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PROGRESS REPORT

Princeton University

SUMMARY

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The existing three-year grant pertaining to "The control of microstructures during consolidation and injection molding of colloidal dispersions" began July 1, 1988 as a continuation of a previous grant. The overall effort seeks to answer fundamental questions relevant to the colloidal processing of submicron particles leading to ceramic materials for structural, electronic, or optical applications. At the outset two distinct projects were envisioned, an exploration of the ultrasonic enhancement of disorder-order transitions and a detailed study of injection molding of very dense dispersions, with each weighted toward experiments but with theoretical components.

As the effort evolved the focus shifted in response to the interests of the students attracted to the project, the identification of interesting related problems through technical meetings, and different insights gained during participation in a DOE sponsored workshop. The scope that has emerged encompasses

-- completion of research begun during the first grant period on disorder-order transitions occurring during sedimentation,

-- the consolidation of flocculated dispersions via filtration, and

-- the assembly of nanometer-sized particle into dense packings.

INTRODUCTION

Our work has encompassed three topics associated with the formation of green bodies from dispersed powders. The first and third focus on

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DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED colloidally stable dispersions, seeking to define conditions under which particles of narrow size distribution can be consolidated into ordered packings. One effort continuing from the first grant examines the disorder-order transition for 0.1 - 1.0 μm hard spheres settling under normal gravity. Weak boundaries between crystallites and the long time scales necessary for ordering may render these microstructures impractical for structural applications. We have sought to understand the process more deeply with the intent of ultimately growing single crystals. The second effort, just beginning, examines much smaller particles, 5-50 nm, for which different modes of consolidation are necessary and little is known.

The third topic, pressure filtration of flocculated dispersions, recognizes their pervasive occurrence in ceramics processing, whether intentional or inadvertent (Lange, 1989). Here we seek to define the conditions required for dense packing, much as observed recently by Velamakanni, et al. (1990).

The first has been completed with the results, described in two PhD theses and the publications cited below and appended, revealing (a) the conditions under which sedimentation of hard spheres yields ordered sediments, (b) the evolution of density profiles throughout the process as delineated by x-ray scans and predicted by a mathematical model, and (c) some insight into the mechanism for the transition from Brownian dynamics simulations. A more fundamental exploration of these and related issues is now being pursued with funding from NASA.

The second project has moved through an initial phase involving design and fabrication of the filtration cell, synthesis and characterization of the colloidal system, and an initial set of x-ray measurements with a CAT scanner at the Schlumberger Corporate Laboratory. The experiments clearly demonstrated the feasibility of the effort, and yielded cakes at 70% of theoretical density, but also identified a minor flaw in the cell design and the need for somewhat larger particles to shorten the time scale of individual runs. The second phase of experiments will begin this spring.

In parallel we are undertaking two modest but interesting theoretical studies: (i) an analysis of the formation of networks via Brownian and sedimentation induced flocculation to complement our previous model for the consolidation of such networks and (ii) a treatment of centrifugal casting in two-dimensional shapes to define how and when bouyancy-driven convection can produce uniform sediments.

The third project addresses particles with sizes in the range of 1-50 nm. The high surface areas for catalytic applications, the appearance of quantum size effects with some semiconductors, and the possibilities of small limiting flaws in structural materials have stimulated the synthesis of a fascinating array of nanosized particles. Our emphasis is on the processing, which requires control over the colloidal stability and different techniques for consolidation since the requisite centrifugal fields or applied pressures for filtration are prohibitive. At present we are preparing and characterizing a model system for studying the assembly of dense phases through osmotic attractions induced by soluble polymer.

SIGNIFICANT ACCOMPLISHMENTS

Our studies of the disorder-order transition during sedimentation of silica dispersions have

-- demonstrated via x-ray scanning and visual observations the kinematics of the process via detailed volume fraction profiles,

-- illustrated the competition between two rate processes, crystallization and sedimentation, that distinguishes between glassy and crystalline sediments, and

-- suggested a simple model for the kinetics of crystal growth.

Our light scattering and rheological measurements for octadecyl silica spheres in hexadecane

-- define a sol-gel transition expressed as the gelation temperature as a function of volume fraction,

-- characterize the shear modulus of the gels, and

-- suggest a means for extracting the strength of attraction from the adhesive sphere model.

This information will be valuable for interpreting our pressure filtration experiments.

PAPERS PUBLISHED OR SUBMITTED

K. E. Davis and W. B. Russel:

"Sedimentation of lyophilic sols", Ceramic Trans. 1B, 693 (1989).

"An asymptotic description of transient settling and ultrafiltration of colloidal dispersions", Phys. Fluids A 1, 82 (1989).

K. E. Davis, W. B. Russel, and W. J. Glantschnig:

"Disorder-order transition in settling suspensions of colloidal silica: X-ray measurements", Science 245, 507 (1989).

"Experiments on settling suspensions of colloidal silica: Observations and x-ray measurements", J. Chem. Soc. Far. Trans. (in press) (1991).

M. Chen and W. B. Russel:

"Characteristics of flocculated silica dispersions", J. Colloid Inter. Sci. 141, 564 (1991).

W. B. Russel:

"Controlling the rheology of colloidal dispersions through the interparticle potential", Ceramic Powder Sci. III, 362 (1990).

"Formulation and processing of colloidal dispersions", MRS Symp. Proc. 177, 281 (1990).

K. E. Davis:

"Sedimentation and crystallization of hard sphere colloidal dispersions", Ph.D. Dissertation, Princeton University, 1989.

C. L. Bolton:

"Brownian dynamics studies of the disorder-order transition in concentrated colloidal dispersions", Ph.D. Dissertation, Princeton University, 1989.

TALKS AT TECHNICAL MEETINGS AND UNIVERSITIES

3rd International Conference on Powder Processing Science, San Diego, CA, February 1990.

Workshop on Self-Assembly, University of Illinois at Urbana-Champaign, November 1990.

DISCUSSION

A. PRESSURE FILTRATION OF DISPERSIONS: EXPERIMENTS

Our investigation of the consolidation process involves a pressure filtration cell for conducting experiments within an x-ray scanning device that utilizes computer assisted tomographic techniques to invert the signal into a three-dimensional density distribution. The compression of a gel requires exceeding the yield stress of the particle network, so we designed a cell (Figure 1) capable of sustaining a pressure in excess of 200 psi while minimizing attenuation of the x-rays, resisting solvents such as cyclohexane and hexadecane, and enabling suitable temperature control.

The cell wall is contructed of polyether sulfone (ICI Americas) with the flanges and supporting rods of nylon (Nylatron GSM from Plastics Center, Conshohocken, PA). A solid teflon disk with several thousand holes of 0.25 mm diameter suffices to support the filter. Filter membranes, with pores of 0.2 μm or 0.02 μm diameter (Anotech, Waukegan, IL) retain the flocs, while spreading a thin cloth of teflon (Zitex A, L-E-M Plastics, Wallington, NJ) on top of the membrane adds a prefilter and prevents adhesion of particles to the membrane surface. An outer wall of polycarbonate surrounds the polyether sulfone to create an annulus for circulation of water to maintain a specified temperature. Nitrogen, supplied by a port at the top, drives liquid flow.

Silica spheres were synthesized following the method of Stober, et al. (1968), coated with octadecyl chains as described by Iler (1979), and then dispersed in hexadecane to provide thermally reversible flocculation as reported by Jansen and coworkers (1986). The particles relevant to the experiments reported here had a number average diameter of 0.167±0.022 μm and a density of 1800±40 kg/m^3. At 50°C they behave as hard spheres but lowering the temperature to 25°C generates a strongly flocculated network at moderate volume fractions.

An extensive study of the structure and rheology of these dispersions, as functions of the volume fraction of particles and the temperature, has been completed (Chen and Russel, 1991). Formation of a gel, or volume filling network, occurs at a temperature that varies with volume fraction (Figure 2). At temperatures below the transition, the shear modulus exhibits a low frequency plateau, characteristic of a solid, with the magnitude varying as a power law function of volume fraction and the exponent increasing with increasing temperature. Static light scattering at volume fractions less than 0.10 suggest a gel formed from fractal clusters with dimension $D = 2.1 \pm 0.1$ and sizes that decrease with increasing volume fraction, in accord with observations of Dietler et al. (1986) on different systems. These results serve to define suitable conditions for the filtration experiments and provide mechanical property data relevant to the consolidation process (c.f. Buscall, 1983).

The CAT scanner was calibrated for quantitative measurement of volume fractions with samples from batches of particles with somewhat different sizes and densities. A linear relationship between the attenuation coefficient and the particle volume fraction correlated all the data within 1%. During an experiment simultaneous scanning of a pure hexadecane sample verifies the continuing validity of the calibration.

Both stable and the strongly flocculated dispersions were consolidated by filtration, with samples prepared at 50°C but the latter then allowed to equilibrate overnight with the circulating water. After an initial CAT scan at the uniform starting density, the driving pressure was imposed by introducing nitrogen into the cell. As the run proceeded filtrate was weighed continuously and scans were taken periodically, every ten minutes initially and then at longer and longer intervals as the cake accumulated and the filtration rate decreased. Thus the physical experiment is standard, but the density profiles will yield new information critical to understanding the mechanics of consolidation. Unfortunately, none of the initial experiments yielded quantitative data due to complications with both the filtration cell and the scanner, most of which have now been resolved. Nonetheless the results demonstrate interesting qualitative features worth some discussion.

With stable dispersions at 50°C that form incompressible cakes, constant pressure filtration leaves the dispersion uniform at the initial volume fraction and produces a cake with depth that increases with time (Figure 3). More interesting is the volume fraction of 0.70 within the cake, suggesting either some ordering or a significant effect of the modest amount of polydispersity. Our future experiments will involve careful checks on the calibration and thorough monitoring of the cake density to ascertain the significance.

Consolidation at 26°C, with a strong gel filling the cell before the beginning of filtration, yielded sediments of similarly high densities. So the mechanical stresses clearly dominate the effects of interparticle attraction at applied pressures of 50-60 psi. However, the density profile evolved quite differently, and reproducibly. As cake accumulated in the early stages of the process, the upper surface of the gel moved downward under the nitrogen pressure but also deformed, as if stresses at the walls retarded motion. Then a rupture appeared above the cake toward the bottom of the gel. As flow continued the rupture closed but a gel-liquid interface disengaged from the liquid-nitrogen interface (Figure 4). This is quite remarkable, implying that the gel is moving faster than the fluid and must be drawn downward by another force. At this point neither the origin nor the significance of this phenomena are clear.

B. CONSOLIDATION OF DISPERSIONS: THEORY

Pressure Filtration

Although development of the ultimate mathematical model must rely on the experiments to identify the key physics, the formulation of a complete framework does seem appropriate now. Previous work of ours (Auzerais, et al., 1988) and others (Buscall and White, 1987) provides a basic model for the consolidation of volume filling networks, though evaluation of existing constitutive equations for the stress borne by the particulate network awaits more data. The formation of the network from initially dispersed particles remains an open issue, however. So we have begun analyzing this process for the fractal growth of flocs due to Brownian and sedimentation-induced collisions. While still rather qualitative, the approach can treat the coupling between sedimentation and floc growth that determines whether a gel forms or discrete aggregates settle before this occurs.

We adopt, in part, the approach of Couch and Hinch (1990) in considering irreversible cluster-cluster aggregation into rigid fractals with the number of particles N, the cluster radius R, and the particle radius a related according to

$$N = (R/a)^d. \tag{1}$$

Then assuming a narrow floc size distribution yields the conservation equation for the number density of clusters n as

$$\begin{aligned} & dn/dt = -kn^2 \\ \text{with}\quad & n = n_o \quad \text{at } t=0 \\ \text{and}\quad & n = n_o/N. \end{aligned} \tag{2}$$

The form of the rate constant k depends on the mechanism of flocculation, for example

$$\left.\begin{aligned} & 4kT/3\mu && \text{for diffusion-limited growth} \\ \text{and} \\ & 4\pi R^2 U = 8\pi N a^3 R \Delta\rho g/9\mu && \text{for sedimentation-induced growth} \end{aligned}\right\} \tag{3}$$

with μ the fluid viscosity, kT the thermal energy, and U the settling velocity for a floc containing N spheres. Since sedimentation does not produce collisions for flocs of equal sizes, the form shown implies a distribution of sizes such that the average velocity difference equals the average velocity, consistent with the cluster-cluster mechanism. Combining (1-3) leads to an expression for the rate of cluster growth, i.e., dN/dt.

Limiting solutions for large and small Peclet numbers (ratio of sedimentation to diffusion) follow directly:

$Pe = 4\pi a^4 \Delta\rho g/3kT << 1$:

$$N(t) = 1 + 3n_o kTt/4\mu \qquad (4)$$

a well-known result for diffusion limited aggregation (Weitz, et al. 1986).

$Pe >> 1$:

$$N(t) = [1 - 8\pi a^4 \Delta\rho g n_o t/8\mu d]^{-d} \qquad (5)$$

In order to estimate the onset of gelation we define an effective volume fraction as

$$\phi_{eff} = 4\pi R^3 n/3 = \phi N^{3/d-1} \qquad (6)$$

with $\phi = 4\pi a^3 n_o/3$. Thus as N increases so does the volume occupied by the flocs until $\phi_{eff} = 1$ at gelation.

While complete solutions incorporating settling during growth have yet to be constructed, the form is reasonably easy to anticipate. For example, the upper boundary of the dispersion H(t) will settle at the velocity of the flocs residing there, i.e.

$$dH/dt = -U(N) \qquad (7)$$

with N increasing with time according to (4) or (5). Integrating and invoking the condition for gelation then determines the total amount of settling. For Pe >> 1 this leads to

$$\Delta H/a = 0.19[\phi^{-1/(1-3/d)} - \phi^{-1}] \qquad (8)$$

which for particles of 1 micron radius suggests settling of 19 cm for ϕ = 0.01 but only 0.19 mm for ϕ = 0.1. Starting with particles small enough that Pe<<1 throughout the process leads to

$$\Delta H/a = [Pe/6\phi(2-1/d)][\phi^{-(2-1/d)/(3/d-1)}-1] \qquad (9)$$

and generally small amounts of settling. Thus one could expect to predict trends with variations in particle size and initial volume fraction, and test the predictions with simple laboratory experiments.

Centrifugal Casting of Two Dimensional Shapes

Recently Beylier, et al. (1990) reported experiments with complex shapes such as the spool mold in Figure 5, in which centrifugal casting of stable dispersions produced perfectly uniform parts. Since the centrifugal field driving the particles into the mold is unidirectional, the ease with which closepacked particles filled the entire mold seems rather surprising. Clearly another driving force must cause radial motion of the particles on the same time scale as the axial motion. Diffusion seems unlikely since the Peclet number is about 10^2 for the conditions of the experiments. In collaboration with Dr. E. Herbolzheimer of the Exxon Corporate Laboratory, we soon identified bouyancy-driven convection arising from density differences associated with variations in the particle concentration and then proceeded through (a) an order of magnitude analysis to confirm this conclusion by predicting the thickness of boundary layers depleted of particles beneath upward facing surfaces and (b) a calculation of the structure of the radially segregated flow within the constriction necessary to permit uniform settling of particles in the lower region.

Given sufficiently strong bouyancy-driven convection to maintain uniform particle volume fractions within the lower chamber, sedimentation will proceed normally, producing a total downward flux of particles equal to

$$\pi R^2 U_o \phi K(\phi) \qquad (10)$$

with ϕ the volume fraction, $U_o = 2\Delta\rho g a^2/9\mu$ the Stokes settling velocity, R the radius of the chamber, and K characterizing hindered settling. Clearly an equal flux of particles must enter the chamber through the neck while that due to sedimentation alone will be smaller by the ratio of the areas, i.e. $(R_t/R)^2$.

This suggests more complex behavior within the neck, with the dispersion forming a core moving downward and an annulus of pure fluid next to the wall moving rapidly upward. The differential motion arises from the different densities and a common pressure gradient. Integration of the equations of motion for fully developed flow and imposition of boundary conditions at the interface $r = R_t - \delta$ yields the velocity profiles. The pressure gradient follows from the requirement that the total volumetric flux must be zero while the flux of particles equals (10).

Scaling the equations identifies the key dimensionless group as the ratio of a characteristic bouyancy-driven velocity within the tube to the Stokes velocity of the particles,

$$\Lambda = (9\phi/2)(R_t/a)^2 >> 1. \qquad (11)$$

Solution as a perturbation expansion for $\Lambda >> 1$ determines the thickness of the annular pure fluid film as

$$\delta/R_t = (3K(\phi)(R/R_t)^2/\Lambda)^{1/3} << 1 \qquad (12)$$

and the dimensionless pressure gradient within the tube as

$$\Delta p R_t{}^2/U_o\mu L = \Lambda[1+(3K(\phi)(R/R_t)^2/8\Lambda)^{2/3}\mu/\eta] \qquad (13)$$

with η the viscosity of the dispersion. Thus for $\Lambda >> 1$ the pure fluid annulus should be very thin and the pressure gradient within the tube should differ only slightly from the hydrostatic value. These features make the phenomena quite similar to the Boycott effect, which enhances settling in inclined tubes by allowing the fluid to disengage from the settling particle phase and move upward rapidly in a thin layer under the downward facing surface. Completion of the analysis to incorporate the motion of the interfaces, i.e. upper surface of the settling particle phase which moves down with time and the rising top of the sediment, should be straightforward.

Perhaps more interesting is a definition of the conditions for which this mode of settling persists. A full theory would necessitate numerical solutions of the momentum and particle conservation equations within the lower chamber, a difficult undertaking. At present we have simply constructed order of magnitude arguments and an equally crude experiment to probe the matter.

If one balances inertial and bouyancy effects in the region just below the neck, a characteristic radial velocity follows as

$$u_r = (\Delta\rho g h \phi/\rho)^{1/2} \qquad (14)$$

with h the thickness of the layer depleted of particles. From the analysis within the tube the characteristic vertical velocity is

$$u_z = U_o K(\phi)(R/R_t)^2. \qquad (15)$$

These determine the trajectory of particles exiting the tube and therefore the interface between the settling particle phase and clear fluid as

$$h/R = u_z/u_r$$

or (16)

$$h/R = (\rho\Delta\rho g\mu^2)^{1/3}\ K^{2/3}(\phi)(a/R_t)^{4/3}.$$

Thus only when $h/R \ll 1$ should the process yield uniform sediments that fill the lower reservoir.

Our experiments were performed in beakers connected by ground glass fittings to a tube as shown in Figure 6. Dispersions of glass beads in water under normal gravity produced sediments that partially filled the lower beaker. The experiment depicted in Figure 7 with 40-50 micron diameter beads initially at $\phi = 0.11$ suggests $h = 1\text{-}5$ mm for $R = 50$ mm, or $h/R = 0.02\text{-}0.1$. Evaluation of (16) gives $h/R = 0.014$, at least of the right order of magnitude.

C. DISPERSIONS OF NANOSIZED PARTICLES

For model studies of consolidation we are assembling a colloidal system consisting of calcium carbonate spheres stabilized with an alkylbenzene surfactant and dispersed in toluene. Previous neutron scattering experiments (Markovic, et al. 1984, 1986a,b) have detected their structure, indicating inorganic cores with radii of 2.5±0.2 nm and a surfactant layer of thickness 1.9±0.1 nm, and soft sphere interactions. In addition, static light scattering by Tong, et al. (1990) has probed the effect of soluble nonadsorbing polymer, finding depletion or volume restriction attractions sufficient to induce phase separation at moderate polymer concentrations. Hence, the dispersion appears well suited for our purposes.

We obtained the particles from Exxon Chemical Company dispersed at a high volume fraction in a viscous mineral oil. The standard procedure for cleaning involves centrifugation, dilution with heptane, and then rounds of precipitation with acetone and washing (McDonald, 1990). Ultimately the particles are dried and then redispersed in toluene. According to the literature approximately 10% oil remains in the final dispersion but does not adversely affect scattering and other experiments.

Our efforts appear to have produced the desired dispersions, and revealed that further cleaning destabilizes the particles, but a definitive assessment awaits results from light scattering experiments currently underway. Given the success of others in preparing and characterizing the particles, obtaining satisfactory systems for this first step of our studies should be only a matter of time.

D. FUTURE WORK WITHIN THE CURRENT GRANT PERIOD

Activity already underway on the topics above should achieve the following between now and the end of the current grant:

- characterization of the calcium carbonate particles and their interactions via static light scattering plus an initial study of the dynamics of consolidation induced by soluble polymer as described more fully in the proposal,
- a complete set of x-ray scans during filtration of dispersions with somewhat larger particles (about 0.4 micron) over a range of temperatures and, therefore, strengths of attraction, and
- completion of the hierarchical model to predict the initial density profiles before consolidation begins, as well as the onset of gelation.

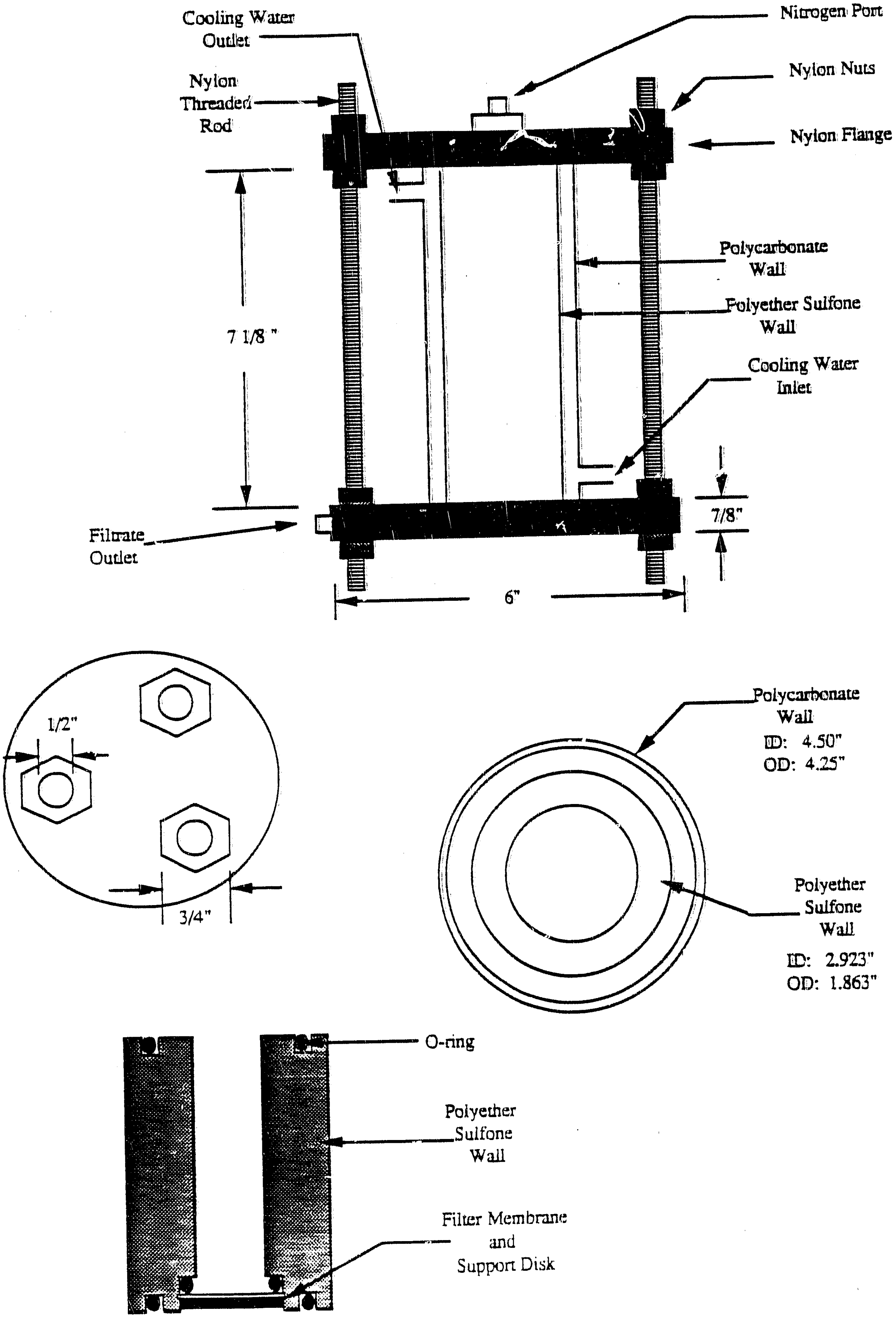

Figure 1 - Drawing of pressure filtration cell.

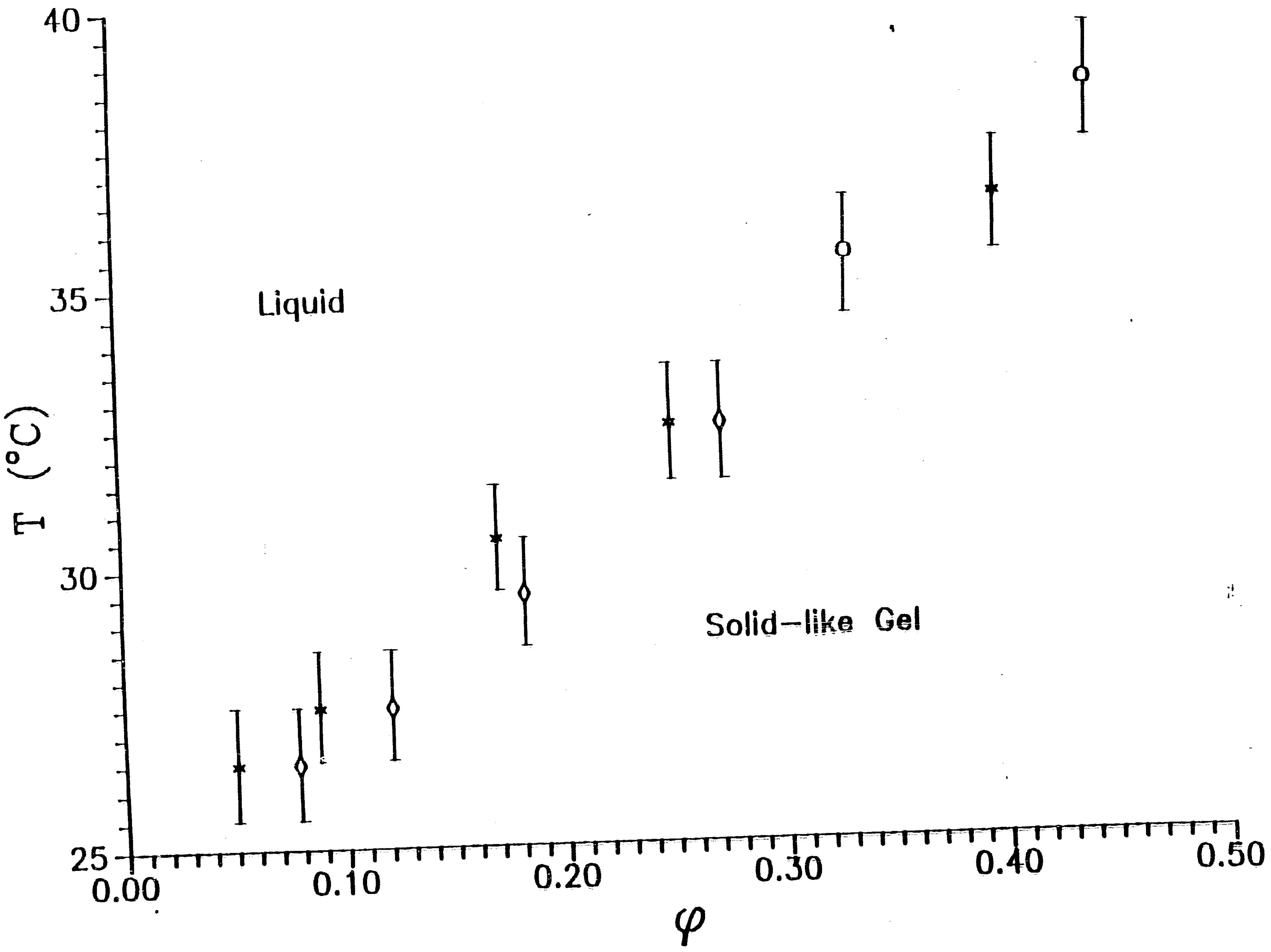

Figure 2 - Gel transition temperature as function of volume fraction for octadecyl-coated silica spheres (* a = 56 nm, ◊ a = 77 nm) in hexadecane (Chen and Russel, 1991).

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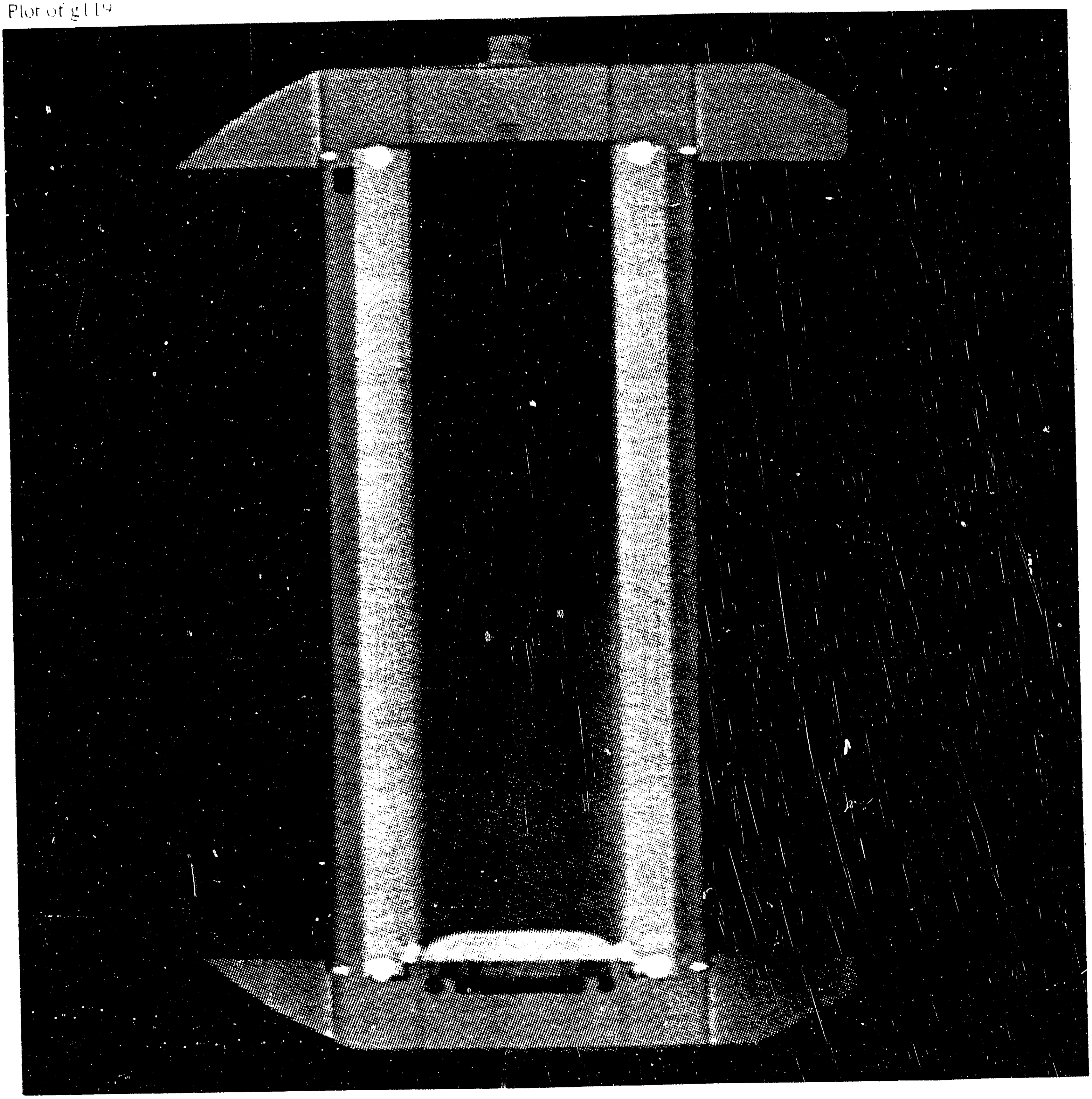

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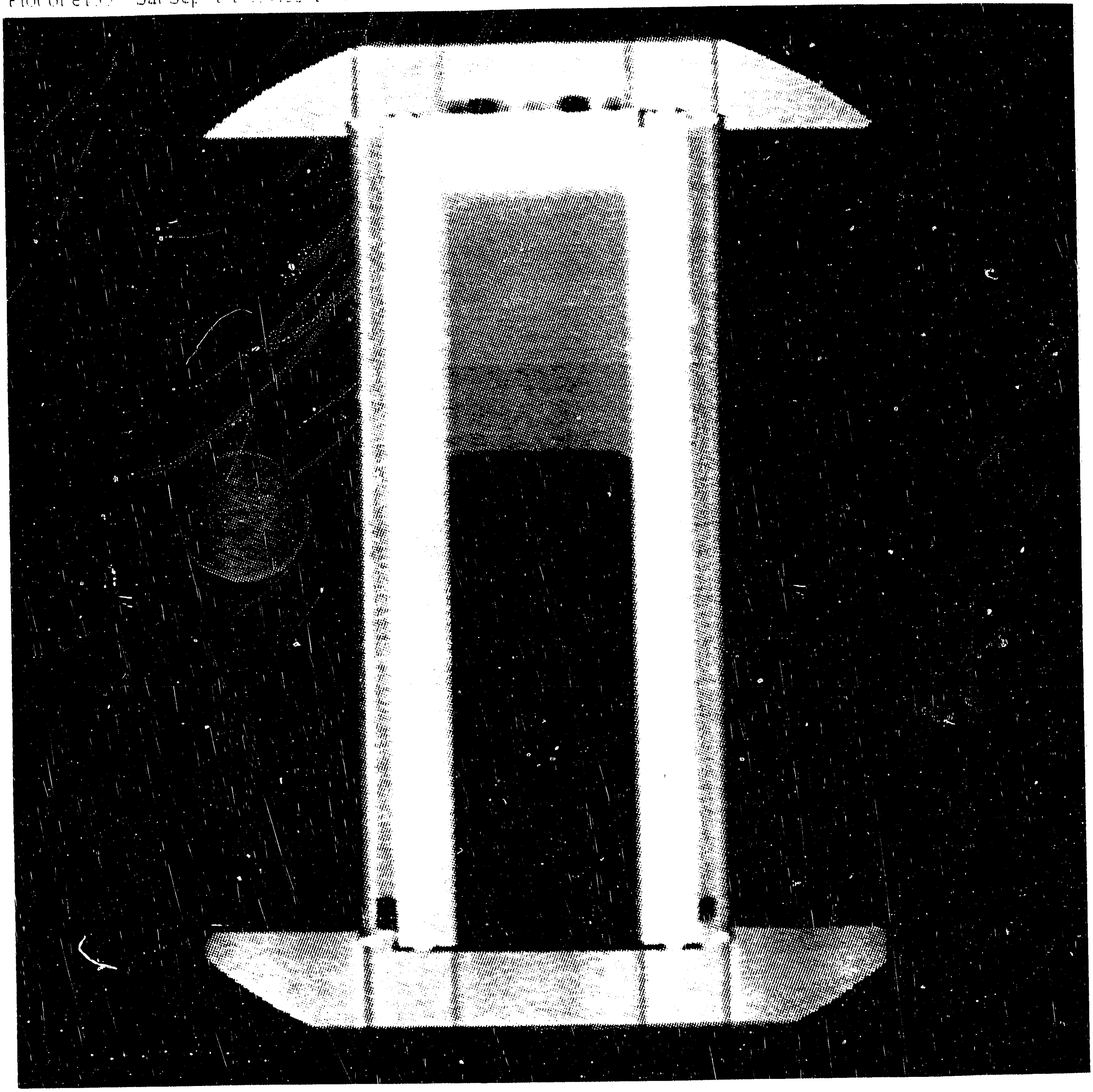

[illegible] graph of silica spheres in [illegible] at [illegible] after [illegible] hour
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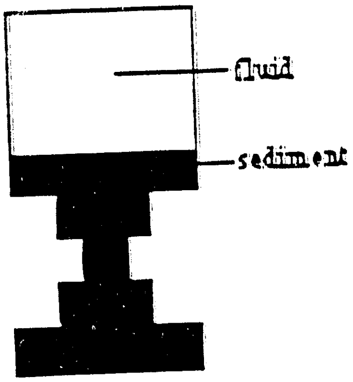

Figure 5 - Schematic of spool mold of Beylier, et al. (1990).

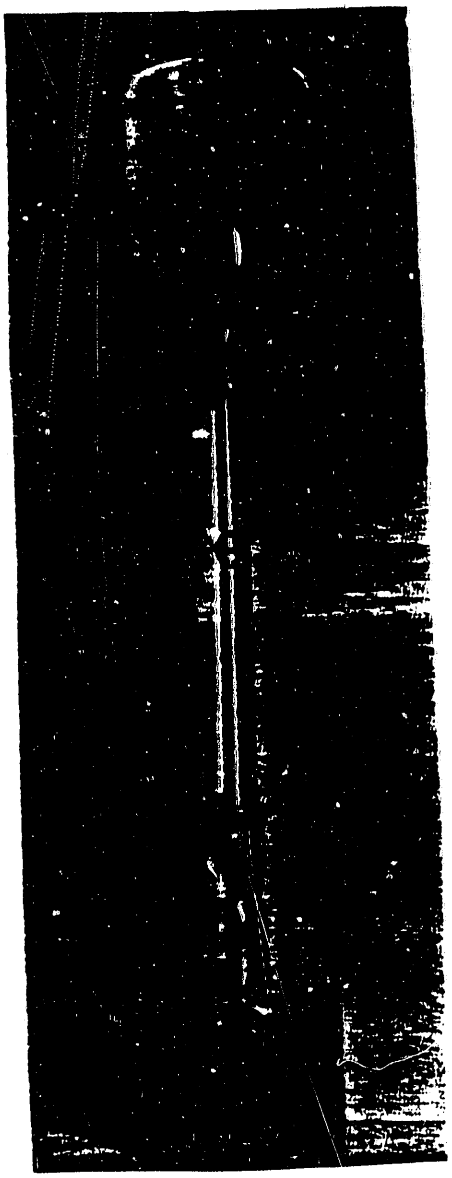

Figure 6 - Apparatus for settling experiment with 95 mm diameter chamber at bottom.

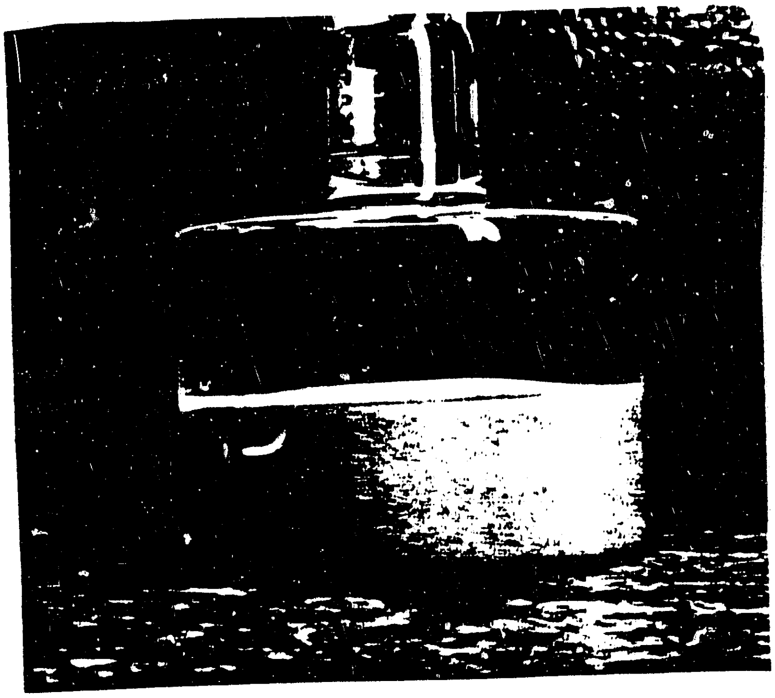

Figure 7 - Results for glass beads with average diameter of 40 μm in water showing slightly humped sediment surface.

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