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Sedimentation Models

D. R. Rector
B. C. Bunker

September 1995

Prepared for
the U.S. Department of Energy
Contract DE-AC06-76RLO 1830

Pacific Northwest Laboratory
Operated for the U.S. Department of Energy
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1.0 Introduction

The nuclear wastes currently stored in tanks at the Hanford site contain complex mixtures of insoluble sludge particles, salts, and supernatant liquids. Treatment and ultimate disposal of these tank wastes will require that the complex solid-liquid mixtures be dispersed in aqueous solutions for retrieval and transport. The mixtures will then require pretreatment steps that will ultimately require the isolation of insoluble particles from supernatant liquids via solid-liquid separation steps such as settle-decant operations, centrifugation, or filtration. There is a perception that sludge treatment in general, and solid-liquid separations in particular, are relatively trivial operations that can easily be transferred to private industry to initiate tank cleanup. Experiences gained over the past few years at Hanford suggest that waste processing is not as trivial as it seems.

The difficulties of tank waste processing can be illustrated by considering a process that appears to be completely mundane: separation of solid particles from supernatant liquids using sedimentation processes. In this process, a slurry of particles in an aqueous solution generated after transport, washing, or leaching of the sludge is left alone in a storage tank. Over time, the solid particles sink to the bottom under gravity. Ideally, this process yields a dense layer of particles on the bottom of the collection tank with a clear layer of supernatant liquids on top of the tank. Solid-liquid separation is then readily achieved by merely pumping off the supernatant liquids and leaving the solids behind. Unfortunately, practical experience on both real sludge and on simulants reveals that the "ideal" sedimentation process is often not observed and that many key issues in sedimentation need to be understood and controlled.

Solid particles do not always settle out, and when they do settle, sedimentation rates are often too slow to be of practical utility. For a viable sedimentation process, current baseline processes assume that a sedimentation velocity of at least 3 cm/hr will be required if a settle-decant step in a single tank is to take less than one month. Such sedimentation velocities often are not achieved. In some instances, the particles appear to interconnect to form low-density networks that settle very slowly. Even when some of the sludge settles rapidly, a fraction of the sludge can remain in supernatant liquids as nonsedimenting fines. Many factors influence the above behavior. Sedimentation rates can vary from tank to tank, and are influenced by parameters such as solids loadings, pH, salt content, organics, and temperature. Even within a given tank, sedimentation behavior can change dramatically. For example, washing and leaching can transform a sediment that settles readily into a sludge that does not appear to settle at all. After sedimentation is complete, the fraction of sludge remaining as "fines" can vary by orders of magnitude, depending on the composition of the mixture and processing conditions.

While sedimentation rates are of concern, final sediment densities are also of critical importance. The total volume occupied by the sediment layer needs to be minimized to minimize the volume required of processing facilities (involving million-gallon tanks in the best-case scenario). In addition, the efficiency of the solid-liquid separation process depends on how effectively the particles in the sediment pack. The total volume of liquid in the tank is partitioned between supernatant liquids that can be pumped away and interstitial liquids that are trapped in the sediment layer. Even if washing or leaching steps completely dissolved desired constituents during processing, the fraction of the solubilized components actually removed in solid-liquid separations is limited to the fraction of the total liquids that are supernatant. Ideally, the goal is to have the sediment achieve maximum packing densities (as high as 60 vol% solids) to minimize the volume of interstitial liquids. In practice, sediment densities seem to span a range from 20 vol% down to as low as 5 vol%. Regarding sedimentation velocities, the final sediment density also appears to be sensitive to both the nature of the sludge and to a wide range of processing parameters. For example, washing and leaching steps can transform a relatively dense sludge into a sediment that occupies 4 to 5 times its original volume. If such expansion is not controlled, or at least anticipated, the results in terms of waste processing could be quite serious.

Given the complexity of Hanford wastes and the wide range of potentially variable processing parameters, one might assume that we will never be able to predict, understand, or control sedimentation behaviors. However, it appears that some relatively simple concepts can be used to rationalize the behavior of tank wastes. One concept that is central to understanding the behavior of sludge is the recognition that the observed behavior is typical of the behavior of agglomerates that are made up of fine particles. Transmission electron micrographs (TEM) show that much of the material in sludge consists of extremely fine (5-10 nm) primary particles. If the particles are dispersed, they are too small to settle. If the particles stick to each other, they form larger agglomerates that can lead to most of the sedimentation behaviors described above.

This report describes the early sedimentation modeling efforts performed by Pacific Northwest Laboratory (PNL) for Westinghouse Hanford Company (WHC) under the Tank Waste Treatment Science task through the TWRS Pretreatment Technology Development Project. Our initial modeling approach started with simple models to describe both agglomeration and sedimentation behaviors. For agglomeration, the initial models have focussed on understanding the interparticle interactions that either promote or discourage agglomeration and relating those interactions back to sludge chemistry. For sedimentation, initial models have focussed on predicting the sedimentation and sediment compaction behavior of ideal particulate suspensions containing hard spheres. Hard sphere models have been used to help understand general sedimentation phenomena. The extension of these models to the sedimentation behavior of colloidal aggregates is described in Rector and Bunker (1995).

In Section 2.0 of this report, we discuss a transient sedimentation model which describes the sedimentation behavior in the bulk and the relative layering of different particle species and compaction of the sediment layer as a function of time. Features of this model include

- hindered settling velocities;
- temperature-dependent diffusion, and
- osmotic pressure.

The transient sedimentation model requires constitutive relationships for the hindered settling factor and compressibility factor. Section 3.0 describes computational and experimental methods for obtaining compressibility factors for nonspherical or interacting particle systems. For example, we describe an equilibrium sedimentation model which uses a Monte Carlo method to determine the density profiles on concentrated colloidal suspensions in sedimentation equilibrium. In many particulate systems, the particles attract each other to form aggregates. To account for this behavior, in Section 4.0 we describe an aggregation model and combine this model with the transient sedimentation model. Finally, in Section 5.0, we show how the hard sphere model predictions compare with experimental results on sludge and sludge simulants. The comparisons will show that many of the features of sedimentation can be rationalized on the basis of the simple hard sphere model by simply replacing a hard sphere by a fractal agglomerate. We also discuss the implications of the models on processing and on future model developments.

2.0 Transient Sedimentation Model

A transient sedimentation model is required which captures all the important features of the sedimentation process. Starting with the simplest possible system, we assume a well-mixed suspension of uniform particles in a closed container, where there are no attractive interparticle interactions which would cause a gel to form. As the suspension begins to settle, certain features become noticeable. A clear liquid layer, devoid of particles, forms at the top and becomes larger with time. A high-density sediment layer begins to form at the bottom of the container and grows with time. As the particles settle, the particle density increases and the rate of settling decreases. As particles continue to accumulate on the top of the sediment layer, the weight of settled particles causes the sediment layer to compress. After a sufficiently long period of time, all the particles have settled and the sediment layer approaches an equilibrium density profile.

In this section, we describe a transient sedimentation model which not only describes the sedimentation behavior in the bulk, but also the relative layering of different particle species and compaction of the sediment layer as a function of time. Features of this model include

- hindered settling velocities,
- temperature-dependent diffusion, and
- osmotic pressure.

We discuss the addition of an aggregation model to this sedimentation model in Section 4.0.

2.1 Description of the Method

At infinite dilution, a small sphere with density, p , differing from that of the surrounding liquid by $\Delta\rho$ moves at the Stokes velocity, U_0 , where

$$U_0 = \frac{2a^2 \Delta\rho g}{9\mu} \quad (1)$$

In Eq.(1), a is the particle radius, μ is the liquid viscosity, and g is the acceleration due to gravity. As particles move closer together, hydrodynamic interactions decrease the sedimentation velocity relative to U_0 . This reduction can be expressed in terms of a hindered settling factor, $K(\phi)$, where ϕ is the volume fraction. As an example, for uniform noninteracting spheres, this factor is given by the expression (Richardson and Zaki 1954)

$$K(\phi) = \frac{U}{U_0} = (1 - \phi)^n \quad (2)$$

where $6.6 > n > 4.5$. Note that at $\phi=0$, $K(\phi)=1$ and as ϕ approaches one, $K(\phi)$ approaches zero. Values of the hindered settling factor for a particular system may be determined either by experiment or by computational modeling using the Stokesian Dynamics method (Brady and Bossis 1988).

As particles approach the sediment layer, they experience a net upward force, or pressure, due to the increased density of particles below. This Brownian force is represented by an osmotic pressure, Π , which is also expressed in terms of a compressibility factor,

$$Z(\phi) = \Pi(\phi) / \rho k_B T \quad (3)$$

where p is the particle number density, k_B is the Boltzmann constant, and T is the temperature. The value of the osmotic pressure as a function of volume fraction, or number density, is also known as the osmotic pressure equation of state. For example, the osmotic pressure for uniform noninteracting spheres is given by a hard sphere equation of state such as the Carnahan-Starling (1969) equation.

$$Z(\phi) = \frac{1 + \phi + \phi^2 - \phi^3}{(1 - \phi)^3} \quad (4)$$

The osmotic equation of state can be used to predict the equilibrium density profile by relating the particle number density at a particular axial level to the osmotic pressure, defined to be the integral of the relative mass (subtracting the density of the liquid) of the particles above that level. The osmotic pressure equation of state can be obtained either experimentally, by measuring axial density profiles, or by performing Monte Carlo sedimentation simulations (described in Section 3.1).

To predict the changing density profile of a sedimenting system, an equation is needed which relates both the gravity and Brownian forces to the number density, or volume fraction, at each elevation. The conservation equation for a single-component, one-dimensional settling process takes the form (Russel, Saville, and Schowalter 1989)

$$\frac{\partial \phi}{\partial t} = D_0 \frac{\partial}{\partial x} \left[K(\phi) \frac{d}{d\phi} [\phi Z(\phi)] \frac{\partial \phi}{\partial x} \right] - U_0 \frac{\partial}{\partial x} [\phi K(\phi)] \quad (5)$$

where $D_0 = kT/6\pi\mu a$ is the Stokes-Einstein diffusion coefficient and x is the elevation. For a uniformly mixed suspension, we would specify an initial condition of $\phi(x,0) = \phi_0$ and zero flux boundary conditions at the top and bottom of the container. The first term on the right hand side represents the net change in particle volume fraction due to temperature-dependent Brownian diffusion. The second term represents the change in volume fraction due to gravity settling. The system reaches equilibrium ($\delta\phi/\delta t = 0$) when the two terms cancel each other.

2.2 Numerical Solution

The conservation equation is solved by using a finite-difference formulation. To express this equation in terms of finite-differences, we must convert it into a more usable form. If we define a dimensionless diffusivity

$$D(\phi) = K(\phi) \frac{d}{d\phi} [\phi Z(\phi)] \quad (6)$$

we can rewrite the conservation equation (5) as

$$\frac{\partial \phi}{\partial t} = \frac{\partial}{\partial x} (D_0 D(\phi) \frac{\partial \phi}{\partial x}) - U_0 \phi K(\phi) \quad (7)$$

where the first term is easily recognized as a diffusion term and the second, a convection term. The diffusion term is solved using a Crank-Nicholson formulation (Anderson, Tannehill, and Pletcher 1984) which is implicit in time and second-order accurate. The convection term is expressed using an upwind-differencing formulation which is explicit in time but more physically representative than higher-order formulations. Because the convection term is explicit in time, the time step, Δt , is

restricted by the Courant limit (Anderson, Tannehill, and Pletcher 1984)

$$\Delta t = \frac{\Delta x}{U}$$

where Δx is the size of the axial level finite-difference nodes.

2.3 Results for Spherical Particle Systems

We demonstrate this computational model by calculating sedimentation as a function of time for two different spherical particle systems to show the effect of the compressibility factor, $Z(\phi)$, on sedimentation behavior. Each system consists of a 10-cm.-high container filled with a 10 vol% solution consisting of 1- μm spherical particles with a specific gravity of 2.0.

The first system has noninteracting spheres with the corresponding Carnahan-Starling equation of state. Figure 2.1 shows the axial volume fraction distribution profiles as a function of time. The time to reach sedimentation equilibrium can be established by plotting the sediment center of mass as a function of time such as shown in Figure 2.2. Note that for the hard sphere system, there is a dense sediment layer (~60-70%) and little compaction as a function of time.

In contrast, many particle systems have aggregating particles (see Section 4.0) which form a gel consisting of particle chains that have packing fractions of 20%, 10%, or less. These particle networks can be elastic, resulting in sediments which are somewhat compressible. The second system

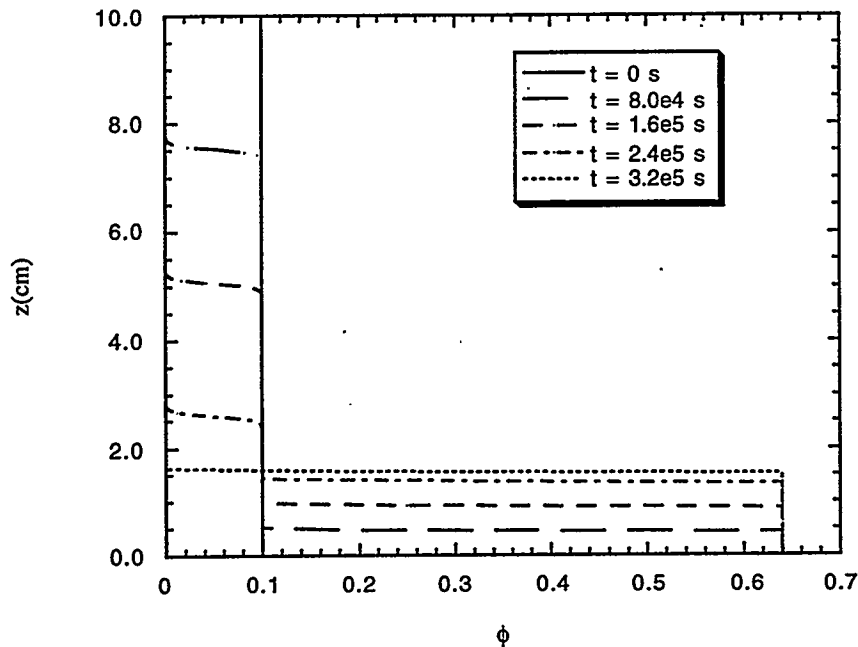


Figure 2.1. Axial Density Profile for Noninteracting Spherical Particles as a Function of Time

is assumed to consist of particles having the compressibility factor shown in Figure 2.3 as a function of volume fraction. Methods for determining the compressibility factor of a system are discussed in Section 3.0. For comparison, the hindered settling factor is assumed to be the same as for the first case. For a real aggregating system, an aggregation kinetics model would be included (see Section 4.3). Figure 2.4 shows the resulting axial volume fraction distribution profiles as a function of time. Note that, in this case, the sediment is nonuniform and the maximum volume fraction is less than 30%. Note also that even after all the particles have reached the sediment layer, the sediment continues to compact.

2.4 Sedimentation of Spherical Particle Mixtures

This model has been extended to predict the transient density profiles of particle mixtures. The primary difference is that a conservation equation is solved for each particle type. For example, for particle type 1, the conservation equation is

$$\frac{\partial \phi_1}{\partial t} = D_0 \frac{\partial}{\partial x} [D_{11} \frac{\partial \phi_1}{\partial x} + D_{12} \frac{\partial \phi_2}{\partial x} \dots] - U_0 \frac{\partial}{\partial x} \phi_1 K(\phi_1, \phi_2 \dots) \quad (8)$$

where D_{ij} are the diffusion coefficients which give the flux of particles of type i resulting from the existence of a gradient of concentration of particles of type j .

The hindered settling factor, $K(\phi_1, \phi_2 \dots)$, and compressibility factor, $Z(\phi_1, \phi_2 \dots)$, are now expressed in terms of volume fraction for each type of particle. Analytical expressions exist for mixtures of noninteracting spherical particles of different sizes. For spherical particles which are somewhat similar in size and density, the hindered settling factor is given by the expression

$$K(\phi) = \frac{U}{U_0} = (1 - \phi)^n \quad (9)$$

where $\phi = \sum \phi_i$. For particles with significantly different sizes or densities, the hindered settling factor is given by (Davis and Gecol 1994)

$$K(\phi_1, \phi_2 \dots) = (1 - \phi)^{-S_0} (1 + \sum_{j=1}^m (S_{ij} - S_{ii}) \phi_j) \quad (10)$$

where S_{ij} are dimensionless sedimentation coefficients given by Batchelor and Wen (1982). The compressibility is given by the mixed hard sphere equation of state (Mansoori et al. 1971)

$$Z(\phi_1, \phi_2 \dots) = [(1 + \xi + \xi^2) - 3\xi(y_1 + y_2\xi) - \xi^3 y_3] (1 - \xi)^{-3} \quad (11)$$

where

$$y_1 = \sum_{j=1}^m \Delta_{ij} (d_i + d_j)(d_i d_j)^{-1/2} \quad (12)$$

$$y_2 = \sum_{j=1}^m \Delta_{ij} \sum_{k=1}^m \left(\frac{\xi_i}{\xi_j} \right) \frac{(d_i d_j)^{1/2}}{d_k} \quad (13)$$

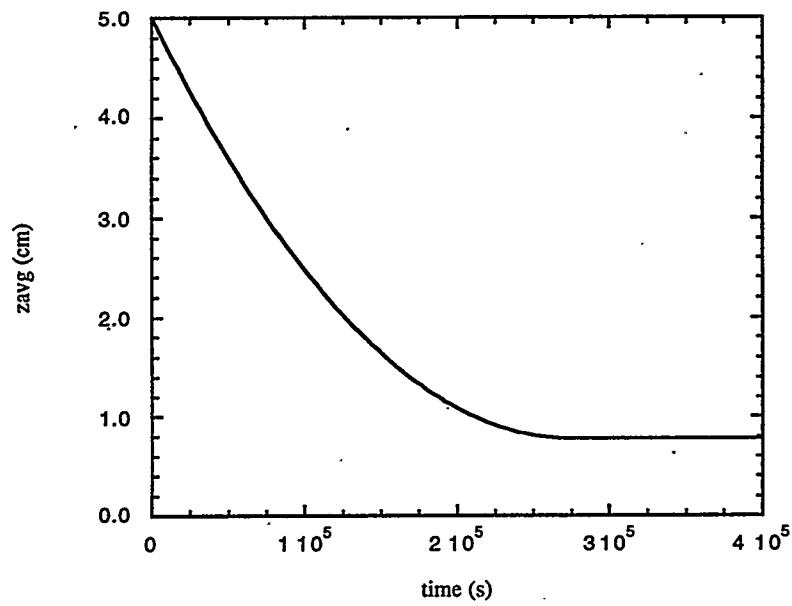


Figure 2.2. Axial Location of the Sediment Center of Mass as a Function of Time

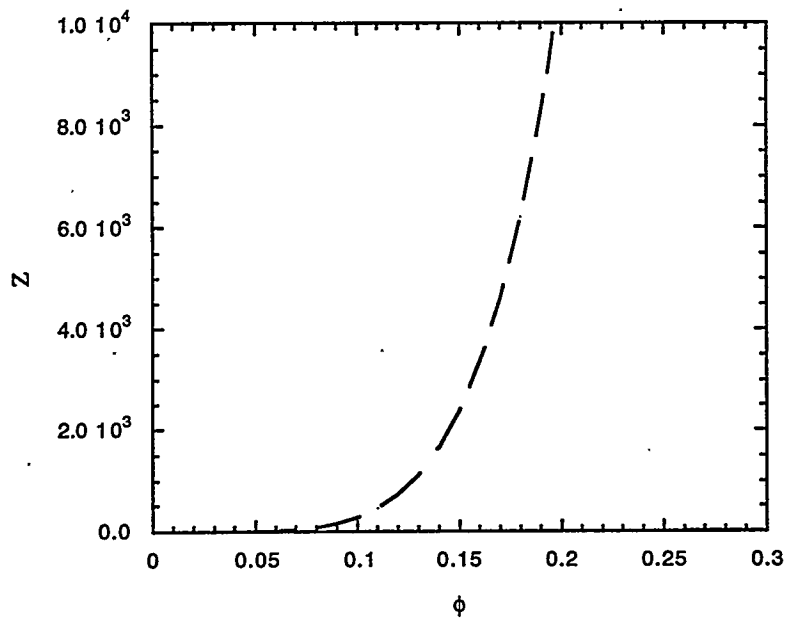


Figure 2.3. Compressibility Factor for Sample Case Representing Aggregating Particles

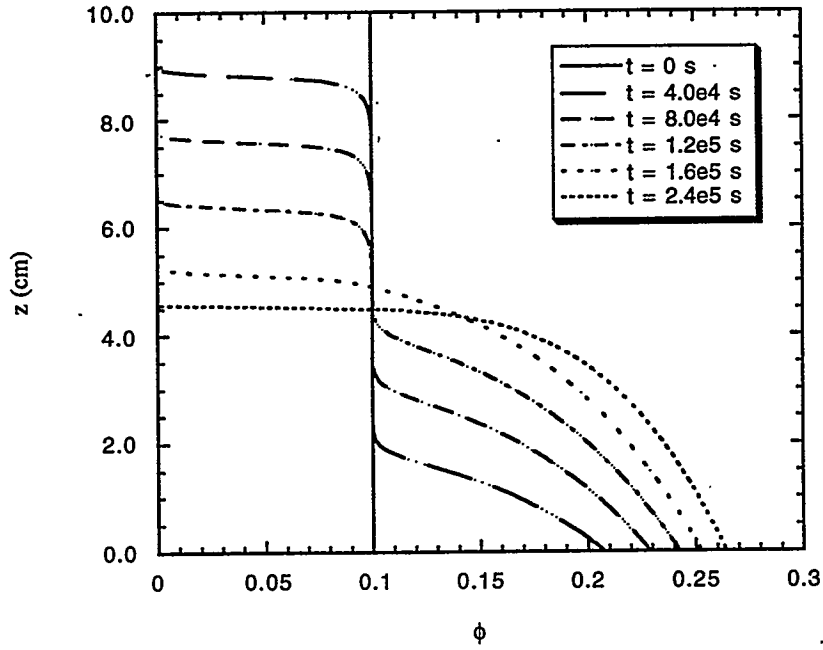


Figure 2.4. Axial Density Profile for Aggregating Spherical Particles as a Function of Time

$$y_3 = \left[\sum_{i=1}^m \left(\frac{\xi_i}{\xi} \right)^{2/3} x_i^{1/3} \right]^3 \quad (14)$$

$$\Delta_{ij} = \left[(\xi_i \xi_j)^{1/2} / \xi \right] [(d_i - d_j)^2 / d_i d_j] (x_i x_j)^{1/2} \quad (15)$$

$$\xi = \sum_{i=1}^m \xi_i; \quad \xi_i = \frac{1}{6} \pi \rho d_i^3 x_i; \quad \sum_{i=1}^m x_i = 1 \quad (16)$$

p is the number density, d_i is the diameter, and x_i is the mole fraction of the i th component.

The ability to do mixture calculations is important because most particle systems of engineering interest consist of mixtures of particles of different sizes and densities. In addition, modeling systems of aggregating particles (described in Section 4.0) will require that we treat particle aggregates as particles of different sizes and densities.

3.0 Determination of Compressibility Factors

The transient sedimentation model described in Section 2.0 requires constitutive relationships for the hindered settling factor, K , and compressibility factor, Z . Analytical expressions were presented for hard spheres and hard sphere mixtures. However, many systems have interacting or nonspherical particles. Therefore, we need methods for determining these factors, especially the compressibility factor, Z , since the hindered settling factor can usually be obtained directly by experiment. The compressibility factor determines the equilibrium density profiles of the sediment and the relative layering of the different components in the sediment.

In this section we describe an equilibrium sedimentation model which uses a Monte Carlo method to determine the density profiles on concentrated colloidal suspensions in sedimentation equilibrium. The osmotic equation of state, which gives the compressibility as a function of volume fraction, can be calculated from the calculated equilibrium density profiles. The osmotic equation of state can also be determined from experimental density profile or sediment height data.

3.1 Description of the Equilibrium Sedimentation Model

A model has been developed to predict equilibrium sedimentation density profiles of colloidal systems by looking at the particle structuring from a microscopic (or rather mesoscopic) point of view, using computational statistical mechanics. The model was developed by Biben, Hansen, and Barrat (1993) and uses a Monte Carlo method to determine the density profiles on concentrated colloidal suspensions in sedimentation equilibrium. This model relates particle size, solid density, interfacial chemistry, and interparticle interactions to sedimentation properties.

Consider a system of interacting colloidal particles suspended in a semi-infinite medium extending from $z=0$ (bottom of the container) to $z=+\infty$. The colloidal particles are assumed to be spherical (other shapes may be included later) but are allowed to vary in size, charge, and mass. If the particles are sufficiently large, the suspending liquid may be regarded as a continuum. The effective mass of the colloidal particle, m , of diameter, σ , is the bare mass of the particle minus the mass of the displaced medium. It is also assumed that the particles interact via a spherically symmetric, effective pair potential, $u(r)$ (other forms may be included later) where r is the particle separation. The total potential energy, U , for N such particles is given by

$$U = \sum_{i=1}^{N-1} \sum_{j=i+1}^N v(r_{ij}) + \sum_{i=1}^N \phi(z_i) \quad (17)$$

where $v(r_{ij})$ represents particle-particle interactions and $\phi(z_i)$ represents the particle potential energies due to the gravitational field. The N particles are confined to a tube with a horizontal (xy) section of area S . The bottom of the tube is taken to be an impenetrable surface. The total number of particles of each species in the system can be expressed in terms of particle surface density, $n_s = N/S$. Another dimensionless parameter used to characterize the system is the inverse gravitational length $\alpha = mg/k_B T$.

Monte Carlo calculations are used to calculate the sedimentation density profiles of both monodisperse and mixed hard sphere systems. The particle number density profiles, $p(z)$, are computed using the standard Metropolis algorithm, with a vertical downward bias controlled by the gravitational Boltzmann factor $\exp\{-\beta mgz\}$. Monte Carlo runs extend over tens of thousands of cycles, each cycle involving one trial move for each of the N particles. The rate of equilibration in the gravitational field is analyzed, among other tests, by monitoring the running average of the altitude of the center of mass, z_c .

3.2 Sample Results

A monodisperse hard sphere system was modeled to demonstrate the effect of temperature on sedimentation. Figures 3.1 and 3.2 show the density profiles for systems with a particle surface density of $n_s^*=40$ and inverse gravitational lengths of $\alpha^*=\alpha\sigma=0.2$ and 0.4 , respectively. The change in inverse gravitational length can result from either doubling the effective mass of the particle or dropping in temperature by one half. The results are expressed in terms of reduced number density $p^*=p\sigma^3$ and reduced elevation $z^*=z/\sigma$. Note that the higher density/lower temperature case (Figure 3.2) shows more structured particle layering, or "crystallization," near the bottom. Note also that the lower density/higher temperature case (Figure 3.1) has a smoother profile, with a "tail" that extends to a higher elevation. These results are similar to those reported by Biben, Hansen, and Barrat (1993).

A set of simulations was performed for a system of mixed hard sphere particles to determine the effect of size and density on the layering of different particle species. The system consisted of equal numbers of large (σ_1) and small particles ($\sigma_2=0.5\sigma_1$), each with a surface density of $n_s^*=20$. In the first case, the solid density of the two particle types is assumed to be the same, therefore the effective masses are related by the expression $m_1/m_2=(\sigma_1/\sigma_2)^3$. The associated inverse gravitational lengths are $\alpha^*=0.4$ and 0.05 , respectively. In the second case, the effective masses of the two particle types are assumed to be equal. The calculated density profiles are presented in Figure 3.3 for the equal solid density case and Figure 3.4 for the equal effective mass case. The results are presented in terms of σ_1 .

The equal solid density results presented in Figure 3.3 show that the larger (and hence, heavier) particles concentrate near the bottom, while the density profile of the smaller particles goes through a maximum around $z^*=40\sigma_1$. Contrast that with the results for the equal effective masses case presented in Figure 3.4. In this case, the smaller particles concentrate near the bottom because of excluded volume effects. The larger particles have a density profile which goes through a maximum around $z^*=18\sigma_1$. Note also that the maximum elevation of the second case is much less than the first, because of the increased effective mass of the smaller particles.

Work has begun on incorporating particle-particle interactions into the sedimentation equilibrium model. The interactions which are being added include a Yukawa potential and a DLVO interaction. The Yukawa potential consists of a hard sphere plus a repulsive screened Coulomb potential. The DLVO interaction (described more fully in Section 4.1) consists of an attractive van der Waals term, specified by an effective Hamaker constant, and a repulsive screened Coulomb potential. Once these particle interaction terms are included, the effect of solution chemistry, such as pH, and particle charge on sedimentation can be explored.

3.3 Compressibilities from Density Profiles or Sediment Height Data

The density and composition of sediment at any axial level depends on the accumulated effective weight of sediment above that axial level, also known as the osmotic pressure, Π . As discussed in Section 2.1, the expression which relates the temperature and density to osmotic pressure is known as the osmotic pressure equation of state. This expression can be determined from density profile information obtained either computationally, by the equilibrium sedimentation model described in the previous section, or experimentally. The change in osmotic pressure with respect to axial location is given by

$$\frac{d\Pi(z)}{dz} = -mg\rho(z) \quad (18)$$

where m is the effective mass of the particle, g is the gravitational force, and $p(z)$ is the number density.

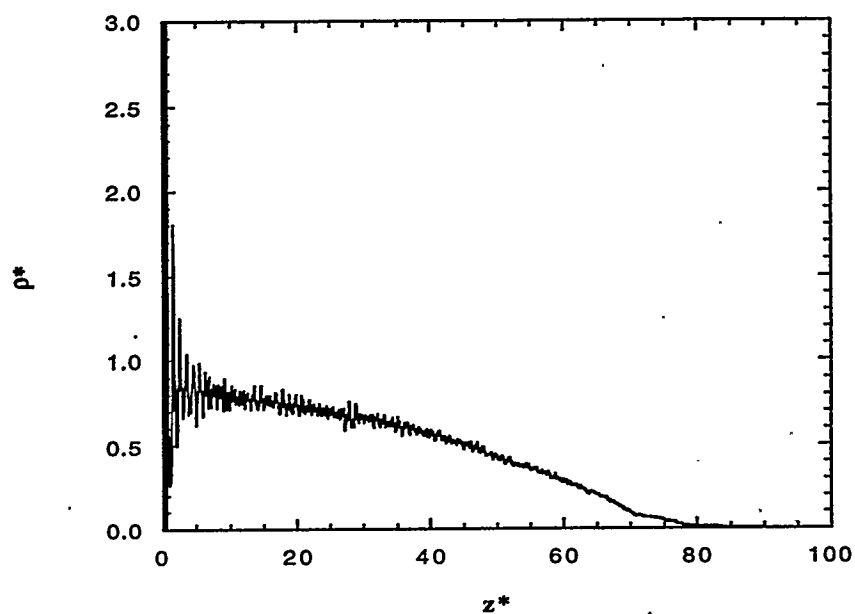


Figure 3.1. Reduced Density Profile of a Hard Sphere Suspension for $n_s^*=40$ and $\alpha^*=0.2$

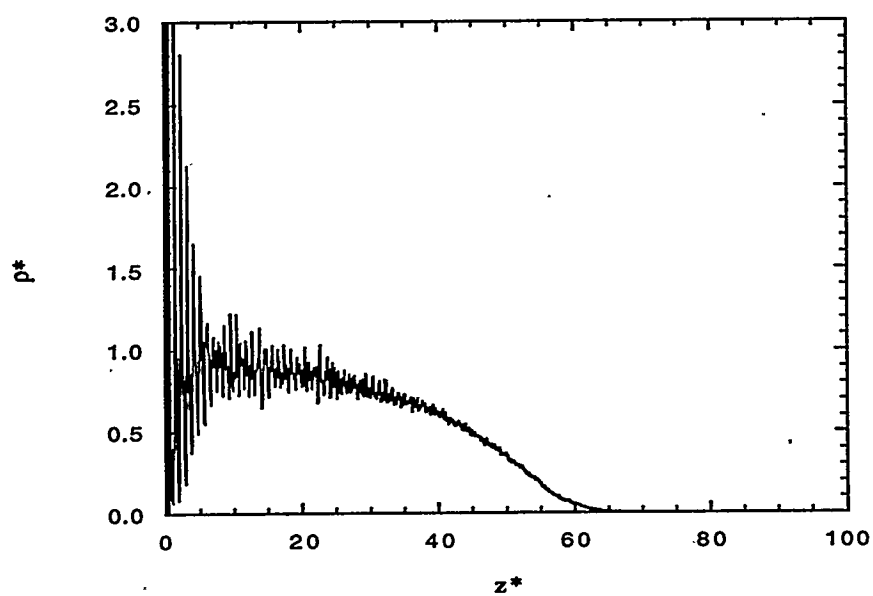


Figure 3.2. Reduced Density Profile of a Hard Sphere Suspension for $n_s^*=40$ and $\alpha^*=0.4$

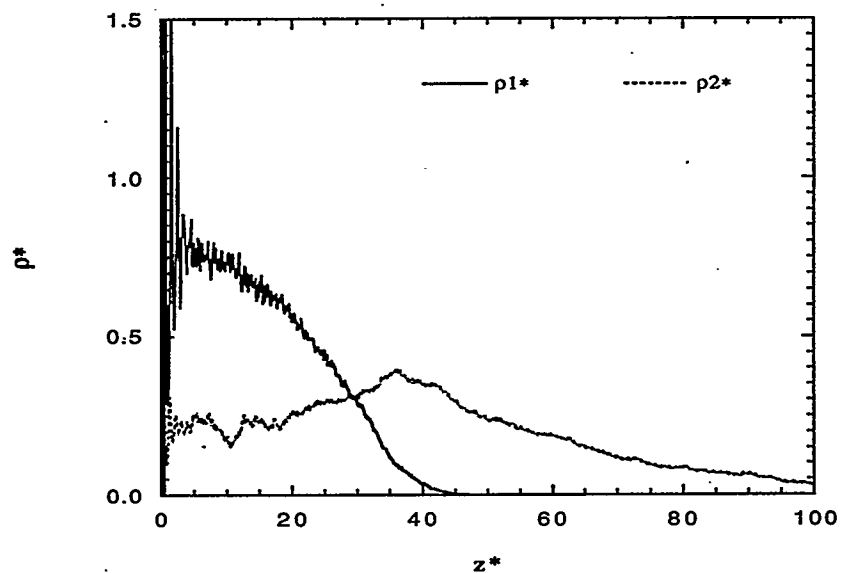


Figure 3.3. Reduced Density Profile of an Equimolar Binary Hard Sphere Suspension with Particle Size Ratio $\sigma_2/\sigma_1=0.5$ and Mass Ratio $m_1/m_2=(\sigma_1/\sigma_2)^3$ (equal density).

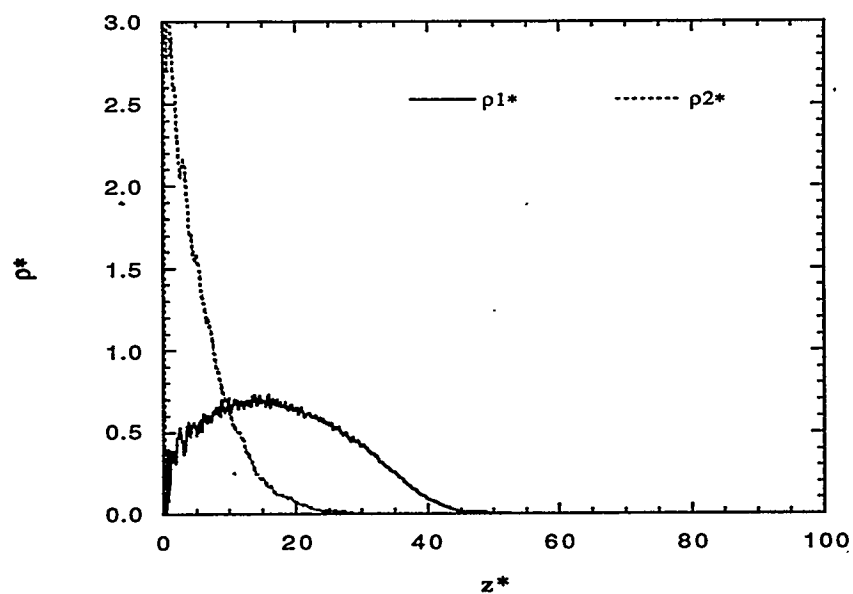


Figure 3.4. Same as Figure 3.3, but for Equal Effective Masses ($m_1=m_2$).

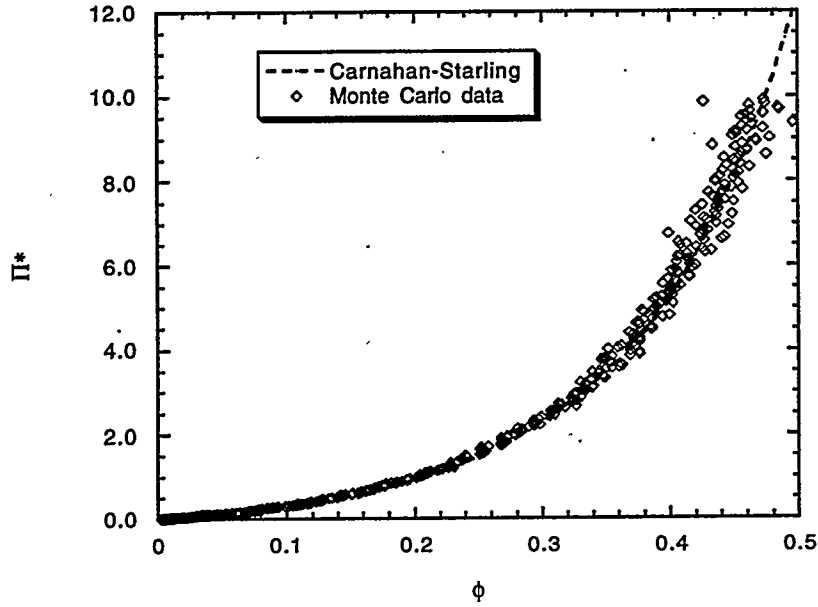


Figure 3.5. Osmotic Pressure as a Function of Volume Fraction. The Monte Carlo Data is From the Results Presented in Figure 2.4. The Dashed Line Represents the Carnahan-Starling Equation of State

Therefore, the osmotic pressure at axial location z is given by

$$\Pi(z) = mg \int_z^{\infty} \rho(z') dz' \quad (19)$$

For example, the relationship between the osmotic pressure, $\Pi^* = \Pi\sigma^3/k_B T$, and volume fraction is shown in Figure 3.5, using the data from Figure 3.2. The dashed curve represents the Carnahan-Starling equation of state for hard spheres. The same information can be obtained by measuring the heights of equilibrium sediment layers with different specified total masses of particulate solids.

4.0 Particle Aggregation

The transient sedimentation model presented in Section 2.0 is valid for systems of independent particles. However, in many suspensions there is an attractive force between particles, resulting in the formation of particle aggregates. In this section, we present a computational model for particle aggregation and combine that model with the transient sedimentation model to predict the sedimentation behavior of aggregating systems.

4.1 Particle-particle Interactions

The properties of particle suspensions depend on the particle-particle interactions, or the potential energy between two particles. For example, under certain chemical conditions, colloidal particles repel each other and, if they are small, may remain dispersed indefinitely. If the chemical conditions change, *i.e.*, the pH changes or the salt concentration increases, the particles attract each other and form aggregates or gels. These forces can be explained using DLVO (Derjaguin, Landau, Verwey and Overbeek) theory (Hunter 1986). This theory simply states that the total interaction between two particles consists of a van der Waals attraction term and an electrostatic term. The relative magnitude of these two terms determines the stability of the colloidal dispersion.

The attractive term arises from the fact that each atom in a particle exerts a van der Waals attraction on each atom in an adjacent particle. The attractive potential energy, V_A , is given by the product of a term which depends only on the materials of the two particles and surrounding fluid, known as the Hamaker constant (Hunter 1986), and a term which describes the geometry of the two particles. For example, the attractive potential energy for two spheres of equal radius, R , at small separations, s , is given by

$$V_A = \frac{AR}{12s} \quad (20)$$

where A is the Hamaker constant.

The electrostatic term arises from electric double layer forces between two adjacent particles. The surface of each particle may be positively or negatively charged, depending on the pH of the surrounding solution. The electric potential at the particle surface may be experimentally determined and is known as the zeta potential, ψ_0 . To satisfy electroneutrality, each surface is surrounded by a cloud of counterions which either come from the surfaces themselves or from salts added to the solution. As the two particles approach each other, the counterion clouds overlap and interfere with each other. The length scale of the double layer interaction is characterized by the inverse Debye length, k , given by

$$k^2 = \frac{2e^2 c z^2 N_A}{\epsilon k_B T} \quad (21)$$

where e is the electronic charge, c is the electrolyte concentration, z is the electrolyte charge, N_A is Avogadro's number and ϵ is the dielectric permittivity. The electrostatic potential energy for two spheres of equal radius, R , is given by

$$V_R = 2\pi\epsilon R \psi_0^2 \ln[1 + \exp(-ks)] \quad (22)$$

for $kR \gg 1$. Note that the electrostatic term depends both on the surface potential, ψ_0 , which in turn depends on the pH of the solution, and the salt concentration, c .

The DLVO pair potential is the sum of the van der Waals attraction term and the electrostatic term

$$V_T = V_A + V_R \quad (23)$$

Figure 4.1 shows an example as a function of separation. For the case of a large surface potential and low salt concentration, the repulsive electrostatic term dominates and there is a large potential barrier to aggregation. As the electrolyte concentration is increased, the Debye length increases (k decreases) and the attractive term becomes increasingly dominant (see Figure 4.2). Note that for a range of salt concentrations, a shallow secondary minimum forms which results in the loose flocculation of particles. When enough salt is added, the potential is purely attractive, resulting in the rapid aggregation of colloidal particles.

4.2 Stability Maps

A colloidal dispersion is said to be stable when significant particle aggregation does not occur, that is, when the potential barrier described in the previous section is sufficiently high to prevent particles travelling at thermal Brownian velocities from contacting each other. Whether a dispersion is stable depends on both the surface electrostatic potential (which depends on the pH of the solution) and the ion concentration of the solution. By using the expressions for the DLVO particle interaction potential presented in the previous section, we are able to determine under which conditions the dispersion is stable or unstable.

This information can be represented in the form of a stability map, which indicates whether a system is stable or unstable for a given pH and ion concentration. The criterion for determining the stability of a dispersion may be based either on the maximum of the DLVO potential, $V_{\max}$, or the stability ratio, W , which is described in the next section.

Figure 4.3 shows a stability map for colloidal boehmite. This map is based on a stability criteria of $V_{\max} > k_B T$. Note that the zero surface potential point is at a pH of approximately 8.5. At lower pH values the surfaces have a positive charge and at higher values the surfaces have a negative charge. Note also that for any pH value there is an ion concentration which sufficiently screens the charge and reduces the DLVO potential maximum to allow aggregation.

4.3 Aggregation Kinetics

If the interparticle interactions are purely attractive, particles or aggregates that collide form a larger aggregate containing k spheres and having an effective radius a_k . For Brownian flocculation, the growth process is controlled by the collision rate between two aggregates (von Smoluchowski 1917)

$$J_{ij} = \frac{2k_B T}{3\mu W_{ij}} (a_i + a_j) \left(\frac{1}{a_i} + \frac{1}{a_j} \right) n_i n_j \quad (24)$$

where n_i and n_j are the corresponding number densities and W_{ij} is the stability ratio. The conservation equation for aggregates of size k can be written as (Sonntag and Strenge 1986)

$$\frac{dn_k}{dt} = \frac{1}{2} \sum_{i=1}^{k-1} J_{ij} - \sum_{i=1}^{\infty} J_{ki} \quad (25)$$

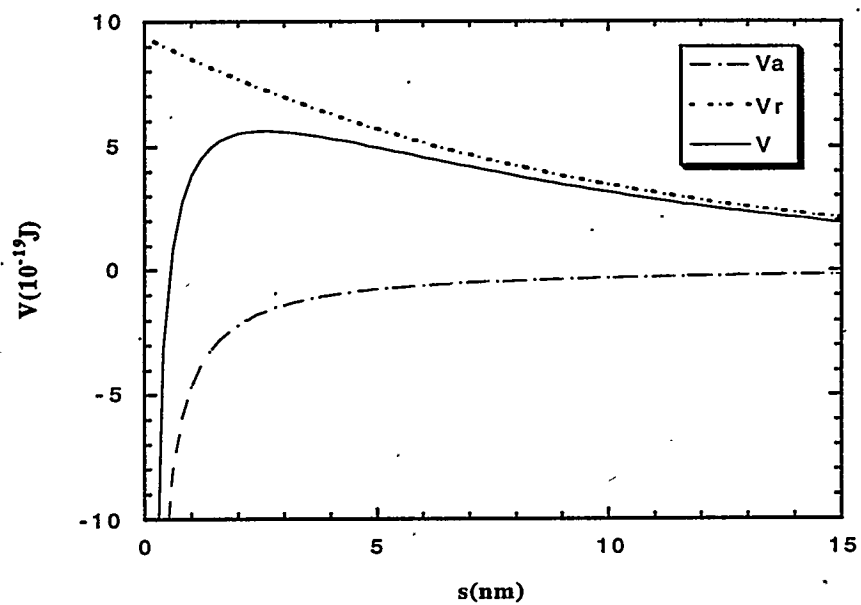


Figure 4.1. DLVO Potential as a Function of Separation.

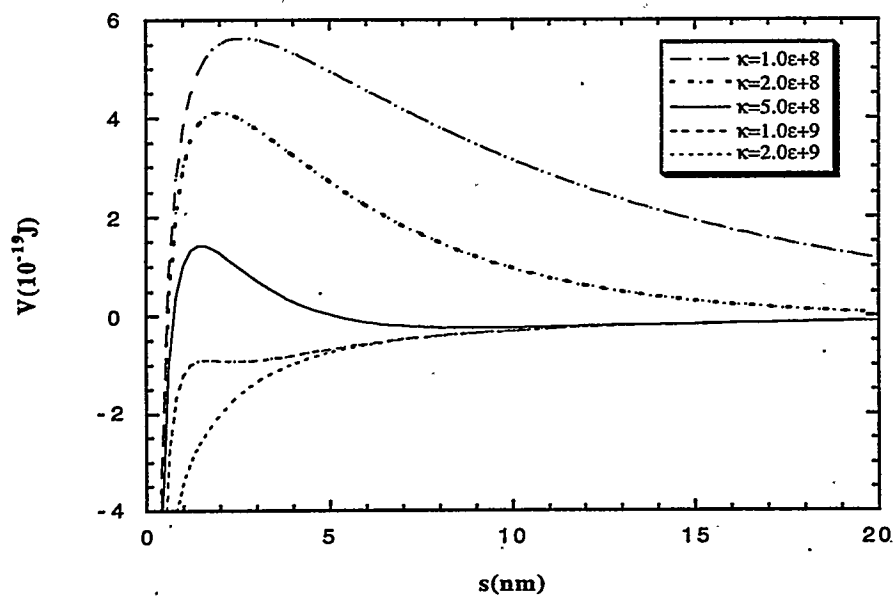


Figure 4.2. Effect of Inverse Debye Length on DLVO Potential

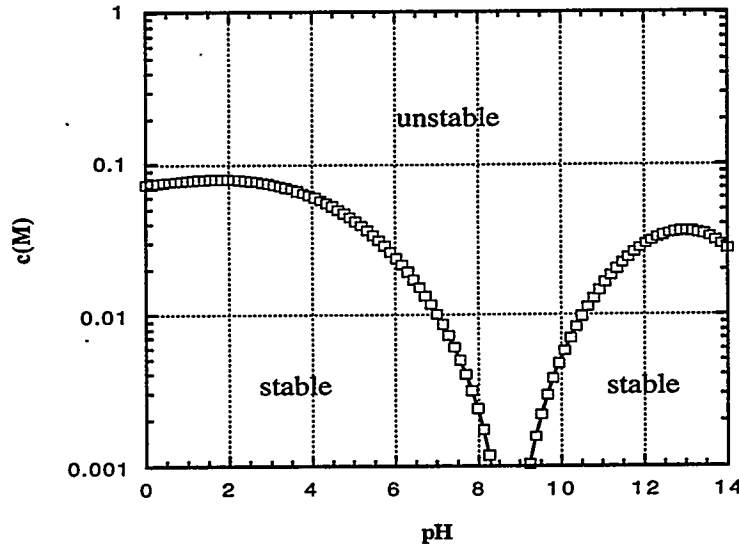


Figure 4.3. Stability Map for Colloidal Boehmite

where the first term is the rate of increase resulting from collision of smaller aggregates and the second term is loss resulting from collision to form larger aggregates. A set of these equations for every aggregate size k can be integrated over time to give the aggregate distribution as a function of time.

The stability ratio, W_{ij} , is the ratio of the total number of collisions between aggregates of size i and j to the number of collisions that result in coagulation. Therefore, the stability ratio measures the effectiveness of the potential barrier in preventing the particles from aggregating. For collisions between particles, this ratio is given by the expression (Sonntag and Strenge 1986)

$$W = \frac{\int_0^{\infty} \frac{\beta(u)}{(u+2)^2} \exp\left[-\frac{V_T(u)}{k_B T}\right] du}{\int_0^{\infty} \frac{\beta(u)}{(u+2)^2} \exp\left[-\frac{V_A(u)}{k_B T}\right] du} \quad (26)$$

where V_T is the DLVO potential energy, V_A is the van der Waals attractive term, and u is the separation scaled by the particle radius. The term β represents a hydrodynamic correction factor which is given by the approximation (Honig, Roeberson, and Wiersema 1971)

$$\beta(u) = \frac{6u^2 + 13u + 2}{6u^2 + 4u} \quad (27)$$

The value for the stability ratio depends only on the particle types involved and the pH and electrolyte concentration of the solution.

Cluster deaggregation may also occur either as a result of fluid shear forces or thermal breakup by Brownian motions. Defining b_{ij} as the rate at which size $i+j$ aggregates break into size i and size j aggregates, the conservation equation for aggregates of size k becomes

$$\frac{dn_k}{dt} = \frac{1}{2} \sum_{i=1}^{k-1} J_{ij} - \sum_{i=1}^{\infty} J_{ki} + \sum_{j=1}^{k-1} b_{jk} n_{j+k} - \sum_{j=1}^{k-1} (1 + \delta_{j,k-j}) b_{j,k-j} n_k \quad (28)$$

where δ is the Kronecker delta.

4.4 Aggregate Fractal Dimension

The aggregation rates used in Section 4.2 are based on an effective radius, a_k , for each aggregate size k . Both experiments and simulation have shown that most colloidal aggregates form fractal structures with a fractal dimension D in the range of 1.6-2.5 (where $D=3.0$ indicates constant packing as a function of radius). The aggregate size k is related to the effective radius by

$$k \sim \left(\frac{a_k}{a}\right)^D \quad (29)$$

where a is the particle radius. The expression for effective aggregate radius becomes

$$a_k = a \left(\frac{k}{\phi_m}\right)^{\frac{1}{D}} \quad (30)$$

where ϕ_m is the maximum packing factor. For spherical particles, $\phi_m=0.74$.

The relative mass of a particle is defined as the mass of the particle minus the mass of an equivalent volume of fluid. The relative density of an aggregate of size k is also calculated using the fractal dimension D by the expression

$$\rho_k = \rho_s k^{1-\frac{3}{D}} \phi_m^{\frac{3}{D}} \quad (31)$$

where ρ_s is the relative density of the solid material.

4.5 Sedimentation of Aggregating Systems

The aggregate size distribution at any point in time is determined by specifying an initial size distribution and then integrating the rate of formation/destruction equations presented in Section 4.2. A computer program has been developed which numerically integrates the rate equations for each aggregate size k . For example, assume an initial distribution consisting only of single particles and a stability ratio $W_{ij}=1$ for all pair combinations. Figure 4.4 shows the change in relative number densities of aggregates of size k as a function of time.

This aggregation model is now being incorporated into the transient sedimentation model described in Section 2.0 to predict the sedimentation behavior of aggregating systems. At each individual time step, the model will perform a sedimentation calculation and an aggregation calculation. The sedimentation calculation will determine the transfer of each aggregate size to

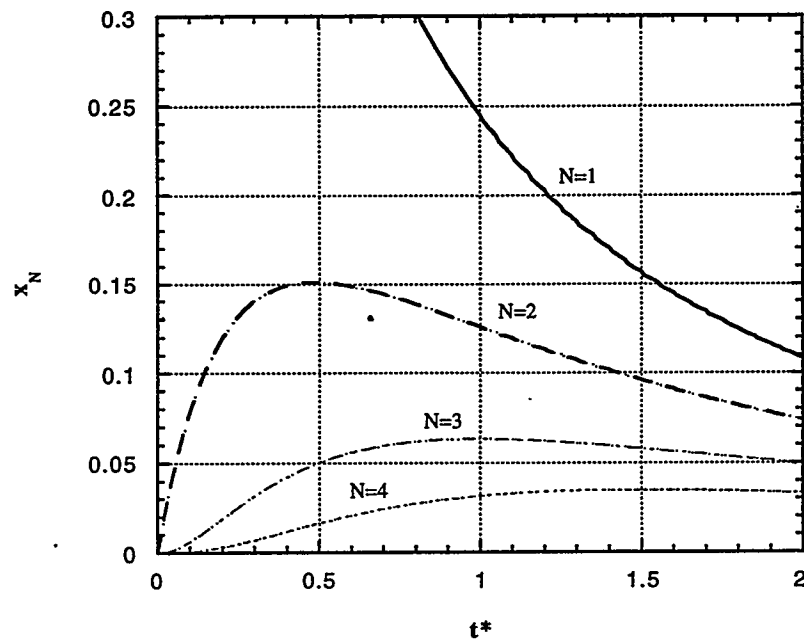


Figure 4.4. Aggregate Size Distribution as a Function of Time

adjacent axial nodes during that time step. The aggregation calculation will determine the creation or destruction of particle aggregates during that time step. Each axial node will be treated as a separate system with its own aggregate size distribution. Issues which may be explored with this model include

- the effect of initial particle concentration on aggregation and sedimentation behavior, and
- the effect of heterogeneous coagulation on sedimentation behavior.

5.0 Comparisons between Models and Experimental Results

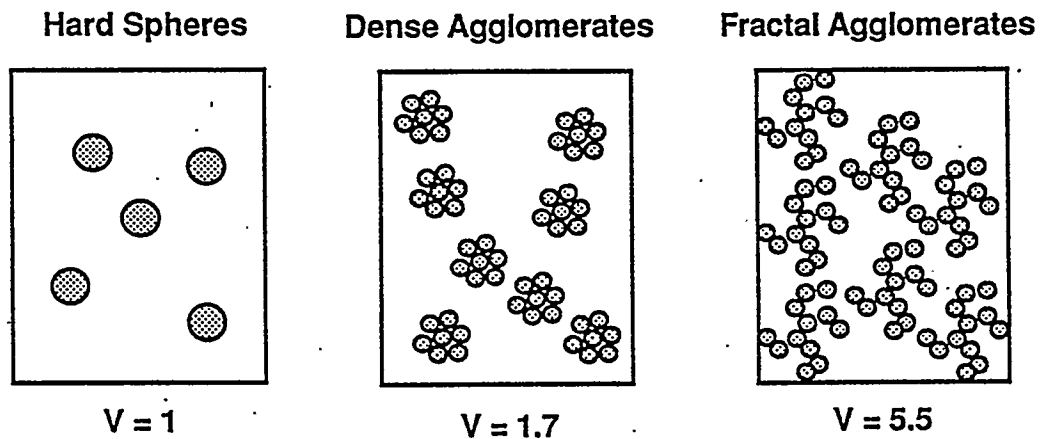
Most of the models presented above have been initially developed to describe the behavior of noninteracting spherical particles. In many cases, the model suspensions are also monodisperse. All of the above parameters were selected to provide computational simplicity for initial models. Clearly, the model systems are dramatically different from tank wastes, which contain a wide range of particles having different sizes, shapes, and compositions in complex solution environments that tend to promote significant interparticle interactions and agglomeration. Given the differences between the models and a real system, one might expect that there would be little correlation between model predictions and behavior that is observed experimentally. However, when such comparisons are made, it is clear that a surprising number of observed phenomena can be rationalized on at least a qualitative basis using the hard sphere model. The direct comparisons also indicate what kinds of information concerning tank sludge will be required to improve our predictive capabilities and what modifications will be required in current hard sphere models to explain sludge sedimentation on a quantitative basis. As will be shown below, it appears that some of the hard-sphere models work surprisingly well if the hard spheres are replaced by low-density, spherical fractal agglomerates. The results suggest that the current hard sphere models may be directly applicable to tank wastes if the size and nature of the agglomerates can be measured and understood.

Before making direct comparisons between the hard sphere models and experimental data, it is important to recognize that the particles in real wastes can be present in three different forms: dense particles, agglomerates formed via dense packing of smaller particles, and fractal agglomerates. As a first approximation, we can assume that all of these agglomerate types are roughly spherical and that the effective diameter of an agglomerate is equal to the hydrodynamic diameter (a circle drawn around the space occupied by both the primary particles and the interstitial water between the particles). Figure 5.1 illustrates that if this assumption is made, the effective volume occupied by the fractal agglomerate is over five times higher than the actual volume occupied by individual particles or the volume occupied by a hard packed agglomerate (in which 60% of the volume is particles and 40% is occupied by interstitial water). (As indicated in Section 4.4, the effective density (and total volume fraction occupied) for fractal agglomerates depends on both the fractal dimension of the agglomerate and the agglomerate radius relative to the radius of the primary particles in the agglomerate. The example given is for a fractal object with a fractal dimension $D = 2.25$ and agglomerates having a diameter ten times greater than the diameter of the primary particle.)

Now that the types of particles have been described, we can examine the behavior of real samples, compare their behavior to the hard sphere models, and see if the observed behavior can be modeled assuming any of the above particle types are predominant. As stated in Section 2.0, both the transient and equilibrium sedimentation models predict that the volume occupied by noninteracting spheres should be around 60 vol% once steady state conditions are reached (Figure 2.1). Such high solids loadings represent the ultimate goal of any sedimentation process. If dense agglomerates are substituted for hard spheres, lower solids loadings are predicted. Each individual agglomerate would have the same maximum solids loading as close-packed spheres (around 60 vol%). If the agglomerates themselves pack as spheres, the net packing density would be around 36 vol% (0.6×0.6). For fractal agglomerates, much less efficient packing is predicted. If the fractal objects pack as hard spheres, the maximum packing density would be represented by the packing density within the agglomerate (dependent on both the fractal dimension and the ratio of primary and agglomerate diameters) times 0.6 (the packing efficiency for the spheres).

Sediment densities have been determined for both real sediments and for simple simulants. The results indicate that final sediment densities range from around 5 vol% up to around 20 vol%. The results suggest that most sludge is heavily agglomerated and contains fractal, rather than hard, agglomerates. Transmission electron micrographs (TEMs) of sludge and particle size analyses (which determine agglomerate size distributions) are consistent with the above conclusion. TEM images indicate that sludge consists primarily of submicron primary particles that stick to each other

Assumption: effective diameter = hydrodynamic diameter



At same solids loading (0.5 vol%), fractal agglomerates occupy a more relative space (V) than either dense agglomerates or dispersed particles.

Figure 5.1. Effect of Aggregation on Effective Volume.

to form fractal agglomerates. Assuming a fractal dimension $D = 2.25$, and given observed primary and agglomerate sizes, equilibrium sediment densities comparable to the observed experimental densities are obtained.

Experimental sedimentation rates are also consistent with the presence of fractal agglomerates. As mentioned in Section 2.0, Stokesian Dynamics models (Brady and Bossis 1988) are capable of predicting how initial sedimentation rates should vary as a function of initial solids loading (Figure 5.2). Sedimentation rates are predicted to decrease as the particles come close enough to have hydrodynamic interactions with adjacent particles. Actual sedimentation data obtained on an agglomerated multicomponent sludge simulant (Figure 5.3) indicates that the functional form of the sedimentation rate vs. solid loading curve is identical to that predicted using hard spheres. However, the normalized sedimentation rate for the real suspension decays with solids loading more rapidly than predicted on the basis of hard spheres. For example, in the hard sphere model, initial sedimentation velocities drop to 10% of the value seen in dilute suspensions by increasing solids loadings to 30 vol%. In the sludge simulant, the particles are interacting with each other to lower sedimentation velocities to 10% at a solids loading of only around 1.5 vol% (4 wt%).

The fact that the particles are interacting with each other at solids loadings as low as 1 vol% can only be explained by assuming that the particles present in the simulant are not dense spheres, but are low-density fractal agglomerates. For hard spheres, the volume fraction of particles at which all particles can form a continuous network by touching each other (called the percolation threshold) is at 16 vol%. For dense agglomerates, the percolation threshold is around 10 vol%. A comparison between Figures 5.2 and 5.3 suggests that the percolation threshold for C-103 simulant (occurring at a relative velocity of 20%) is around 1 vol% (3 wt%). Note that the packing density required to form a continuous network of fractal particles is significantly lower than the volume fraction occupied by fractal particles in the sediment at equilibrium.

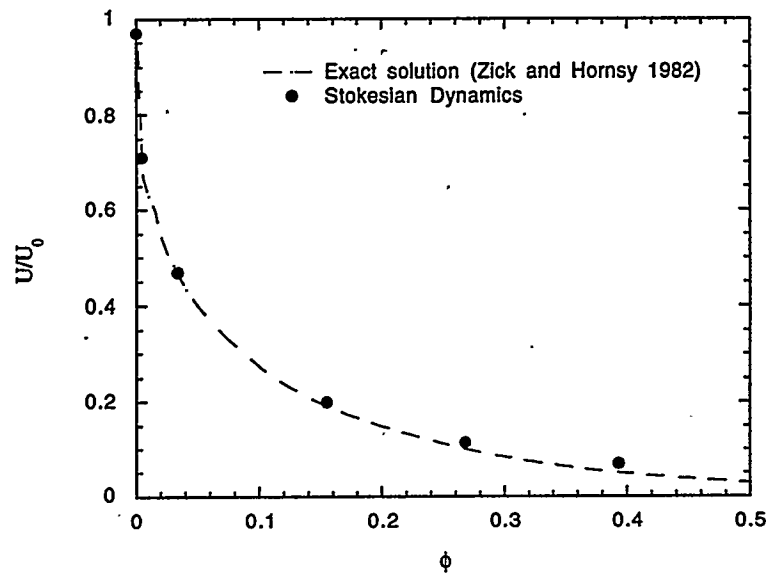


Figure 5.2. Calculated Settling Rates for a Cubic Array of Spheres.

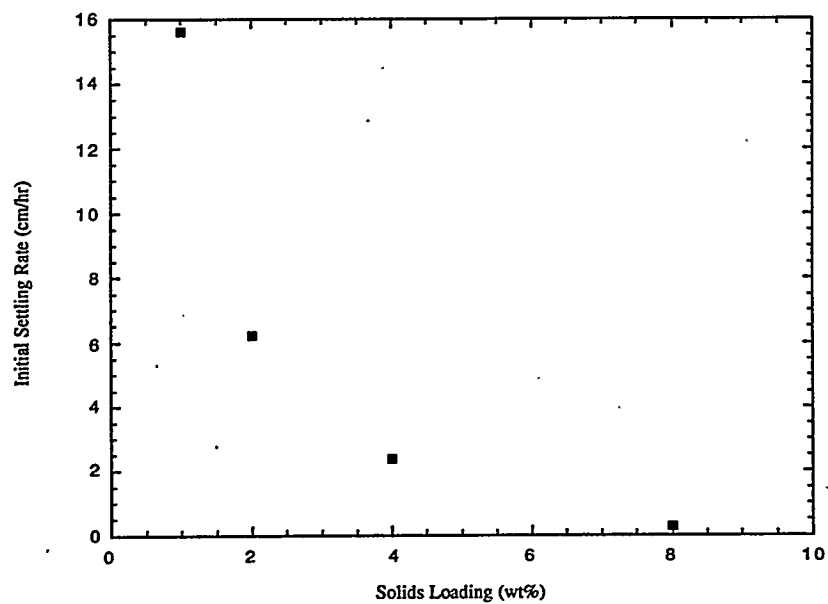


Figure 5.3. Measured Initial Settling Rates for S-103 Tank Waste Simulant.

The concept of a percolation threshold is consistent with experimental data showing how sedimentation rates vary as a function of time for different solids loadings. Figure 5.4 shows the range of sedimentation behaviors that have been observed for both complex and simple simulants. At low initial solids loadings, sedimentation rates decrease as a function of time. This is because as the sediment sinks, the particle concentration increases, increasing the volume fraction occupied by solids. In the dilute regime, a plot of sedimentation rate vs. time has almost the same shape as a plot of initial sedimentation rate vs. volume fraction (Figures 5.2 and 5.3). At higher solids loadings, sedimentation rates start slow, then increase, and finally decrease, producing an "S-shaped" sedimentation curve. The solids loading at which "S-shaped" curves are seen is around 2 vol% for the example shown. At higher solids loadings, the "S-shaped" curves disappear, and slow to negligible sedimentation is observed.

The above behavior can be explained on the basis of the formation of a continuous "percolation" network at solids loadings of around 2 vol%. While fractal agglomerates are capable of forming such a network at 2 vol%, such a network is expected to be quite fragile. Even in a completely immobile solution, the density of weak contact points in the network can be low enough that the structure can eventually collapse under its own weight. At initial solids loadings above 2 vol%, the number of contact point between the particles should be higher, resulting in a stronger, more rigid network that is resistant to sedimentation. To predict the behavior of fractal networks (both before and after collapse), the nature of the network and the magnitude of interactions between the agglomerates must be known. This is one area where the compressibility calculations described in Section 3.0 are relevant once the interaction potential is included in the calculations.

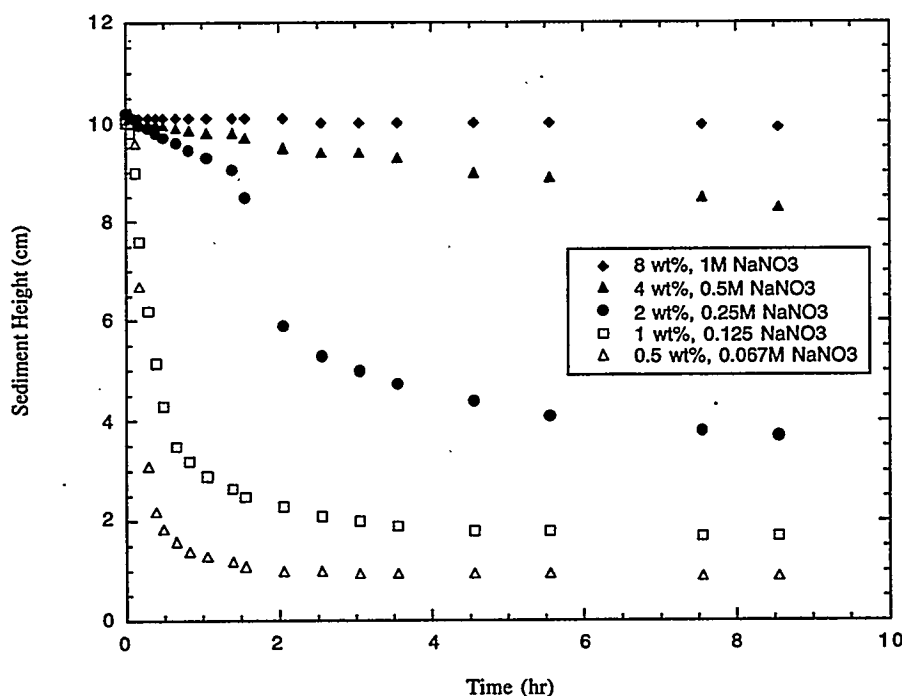


Figure 5.4. Effect of Initial Solids Loading on Sedimentation Behavior

A final example of how the model calculations can be used to predict the behavior of sludges during sedimentation involves predicting whether solution conditions should either agglomerate fine particles or promote agglomerate dispersion and the production of fines. For example, it has been observed that washing sludge samples can greatly increase the volume of fines left in supernatant liquids. Colloidal stability diagrams such as those depicted in Figure 4.3 can be used to predict such behavior. In some washing operations, the effective ionic strength of the solution is lowered. The expansion of the electrical double layer as the ionic strength decreases can lead to electrostatic stabilization of certain suspensions, breaking up agglomerates and producing more fines.

6.0 Conclusions and Task Status

Models have been developed to describe sedimentation behavior of sludge samples. For simplicity, the models are initially based on monodisperse, noninteracting spheres. If the models are modified to include the kinds of particles expected to be predominant in tank wastes, namely fractal agglomerates rather than hard spheres, it has been demonstrated that the simple models are capable of rationalizing a wide range of observed sedimentation behaviors. If the models developed to date are to be made quantitative, experimental data will have to be supplied concerning the types of both primary particles and agglomerates present in tanks. More information will also be required concerning the strength of interactions between the agglomerates (to determine sediment compressibilities). The latter task will involve improving agglomeration models, such as those described in Section 4.0, as well as better characterization of the chemistry of both solids and supernatant liquids. While the models outlined here are far from complete, these initial modeling efforts have provided us with considerable insights into the sedimentation process and are paving the way for more sophisticated models that may eventually allow us to predict sedimentation on a quantitative basis.

The understanding that has been gained from using these models can be used to develop remediation strategies for sedimentation problems. The degree of particle aggregation is dependent on a number of factors, including solution chemistry. By using colloidal stability diagrams such as those depicted in Figure 4.3, the stability of the suspension may be controlled by adjusting the pH and salt concentration of the solution. Heterocoagulation may be induced by adding particles with different surface potentials at the desired pH. It was noted that some aggregating systems produce intermediate structures which slow the sedimentation process. The formation of these structures may be prevented through some means of agitation, such as acoustic waves or mechanical mixing.

To this point, the effort on this task has been primarily on developing computational models which describe the sedimentation and aggregation behavior of particulate suspensions. This report documents the mathematical basis for these models. Accomplishments to date for the Tank Waste Treatment Science Colloidal Modeling Sub-Task include:

- Development of a transient sedimentation model which predicts the axial density profiles of particles and particle mixtures as a function of time. This model accounts for hindered settling, the effect of osmotic pressure on the compression of the sediment layer, and the relative layering of different components within the sediment.
- Development of an equilibrium sedimentation model which uses a Monte Carlo method to determine the density profiles for concentrated colloidal suspensions in sedimentation equilibrium. This information can be used to derive the osmotic equation of state for any system of particles.
- Development of a kinetic aggregation model which predicts the rate of formation and breakup of particle aggregates based on the interparticle potential.
- Construction of colloidal dispersion stability maps which predict the stability with respect to aggregation of a suspension based on the pH and ion concentration of a solution. The maps are based on the DLVO interparticle potential.

The major emphasis of this work will now be to extend these models to aggregating systems and validate by comparing results with data from experimental sedimentation tests using both real tank waste and simulants.

7.0 References

- Anderson, D.A., J.C. Tannehill and R.H. Pletcher. 1984. *Computational Fluid Mechanics and Heat Transfer*. Hemisphere Publishing Corp, New York, New York.
- Batchelor, G.K. and C.S. Wen. 1982. "Sedimentation is a Dilute Polydisperse System of Interacting Spheres: 2. Numerical Results," *J. Fluid Mech.*, **124**, 495.
- Biben, T., J-P. Hansen and J-L Barrat. 1993. "Density Profiles of Concentrated Colloidal Suspensions in Sedimentation Equilibrium," *J. Chem. Phys.*, **98**, 7330.
- Brady, J.F. and G. Bossis. 1988. "Stokesian Dynamics." *Ann. Rev. Fluid. Mech.* **20**,111-57.
- Carnahan, N.F. and K.E. Starling. 1969. "Equation of State for Nonattracting Rigid Spheres," *J. Chem. Phys.*, **51**, 635.
- Davis, R.H and H. Gecol. 1994. "Hindered Settling Function with No Empirical Parameters for Polydisperse Suspensions," *AIChE J.*, **40**, 570.
- Honig, E.P., G.J. Roeberson and P.H. Wiersema. 1971. *J. Colloid Interface Sci.* **36**, 97.
- Hunter, R.J. 1986. *Foundations of Colloid Science*. Clarendon Press, Oxford.
- Mansoori, G.A., N.F. Carnahan, K.E. Starling and T.W. Leland, Jr. 1971. "Equilibrium Thermodynamic Properties of the Mixture of Hard Spheres," *J. Chem. Phys.*, **54**, 1523.
- Rector, D.R. And B.C. Bunker. 1995. *Effect of Colloidal Aggregation on the Sedimentation and Rheological Properties of Tank Waste*. PNL-10761, Pacific Northwest Laboratory, Richland, Washington.
- Richardson, J.F. and W.N. Zaki. 1954. *Trans. Inst. Chem. Eng.*, **32**, 35.
- Russel, W.B., D.A. Saville and W.R. Schowalter. 1989. *Colloidal Dispersions*. Cambridge University Press.
- Sonntag, H. and K. Streng. 1986. *Coagulation Kinetics and Structure Formation*. Plenum Press.
- von Smoluchowshi, M.. 1917. *Z. Phys. Chem.*, **92**, 129.
- Zick, A. and G.M. Homsy. 1982. "Stokes Flow through Periodic Arrays of Spheres," *J. Fluid Mech.*, **115**, 13.