

# Precipitation and Deposition of Aluminum-Containing Species in Tank Wastes

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## Research Objectives

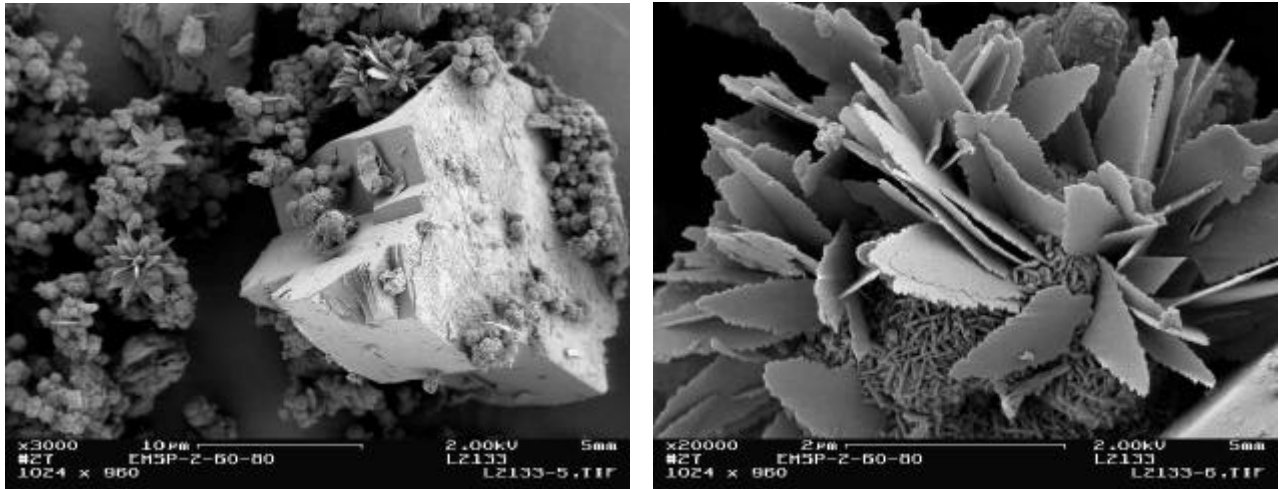
Aluminum-containing phases represent the most prevalent solids that can appear or disappear during the processing of radioactive tank wastes. Processes such as sludge washing and leaching are designed to dissolve Al-containing phases and thereby minimize the volume of high-level waste glass required to encapsulate radioactive sludges. Unfortunately, waste-processing steps that include evaporation can involve solutions that are supersaturated with respect to cementitious aluminosilicates that result in unwanted precipitation and scale formation. Of all the constituents of tank waste, limited solubility cementitious aluminosilicates have the greatest potential for clogging pipes and transfer lines, fouling highly radioactive components such as ion exchangers, and completely shutting down processing operations. For instance, deposit buildup and clogged drain lines experienced during the tank waste volume-reduction process at the Savannah River Site (SRS) required an evaporator to be shut down in October 1999. The Waste Processing Technology Section of Westinghouse Savannah River Company at SRS now is collaborating with team members from Pacific Northwest National Laboratory (PNNL) to verify the thermodynamic stability of aluminosilicate compounds under waste tank conditions in an attempt to solve the deposition and clogging problems. The primary objectives of this study are 1) to understand the major factors controlling precipitation, heterogeneous nucleation, and growth phenomena of relatively insoluble aluminosilicates; 2) to determine the role of organics for inhibiting aluminosilicate formation, and 3) to develop a predictive tool to control precipitation, scale formation, and cementation under tank waste processing conditions. The results of this work will provide crucial information for 1) avoiding problematical sludge processing steps and 2) identifying and developing effective technologies to process retrieved sludges and supernatants before ultimate vitrification of wastes.

## Research Progress and Implications

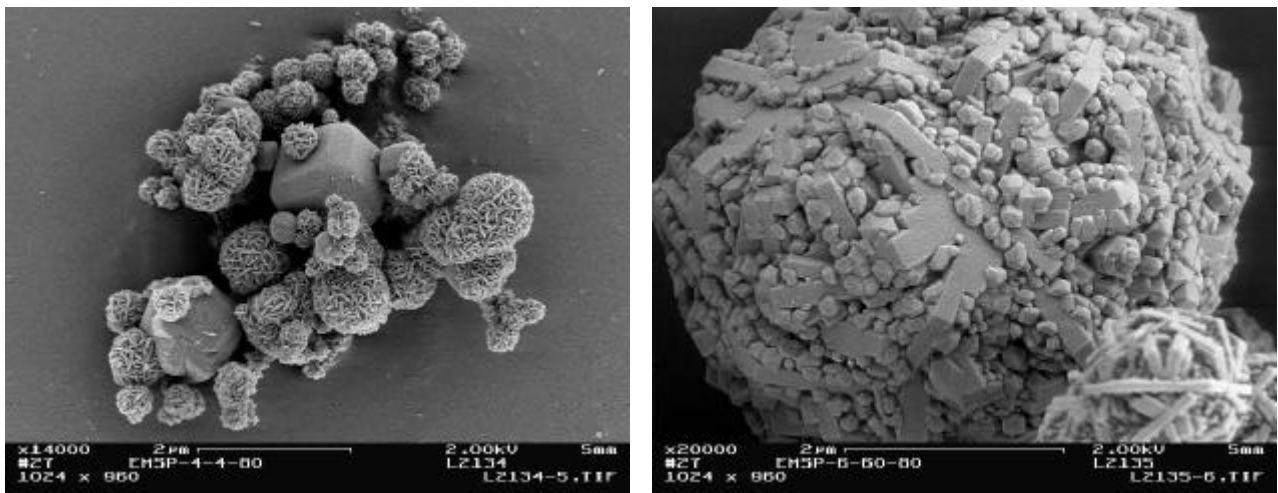
This report summarizes work completed after 1 year of a 3-year project. Studies conducted so far have focused on identifying the insoluble aluminosilicate phase(s) and characterizing their chemistry and microstructure by determining the kinetics of the phase formation and transformation of such aluminosilicate phases under hydrothermal conditions.

The data we obtained from tests conducted at 40°C showed that formation and persistence of crystalline phases were dependent on the initial hydroxide concentrations. The formation and persistence of a zeolitic phase (zeolite A) occurred only at lower hydroxide concentrations, whereas increasing hydroxide concentrations appeared to promote the formation of sodium aluminosilicate phases such as sodalite and cancrinite. The results showed that although zeolite A forms during the initial period of reaction, it converts to more stable crystalline phases such as sodalite and cancrinite because of its metastability. We also observed that the rate of transformation of zeolite A increased with increasing hydroxide concentration. The data from

tests conducted at 80°C revealed relatively rapid formation of sodalite and cancrinite. Although minor amounts of zeolite A were detected initially in some cases, the higher reaction temperatures seemed to promote very rapid transformation of this phase into more stable phases. Also, the higher temperature and hydroxide concentrations appeared to initiate kinetically fast crystallization of sodalite and cancrinite. Figures 1 and 2 illustrate our findings.



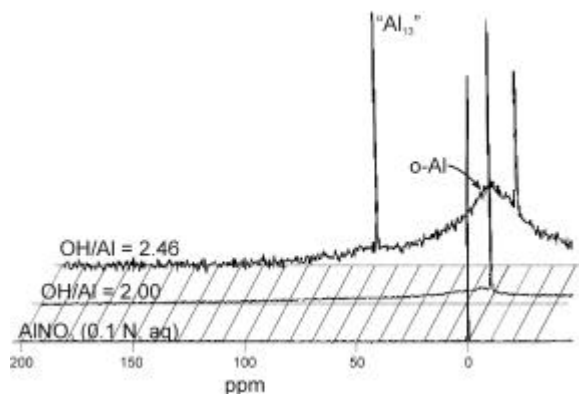
**Figure 1.** (Left) Massive crystals of gibbsite with minor quantities of bladed nordstrandite and textured spherical cancrinite formed after 60-day reaction period at 80°C from low Si (0.01 M), high Al (0.5 M), and low OH (0.1 M). (Right) A close-up of nordstrandite and cancrinite crystals.



**Figure 2.** (Left) Aggregates of cubic zeolite A and spherical cancrinite crystals formed after 4-hr reaction period at 80°C from low Si (0.01 M), high Al (0.5 M), and high OH (1.0 M). (Right) A magnified view of well-crystallized cancrinite formed after 60-day reaction period at 80°C from low Si (0.01 M), high Al (0.5 M), and very high OH (4.5 M).

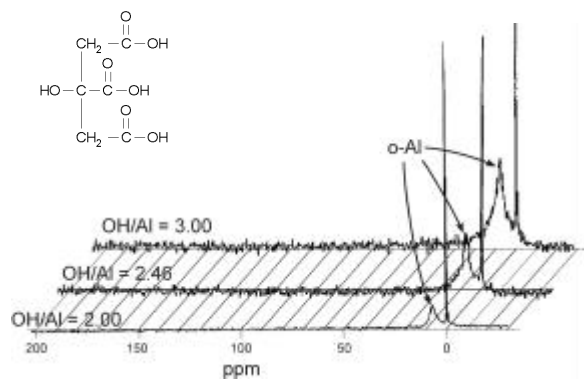
The data we have obtained so far are unique because we have examined aluminosilicate formation under very low silica-high aluminum (Al/Si) mol ratio conditions (20 to 50) and a range of hydroxyl conditions (0.1 to 4 M) that are similar to actual waste processing conditions. Our literature review indicated that all previous studies on aluminosilicate (zeolites) formation were typically conducted at Al/Si mol ratios approaching unity. Therefore, the implications of our study are that during waste concentration in evaporators, hard scale-forming aluminosilicates can form even in the presence of very low concentrations (0.01 M) of silica in the feedstock. More recent testing at the SRS in support of the high-level waste evaporator plugging issue has shown similar trends in the formation of aluminosilicate phases. Comparison of our results with those reported above show very similar trends - that is, initial formation of an amorphous precipitate followed by a zeolite phase that transforms to sodalite, which finally converts to cancrinite. Our results also show the expected trend of an increased rate of transformation of initial precipitates into denser scale-forming aluminosilicate phases (sodalite and cancrinite) at higher temperature. The results of our studies can be used to avoid feedstock compositions that would result in rapid formation of enhanced quantities hard scale-forming aluminosilicate phases such as sodalite and cancrinite. Two manuscripts that describe the studies are being prepared for submission to selected peer-reviewed journals.

The work conducted by our collaborators at the Princeton University focused on understanding the mechanisms by which organics inhibit the nucleation and growth of insoluble aluminum oxyhydroxides, specifically to evaluate the ability of an organic to chelate with the aluminum cation or active sites on the surfaces of complexes and particles. The initial focus has been on the use of simple carboxylic acids, to stabilize colloidal alumina particles in aqueous suspension. Our investigations demonstrated the very complex chemistry that appears to exist within deceptively simple solutions containing only aluminum oxyhydroxides and/or aluminum cations, the organic moiety, NaOH, and water. Nuclear magnetic resonance with  $^{27}\text{Al}$  solution on control solutions containing aluminum nitrate in water demonstrated the development of a large aluminum complex  $(\text{Al}_{13}\text{O}_4(\text{OH})_{24}(\text{H}_2\text{O})_{12}^{7+}$  polycation, “Al<sub>13</sub>”) at OH/Al molar ratios near 2.46 (Figure 3), assumed to be the precursor to aluminum oxyhydroxide particle formation and precipitation. The effect of citric acid  $(\text{HOOCCH}_2\text{COH}(\text{COOH})\text{CH}_2\text{COOH})$ , a tricarboxylic acid, is to inhibit particle formation, apparently by preventing the formation of or breaking up the large aluminum complex, directly chelating to and stabilizing the  $\text{Al}^{3+}$  cation in solution (Figure 4).

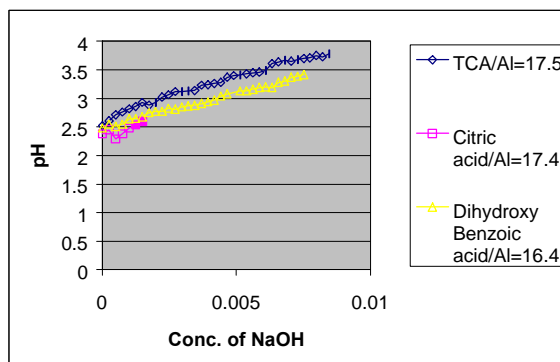


**Figure 3.** Addition of NaOH to aqueous solutions of aluminum nitrate results in the formation of a soluble 13-Al oxyhydroxide complex (“Al<sub>13</sub>”).

Although effective at low pH and high reactant concentrations, citric acid is ineffective in high-pH solutions and low reactant concentrations, as shown by quasi-elastic light scattering. Under these conditions, precipitation occurs in spite of the presence of the acid. Other carboxylic acids—tricarballic acid (TCA) and 2,4-dihydroxy benzoic acid—are effective under these same conditions, although at very high ratios of acid to aluminum (Figure 5). Tricarballic differs chemically from citric acid in the absence of a hydroxide group on the central carbon ( $\text{HOOCCH}_2\text{CH}(\text{COOH})\text{CH}_2\text{COOH}$ ), which appears to improve citric acid solubility in water relative to TCA.



**Figure 4.** Citric acid (inset structure) prevents precipitation of aluminum-containing materials by inhibiting or decomposing the large soluble complexes believed to provide the seeds for the nucleation and growth of insoluble species.



**Figure 5.** At higher pH and low reactant concentrations, citric acid fails to prevent precipitation of aluminum-containing phases. TCA and 2,4-dihydroxy benzoic acid, although having lower solubility in water, effectively prevent the formation of insoluble species, albeit at very high acid to aluminum ratios (plots truncate at point of precipitation).

## Planned Activities

We will be conducting experiments at higher temperatures (120°C and 175°C) to examine the rate of formation and transformation of aluminosilicate phases (to be completed March 2003). We will conduct low angle x-ray scattering studies to understand formation of clusters during the very early stages of the reaction period; these studies are scheduled for completion by June 2003. Following these activities, we plan to initiate solution thermodynamic studies. Our collaborators at Princeton University will be conducting  $^{27}\text{Al}$  nuclear magnetic resonance spectrometry to determine the structure of the stabilized aluminum-containing species in solution in the presence of TCA and 2,4-dihydroxy benzoic acid. Additional studies would include the use of polyelectrolytes such as poly(acrylic acid) to stabilize or dissolve aluminum complexes.