\text{O})_6^{3+}$ and $\text{Al}(\text{OH})(\text{H}_2\text{O})_5^{2+}$. Under near-saturation conditions, the polycation $\text{Al}_{13}\text{O}_4(\text{OH})_{24}(\text{H}_2\text{O})^{7+}$ appears. Above $\text{OH}/\text{Al} = 2.46$, insoluble particles form in suspension.

The Role of Citric Acid in Aluminum-Containing Solutions

At OH/Al ratios below the critical value of 2.46, the presence of citric acid in the titrated solution acted to retard the dissolution of particles (Fig. 3, upper) formed by the addition of the alkaline to the solution. The particles did eventually disappear, albeit after 10 h from the time of mixing. Citric acid also slowed the growth of these transient particles to their maximum diameter, which were also smaller than the maximum achieved in solutions without citric acid present (Fig. 1). At higher OH/Al ratio (Fig. 3, lower) particles nucleated and grew in the presence of citric acid at ratios well below 1:1 citric acid/aluminum (mol/mol) until precipitation. Increasing the citric/aluminum ratio to nearly one prevented particle nucleation and solutions remained clear of detectable particles for several weeks when sealed against solvent evaporation and held at room temperature.

Changes in the structures of the soluble aluminum complexes in the presence of citric acid were observed using ^{27}Al nmr on solutions containing AlCl_3 , NaOH , and citric acid (Fig. 4). The most obvious difference is the loss of the 13-Al polycation peak at $\delta = 63$ ppm under $\text{OH}/\text{Al} = 2.46$, indicating that the

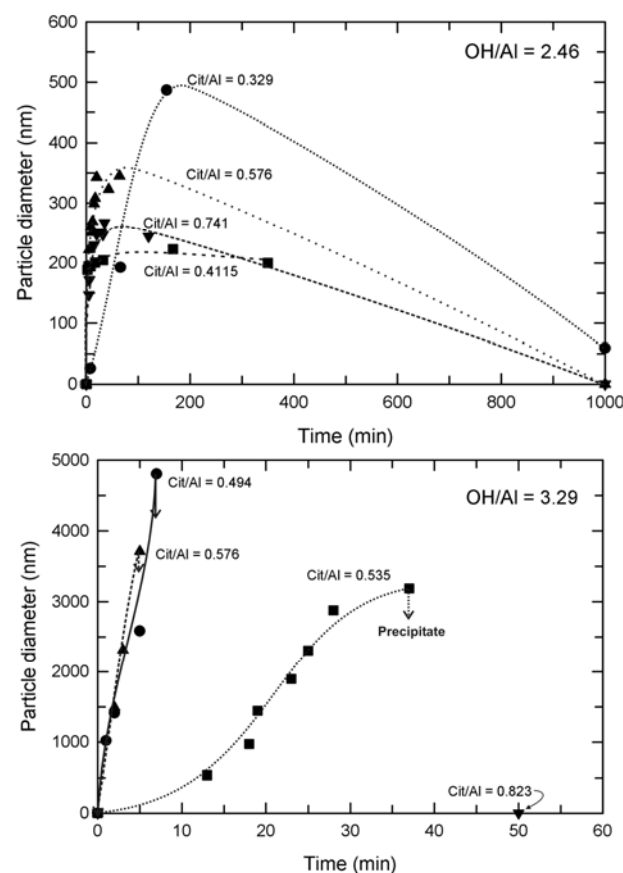


Figure 3: The formation and shrinking (upper) or growth and precipitation (lower) of particles in the presence of citric acid.

polycation either did not form or fragmented in the presence of citric acid. The exact mechanism cannot be determined from these nmr measurements due to the long time between titration and nmr characterization. Under fragmentation, it is possible that the polycation may first be protected by interaction with citric acid, as with particles, but strong complexation between the aluminums of the polycation and citric acid could eventually lead to the fragmentation of the polycation, a mechanism supported by the lack of the signature nmr peaks. Or the citric acid preferentially complexes with free aluminum cations in solution, reducing the concentration of the monomeric aluminum and thereby increasing the likelihood that the (complexed) polycation would become more susceptible to fragmentation into smaller aluminum-containing units.

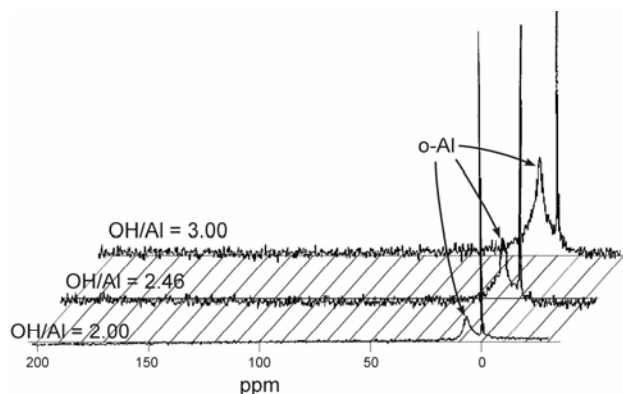


Figure 4: ^{27}Al nmr scans on aluminum-containing aqueous solutions composed of NaOH, AlCl_3 , and citric acid (citric/Al = 0.8) in water. The ^{13}Al polycation does not exist in the presence of citric acid. Polymeric octahedral Al are indicated by the growth of the broad band around $\delta = 10$ ppm. The primary soluble species remain the monomeric aluminum species, $\text{Al}(\text{H}_2\text{O})_6^{3+}$ and $\text{Al}(\text{OH})(\text{H}_2\text{O})_5^{2+}$, but the increasing polymeric content indicates the presence of seed molecules or clusters undetected by light scattering.

The loss of the ^{13}Al -aluminum polycation does not presage the loss of suitable seeds for the eventual growth of particles. A broad peak at $\delta = 10$ ppm appeared in all solutions for all values of OH/Al in Fig. 4, assigned to “polymeric” aluminum-containing species composed of octahedrally coordinated aluminum centers.⁵ Comparing Fig. 4 with Fig. 2, in the solutions containing citric acid all aluminum atoms appear as octahedrally coordinated, both in monomeric ($\delta = 0$ ppm) and polymeric forms ($\delta = 10$ ppm). The increased content of larger aluminum-containing molecules suggests the increased concentration of possible seed molecules or clusters, of size too small to be visible in light scattering. The presence of larger polymeric species would reduce the amount of citric acid needed to coordinate all aluminum centers. Since monomeric aluminum species exhibit one-to-one association with citric acid, the slightly lower citric acid/aluminum ratio required in our solutions to completely arrest particle formation is simply explained by the existence of these soluble polymeric aluminum oxyhydroxides.

Our observations suggest that the citric acid is a complexing agent whose interaction with aluminum containing species is strong enough to enhance solvation of the same but weak enough that the molecule also acts as an effective inhibitor, protecting oxyhydroxide surfaces from dissolution. Both activities are observed in similar solutions in the presence of citric acid: Where particles exist, dissolution, even under conditions of high hydrolysis, is slowed. If citric acid is present, large polycations do not exist in solutions that would otherwise be expected to contain such molecules. The acid effectively complexes with smaller cations and either causes the breakup of larger cations or prevents formation of the same. Likewise, with sufficient citric acid present, particles do not form and below a critical ratio of citrate/Al, particle growth is slowed under conditions in which spontaneous nucleation and rapid growth is expected.

The Effect of Polyols on the Nature of Silicon in Alkaline Solution

The chemistry of silicon in alkaline solutions is complex, with a large number of oligomeric silicon (IV) species shown to exist under alkaline conditions.⁶ Slight increases in local silicon content readily induces nucleation of stable particles that persist in solution even under highly alkaline solutions. The nature and distribution of oligomers is dependent upon the cation present

in solution, especially the sodium ion.⁶ Since attempts to dissolve silicon typically used sodium silicate as the silicon source, even high pH solutions were often observed to contain a significant quantity of stable particles. This stability hampered our studies of silicon in solution. Unlike aluminum-containing solutions, citric acid was determined to have little effect on the increasing the solubility of silicon, probably due to the stability of Si(IV) in tetrahedral coordination relative to that of Al(III). As described in literature, the more soluble octahedrally coordinated silicon has been stabilized using polyols.⁷ Accordingly, we selected a series of such molecules in an attempt to increase silicon solubility and solution stability under highly alkaline conditions.

In baseline trials, solutions of sodium silicate of 0.01M and 0.035M silicon were determined *via* dynamic light scattering (DLS) to form stable particle suspensions of 1.25 μ m and 1.50 μ m average diameter particles respectively in solutions with pH of 10.45.⁸ Adding any one of three polyols—sorbitol, gluconic acid, or xylitol—had a marked effect on the appearance of the solutions. In the test solutions, polyol was added to achieve a molar ration of 3 polyol to one silicon. In the 0.01M silicon solutions, the addition of polyol effectively cleared the suspensions. In the 0.035M silicon solutions, particles remained in suspension, albeit at reduced average particle size around 0.8 μ m regardless of polyol used. As in the case of aluminum particle suspensions, laser light scattering has a detection limit of around 3-5nm diameter, so the apparent absence of particles cannot be interpreted as complete dissolution into solution.

Aluminosilicates in Solution and in Suspension

The tabulated solubilities of aluminum and silicon are offset by the chemical affinity between silicon-containing oxyhydroxides and aluminum cations. A variety of metastable aluminosilicate solutes have been found to exist under alkaline conditions, with smaller, more reactive molecules favored at higher alkalinity.⁶ Although silicate solutes are deprotonated at high pH, the aluminosilicates retain sufficient –OH functionalities to drive condensation between the smaller components to form virtually insoluble gels. These aluminosilicates are also thought to provide the building blocks for zeolite formation and have more recently given rise to high pH synthesis of “geopolymers,” polymeric aluminosilicates with sialate [–Si–O–Al–O–] or silicate siloxo [–Si–O–Al–O–Si–O–] backbones.⁹ The composition and structures of these geopolymers are very similar to molecular precursors designed for use in the low temperature synthesis of mullite (3Al₂O₃·2SiO₂).¹⁰

Our work on the separate aluminate and silicate solutes described above and our past studies using aluminosilicate gels in the synthesis of mullite¹¹ have demonstrated the difficulties of working with aluminum and silicon solutes at high pH. The affinity between the aluminum and silicon and the presence of large, metastable structures suggest that we should not focus on the improving solvation of the aluminosilicates, but, rather, shift emphasis to the stabilization of small particles, or “nuclei,” within a long-lived suspension. The chemical stability of aluminosilicates is demonstrated by mullite, a thermodynamically stable solid solution in the Al₂O₃–SiO₂ system, which is extremely resistant to alkali corrosion at high temperatures.¹²

The high sodium content found in nuclear waste at sites such as Savannah River^{1,2} has a significant effect on the formation and stability of geopolymers^{9,13} and should not be ignored in future studies. Indeed, our difficulties with silicate solutes in part arose from using sodium silicate for the source of silicon; we did not fully appreciate the effect of high sodium content.

References

1. *Tanks Focus Area, 1997 Annual Report* (National Technical Information Service, U.S. Department of Commerce, Springfield, VA 1998).
2. Barney, G.S. *Vapor-liquid solid-phase equilibria of radioactive sodium salt wastes at Hanford ARH-ST-133* (U.S. Energy Research and Development Administration: Richland, WA, 1976).
3. Dabbs, D.M.; Ramachandran, U.; Lu, S.; Liu, J.; Aksay, I.A. "Stabilization of Aluminum Oxyhydroxides using Citric Acid" *manuscript in preparation*.
4. Delgado, A.; Matijevic E., *Particle & Particle Systems Characterization*, **1991**, 8 [2], 128-135.
5. Fu, G.; Nazar, L.F.; Bain, A.D., *Chem. Mater.*, **1991**, 3, 602-10.
6. Swaddle, T.W. *Coord. Chem. Rev.*, **2001**, 219, 665-86.
7. Kinrade, S.D.; Maa, K.J.; Schach, A.S.; Sloan, T.A.; Knight C.T.G. *J. Chem. Soc., Dalton Trans.*, **1999**, 3149-50.
8. Coleman, C.; Senior Thesis, **2003**, Princeton University (Thesis number 15926).
9. For example, see Barbosa, V.F.F.; MacKenzie, K.J.D. *Mater. Res. Bull.*, **2003**, 38, 319-31.
10. Treadwell, D.R.; Dabbs, D.M.; Aksay, I.A. *Chem. Mater.*, **1996** 8 [8] 2056-60.
11. Aksay, I.A.; Dabbs, D.M.; Sarikaya, M. *J. Am. Ceram. Soc.*, **1991** 74 [10], 2343-58.
12. For example, see Scanu, T.; Colomban, P. *J. Phys. IV*, **1993**, 3 (C7), 1927-30.
13. Bao, Y.; Kwan, S.; Siemer, D.D.; Grutzeck, M.W. *J. Mater. Sci.*, **2004**, 39, 481-8.