Project 90162

Physical Properties of Hanford Transuranic Waste Sludge

Berg, John C.
University of Washington

RESULTS TO DATE: Equipment that was purchased in the abbreviated year 1 of this project has been used during year 2 to study the fundamental behavior of materials that simulate the behavior of the Hanford transuranic waste sludge. Two significant results have been found, and each has been submitted for publication. Both studies found non-DLVO behavior in simulant systems. These separate but related studies were performed concurrently. It was previously shown in Rassat et al.'s report Physical and Liquid Chemical Simulant Formulations for Transuranic Wastes in Hanford Single-Shell Tanks that colloidal clays behave similarly to transuranic waste sludge (PNNL-14333, National Technical Information Service, U.S. Dept. of Commerce). Rassat et al. also discussed the pH and salt content of actual waste materials. It was shown that these materials exist at high pHs, generally above 10, and at high salt content, approximately 1.5 M from a mixture of different salts. A type of clay commonly studied, due to its uniformity, is a synthetic hectorite, Laponite. Therefore the work performed over the course of the last year was done mainly using suspensions of Laponite at high pH and involving high salt concentrations. One study was titled "Relating Clay Rheology to Colloidal Parameters." It has been submitted to the **Journal of Colloid and INterface Science** and is currently in the review process. The idea was to gain the ability to use measurable quantities to predict the flow behavior of clay systems, which should be similar to transuranic waste sludge. Leong et al. had previously shown that the yield stress of colloidal slurries of titania and alumina could be predicted, given the measurement of the accessible parameter zeta potential (Leong YK et al. J Chem Soc Faraday Trans, 19 (1993) 2473). Colloidal clays have a fundamentally different morphology and surface charge distribution than the spheroidal, uniformly charged colloids previously studied. This study was therefore performed in order to determine the applicability of the previous findings to the systems of interest. The yield stress of clay slurries was measured using the Physica MCR 300 purchased in year 1 of this project. The zeta potential of these systems was then measured using the Brookhaven Zeta PALS, also purchased in year 1. These two parameters were then plotted and compared with the Leong result. It was found that this system behaved in a non-DLVO manner. Leong found that colloidal slurry yield stress decreases with increased zeta potential which is consistent with the DLVO theory's assertion that particle attractions decrease as their electrostatic repulsion increases. Clay systems, however, show an increase in yield stress as zeta potential is increased. This is due to the nature of the charge distribution on the surface of clay particles. Clay particles are in the form of platelets. It is generally accepted that the charge on the face of the platelet is negative and the charge on the edge of the platelet is positive. This can lead to electrostatic attractions between particles which would increase in strength as the magnitude of the charge on the face or edge is increased. In this case the van der Waals and electrostatic forces are additive unlike the DLVO case where these forces compete. Leong et al. wrote an equation that related slurry yield stress to the number and strength of particle interactions based on DLVO where electrostatic forces were subtracted from van der Waals. In this work Leong et al.'s equation was modified to make these two forces additive. The resulting equation was compared to laboratory data and showed good agreement. A system of naturally occurring clays, kaolinites and bentonites, was used to help confirm the result. The experimental data from this system also fit the model well. These results are thought to be a significant contribution to the field and have been submitted for publication. Beyond being interesting academically, these results have implications for designing processes for the removal of transuranic wastes from storage tanks. In particular it may not be intuitive to think that dilution of sludge may actually make moving the sludge more difficult. The yield stress of these systems increases as zeta potential increases. Zeta potential increases as salt concentration decreases. Therefore, as water is added to the system, thereby decreasing salt concentration, the yield stress of transuranic wastes may actually increase. Fortunately, there is a significant competing effect. The yield stress is directly related to the square of the volume fraction of solids available, which would tend to reduce yield stress as water is added. The proposed relation accounts for this volume fraction dependence and could potentially be used to determine an optimum dilution for waste removal. The second study, titled "Re-stabilization of Laponite Clay Particles in High Salt Media," also showed a non-DLVO phenomenon. The paper was submitted for publication in the Journal of Colloid and Interface Science and is currently in the review process. The Zeta PALS was used to characterize aggregation behavior of the simulant material, Laponite slurries, in conditions similar those found in storage tanks (high salt and pH). The results of the study were written and submitted for publication. It was demonstrated that in high salt and high pH media, specific salts slow the aggregation rates, or re-stabilize, colloidal suspensions leading to the formation of compact aggregates mimicking behavior typically observed at very low salt concentrations. This stands in contrast to the classical theory applied in the description of colloidal stability, DLVO theory, i.e., once the surface charge of the particles has been screened by counterions in solution, further addition of salt should not slow down the expected rapid aggregation. This finding in addition to the expected microstructure of aggregates in different salt concentrations advanced the knowledge needed in the efforts to transport and package the waste for permanent disposal. Specifically it was shown that under certain conditions aggregates may exist in a more dense state than predicted by the classical theory. Over the course of the second year of this project significant progress has been made. The equipment purchased in year 1 has been used to perform fundamental studies of systems that simulate transuranic waste behavior. These studies have resulted in significant contributions to the field of colloid science as well as produced results that may prove important in handling actual waste materials. The work over the course of this past year has been significant and sufficient to submit two separate journal articles.

DELIVERABLES: A study relating TRU waste simulant rheological parameters to accessible colloidal properties was submitted for publication to the Journal of Colloid and Interface Science on July 7, 2005 under the title Relating Clay Rheology to Colloidal Parameters with the authors P. B. Laxton and J. C. Berg. The abstract was submitted as follows: The ability to predict rheological behavior of clay dispersions would be useful in formulating systems rheologically modified by clays as well as designing equipment to handle clay based materials. Deriving predictive equations for these materials has been hindered by poor understanding of the mechanism by which clay systems develop microstructure. This work seeks to observe the relationship between the yield stress and the zeta potential and determine the nature of the particle interactions for dispersions of Laponite synthetic clay) and dispersions of a mixture of naturally occurring kaolinites and bentonites. It is found that the relationship of yield stress to the squared zeta potential for clay suspensions is opposite to that found for homogeneously charged spheroidal colloids. This result can be traced to the type of particle interactions occurring, which for the systems studied appear to be edge-to-face attractions.

Also submitted to the Journal of Colloid and Interface Science was a paper describing a study of the phenomenon of restabilization of clay dispersions in high salt media. This paper was submitted on June 20, 2005 under the title Restabilization of Laponite Clay Particles in High Salt Media by the authors A. Y. Huang and J. C. Berg. The abstract was submitted as follows: The present work characterizes the aggregation behavior of Laponite RD clay particles in barium chloride solutions. Aggregation kinetics in conjunction with the resulting cluster structure are utilized to describe the growth process of these disk-like colloids. Two distinct, limiting regimes (reaction limited and diffusion limited cluster-cluster aggregation) are identified for this system with the Derjaguin-Landau-Verwey-Overbeek (DLVO) theory used to describe the interaction between colloids. However, aggregation rate in high salt media unexpectedly decreases (restabilization) even though electrostatic repulsion has completely been screened out. This slow down results in more compact structure resembling the cluster structure often observed for reaction limited cluster-cluster aggregation. Non-DLVO forces, explained in terms of a polarization theory proposed by Manciu and Ruckenstein, are believed to be the cause of restabilization. Zeta potentials measurements show that charge reversal does not occur in high salt concentrations supporting the polarization theory. In addition, aggregation kinetics for two different suspension methods is examined. Comparison of the two cases suggests that dispersing Laponite at pH 10, which prevents dissolution of particles, deprotonates the hydroxyl groups on the edge of the face requiring more electrolyte to screen out a more negative surface charge.