

Progress Report 2002 – 2003 (EMSP Project 81887)

Precipitation and Deposition of Aluminum Containing Species in Tank Wastes

Shas V. Mattigod, Pacific Northwest National Laboratory; David T. Hobbs, Westinghouse Savannah River Company; L. Wang, Pacific Northwest National Laboratory; Daniel M. Dabbs and Ilhan A. Aksay, Princeton University

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 after 2 years 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, and studying 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 initial period of reaction, due to its metastability, it converts to more stable crystalline phases such as sodalite and cancrinite. 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 formations of sodalite and cancrinite. Although minor amounts of zeolite A were initially detected 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.

The results of the experiments conducted at 120 °C and 175 °C were similar to the data obtained from 80°C. However, the rates of formation of crystalline phases at 120 °C and 175 °C were, respectively, about one and two orders of magnitude faster than what was observed at 80°C. 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 20 – 50), a range of hydroxyl conditions (0.1 – 4 M), and temperatures (40 – 175°C) 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 (0.01M) 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. Comparison of our results with those reported above showed very similar trends, i.e., initial formation of an amorphous precipitate followed by a zeolite phase that transforms to sodalite, which finally converts to cancrinite. Our results also showed the expected trend of an increased rate of transformation of initial precipitates into denser scale-forming aluminosilicate phases (sodalite and cancrinite) at higher temperatures. The results of our studies can be used to avoid feed stock compositions that would result in rapid formation of enhanced quantities hard scale-forming aluminosilicate phases such as sodalite and cancrinite.

Inhibition of nucleation of insoluble aluminum hydroxides by chelating organics was studied by our collaborators at Princeton University. The results showed that particle formation was significantly retarded in solutions containing citric acid at $\text{Cit}/\text{Al} > 0.7$, and that the hydroxyl group on citric acid acted as complexant at high pH. The ^{27}Al NMR data indicated the formation of Al_3 polycation precursor at the critical OH/Al molar ratio of ~ 2.46 . Stable particle formation was observed only when the critical OH/Al ratio was exceeded. Although effective at low pH and high reactant concentrations, citric acid was ineffective in preventing precipitation under high pH-low reactant conditions. Therefore, to prevent nucleation under these conditions, a chelating agent that forms more stable linkages with Al is necessary.



Aggregate of hexagonal cancrinite crystals formed after 24 hr of reaction at 175 °C under low Si (0.01M), high Al (0.5M), and high OH (4.5M) conditions.

3. Planned Activities

We will be conducting experiments to examine the rate of formation and transformation of aluminosilicate phases under higher silica conditions (to be completed 9-2003). We plan to conduct low angle X-ray scattering studies to understand formation of clusters during very early stages of reaction period, and use insitu X-ray diffraction to determine the rate of crystallization (2004). We also plan to select and tailor better chelates for aluminum under high pH conditions (2004).

4. Information Access

S. V. Mattigod, D. T. Hobbs, K. E. Parker, D. E. McCready, and L. Wang. 2003. Precipitation of Aluminum-Containing Species in Tank Wastes. ACS Abstracts.

X. Gong, Z. Nie, M. Qian, J. Liu, L. A. Pederson, D. T. Hobbs. 2003. Gibbsite to Boehmite Transformation in Caustic and Salty Environment. Ind. Eng. Chem. Res. (In Press).

S. V. Mattigod, L. Wang, D. 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>

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

S. V. Mattigod, L. Wang, D. 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>