

**FY-04 Annual Report: Physical Properties of Hanford Transuranic Waste Sludge**  
**EMSP Project Number: 90162**  
**Lead PI: A.P. Poloski, Pacific Northwest National Laboratory, WA**

## **RESEARCH OBJECTIVES**

This project has two primary objectives. The first is to understand the physical properties and behavior of the Hanford transuranic (TRU) tank sludges under conditions that might exist during retrieval, treatment, packaging, and transportation for disposal at WIPP. The second primary objective is to develop a fundamental understanding of these sludge suspensions by correlating the macroscopic properties with particle interactions occurring at the colloidal scale in the various liquid media. The results of this research effort will enhance the existing understanding of agglomeration phenomena and the properties of complex colloidal suspensions. In addition, the knowledge gained and capabilities developed during this effort will aid in the development and optimization of techniques to process the wastes at various DOE sites. These objectives will be accomplished by: 1) characterizing the TRU sludges contained in the Hanford tanks that are intended for shipment to WIPP; 2) determining the physical behavior of the Hanford TRU tank sludges under conditions that might exist during treatment and packaging; 3) and modeling the retrieval, treatment, and packaging operations that will be performed at Hanford to dispose of TRU tank sludges.

## **RESEARCH PROGRESS AND IMPLICATIONS**

As of September 2004 (i.e. 1 year of a 3 year project), four main tasks have started. Progress and implications of each of these tasks are summarized below:

1. **Physical and Rheological Data for Actual TRU Waste** - The first task is to gain basic physical property data on actual TRU sludges that are the focus of this EMSP proposal. In order to maximize the usefulness and applicability of this data the TRU sludges selected for study are significant to the current Hanford cleanup process. CH2M HILL Hanford Group, Inc. (CH2M HILL) is in the process of identifying and developing supplemental process technologies to accelerate the Hanford tank waste cleanup mission. A range of technologies are being evaluated to allow disposal of Hanford waste types, including TRU process wastes. For the TRU process wastes, the current tank retrieval process is a water dilution and pumping system. Thirteen Hanford waste tanks have been identified as containing waste that may meet the criteria for designation as TRU waste. Samples from four of these TRU tanks have been previously studied at Pacific Northwest National Laboratory (PNNL) in support of the CH2M HILL retrieval activities. These tanks include B-203, T-203, T-204, and T-110. For tank retrieval purposes, PNNL developed correlations between rheological properties and dilution level. The correlations have been reported to CH2M HILL in previously published PNNL reports. However these correlations are suitable for engineering and not research purposes. Therefore, these data were augmented with additional experimental data to prepare updated correlations based upon current models in the rheological literature. The supplemental experimental data obtained include density of interstitial liquid, density of dried dissolved solids, density of dried TRU sludge, and particle size distribution. These data allowed for the calculation of mass and volume fraction of solids in the sludge samples at each dilution level which are typically correlated with rheological data. Additionally, particle size and shape information can be obtained from these measurements.

Actual TRU sludge flow curve data follows the Bingham Plastic rheological model. These data were fit with correlations previously developed in the rheological literature between Bingham plastic consistency and yield stress against reduced volume fraction solids (e.g. volume fraction solids / volume fraction solids at maximum packing). Mathematically, these correlations were developed for situations where the interstitial liquid composition remains constant. For tank retrieval, a water dilution process will be used that changes interstitial liquid composition. This limits the direct applicability of these correlations. Despite this fact, good agreement was observed between the Bingham consistency parameter and reduced solids loading correlations. Since the model used to develop these correlations is similar to the Krieger-Dougherty equation which assumes non-interacting solid particles, the Bingham consistency data for Hanford TRU sludges appears to be primarily frictional based and is a weak function of dissolved species composition. Therefore, a master curve for Bingham consistency of TRU sludges has been identified as a function of moisture content. For the Bingham yield stress parameter, a relatively good fit is obtained with previously developed empirical models. Again, these empirical models are a function of reduced solids loading and do not consider inter-particle forces governed by interstitial

liquid species composition. A subtask with the purpose of considering these aspects and improving these models is described in subtask 3 below.

Shear strength of the TRU sludge is a significant property during tank retrieval and various process restart operations. The empirical model for Bingham plastic yield stress as a function of solids loading provides a relatively good fit for shear strength data of TRU sludges. Again, an improved model based on physical models should be developed to predict shear strength under various processing conditions. A subtask with the purpose of developing this model is described in subtask 4 below.

The particle size distribution of the TRU tank sludges is predominantly a bimodal distribution of particles with one mode peak at approximately 10  $\mu$ m and another peak at approximately 100  $\mu$ m. As the level of water dilution increases the relative amount of 100  $\mu$ m mode particle decreases indicating solids dissolution in this size range. Particle shape data indicate that the sludges consist of particles with an aspect ratio significantly greater than unity. This suggests the presence of oblate spheroid particles. The maximum volume packing of oblate spheroid particles is relatively low values (< 30%) and is consistent with calculated values from physical properties measurements. Since maximum packing of solids is a significant parameter in the rheological models and particle shape greatly affects this value, particle shape effects on rheological parameters should be further investigated.

- 2. Anisotropic Plastic Deformation of Colloids due to Alpha Radiation** - Recently published data indicate that colloid particles can deform under the influence of ion irradiation. The data presented show the formation of oblate spheroid silica and titania particle under Xe irradiation. The authors developed a model for this deformation based on the electronic stopping of the ions in the colloid particles. In the immediate vicinity of the ion path, the colloid melts and solidifies on a time scale of nanoseconds. This melting and solidification process creates a cumulative stress on the colloid particle that deforms the particle over time. For TRU tank sludges, a high degree of  $\alpha$  radiation may provide a similar mechanism for deformation. Using the published model with  $^{238}\text{Pu}$   $\alpha$  radiation rather than Xe ion irradiation, a fluence of approximately  $10^{15} \text{ cm}^{-2}$  would be required before significant deformation is observed. Considering the relatively high degree of TRU isotopes in the sludge and the creation date of these wastes (1940s-1950s), fluences of this magnitude are expected in the actual waste and provide a potential mechanism for the creation of oblate spheroids in the TRU sludge.
- 3. Mechanistic Modeling of Flow Curves** – As discussed in subtask 1, interstitial liquid composition is significant to inter-particle forces in TRU sludges. Additionally, particle shape is critical to maximum packing fraction of the solid phase. Both of these parameters have an effect on the flow behavior of TRU sludges. Professor John Berg at the University of Washington is investigating the effects of these parameters under a collaborative DOE grant (DE-FG02-04ER63796). Model slurries with various particle shapes and liquid phase compositions have been identified. Rheological properties of these model systems will be examined for model development. For more information, the annual report for the University of Washington grant can be seen as attachment 1.
- 4. Mechanistic Modeling of Shear Strength** – As discussed in subtask 1, shear strength data of TRU sludges has only been modeled empirically rather than mechanistically. Recently published data on shear strength of bimodal slurries, such as the Hanford TRU sludges, indicate two primary physical origins for shear strength, inter-particle friction and bonding due to static and Vander Waals forces. If the large particles in the slurry settle and come into direct contact with one another, frictional forces become significant. If the large particles remain suspended in the slurry, inter-particle bonding is the significant shear strength regime. Shear strength measurements on a bed of dry glass beads were used to investigate the frictional origins of shear strength. A model based on Janssen's law of stress distribution of granular materials was developed to explain the measured shear strength behavior. A journal article presenting these results has been written and is in the process of being submitted to the *Journal of Rheology*. Attachment 3 is the abstract from this journal article. Investigation of the settling criteria for large particles suspended in non-Newtonian fluids was investigated by University of Washington. A new settling criterion based on the ratio of the viscous and elastic behavior of the suspending gel was established from this investigation. A journal article detailing these results was submitted to *Journal of Colloid and Interfacial Science*. Attachment 2 is the abstract from this journal article. Several models have been previously published describing the shear strength regime based on inter-particle bonding. Future work will focus on combining all of these aspects into a unified model for shear strength of bimodal slurries.

## PLANNED ACTIVITIES

1. **Physical and Rheological Data for Actual TRU Waste** – In FY05, additional physical and rheological characterization data will be obtained on the Hanford TRU sludge. Zeta potential measurements will be performed to quantify the inter-particle forces. Oscillatory rheometry techniques will be performed on the samples to measure the ratio of viscous to elastic behavior of the TRU sludges to determine settling criterion for large particles. The solid phases present in the slurries will be examined using microscopy techniques to identify the type, size, and shape of the particle present in the TRU sludges. Chemical and radiochemical analysis will be performed on separately the liquid and solid phases to identify significant species present in each phase.
2. **Particle Deformation Due to Alpha Radiation** – In FY05-FY06, anisotropic plastic colloid deformation due to  $^{238}\text{Pu}$   $\alpha$  radiation will be examined. A proposal will be placed with the [ATLAS facility](#) at Argonne National Laboratory to irradiate silica and titania particles to fluences in the range of  $10^{15} \text{ cm}^{-2}$  with He-4 nuclei at energies to mimic natural  $^{238}\text{Pu}$   $\alpha$  radiation. The particles will be examined for particle deformation. If particle deformation occurs, an anisotropic plastic deformation mechanism for colloids under  $\alpha$  irradiation will be confirmed. This deformation would explain rheological aging effects for Hanford tank wastes. Follow on work in FY06 would include precipitation of TRU simulant colloids doped with  $^{238}\text{Pu}$ . Colloid shape would be monitored as a function of time to confirm the presence of anisotropic plastic deformation in Hanford TRU waste tanks. Lastly, computer simulations of this irradiation process would be performed to predict geometric effects of this in large scale Hanford waste tanks.
3. **Mechanistic Modeling of Flow Curves** – In FY05-FY06, investigation of the influence of particle size, shape and interstitial liquid composition will be performed at the University of Washington. See attachment 1 for further details on these activities.
4. **Mechanistic Modeling of Shear Strength** – In FY05 a unified model for shear strength capturing frictional, inter-particle bonding and gel trapping components for bimodal slurry systems will be mathematically developed. In FY05-FY06 this mathematical model will be tested with model bimodal slurry systems likely consisting of large glass beads and smaller clay particles. This work will be performed at both PNNL and University of Washington.

## INFORMATION ACCESS

Data is available upon request to the principle investigator, Adam Poloski ([adam.poloski@pnl.gov](mailto:adam.poloski@pnl.gov) ; 509-376-1684)

## OPTIONAL ADDITIONAL INFORMATION

- ?? Attachment 1 is a summary of FY04 activities for the University of Washington activities funded under DOE grant no. DE-FG02-04ER63796.
- ?? Attachment 2 is an abstract for a University of Washington authored paper submitted to *Journal of Colloid and Interfacial Science* in collaboration with this EMSP project under DOE grant no. DE-FG02-04ER63796.
- ?? Attachment 3 is an abstract for a PNNL authored paper submitted to *Journal of Rheology* in under this EMSP project.

## OPTIONAL PROPRIETARY INFORMATION

Not applicable.

## Attachment 1

Since the start of this project in March of 2004 two main goals have been achieved. First, the laboratory facilities of the Center for Surfaces, Polymers and Colloids (SPC) at the University of Washington have been updated with the purchase and installation of two state-of-the-art analysis tools. Second, a study of the sedimentation behavior of high density colloidal solids in complex media has been performed. The results of this study were presented at the 78th ACS Colloid and Surface Science Symposium at Yale University in New Haven, CT, and have been submitted for publication to the Journal of Colloid and Interface Science. Both the new equipment and the results of the initial study will help to gain insight into the physical properties of Hanford transuranic waste sludge.

The first piece of equipment purchased was the Brookhaven Zeta PALS. The Zeta PALS has been installed and professional training in its operation has taken place. This tool has a wide range of capabilities that will prove vital to the project. First, it can operate in a dynamic light scattering (DLS) mode. This mode of operation provides quick particle size information when the standard photon correlation analysis is used. DLS has also been used in the past to perform analyses that provide other system information that could be useful in this project.

The second and more exceptional capability of the Zeta PALS is phase analysis light scattering (PALS). This type of light scattering is used in combination with an electrophoretic cell where zeta potential measurements can be performed. The unique PALS system allows for the measurement of very low zeta potentials previously inaccessible by traditional zeta potential analysis tools. This is essential for this project since the Hanford transuranic waste sludge is a system of colloidal solids in a high salt medium. These types of systems typically have imperceptibly small zeta potentials. However, the Zeta PALS system should allow measurement of zeta potentials in these types of systems. Zeta potential studies of waste sludge simulants in combination with rheological and other light scattering studies will provide insight into the cause and rate of aggregate formation under quiescent conditions as well as under shear.

The second piece of equipment purchased was the Physica Modular Compact Rheometer (MCR) 300. This instrument has been installed and professional training has taken place. The major reason for choosing this particular rheometer is its modular design. This feature allows for future add-ons that will likely prove indispensable for research in this project.

The MCR 300 is a versatile device that will measure system response to multiple types of applied force. It is capable of running in a controlled strain as well as controlled stress modes which give stress-strain curves and viscosity as a function of either stress or strain rate. The MCR 300 will also run in an oscillatory mode which gives us the capability of probing the viscoelastic nature of a sample. These types of measurements can be made on any of four different measuring systems each with their own benefits. A temperature control unit for this rheometer is a valuable addition to the lab that will help investigate the dependence of rheological properties on system temperature.

The modular nature of this unit will become important when optical access capabilities are installed. There is an off the shelf small angle light scattering (SALS) unit that can be attached to the rheometer making what is referred to as rheo-SALS measurements possible. This along with direct microscopic optical access to samples under shear will make it possible to investigate the relationship between rheological properties and colloid aggregate structure. Also aggregate formation and structure under shear will be directly observable. This capability will make a large impact in learning about the physical nature of Hanford transuranic waste sludge.

Over the past five months while this equipment were being chosen, specified, purchased, installed, and trained upon, there was experimental work going on with existing SPC center lab equipment. This work was concerned with the sedimentation behavior of heavy, or dense, colloids in complex media. It was found that the current criterion for stability against sedimentation was not sufficient to predict stability. These results could provide useful insight into the sedimentation behavior of tank wastes.

Model systems of large dense colloidal spheres suspended in a fluid with a yield stress were studied. Rotational and oscillatory rheometry in combination with sedimentation and centrifugation experiments were performed to investigate the validity

of the accepted criterion for sedimentation stability. It was previously argued that if the normal force due to the yield stress of a suspending medium is greater than the gravitational force on a suspended particle then the particle would be suspended indefinitely. It was found, however, that this condition is not sufficient. A second requirement for stability against sedimentation involves the viscoelastic character of the suspending medium. For a medium to prevent the sedimentation of a suspended particle the elastic nature of the medium must dominate the viscous nature. This can be easily quantified by the loss tangent with the critical value being unity. That is, if the loss tangent is greater than one the suspension is unstable and will settle under gravity. As mentioned, these results were presented at a major symposium and have been submitted for publication in a well respected scientific journal.

Over the initial five months of the project significant progress has been made. The laboratory is now ideally set up for the type of fundamental work that will be necessary in this project. Also, enough research progress has been made to publish a full journal article.

## Attachment 2

Work concerning sedimentation behavior of dense colloids in complex media was presented at the 78th ACS Colloid and Surface Science Symposium at Yale University in New Haven, CT. It was presented on Tuesday June 22, 2004 at 4:20 pm under the title **Gel Trapping of Dense Colloids** as paper #404 with authors P.B. Laxton and J.C. Berg. The abstract was submitted as follows:

Phase density differences in sols, foams, or emulsions often lead to sedimentation or creaming, causing problems for materials where spatial uniformity is essential. The problem may be addressed through the use of rheology modifiers in the continuous phase. Weak polymer gels have found use for this purpose in the food industry. They appear to be capable of trapping dispersoid particles in a three-dimensional matrix under quiescent conditions, while producing water-like viscosities at low shear. Attempts to predict sedimentation stability in terms of particle properties (size, shape, density difference) and gel yield stress, however, have led to only mixed success. The present work seeks to determine useful stability criteria under both quiescent and shear conditions in terms of readily-accessible viscoelastic descriptors. Results are reported for systems consisting of 10.5 micrometer polymethylmethacrylate (PMMA) spheres dispersed in aqueous gellan gum. Monovalent salt concentration is varied to control rheological properties, and sedimentation/centrifugation experiments are performed to determine dispersion stability. Necessary and sufficient conditions for stability consist of a minimum yield stress together with a value of the loss tangent less than unity.

This same work was submitted for publication to the Journal of Colloid and Interface Science on July 22, 2004. With the same title as the presentation, **Gel Trapping of Dense Colloids**, and the same pair of authors Peter B. Laxton and John C. Berg. The abstract was submitted as follows:

Phase density differences in sols, foams, or emulsions often lead to sedimentation or creaming, causing problems for materials where spatial uniformity over extended periods of time is essential. The problem may be addressed through the use of rheology modifiers in the continuous phase. Weak polymer gels have found use for this purpose in the food industry where they appear to be capable of trapping dispersoid particles in a three-dimensional matrix while displaying water-like viscosities at low shear. Attempts to predict sedimentation stability in terms of particle properties (size, shape, density difference) and gel yield stress have led to qualitative success for suspensions of large particles. The effect of particle size, however, in particular the case in which colloidal dimensions are approached, has not been investigated. The present work seeks to determine useful stability criteria for colloidal dispersions in terms of readily-accessible viscoelastic descriptors. Results are reported for systems consisting of 12 micrometer poly(methyl methacrylate) (PMMA) spheres dispersed in aqueous gellan gum. Monovalent salt concentration is varied to control rheological properties, and sedimentation/centrifugation experiments are performed to determine dispersion stability. Necessary conditions for stability consist of a minimum yield stress together with a value of the loss tangent less than unity.



## Attachment 3

Work concerning frictional aspects of shear strength behavior is going to be submitted to the Journal of Rheology. The title of the paper is **A Janssen's Law Model for Shear Strength of Granular Materials**. Authors are Adam Poloski, Paul Bredt, and Nathan Lester. The abstract is as follows:

In an effort to better understand shear strength measurements using a vane impeller two equations describing a frictional based mechanistic model of granular materials were derived. A hydrostatic pressure profile as a function of vane depth and a pressure profile for granular materials described by the Janssen equation were the basis for the two equations. These equations can be used to calculate expected torque values during shear vane measurements. To test these equations, shear vanes of various dimensions were attached to a Haake M5 viscometer. The shear vanes were immersed to a known depth, rotated at a constant rate, and a resulting torque versus time profile was obtained. Peak and equilibrium values were determined from the torque/time profiles corresponding to the static and kinetic frictional cases respectively from the mechanistic equations. A least squares regression was performed on the experimental data to calculate two fitting parameters in the mechanistic equations. These fitting parameters represent 1) the number and orientation of contact points in a differential element on the surface area of the cylinder formed by rotating the vane 2) the ratio of the lithostatic axial stress to radial stress that Janssen demonstrated as significant to granular materials. Good agreement,  $\pm 15$  to 40% , is observed between the measured and modeled kinetic values using these

techniques. This agreement demonstrates an initial understanding of granular material mechanics during shear vane measurements.