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Title: RHEOLOGICAL CHARACTERIZATION OF NUCLEAR WASTE USING FALLING-BALL RHEOMETRY

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ABSTRACT
Knowledge of the rheological properties of saturated solutions containing solid particles is very important in nuclear waste management technology. For example, the nuclear waste in the Hanford Site high-level radioactive waste tanks contains strong electrolyte solutions with a high concentration of solids. Previous attempt using rotational viscometers to determine the rheology has shown unusual thixotropic and shear thinning behaviors with a lack of reproducibility. Using falling-ball rheometry, the rheology of the undisturbed simulant may be determined with much better reproducibility.

In this study, a well-mixed simulant which has similar chemical composition to the actual waste will be tested. Falling-ball size and density will be varied to get data in a wide range of shear rates. To determine the rheogram, several methods will be tried to match the observed data. Based on these tests, a rheogram can be determined from the model and its best-fit parameters.

The simulant shows shear-thinning behavior and a yield stress. This would suggest a H-B model. But when fitting to one of the simulants which showed a very low yield stress, the predictions assuming no yield and assuming yield resulted in no improvement in the fit when assuming yield.

1. INTRODUCTION

Success of many of the mitigation/remediation and retrieval schemes proposed for the Hanford Site high-level radioactive waste tanks requires the knowledge of the rheological properties for the material contained within these tanks. The mitigation of tank 101-SY has received most of the attention because it is known to release flammable and toxic gases periodically.

Prior the mixer pump operation, the waste in tank 101-SY exhibited four distinct layers; a-crust, a-convective layer (CV), c-nonconvective layer (NC), and d-sludge at the bottom. Because the convective and nonconvective layers compose also all of the tank volume, the rheological properties of these layers are of interest. Core samples have been taken from various regions of the tank to characterize the chemical and rheological properties of the waste (Tingey 1992). The two samples are known as the windows C and E.

However, these samples were not the same in either the CV or NC layers. For example, there is a considerable difference in the CV layer viscosity for samples from windows C and E. Rheology measurements for the NC layer show scatter over 1-2 orders of magnitude. NC layer data also indicate that over a certain range of temperatures and strain rates, viscosity increases with increasing temperature. In addition, there was a lack of repeatability of tests. The waste consists mostly of seven different salts in water. These seven salts are used to create a simulant that is chemically similar to the waste.

Attempts were made to obtain rheological properties of CV and NC layers using a cone and plate viscometer (Tingey, 1992). The test lacked reproducibility probably because the clearances of the cone-and-plate viscometer was on the same order as the crystalline sizes existing in the waste (the crystalline particles in the waste slurry are believed to be 1 to 100 μm in size).

Additional study performed at Los Alamos National Laboratory (Pasamehmetoglu, Unal, Edwards, 1993) demonstrate that the cone-and-plate viscometer yields reasonably reproducible results for Newtonian fluids and non-Newtonian fluids with very fine particles. However, the reproducibility of the cone and plate experiments using a waste simulant had an unacceptable amount of scattering.

Spindles also were used to measure the viscous behavior of the waste simulant. Although spindles gave repeatable results, the measured quality was in question because of the concern associated with the particle migration and wall slip in the shear flow fields.

Using falling ball rheometry, additional tests were performed. These preliminary tests showed shear thinning behavior. However, the measured values were similar to those obtained using the spindle method. To see if falling ball

rheometry was a better technique than spindle tests, more accurate falling-ball experiments needed to performed.

The waste consists of a saturated salt solution containing solid salt crystals. Because of the various crystal types, the waste can be thought of as a suspension with various sizes and shapes of suspended particles. The settling time for the particles is slow.

Suspension rheology in concentrated systems have been determined using falling-ball rheometry (Mondy *et al.*). However, the waste exhibits also shows strong time dependency. This is believe to be caused by the continuos evolution of salt crystal structures. This structures then trap gas generated by the waste in the lower settled (NC) layer. This occurs until the NC layer has accumulated enough gas so that its average density is less than the CV layer. The roll-over shears the NC layer releasing the trap gases. Also the large pressure head (5-10 meters) can cause swell in the tank before the gas release. Therefore the properties of the well-mixed and settled simulant are of interest. In this paper, only the experiments on the well-mixed simulant are described.

In most techniques, the bulk of the fluid is continuous sheared (cone and plate, spindle) or is shear at high rates for short amounts time (capillary). However, the settling ball in a falling-ball experiment is continuously encountering undisturbed fluid as it falls, and the bulk amount of the fluid is sheared very little, if at all. This minimizes suspend particle interactions which can cause particle migration (Abbott *et al.* 1991).

Because the waste exhibits a very complex time-dependent fluid behavior, the applicability of falling ball rheometry has to determined. The most important issue is that whether or not the well-mixed waste can be treated as a homogenous media. If the waste does behave as a homogenous fluid, then the apparent viscous behavior of the simulant can be determined using various sizes and densities of fall balls.

The first objective of this study is to test the reproducibility of falling ball tests in the various waste simulants. Secondly, the settling velocities will be analyzed assuming various shear-rate dependent viscosities, until the assumed behavior matches the observed behavior. Two chemically similar simulants will be used to determine the characteristics of the mixed waste. The major difference between the two simulants in when they were created. Therefore, the differences will highlight any differences due to aging.

The results of this study will be used to design an *in situ* viscometer and determine a procedure for determining the viscosity from *in situ* tests. A brief summary of the state of art of the falling ball rheometry will be given as it applies to concentrated suspensions. Also some of the issues in regard to our

current experiments will be discussed. Following the description of the simulant used in these experiments, the results and conclusions will be presented.

2. FALLING-BALL RHEOMETRY

Determining the viscosity of liquid from the terminal settling velocity of a ball is a well known technique and has been the subject of numerous experimental, numerical, and theoretical papers. The solution of the equation of motion for a ball falling in an unbounded Newtonian fluid at a low Reynolds number (Re < 0.1, also known as creeping flow) is known as Stokes's law:

$$u = \frac{d^2(\rho_b - \rho)g}{18\mu} \tag{2-1}$$

where

u is the terminal velocity,
d is the sphere diameter,
ρ_b is the sphere density,
g is the gravitational acceleration, and
ρ and μ are the density and viscosity, respectively, of the Newtonian fluid.

This equation is obtained by balancing the drag force on the sphere with its buoyancy force. Beyond a Reynolds number of 0.1, corrections for inertia are needed. Also, in many problems, wall effect corrections are needed. For Newtonian and many non-Newtonian fluids, these corrections are known. However, for materials exhibiting a significant yield stress or in large containers, wall effects can be insignificant.

Falling-ball rheometry recently has been used for dilute and concentrated suspension by several researchers (Mondy, *et al.* (1986), Powell and Walla (1991), Abbott (1993), Abbott *et al.* (1991), Milliken *et al.* (1989), Mondy *et al.* (1990). Although suspensions are not always represented as Newtonian continua, they may be partially characterized by an apparent viscosity if the suspended partials only interact hydrodynamically. However, this assumes that a reproducible settling velocity can be determined. This definition goes back to Einstein's (1906, 1911) original works, which concentrated on neutrally buoyant suspensions subjected to elongation. Subsequently, Burgers (1939) obtained an identical result for simple shear flow between parallel plates.

Two ways in which suspensions differ from homogeneous fluids are the turbulence dissipation and migration of suspended particles caused by hydrodynamic interactions. The differences between suspensions and

homogeneous fluids under turbulence are believed to be caused by the interaction between the particle size and the size of turbulent eddies.

Particle migration occurs when initially well-mixed suspensions are subjected to inhomogeneous shear flows (Abbott *et al.*, 1991). The suspended particles migrate from the regions of high shear rate to regions of low shear rate. This migration can occur over relatively short shearing lengths and results in the development of large concentration gradients.

The above test assume that the suspension could be modeled as a homogenous Newtonian fluid. From test performed earlier, the actual waste has appears to have a yield stress and shear-thinning behavior. Therefore, models assuming Bingham and/or shear-thinning behavior will be tested when reducing the data. Again, a homogenous fluid models may not be applicable to two-phase suspension media.

Evaluation of yield stress and Bingham viscosity for high shear rates may not be obtained by the analytical solution of Beris *et al.* (1985), because this case includes inertial effects. However, as a second alternative, we also can reduce this data from empirical experimental correlations available by Ansley and Smith (1967), Ito and Kajiuchi (1969), and Brooks and Whitmore (1969); these researchers obtained the drag coefficient as a function of the Bingham number and plastic Reynolds number. They used clay and other types of Bingham plastics and dragged the ball up to the plastic Reynolds number of 1000. Ansley and Smith (1967) were able to collapse all drag coefficient data to a single curve by defining a dynamic parameter in terms of the Bingham number and plastic viscosity number. Thus, tests theoretically can be run with high velocities if these correlations hold. The danger of this approach is the limited range of the dynamic parameter (between 0.01 to 2000) in Ansley and Smith's(1967) study because their Bingham fluids had very low yield stress. If the waste yield stress is high, as suggested, the dynamic parameter becomes very low for reasonable plastic viscosities. In this case, we may need to extrapolate the correlation, which is always difficult to justify. This extrapolation approach was taken in the preliminary drag force evaluation analysis of Pasamehmetoglu *et al.* (1993)

This research will attempt to answer questions asked above, in a step by step approach. We have discussed some of our alternatives for data reduction. The final approach will be determined on the basis of experimental results we obtain from the tests.

3. SIMULANT CHARACTERISTICS

The wastes that were added to tank 101-SY consisted of double-shell slurry (DSS) and complexant concentrate (CC) waste. Both of these wastes were concentrated by evaporation prior to storage. The complexants added to the CC waste consists

primarily of Na_4EDTA, Na_3HEDTA, sodium citrate, and sodium hydroxy acetate (glycolate). Both wastes consisted mostly of precipitated, inorganic salts.

To adequately predict the behavior of the waste in the tank, it is essential to perform falling-ball experiments with a representative waste simulant. A chemically similar simulant (described below) has shown, like the waste, that long amounts of time (month to years) are necessary for the simulant to stabilize. Because this study needed to be performed in a 6-7 month time frame, an aged simulant was needed. Also to perform large scale experiments and to determine the effects of aging, a fresh simulant was made. These two simulants are described below.

3.1 Composition

Based on the chemical analysis of the core samples from tank 204-SY-101, Agnew (1993) suggested the following mixture as a chemically accurate reproduction of the waste in the tank.

TABLE 1 : COMPONENTS USED IN AGNEW'S SIMULANT

Component	Amount in Moles/l (M)
$NaNO_3$	3.7
$NaNO_2$	3.6
NaOH	3.5
$NaAlO_2$	2.3
$NaCO_3$	0.5
Na_4EDTA	0.12
Na_3HEDTA	0.13

Agnew (1993) prepared his simulant in a progressive manner. The least soluble components are added to an appropriate amount of tap water first (complexants). 2.3 M NaOH was added next. Addition of NaOH heats the solution. The aluminate was added after NaOH. However, Agnew later found that the sodium carbonate was much less soluble than aluminate. As we will mentioned we add the sodium carbonate before aluminate in the preparation of our fresh simulant. After adding aluminate, sodium nitrite, carbonate, and nitrate were added. After this mixture stood for a few days at 60 °C in a 33.4 L model tank, it was observed that the settled solids were not correct, comprising only 1 inch of settled solids. The total sodium was increased by adding an additional amount of sodium hydroxide from 2.3 to 3.3 M to compensate for the lack of other cations that are present in the actual waste. Some of the components which are not added to the simulated waste are citrate, glycolate, nitrilo triacetate, phosphate, fluoride, chloride, and other anions, potassium, calcium and other common cations, chromium, iron and other transition metals. The

simulated waste made by Agnew includes the major chemical species believed to adequately represent the physical and chemical nature of the tank slurry.

Agnew's slurry showed characteristics of four layers; a-foam layer, b-clear supernate layer, c-soft slurry layer, d-much stiffer bottom layer. This simulant waste was prepared approximately 2 years ago and kept at typical tank temperatures in a model tank.

We obtained 4 L of this aged waste simulant from the Agnew's model tank after the waste simulant was mixed homogeneously. These individual 1 L samples were kept in a vacuum oven to maintain the temperature around 50-60°C. Later tests showed that the temperature would vary between 52°C and 58°C in each cycle.

The four liter samples are indicated as AS1, AS2, AS3, and AS4 (aged simulant). Each simulant taken from Agnew's tank is treated separately, because they have different temperature and shear history. For example two of the samples were taken about a month after the first two. Also all the samples were allowed to cool before they were moved.

To complete this study, 20-30 gallons of simulant was needed. Because there was less than 10 gallons of aged simulant, some simulant had to be created.
Using the recipe and procedure suggested above, a sample liter was made. The chemical components are listed in the following table. The composition given below is identical to those shown in Table 1, except in g/1 versus moles/l

TABLE 2 : COMPONENTS USED IN THE FRESH SIMULANT

Component	g/l
Na_4EDTA	50.00
Na_3HEDTA	50.00
Na_2CO_3	56.19
$NaAlO_2$	196.07
$NaNO_3$	317.05
$NaNO_2$	244.95
NaOH	139.60
H_2O*	536.14

* amount calculated such that there would be 1590 g/l total.

The components are listed in the order they are added to the water. All the salts dissolved at room temperature up to the addition of the sodium nitrate. At 50°C, the carbonate (and possible the EDTA and HEDTA) come out of solution after the addition of the aluminate. The simulant was then transferred into a plastic container with a lid to reduce evaporative loses. The container was placed in the same oven with the Agnew's simulants to maintain its temperature

Using the test procedure given above, a 113.6 liter (30 gallons) batch of simulant was made in a 55 gallon barrel. Initially, the temperature of the simulant caused by the heat of solution (mainly from the aluminate and sodium hydroxide) was 30°C. Over two days the simulant temperature was raised to the set point of 50°C. This mixture was constantly stirred using a barrel mixer. After several months, a sample of this simulant (fresh simulant or FS2) was taken from the barrel.

To prepare the new simulant for experimental use, the simulant is taken to 70 °C for at least overnight. Then the simulant (still above 60°C) is mixed vigorously for 30-60 minutes. Then the simulant is cooled to 50 °C. At 70°C, the nitrate and nitrite salts crystals have dissolved completely. When the temperature is reduced, the resulting crystals are more representative of crystals seen in the NC layer. This is equivalent to redistributing the sludge layer in the tank. This diminishes the variability of the simulant taken from the barrel at different times.

3.2. Density and Particle Shapes and Sizes

The shape and size of solid particles and the solid fraction are very important parameters controlling the rheological properties of suspensions. They also determine the settling rate of the suspension. The other physical properties are important such as densities of the mixed simulant, saturated liquid, and the precipitated crystals.

For the simulant received from Agnew (1992), the densities were measured, along with information on the size and shape of the solid particles. Densities of Agnew's simulant and their comparison with waste measurements are given in the following table.

TABLE 3. PROPERTIES OF AGNEW'S SIMULANT

Density (g/cc)	Supernate (g/cc)	Convective Layer (g/cc)	NonConvective Layer (g/cc)	Average (g/cc)
Agnew-Simulant	1.51			1.59
E-Core Sample	1.50	1.57	1.70	
C-Core Sample		1.49	1.63	

Agnew's simulant showed certain pattern of particle sizes that may be a trend for the actual waste. There were larger crystals made of sodium nitrate, sodium nitrite, and sodium carbonate. Sodium nitrate crystals are rhombohedral and tend to be very symmetrical prisms, while the sodium nitrite crystals are

monoclinic and grow in variety of different ways. Generally, they are present as flat, triangular plates, although dendritic forms grow readily out of rapidly cooled solutions. The sodium carbonate crystals most often appear as needles clustered like haystacks (Agnew, 1993). These forms only appear in waste that is cooler than about 30 °C, and it appears that the carbonate exists in another much smaller crystal at the tank temperature. The complexant present in Agnew's slurry primarily as small crystals, since it is fairly insoluble in the 12 M sodium supernatant. HEDTA components could not be found in the actual waste or in Agnew simulant, even though it was present initially in both. It is assumed that the HEDTA degrades quickly into some as yet undetermined products very quickly(Agnew, 1993).

The rate of crystal growth/dissolution is unknown. Indirect evidence, such as change in appearance and viscous behavior of simulant, suggests that the rate is weeks, not hours.

In this study, the density of Agnew's simulant was measure. The density of supernate at 50 °C was determined to be 1.544 g/cc (±0.004). The well mixed simulant was measured as 1.593 (±0.004) and 1.561 (±0.004) for AS1 and AS2, respectively.

The solid fraction in a given simulant can also be changed by varying the temperature. Falling-ball tests were conducted at different temperatures with the well-mixed aged simulant to investigate the solid fraction effect. The base viscosity of the saturated liquid will decrease with increasing temperature, making a direct analogy between solid loading variations due temperature variation with variation due to an actual decrease in solids concentration (by settling or filtration).

4. DESCRIPTION OF EXPERIMENTS

4.1. Description of Falling Ball Tests and Real-Time Radiography

A good description of falling ball rheometry in opaque suspensions can be found in Mondy *et al.* (1986). Here, only the parts unique to this study will be presented.

The falling ball paths were recorded using a standard VHS, editing video system. This system records 30 frames per second and the VCR could be advanced one frame at a time, yielding the highest accuracy within the limitations of the technique. The accuracy in position and time are estimated to be ±0.2 cm in the position and ±0.03 s in time, respectively. Because objects placed closer to the x-ray source would appear larger in the recorded image than objects further away, rulers with 1/8" markings were place in front on the right side and in back on the left side of the column. First order corrections for errors due to perspective could be determined. Second order corrects would be on the scale of other errors.

The test cylinder has a inside diameter of 2 inches and a length of 18-20 inches. A cylindrical jacket, through which water was pumped to maintain a constant temperature, surrounded the test cylinder. The water temperature was maintain by using a constant temperature bath which controlled the temperature in the bath to within ±0.01°C and in the column to within ±0.03°C. The top of the test cylinder was covered with a lid to reduce evaporative losses.
The falling ball used in this study varied from 1/8 inch to 3/4 inches. Tungsten carbide, brass, steel, aluminum oxide (ruby), ceramic and aluminum balls were used to get various densities. Aluminum balls did settle under low shear rate, but the simulant (like the real waste) corrodes aluminum. The initial experiments completely dissolved 1/4" aluminum balls in less than 3 days.

While inertial effects will be important in many of the experiments performed in either the simulant or the actual waste, the low Reynolds number data will be useful as a starting point to understand the more complex behavior at higher Reynolds numbers.

To get to lower shear rates, 1/2" and 1/4" plastic balls were used. The plastic balls used had a density 1.18, much less than the simulant density of 1.6. To increase the 1/2" ball average density, 1/8" to 3/16" holes were drilled in the ball and filled with various sizes of Tungsten carbide, brass, and steel balls. These balls are referred to as PFB's. Similarly, 1/16" holes were drilled in the 1/4" plastic balls and filled with 1/16" gold wire to increase the average density of the ball. These balls are referred to as PFG's. All the holes were sealed with an acrylic epoxy.

4.2. Description of Couette Viscometer Tests

In addition to falling-ball tests, rheological were performed measurements using Couette viscometer. Couette viscometer is based upon a rotational principal. As we mentioned in the introduction, the particle migration and wall slip can be seen in the rotational viscometers. To compare the falling ball results with results from a rotational viscometer, a Couette device was selected. The simulant used in Couette experiments was aged simulant of Agnew (1993).

Approximately 200 ml of aged simulant (AS4) was provided to the Naval Air Warfare Center Weapons Division at China Lake (NAWCWPNS, CL) to perform Couette flow tests. The sludge was send in two 125 ml polyolefin screw-top bottles. When not in use, the sludge was stored at room temperature (20 to 25 °C). Before making measurements, the bottles of simulant were stored for several days in an environmental chamber at the test temperature. The sludge was stirred by inverting or shaking the bottles. Air bubbles introduced by shaking were allowed to rise to the surface before pouring samples of the sludge into a viscometer for viscosity measurements. Only a few seconds were required to allow bubbles to rise to the surface. It was noticed that the simulant gave off a slight ammonia odor at 40 °C.

A Couette (cup and bob) viscometer was used, though a parallel plate viscometer was tried. The parallel plate was 50 mm in diameter. In loading the parallel plate viscometer, sludge was poured onto the center of the lower plate, then the upper plate was lowered to squeeze the sample to the edge of the plates. During the measurement, a crust appeared to form over part of the exposed surface at the edge of the sample. The torque was measured was at various rotation rates. The torque appeared to decrease with increasing rates, which may have resulted from breakup of the crust at higher rates. The torque may have also been influenced by sedimentation of the suspended particles. For these reasons, the parallel plate viscometer was not used further.

Samples measured in the Couette viscometer were loaded by pouring between 28 and 29 grams of simulant into the cup, mounting the cup into the viscometer, then lowering the bob into the sample, then spreading a layer of mineral oil on top of the sample. The mineral oil was added drop-wise from an eye-dropper to form a 1 to 2-mm thick layer, floating on top of the simulant. This oil layer kept the simulant from evaporating and prevented the formation of any crust. For samples run without the oil layer, a crust was seen to form on the exposed surface, and these runs showed higher and less reproducible torques than runs made with the oil layer in repeat experiments. The oil was low in viscosity (0.3 Poise at 23 °C), and the layer was thin enough that its contribution to the measure torque was negligible.

The Couette was in a temperature-controlled environmental chamber heated by convection. A thermocouple in the base of the cup was used to measure the sample temperature. In all cases, the simulant was held at the test temperature in a separate environmental chamber before pouring it into the Couette. The Couette was allowed to equilibrate to the test temperature in its environmental chamber before loading the sample.

4.3. Test Procedure for Falling Ball Tests

For mixed-simulant tests, the simulant was poured into the cylindrical cylinder after taking it out from the constant temperature oven. The column was kept at a constant temperature as described in Section 4.1. The stirring apparatus consisted of a hub with eight equally spaced rods projecting radially. A long axial rod connected the hub to a stirring handle. By moving the handle up and down while rotating it, the simulant was mixed for approximately 5 minutes. After the mixing, x-ray equipment and columns were moved such that the appropriate part of the column could be recorded.

Prior to being used in an experiment, the balls were stored to within 2°C of the bath temperature. However, the column was normal 1-2°C cooler than the water bath due to convective loses to the surrounding air.

Before the constitutive behavior can be determined, the reproducibility of the settling experiments needs to be checked. In Fig. 2, the results are shown for AS1, although equivalent experiments were perform in all the simulants shown in this study. The first set of falling balls consisted of sets of 1/4-inch-aluminum, 1/4-inch-steel, and 3/16-inch-steel balls. To determine if the simulant behaved like a single-phase, homogenous fluid, each set consisted of 3-5 balls dropped. As can be seen in Fig. 2, the reproducibility of the settling times is with a few percent. Most of this error is due to the low resolution in time, because the standard speed of thirty frame per second was used in taping these experiments.

Using the fresh simulant (FS2), the PFB and PFG balls did not settle through the well-mixed simulants. Higher shear rate balls did settle reproducibly through the simulant. This bounded the yield stress. However, using 1/8" ruby spheres, the balls did not settle reproducibly.

In earlier drops a similar phenomenon was observed with the PFB and PFG balls in AS1 Some ball with a higher apparent density settled slower than less dense balls. At that point it was assumed that the differences were caused by the non-

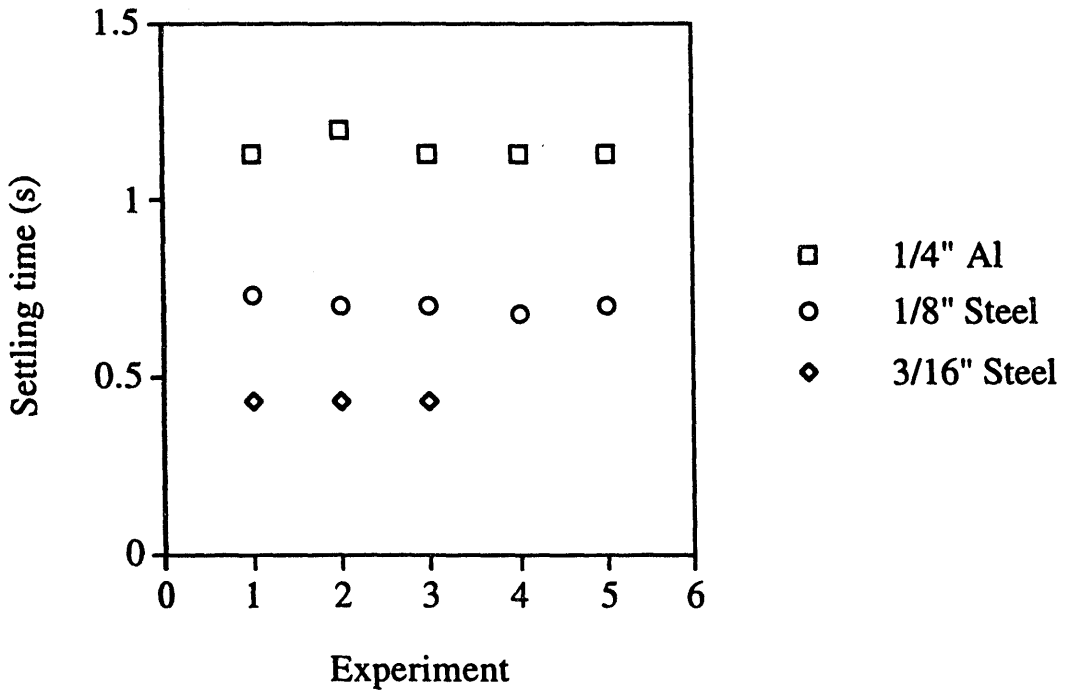

Figure 2: Balls of the same density and size give good reproducibility. The shear rate for the 1/4" aluminum, 1/8" steel, and 3/16" steel are 22, 70, and 78 1/s, respectively. (Note that the frame rate was 30 frames per second, therefore the above difference for a given ball type are caused by differences of ±1 frame).

uniform nature of the plastic ball (i.e. roughness, asymmetry, etc.). Also some balls did not settle when less dense balls did settle. Because only 8" of the column can be observed at one time, the section chosen was normally far below the upper interface where ball did get stuck in later drops. In a ball was trap in this upper layer, stirring for the next ball would send it to the bottom.

The 1/8" spheres were the best spheres used in this study, and they have given very reproducible results at high sphere rates. In FS2, their velocities were not constant over all the drops. In fact, the first ball settled twice as fast as the second ball. What this seems to suggest is that the yield stress may not be uniform throughout the simulant or not uniform upon mixing. This would only manifest itself for balls that are near the yield point as the settle. There a small change in the yield would cause large changes in the settling velocity. When using the in situ viscometer, where the velocity, this effect will give cause a small change in the force required to pull the ball.

5.2. Flow Curves and Rheograms

Above we demonstrated that the well mixed simulant (especially the aged one) behaves as a homogenous fluid (continua). To estimate the flow curves (e.g. the relation between the shear stress and shear rate) a systematic method will be followed. First, the simulant will be assumed to be a Newtonian fluid. Then the measured terminal velocity will be used to calculate the shear stress and shear rate. If the simulant is a Newtonian simulant, the calculated effective (apparent) viscosity will not be a function of the shear rate. If the viscosity depends upon the shear rate, then a non-Newtonian fluid model will be used. However, the apparent Newtonian viscosities behavior as a function of shear-rate should be used a guild to select the non-Newtonian models to test. In this case, the apparent Newtonian viscosity was shear-thinning with a possibility of a yield stress. Below, these cases will be discussed in a progressive order.

As a first iterate, the settling rate of the falling-balls were analyzed assuming the fluid behaved as a Newtonian fluid at low Reynolds numbers. Making this assumption, the apparent Newtonian fluid viscosity can be calculated directly from the settling velocities using the drag on a sphere in the cylinder as given by Happel & Brenner (1983) as Eq. 2.1 or

$$F_s = -\frac{3\pi\mu du}{\chi} \tag{5.1}$$

where χ is the wall effect correction given by Faxen (1923)

$$\chi = 1 - 2.149\frac{d}{D} + 2.05\left(\frac{d}{D}\right)^3 - 0.95\left(\frac{d}{D}\right)^5 + O\left(\frac{d}{D}\right)^6, \tag{5.2}$$

and where d, u, μ, and D are the diameter and velocity of the ball, the viscosity of the fluid, and the diameter of the cylinder, respectively. However, all the balls did not predict the same viscosity. From examining the apparent viscosity as a function of the shear rate , the fluid appeared to be a shear-thinning, and possibly a power-law fluid. While the drop at different temperatures and in the different simulant could also be subjected to a Newtonian analysis, they were not, because the power-law analysis appeared to work satisfactorily.

The first constitutive equation tried was for a power-law fluid, based on the behavior seen in the Newtonian analysis. The analysis assumes that the drag coefficient as a function of Reynolds number is the same for power-law fluids as for Newtonian fluids. Making this assumption introduces a 30% uncertainty into the results. While this is normally consider satisfactory, better results should be obtained if the drag coefficient depended on the Reynolds number and the power-law index. However, other proposed analysis methods have not improved upon the accuracy of this seemly first-order assumption.

The constitutive relationship for a power-law fluid is

$$\nu = m|\dot{\gamma}|^{n-1}\dot{\gamma} \tag{5.3}$$

where ν is the non-Newtonian viscosity, $\dot{\gamma}$ is the shear rate, and m and n are the power-law coefficients. For $n = 1$ the Newtonian behavior is recovered with $m = \mu$. If $n < 1$ then the fluid is considered shear-thinning.

At moderate Reynolds numbers, the wall effects depend on the Reynolds number and the diameter of the settling ball relative to the diameter of the column. For a power-law fluid the following relationships (Chhabra, 1993) were used to determine the wall-effect f

$$\frac{1/f - 1/f_\infty}{1/f_0 - 1/f_\infty} = \left\{1 + 1.3\,\mathrm{Re}_{PL,m}^2\right\}^{-0.33} \tag{5.4}$$

where

$$f_0 = 1 - 1.6(d/D), \tag{5.5}$$

$$f_\infty = 1 - 3(d/D)^{3.5}, \tag{5.6}$$

$$f = \frac{u_0}{u}, \tag{5.7}$$

and

$$\mathrm{Re}_{PL,m} = \frac{\rho_f d u}{m\left(u/d\right)^{n-1}} = \frac{\rho_f d^n u^{2-n}}{m}. \tag{5.8}$$

where u_0 is the measured velocity, u is the theoretical settling velocity in an infinite sea of fluid, d is the diameter of the sphere, and D is the diameter of the container. Also the drag coefficient C_D is defined as

$$C_D = \frac{4(\rho_b - \rho_f)gd}{3u^2\rho_f} \tag{5.9}$$

where ρ_b and ρ_f are the densities of the ball and fluid respectively, and g is the gravitational constant. The densities of the simulant were measured and reported in an earlier section. Everything but the settling velocity is known *a priori*. Note that the velocity used is the velocity corrected for wall-effects, which depends on the Reynolds number.

The procedure consists of guessing a plastic Reynolds number, calculating the wall effect (Eqs. 5.4-5.6), modifying the velocity (Eq. 5.7), determining the drag coefficient (Eq. 5.9), and finally calculating the Reynolds number from the drag coefficient assuming Newtonian behavior. From data found in Perry's handbook (1984), the following inverse relationship was determined for $0.5 \leq \mathrm{Re} \leq 50$,

$$\log(\mathrm{Re}) = 2.0292 - 1.999\log(C_D) + 0.60542\log(C_D)^2 - 0.14072\log(C_D)^3 \,. \tag{5.10}$$

Higher Reynolds numbers were not encountered, and for lower Reynolds numbers the creeping flow result could be used where

$$C_D = \frac{24}{\mathrm{Re}} \,. \tag{5.11}$$

Using the calculated Reynolds number as a guide, new Reynolds numbers are guessed until the calculated Reynolds number matches the guessed Reynolds number to three places. This procedure is repeated until all the different ball drops have self consistent Reynolds numbers. From the plastic Reynolds number and the power-law index n, the apparent m can be determined. By calculating the variance of m as a function of n, the best power-law index can be determined. Because the wall effect is independent of the power-law coefficients m and n, the determination of the Reynolds numbers can be separated from the determination of the power-law coefficients.

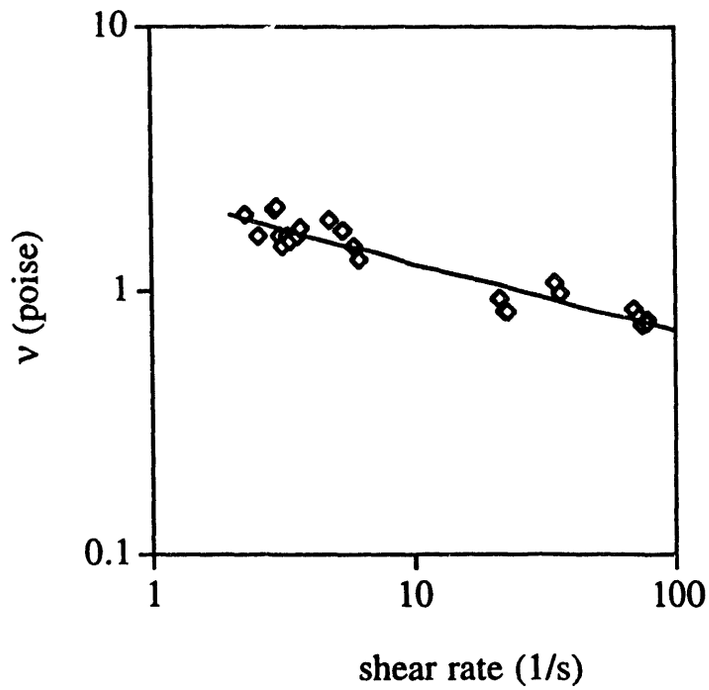

Figure 3: Settling data reduced assuming power-law behavior and resulting wall-effects gives power-law behavior.

Table 4: Power-law coefficients determined by falling ball.

Temperature [°C]	m [dyn s^n / cm^2]	n
51.2	1.59	0.72
25.2	11.7	0.72
40.8	4.34	0.72
50.0	1.59	0.78

In Fig. 3, the results of this analysis are shown. The power law coefficients are 0.74 and 2.29 for the power law index and fluid consistency index, respectively. Next the temperature was changed to 40.8°C, followed by a changed to 25.2°C. After that the balls were recovered, except for the aluminum balls . Because the off gassing occurred during the drops at 51.2°C (set A and B), the simulant was reheated back up to 50.0°C, and the initial test were repeated (set C). The results of all this can be seen in Fig. 4 and tables 4.

In Fig. 5, the stress versus strain was plotted to determine if the well-mixed simulant had a yield stress (either real or apparent). As can be seen in the figure, if a yield exists it was less than 10 dynes/cm^2 or 1 Pascal. Shown in Fig. 6, FS2 is compared with AS1, and FS2 appears to have a yield stress greater than 10

dynes/cm^2. If the yield stress is subtracted from the overall stress, the two simulants look pretty much the same.

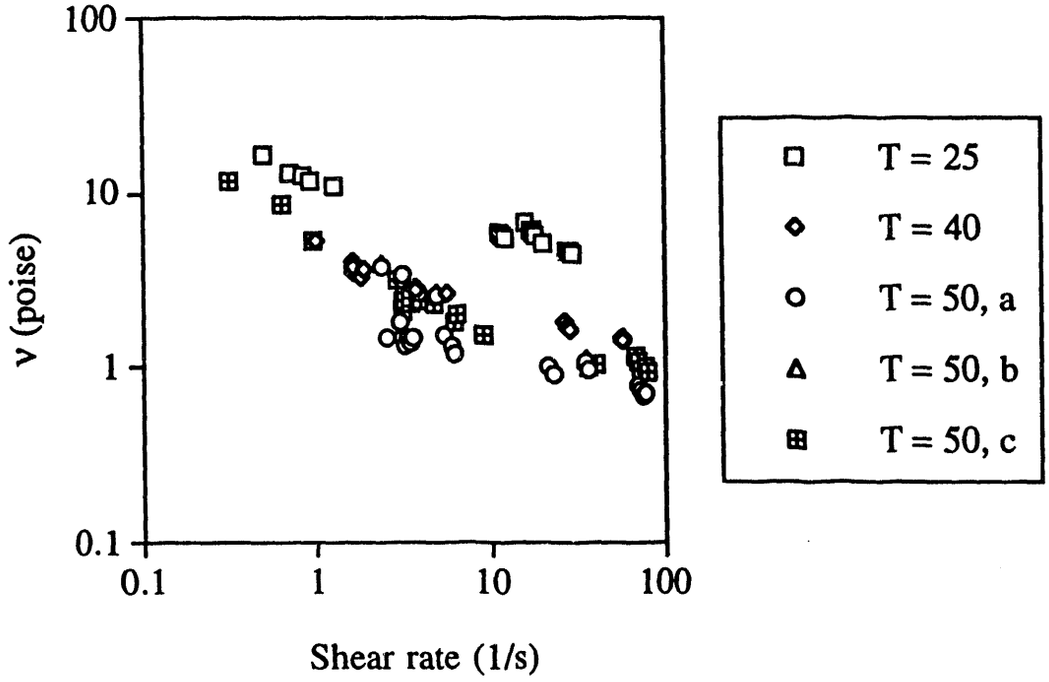

Figure 4: Rheogram for AS1 at various temperatures. Note that the first two tests at 50°C were performed during or soon after the aluminum balls were introduced into the simulant.

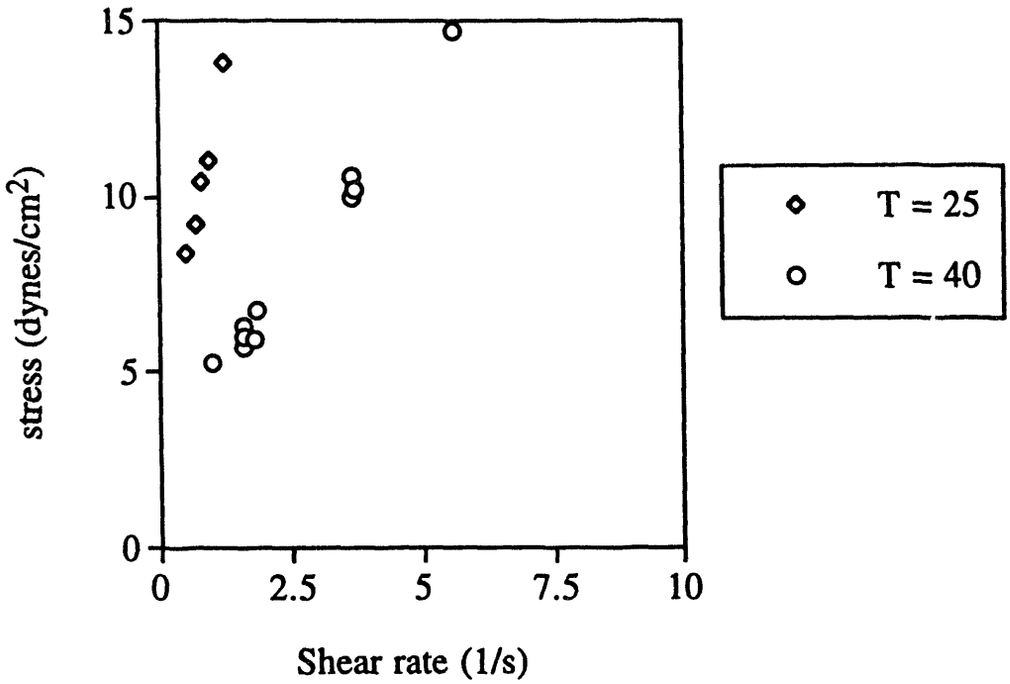

Figure 5: Low shear behavior of AS1 shows that the yield stress is less than 10 dynes/cm^2 or 1 Pascal.

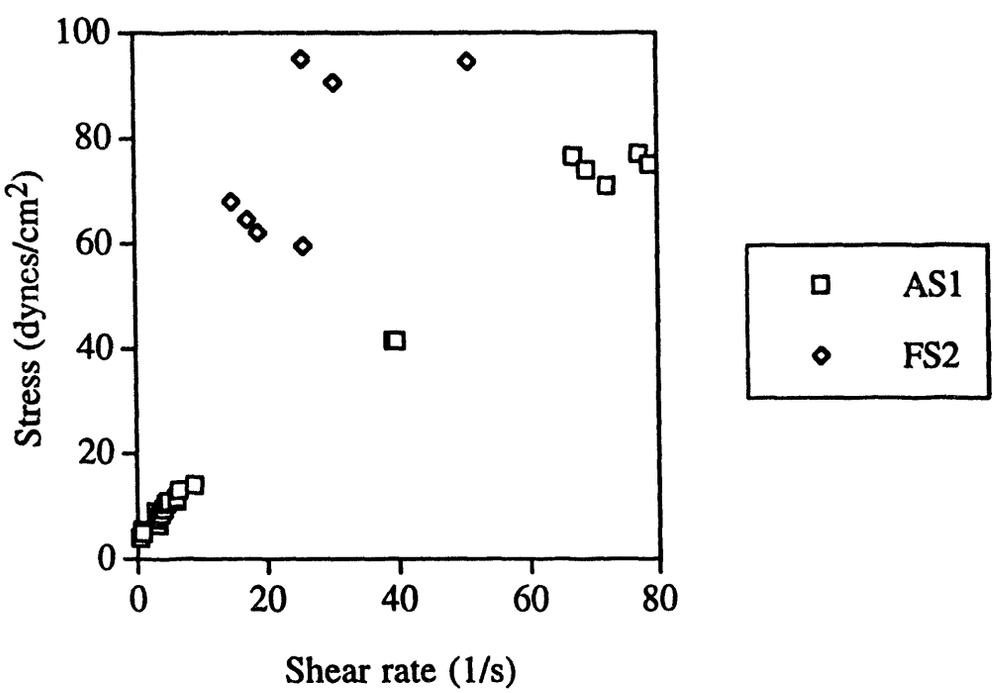

Figure 6: Stress-strain diagram for two types of simulants. AS1 has a lower effective viscosity than FS2 due to a corresponding lower yield stress.

5.3. Couette Viscometer Tests

The viscosity was measured by using a Couette viscometer with a bob radius of 1.9 cm and a cup radius 0f 2.3 cm. The bottom of the bob was concave and captured a bubble of air beneath the bob to provide a shear-free surface. It was therefore assumed that the measured torque was due only to sample being sheared in the annular gap between the cup and the bob. The shear stress in the gap was not uniform. From the conservation of momentum, it can be shown that the shear stress varies as the reciprocal of the radius squared. Thus the shear stress varied from its maximum at the surface of the bob to $(R_i/R_o)^2$ of the maximum value at the inner surface of the cup. For the Couette used, the ratio of the minimum stress to the maximum stress was 0.682.

The mean shear stress was calculated as the arithmetic average of the stress at the bob and the stress at the cup. The shear rate corresponding to this shear stress was calculated by using a series solution given by Mooney (1930). This series requires estimating the second derivative of the raw data. Derivatives were calculated by finite differences. Second derivatives were found to be small, so that only the leading term was important in calculating shear rates. The series solution is valid assuming:

a) the material has a yield stress lower than the minimum stress in the gap, so that all the material in the gap is shearing,
b) the material does not slip at the wall, and
c) the material remains homogeneous (sedimentation and particle migration are negligible).

Data were consistent with a zero or very small yield stress (lower than is measurable on the viscometer used), and the entire sample appeared by visual inspection to be sheared during measurements. No wall slip was detected by visual inspection either through the transparent cup wall or at the top surface in contact with the bob. Repeated runs on the same sample were reproducible to within ±15% except at the lowest torques, where the noise in the torque signal was a significant fraction of the measured torque.

The measured viscosities at the three temperatures are listed in Table 5

Table 5. Measured viscosity of Aged Simulant Using Couette Viscometer

Mean Shear Rate [1/s]	Mean Shear Stress [dyn/cm2]	Viscosity [Poise]	Temperature [°C]
0.473	2.17	4.59	24.2
0.841	3.75	4.46	24.2

1.50	4.65	3.11	24.2
2.66	7.29	2.74	24.3
4.73	10.95	2.31	24.3
0.841	2.88	3.42	30.6
1.50	4.44	2.97	30.5
2.66	5.98	2.25	30.6
4.73	8.24	1.74	30.6
0.472	1.56	3.30	40.4
0.840	2.30	2.73	40.4
1.50	2.83	1.89	40.4
2.66	3.87	1.45	40.5
4.73	5.12	1.08	40.5

The viscosity was found to obey a power law relation, see Eq. 5.3. The power law parameters are listed in Table 6.

Table 6. Power Law Parameters of Aged Simulant Obtained From Couette Viscometer

Temperature [°C]	m [dyn s^n / cm^2]	n
24.2	3.78	0.678
30.6	3.31	0.600
40.4	2.36	0.503

Comparison of results obtained from Couette and falling-ball rheometers are given in the following figure. As seen from this figure, the viscosity measured by the Couette viscometer at a given shear rate is less than measured by a falling-ball viscometer. Also the power-law index obtained from the Couette is less (more shear thinning) than for the fall ball. There are four possible explanations for this effect, a) particle migration, b) slip at the walls, c) yield stress with a short recovery time, or d) the different histories make comparisons between simulants futile.

The first explanation would either be a function of the amount of migration, stabilizing only upon reaching the steady-state concentration profile. As seen in earlier studies (Abbott et al. 1993), particle migration depends on the amount of shear, not the shear rate used to get there. These tests were performed by ramping the velocity up in a stepwise fashion from lowest to highest and then ramping down. Because, the viscosities measured on the way up matched those

on the way down, the particle migration would have to be completed during the first test at low shear rates. This seems unlikely.

The second explanation has been checked for as described above. For the last explanation, it seems more probably for our experience that the long times at room temperature would result in a more viscous, not less viscous, simulant. Therefore the third explanation appears mostly likely. To test this assumption, two tests could be performed to verify of bound the time scale of the yield behavior. First, using the Couette viscometer, stop the viscometer and wait a short period of time (a few seconds up to a couple of minutes). Then restart the viscometer and check for a transient reduction in torque. Second, using the falling-ball experiment and a fast settling ball (less than 2 seconds to move 8"), drop one ball a short time after dropping the first ball. Here, in the well mixed simulant, a faster settling velocity should be observed.

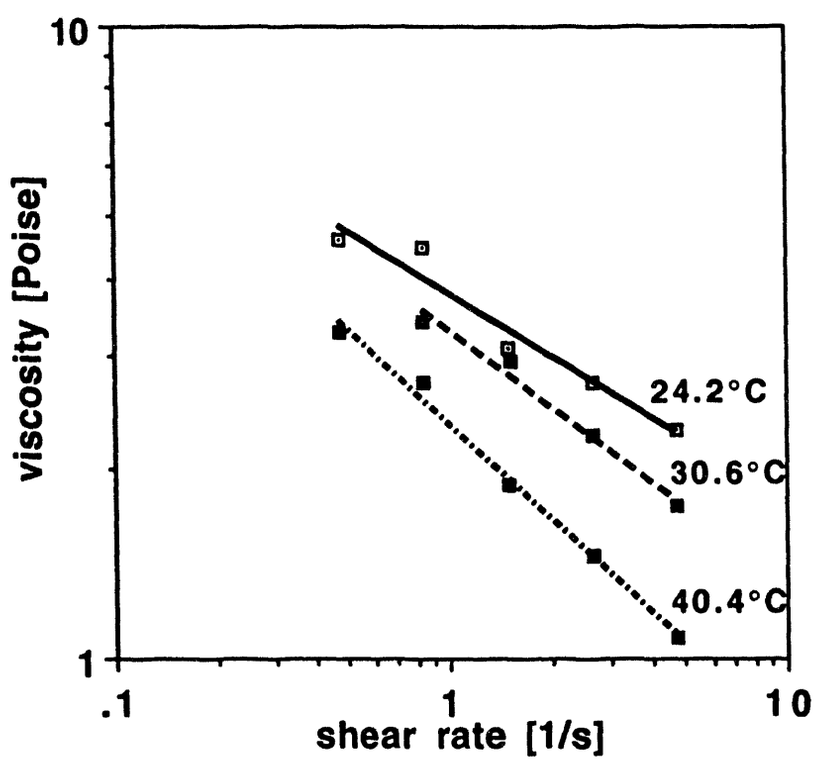

Figure 7. Viscosity of Hanford waste sludge at the temperatures indicated.

6. SUMMARY AND CONCLUSIONS

To model the viscous behavior of the simulant at moderate Reynolds number, it was clear from the beginning that inertial effects would have to be accounted for. Additionally, because of the size of falling balls relative to the size of the column, wall effects corrections would be important. The convective layer is expected to behave as a Newtonian suspension. These falling-ball experiments performed with well-mixed waste simulants, clearly shows that the mixed waste (and probably the nonconvective layer) are not Newtonian suspensions.

At high shear rates, a power-law analysis appeared to adequately model the data. For the fresh simulant, which has a higher yield stress, a correction for the yield stress appears to be necessary. As a function of temperature, the yield stress did not scale with the increased viscosity.

At low shear-rates, a yield stress appeared to exist. However, a Bingham plastic analysis did not improve the fit of the measurements. Part of the problem is that more dense balls do not always settle faster than less dense balls. This suggests that mixing the suspension does not make it homogeneous. Most of the mixing studies to date have concentrated on the uniform, single material balls, which settled at high shear rates. The possible explanations are that the simulant is inhomogeous or that the simulant recovers some yield stress after mixing. For the latter explanation, the recovery time would have to be on the order of one minute. This suggests that a history-dependent Bingham plastic model may be necessary.

The physics behind the time dependent Bingham plastic appear to be related to structure formation of the precipitated salts. This would depended on the rate of crystal dissolution/recrystalization, which would increase with increasing temperature. This would explain why the yield stress did not increase with decreasing temperature.

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8. REFERENCES

Abbott, J. R.., 1992, "Dispersive Process in Concentrated Suspensions," Ph.D. Thesis, Department of Chemical Engineering, Massachusetts Institute of Technology, Cambridge, MA.

Abbott, J. R., N. Tetlow, A. L. Graham, S. A. Altobelli, E. Fukushima, L. A. Mondy, and T. S. Stephens, 1991, "Experimental Observations of Particle Migration in Concentrated Suspensions: Couette Flow," *J. Rheology* **35**(5).

Agnew, S. F. and Sullivan, L. H., 1993, "Evaluation of Ultrasonic for the Mitigation of episodic Gas Release in Hanford waste Tank 241-SY-101,' Draft Report.

Anderson, J. L. and Reed, C. C., 1990, Diffusion of spherical macromolecules at finite concentration," *Int. J. Multiphase Flow,* **16**(4):579-596.

Ansley, R. W. and T. N. Smith, 1967, "Motion of Spherical Particles in a Bingham Plastic," *AIChE J* **13**:1193–1196.

Batchelor, G., 1982, "Sedimentation in a dilute polydisperse system of interacting spheres. Part 1. General theory, " *J.Fluid Mech.,* **124**:379-408.

Batchelor, G. and Wen, C-S., 1982, " Sedimentation in a dilute polydisperse system of interacting spheres. Part 2. Numerical Results, " *J. Fluid Mech.,* **124**:495-528.

Beris, A. N., J. A. Tsamopoulos, R. C. Armstrong, and R. A. Brown, 1985, "Creeping Motion of a Sphere through a Bingham Plastic," *J. Fluid Mech* **158**, 219–244.

Bohlin, T. ,1960, "On the drag on a rigid sphere moving in a viscous liquid inside a cylindrical tube, "Trans. *R. Inst. Tech. (Stockholm),* **155**:1-63.

Brenner, H., Graham, A. L., Abbott, J. R., and Mondy, L. A. , 1990, "Theoretical basis for falling-ball rheometry in suspensions of neutrally buoyant spheres. *Int. J. Multiphase Flow,* **16**(4):579-596.

Brookes, G. F. and R. L. Whitmore, 1969, "Drag Forces in Bingham Plastics," *Rheologica Acta* **8** (4), pp. 472–482.

Brookes, G. F. and R. L. Whitmore, 1968, "The Static Drag on Bodies in Bingham Plastics," *Rheologica Acta* **7**(2), pp. 188–193.

Burgers, J. M. , 1939, " *On the Motion of Small Particles of Elongated Form Suspended in a Viscous Liquid,"* , Chapter 3. Second Report on Viscosity and Plasticity. Nordemann, Amsterdam.

Chhabra, R. P., 1993 Bubbles, *Drops, and Particles in Non-Newtonian Fluids* (CRC Press.

Einstein, A. ,1906, "A new determination of molecular dimensions, " *Annln Phys.*, 19:2S9-306.

Einstein, A. ,1911, " Correction to my work: a new determination of molecular dimensions," *Annln Phys.*, 34:591-592.

Faxen, H., 1923, " Die Bewegung Einer starren Kugel lang~ der Achse eines mit zaher Flussigkeit gefullten Ruhres," *Ark. Mat. Astr. Fys,* 17(1).

Faxen, H., 1927, " Simplified representation of the generalized green's equations for the constant motion of translation of a rigid body in a viscous fluid," *Ark. Mat. Astr. Fys,* 20(8):5.

Glasrud, G. G., Navarrete, R. C., Scriven, L. E. and Macosko, C. W., 1993, Settling behaviors of iron oxide suspensions," *AIChE Journal,* 39:4.

Hancock, G. J., 1953, " The self-propulsion of microscopic organisms through liquids," *Proc. Roy. Soc.*, A 217:96.

Happel, J. and Brenner, H. , 1983," *Low Reynolds Number Hydrodynamics,"* Martinus Nijhoff Publishers.

Ito, S. and T. Kajiuchi, 1969, "Drag Force on a Sphere Moving in Plastic Fluid," *Journal of Chemical Engineering of Japan* 2(1), 19–23.

Jeffrey, D. J. and Onishi, Y. , 1984, " Calculation of the resistance and mobility functions for two unequal rigid spheres in low-Reynolds number flow," *J. Fluid Mech.*, 139:261-290.

Michaels A. S. and Bolger, J. C., 1962, "Settling Rates and Sediment Volumes of Flocculated Kaolin Suspensions", *I&EC Fundm.* 1(1), 24.

Milliken, W., Gottlieb, M., Graham, A. L., Mondy, L. A., and Powell, R. L., 1989a, " The viscosity-volume fraction relationship of a randomly oriented suspension of rods", *J. Fluid Mech.*, 202:217-232.

Milliken, W. J., Gottlieb, M., Graham, A. L. Mondy, L. A. and Powell, R. L., 1989b, "The Viscosity-Volume Fraction Relation for Suspensions of Rod-Like Particles by Falling-Ball Rheometry," *J. Fluid Mechanics* 22. 217–232.

Milliken, W., Mondy, L. A., Gottlieb, M., Graham, A. L., and Powell, R. L., 1989b, " The effect of the diameter of falling ball on the apparent viscosity of suspension of spheres and rods" *Phys.* 11 (3):341-355.

Mondy, L. A., A. L. Graham, and J. L. Jensen, 1986, "Continuum Approximations and Particle Interactions in Concentrated Suspensions," *J. Rheology* **30**(5), 1031–1051.

Mondy, L. A., Morrison, T. G., Graham, A. L. and Powell, R. L., 1990, "Measurements of the Viscosity of Suspensions of Oriented Rods Using Falling Ball Rheometry," *Int. J. Multiphase Flow* **16** (4), 651–662.

Mooney, M., 1930, "Explicit formulas for slip and fluidity," J. Rheol. 2(2), 210-222.

O'Neill, M. E. and Majumdar, S. R., 1970, "Asymmetrical slow viscous fluid motions caused by the translation or rotation of two spheres. part I: The determination of exact solutions for any values of the ratio of radii and separation parameters," Z. *angeu~. Math. Phys.*, 21:164-179.

Pasamehmetoglu, K., Unal, C., and Edward's, J. N. ,1993, " Evaluation Methods for Rheology of the Waste Contained in Hanford Tank 241-SY-101," Los Alamos National Laboratory draft report (October).

Perry's Chemical Engineering Handbook, 1984 6th edition, Don Green, Ed. MacGraw Hill.

Phan-Thien, N., Jin, H., and Zheng, Rong, 1993, "On the Flow Past a Needle in a Cylindrical Tube," *Journal of Non-Newtonian Fluid Mechanics*, **47**:137-155.

Powell R. L., and L. A. Walla, 1991, "Viscosity Measurement of Suspensions of Rod Mixtures," *Liquid-Solid Flows-1991* (American Society of Mechanical Engineers, New York, New York), FED-Vol.. 118, pp. 117–122.

Richardson, J. F. and Zaki, W. N., 1954, "Sedimentation and Fluidization: Part I, " Trans. Inst.. Chem. Engrs. 32,35-53,

Richardson, J. F. and Zaki, W. N., 1954, ", Sedimentation and Fluidization: Part III The Sedimentation of Uniform Fine Particles and Two-Component Mixtures of Solids" Trans. Inst.. Chem. Engrs. 32, 348-356.

Tingey, J. M., 1992, "Rheological Properties of Waste from Tank 101-SY," Pacific Northwest Laboratory draft report (May).

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