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Microstructural Properties of High Level Waste Concentrates and Gels with Raman And Infrared Spectroscopies

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Research Objective

The concentrated caustic waste slurries stored in waste tanks at Hanford and Savannah River have large amounts of aluminate along with nitrate, nitrite, hydroxide, carbonate, and phosphate—all species are present both in solution and as solids. The dominant cation is sodium with few percent potassium and other species. These slurries have sodium concentrations on the order of 10-15 mol/L and therefore very high ionic strengths and low water activities. These slurries have been the source of many safety problems at Hanford and Savannah River Sites and the slurry rheologies, gelling points, and gas retention properties are largely responsible for those safety issues.

Even though both Hanford and Savannah River have produced large volumes of these slurry concentrates, the microstructural properties that are important for understanding slurry behavior are not well understood. For example, aluminate solid formation has been associated with Hanford concentrates, but is not observed at Savannah River. Another example is that although hydrogen gas retention in slurries is a prevailing safety issue at Hanford, it is only a relatively minor issue in SRS tanks.

Research Progress and Implications

This project is in the second year of a three year effort. A very important property of these slurry concentrates is water activity. Water activity is manifest as its vapor pressure in equilibrium with each slurry. We have found that aluminate in both solution and solid have dramatic effects on water activity. For example, the monosodium aluminate solid, MSA, is only stable at around 22% relative humidity at 20° C. If one attempts to store MSA at humidities greater than this equilibrium, the solid rapidly deliquesces or absorbs water until it redissolves.

This behavior of MSA explains why it can never be stored in waste tanks at Savannah River. The seasonal average relative humidity at Savannah River is on the order of 40%, which therefore precludes long term MSA storage.

With increasing aluminate concentration, the aluminate dimerizes thereby releasing water. Concentrating aluminate solutions normally produces increasing amounts of dimer. However, the dimer can only exist in particular ranges of water activity. If the water vapor pressure increases, the solution readily absorbs water as the dimer shifts to the monomer. We have found that the water activity for aluminate solutions can be predicted based on the extent of dimerization as well as excess hydroxide. Thus, a particular aluminate concentration is only stable up to some limiting water vapor.

Precipitation of monosodium aluminate from solution releases water as

The solution aluminate, then, actually ties up much more water than does the MSA solid. The waters of hydration in MSA are strongly hydrogen-bonded in channels within its lattice as shown in [Fig. 1](#).

Fig. 1. View down the unusual ion channel of monosodium aluminate (MSA), tetragonal, $P\bar{4}2_1m$ $Na[AlO_{1.5}(OH)] \cdot 0.75H_2O$.

These waters of hydration are much more strongly perturbed than, for example, waters of hydration in clay minerals. The “free” water is characterized by HOH stretch doublet at 3250 and 3440 cm^{-1} and an HOH deformation at 1660 cm^{-1} . There is a “bound” form of water with a very broad HOH stretch at 3040 cm^{-1} and an HOH deformation shifted to 1590 cm^{-1} . This highly perturbed water is evidently associated with a hydrogen-bonded solution and solid form since these features persist in MSA solid. We have further explored the effect of nitrate, nitrite, and carbonate ions on the solution and slurry properties. Sodium nitrate and nitrite seem to act primarily as diluents when combined with aluminate. The aluminate dimer equilibrium shifts in a manner similar to that of simply diluting with increasing water concentration.

Carbonate ion, on the other hand, has a much more pronounced affect on the solution aluminate equilibrium. The source of carbonate in concentrated wastes has been primarily that absorbed from the atmosphere by reaction with the caustic waste. Aluminocarbonate solids are well known, but the nature of the aluminocarbonate solution interaction in caustic solution is not known. The presence of carbonate somehow destabilizes the aluminate dimer causing a shift back to monomer for reasons that we still do not entirely understand. However, infrared spectroscopy suggests that the carbonate is weakly monodentate in these solutions, showing a doublet absorption at 1380 and 1440 cm^{-1} . This suggests that there is an aluminocarbonate species formed in these solutions.

Planned Activities

We plan to explore the nature of the aluminate in the presence of carbonate and obtain infrared absorption of solutions and solids, and better correlate the water activity with its Raman and infrared features. In particular, we will correlate the two types of water present in these mixtures with the slurry water vapor pressure. Finally, we hope to explore the interaction of soluble organic complexants with aluminate in solution. We feel that there will be an interaction similar to that we observe for carbonate.

Other Access To Information

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