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IMPROVED BETA"-ALUMINA OXIDE ELECTROLYTES
THROUGH TRANSFORMATION TOUGHENING
Final Report

F.F. Lange and K.T. Miller

October 1986

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by

F.F. Lange and K.T. Miller

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for

Technology Base Research Project
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Section 1

A COLLOIDAL METHOD TO ENSURE PHASE HOMOGENEITY IN β''-Al_2O_3/ZrO_2 COMPOSITE SYSTEMS

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ABSTRACT

A colloidal method which ensures phase homogeneity has been developed for processing β''-Al_2O_3/ZrO_2 composites. High volume fractions ($\leq$ 55 vol%) of β''-Al_2O_3 and limited volume fractions ($\leq$ 5 vol%) of ZrO_2 powders would disperse in isopropanol. It is suspected that ions associated with the powders (e.g., Na^+), and, possibly, trace amounts of water produce the needed coulombic repulsive forces. All particles larger than a predetermined size were eliminated by sedimentation. To concentrate the fine solids of the slurry and to prevent mass segregation during storage, the ZrO_2 powder was flocced with small additions of nitric acid. Since water leaches Na^+ from β''-Al_2O_3, this powder was sedimented from a concentrated (35 vol%) dispersed slurry and was not flocced. The two-phase slurry, which exhibited the thixotropic rheology indicative of a flocced system, was mixed by passing through an ultrasonic mixing chamber. The viscosity and mixing uniformity, quantified by high spatial resolution phase analysis of sintered materials, increased with ultrasonification time. These observations suggest that when the flocced ZrO_2 globules were sheared apart they recombined with the dispersed β''-Al_2O_3 phase, causing two-phase heteroflocculation. Viscosity measurements can, therefore, be used as a measure of phase homogeneity. The two-phase slurries could be consolidated by slip casting or pressure filtration.

1.0 INTRODUCTION

Previous studies have shown that additions of ZrO_2 can significantly increase the strength of β''-Al_2O_3.[1-3] The ZrO_2 dispersion plays two roles in strengthening. First, the ZrO_2 dispersion prevents the abnormal growth of plate-like β''-Al_2O_3 grains, which is the strength-controlling flaw population in single-phase β''-Al_2O_3.[3] Second, if the ZrO_2 is retained in the tetragonal phase, the material is transformation toughened.[1-3] Composites containing 15 vol% ZrO_2 (+ 2.5 mol% Y_2O_3) can be two to three times stronger than single-phase β''-Al_2O_3, having strengths ranging between 300-400 MPa[2] and resistivities of 8 Ω-cm at 300°C.[1,2]

Past experience has shown that the ZrO_2 powder can contain large, partially sintered agglomerates which produce crack-like voids during densification. These hard agglomerates are produced when small (< 30 nm) crystallites, formed from precursor salts (eg., $ZrOCl_2$), sinter together during the calcining step of powder manufacture. Some agglomerates survive the subsequent milling.[4] For maximum strength, these agglomerates must be removed.

Colloidal processing of powders can remove hard agglomerates and break up soft agglomerates (particle groups bound by Van der Waals forces).[5] In this method, a powder is dispersed in a fluid using a surfactant that produces repulsive interparticle forces, breaking apart soft agglomerates. Using Stoke's Law, all particles larger than a predetermined size, including hard agglomerates, are then eliminated by sedimentation. Centrifuging the slurry can accelerate this step. The portion of slurry containing the fine particles

is removed, stirred, and immediately flocced to prevent mass segregation by sedimentation. Floccing also concentrates the slurry by producing a weak network of touching particles which consolidates under its own body forces. The flocced slurry, which has the consistency of latex paint, can be washed to remove excess surfactant products (e.g., salts) produced by cycling between the dispersed and flocced states (repulsive and attractive interparticle forces).

To produce composites, two or more powders treated in this manner can be mixed in a high shear rate field. The high shear rate produced, for example, with a high-speed blender, momentarily redisperses the flocced mixture, allowing intimate mixing of particles; upon leaving the field, a heteroflocced mixture is produced.[6] The continuous network of touching particles prevents phase separation of the mixed constituents. Consolidation of the powder into the desired final shape must be accomplished directly from the slurry state, since drying will cause detrimental agglomerates to reform. Currently, consolidation can be accomplished by slip casting (filtration) and electrophoresis (which requires redispersion of the slurry). Since these two methods are limited, other slurry state consolidation techniques, consistent with the colloidal method of treating powders, are under investigation.

Previous attempts to produce β''-Al_2O_3/ZrO_2 composites using the colloidal method[2,3] were not successful. It was recognized that water could not be used as the dispersing fluid since it reacts with β''-Al_2O_3, so nonaqueous fluids were explored. Various alcohols were found to effectively disperse β''-Al_2O_3. Zeta potential measurements suggested that the repulsive interparticle

forces were produced by an electrostatic double-layer effect, consistent with Powers'[7] previous observations. Unfortunately, these alcohols did not appear to disperse the ZrO_2 powder. A compromise was used. β''-Al_2O_3 powder was dispersed at high volume fractions in butanol and sedimented to eliminate the very large particles and agglomerates (e.g., > 5 μm). The retained β''-Al_2O_3 dispersion was not flocced. ZrO_2 powder was colloidally treated in water, as described above. The resultant flocced slurry was then washed with acetone and calcined at 320°C. Proper weight fractions of this dried ZrO_2 powder and the dispersed β''-Al_2O_3 slurry were mixed in a high shear rate field. Samples were consolidated by slip casting. Unfortunately, not all of the ZrO_2 agglomerates produced during drying were broken apart during mixing. The few ZrO_2 agglomerates retained in the consolidated powder compact produced crack-like voids that resulted in the large scatter in observed strengths (300-400 MPa).

The object of the current work was to fabricate β''-Al_2O_3/ZrO_2 composite materials using a process consistent with the colloidal method and to examine the limitations of pressure filtration as a slurry consolidation method (to be reported in a companion paper).

2.0 EXPERIMENTAL APPROACH

Commercial β''-Al_2O_3* and ZrO_2 (+ 3 mol% Y_2O_3)** powders were used for this investigation. Effort was concentrated on determining the dispersion characteristics of ZrO_2 in the alcohols known to disperse β''-Al_2O_3. Flocculating conditions for the dispersed powders were then investigated. Using this information, a modified colloidal powder processing method was developed.

Composite slurries with the solid composition β''-Al_2O_3/15 vol% ZrO_2, previously determined to be optimum,[2] were mixed in a high shear rate mixing chamber (Fig. 1) for total residence times of 6, 58, and 292 s. A constant flow rate of 1.5 cm^3/s was used. To mix a slurry for longer periods than the residence time of a single pass, reservoirs 1 and 2 were exchanged, and the entire slurry volume was again passed through the chamber. During mixing, the ultrasonic horn‡ in the chamber operated at 70% of its maximum output of 1500 W. Viscosity was measured as a function of shear rate using a cone-plate geometry‡‡ to determine the rheology, and thus the type of interparticle forces, of these slurries.

Specimens mixed for the above periods were slip cast, dried, sintered, and polished for phase distribution studies. The mixing homogeneity was quantified using a scanning electron microscopy technique which identifies

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*Ceramatec, Inc., Salt Lake City, UT.
**TZ-3Y, Toyo Soda Manufacturing Co., Ltd., Tokyo, Japan.
‡Sonic Dismembrator Model 300, Fischer Scientific Co., Pittsburgh, PA.
‡‡Wells-Brookfield Cone/Plate Viscometer, Model RVTD, Brookfield Engineering Laboratories, Inc., Stoughton, MA.

the smallest volume that maintains the overall phase distribution of the sample.[8] The smaller this volume, the better the mixing. In this technique, relative compositional analyses, obtained by dispersive x-ray spectra, are performed on arbitrarily chosen sample areas at each of a series of specimen magnifications. It is assumed that the standard deviation of a series of analyses performed at low magnifications will reflect only counting errors. At some magnification level, the standard deviation of a series becomes significantly greater than the base amount, reflecting the threshold of inhomogeneous phase distribution. At magnifications below this threshold level, the sample is homogeneously mixed.

To determine the relative amounts of β''-Al_2O_3 and ZrO_2, the fractional ratio, $[Z/(A + Z)]$, of integrated energy dispersive x-ray peak intensities of the Al K-α_1 (1.34 - 1.64 keV) and the Zr Lβ_1 (1.89 - 2.19 keV) peaks were taken. Between five and ten spectra were taken at each magnification level. To speed the process from that previously reported,[8] the magnification was increased until the results of a single spectrum were significantly different from the mean obtained at the lowest magnification. This estimate of threshold magnification was used as a starting point for obtaining spectra.

Mixed slurries were consolidated by slip casting and pressure filtration, dried, and sintered for 1 h at 1550°C. Pressure filtration results will be reported in a companion paper. X-ray diffraction analysis was used to determine the phase content (β vs β''-Al_2O_3 ratio, and ZrO_2 structure) of the sintered bodies.

3.0 RESULTS

3.1 Dispersion and Flocculation Conditions

Experiments showed that ZrO_2 volume fractions ≤ 0.05 could be dispersed in both isopropanol and butanol, provided that they were "water-free." Such dispersions were stable for an observed period of 64 h. Volume fractions greater than 0.05 caused slow flocculation over a period which prevented sedimentation of particles and agglomerates larger than 1 μm. Both alcohols could disperse β"-Al_2O_3 volume fractions of approximately 0.55, where the slurry was still pourable, but dilatant.

The initial size distribution of particles and agglomerates was examined by mixing low volume fraction (< 5 vol%) dispersions of each powder and then slip casting the composite slurry to form a consolidated body, which was dried and sintered. After cutting and polishing a cross section, the size distribution of each phase was observed using optical microscopy. The largest particles in each phase very quickly sedimented to the filter interface, while the smallest particles sedimented much more slowly and so were seen at the top of the sintered specimen. Figure 2 shows the very large particles and agglomerates found at the filter interface. β"-Al_2O_3 particles larger than 100 μm were observed.

Small quantities of water (approximately 1 vol% of the alcohol) spontaneously flocced the ZrO_2/alcohol dispersions. Smaller quantities (< 0.5 vol%) of nitric acid produced the same effect. Much larger quantities

of either water or acid were required to floc the β"-Al_2O_3/alcohol dispersions, and both reacted with the β"-Al_2O_3. These observations are consistent with those of Powers,[7] who showed that additions of water to various β"-Al_2O_3/organic slurries could reverse the sign of the zeta potential. X-ray diffraction analysis of the wet slurry, flocced with nitric acid, revealed sharp diffraction peaks identified as $NaNO_3$. When flocced slurries of β"-Al_2O_3 and ZrO_2 were mixed, consolidated, and sintered, the $NaNO_3$ crystals produced large voids in the dense material, as seen in Fig. 3. The β"-Al_2O_3 slurry, therefore, was not flocced in the colloidal preparation of β"-Al_2O_3/ZrO_2 composites.

Figure 4 schematically illustrates the colloidal procedure as adapted to prepare β"-Al_2O_3/ZrO_2 composites. 3 vol% of ZrO_2 powder is dispersed in isopropanol, the fluid chosen for this study. The slurry is passed through a high shear rate mixing chamber, schematically shown in Fig. 1, to break apart soft ZrO_2 agglomerates. The ZrO_2 particles were then allowed to sediment until all those with a Stoke's diameter > 2 μm were removed. The slurry containing the desired fine particles was pumped into a container and immediately flocced by adding approximately 0.5 vol% of a 5 M solution of nitric acid. The continuous network formed after flocculation consolidates, producing a clear supernatant which is later removed to reduce the storage volume. Since the rejected portion of the slurry still contains many desirable particles, it is again mixed with isopropanol and the process repeated. Experience indicates that approximately 90% of the desirable particles are removed after three cycles.

A different procedure was used to prepare the β''-Al_2O_3. 35 vol% of β''-Al_2O_3 powder was dispersed in isopropanol and sedimented to remove particles > 5 μm. The desirable fraction of the slurry is pumped to a storage container, but is not flocced. Before being used, this slurry is stirred to eliminate any mass segregation caused by sedimentation during storage. Because the initial slurry contained a high volume fraction of powder, the concentration of particles in the retained, dispersed slurry (9.8 vol% solids) was similar to that of the flocced slurry.

3.2 High Shear Rate Mixing

Before mixing, the concentration of each of the component slurries must be determined, either by using a pycnometer to measure slurry density or by weighing a portion of slurry before and after drying. Appropriate weight fractions of each slurry are hand-mixed and the resultant composite is then passed through a high shear rate mixing chamber (Fig. 1).

Viscosity as a function of shear rate for a β''-Al_2O_3/15 vol% ZrO_2 slurry is shown in Fig. 5. The two-phase slurry contained 9.4 vol% solids. The three curves correspond to mixing chamber residence times of 6, 58 and 292 s. The observed decrease in viscosity with increasing shear rate is typical of a flocced slurry and indicates thixotropic rheology. The increase in viscosity with mixing time suggests that the ultrasonic mixing procedure increases the strength of the flocced particle network.

Figure 6 illustrates the results of the phase distribution analysis. The standard deviation of [Z/(A + Z)] vs magnification is plotted for the three mixing times. As shown, the mixing homogeneity threshold decreases with increasing ultrasonification period. Figure 7, which illustrates the microstructure of these same specimens, shows that the size of the single phase regions decreases with increasing ultrasonification period. Figure 7a shows the inhomogeneous microstructure developed when the two phases are only hand mixed.

X-ray diffraction analysis of slip cast and pressure filtered bodies sintered at 1550°C for 1 h revealed β''-Al_2O_3, tetragonal ZrO_2 and a trace (estimated at < 5%) of β-Al_2O_3.

4.0 DISCUSSION

Observations show that hand mixing the flocced ZrO_2 and dispersed β"-Al_2O_3 slurries produces a microstructure in which the ZrO_2 phase is present as large globules. The quanitative phase distribution studies show that the ZrO_2 agglomerate size decreases with increasing ultrasonification period. The viscosity was also observed to increase with the ultrasonification period. These observations strongly suggest that the degree of heteroflocculation increases as the ZrO_2 globules are broken down. Heteroflocculation would increase the strength of the particle network, increasing viscosity. Thus, the viscosity of the two-phase slurry is a measure of the phase homogeneity and can be used to determine the homogeneity of the slurry prior to consolidation.

5.0 ACKNOWLEDGEMENT

This work was performed with support from the Lawrence Berkeley Laboratory Advanced Battery Program under Contract Number 4530910.

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7.0 FIGURE CAPTIONS

Fig. 1 Schematic diagram of the ultrasonic mixing chamber.

Fig. 2 Microstructure near the filter interface of a β"-Al_2O_3/15 vol% ZrO_2 composite slip cast from the as-received powders. The light phase is ZrO_2 and the dark phase is void space.

Fig. 3 Large voids caused by volatilization of $NaNO_3$ crystals present in a β"-Al_2O_3/ZrO_2 composite formed using β"-Al_2O_3 flocced with HNO_3.

Fig. 4 Colloidal processing flowchart adapted for β"-Al_2O_3/ZrO_2 composites.

Fig. 5 Viscosity as a function of shear rate for a β"-Al_2O_3/15 vol% ZrO_2 composite slurry mixed in the ultrasonic chamber for 6, 58, and 292 s.

Fig. 6 Percentage standard deviation from the mean phase distribution plotted against magnification (or sampling area) for β"-Al_2O_3/15 vol% ZrO_2 composite slurries mixed for 6, 58, and 292 s.

Fig. 7 Microstructures of β"-Al_2O_3/15 vol% ZrO_2 composites ultrasonically mixed for increasing periods. (a) No ultrasonic mixing (hand mixing only), (b) 6 s, (c) 58 s, (d) 292 s.

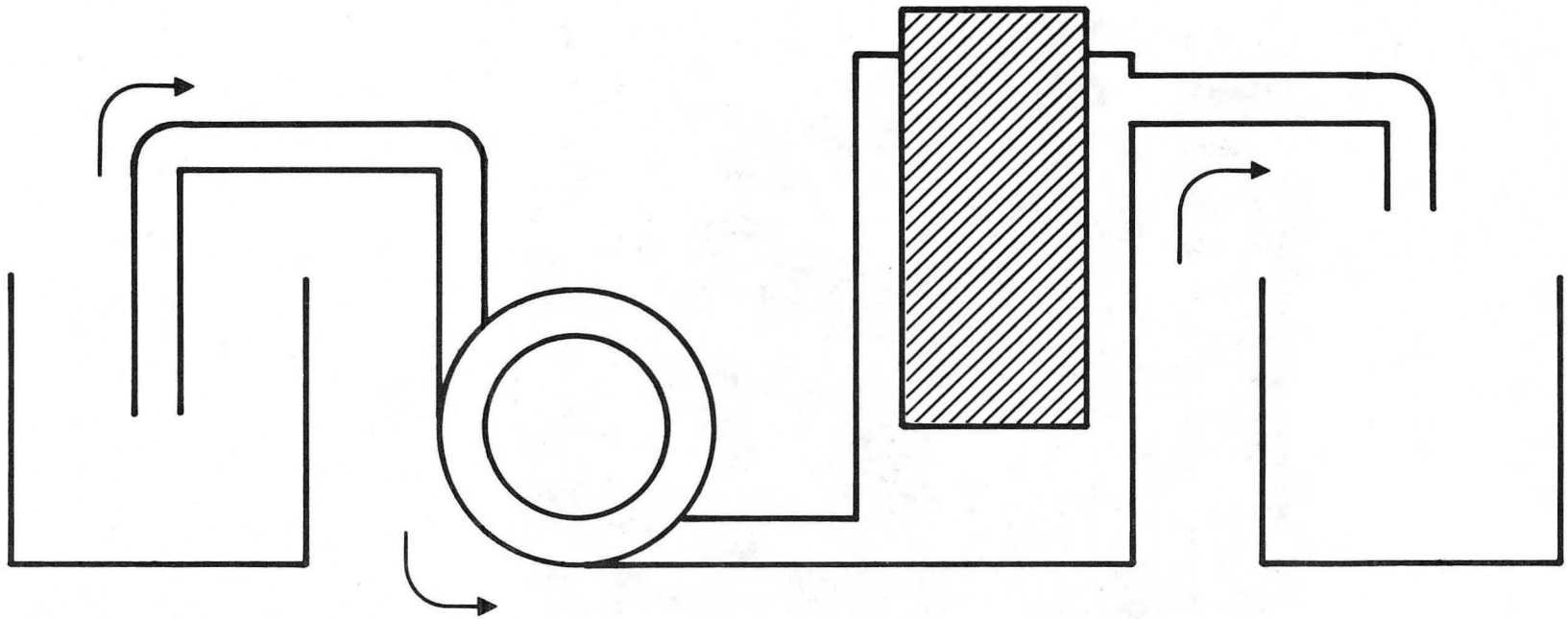
RESERVOIR 1
PERISTALTIC PUMP
MIXING CHAMBER WITH ULTRASONIC HORN
RESERVOIR 2

Figure 1

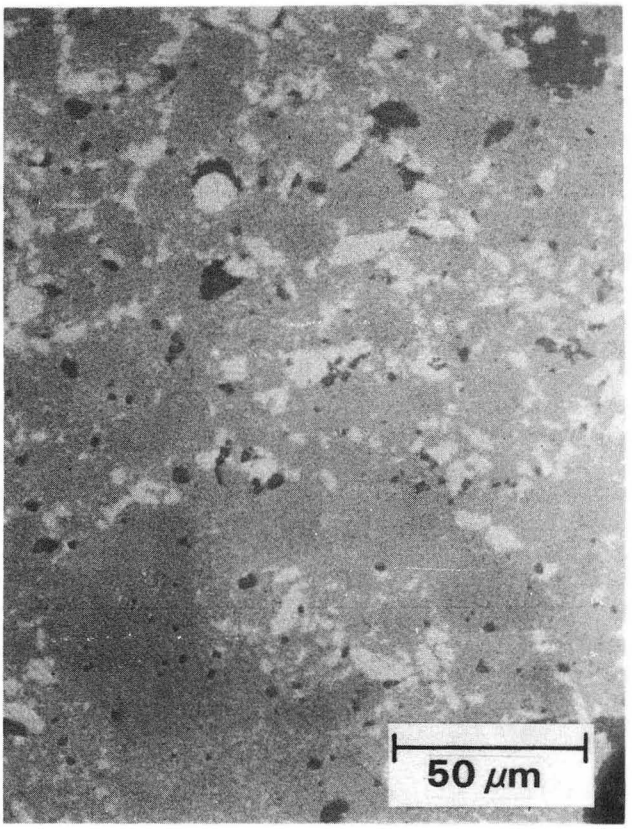

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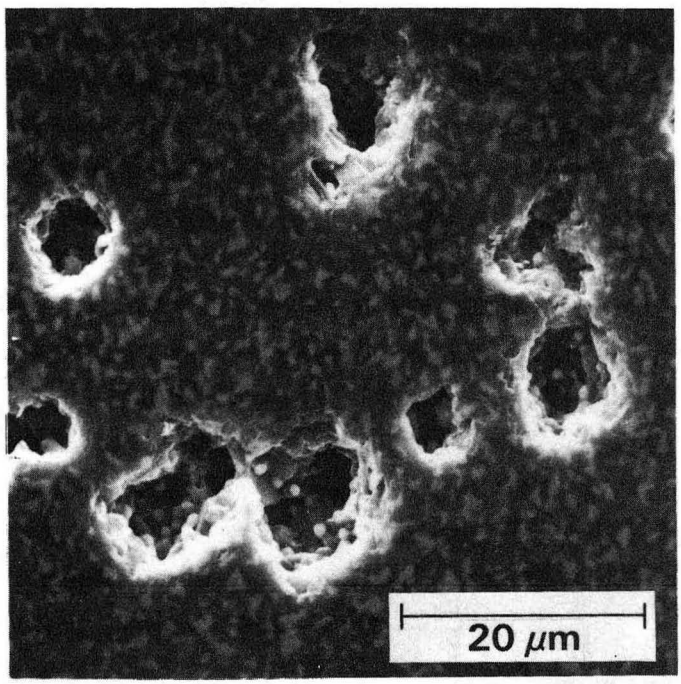
Figure 2



XBB 8612-10407

Figure 3

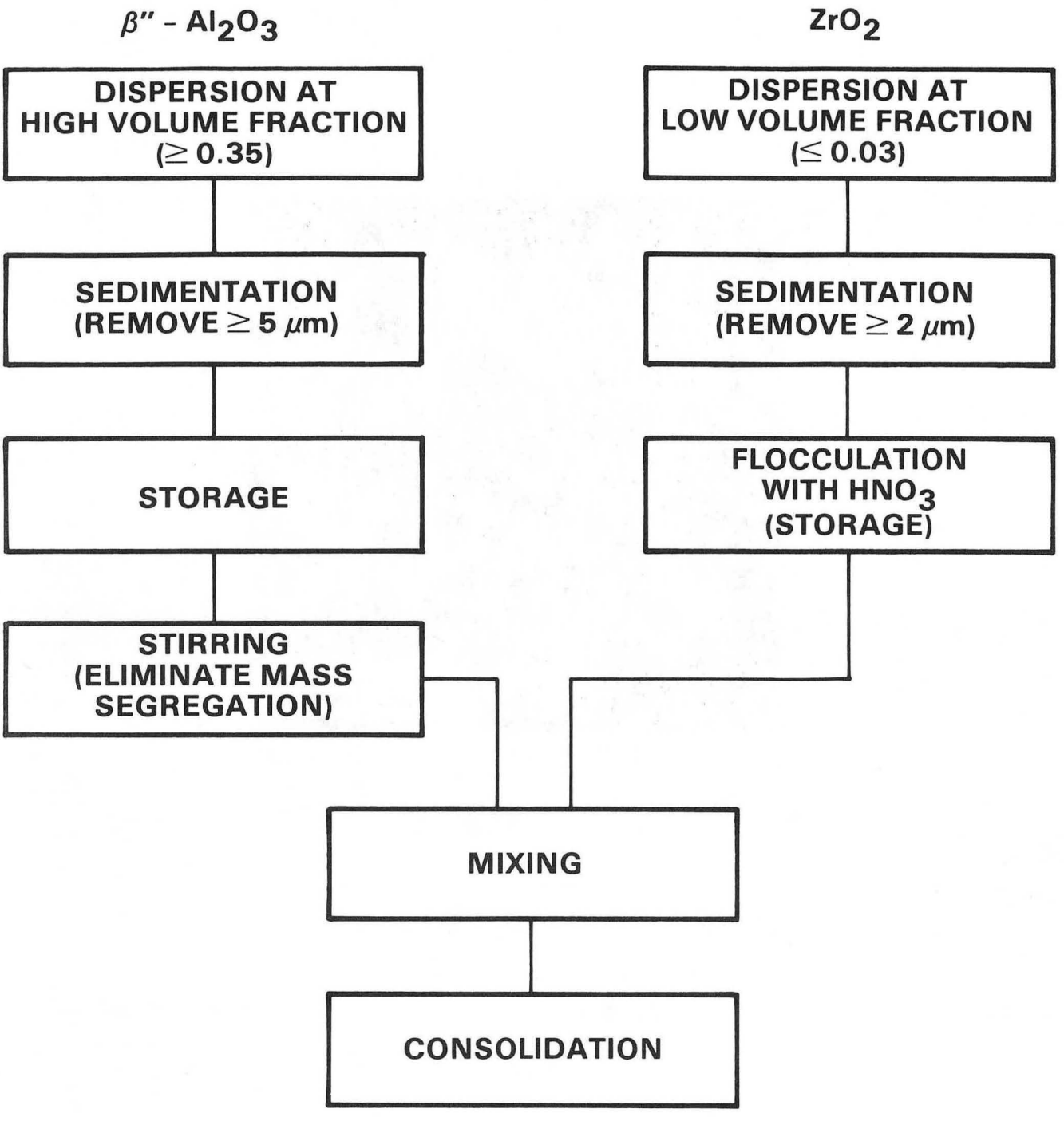

β'' - Al_2O_3
ZrO_2
DISPERSION AT HIGH VOLUME FRACTION (≥ 0.35)
DISPERSION AT LOW VOLUME FRACTION (≤ 0.03)
SEDIMENTATION (REMOVE $\geq 5\ \mu m$)
SEDIMENTATION (REMOVE $\geq 2\ \mu m$)
STORAGE
FLOCCULATION WITH HNO_3 (STORAGE)
STIRRING (ELIMINATE MASS SEGREGATION)
MIXING
CONSOLIDATION

Figure 4

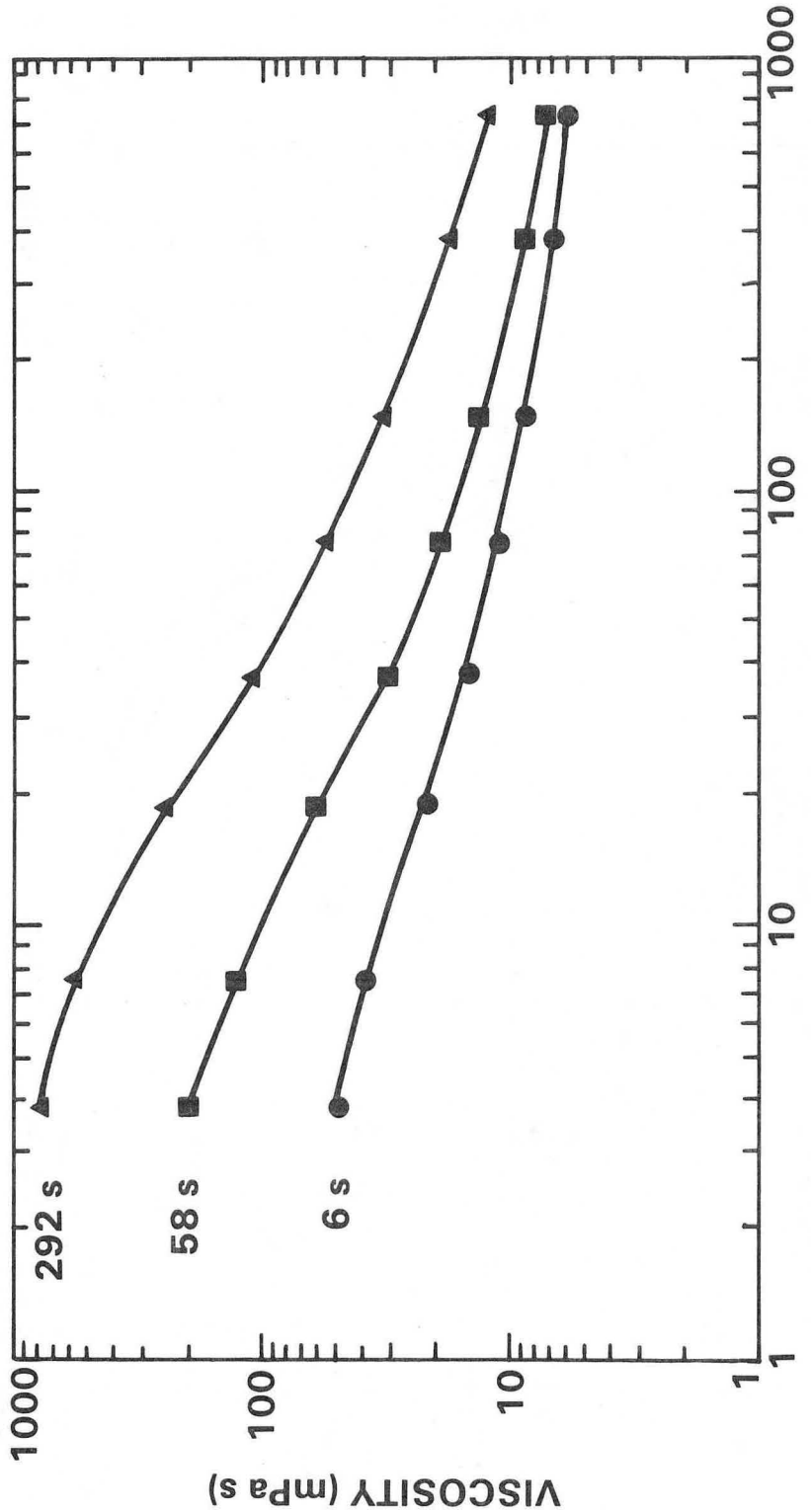

VISCOSITY (mPa s)
1000
100
10
1
1
10
100
1000
SHEAR RATE (s^{-1})
292 s
58 s
6 s

Figure 5

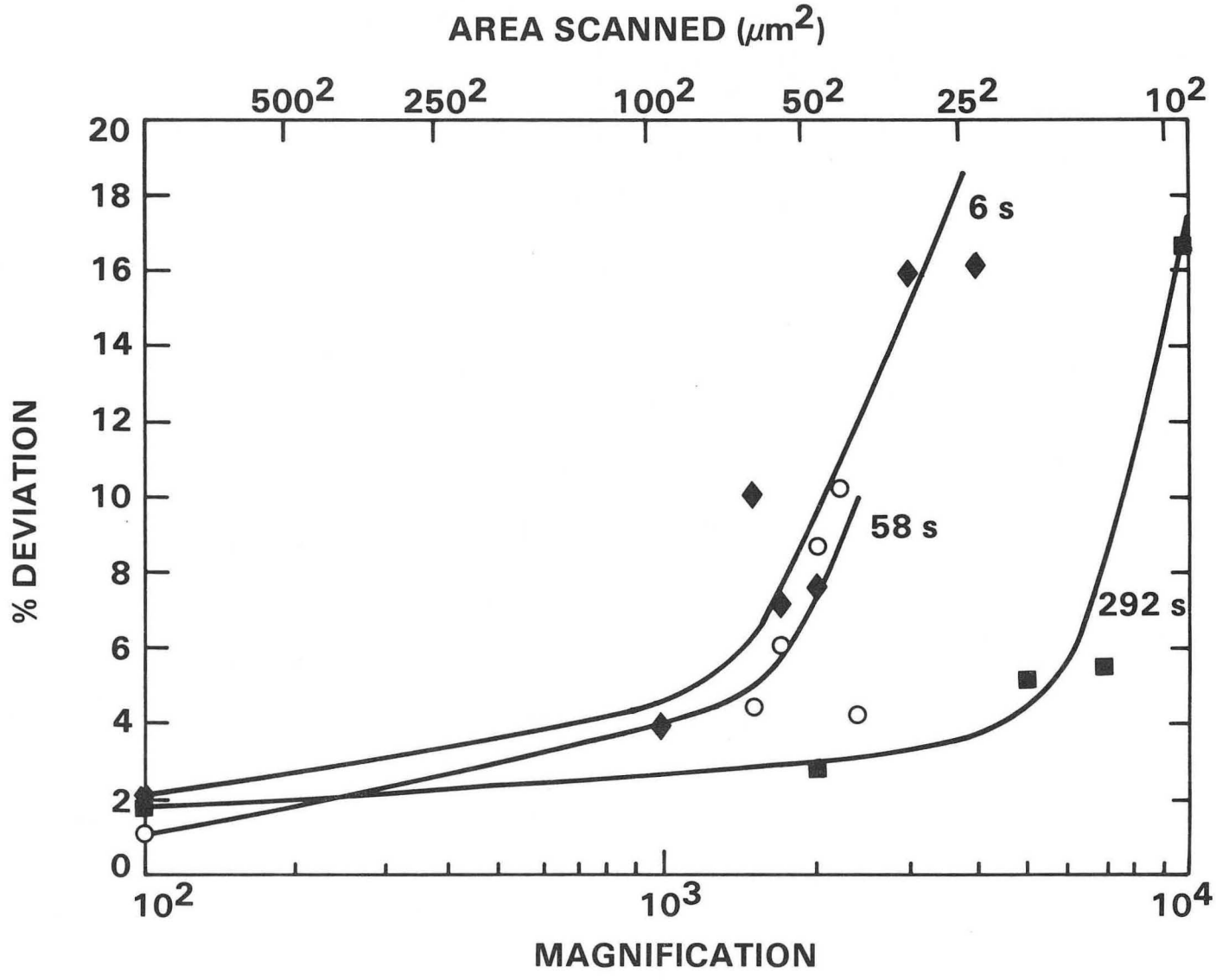

AREA SCANNED (μm^2)
500^2
250^2
100^2
50^2
25^2
10^2
20
18
16
14
12
10
8
6
4
2
0
% DEVIATION
6 s
58 s
292 s
10^2
10^3
10^4
MAGNIFICATION

Figure 6

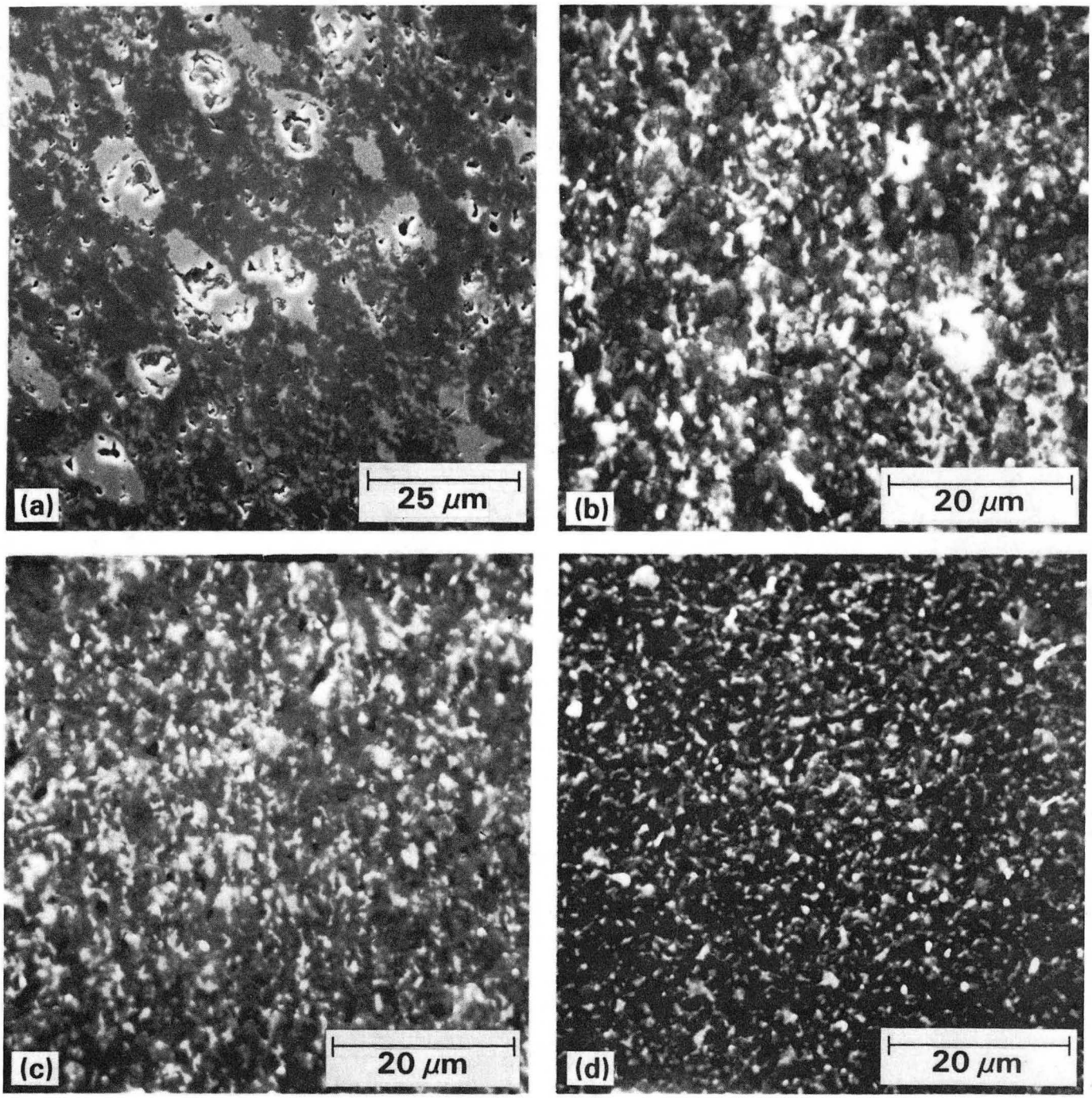


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Figure 7

Section 2

PRESSURE FILTRATION: CONSOLIDATION KINETICS AND MECHANICS

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ABSTRACT

Pressure filtration kinetics and mechanics were examined for flocced and dispersed Al_2O_3 slurries over the applied pressure range of 0.04 to 80 MPa. Two-phase β''-Al_2O_3/ZrO_2 flocced slurries were also studied. The packing density, and thus permeability, of bodies consolidated from flocced slurries was very pressure-sensitive (solid fractions from 0.42 to 0.63), while that of the dispersed slurry was pressure-insensitive (0.70 ± 0.02). The Kozeny-Carman relation appeared to be valid over the total range of observed packing density, suggesting that the distribution of pore channels was not affected by packing density. Apparent permeabilities decreased with increasing polymer addition; a large fraction (25 to 40%) of the polymer added to the slurry was retained in the consolidated body. Measurable shrinkage strains (> 1%) were not observed for bodies consolidated at pressures greater than approximately 1 MPa, suggesting that the capillary pressures that produce drying shrinkage are of this order. The recovery of strain (up to 3%) stored in the body during consolidation was time-dependent, suggesting that fluid flow accompanied strain recovery. This time-dependent strain relaxation imposes macroscopic stresses on the consolidated body, which appear to be responsible for slow crack extension observed in some bodies consolidated at the higher applied stresses. Small additions (0.5 w%) of certain polymers (e.g., PVA) that appeared to increase the interparticle strength, and thus fracture toughness, were used to avoid the cracking problem. An isopressure filtration system, which eliminates problems associated with die wall friction and die release, demonstrated the ability to form complex shapes.

1.0 INTRODUCTION

Agglomerates degrade the properties of ceramics, decreasing powder sinterabilities and producing crack-like voids during densification. Colloidal powder processing can overcome these detrimental effects;[1] dispersion breaks weakly bonded agglomerates, and sedimentation eliminates grains and strongly bonded agglomerates larger than a chosen size. The resultant slurry containing desirable particles is flocced for storage, preventing mass segregation. Various slurries so prepared can be mixed at high shear-rates to produce a multiphase flocced slurry, with phase separation prevented by the floc's continuous network of touching particles. Experience has shown that single-phase, aqueous slurries of Al_2O_3, Si_3N_4, and ZrO_2, flocced by maximizing attractive (Van der Waals) interparticle forces, can be redispersed with either a high shear-rate field or an appropriate surfactant after storage periods exceeding one year.

Colloidally treated slurries should not be dried before consolidation. Drying causes the spontaneous reformation of agglomerates, which can be relatively strong due to cementatious hydroxides and salts. Consolidated shapes, therefore, must be formed from the slurries themselves.

Pressure filtration is widely used by industry to concentrate the solids in slurries. With some imagination, pressure filtration can also be conceived to consolidate complex shapes. Particles within the slurry form a consolidated layer on the filter as the fluid is forced through the system. The consolidated layer offers the greatest resistance to fluid flow; its per-

meability and thickness control the filtration kinetics. Filtration kinetics are known to obey Darcy's Law,[2] which states that the flux of fluid (J = fluid volume per unit area per unit time) through a consolidated layer of thickness h is given by

$$J = (k\Delta P)/(\mu h) \tag{1}$$

where ΔP is the pressure difference across the consolidated layer, k is the permeability of the layer, and μ is the fluid's viscosity. The permeability of the consolidated layer depends on the size and number of the percolation channels in the consolidated layer, which, in turn, depend on particle size and arrangement.

It is well recognized that particle arrangement is influenced by the applied pressure. Generally, particle packing density increases with pressure, i.e., permeability decreases with increasing pressure. Fennelly and Reed[3] studied the pressure filtration of a 50 vol% Al_2O_3 aqueous slurry in which the repulsive interparticle forces where systematically increased with additions of an ammonium polyacylate polyelectrolyte. They showed that the packing density of the consolidated layer, and thus its permeability, was strongly dependent on the polyelectrolyte concentration. Concentrations that produced the higher electrophoretic mobility (greater interparticle repulsive force) produced the highest packing density (relative density of 0.72). For these slurries, packing density was relatively insensitive to pressure. The packing density was very pressure-sensitive for slurries where the electro-

phoretic mobility was low (but still sufficiently high to produce a pourable slurry). The maximum relative density obtained for these consolidated layers was 0.64.

The purpose of the present work was to further explore the potential of consolidating ceramic slurries by pressure filtration. Preliminary work showed that, although pressure filtration appeared to be potentially useful, large cracks would sometimes slowly propagate through the specimen shortly (seconds to minutes) after the specimen was removed from the pressing die. The propensity for crack extension appeared to increase with the filtration pressure. Although crack extension was not observed after filtration at low pressures, the dried bodies were relatively weak. A systematic study was then initiated to investigate the kinetics and mechanics of pressure filtration. Emphasis was placed on flocced slurries, the more likely state for two-phase systems; for comparison, dispersed slurries were also studied. The effect of polymer additions on filtration kinetics was also investigated, since polymer additions might be used to strengthen the interparticle bonds in consolidated bodies. In addition, studies were initiated to determine the feasibility of using isostatic pressure systems to consolidate complex shapes by pressure filtration.

2.0 EXPERIMENTAL APPROACH

2.1 Slurries

Pressure filtration studies primarily used aqueous Al_2O_3 slurries. Additional studies used two-phase composite slurries of β"-Al_2O_3/ZrO_2 in isopropanol.

The Al_2O_3 slurries were prepared by directly dispersing the as-received powder* in deionized water with sufficient additions of HCl to maintain a pH of 2 during preparation. A high shear-rate field, obtained by immersing an ultrasonic horn‡ in the slurry, aided the dispersion. Previous work has shown that the maximum electrophoretic mobility, and thus the maximum interparticle repulsive forces, can be obtained at pH = 2. Up to 55 vol% of the Al_2O_3 powder could be dispersed in this manner to produce a pourable but somewhat dilatant slurry. The dispersed slurries were flocced by increasing the pH to 8.5 with appropriate additions of NH_4OH. When the initial slurry contained < 15 vol% Al_2O_3, floccing would produce a continuous network of touching particles that would consolidate under its own body forces, producing a clear supernatant. Flocced slurries containing up to approximately 20 vol% Al_2O_3 were pourable. Figure 1 illustrates the particle size distribution of the dispersed Al_2O_3 powder, indicating a mean particle size of 0.5 μm.

*A-HPS40, Sumitomo Corporation of America, New York, NY.
‡Sonic Dismembrator Model 300, Fisher Scientific Co., Pittsburgh, PA.

The flocced, isopropanol, β"-Al_2O_3/15 vol% ZrO_2 slurries were prepared by a colloidal method described elsewhere.[4] These slurries contained 10 vol% solids.

Either methylcellulose* (average molecular weight = 15,000) or fully hydrolyzed polyvinyl alcohol‡ (molecular weight = 86,000), predissolved in water, was mixed into the flocced Al_2O_3 slurries. Ethylcellulose,§ predissolved in isopropanol, was mixed into the β"-Al_2O_3/ZrO_2 slurry. The ultrasonic horn aided mixing. The weight fraction of the added polymer was based on the powder in the slurry. The effect of the polymer on the viscosity of the fluid was reported by the manufacturer of the methylcellulose and directly measured for the ethylcellulose with a cone-plate viscometer.**

2.2 Consolidation and Strain Recovery Experiments

The pressure filtration device schematically shown in Fig. 2 was used to obtain data for consolidation kinetics and, upon load removal, strain relaxation. The device consisted of a moving plunger sealed from the outer cylinder with an O-ring. The filter was a partially sintered stainless steel disc,‡‡ 0.125 in. thick, backed with a solid steel disc containing several holes. A single sheet of filter paper, which sealed the outer rim of the

*Methocel A15-LV, Dow Chemical Company, Midland, MI.
‡Aldrich Chemical Company, Inc., Milwaukee, WI.
§Ethocel Standard 10 Industrial, Dow Chemical Company, Midland, MI.
**Wells-Brookfield Cone/Plate Viscometer, Model RVTD, Brookfield Engineering Laboratories, Inc., Stoughton, MA.
‡‡FCR-25-32-2, Pacific Sintered Metals, Inc., Los Angeles, CA.

cylinder and the metal filter, was used to initiate the consolidated layer build up.

To fill the device with slurry, it was inverted and the plunger moved to create a chamber of known volume (27.2 cm^3). After filling, the wet filter paper, followed by the metal filter assembly, was placed over the slurry surface. A retaining ring was then screwed in place to secure the filter assembly. Tests showed that the filter system offered no significant resistance to fluid flow and that an insignificant force was required to move the plunger.

A predetermined load was rapidly applied to the plunger with the moving crosshead of a mechanical testing machine.* To maintain a constant load, the testing machine was used in its load cycle mode, in which the crosshead would stop upon reaching the desired load and reactivate when that load relaxed by 1%. The load cycle period increased as consolidation proceeded. The displacement between the moving plunger and the outer cylinder during consolidation was measured with a calibrated, clip-on extensometer. Both load and displacement were recorded during consolidation. The consolidation experiment was terminated when the load cycle period exceeded 1 min, corresponding to a displacement rate near zero. Pressure exerted on the slurry was calculated by dividing the applied load by the cross sectional area of the plunger. After consolidation, the specimen was either ejected, weighed, and dried, or prepared for a strain recovery experiment. Assuming that the consolidated body contained only solids and fluid, its solids volume fraction could be

* Model 1125, Instron Corporation, Canton, MA.

measured by weighing the consolidated body before and after drying. The bulk density of the dried body was determined by dimension and weight measurements.

Assuming that the volume displaced by the moving plunger is equal to the volume of fluid forced through the filter, Darcy's Law (Eq. (1)) can be integrated to obtain

$$d = [2k/\mu(v_1/v_0 - 1)Pt]^{1/2} \qquad (2)$$

where

d = plunger displacement

t = filtration time

P = pressure applied to slurry

k = permeability of consolidated layer

μ = viscosity of fluid

v_1 = volume fraction of solids in consolidated layer

v_0 = volume fraction of solids in slurry.

Equation (2) shows that pressure filtration should exhibit parabolic rate kinetics. A plot of d vs $t^{1/2}$ should result in a straight line with a slope equal to $[2\ k/\mu\ (v_1/v_0 - 1)\ P]^{1/2}$. The consolidated layer permeability can be obtained by measuring v_1 after the test termination if the controllable experimental parameters are known.

Strain recovery specimens were prepared by consolidating a slurry at a low applied load, as described above. The filter assembly was then removed and replaced with a solid steel disc to increase the stiffness of the system. A ring of filter paper was placed between the solid disc and outer cylinder rim to ensure that fluid could flow during subsequent reloading and unloading. The clip-on extensometer used during consolidation was replaced with one of lower total displacement, but of greater accuracy (±2 μm). The consolidated specimen was then reloaded as described above. When the load cycle period exceeded 1 min, the load was quickly removed by rapidly raising the cross-head. Plunger displacement was continuously recorded during and subsequent to unloading. After a sufficient relaxation period, a higher load was reapplied and relaxation displacement was again measured. Load-deflection data were also obtained for the loading system without a consolidated body, since these data were needed to calculate the relaxation displacement associated with the consolidated body. The thickness of the consolidated body was measured after the experiment was terminated, and the thickness prior to each unloading cycle was determined by subtracting subsequent unloading displacements. In this manner, relaxation strain was determined by dividing the displacement by the thickness of the consolidated layer prior to load removal.

3.0 RESULTS

Most of the kinetic data for the Al_2O_3 slurries was obtained for slurries containing 0.20 volume fraction solids. Complete kinetic experiments were not carried out on dispersed slurries at pressures < 1 MPa due to their extremely long consolidation periods. Kinetic data were also limited to pressures < 10 MPa; the immediate application of higher pressures would cause the filter paper seal to rupture. This problem could be circumvented by first applying a low pressure to produce a substantial consolidated layer and then completing the consolidation at the higher, desired pressure. Strain relaxation experiments were carried out on flocced slurries containing 0.10 volume fraction solids and dispersed slurries containing 0.35 volume fraction solids.

The rheological behavior of the consolidated bodies was markedly different. Flocced slurries filtered at pressures exceeding approximately 1 MPa appeared similar to dry pressed bodies despite fluid volume fractions between 0.36 and 0.46. These bodies retained their pressed shape. Bodies consolidated from dispersed slurries were dilatant and would flow slightly after they were ejected from the pressing die.

For the set of experiments reported below, slow crack extension after die ejection was only observed for the β''-Al_2O_3/ZrO_2 consolidated bodies. For these bodies, the addition of the 2 w% polymer did not prevent spontaneous cracking. Crack extension was also observed for Al_2O_3 bodies consolidated with the isopressing device described in the Appendix. Additions of 0.5 w% polyvinyl alcohol (PVA) prior to consolidation prevented this crack extension.

PVA additions to the starting slurry appeared to make the consolidated bodies much stronger. After drying, consolidated bodies containing as little as 0.5 w% PVA were strong enough to be dropped without breaking. Similar additions of PVA to Si_3N_4 and ZrO_2 slurries also prevent the slow crack extension prevalent in these materials. Additions of methylcellulose to the Al_2O_3 slurries did not produce any apparent strengthening.

3.1 Permeability

For the flocced slurries, plots of d vs $t^{1/2}$ were slightly nonlinear. The linearity of these plots increased with applied pressure. As discussed below, the strong dependence of packing density, and thus permeability, on the applied pressure suggests that a density gradient exists within the layer during consolidation and that this gradient diminishes with consolidation time. This behavior would produce an apparent permeability which would increase with time, and thus the observed nonlinear d vs $t^{1/2}$ behavior.

Figure 3 shows that the consolidated layer permeability, k, is strongly pressure-dependent for the flocced slurries and pressure-insensitive for the dispersed slurries. Figure 4 shows log k plotted against volume fraction of solids (v_1) in the wet consolidated body. These data suggest that k and v_1 are related by

$$k = e^{-(mv_1+A)} \tag{3}$$

where m = 11 and A = 31.

Polymer additions to the flocced slurries dramatically increased the filtration period without changing the packing density (v_1) of the consolidated body. Figure 5 illustrates the apparent permeability as a function of added polymer for the Al_2O_3 and β''-Al_2O_3/ZrO_2 slurries. The lower curve in each plot assumes that the polymer has not affected the fluid viscosity and is used to illustrate the extended filtration time. Weight loss measurements after sintering suggest that between 25 to 40% of the polymer added to the slurry is retained in the body after consolidation. The upper curve shown in Fig. 5a was determined assuming that, while particle packing was unchanged by the polymer, the viscosity of the water within the consolidated layer was increased by an amount corresponding to 25% retention of the total polymer added to the initial slurry. Similarly, the upper curve in Fig. 5b was determined assuming the viscosity of the isopropanol increased due to 35% polymer retention. These results suggest that the polymer collected in the consolidated layer (either trapped or absorbed on the particle surfaces) effectively increases the viscosity of the filtrate.

3.2 Packing Density

Figure 6 illustrates that a linear relation is obtained when the volume fraction of solids (v_1) in bodies consolidated from the flocced Al_2O_3 slurries is plotted as a function of the log of the applied pressure. The few data obtained for the dispersed slurries show that v_1 is relatively insensitive to the applied pressure, varing from 0.68 at low pressures to 0.70 at 80 MPa, suggesting that $v_1 = 0.70 \pm 0.02$ is the maximum packing density for the as-received Al_2O_3 powder.

Upon drying, the only bodies that exhibited measurable shrinkage ($\geq$ 1%) were those consolidated from the flocced slurry at pressures below approximately 1 MPa. All of these bodies increased their relative densities to 0.54 $\pm$ 0.01 during drying. This information, correlated with the data presented in Fig. 6, suggests that the capillary pressure responsible for further consolidation during drying is equivalent to an applied pressure between 0.5 MPa to 1 MPa.

3.3 Strain Relaxation

As the last portion of slurry consolidates, the pressure gradient within the fluid decreases to zero and the applied pressure is completely transferred to the consolidated particle network. The strain energy stored in the network will be released when the applied pressure is removed. This release of stored strain energy is manifested by an increase in specimen dimensions. Preliminary experiments showed that, as expected, this release of strain energy was time-dependent. The dimensional changes that accompany the release of the stored strain energy are expected to require fluid flow through the saturated body, which is restricted by the permeability of the particle network. The object of the current work was to characterize the time-dependent strain energy recovery phenomenon for bodies consolidated from the Al_2O_3 slurries. Cavitation would reduce this time-dependent strain energy release phenomena.

The time-independent compliance of the loading system contributed approximately 50% of the total strain recovered upon unloading. Since the

largest recovery displacement associated with the consolidated specimen did not exceed 150 μm, and since the accuracy of the extensometer was ±2 μm, the behavior calculated at the lower applied stresses was somewhat erratic; at lower stresses, some specimens appeared to exhibit a compressive displacement during unloading. Experiments repeated upon the same specimen did record the same displacements, within the accuracy of the extensometer.

Figure 7 illustrates the time-dependent strain recovery upon rapid unloading (~ 3 s) from 80 MPa for bodies consolidated from both flocced and dispersed slurries. As shown, a larger percentage (85%) of the strain was quickly recovered (< 20 s) for the dispersed body. For the dispersed body, the fraction of quickly recovered strain increased linearly with stress, while for the flocced body it was nearly constant (between 50 to 60%). Although > 90% of the strain was recovered within a 15 min period, total recovery required hours for the flocced bodies and much shorter periods (< 20 min) for the dispersed bodies.

Figure 8 illustrates the strain recovered after 15 min as a function of the applied stress. As shown, the recovery strain can be substantial (2 to 3%). The nonlinear stress-strain behavior is indicative of the Hertzian stress-strain behavior of powders, in which the elastic deformation at contact positions is nonlinearly related to stress.[5]

4.0 DISCUSSION

As expected, touching particle networks formed by attractive interparticle forces are more difficult to rearrange during consolidation than strongly repulsing particles, which quickly pack to their optimum density under relatively low consolidation pressures.

From Darcy's Law, the units for permeability are (meters)^2, suggesting that permeability is related to the square of the mean particle diameter, D, of the powder in the consolidated layer. Assuming that the fluid flow through the consolidated layer can be modeled as a bundle of capillary tubes using Poiseuille's Law modified in terms of a hydraulic diameter and assumed tortuosity of flow, the permeability can be expressed as the Kozeny-Carman Equation (see Ref. 2 for a recent review):

$$k = D^2(1 - v_1)^3/(36\ h\ v_1^2) \tag{4}$$

where h is the Kozeny constant which defines the shape factor and tortuosity of the flow channel. It has been found that h = 5 for many different powder systems. The major assumption in the Kozeny-Carman relation is that the distribution of flow channels is unaffected by changes in v_1 (the area associated with these channels is expected to decrease with increasing v_1).

Using the empirical relation between k and v_1 expressed in Eq. (3), and h = 5, the particle size, D, was calculated using the Kozeny-Carman relation (Eq. 4). The resulting particle size obtained from this calculation was 0.222 μm ±3% over the range $0.4 \leq v_1 \leq 0.7$. The invariance of the calulated particle size over the large range of packing density strongly suggests that the same channels support fluid flow over the whole range of packing density. The reason why the calculated particle size is approximately 1/2 the mean particle size determined from particle size distribution measurements (Fig. 1) is currently unknown.

It is generally assumed that during consolidation a sharp demarcation exists between the slurry and the consolidated layer. The pressure gradient associated with the consolidated layer fluid means that the opposite gradient must exist in the consolidated particle network (neglecting die wall friction). A sharp demarcation should exist for the dispersed slurry since its packing density is independent of applied pressure. The pressure dependence of particle packing for flocced slurries (Fig. 6) means that a density gradient should exist within the layer during consolidation, indicating a diffuse interface between the slurry and consolidated layer. The increasing linearity of the d vs $t^{1/2}$ curves (see Section 3.1) with increasing pressure suggests that the density gradient within the consolidated layer decreases with increasing pressure. It should also be noted that die wall friction can produce density gradients in bodies consolidated from flocced slurries, as it does in dry powders.

The time-dependent strain relaxation observed for bodies consolidated from both flocced and dispersed slurries was not unexpected. Upon unloading, the compressed particle network expands and places the fluid within the saturated body in a state of negative pressure. This causes fluid (or air) to reenter the body from the surface. At the surface, the fluid pressure is equal to the ambient pressure, while the negative fluid pressure within the body is initially proportional to the applied consolidation pressure. Because the pressure gradient in the fluid (e.g., surface to center) is a function of relaxation time, the observed strain recovery data (Fig. 7) cannot be analyzed without solving the differential form of Darcy's Law (Eq. 1).

If air enters the body instead of fluid, one would expect that the curved menisci between particles (drying front) would move into the body with an irregular morphology, as observed by Shaw for the case of conventional drying. Shaw has described this irregular and abrupt motion as invasion percolation. The velocity of the drying front would be expected to depend on the negative pressure in the fluid, which is initially proportional to the applied consolidation pressure and decays with time. This explains why the surfaces of the bodies consolidated from flocced slurries appeared dry shortly after being ejected from the consolidation die.

The pressure gradient within the consolidated body will also depend on how fluid (or gas) can reenter the body; different pressure gradients will arise for the cases of fluid reentering from all sides (free standing body completely immersed in the filtrate), from one side (strain relaxation with the filter in place), or from the perimeter (suspected for the present strain

relaxation experiments). With any case, one region of the consolidated body will relax first. This implies that the body will be subjected to macroscopic stress gradients upon unloading and during relaxation. The gradient's magnitude will depend on the size and shape of the region that relaxes first. The magnitude of the largest stress will be proportional to the applied consolidation pressure.

If fluid (or air) reenters the surface at one location first, the volume element beneath this surface area will attempt to expand. Because the volume element is constrained from expanding by the surrounding body, the element will be placed in compression, and the body will be placed in tension, promoting crack extension radial to the compressed element. This problem is directly analogous to the inclusion problem, where a similar stress distribution arises when an inclusion has a lower thermal expansion and contracts less during cooling than its surrounding matrix.

Similar highly localized stresses that will promote radial crack extension will arise when an air bubble (or dissolved gases that produce cavitation upon unloading) is trapped in the slurry. During consolidation, such a bubble will collapse and be broken into much smaller voids, localized in a lenticular region. Upon unloading, the small pressurized voids will expand as an internal drying front and release stored strain energy. The 'inclusion' defined by the internal drying front will be constrained from expanding by the surrounding body and thus be placed in compression. Tensile stresses are concurrently induced in the body surrounding the 'inclusion,' which can promote the extension of a radial crack (for example, the extension of one of the drained, irregular regions associated with the drying front).

In all cases, crack extension will be time-dependent due to the need for fluid flow defined by Darcy's Law. As in the inclusion problem, the growing cracks arrest when sufficient strain energy has been released. The probability for crack extension after unloading will increase with the amount of released strain, and thus with the applied consolidation pressure. These expectations are consistent with the observed phenomena.

The resistance to crack extension, or fracture toughness, of the consolidated body will depend on the strength of the interparticle bonds. Absorbed polymers that strengthen the interparticle bonds, for example, glues like PVA, might be expected to increase fracture toughness sufficiently to prevent crack extension.

By rearranging Eq. (2), the time required to consolidate a body that will have a thickness h after it is fully densified by sintering is:

$$t = C\, h^2 \tag{5}$$

where

$$C = (\mu/[2kP])(v_\ell/v_0 - 1)v_\ell^{-2/3} \quad .$$

The coefficent C may be calculated using permeability values given by Eq. (2), $\mu = 1 \times 10^{-3}$ Pa s (viscosity of water), and appropriate values of the solid fractions of Al_2O_3 in the slurry (v_0) and consolidated layer (v_ℓ). Assuming pourable slurries ($v_0 = 0.15$ for the flocced state and $v_0 = 0.50$ for the dis-

persed state) and a reasonable applied pressure of 70 MPa (10 kpsi) (resulting in v_ℓ = 0.6 for the flocced slurries, and v_ℓ = 0.7 for the dispersed slurries), the coefficients are 1 min/cm^2 for flocced and 0.4 min/cm^2 for dispersed slurries. Conventional slip casting periods (P = 0.14 MPa, or 20 psi) would be 500 times greater.

Pressure filtration appears to offer many other advantages. For example, after consolidation much of the filtrate can be removed with a high pressure gas before the body is removed from the molding die. This process is commonly known as 'dewatering'. Also, as suggested in the Appendix, the process could be adapted to an isopressure apparatus, with potentially great advantages over dry powder isopressing for production of complex shapes. The major problems associated with pressure filtration appear to the related to the dilatent nature of bodies consolidated from dispersed slurries and the time-dependent cracking phenomena observed in some bodies consolidated from flocced slurries. The latter problem could be avoided with small additions of certain polymers that appear to increase the strength of the interparticle bonds in the consolidated body. Both problems might disappear if the consolidated body was 'dewatered' prior to die ejection. With further knowledge of pressure filtration as applied to ceramic forming and the imaginative adaptation of pressure systems, pressure filtration might displace many of the currently used forming methods.

5.0 APPENDIX

ISOPRESSURE FILTRATION

The major disadvantage of die pressing is the constraint of the molding die itself. First, die wall friction during consolidation leads to pressure gradients, and therefore density gradients, within the consolidated powder compact. Second, when the pressure is released, the large release of stored strain energy in the consolidated body is constrained by the relatively stiff die, leading to disruptive stresses. Both of these effects are eliminated when the body is consolidated within a highly compliant polymer mold under isostatic pressure. The consolidation pressure is applied normal to the polymer mold, minimizing the need to shear powder along the mold wall and thus eliminating mold wall friction. Additionally, upon stress release the polymer mold expands and separates from the consolidated body.

Figure A1(a) illustrates one of the configurations tested to examine the feasibility of isopressure filtration. Once filled with a slurry and sealed, the whole device was immersed in an isopressure vessel.* A very compliant thermoplastic was used to fabricate the mold, which contained the shape to be formed (lower portion of mold) and a chamber to contain excess slurry (upper portion). The excess slurry chamber would distort as slurry was drained from the system into filtrate chamber, but the lower portion of the

*Autoclave Engineering

mold would retain its shape (subject to the constraint of the metal filtrate chamber) producing the desired consolidated shape.

Neglecting the volume occupied by the filter and filtrate chamber, the pressure exerted on the consolidated layer, slurry, and thermoplastic mold will be identical to that of the pressurized fluid surrounding the device. As the consolidated layer forms, it supports the applied pressure. Although the net pressure exerted on the consolidated layer is identical to the external fluid pressure, the fluid within the consolidated layer will be subject to a pressure differential that produces filtration, since the pressure applied by the isopressure system is greater than the atmospheric pressure within the filtrate chamber. Thus, unlike dry powder isopressing, the consolidated layer is formed without a pressure differential between the isopressure fluid and the material within the mold.

Under isostatic pressures, the compliant mold material will change its dimensions without changing shape; the dimensional change will depend on the material's compressibility. Neglecting the dimensional changes due to the constraint from the metal filtrate chamber, the volume and shape of the consolidated body at the end of filtration will be identical to the compressed mold. Shape changes, however, are expected where the highly compliant mold is attached to the stiffer metal filtrate chamber. Figure A1(b) shows a schematic of the shape change expected and observed after isopressure filtration.

Upon removal of the pressure, all bodies within the isopressure system will relax back to their original dimensions. If the compressibility of

the mold material is greater than the particle network forming the consolidated body, it will separate from the consolidated body during pressure release. If an object stiffer than the consolidated body is placed within the mold, then the consolidated body will also separate from it during pressure release. In this manner, no resistance is offered in removing the consolidated body. This is illustrated in Fig. A1(b), in which a tube is formed around a metal plug.

Isopressure filtration experiments carried out at 80 MPa in a conventional isopress using a flocced Al_2O_3 slurry (v_0 = 0.20) with and without additions of PVA (1 wt%) demonstrated the feasibility of the method to make thick-walled tubes (shown in Fig. A1(b)). Additions of PVA increased the consolidation period as expected (see Fig. 5a) but were needed to prevent cracking of the consolidated body after removal from the mold. Small details inadvertently incorporated into the mold surface (parting lines, scratches, etc.) were replicated in the surface of the consolidated body, demonstrating the ability of this technique to produce fine detail in ceramic bodies.

6.0 ACKNOWLEDGMENT

Work concerning the β''-Al_2O_3/ZrO_2 composite, the effect of polymer additions to all slurries, and the demonstration of the isopressure filtration system were supported by the Lawrence Berkeley Laboratory Advanced Battery Program under contract No. 4530910. The other work was supported by the IR&D Program at the Rockwell International Science Center.

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8.0 FIGURE CAPTIONS

Fig. 1 Particle size distribution for the as-received Al_2O_3 powder.

Fig. 2 Schematic diagram of the pressure filtration device.

Fig. 3 Consolidated body permeability as a function of applied pressure for flocced and dispersed slurries.

Fig. 4 The log of permeability as a function of volume fraction solids for bodies consolidated from Al_2O_3 slurries.

Fig. 5 The effect of polymer additions on the apparent permeability of consolidated bodies. (a) Al_2O_3, (b) β''-Al_2O_3/ZrO_2.

Fig. 6 The pressure dependence of the solids concentration of bodies consolidated from 20 vol% Al_2O_3 slurries.

Fig. 7 The time-dependent strain recovery for bodies consolidated from flocced and dispersed slurries upon unloading of 80 MPa pressure.

Fig. 8 Total strain recovered after 15 minutes relaxation time plotted as a function of applied pressure for bodies consolidated from flocced and dispersed slurries.

Fig. A1 (a) Schematic diagram of the isopressure filtration apparatus.
(b) Schematic shape change of a thick-walled tube formed by isopressure filtration.

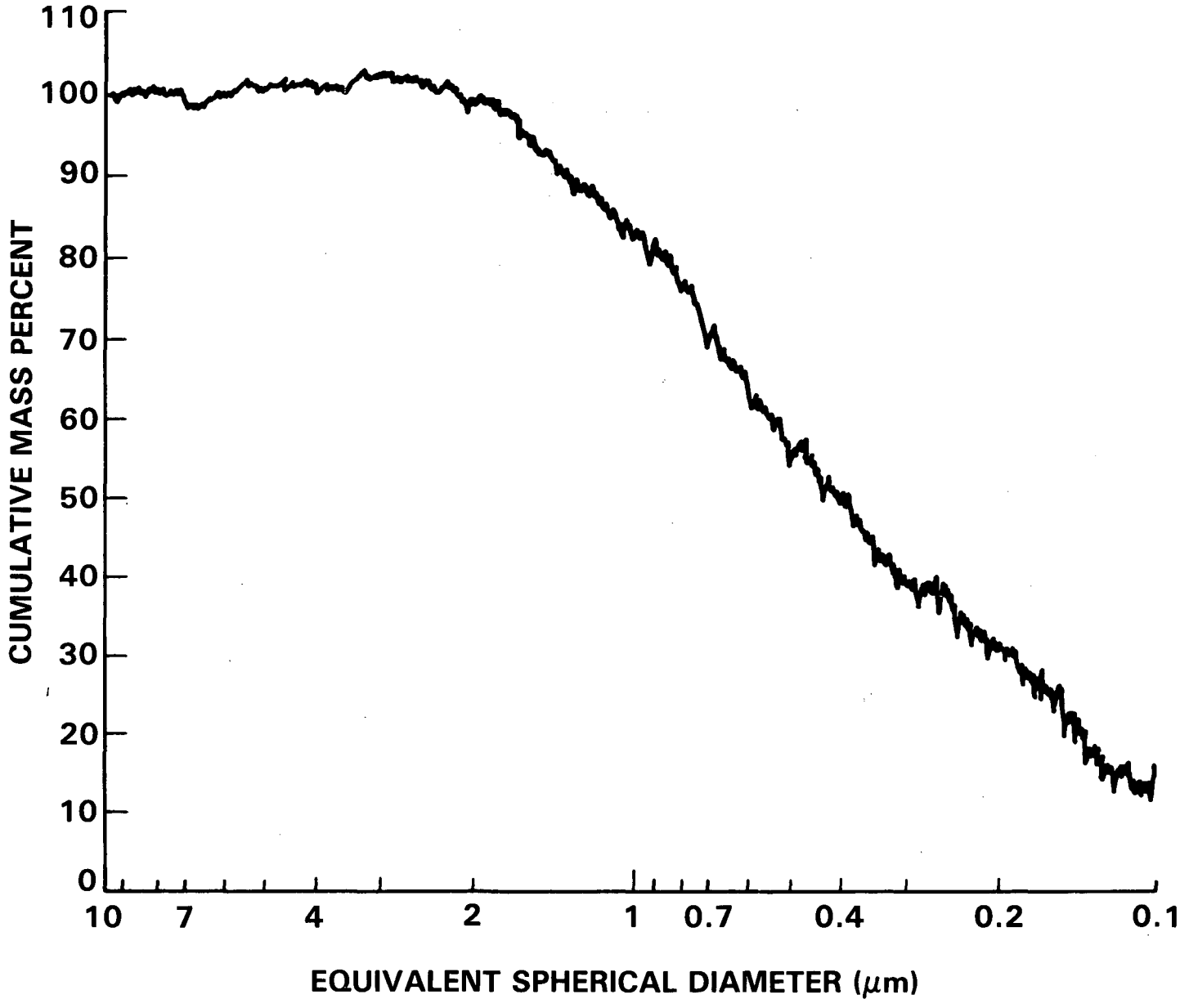

110
100
90
80
70
60
50
40
30
20
10
0
CUMULATIVE MASS PERCENT
10
7
4
2
1
0.7
0.4
0.2
0.1
EQUIVALENT SPHERICAL DIAMETER (μm)

Figure 1

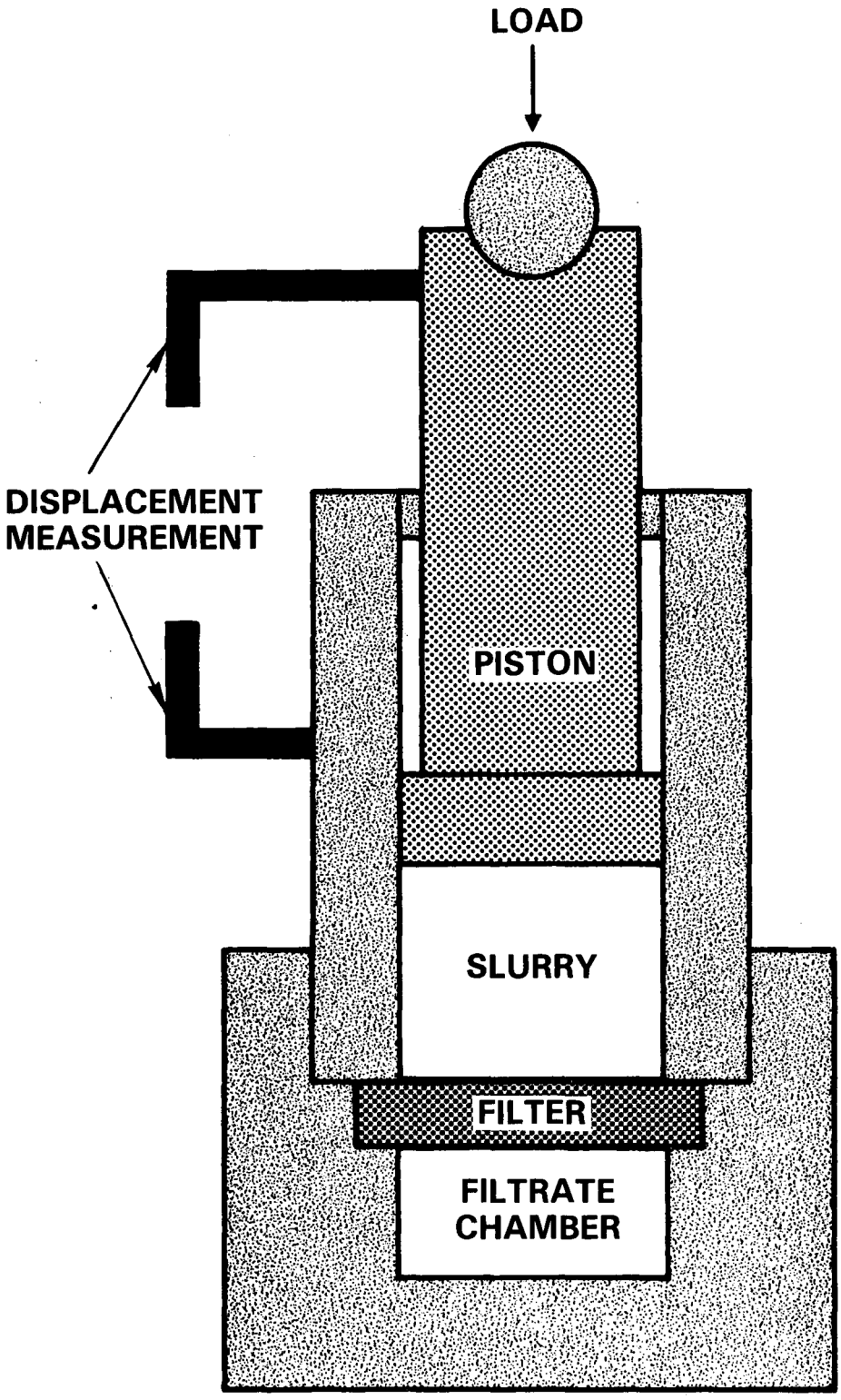

LOAD
DISPLACEMENT
MEASUREMENT
PISTON
SLURRY
FILTER
FILTRATE
CHAMBER

Figure 2

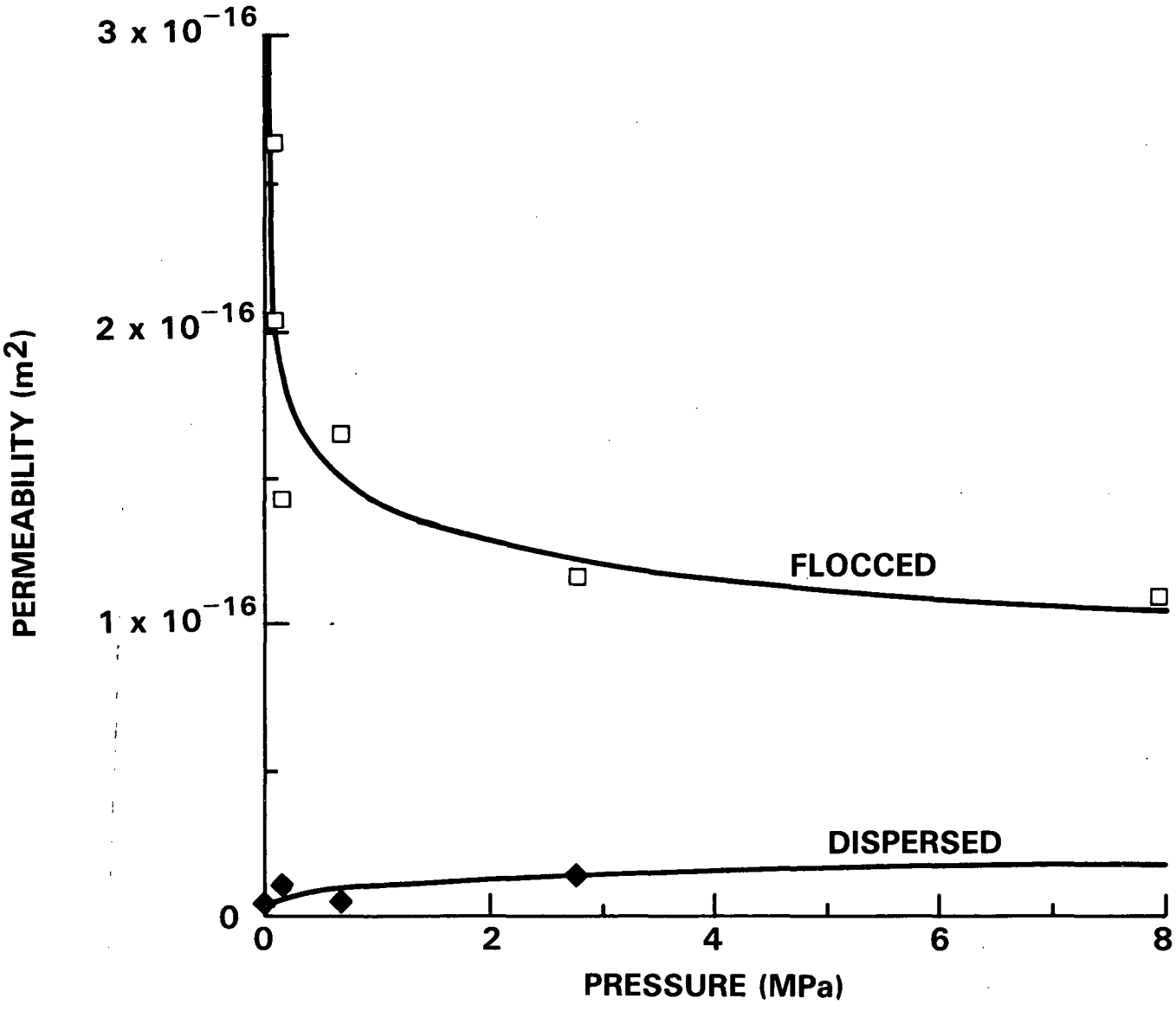
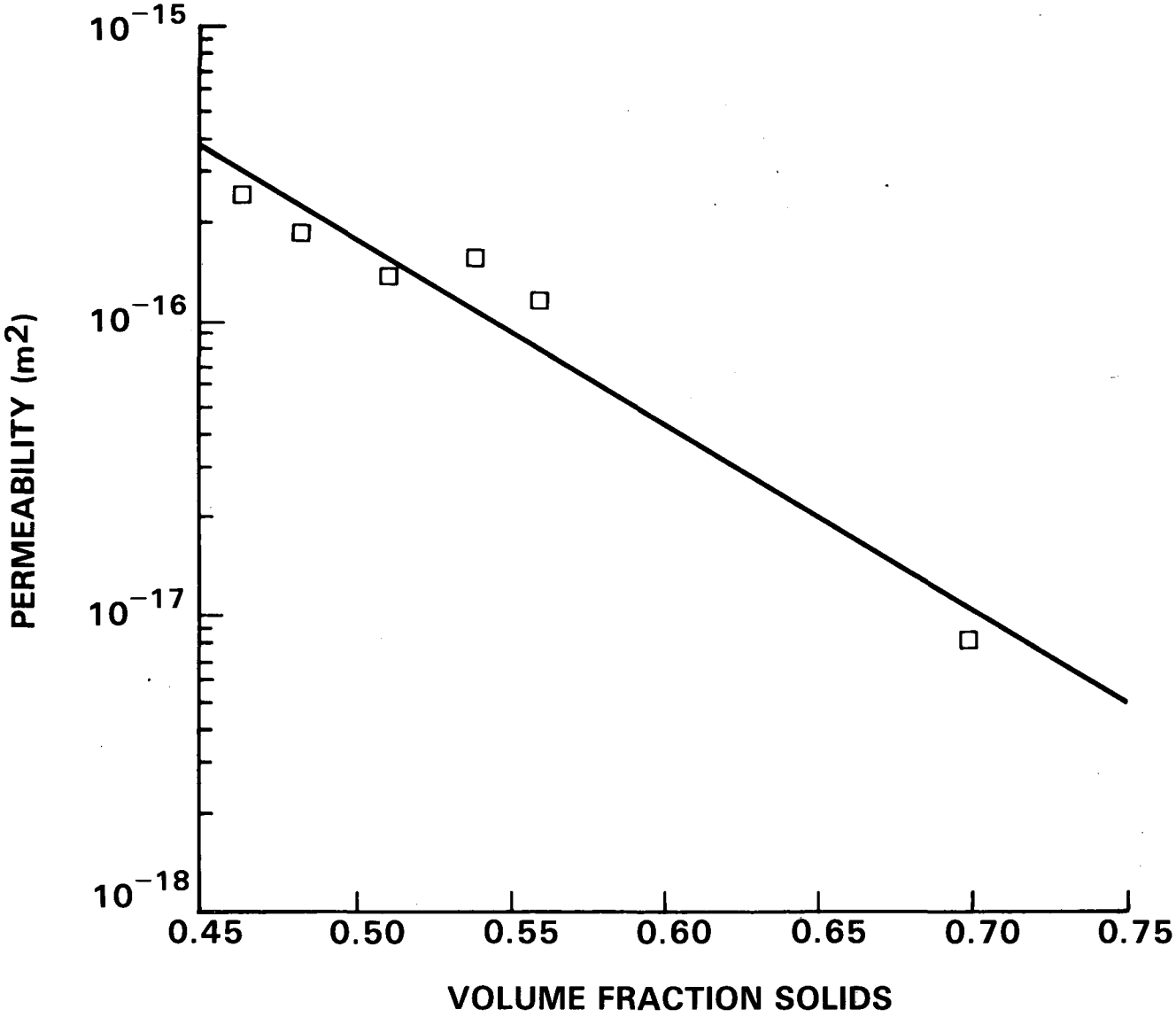

3 x 10⁻¹⁶
2 x 10⁻¹⁶
1 x 10⁻¹⁶
0
PERMEABILITY (m2)
FLOCCED
DISPERSED
0
2
4
6
8
PRESSURE (MPa)

Figure 3


10^{-15}
10^{-16}
10^{-17}
10^{-18}
PERMEABILITY (m^2)
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0.50
0.55
0.60
0.65
0.70
0.75
VOLUME FRACTION SOLIDS

Figure 4

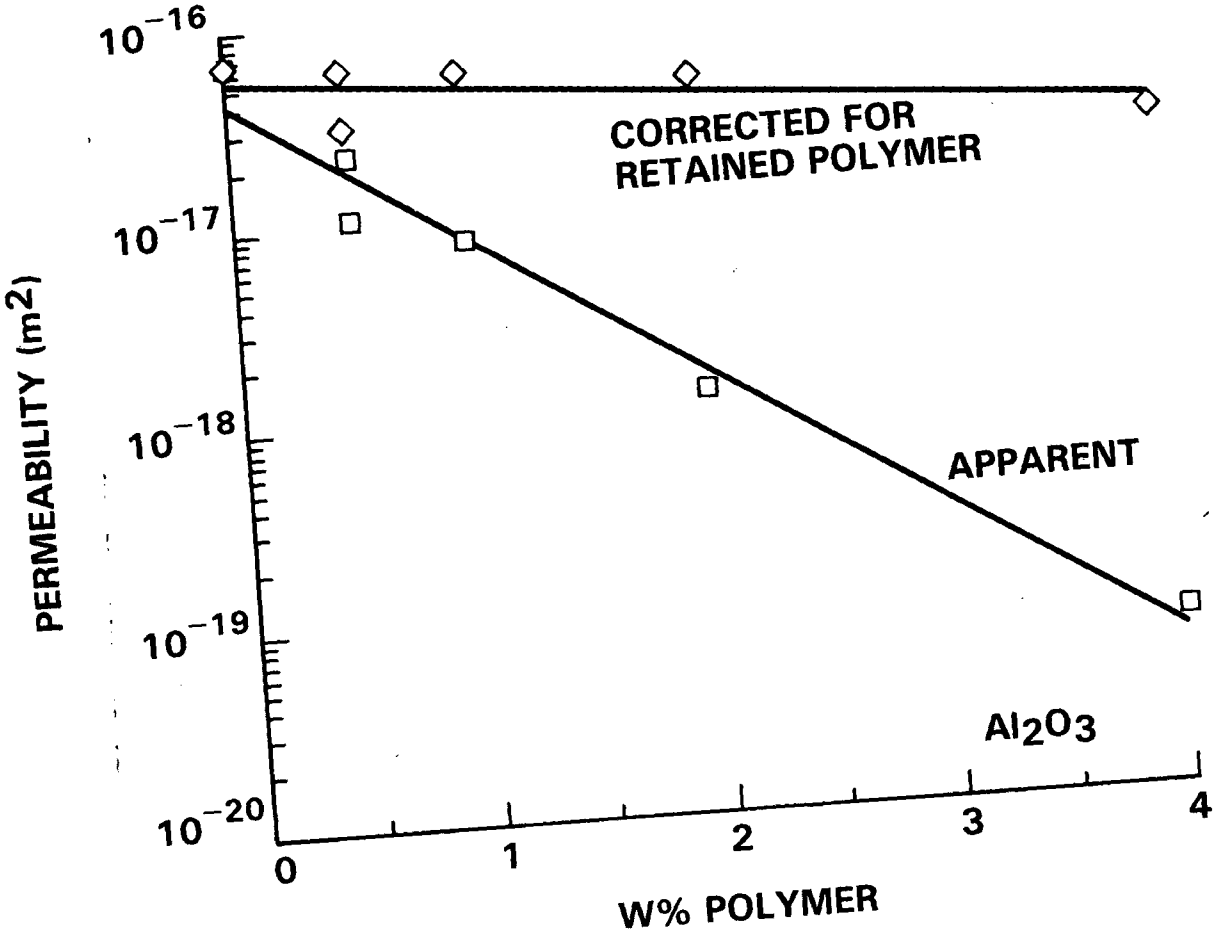

10^{-16}
10^{-17}
10^{-18}
10^{-19}
10^{-20}
PERMEABILITY (m^2)
CORRECTED FOR
RETAINED POLYMER
APPARENT
Al_2O_3
0
1
2
3
4
W% POLYMER

Figure 5a

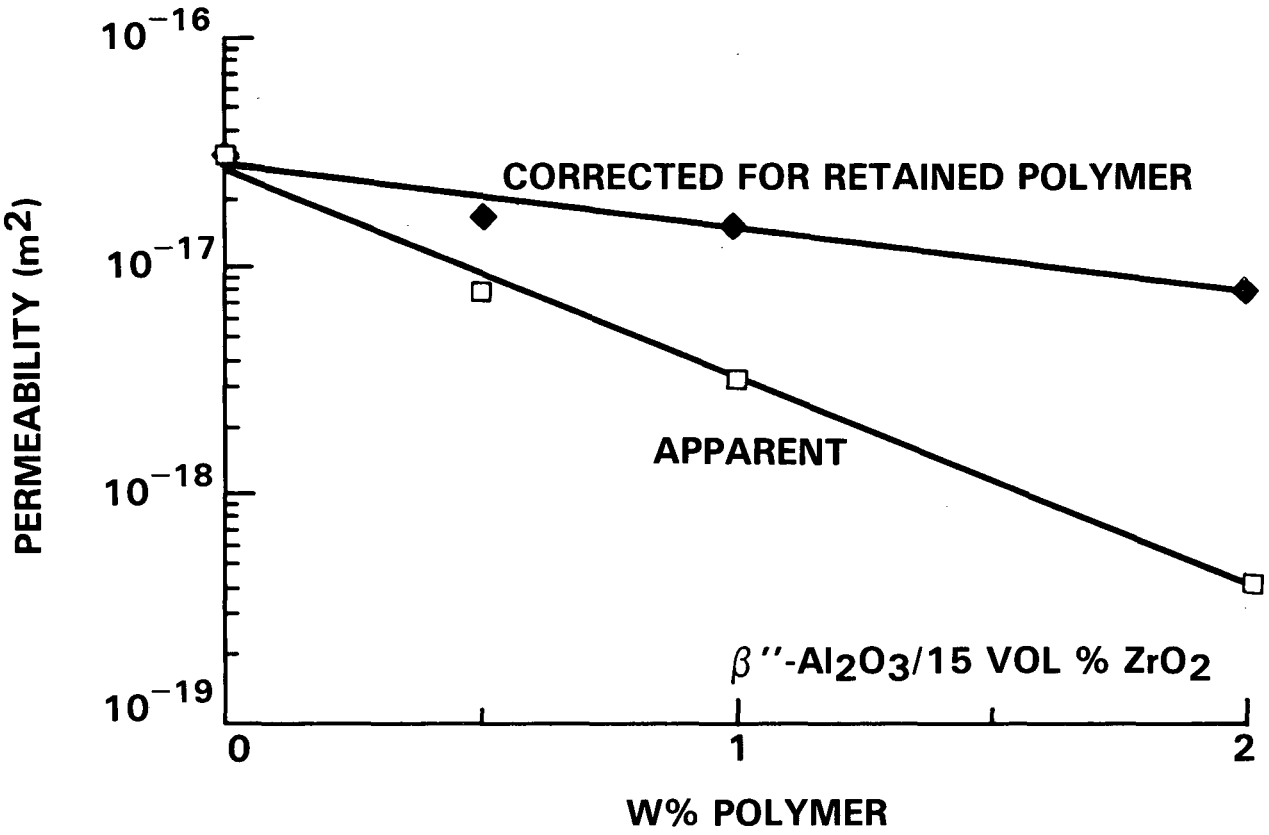
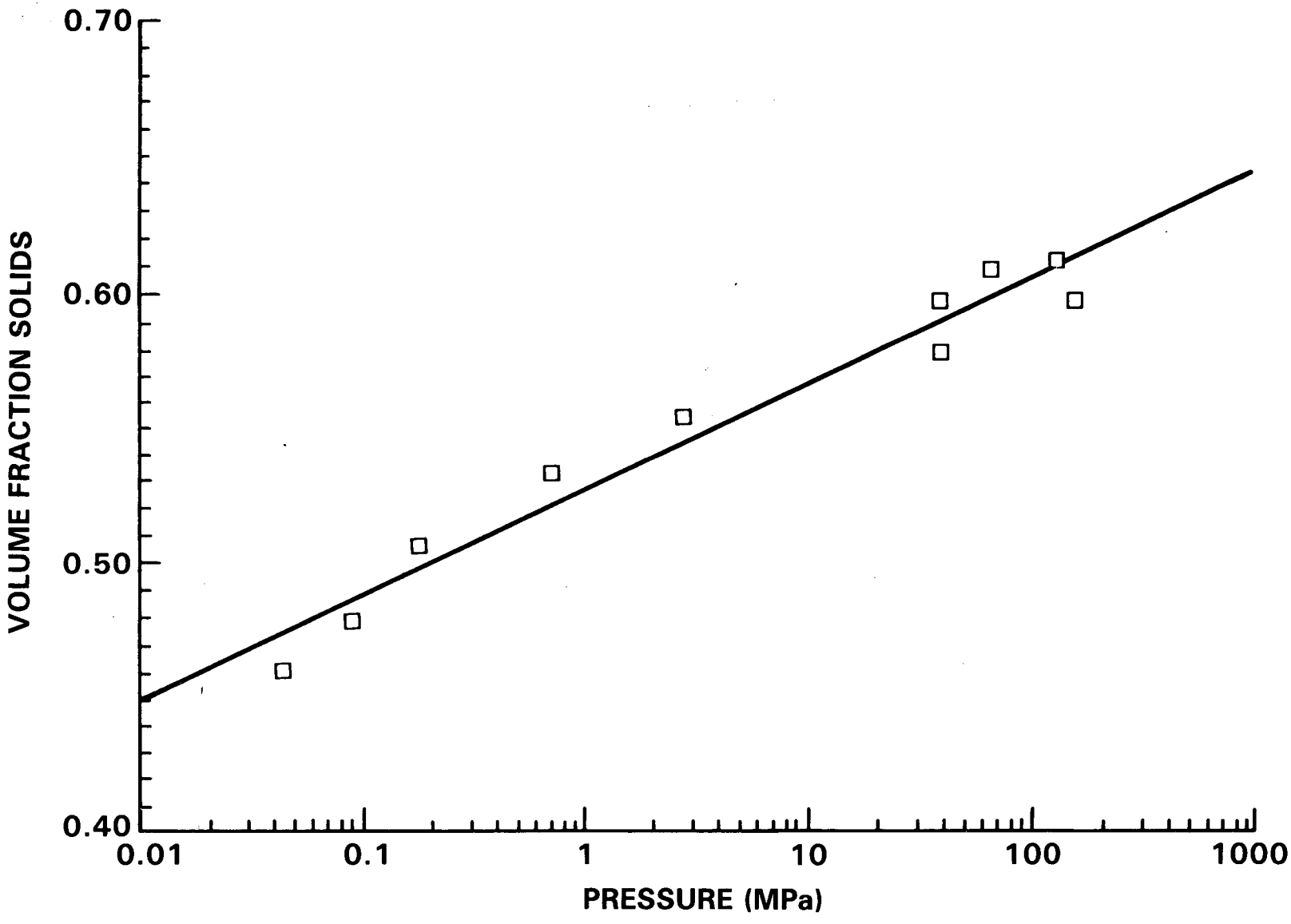

10^{-16}
10^{-17}
10^{-18}
10^{-19}
PERMEABILITY (m^2)
CORRECTED FOR RETAINED POLYMER
APPARENT
β''-Al_2O_3/15 VOL % ZrO_2
0
1
2
W% POLYMER

Figure 5b


0.70
0.60
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0.40
VOLUME FRACTION SOLIDS
0.01
0.1
1
10
100
1000
PRESSURE (MPa)

Figure 6

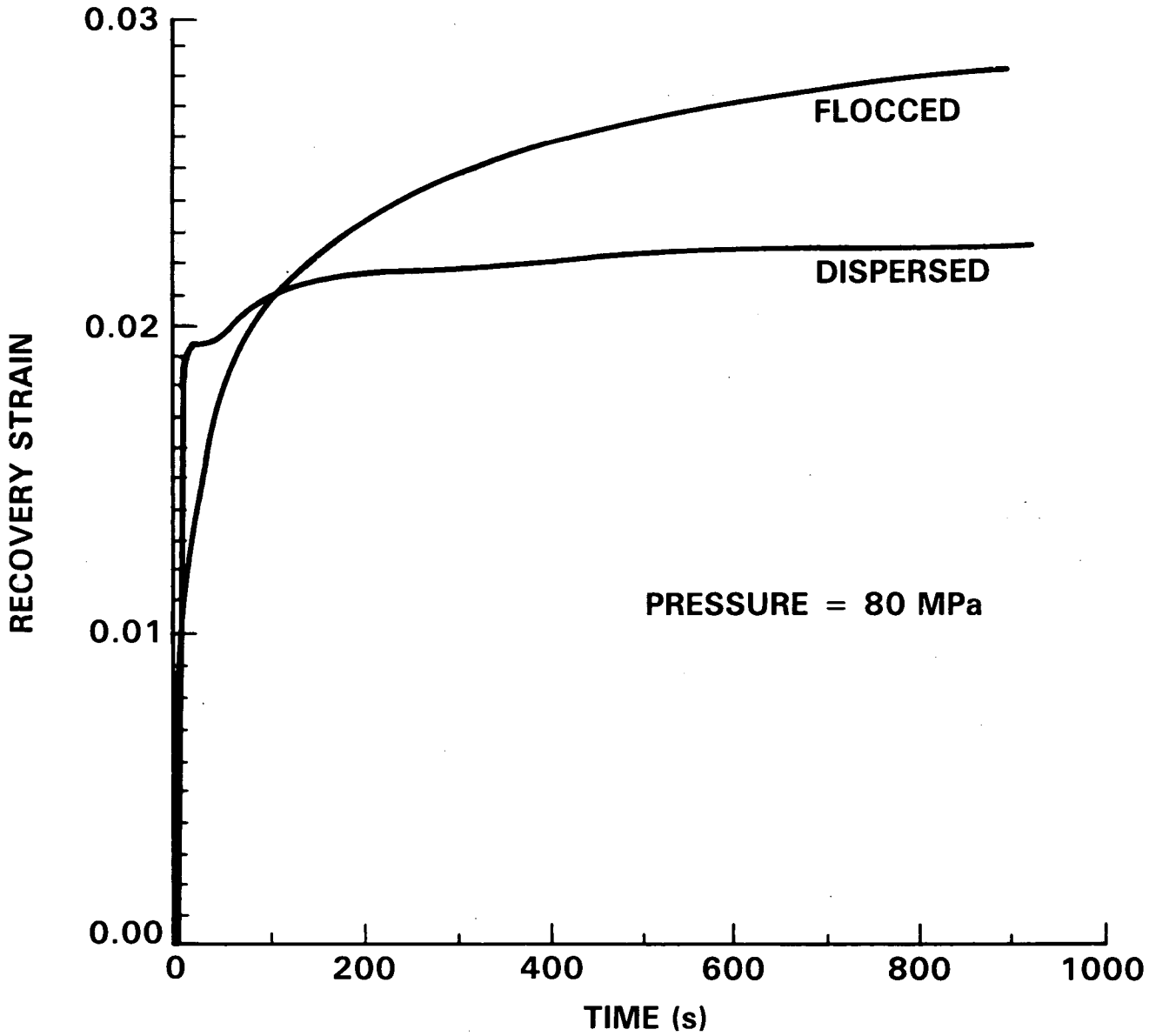
0.03
0.02
0.01
0.00
RECOVERY STRAIN
FLOCCED
DISPERSED
PRESSURE = 80 MPa
0
200
400
600
800
1000
TIME (s)

Figure 7

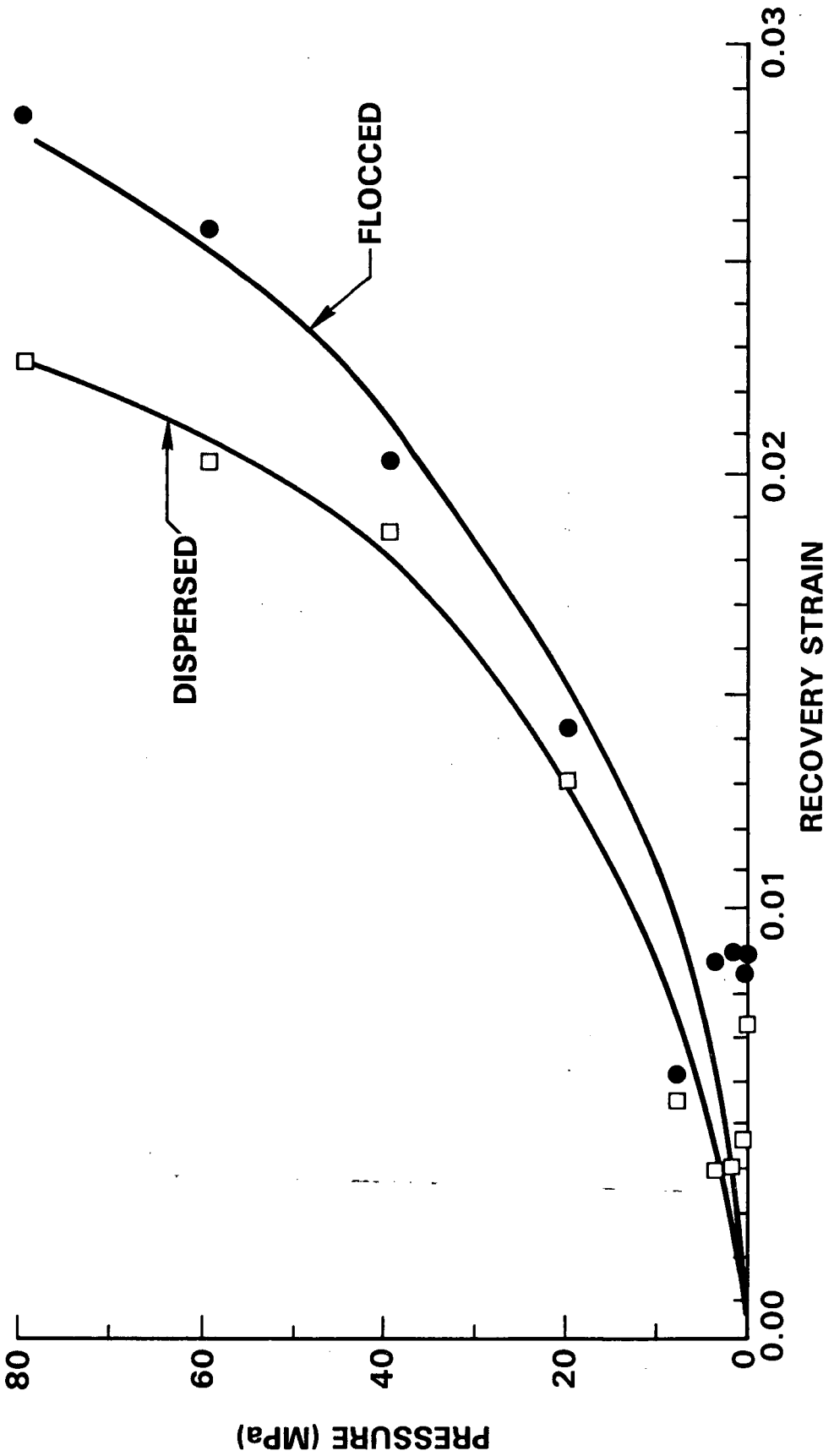
FLOCCED
DISPERSED
PRESSURE (MPa)
RECOVERY STRAIN
0
20
40
60
80
0.00
0.01
0.02
0.03

Figure 8

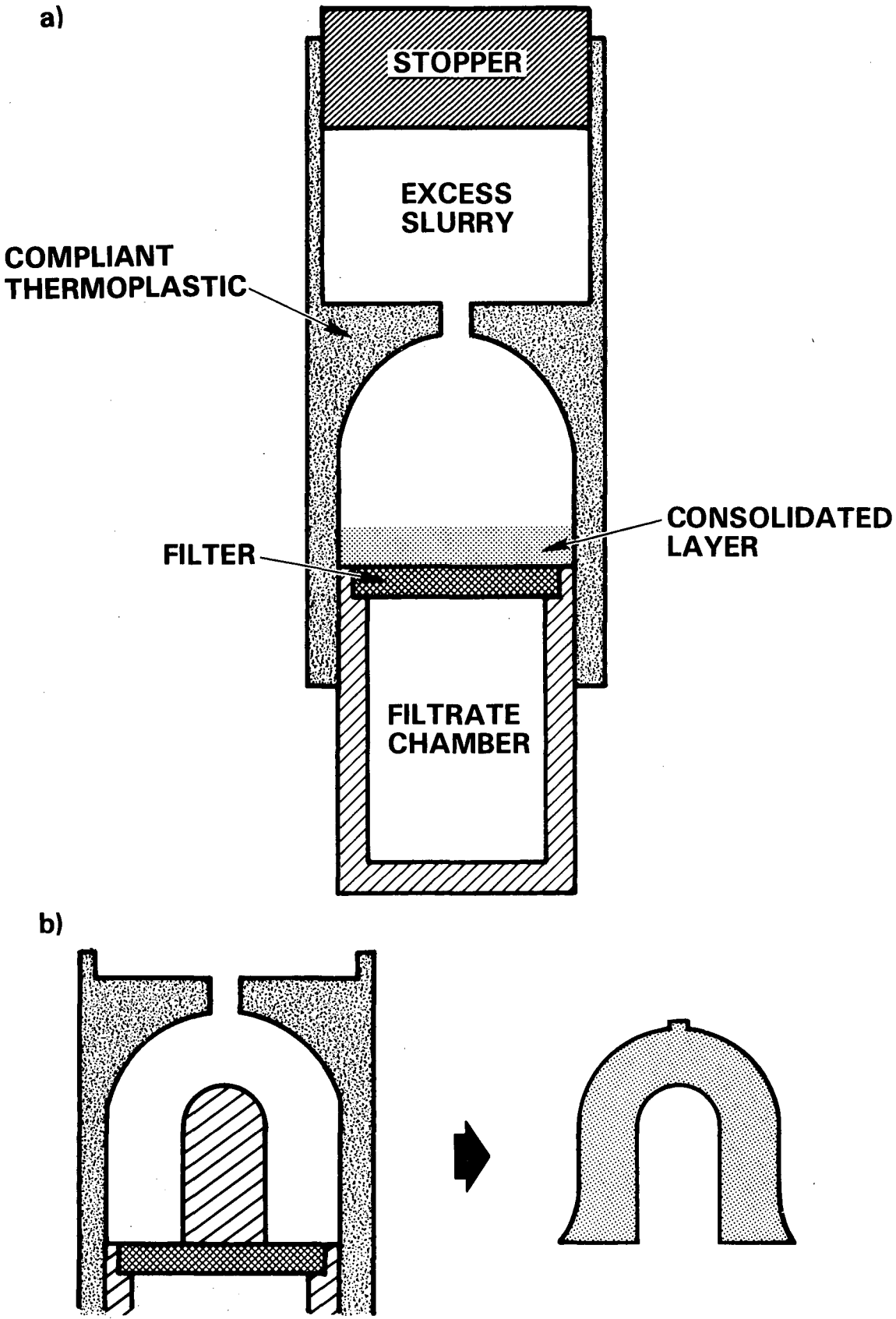
a)
STOPPER
EXCESS SLURRY
COMPLIANT THERMOPLASTIC
CONSOLIDATED LAYER
FILTER
FILTRATE CHAMBER
b)

Figure A1

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