

Project 95016

Precipitation and Deposition of Aluminum-Containing Phases in Tank Wastes

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RESULTS TO DATE: Precipitation and Deposition of Aluminum-Containing Phases in Tank Wastes
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In the first phase of our study, we focused on the use of simple organics to raise the solubility of aluminum oxyhydroxides in high alkaline aqueous solvents. In a limited survey of common organic acids, we determined that citric acid had the highest potential to achieve our goal. However, our subsequent investigation revealed that the citric acid appeared to play two roles in the solutions: first, raising the concentration of aluminum in highly alkaline solutions by breaking up or inhibiting ?seed? polycations and thereby delaying the nucleation and growth of particles; and second, stabilizing nanometer-sized particles in suspension when nucleation did occur. The results of this work were recently published in *Langmuir*: D.M. Dabbs, U. Ramachandran, S. Lu, J. Liu, L.-Q. Wang, I.A. Aksay, "Inhibition of Aluminum Oxyhydroxide Precipitation with Citric Acid" *Langmuir*, 21, 11690-11695 (2005). The second phase of our work involved the solvation of silicon, again in solutions of high alkalinity. Citric acid, due to its unfavorable pKa values, was not expected to be useful with silicon-containing solutions. Here, the use of polyols was determined to be effective in maintaining silicon-containing particles under high pH conditions but at smaller size with respect to standard suspensions of silicon-containing particles. There were a number of difficulties working with highly alkaline silicon-containing solutions, particularly in solutions at or near the saturation limit. Small deviations in pH resulted in particle formation or dissolution in the absence of the organic agents. One of the more significant observations was that the polyols appeared to stabilize small particles of silicon oxyhydroxides across a wider range of pH, albeit this was difficult to quantify due to the instability of the solutions. In our previous 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 micrometer and 1.50 micrometer 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 ratio 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 micrometer regardless of polyol used. Laser light scattering has a detection limit of around 3-5nm diameter, so the apparent absence of particles cannot be interpreted as the complete dissolution of the particles. Light scattering, as used in the previous aluminum oxyhydroxide systems, was crippled by the loss of the instrumentation for several months, and efforts were directed to correcting this. We are in the process of upgrading our light scattering facility and it should be back online by the end of the report period. Our current plans involve the solubility of aluminosilicon oxyhydroxides. As with the silicon solutions, these systems are very sensitive to small changes in pH. Literature values are inconsistent and little work appears to exist at high pH. To date, our experience has demonstrated that such solutions are very unstable in the absence of organic agents, easily precipitating to form insoluble scales on container surfaces or forming particles which all too often agglomerate to form gels. We are working on improving our solution preparation procedures to get a viable series of baseline measurements. Solutions studies using CIR-IR in a modified CIRcle (registered trademark) cell are also underway. For the near term we are continuing our work with the aluminosilicon oxyhydroxide solutions and polyols. Another system of interest are the so-called ?sugar acids?, such as gluconic, saccharic and glucoheptonic acid, which show great affinity for aqueous silicate anions at high pH (S.D. Kinrade et al., ?NMR evidence of penta-oxo organosilicon complexes in dilute neutral aqueous silicate

solutions? Chem. Commun., 2001, 1564-1565). Our interest in these compounds dovetails with another project within our laboratory. Coincident with the work on aluminum remediation, our group has been working on corrosion inhibition using organic surfactants, in collaboration with Harvard University and sponsored by ARO/MURI. Although the primary interest here is in the corrosion of copper, the study includes aluminum surfaces as well. The sugar acids have been found to inhibit corrosion rates on aluminum substrates at low pH and a series of measurements is now underway at high pH. Surface analysis using ATR-IR is being tested as a method for determining surfactant content on the metal surfaces (N. Teelucksingh and K. B. Reddy, ?Pharmaceutical Ingredients on Metal Surfaces Using a Mid-IR Grazing Angle Fiber Optics Probe? Spectroscopy 20, 16-22 (2005)). We expect to extend this technique to the study of aluminosilicate surfaces exposed to high pH.

DELIVERABLES: D.M. Dabbs, U. Ramachandran, S. Lu, J. Liu, L.-Q. Wang, I.A. Aksay, "Inhibition of Aluminum Oxyhydroxide Precipitation with Citric Acid" Langmuir, 21, 11690-11695 (2005).

Abstract: Citric acid has been shown to act as an agent for increasing the solubility of aluminum oxyhydroxides in aqueous solutions of high (>2.47 mol/mol) hydroxide-to-aluminum ratios. Conversely, citric acid also colloidally stabilizes particles in aqueous suspensions of aluminum-containing particles. Solutions of aluminum chloride, with and without citric acid added, were titrated with NaOH (aq). The presence and size of particles were determined using quasi-elastic light scattering. In solutions that contained no citric acid, particles formed instantaneously when NaOH (aq) was added but these were observed to rapidly diminish in size, disappearing at OH/Al ratios below 2.5 mol/mol. When the OH/Al ratio was raised beyond 2.5 by adding more NaOH (aq), suspensions of colloidally stable particles formed. Large polycations containing 13 aluminum atoms were detected by ^{27}Al solution NMR in citric-acid-free solutions with OH/Al ratios slightly lower than 2.5. In comparison, adding citric acid to solutions of aluminum chloride inhibited the formation of large aluminum-containing polycations. The absence of the polycations prevents or retards the subsequent formation of particles, indicating that the polycations, when present, act as seeds to the formation of new particles. Particles did not form in solutions with a citric acid/aluminum ratio of 0.8 until sufficient NaOH(aq) was added to raise the OH/Al ratio to 3.29. By comparison, lower amounts of citric acid did not prevent particles from forming but did retard the rate of growth.