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Project Title: **Precipitation and Deposition of Aluminum-Containing Phases in Tank Wastes**

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Dissolution, Precipitation, and Deposition of Aluminum-Containing Phases in Tank Wastes

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Research Objective

The goal of this work is to understand the kinetics of dissolution, precipitation, and scale formation involving aluminum-containing phases in alkaline salt solutions representative of tank wastes. This research will identify aluminum-containing phases that are likely to form or be present, and predict conditions under which such phases are likely to form or be present. Experiments will identify processing conditions that either promote or inhibit the heterogeneous or homogeneous nucleation and growth of aluminum-containing phases to form precipitates or scales. Test conditions will encompass conditions anticipated for waste storage, washing, leaching, concentration in evaporators, and contact with pipes, ion exchangers, and other processing media.

Problem Statement

Aluminum is one of the principal elements in alkaline nuclear wastes stored at DOE sites, including Hanford and Savannah River. Both the insoluble and soluble fractions pose serious challenges to waste processing. Aluminum removal during processing is desired because it is a major waste component that dictates the volume of waste glass produced via vitrification of both high- and low-level waste streams. It is critical to understand factors controlling the extent and rate of dissolution for aluminum-containing phases.

Soluble aluminates represent a major component of supernatant liquids in most tanks even prior to sludge dissolution. Aluminum concentrations in many solutions are near saturation levels. Changes in solution conditions can lead to supersaturation, promoting precipitation and scale formation. Aluminate precipitates are known to have clogged pipes in the tank farms at Hanford. Scale formation may have contributed to the clogging of cross-site transfer lines. At Savannah River, precipitation of aluminosilicates led to the clogging of evaporator gravity drain lines. Precipitation due to pH, temperature, or ionic strength gradients within ion exchange columns and filters could lead to fouling and clogging of units having high radioactive inventories.

While the solubility of aluminum oxides and hydroxides has been studied extensively, limited information is available regarding the behavior of solid phases or soluble aluminum species in highly basic salt solutions, especially in the presence of silicate or phosphate species. Almost nothing is known about the kinetics of nucleation and growth leading to precipitation and/or scale formation from supersaturated aluminate solutions.

Research Progress

Interaction with Savannah River Technology Center and Hanford to Address Specific Tank Waste Needs

After detailed discussion with Savannah River Technology Center (SRTC) staff, the following areas have been identified as significant tank waste problems at SRTC.

1. Effect of aging of aluminum-containing sludges: One of the main processes of the Extended Sludge Processing operation at the Savannah River Site (SRS) is aluminum leaching. Aluminum leaching is

accomplished by treating the sludge with hot caustic solution. Despite many theoretical models on aluminum speciation during leaching and washing, there are still many questions regarding the effects of other variables (such as temperature, chemical environment, and radiation) on the formation and transformation of aluminum-containing phases in high-level nuclear wastes. Much of the testing performed to determine parameters for aluminum leaching in sludges used freshly precipitated sludges. Aging of the sludge is known to convert aluminum phases. Thus, aluminum leaching characteristics of aged waste solutions may be vastly different than freshly prepared materials. Testing is needed to determine the important parameters and the rates of phase transformations.

2. Interaction with silicate: The introduction of elevated quantities of silicon in the 2H-evaporator system at SRS from the DWPF recycle stream resulted in the formation of aluminosilicate solids that plugged the evaporator gravity drain line. Several million dollars were spent on cleaning the line because this evaporator is critical to maintain adequate storage space for HLW at the SRS. Testing is needed to determine allowable solution-phase concentrations of aluminum and silicon so that aluminosilicate formation can be prevented.

At the Hanford Site, ESP models have been widely used to predict the mineral contents in the tank wastes. Experimental verification of the ESP models, especially in the high aluminum tank wastes, remain critical.

Main Solid Phases and Implication on Tank Waste Processing

TEM studies have been performed on many tank waste samples in the past several years (Lafemina 1995), and the main results are summarized below.

Although the tank composition and history are very complicated, the most abundant elements in many tanks include Fe, Al, P, Ca, Si, and Bi. Among these, aluminum is one of the most prevalent elements in tank wastes. The major component in C-112 is large gibbsite ($\text{Al}(\text{OH})_3$) particles, ranging from micrometers to tens of micrometers in size. Other phases are also observed, including uranium phosphate, calcium phosphate, and boehmite. The boehmite (AlOOH) and calcium phosphate are in the nanometer size range and exist as agglomerates. Besides gibbsite, aluminum-containing phases also exist as boehmite, hydrated alumina, although in some tanks they also exist as sodium aluminate, aluminum phosphate, and aluminosilicate. Boehmite is the main crystalline phase in many tanks from the redox process (S101, S111, S102, S107, S103, and S104). The boehmite exist as rectangular plate-like particles, with a thickness ranging from 1 to 10 nm, and a width ranging from 10 to a few hundred nanometers. The aluminum hydroxide and aluminosilicate usually are in the micrometer size range.

Another commonly encountered phase is iron oxyhydroxide (FeOOH). The FeOOH was usually formed as particles less than 10 nm in size and incorporated into hard agglomerates of spherical shapes about one micrometer in size. The crystallinity of the particles and the density of the agglomerates vary from tank to tank, most likely depending on the composition and history of the tank. When bismuth and silicon are also present, iron will mix with them to form iron bismuth silica agglomerates of similar size and shape. It is interesting that the agglomerate shows single crystalline diffraction pattern even though the primary particles can still be distinguished within the agglomerates, indicating the particles are sintered together. This is most likely due to the long heating history inside the tank. In other tanks, like B-111, T-111, and T-104, the primary particles in agglomerate of similar shape are much less crystalline.

Although it is impossible to list all the minerals found even in one tank waste sample, different types of tank wastes have different degrees of complexity. S-101, S-102, S-103, S-104, S-107, S-111, SY-102, and SX-108 only have one mineral phase, boehmite, as the major constituent. B-111, T-111, and T-104

also have only one major morphology: spherical agglomerates of amorphous bismuth silicate ($\text{Fe}_2\text{Bi}(\text{SiO}_4)_2\text{OH}$). Many tank sludges, like C-106, C-107, C-112, and C-108, have two major solid phases, aluminum oxyhydroxide (gibbsite or boehmite) and iron oxyhydroxide (FeOOH). Even in more complicated tank sludges that contain many other phases, like BY-104, BY-108, BY-110, BX-112, and BX-110, gibbsite, boehmite, and iron oxyhydroxide are still the majority phases. These observations give some useful lessons about the solid phases in tank waste sludges: 1) the major solid phases can be classified either as micrometer-sized colloidal particles, such as $\text{Al}(\text{OH})_3$, or as agglomerates of nanometer-sized particles, such as AlOOH , FeOOH , or $\text{Fe}_2\text{Bi}(\text{SiO}_4)_2\text{OH}$; 2) although many phases are present in the tank, the different phases have not mixed with one another on a fine scale – it seems common for the fine particles to form aggregates of their own, rather than forming hetero-aggregates.

The TEM observations suggest that it is possible to use simple models to understand and predict the colloidal properties of the tank wastes: 1) under many conditions, the tank waste slurries can be simulated using one component system containing fine particles (boehmite, for example), or a two-component system consisting of fine particles and coarse particles; 2) because hetero-aggregation is not commonly observed, the model systems can be prepared by mixing different colloidal components.

We studied the sedimentation density of binary agglomerates of goethite (fine particles, primary particle sizes of less than 10 nm) and gibbsite (coarse particles, 1.3 μm). The sedimentation density decreases rapidly as the volume fraction of the fine particles increases. This behavior can be explained by a biphasic mathematical model in which the two components are not intimately mixed; the fine particles form lower-density agglomerates by themselves, and the large particles form higher-density agglomerates by themselves. The sedimentation density of the fine particles is about 0.18 by volume, and the sedimentation density of the coarse particles is 0.5 by volume. The sedimentation density of the binary mixture can be calculated: $V = V_c V_f / [V_f(1-X) + V_c X]$, where V is the sedimentation density in the mixture, V_c the sedimentation density of coarse agglomerates, V_f that of the fine agglomerates, and X the weight fraction of the fine agglomerates. The expected density from this biphasic model is plotted as the solid line. Over the whole range, the biphasic model gives a good estimate for the sedimentation density compared with the experimental results. This biphasic model is based on the TEM observation that the different phases do not mix intimately with one another. It does not make any assumptions about the agglomerate structure (size, density, fractal dimension, etc.) and provides a reasonable picture of the distribution of the two major phases in the tank waste. The only information needed is the maximum sedimentation density of the coarse and fine particles, which can be easily estimated.

Hydrothermal Treatment of Gibbsite

1. Gibbsite in caustic solution: (about 1.3 μm in diameter) Gibbsite was treated in caustic solutions containing high concentrations of sodium aluminate. After heating the solutions in sealed Teflon containers for up to 10 days at 80 and 100°C, TEM and XRD characterization indicated that there was no significant change in the crystalline phase and the particle morphology.
2. Hydrothermal treatment of gibbsite with silicate: 100 mL solution with 1 M sodium silicate solution (27%) and 2 M NaOH were heated to 100°C to dissolve the sodium silicate. The solution was then cooled to room temperature. Five grams of gibbsite were added to the above solution and stirred in a Teflon container for 30 minutes. These solutions were heated in the sealed Teflon containers for up to 10 days. After the hydrothermal treatment, the samples were centrifuged and washed several times until the pH value of the supernatant reached 6. The solid materials were dried and analyzed by TEM and XRD.

In the first two hours, at both 80 and 100°C, no significant reaction was observed. Between two hours and one day, many intermediate products were formed, including cristobalite, quartz, faujasite, and tridymite. After seven days, the principal reaction product is zeolite P2 (sodium-exchanged, artificial).

These results suggest that the presence of silicate has a drastic effect on the activities of aluminum hydroxide. Although this phenomenon has been well documented, there is no detailed study of how gibbsite reacts with silicate in caustic solutions. These reactions will be the subject of future study.

Control of Aluminum Solubility

The program goals of the Princeton University team are 1) to maintain and enhance the solubility of aluminum-containing species in high-pH aqueous solutions and 2) to stabilize suspensions of ultrafine aluminum-containing nuclei or submicron particles and thereby prevent deposition of insoluble materials in waste tanks and transfer lines. To these ends, three areas of study were emphasized: 1) the solubility of aluminum in high-pH solutions in the presence of organic molecules, 2) the kinetics of aluminum-containing phase precipitation, and 3) the composition and structure of aluminum-containing precipitates and soluble species. Additionally, the chemistry of hydration and the mechanisms of nucleation and growth of hydrated alumina solids will be studied to control the precipitation of aluminum-containing materials and thereby prevent unwanted precipitation.

In the initial stage we are screening simple organic molecules that might affect the solubility of aluminum-containing anions in solution through the complexation of the aluminum or aluminum oxyhydroxides. We have started with simple, water soluble carboxylic acids: hexanoic acid, butyric acid, and glutaric acid, examining and contrasting their behavior in alkaline solutions with respect to the presence of soluble aluminum-containing species. Solutions of the stable polycation $\text{Al}_{13}\text{O}_4(\text{OH})_{24}(\text{H}_2\text{O})_{12}^{7+}$ ("Al-13") were used as the test matrix. The Al-13 solutions were made by the following procedure:

1. 0.5 M solution of Al^{3+} prepared from dissolving either aluminum nitrate nonahydrate ($\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$) or aluminum chloride (AlCl_3) in deionized water.
2. The Al^{3+} solution was refluxed at 60°C for two hours; after two hours, 0.2 M NaOH was slowly added to the solution by dropwise addition until the OH/Al ratio was 2.46.
3. The solution was refluxed at 60°C for two more hours following the addition of NaOH (aq), then set aside to cool.

Solutions made by this procedure remained stable for several weeks. Varying amounts of the simple carboxylic acids listed above were added to separate Al-13 solutions to achieve acid/aluminum ratios ranging from 1:4 up to 1:1. Across all acid/aluminum ratios, the glutaric acid (a dicarboxylic acid) served to immediately precipitate the aluminum oxyhydroxide from solution when added. Butyric acid and hexanoic acid solutions remained clear. Once stabilized, the acid-containing solutions were then titrated with 0.2 M NaOH (aq) to raise the OH/Al ratio in solution. Butyric acid solutions precipitated as the OH/Al ratio approached 2.46; hexanoic acid solutions remained clear up to an OH/Al ratio of 2.46, at which point titration was stopped. The hexanoic acid solutions were stable (e.g., free of visible precipitate) for several weeks. Dynamic light scattering on the hexanoic acid solutions failed to detect any submicron particles in suspension.

These results indicate that short-chain carboxylic acids have a large effect on aluminum oxyhydroxides in solution. We hypothesize that the glutaric acid acts as a bridge molecule, bringing the

aluminum oxyhydroxides near each other through the presence of acid groups at either end of the molecule, thereby facilitating precipitation. The difference in behavior between the butyric acid ($C_4H_8O_2$) and hexanoic acid ($C_6H_{12}O_2$) may be explained by the two-carbon difference between the molecular structures. If so, this indicates the sensitivity of the aluminum oxyhydroxide system to chain length, and provides a direction for additional studies. We plan to characterize the structure of the oxyhydroxide in solution with hexanoic acid by NMR to determine whether the hexanoic acid is indeed stabilizing the Al-13 structure or perhaps maintaining another molecular species in solution.

Planned Activities

1. Map the solubility limit and the phase-stability limit of gibbsite in the presence of silicate by changing its composition and temperature. This study will provide information to SRTC.
2. Achieve phase transition of gibbsite during hydrothermal treatment.
3. Perform simulations studies to support the ESP modeling work at the Hanford Site, in collaboration with Dr. Albert Hu of Lockheed Martin Hanford Company.
4. Perform dissolution and phase transition of zeolites in caustic aluminate solutions.
5. Screen organic molecules as possible complexing agents. Bidentates and polyelectrolytes are two areas we plan to investigate, the latter involving the commercial polymers PMAA and PAA.

Reference

Lafemina JP. 1995. *Tank Waste Treatment Science Task Quarterly Report for April-June 1995*. PNL-10764, Pacific Northwest Laboratory, Richland, Washington.

Publication and Presentation

Liu J, GJ Lumetta, JW Virden, GL Graff, NG Colton, BC Bunker, and JL Krumhansl. 1999. "Characterization of Colloidal Phases in Tank Wastes." To be published in the *Proceedings of American Ceramic Society*, Indianapolis.