

Progress Report 2003 – 2004 (EMSP Project 81887)

Precipitation and Deposition of Aluminum Containing Species in Tank Wastes

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1. Research Objective

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 Savannah River Site (SRS) required an evaporator to be shut down in October 1999. The Waste Processing Technology Section (WPTS) of Westinghouse Savannah River Company (WSRC) at SRS is now 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 goals of this study are to understand the 1) the major factors controlling precipitation, heterogeneous nucleation and growth phenomena, of relatively insoluble aluminosilicates, 2) 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 obtained from this 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.

2. Research Progress and Implications

This report summarizes work completed during the last year of a 3-year project. Studies conducted so far have focused on identifying the insoluble aluminosilicate phase(s), characterizing the chemistry and microstructure of these phases, studying the kinetics of the phase formation and transformation of such aluminosilicate phases under hydrothermal conditions, and the role of organics for inhibiting aluminosilicate formation.

A series of experiments were conducted with the salt concentrations that represented average compositions reported from Tanks 38H, 43H, and the evaporator from the Savannah River site. Some of the most important salts included NaAlO_2 , NaNO_3 , with varying silica and hydroxide concentrations. The initial experimental strategy, was to vary the hydroxide (from 0.01 M to 4.5 M) and aluminum concentrations (0.2M and 0.5M) for a fixed silica concentration of 0.01M. Sodium nitrate concentrations were fixed at ~3M. Four reaction temperatures were studied: 40 °C, 80 °C, 120 °C, and 175 °C. These temperatures were selected to cover the range of temperatures encountered during the storage and evaporation of waste solutions.

Crystallization kinetics (time to attain 50% crystallization of initially precipitated precursor phase) indicated that both temperature and increasing hydroxyl concentration promoted more rapid crystallization (Figure 1). Highest rates of crystallization at all temperatures above 80 °C were observed in solutions (5 and 6) containing the highest NaOH concentration (4.5M).

These data were used to generate predominance diagrams for solid phases in temperature-hydroxyl concentration field (Figure 2). These diagrams illustrate the relative mass distribution of various crystalline and the precursor amorphous phases as a function of temperature, hydroxide concentration, and Al/Si molar ratios. At lower temperatures and low hydroxide concentrations zeolite A appears to be a dominant phase whereas, at higher temperatures and hydroxide concentrations sodalite and cancrinite constitute the bulk of crystalline mass. Our literature review indicated that all previous studies on aluminosilicate (zeolites) formation were typically

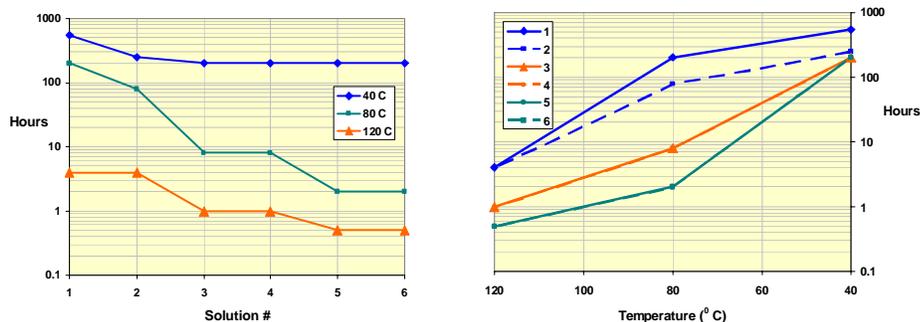


Figure 1. Rate of crystallization as a function of solution composition (left) and temperature (right). Initial solution compositions: Al/Si Mole ratio Solutions 1, 3, and 5 = 30. Solutions 2, 4, and 6 = 50. NaOH conc; Solutions 1 and 2 = 0.01M, 3 and 4 = 1.0 M and 5 and 6 = 4.5 M NaOH.

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 (0.01M) of silica in the feed stock. 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.

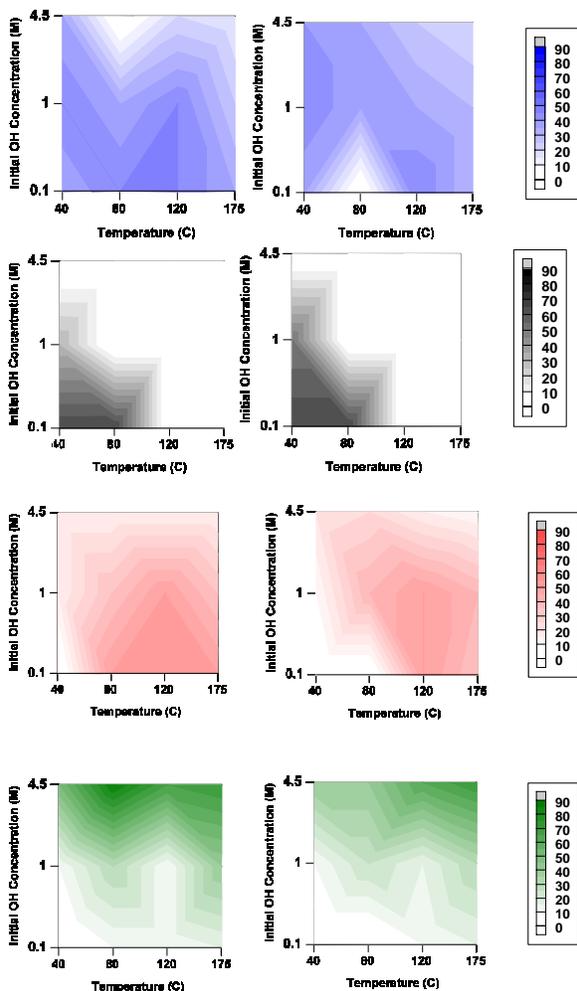


Figure 2. Predominance diagram for precursor phase (blue), zeolite A (gray), sodalite (red) and cancrinite (green). The diagrams on the left represent Al/Si mole ratio of 20 and on the right represent Al/Si mole ratio of 50.

Comparison of our results with those obtained at SRS showed very similar trends, i.e., initial formation of an amorphous precipitate followed by zeolite A that transforms to sodalite, which finally converts to cancrinite. Our results also showed an increased rate of transformation of initial precipitates into denser scale-forming aluminosilicate phases (sodalite and cancrinite) at higher temperatures and hydroxyl concentrations (Figures 1, 2).

Inhibition of nucleation of insoluble aluminum hydroxides by chelating organics was studied by our collaborators at Princeton University.

The data indicated 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 were observed in similar solutions in the presence of citric acid: Where particles existed, dissolution, even under conditions of high hydrolysis, was slowed. If citric acid was present, large polycations did not exist in solutions that would otherwise be expected to contain such molecules. The acid effectively complexed with smaller cations and either caused the breakup of larger cations or prevented formation of the same. Likewise, with sufficient citric acid present, particles did not form and below a critical ratio of citrate/Al, particle growth was slowed under conditions in which spontaneous nucleation and rapid growth was expected.

The chemistry of silicon in alkaline solutions is complex, with a large number of oligomeric silicon (IV) species shown to exist under alkaline conditions. 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. 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).

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. 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.

3. Planned Activities

The remaining part of our studies will consist of data analysis and interpretation and preparation of manuscripts for publication in peer-reviewed journals.

4. Information Access

Mattigod, S.V., D.T. Hobbs, K.E. Parker, D.E. McCready, L.Q. Wang. Precipitation of scale-forming species during processing of high-level wastes. Abs. 227th ACS National Meeting, Anaheim, CA, Mar, 28 – Apr 1 2004 (2004).

Mattigod, S.V., D.T. Hobbs, K.E. Parker, D.E. McCready and L.Q. Wang. Precipitation of Aluminum Containing Species in Tank Wastes (2004 In Press). ACS Symp. Ser. Am. Chem. Society, Washington DC.

Mattigod, S.V., D.T. Hobbs, K.E. Parker, D.E. McCready, L.Q. Wang. Precipitation of aluminum containing phases in tank wastes. Abs, 226th ACS National Meeting, New York, NY, Sep 7 – 11, 2003 (2003).

Gong, X., Z. Nie, M. Qian, J. Liu, L.A. Pederson, D.T. Hobbs, N.G. McDuffie. Gibbsite to Boehmite Transformation in Strongly Caustic and Nitrate Environments. Ind Eng. Chem. Res, 42 (2003), 2173 – 2170.

Jantzen, C.M., J.M. Pareizs, J.M. and T.B. Edwards. Thermodynamic Modeling of the SRS Evaporators: Part IV. Incorporation of High Caustic Aluminosilicate Solubility Data (U), WSRC-TR-2001-00330, revision 0, 2003.

Pareizs, J.M. and C.M. Jantzen. Thermodynamic Modeling of the SRS Evaporators: Part V. Validation, WSRC-TR-2001-00331, revision 0, 2003.

Mattigod, S.V., D.T. Hobbs, K.E. Parker, D.E. McCready. Precipitation of aluminum Containing species in tank Wastes. PNNL-13881 Pacific Northwest National Laboratory, Richland, Washington. 2002

Hobbs, D. T.; S.V. Mattigod, J. Liu, Z. Nie. Formation of aluminosilicate phases pertinent to the evaporation of high-level nuclear wastes. Abs. 222nd ACS National Meeting, Chicago, IL, Aug 26 -30, 2001

Mattigod, S.V., L.Q. Wang, D.T. Hobbs, D. Dabbs, and I. Aksay. 2001. Precipitation and Deposition of Aluminum-Containing Phases in Tank Wastes. EMSP Workshop, Richland, WA. November 7-8, 2001. <http://www.pnl.gov/emsp/presentations.stm>

Mattigod S.V., L.Q. Wang, D.T. Hobbs, D. Dabbs, and I. Aksay. 2003. Precipitation and Deposition of Zeolite Phases in Tank Wastes. EMSP Workshop, Richland, WA. <http://www.pnl.gov/emsp/presentations.stm>