

Colloidal Agglomerates in Tank Sludge: Impact on Waste Processing

Pacific Northwest National Laboratory
June 1, 1997

Progress Report

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Research Objective

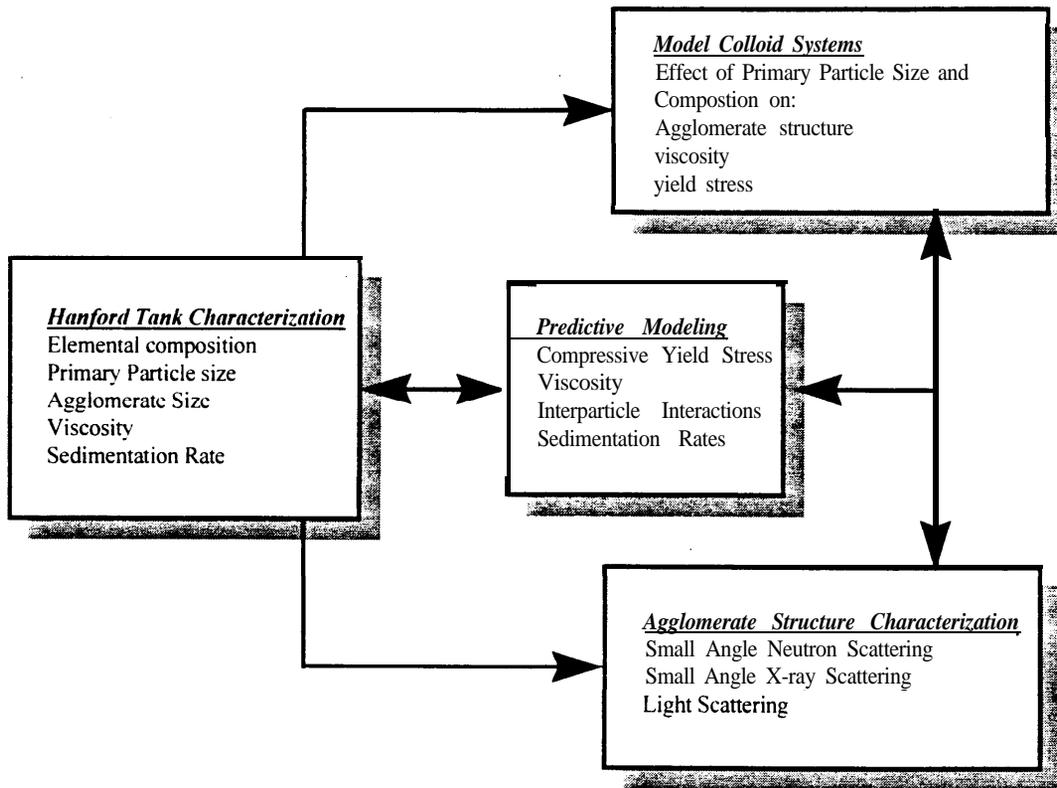
Disposal of millions of gallons of existing radioactive wastes is a major remediation problem for the Department of Energy (DOE). Although radionuclides are the most hazardous waste constituents, the components of greatest concern from a waste processing standpoint are insoluble sludges consisting of submicron colloidal particles. Depending on processing conditions, these colloidal particles can form agglomerate networks that could clog transfer lines or interfere with solid-liquid separations such as settle-decant operations. Under different conditions, the particles can be dispersed to form very fine suspended particles that will not create sediment in settle-decant steps and that can foul and contaminate downstream treatment components including ion exchangers or filtrations systems. Given the wide range of tank chemistries present at Hanford and other DOE sites, it is impractical to measure the properties of all potential processing conditions to design effective treatment procedures. Instead, a framework needs to be established to allow sludge property trends to be predicted on a sound scientific basis. The scientific principles of greatest utility in characterizing, understanding, and controlling the physical properties of sludge fall in the realm of colloid chemistry. The objectives of this work are to accomplish the following:

- understand the factors controlling the nature and extent of colloidal agglomeration under expected waste processing conditions
- determine how agglomeration phenomena influence physical properties relevant to waste processing including rheology, sedimentation, and filtration
- develop strategies for optimizing processing conditions via control of agglomeration phenomena.

Research Statement

Technical Approach

The technical approach is shown schematically below. This project will use characterization data obtained from *real* Hanford tank sludge samples to guide and validate all model studies. The physical characterization data obtained on real tank sludge will be utilized in three areas: model colloid systems, predictive modeling, and agglomerate structure characterization. Model colloidal systems will investigate the effect of particle size, solid loadings, agglomerate structure, and particle composition on dispersion rheology and sedimentation behavior as a function of proposed processing conditions. Agglomerate structure will utilize Small Angle Neutron Scattering (SANS, Oak Ridge National Laboratory [ORNL]), Small Angle X-ray Scattering (SAXS, Pacific Northwest National Laboratory [PNNL]), and light scattering (Sandia National Laboratory [SNL]) to characterize agglomerate structure. The information discovered in model colloid systems and agglomerate structure will serve as input into the predictive modeling task. The predictive modeling task will be compared to such measurements as viscosity and sedimentation rate on Hanford tank waste.



Research Progress

Project Status

This project was initiated in FY97 and is being performed cooperatively with PNNL, SNL, and the University of Washington. The small angle neutron scattering facility at ORNL is being utilized for sample characterization.

Progress in the first six months has focused on characterization and modeling of colloidal systems similar to those found in Hanford tank waste. Experimental and modeling work is ongoing at PNNL and the University of Washington. Initial results have revealed a restabilization of colloidal dispersions at high salt concentrations. These results are very interesting and will require further study to fully explain. A series of computer programs are being developed based on the Brownian dynamics method to simulate the formation of colloidal gels and determine their physical properties. Brownian dynamics simulations is proving to be a useful tool for understanding the link between microstructure and the physical properties of a suspension or gel.

In the second half of FY97, SNL will have received their funding and will be focusing on modeling and validating colloidal agglomerate structures under a variety of conditions. Results from SANS will be interpreted and used to correlate agglomerate structure for colloidal dispersion under different solution conditions. The SAXS equipment at PNNL will be operational and

will investigate the relationship between agglomerate structure and colloidal dispersions. Work on model colloidal systems and the modeling dispersion behavior will continue. Specific results are described in detail below.

Technical Progress

Model Colloid Systems

The primary emphasis of the colloidal studies work has been the investigation of binary colloid systems at solution pH (pH=12-13.5) and salt concentrations (2-5M NaNO₃) analogous to conditions existing in Hanford waste storage tanks. Sedimentation, particle size determination, and rheological measurements were used to probe the agglomeration, particle packing, and flow behavior of Al- and Fe- hydroxide mixtures in addition to aluminum hydroxide suspensions containing varying ratios of large (1.3 mm) and small (50 nm) particles. Initial experiments were also conducted to investigate the effect of high electrolyte concentration (2-5M) on the sedimentation and rheological properties of nanometer- and micron-sized particles at high solution pH.

Gibbsite: Ferrihydrite Binary Mixtures

Previous work⁷ has shown that the presence of very small quantities (<1 volume %) of nanometer-sized particles can have dramatic effects on the sedimentation, filtration, rheological, and consolidation behavior of sediments and suspensions. Any condition such as dissolution of larger particles, separation of hard agglomerates, or dissolution/reprecipitation reactions that increase the volume fraction of fines in suspension or decrease the overall particle size could significantly affect the colloidal behavior of the system. Of particular concern are possible reactions between alumina or silica and other colloids existing in the tanks upon mixing and/or transport, because the solubility of Al³⁺ is high at pH 13 (> 10⁻³M). Elemental chemical analysis and Transmission Electron Microscopy/Energy Dispersive X-Ray Spectroscopy (TEM/EDS) investigations performed on core tank samples have shown aluminum and iron to be major components in the insoluble fraction of many tank sludges. For this reason, we are investigating the sedimentation, agglomeration, and viscosity behavior of binary mixtures containing Al and Fe hydroxides.

For these studies, a commercially available gibbsite (Al(OH)₃) powder (Alcoa S-3) with mean particle size of 1.3 mm was mixed with a hydrated ferrihydrite (Fe(OH)₃) slurry (Noah) containing hard agglomerates (1.6 mm) of nanometer-sized primary particles (approximately 50 nm). 1 volume % (total solids loading) suspensions were prepared with varying ferrihydrite:gibbsite (Fe:Al) ratios and aged at 22°C and 40°C. Figure 1 shows the sedimentation behavior of the Fe:Al mixtures as a function of time at ratios from 0: 100 to 100:0 volume percent. The sediment cake volume increases in proportion to the concentration of nanometer-sized ferrihydrite in the mixture with little or no effect of time or temperature on this trend. The introduction of small particles typically leads to lower packing densities in sediments due to the open, ramified nature of the agglomerates formed. The trend measured in the sedimentation experiments was also seen using viscosity measurements. Figure 2 shows the viscosity measured

on 1 volume % Fe:Al slurries after 5 days of stirring at room temperature. As the concentration of fine particles in suspensions increases, the viscosity increases and the particle-packing density decreases, consistent with an increasing number of loosely packed aggregates in suspension. Future efforts will focus on measuring agglomerate structure of these dispersions and relating structure to measured properties.

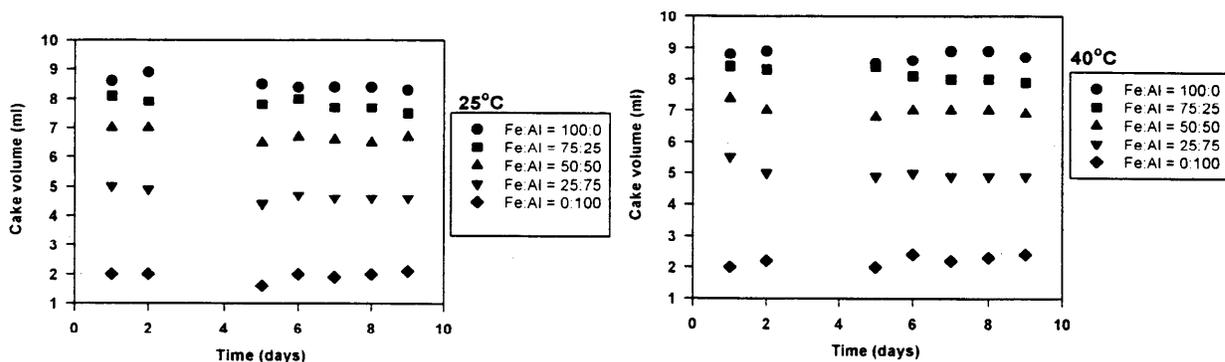


Figure 1. Sediment Volume Measured for Binary Ferrihydrite: Gibbsite Mixtures. 1 volume % total solids loadings, 10 ml total sample volume.

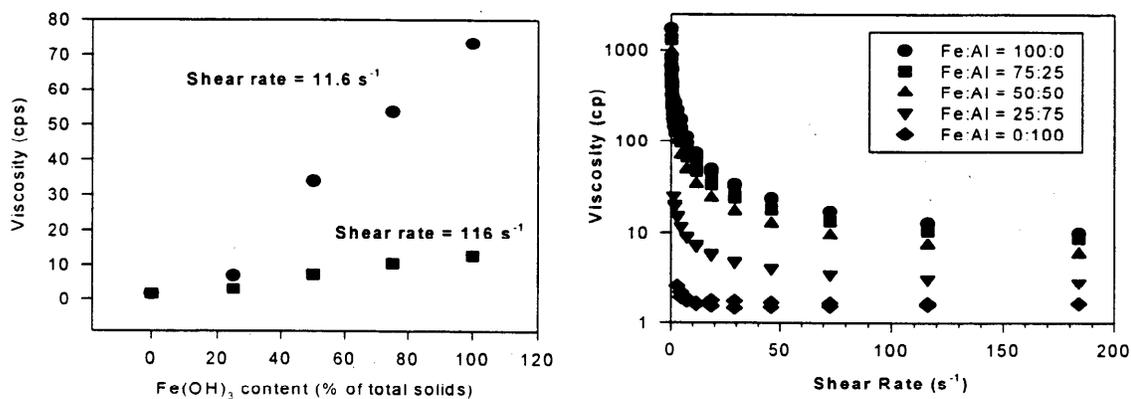


Figure 2. Viscosity of 1 volume % Ferrihydrite: Gibbsite Binary Mixtures at 5M NaNO₃ and pH 12. Particle concentrations are expressed as percentages of the total solids loading.

Salt Effects

One novel aspect of tank conditions is the extremely high salt (electrolyte) concentration. At counterion concentrations of 2-5M, existing colloidal interaction theories (DLVO) predict complete collapse of any electrostatic repulsion between particles, and strong aggregation of particles due to long range van der Waals attractive forces. More recently, the existence of very short range (1-5 nm) hydration and/or steric forces, resulting from surface/cation hydration or

surface reactions, are being suggested to explain particle-particle interactions observed at very small separation distances (< 10 nm). Velamankani² and Lange³ have conclusively shown that electrostatically dispersed systems that have been “salted out” (coagulated) will pack to higher green densities than agglomerated (electrostatically attractive) suspensions of colloidal particles. The “coagulated” systems of Velamankani are produced at salt concentrations of 1M or less. To our knowledge, there are no studies of colloidal behavior at electrolyte concentrations approaching those relevant to tank waste (5M).

For this reason, sedimentation experiments were conducted on boehmite (AlOOH), ferrihydrite ($\text{Fe}(\text{OH})_3$), and gibbsite ($\text{Al}(\text{OH})_3$) particles at NaNO_3 concentrations ranging from 0.01M to 5M. The sedimentation results for 1.3mm gibbsite particles at pH 12 are shown in Figure 3. Interestingly, the particle-packing densities do not simply reach some minimal value due to particle-particle attraction into the primary minimum. The improved packing densities (lower cake volumes) at 0.01M NaNO_3 can be explained by the presence of weak electrostatic repulsion arising from the negative surface charge on the aluminum hydroxide particles at this pH, but at 1M salt, particle surface charges are effectively screened (neutralized) within nanometers of the particle surfaces. This fact would suggest that once the electrostatic contribution is effectively screened, particles would attract (aggregate) strongly due to the strength of van der Waals forces at these small separation distances. The data in Figure 3 follow this trend between 0.01-1M NaNO_3 , but deviate at higher salt concentrations. Particle-packing densities at 5M salt are higher than those at 0.1M and 1M. To further substantiate this finding, 10 volume % suspensions were prepared at pH=12 and stirred for 2 hours and 5 days. Suspension viscosities were then measured using the Bohlin VOR rheometer. The results are plotted in Figure 4 for shear rates of 11.6 and 116 s^{-1} . The viscosity data show identical trends to the sedimentation results with the highest viscosity suspensions (lowest packing densities) at approximately 1.0M NaNO_3 . At this time, the exact mechanisms for the restabilization of the dispersions at high salt concentrations are not fully understood. Future efforts will concentrate on understanding the mechanisms responsible for the observed behavior.

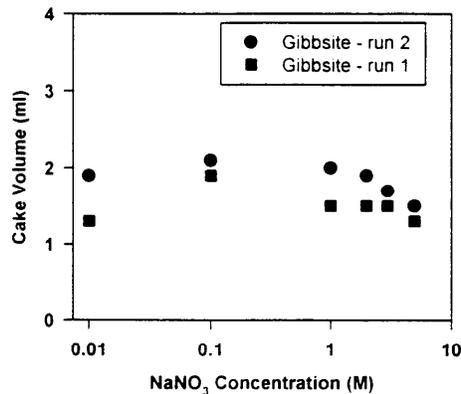


Figure 3. Sedimentation Volume for 1 volume % Gibbsite Slurries Prepared at pH 12 and Varying NaNO_3 Concentrations. 10 ml total suspension volume.

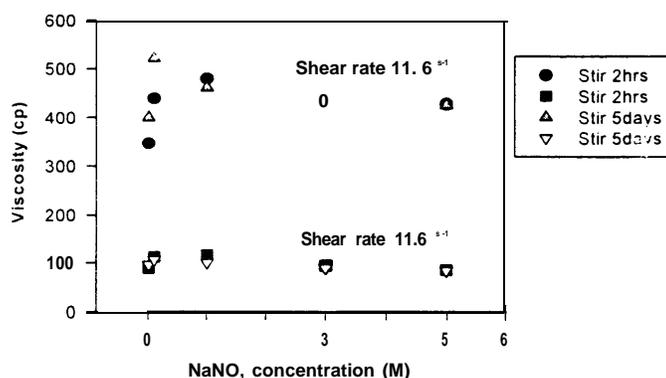


Figure 4. Viscosity of 10 volume % Gibbsite Suspensions versus NaNO₃ Concentration at pH 12. Gibbsite mean particle size of 1.3 μm.

Rheological Studies - Binary Systems

The ultimate objective of this work is the ability to predict the rheological properties of tank sludges if given accurate measurements of particle size and size distributions, solution pH, salt concentration, and total insoluble solids loading. In essence, we hope to use a standard set of readily measurable slurry parameters to predict the relative viscosity, sedimentation, and filtration behavior of actual tank waste and simulate this behavior using simple 1, 2, or 3 component systems. Figure 5 shows the complex rheological behavior measured for tank 241-C-107 (hereinafter referred to as C-107) compared with rheological measurements on ferrihydrite slurries at 0.5, 1.0, and 2.0 volume % at pH 13.5 and 5M NaNO₃. One can readily see that the viscosity behavior of C-107 can be simulated by colloidal slurries of fine iron hydroxide particles (particle size approximately 50 nm). Figures 6 and 7 show similar measurements made using 50 nm boehmite (AlOOH) and 1.3 mm gibbsite (Al(OH)₃). A striking feature of the C-107 viscosity data is the existence of a large discontinuous region between approximately 0.1 s⁻¹ and 1.0 s⁻¹. This feature is due to the highly attractive state of the particles in suspension, and the existence of a 3-dimensional gel network in suspension. In essence, the network structure of particle agglomerates in the suspension is capable of partially reforming at a rate comparable to network disruption caused by the shear forces induced in the rheometer. Note that this region is clearly present in suspensions prepared from nanometer-sized iron and aluminum oxides, but is absent in suspensions of the larger gibbsite particles. We found that in the gibbsite system (1.3 mm) the observed discontinuity was only observed at much higher solids loadings (10 volume %) and at viscosities several orders of magnitude higher than that measured for C-107. These measurements support previous TEM micrographs that show the existence of nanometer-sized particles in the C-107 sludges, and that these line particles play a significant role in the colloidal behavior of the system.

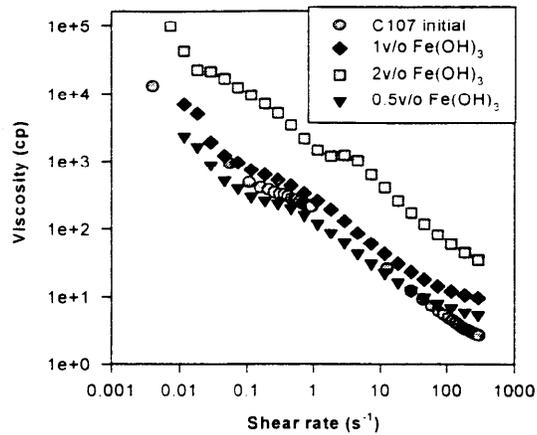


Figure 5. Viscosity as a Function of Shear Rate for Agglomerated Ferrihydrite (50 nm) Suspensions Compared to the Rheological Behavior of C-107 Tank Sludge. Suspensions pH=13.5 electrolyte concentration was 5M NaNO₃.

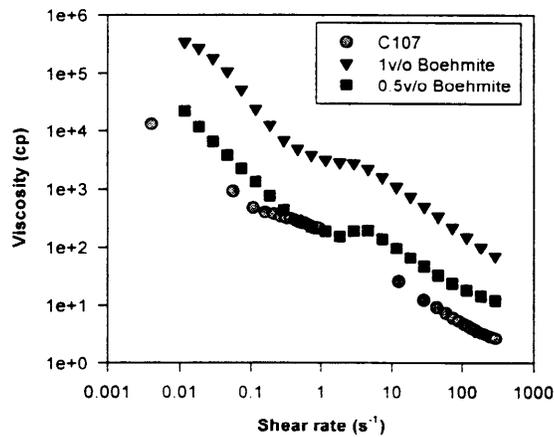


Figure 6. Viscosity as a Function of Shear Rate for Agglomerated Boehmite (50 nm) Suspensions Compared to the Rheological Behavior of C-107 Tank Sludge. Suspensions pH=13.5 electrolyte concentration was 5M NaNO₃.

Though the single component, fine particles seemed to simulate the rheological properties of C-107 sludges, the low solids loadings in the simulants (0.5-1.2 volume %) are nowhere near the values measured on actual core samples. Though the value reported for total solids in tank C-107 varies in different reports, and different measuring techniques, Thermal Gravimetric Analysis (TGA) techniques generally report solids loading of approximately 40-50 volume %. Such measurements would, by necessity, include the soluble as well as insoluble solids. In careful measurements performed by PA Smith and DR Rector in 1996 on C-107 samples, the solids loading for **insoluble** particles was measured at 6.8 volume %. In addition, TEM micrographs of the same C-107 sample showed the presence of fine (10-50 nm) Al-containing

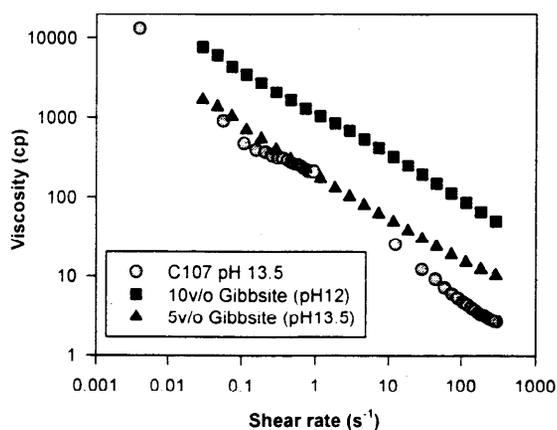


Figure 7. Viscosity as a Function of Shear Rate for Agglomerated Gibbsite (1.3 μm) Suspensions Compared to the Rheological Behavior of C-107 Tank Sludge. Suspensions electrolyte concentration was 5M NaNO_3 .

particles. many 1-10 micron-sized particles of AlOOH or $\text{Al}(\text{OH})_3$ with some larger particles ($>50\text{nm}$). Based on this information, we initiated a series of rheological studies on binary systems containing large (1.3 μm gibbsite) and small (50 nm boehmite) particles in an attempt to simulate the viscosity behavior of C-107 samples using particles of similar size, composition, and total solids loadings as those measured in the actual sample. In addition, solution conditions of $\text{pH}=13.5$ and 5M NaNO_3 were used to simulate tank conditions. Our goal is to reproduce the complex viscosity behavior (particularly the discontinuity) with mixtures of micron- and nanometer-sized particles at total solids loadings near those measured in C-107.

Figure 8a shows the viscosity versus shear rate data for a fixed boehmite concentration of 0.5 volume % (fine particles) and gibbsite concentrations ranging from 0-7 volume % (large particles). In all cases the viscosity of the binary simulant exceeds that of C-107. Figure 8b is the same data replotted to emphasize the region of discontinuity ($0.1-1 \text{ s}^{-1}$). The effect of the larger particles is clearly seen in disrupting the network formed by agglomerated fine particles as the restructured region lessens in magnitude and shifts towards lower shear rate upon increasing additions of gibbsite particles. By lowering the initial boehmite concentration to 0.3 volume %, the rheological behavior of C-107 could be closely approximated with gibbsite:boehmite mixture ratios of 3.0:0.3 and 5.0:0.3. These findings hold promise that binary or ternary systems of particles that match the approximate size distribution and solids loadings may serve as colloidal properties simulants for engineering studies.

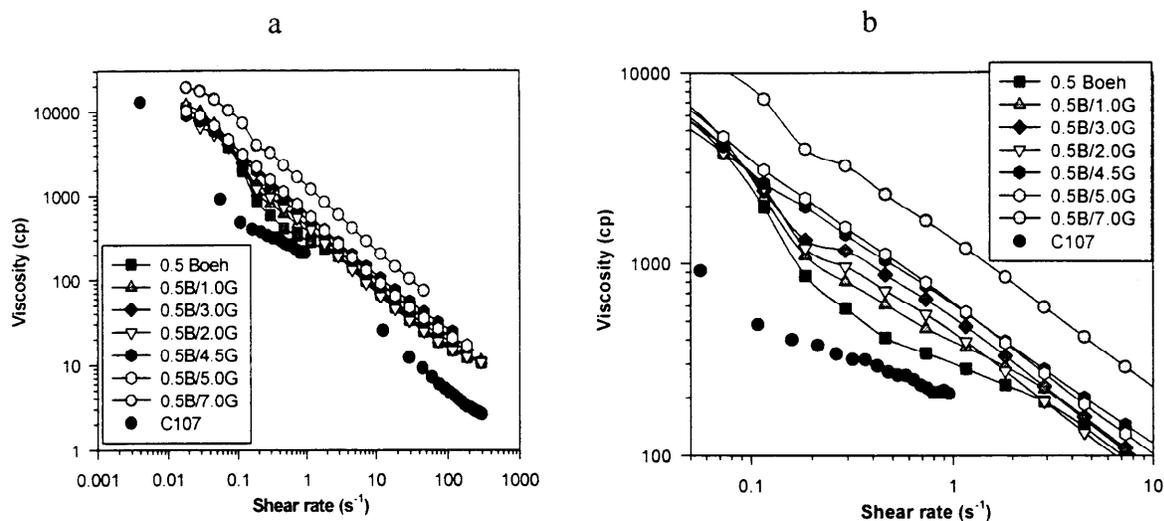


Figure 8. a) Viscosity Versus Shear Rate for Binary Mixtures of Gibbsite and Boehmite Particles. Ratios are expressed in volume percent. Suspension pH= 13.5 with 5M NaNO₃ Electrolyte concentration. b) Enlarged Region of Figure 8a Emphasizing Shear Rate Region Between 0.1 s⁻¹ and 10 s⁻¹ for Binary Mixtures of Gibbsite and Boehmite Particles.

Predictive Modeling

A large fraction of the insoluble solids that exists in Hanford tank waste is in the form of sub-micron-sized particles. Under the high pH and salt concentration conditions that exist in the tanks, these colloidal particles tend to attract each other to form porous aggregates and gels. Recent work related to tank waste processing indicates that the aggregation of these particles to form colloidal gels can have an enormous impact on tank waste processing. For example:

- The efficiency of solid-liquid separation through sedimentation depends on how effectively the particles in the final sediment pack. The formation of a colloidal gel can reduce or even eliminate the degree of settling that occurs during a pretreatment wash or leach procedure.
- The retrieval and transport of tank sludge depends on the viscosity of the suspension. The formation of a colloidal gel can change a low-viscosity Newtonian suspension into a high-viscosity shear-thinning fluid.

The objective of this task is to use computer simulation to model the aggregate or gel microstructure formation based on the known interactions between colloidal particles, and to predict the physical properties resulting from the microstructure. The primary physical properties of interest are the compressive yield stress for sedimentation and rheological properties for tank waste mobilization and transport.

Method

The physical properties of a colloidal gel depend both on the microstructure of the gel and the interaction potential between particles. The microstructure, in turn, depends on the Brownian motion and aggregation history of the individual particles. This transient aggregating behavior is modeled using the Brownian dynamics method.

The first part of this year has been spent on developing a series of computer programs based on the Brownian dynamics method to simulate the formation of colloidal gels and determine their physical properties. In Brownian dynamics, the motion of individual particles are determined based on the random forces exerted by the surrounding fluid and particle-particle potential interactions. The translational motion is described by the Langevin equation

$$m \frac{dv_i(t)}{dt} = -\zeta v_i(t) + F_i(t) + F_i^R(t)$$

where ζ is the Stokes friction coefficient, $F_i(t)$ are the interparticle forces, and $F_i^R(t)$ is a random component with Gaussian distribution. For solutions with a high salt concentration, such as those in tank waste, the repulsive electrostatic double-layer collapses resulting in a van der Waals attraction potential. The momenta decay rapidly and the update algorithm can be written as

$$r_i(t + \Delta t) = r_i(t) + [F_i(t) + R_i(t, \Delta t)](\Delta t / \zeta)$$

where R_i is the random force. The motions of the individual particles are integrated over time until the particles have aggregated to form a continuous network. Simulations of several thousand particles are typical.

Two different Brownian dynamics algorithms have been developed to model colloidal aggregation and gel formation. One algorithm tracks individual particles until they contact another particle or cluster of particles. The new cluster is then treated like a rigid body with the appropriate Brownian and cluster-cluster interactions. This algorithm is useful for efficiently creating gels for diffusion-limited aggregation systems. The cluster size distribution as a function of time and the fractal dimension of the clusters compare favorably with values in the literature.

Another Brownian dynamics algorithm has been developed that connects contacting particles with a center potential, which allows each particle to rotate around the surface of the connected particle. Using this method, the fractal agglomerates are formed with truss-like structures rather than individual rigid bonds.

A colloidal gel is formed by running the Brownian dynamics transient until all particles and clusters connect to form a single structure. Information about the structure of a suspension or gel is obtained using the particle-particle correlation functions, $g(r)$, and the structure factor, $S(q)$. To evaluate $g(r)$, one momentarily stops the aggregation process at predetermined times and

obtains a histogram giving the number of pairs of particles that are found within the spherical shells of radii r and $r+dr$, irrespective of whether the particles belong to the same cluster or different ones. The pair correlation function is calculated from this histogram with the formula

$$g(r) = \frac{\text{density of pairs in } (r, r + \delta r)}{\text{average density of pairs}}$$

The scattered intensity, $S(q)$, of a macroscopic system containing identical particles with number density ρ , assuming single scattering, is given by

$$S(q) = 1 + \frac{4\pi\rho}{q} \int_0^{\infty} r \sin(qr) (g(r) - 1) dr$$

The structure factor, $S(q)$, can be related to the intensity results from neutron and x-ray scattering experiments.

The physical properties of a colloidal gel are determined by applying forces to the simulated gel network and measuring the response. For example, the compressive yield stress is defined as the relative weight per unit area of sediment that can be supported by a colloidal gel as a function of solids volume fraction. This is simulated by forming a colloidal gel between two parallel walls, one of which remains fixed while the other acts as a freely moving piston. A force is applied to the moving wall and the system is allowed to compress until it reaches a new equilibrium value. By repeating this procedure, the compressive yield stress vs. solid fraction is determined. A similar approach can be taken to determine rheological properties.

Preliminary Results

The methods described in the previous section will be used to examine a variety of homogenous and heterogenous particle systems in support of the experimental efforts of this project. The first system to be modeled is a mixture of large and small particles to understand the properties of the suspensions as a function of solids loading and particle size distribution.

The gel structure of binary particle mixtures was modeled using Brownian dynamics simulations. The simulation begins with a suspension of large and small spherical particles with a 10:1 diameter ratio. The solids loading is 2 vol%, divided evenly between the large and small particles, using a total of 10,010 particles. Before starting the transient, the particles are randomly placed on a lattice and then the system is relaxed using a series of Monte Carlo moves. The particles combine based on diffusion-limited aggregation.

After a specified period of time, the pair distribution function between large and small particles, $g(2,1)$, is determined and is presented in Figures 9 and 10. The small particle density is normalized with respect to the bulk small particle number density. The radial distance is in terms of the small particle diameter, $s(1)$. Note that there is a peak near $5.5 s(1)$, which

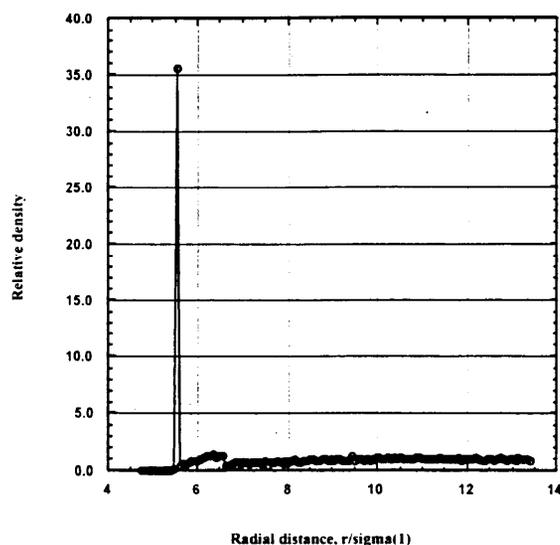


Figure 9. Pair Distribution Function Between Large and Small Particles. Normalized to Small Particle Density. $s(2)/s(1)=10$, $N=10010$, $f(1)=f(2)=0.01$.

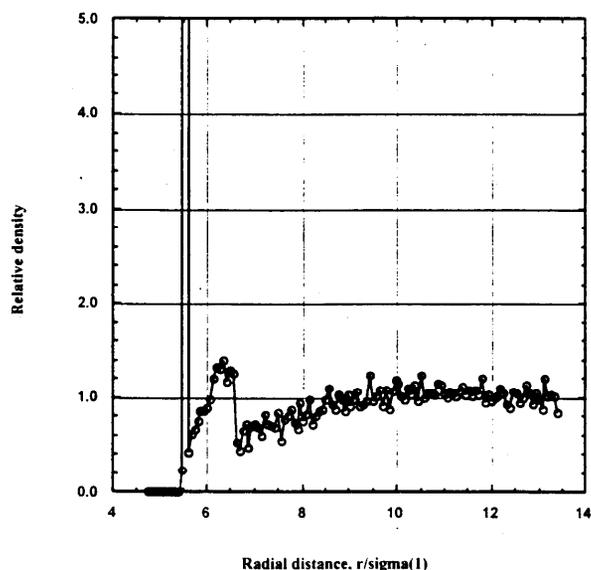


Figure 10. Pair Distribution Function Between Large and Small Particles. Normalized to Small Particle Density, $s(2)/s(1)=10$, $N=10010$, $f(1)=f(2)=0.01$. (Expanded to show detail.)

represents the small particles adsorbed on the surface of the large particle. Then there appears to be a depletion region between $5.5-7.5 s(1)$ where the small particle density is less than the bulk average. For greater distances, the density is equal to that of the bulk density. These results appear to be relatively insensitive to the concentration of large particles but very sensitive to the small particle number density, which determines the mean path of a small particle before it becomes part of the gel.

These results indicate that the adsorbed particles are removed from the depletion region, but that the presence of the large particles is felt only a few small particle diameters into the gel. Beyond this distance, the gel is essentially the same as that for a pure small particle gel with the same bulk number density. The small particle structure appears to dominate the properties of the gel, and the addition of large particles at these concentrations appear to perturb the structure slightly. The effect on the strength of the gel will be determined by performing a series of compressive yield stress simulations for both the monotonic and binary systems and comparing results.

Conclusions

Brownian dynamics simulations provide a useful tool for understanding the link between the microstructure and the physical properties of a suspension or gel. The preliminary results for a binary system of large and small particles indicates that the small particles dominate the structure of the gel. However, this must be verified by determining the effect on the strength of the gel by performing a series of compressive yield stress simulations for both the monotonic and binary systems.

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