

Microdivers to Study Sedimentation in Polydisperse, Concentrated Colloidal Suspensions

P. Maarten Biesheuvel and Henk Verweij

Dept. of Chemical Technology, University of Twente, P.O. Box 217, 7500 AE Enschede, The Netherlands

Victor Breedveld

Dept. of Chemical Engineering, College of Engineering, University of California, Santa Barbara, CA 93106

A small amount of polymer particles with diameters in the 100 μm range can be used as an ensemble of "microdivers" to study sedimentation velocities of polydisperse sub-micron particles in concentrated opaque suspensions. This tracer technique, based on Berg's (1941) diver method, is simple, measures velocities directly, and does not require underlying theory beyond conservation of momentum. It confirms that the polymer tracers reside at the position in the suspension where the suspension density corresponds to their own density. Aqueous inorganic suspensions of 250–750 nm α -alumina particles were studied, which is electrostatically stabilized with nitric acid in water, using ~ 100 μm polymethylmetacrylate and polystyrene particles as tracers. Experiments were compared with predictions by state-of-the-art continuum models for multicomponent sedimentation to underpin the validity of the tracer technique.

Introduction

Sedimentation of polydisperse colloidal (submicron) particles in concentrated suspensions is of importance to many fields ranging from geology to food processing (Zeng and Lowe, 1992, p. 393; Hunt and Zukowski, 1999, p. 343; Hoyos et al., 1994, p. 3809). However, sedimentation in concentrated and/or colloidal suspensions cannot be observed with the naked eye and is very difficult to measure by other means (Williams et al., 1990, p. 1). We performed experiments with different suspensions of 6–33 vol. % α -alumina of an average size of 250–750 nm dispersed ultrasonically in nitric acid (pH = 4) in which sedimentation cannot be observed visually. In the course of days the suspension remains opaque from top to bottom, although the presence of a sediment layer becomes clear when the flask is tilted slightly. It takes days before a transparent supernatant layer forms at the top of the flask. However, at this stage, practically all particles have already sedimented as can be inferred from the thickness of the sediment. The persistence of the opaqueness of the sus-

pension is due to the polydispersity of the powder. The finest particles, initially present in the powder, either sediment very slowly or remain in suspension due to Brownian motion or the slightest form of thermal convection as a result of temperature gradients in the sedimentation vessel. Due to their small size and resulting high specific surface area, these fines scatter light even when present in tiny amounts.

Many techniques, mostly based on the response of the system to electromagnetic waves, are currently being investigated for the study of such "complex polydisperse suspensions" (Williams et al., 1991). An overview of the bewildering range of these techniques is given by Allen (1981), Williams et al. (1990, 1991), Pal (1994) and Bernhardt (1994); see also Jiang (1998) and Bartlett and Jiang (2001) who describe the photon migration technique. Ultrasound seems to be the most promising technique for opaque systems, but requires, as most other techniques, extensive modeling to convert raw measurement data to velocities and concentrations.

To study sedimentation in these systems by visual means, we modified the diver technique devised by Berg (1941, 1959) and described by Jarrett and Heywood (1954), Whitmore (1955), Herdan (1960), Weiland and McPherson (1979), Allen (1981, p. 289), Bernhardt (1994, p. 124) and Williams et al.

Correspondence concerning this article should be addressed to V. Breedveld.

Current address of P. M. Biesheuvel: Shell Global Solutions International B.V., Badhuisweg 3, 1031 CM Amsterdam, The Netherlands.

Current address of H. Verweij: Materials Science and Engineering Dept., Ohio State University, Columbus, OH 43210.

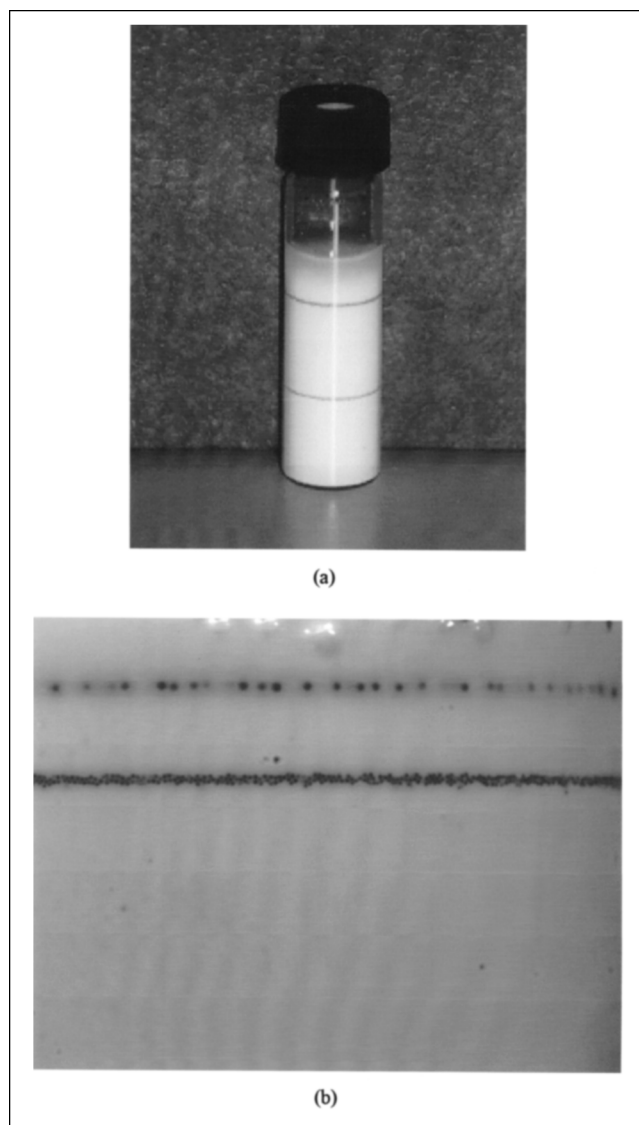


Figure 1. Polymer microdivers in alumina suspension.

PS (upper) and PMMA (lower) tracer layers in a suspension of α -alumina prepared by method 1. (a) mixture of 4 vol. % AKP-30 and 5 vol. % AKP-15, 22 h after resuspension, see Figure 6. Flask and cap have a height of 63 mm. (b) 14 vol. % AKP-15 1 h after resuspension. The bubbles on top indicate the gas/liquid interface. Magnification $\sim 20\times$.

(1990, p. 16). Divers are tracer particles that are added to a suspension and move to the suspension location (height) which corresponds in suspension density ρ_s to their own density ρ_T . We decreased the diver size from the order of 10 mm to the order of 0.1 mm (thus, a change in particle volume in the order of 10^6) and used a polymer powder, instead of individually engineered divers (see Figure 1). Besides decreasing the size of the divers, we simultaneously increased the number of divers from one to the order of 10^4 per cm^2 , which results in a huge assembly of tiny “microdivers” that will form a horizontal (mono-)layer in the suspension. Advantages of using a monolayer of microdivers are the improved spatial accuracy; a monolayer of $\sim 100\ \mu\text{m}$ vs. a diver of a height of 10 mm results in an increase in accuracy by a factor 10^2 .

Furthermore, when using an assembly of microdivers, some microdivers will always be present at the wall of the flask; these particles are directly visible to the naked eye. Finally, lateral effects are absent: a single diver with a significant diameter compared to the vessel diameter induces undesired flow phenomena (such as liquid being pushed to the sides along the diver), which are absent using a layer of microdivers.

The microdiver technique requires tracer particles of a bright color contrasting with the suspension. (In this article, the words “tracer,” “tracer particle,” “diver,” and “microdiver” are used alternatively). In that case, the tracer particles form distinct horizontal planes floating in an opaque background (see Figure 1). The diver technique does not require model assumptions to convert raw measurement data into sedimentation velocities and can be used for very concentrated suspensions of polydisperse, submicron powders. The technique is Lagrangian: the change of location with time of a certain parameter is followed, whereas most other techniques (electromagnetic waves, ultrasound, sampling, pressure points) are Eulerian in nature and measure at a certain height in the vessel/column the change of a characteristic quantity (typically, a concentration) with time. The latter techniques are not naturally suited to the measurement of sedimentation velocities, but information gathered at different heights at different times can be combined to obtain a sedimentation velocity. Another advantage of the diver technique is the fact that the suspension is not required to be (considered) exactly monodisperse. On the contrary, the diver technique is especially suited to cope with the polydispersity of as-received powders used in industrial applications. Note, however, that the diver technique measures the velocity of a front of a fixed density. It does not trace individual particles, such as is being done by Nicolai et al. (1995) and Delnoij et al. (1999).

In the remainder of this article we show typical results of adding—by choice—two polymers as tracer particles to different submicron alumina suspensions and compare these results with theoretical predictions to validate the microdiver technique. We will use this technique to study deagglomeration by ultrasound and present preliminary results of this technique applied in a centrifugal field.

Theory

In this section we provide the theoretical framework that is used to compare our experiments with predictions based on state-of-the-art models for the particle sedimentation velocity in polydisperse suspensions. To describe batch sedimentation of a polydisperse powder, the continuous size distribution is usually partitioned into m particle types (Davis and Hassen, 1988). This discretization allows for the derivation of analytical expressions for the sedimentation velocity of the different species as a function of composition of the suspension. These expressions can then be linked through mass conservation equations; thus, a solution of the full problem can be obtained. The last step is made by means of an iterative numerical integration scheme, as will be described in the Materials and Methods section.

The discretization of the particle distribution into m particle types results in the development of m suspension phases.

In addition there is a sediment layer and clear supernatant. Here we only consider particles of equal mass density ρ . Furthermore, the particle types are numbered from 1 (the smallest) to m (the largest), which leads to the following identification of the suspension phases: the bottom suspension phase m contains all particles, in phase $m-1$ right above phase m , particle type m —which is larger and thus sedimenting faster than $(m-1)$ —is absent, and so on. The top phase 1 only contains the smallest particles of type 1.

We denote velocities and concentrations as $U_{i,j}$ and $\phi_{i,j}$ with i the particle type and j the suspension phase ($i \leq j$). The sharp boundary between phase j and $j-1$ (with velocity $U_{j,j}$) results in $j-1$ mass balances for the particle types $1 \dots j-1$, which gives rise to the following equations for the concentrations of particles $1 \dots j-1$

$$\phi_{i,j} = \phi_{i,j+1} \frac{U_{i,j+1} - U_{j+1,j+1}}{U_{i,j} - U_{j+1,j+1}} \quad (1)$$

To solve this set of equations, a model is needed for the sedimentation velocities $U_{i,j}$. The Patwardhan and Tien (1985) model is the state of the art for describing particle velocities in polydisperse systems by closed-form continuum equations (Biesheuvel et al., 2001a,b). These equations can be derived from macroscopic momentum balances (Syamlal and O'Brien, 1988) and show that the driving force for sedimentation is the density difference of a given particle ρ with the entire suspension density ρ_s at that location (see Eq. 5). The expressions for particle velocity incorporate empirical hindrance functions for polydisperse systems based on those derived in 1954 by Richardson and Zaki for monodisperse systems. These hindrance functions solely take into account retardation due to hindrance and do not change the uniqueness of $\rho - \rho_s$ as the driving force for sedimentation. For phase j containing particles $1 \dots j$, the velocity of particle i is given by (Biesheuvel et al., 2001a,b).

$$U_{i,j} = U_{i0} h_{i,j} \frac{\rho - \rho_{s,j}}{\rho - \rho_0} - \sum_{k=1}^j U_{k0} h_{k,j} \frac{\rho - \rho_{s,k}}{\rho - \rho_0} \phi_{k,j} \quad (2)$$

with the particle velocity at infinite dilution U_{i0} given by Stokes' law

$$U_{i0} = \frac{d_i^2 (\rho - \rho_0)}{18\eta} g \quad (3)$$

which is valid in laminar flow for spherical particles in the absence of wall effects. Following our definition, j again denotes the phase index (which equals the number of different particle types in the phase), i is the particle type index, d_i is the particle diameter, ρ is the particle density, ρ_0 is the liquid density, g is acceleration due to gravity, η is the Newtonian viscosity of the liquid, and h_i is the hindrance function incorporating variations in local porosity (volume fraction of the continuous phase) $d_{\epsilon,i}$ around particles of different size

(Patwardhan and Tien, 1985)

$$h_{i,j} = \left[1 - \left(1 + \frac{d_{\epsilon,i}}{d_i} \right)^{-3} \right]^{n-2},$$

$$d_{\epsilon,j} = \frac{\sum_{k=1}^j d_k \phi_{k,j}}{\phi_{\text{tot},j}} (\phi_{\text{tot},j}^{-1/3} - 1) \quad (4)$$

Here, n is an empirical factor which for low Reynolds numbers and neglect of wall effects is equal to $n = 4.65$ (Wallis, 1969). The suspension density $\rho_{s,j}$ is given by

$$\rho_{s,j} = (1 - \phi_{\text{tot},j}) \rho_0 + \phi_{\text{tot},j} \rho \quad (5)$$

$\phi_{\text{tot},j}$ being the total volumetric particle concentration (unity minus porosity) in phase j

$$\phi_{\text{tot},j} = \sum_{k=1}^j \phi_{k,j} \quad (6)$$

When the local particle concentration $(1 + d_{\epsilon,i} d_i^{-1})^{-3}$ (local at the particle scale) is set equal to the total particle concentration $\phi_{\text{tot},j}$, the model by Masliyah (1979) is obtained. In this case, Eqs. 2–6 result in

$$U_{i,j} = \frac{\rho - \rho_0}{18\eta} \left(d_i^2 - \sum_{k=1}^j d_k^2 \phi_{k,j} \right) (1 - \phi_{\text{tot},j})^{n-1} g \quad (7)$$

We will calculate predictions for both models in the remainder of this article. The above equations suffice to describe the sedimentation problem if the composition of the powder (and therewith of the initial phase m) is known (in terms of $\phi_{i,m}$).

Materials and Method

Materials

The submicron α -alumina powders (Sumitomo, Tokyo, Japan) were AKP-15 (average size $d_{\text{av}} = 750$ nm, $\sigma = 170$ nm, with σ being the mean deviation based on a normal distribution (Montgomery et al., 1998), AKP-30 ($d_{\text{av}} = 375$ nm, $\sigma = 85$ nm) and AKP-50 ($d_{\text{av}} = 250$ nm, $\sigma = 55$ nm). The particle-size distribution of the powders is depicted in Figure 2. The volumetric dimensionless concentration ϕ_i is given by $f_i \cdot \phi_{\text{tot}}$ with f_i the fraction of size d_i , meeting the requirement of

$$\sum_{i=1}^m f_i = 1.$$

As polymer tracers, we used spherical particles of polystyrene (PS, density $1,050$ kg/m³) and polymethylmethacrylate (PMMA, $1,190$ kg/m³). The PS particles (PB-4, Maxi-Blast Inc., South Bend, IN) have sizes in the range 150 – 250 μm . We applied sedimentation fractionation in a water-glycerol mixture to reduce the density variation to below 1 kg/m³. We used the 75 – 106 μm size fraction of sieved PMMA particles (Lucite 4-F, ICI Acrylics, London, U.K.). The polymer particles were colored black (PMMA) and blue (PS) using standard fabric dyes (Rit, CPC Specialty Markets,

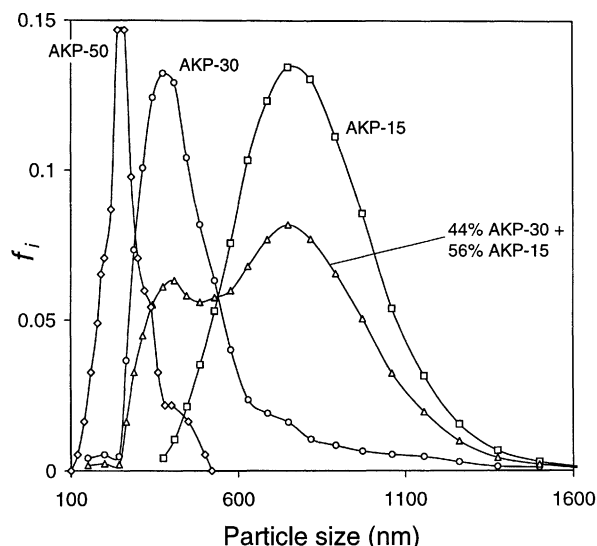


Figure 2. Size distribution of alumina powders.

The pure alumina powders are depicted as well as the mixture used in the experiment of Figure 6.

Indianapolis, IN). We did not detect changes in (the density of) the polymer particles due to the dyeing process.

The alumina powders were added to HNO_3 acidified distilled water and were electrostatically stabilized—and dispersed—using ultrasonification. Two methods were used. In method 1 we added the alumina powder to 0.05 M HNO_3 , after which the glass beakers with suspension were placed in an ultrasonic bath filled with tap water (Ultrasonic Cleaner B2200E-3, Branson Ultrasonics, Danbury, CT; constant output power 60 W, frequency 47 kHz) for ~15 min with intermediate stirring and were subsequently sieved over a 200 μm filter to remove possible large agglomerates. In method 2, while adding the alumina to the HNO_3 solution, the pH is kept at pH = 4. The tip of an ultrasonic horn is placed directly in ~140 mL of this suspension for 5 min (Ultrasonic processor W-380, Heat Systems-Ultrasonics, Farmingdale, NY; output power ~50 W for 2.5 s per 5 s period, frequency 20 kHz). The resulting suspension is not sieved.

Next, part of the dispersed suspension is transferred to 8 mL flasks with teflon caps. We added tiny amounts of polymer (typically 20 mg per type) and a drop of anionic soap (Triton X-100, Acros Organics, NJ) to improve wetting of the polymer tracers and thus inhibit flotation. An ionic soap would also prevent flotation, but causes agglomeration of the alumina suspension, probably due to bridging flocculation. The viscosity of the suspending fluid (0.3 mass % Triton in distilled water) was measured with an Ubbelohde capillary viscometer (type 532-01, Schott Geräte, Hofheim a. Ts., Germany) and was found to be 1.064 mPa·s at 18°C, which is only 1.7% above the literature data for pure water.

Measurement

The contents of the flasks were homogenized by swirling, shaking or rolling gently, ensuring that any sedimented alumina and polymeric particles were fully redispersed while

minimizing foam formation. Then the flasks were put on a lab table to start the sedimentation process. The polymer tracers rapidly moved (within 1 min) upward to the top of the suspension to form two distinct layers (see Figure 1). The position of the tracer layers above the surface on which the flasks were placed was measured with a sliding gauge (accuracy of instrument 10 μm) at intervals of several hours for the duration of 24 h to one week. The sedimentation velocity of the tracers was determined by linearly least-squares fitting the displacement curves of the tracers. This velocity represents the velocity of a constant density front in the suspension and is not the same as the sedimentation velocity of individual colloidal particles. The fact that the observed sedimentation velocity of the tracer particles was always stationary is quantified by the fact that the R^2 -values of the linear fit were always $\gg 99\%$.

Numerical calculations

The set of Eqs. 1–7 was solved with the “Newton” routine of the commercial software package Maple V (Waterloo Maple Inc., Waterloo, Ontario, Canada). To minimize the number of equations that need to be solved simultaneously, our code determines the concentrations $\phi_{i,j}$ and velocities $U_{i,j}$ layer by layer (starting at phase $j = m - 1$) giving a maximum of $2 \cdot (m - 1) = 48$ equations to be solved at the same time (for the AKP-15/AKP-30 mixture). The location of the height of the tracers PMMA and PS was determined numerically by considering at which of the m interfaces each particle would be located: such as if the density of phase $j = 5$ would be 1,140 kg/m^3 and that of phase 6 be 1,210 kg/m^3 , PMMA (of density 1,190 kg/m^3) will trail the interface between phase 5 and 6 and have velocity $U_{6,6}$.

Results and Discussion

Sedimentation of a slightly polydisperse suspension

As described in the Theory section, we partition the polydisperse suspension into a set of m discrete particle sizes. For m particle sizes, the sedimentation models predict the development of as many suspension phases right from the start of the sedimentation process. This is illustrated in Figure 3 where the position of zones with constant density is shown as a function of time. Calculations in Figure 3 were made for AKP-15 with $m = 18$ discrete particle sizes (m suspension phases). For clarity, several suspension phases are lumped together in Figure 3.

Clearly, the densities of the suspension phases are independent of time, while the suspension density decreases shockwise with height at the separations between the particle phases. The vertical height of each phase trailing the original bulk suspension phase ($\rho = 1,594 \text{ kg}/\text{m}^3$) increases steadily in time, until the sediment is reached. The boundaries between the m phases—the constant density fronts—have a constant velocity.

The assumption of the tracer technique is that the tracers (of density ρ_T) will reside at that constant density front (lines in Figure 3) that separates two suspension phases of which the lower phase has density $\rho_L > \rho_T$ and the upper phase has density $\rho_U < \rho_T$.

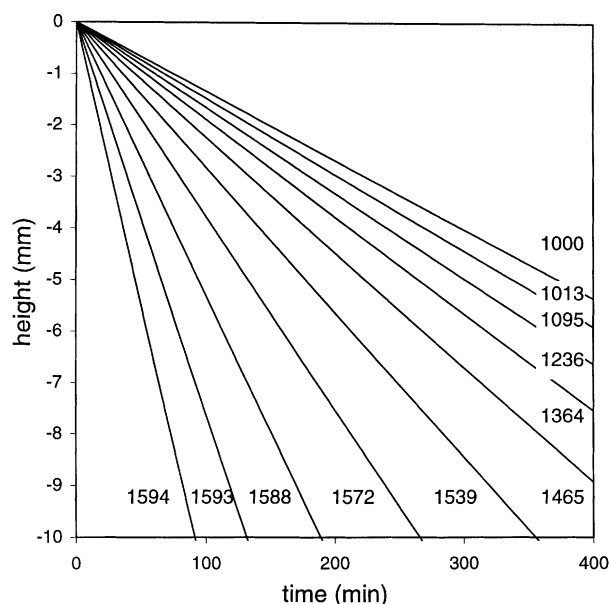


Figure 3. Change of suspension density (kg/m^3) as function of time and height.

AKP-15 suspension at 20 vol. % total concentration calculated with the Masliyah model. Height “0” is the top of the liquid, “1000” denotes the clear liquid of density ρ_0 and “1594” the original “bulk” suspension of $\rho_{s,\text{ini}}$.

Microdivers

Experiments with PS and PMMA in a suspension of submicron α -alumina show two discrete layers of microdivers (PS above PMMA) moving with different velocities away from the gas-liquid interface (see Figure 1a,b). In Figure 1b, the monolayer of PS is not completely filled, while the PMMA forms a stacking of two to three dense monolayers of particles. Obviously, by adding more or less polymer, we can obtain perfectly filled monolayers of each particle type.

Experiments in AKP-15 suspension

For a suspension consisting only of AKP-15 (Figure 1b), the velocity of the tracer layers was measured ($6.1 < \phi_{\text{tot}} < 33.5$ [vol. %]) and calculated ($5 < \phi_{\text{tot}} < 40$ [vol. %]) as function of suspension concentration (see Figure 4). The lowest measured suspension concentration (6.1 vol. %) corresponds to an initial suspension density of $\rho_{s,\text{ini}} = 1,182 \text{ kg}/\text{m}^3$, which is lower than the density of the PMMA tracers ($\rho_T = 1,190 \text{ kg}/\text{m}^3$). Indeed, in this experiment, the PMMA did not cream to the top of the suspension, but immediately settled to the bottom of the flask. In the next experiment at 6.6 vol. % ($\rho_{s,\text{ini}} = 1,197 \text{ kg}/\text{m}^3$), the PMMA moves to the top of the suspension, as expected, while it has a very high sedimentation velocity.

The numerical curves in Figure 4 show discontinuities that are an artifact of the calculational method: as a function of the initial suspension concentration the tracers exhibit discrete jumps in sedimentation velocity. This is the result of moving from one to the other interface at several critical concentrations. For example, when the suspension concentration is decreased a certain critical concentration will be reached

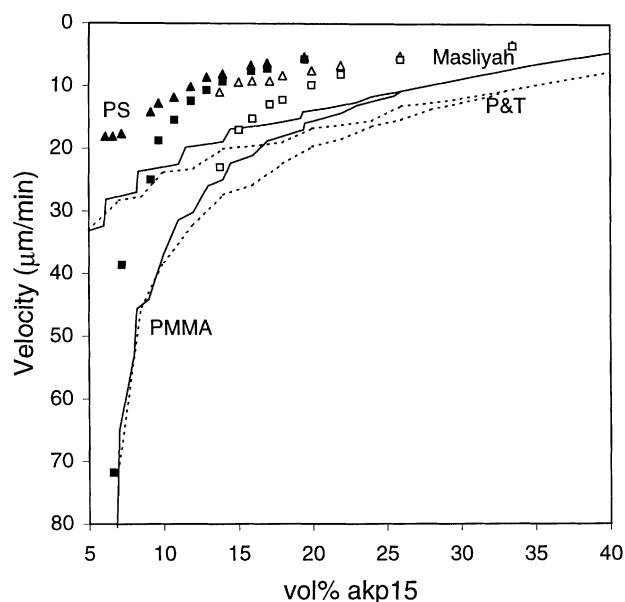


Figure 4. Sedimentation velocity of microdivers in alumina suspension.

Experiments (dots) and model results (lines) for PS (above, triangles) and PMMA (below, squares) in an AKP-15 suspension as function of overall initial volume concentration $\phi_{s,\text{ini}}$. Open signs indicate use of method 1 for suspension preparation, solid signs method 2. The lines are based on the Masliyah (solid) and the Patwardhan and Tien-models (dashed).

at which the tracers are no longer supported by suspension phase j and “move down” through phase j to be supported by the next interface which is the back of phase $j + 1$. Thus, the sudden jumps in the theoretical curves of Figure 4 are the result of partitioning the original continuous-size distribution into a discrete set of monodisperse fractions of distinct sizes. Increasing the number of species in the calculations would smoothen the curves, but also lead to larger computational costs.

It must be stressed once more that the discontinuities in the curves in Figure 4 reflect a change of (initial) suspension concentration: in each experiment—of a given initial suspension concentration—the tracers have a constant velocity during the sedimentation process as demonstrated in Figure 3 and Figure 6.

There is good, qualitative, agreement between experiments and calculations—both data sets show the same variation with suspension concentration as is theoretically predicted—suggesting that our understanding of the physics behind the tracer technique is correct. Interestingly, the tracer velocities markedly differ between the two data sets, which reveals the sensitivity of the microdiver technique to the suspension preparation method. The difference between the data sets might be related to the degree of agglomeration, or to the difference in interparticle electrostatic repulsion (see further on).

The shape of the curves in Figure 4 is the same for both experiment and theory: at low concentrations, the velocity difference between PMMA and PS is large, while, at high concentrations of AKP-15, the two layers move at almost the

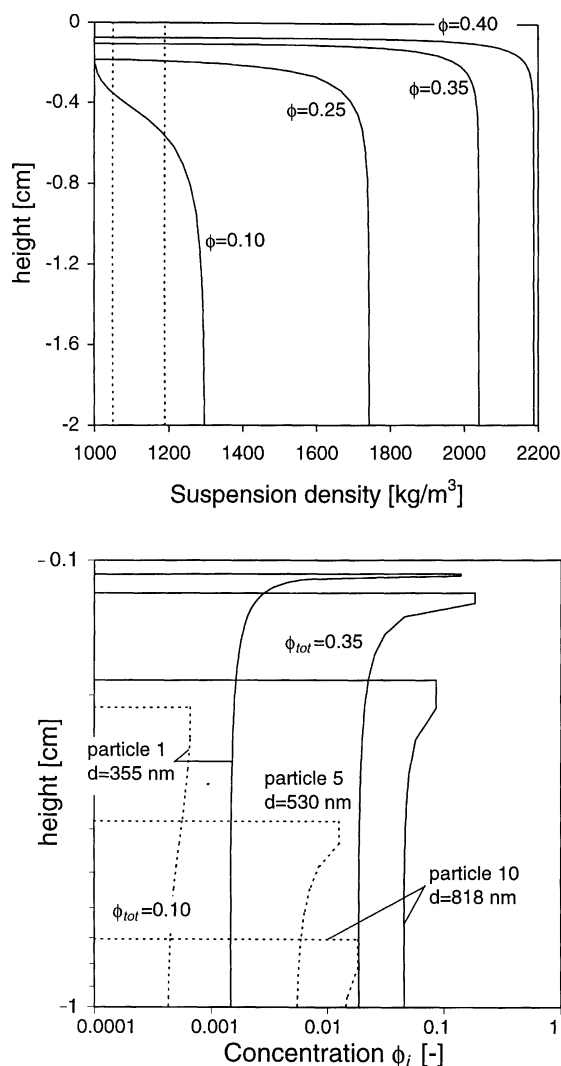


Figure 5. Self-sharpening at the top of a sedimenting suspension.

(a). Suspension density as function of height from top (after 10^4 s) for four initial concentrations ϕ_{tot} showing self-sharpening at higher concentration. The two dashed vertical lines correspond to the density of the two tracer particles. (b). Concentration profiles for particle types 1 (smallest), 5 and 10 for initial concentration ϕ_{tot} of 10 vol. % (broken lines) and 35 vol. % (solid lines). Note the logarithmic scales.

same velocity. This is caused by self-sharpening (Davis and Hassen, 1988; Richardson and Meikle, 1961, p. 349), which is the phenomenon that the change of suspension density ρ_s from the initial value $\rho_{s,ini}$ in phase m , to the liquid phase value ρ_0 occurs in an increasingly small region when the (initial) suspension concentration ϕ_{tot} is increased. To numerically elucidate the narrowing of the density gradient zone, we plot in Figure 5a the suspension density ρ_s as a function of height h for four initial concentrations of the AKP-15 suspension. The suspension-air interface is located at $h = 0$ and the results of the calculations are presented for $t = 10^4$ s. The densities of PMMA and PS are indicated as vertical lines and the intersects of the suspension density profiles with these lines correspond to the tracer locations. The figure clearly

shows that the two polymer layers must become indistinguishable at high concentrations, just as is observed.

Self-sharpening is closely associated to the fact that the concentration of a particle type i increases steeply with height (with decreasing phase number j) and reaches a maximum in the highest layer j in which it is present ($i = j$). Numerical calculations on the increase of concentration with height are plotted in Figure 5b for a low (10 vol. %) and a high concentration (35 vol. %) and for three particle types (namely 1, which is the smallest, 5 and 10). In the 10% suspension, without appreciable self-sharpening, the concentration gradient is small for each of the particle species. However, in the 35% suspension, particles of type 1 and 5 are concentrated in the upper layer of their presence. This is related to the fact that the hindrance function increases strongly as a function of volume fraction. Therefore, at high concentrations, the large particles sediment relatively slowly and the upper layers, which consist only of fines, are able to stay much closer to the bulk phase. In a sense, by increasing the volume fraction in the uppermost layers, the system ensures that the velocity of the interfaces $U_{i,j}$ decreases with increasing phase number j (Davis and Hassen, 1988).

Another characteristic feature of Figure 4 is that the sedimentation velocity is consistently underestimated by the theoretical models. We suggest that this discrepancy is caused by the electrostatic repulsive forces between individual particles. Indeed, Thies-Weesie et al. (1995) and Keh and Ding (2000) demonstrate both experimentally and theoretically that, for colloidal particles, (size $< 1 \mu\text{m}$) interparticle electrostatic repulsion significantly decreases the sedimentation velocity, even for very dilute suspensions. Both literature sources present alternative hindrance functions h_i in which the retarding influence of electrostatic repulsion is implemented. We suggest that the tracer technique can be used to validate these functions—derived for monodisperse colloidal systems—and develop extended functions for multicomponent colloidal suspensions.

That electrostatic repulsion plays a role in the gravity-sedimentation experiments is underpinned by our work on the same AKP-powders in a centrifuge (Biesheuvel et al., 1998, 2001b). In that case, much better agreement was obtained between experiment and calculation. In these experiments the driving force for sedimentation was typically increased a thousandfold (to 1,000 g), resulting in the fact that the electrostatic surface forces—that are independent of g —could well be neglected.

Experiments in AKP-15/-30 mixture

A second set of experiments was performed with a mixture of two α -alumina powders having a bimodal particle-size distribution (see Figure 1a, Figure 2 and Figure 6). The powder concentrations and sizes were chosen such that the PS would reside on top of the smaller AKP-30 fraction and the PMMA in between the two peaks of Figure 2. To that end, we prepared a suspension by method 1 consisting of a mixture of 5 vol. % AKP-15 together with 4 vol. % AKP-30. Measurements were done in duplo and continued until both tracer particles had settled to the sediment, in order to show once more that velocities do not change in time (see Figure 6). The missing sections of the curves mark the overnight peri-

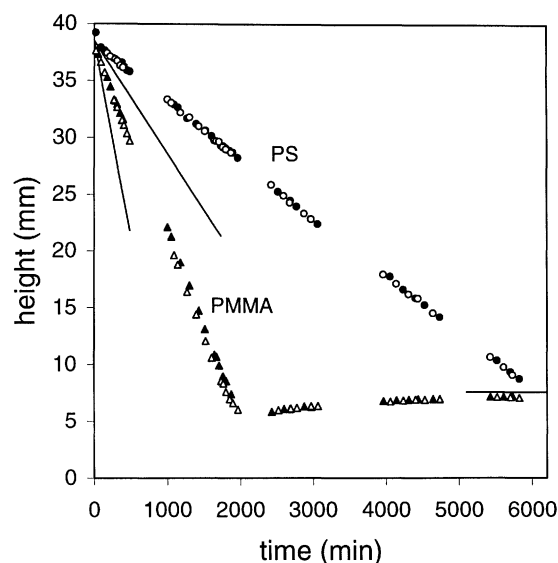


Figure 6. Sedimentation of a bimodal mixture of AKP-30 and AKP-15 powder.

The tracers are PS (open and closed circles) and PMMA (open and closed triangles). The final position of both tracer types measured at $t \sim 10^4$ min is indicated by the horizontal line. Lines at short times are predictions based on the Masliyah model for $m = 25$ (see Figure 2) and $n = 4.65$.

ods. Note the behavior of the PMMA after it has settled at $t \sim 2,000$ min. Trailing α -alumina particles that reach the sediment later than the PMMA fill up the pores between the tracer particles, thereby raising the local suspension density ρ_s to above the tracer density ρ_T , which results in an upward motion of the PMMA tracer. The tracer thus always remains at the sediment-suspension boundary. The creaming of the PMMA provides convincing experimental validation of the fact that the tracer remains at the height that corresponds with its own density. The final position of both tracer particles was measured after $\sim 10^4$ min and is indicated by the horizontal line. The two lines represent the theoretical tracer velocities according to the Masliyah model ($m = 25$, $n = 4.65$). Again, the theory overestimates the velocity, just as for the experiments with pure AKP-15.

Test for degree of agglomeration

A practical application of the microdiver technique might include an easy check on the degree of agglomeration obtained with various dispersion techniques in both laboratory experiments and industrial applications. To show that this is feasible, we suspended AKP-50 by method 2, varied the time of ultrasonification and measured the fall velocity of a PMMA tracer layer (see Figure 7). The fall velocity levels off after 3 min in ultrasound showing that particles have reached the primary particle size, and aggregates are dispersed.

Experiments in centrifugal field

In industrial applications, a centrifugal, thus faster, variant of the present technique might be very useful. Indeed, in a preliminary experiment an 8 mL flask filled with 12 vol. % AKP-50 suspension (prepared by method 2) together with

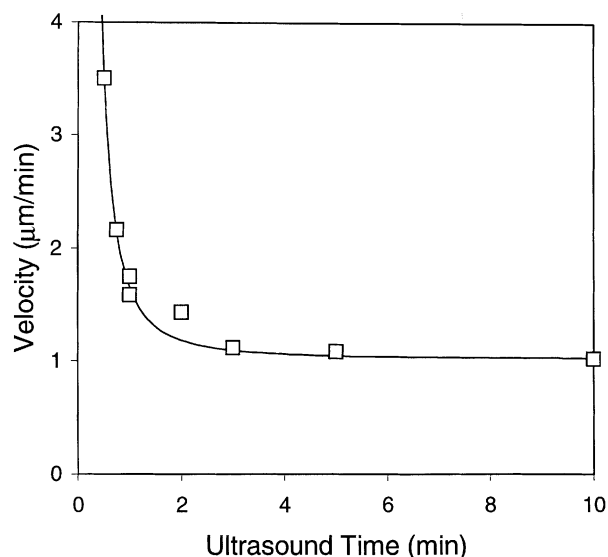


Figure 7. Influence of ultrasonification time on agglomeration.

The degree of agglomeration of an 11.7 vol. % AKP-50 suspension (prepared by method 2) is studied via the fall velocity of a PMMA tracer layer as function of time of ultrasonification.

PMMA tracer was placed in a swinging bucket laboratory centrifuge (Model HN-SII, Damon IEC, Needham Hts, MA; rotation at $\sim 2,500$ rpm; flask at ~ 12 cm from axis of rotation). In this experiment, the PMMA layer has a velocity of 1.31 mm/min which corresponds to 1.47 $\mu\text{m/min}$ in a gravity field and is higher than the corresponding value of 1.09 $\mu\text{m/min}$ measured in gravity (Figure 7). The higher value in centrifugation (after re-scaling of the driving force) is in agreement with the foregoing discussion on the discrepancy between simulations and experiments in a gravity field. A disadvantage of a centrifugal variant is the fact that the effective g -force $\omega^2 \cdot r$ (with ω the rotational velocity in rad/s and r the distance from the axis of rotation) should only change slightly from the top to the bottom of the sedimenting suspension; else, computations become much more difficult (Biesheuvel and Verweij, 2000). Further, the periods of spin-up and spin-down (changing ω) have to be included in the calculations, while induced vibrations, especially during spin-down and handling (height measurement), result in reduced accuracy. A final, slight inconvenience is the fact that the sediment cannot be resuspended easily because of the high g -forces that result in particles packing into their primary potential minimum (Biesheuvel et al., 1998).

Diver selection

To study sedimentation with microdivers, the following two criteria must hold. First, the density of the diver ρ_T has to be in between the initial suspension density $\rho_{s,\text{ini}}$ and the density of the liquid ρ_0 : $\rho_0 < \rho_T < \rho_{s,\text{ini}}$. Also, for $\rho_{s,\text{ini}}$ just above ρ_T (such as ~ 10 kg/m³), the tracer layer becomes unstable (see Figure 8). The layer expands in vertical direction to have a more “cloudy” appearance, particles of the tracer layer start to “rain out” of the layer as small strings (once we observed particle strings “raining” upward out of the layer, but could

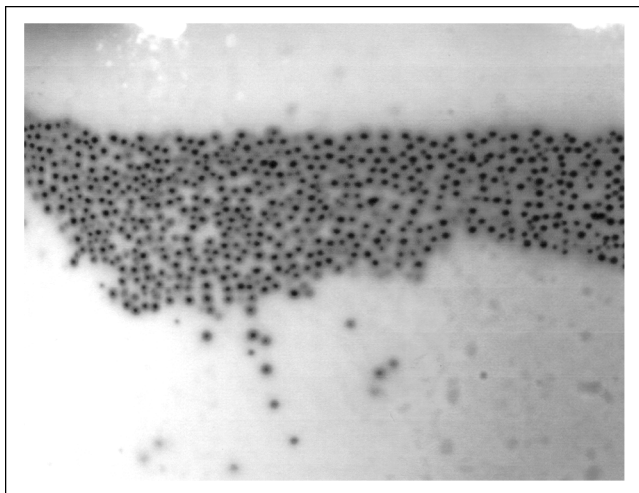


Figure 8. Instable tracer layer.

A thick layer of PMMA tracer particles floats in a suspension of a density just above that of the tracer. The variation of thickness in circumferential direction is clear, as well as a string of particles raining down.

not reproduce these experiments), and the layer becomes very asymmetric in horizontal direction. The instability follows from the fact that the driving force $(d/dh)(\rho_s - \rho_T)$ for a straying tracer particle to return to the tracer layer decreases when $\rho_{s,ini}$ approaches ρ_T . This can be understood by considering the $(h-\rho_s)$ -curves of Figure 5a (such as for $\phi_s = 0.10$). For $\rho_{s,ini}$ approaching ρ_T , $d\rho_s/dh$ at the location of the tracer layer (namely, where $\rho_T = \rho_s$) goes to zero (for $\rho_s \rightarrow \rho_{s,ni}$, $dh/d\rho_s \rightarrow -\infty$ in Figure 5a).

Secondly, an appropriate diver should be large enough to rapidly move to its correct location in the sedimenting suspension. Small (and therefore slow) tracers cause a long startup time. This requirement can be quantified by stating

$$\left\{ \left(\frac{(\rho_T - \rho_s)d_T^2}{(\rho - \rho_s)d_{av}^2} \right) = C \right\} \gg 1 \quad (8)$$

in which d_T is the diameter of the diver particles, and d_{av} is the average size of the submicron powder. The conditions and materials chosen in this article are given by $36 < C < 33 \times 10^3$, a range which is significantly above unity.

Finally, divers should not disturb the colloidal behavior of the suspension. In our experiments we had to add (a very small amount of) anionic soap to the suspension to inhibit flotation of the tracers, while assuming that this addition does not change the sedimentation of the alumina particles. However, in other systems, such an addition might certainly change the system (as occurs in our system if we use ionic soap). Therefore, flotation of the polymer tracer particles is ideally avoided by other means, such as the use of hydrophilic(-ally coated) polymer particles (in the case of an aqueous system) or by anchoring the polymer chains onto the surfaces of the tracers.

Once these criteria are fulfilled, the microdiver technique provides a simple and accurate technique to study sedimentation of polydisperse, concentrated, colloidal suspensions.

Conclusions

Velocities of fixed density fronts in sedimenting, concentrated, submicron, polydisperse alumina suspensions were studied by the addition of larger (order 100 μm) polymer tracer particles ("microdivers") that float in the suspension at the location where they have the same density as the suspension.

The technique requires tracer particles of an intense color different from the suspension. To support the new technique fundamentally, state-of-the-art multicomponent particle transport models of Patwardhan and Tien and of Masliyah were solved. This resulted in sufficient agreement with the experiments to indicate that the tracer technique is valid.

The density of the microdivers must be in between that of the liquid and the original suspension, while the microdivers' mobility must be significantly higher than that of the particles in suspension. These criteria are met when polymer divers in the 100 μm range are used to study sedimentation of concentrated submicron oxidic powders.

Acknowledgments

We thank the Rheology Group, Dept. of Applied Physics & Twente Institute of Mechanics, University of Twente, The Netherlands for providing experimental facilities for a portion of this study, as well as the Materials Department, College of Engineering, University of California at Santa Barbara.

Literature Cited

- Allen, T., *Particle Size Measurement*, 3rd Ed., Chapman & Hall, London (1981).
- Bartlett, M., and H. Jiang, "Particle Sizing in Dense, Rapidly Flowing KCl Suspensions by Photon Migration Techniques," *AIChE J.*, **47**, 60 (2001).
- Berg, S., "Untersuchungen über Korngrößenverteilung," *Kolloid-chemische Beihefte*, **53**, 149 (1941).
- Berg, S., "Determination of Particle Size Distribution by Examining Gravitational and Centrifugal Sedimentation According to the Pipet Method and with Divers," Symp. on Particle Size Measurement, Boston (June 1958), ASTM Special Techn. Publ., **234**, 143 (1959).
- Bernhardt, C., *Particle Size Analysis*, Chapman & Hall, London (1994).
- Biesheuvel, P. M., A. Nijmeijer, and H. Verweij, "Theory of Batchwise Centrifugal Casting," *AIChE J.*, **44**, 1914 (1998).
- Biesheuvel, P. M., and H. Verweij, "Calculation of the Composition Profile of a Functionally Graded Material Produced by Centrifugal Casting," *J. Amer. Ceram. Soc.*, **83**, 743 (2000).
- Biesheuvel, P. M., H. Verweij, and V. Breedveld, "Evaluation of Instability Criterion for Bidisperse Sedimentation," *AIChE J.*, **47**, 45 (2001a).
- Biesheuvel, P. M., V. Breedveld, A. P. Higler, and H. Verweij, "Graded Membrane Supports Produced by Centrifugal Casting of a Slightly Polydisperse Suspension," *Chem. Eng. Sci.*, **56**, 3517 (2001b).
- Davis, R. H., and M. A. Hassen, "Spreading of the Interface at the Top of a Slightly Polydisperse Sedimenting Suspension," *J. Fluid Mech.*, **196**, 107 (1988).
- Delnoij, E., J. Westerweel, N. G. Deen, J. A. M. Kuipers, and W. P. M. van Swaaij, "Ensemble Correlation PIV Applied to Bubble Plumes Rising in a Bubble Column," *Chem. Eng. Sci.*, **54**, 5159 (1999).
- Esipov, S. E., "Coupled Burgers Equations: A Model of Polydisperse Sedimentation," *Phys. Rev. E*, **52**, 3711 (1995).
- Herdan, G., *Small Particle Statistics*, Butterworths, London (1960).
- Hoyos, M., J. C. Bacri, J. Martin, and D. Salin, "A Study of the Sedimentation of Noncolloidal Bidisperse, Concentrated Suspensions by an Acoustic Technique," *Phys. Fluids*, **6**, 3809 (1994).

- Hunt, W. J., and C. F. Zukoski, "The Rheology of Bimodal Mixtures of Colloidal Particles with Long-Range, Soft Repulsions," *J. Colloid Interface Sci.*, **210**, 343 (1999).
- Jarrett, B. A., and H. Heywood, *Brit. J. Appl. Phys.*, suppl. No. 3, S21 (1954).
- Jiang, H., "Enhanced Photon-Migration Methods for Particle Sizing in Concentrated Suspensions," *AIChE J.*, **44**, 1740 (1998).
- Keh, H. J., and J. M. Ding, "Sedimentation Velocity and Potential in Concentrated Suspensions of Charged Spheres with Arbitrary Double-Layer Thickness," *J. Colloid Interface Sci.*, **227**, 540 (2000).
- Masliyah, J. H., "Hindered Settling in a Multi-Species Particle System," *Chem. Eng. Sci.*, **34**, 1166 (1979).
- Montgomery, D. C., G. C. Runger, and N. F. Hubble, *Engineering Statistics*, Wiley, New York (1998).
- Nicolai, H., B. Herzhaft, E. J. Hinch, L. Oger, and E. Guazzelli, "Particle Velocity Fluctuations and Hydrodynamic Self-Diffusion of Sedimenting Non-Brownian Spheres," *Phys. Fluids*, **7**, 12 (1995).
- Pal, R., "Techniques for Measuring the Composition (Oil and Water-Content) of Emulsions—A State-of-the-Art Review," *Colloids and Surfaces A*, **84**, 141 (1994).
- Patwardhan, V. S., and C. Tien, "Sedimentation and Liquid Fluidization of Solid Particles of Different Sizes and Densities," *Chem. Eng. Sci.*, **40**, 1051 (1985).
- Richardson, J. F., and R. A. Meikle, "Sedimentation and Fluidisation: III. The Sedimentation of Uniform Fine Particles and of Two-Component Mixtures of Solids," *Trans. Instn. Chem. Engrs.*, **39**, 348 (1961).
- Syamlal, M., and T. J. O'Brien, "Simulation of Granular Layer Inversion in Liquid Fluidized Beds," *Int. J. Multiphase Flow*, **14**, 473 (1988).
- Thies-Weesie, D. M. E., A. P. Philipse, G. Nägele, B. Mandl, and R. Klein, "Nonanalytical Concentration Dependence of Sedimentation of Charged Silica Spheres in an Organic Solvent: Experiments and Calculations," *J. Colloid Interface Sci.*, **176**, 43 (1995).
- Wallis, G. B., *One-Dimensional Two-Phase Flow*, McGraw-Hill, New York (1969).
- Weiland, R. H., and R. R. McPherson, "Accelerated Settling by Addition of Buoyant Particles," *Ind. Eng. Chem. Fundam.*, **18**, 45 (1979).
- Whitmore, R. L., "The Sedimentation of Suspensions of Spheres," *British J. of Appl. Phys.*, **6**, 239 (1955).
- Williams, R. A., C. G. Xie, R. Bragg, and W. P. K. Amarasinghe, "Experimental Techniques for Monitoring Sedimentation in Optically Opaque Suspensions," *Colloids and Surfaces*, **43**, 1 (1990).
- Williams, R. A., C. G. Xie, F. J. Dickin, S. J. R. Simons, and M. S. Beck, "Multiphase Flow Measurements in Powder Processing," *Powder Tech.*, **66**, 203 (1991).
- Zeng, J., and D. R. Lowe, "A Numerical Model for Sedimentation from Highly-Concentrated Multi-Sized Suspensions," *Math. Geology*, **24**, 393 (1992).

Manuscript received May 26, 2000, and revision received Mar. 15, 2001.