

Influence of pH on rheological properties of Al₂O₃ slips

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The slip-casting technique is commonly used for the production of complex-shaped ceramic components. Various commercial powders have been used, which were characterized with respect to morphology, particle-size distribution and specific surface area. Alumina slips with 80% solid content were prepared with distilled water and ethanol as dispersing agent, with and without deflocculant. HCl and C₄H₁₃NO (tetramethylammonium hydroxide) were used for controlling the pH. Investigations into rheology, i.e. the dependence of viscosity and shear stress on shear rate, were performed. The slip, green and sedimentation bulk density were measured.

1. Introduction

Manufacturing processes which allow the production of near-net-shape ceramic parts are of crucial importance for the large-scale use of ceramics. Several shaping methods can be used for the production of ceramic parts which need no or only minor treatment after being fired: slip casting to obtain green bodies; injection moulding to obtain green bodies; hot isostatic pressing (HIP) of canned powders or presintered bodies; chemical vapour deposition — preparation of bulk parts; preparation of ceramics from polymer precursors.

Slip casting as a forming method is used for the production of large or complicated shaped components or for the development of prototypes or small production series because of low forming costs. It is a versatile process which is used both by the ceramic artist and the manufacturer of highly sophisticated technical ceramics. The versatility of the process has led to the development of slip-casting techniques for many different materials.

Slip casting consists of the following steps:

- (a) preparation of mixture of a powdered material and a liquid into a stable suspension, called a slip;
- (b) pouring this slip into a porous mould, usually made from plaster of Paris and allowing the liquid portion of the slip to be partially absorbed by the mould. A layer of semihard material is formed against the mould surface as liquid is removed from the slip;
- (c) (i) drain casting — pouring the excess slip out of the cavity, when a suitable wall thickness has been formed; (ii) solid casting — solid object may be made by hard material;
- (d) removal of the solid object from the mould;
- (e) drying the material in the mould to provide

adequate green strength. Some shrinkage usually occurs in this step.

A number of investigation [1, 2] of the mechanisms of stability (against flocculation) in nonaqueous systems have been carried out with low relative dielectric constant ($\epsilon_r \leq 10$) solvents (e.g. hydrocarbons). Studies using more polar liquid have been reported for nonplastic materials such as Al₂O₃, CaF₂, CaO-stabilized ZrO₂, MgO, β -alumina, silicon, etc. [3–10].

To obtain defect-free bodies, the slips are required to be concentrated stable suspension with low viscosity. The shape of a flow curve (shear stress against shear rate) gives information about the effectivity of deflocculation process. A well deflocculated suspension shows nearly Newtonian flow behaviour, in contrast to a flocculated slurry which behaves in a pseudoplastic manner. Moreover, they should be castable at intermediate pH values in order to avoid corrosive attacks on the plaster moulds as well as on particle surfaces [5, 6, 11–13]. It is also desirable that the slips should be stable in the long term. Today the most frequently used method to obtain well-stabilized slips is to work at very high or very low pH values. At these pH values the particles in the slip have a high surface potential, which causes electrostatic repulsive forces between the particles. In the present study the slips of Al₂O₃ in polar solvent (e.g. water and ethanol) were used at different pH values. The rheological behaviour, slip, green and sedimentation bulk density were also studied.

2. Basic principles

Most theories agree that solid particles, when suspended in polar liquid, are charged at the surface and move randomly in the dispersion medium. This

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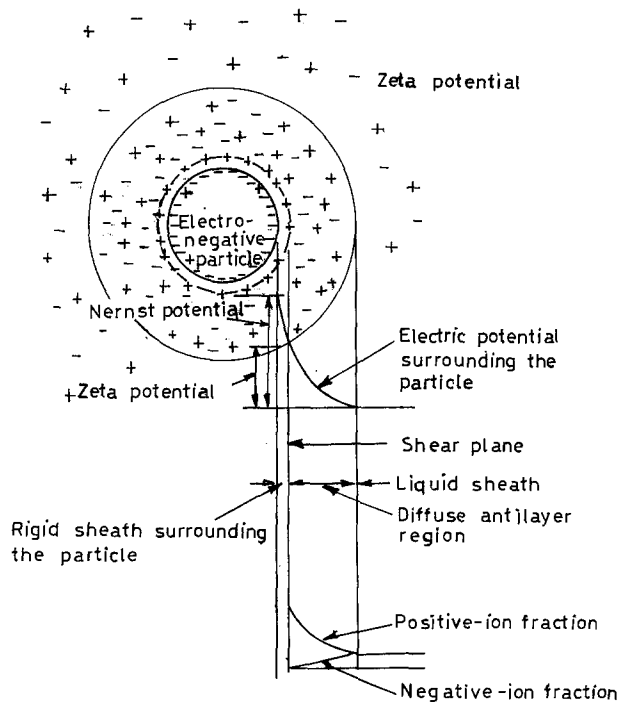


Figure 1 The electrical double layer of particles.

motion, the Brownian motion, causes particle-particle collisions. The stability of the dispersion is directly dependent on how the particles interact during the collision moment. If the attractive van der Waals forces dominate, the particles attract each other during the particle collisions and the dispersion flocculates. To achieve stable dispersions the repulsive forces must exceed the attractive forces. The repulsive forces are caused by electrostatic interaction between the particles or by a steric hindrance through an adsorbed polymer layer [14]. The charged particle surfaces adsorb a layer of oppositely charged ions, i.e. counter ions, form the surrounding medium in order to achieve electrical neutrality. Beyond the counter ions there is a layer of diffusively distributed ions. The charged particle surface, the counter ions and the diffuse part are together termed the electrical double layer (Fig. 1). When the diffuse parts of the double layer of two particles are brought into contact with each other the interaction gives rise to a repulsive force between the particles. The magnitude of the repulsive force depends on the size of the particle and thickness of the electrical double layer. At high electrolyte concentration the electrical double layers are compressed which causes a reduction of the repulsive forces between the particles [14]. Through adsorption of a polymer layer onto the particle surfaces a steric barrier is obtained between the particles. The magnitude of the attractive forces is reduced by the fact that the smallest possible distance between the particles is increased by the polymer layers. The interaction between the adsorbed polymer layers also gives rise to a repulsive force between the particles. If the polymer is charged, the polyelectrolyte charge will decrease or increase, depending in the charge of the polyelectrolyte [15]. When a dispersion is stabilized by an adsorbed polymer layer, causing a repulsive force by the interaction between polymer layers, the dispersion is sterically stabilized. Steric stabilization has

great importance in dispersions where the electrostatic stabilization is insufficient, i.e. in non-polar dispersion medium, in highly concentrated dispersions or water-based dispersions with high electrolyte concentrations.

Viscosity measurements can be used to determine the optimum pH and counter-ion concentration. At the zero point of charge the slip will be flocculated due to the absence of repulsive forces, and it will exhibit a high viscosity. As the pH is changed from the zero point of charge by the addition of acid or base, the zeta-potential will increase and the viscosity will decrease. The increase in zeta-potential will be limited when maximum adsorption of the potential-determining ion on the particle surface is reached. Further addition of the potential-determining ion only increases the charge in the liquid phase and reduces the potential difference between the surface and the liquid. The reduction in surface potential leads to a corresponding reduction in the zeta potential; hence the zeta-potential goes through a maximum. The viscosity of the slip reaches a minimum which corresponds to the maximum in the zeta-potential [16].

There are many factors affecting the casting characteristics of an oxide slip system, namely morphology and dimensional characteristics of the starting powders. Other factors such as viscosity, pH measurements, deflocculant concentration, suspension concentration and moulding conditions are also important in the slip-casting process.

3. Experimental details

Commercial powders of different aluminium oxide (Al_2O_3) were used. The as-received powders were analysed by scanning electron microscopy (particle size), Lasergranulometer (particle-size distribution) and the BET method (specific surface area). Alpha- Al_2O_3 powder B (Al7*, Alcoa Deutschland GmbH, Frankfurt) was used as starting material for the investigation of the slip behaviour. This powder has a composition (wt %) of Al_2O_3 99.5, SiO_2 0.08, Fe_2O_3 0.03, Na_2O 0.1 to 0.2, MgO 0.02 and the average particle size was $\sim 3 \mu\text{m}$. Water, as well as ethanol, were used as a dispersion medium. Suspensions containing 80 wt % powder, 20 wt % distilled water or ethanol plus 0.2 wt % Dolapix CE64 (Zschimmer and Schwarz GmbH, Lahnstein) (deflocculant) were prepared. The deflocculant contains alkali-free carboxylic acid groups.

The suspension was placed in a polyethylene bottle with alumina balls and milled for 24 h to achieve good homogeneous dispersion. After dispersing, the suspension was degassed for several minutes under a rotary vacuum pump. A Sargent-Welch Model LS pH-meter with a glass combination electrode was used to measure the pH in all slips. Hydrochloric acid (HCl) and tetramethyl ammonium hydroxide ($\text{C}_4\text{H}_{13}\text{NO}$) solutions were used to adjust the suspension pH. The slip density of the suspension was measured from the known volume (100 ml) and weight method. Suspension rheological flow characteristics (i.e. variation of shear stress and viscosity with shear rate) were determined with a Rotation viscosimeter (Physica, Viscolab VC 10).

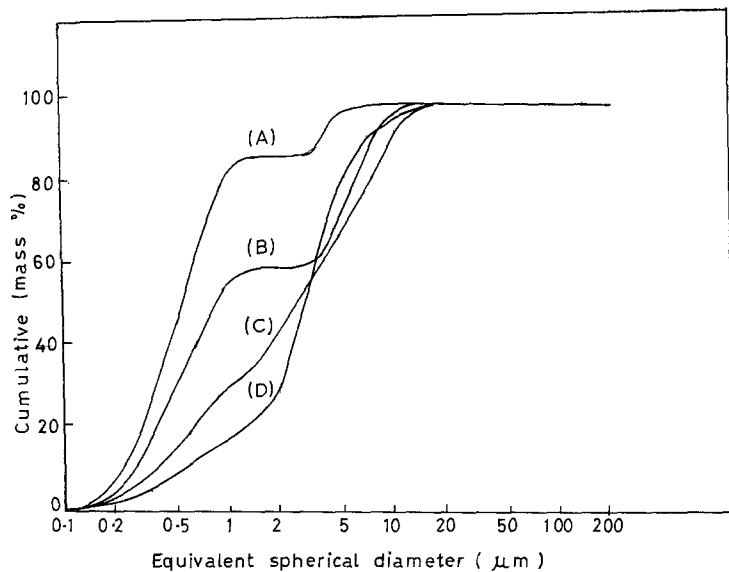


Figure 2 Particle-size distribution and specific surface area of Al_2O_3 powder. (A) CT3000 SG, (B) A17(Alcoa Deutschland GmbH, Frankfurt); (C) ZPS 402 (VAW, Schwandorf); (D) 625-25-10 (Martinswerk GmbH, Bergheim).

Sedimentation bulk density was determined by pouring the suspension (of known weight) into a 50 ml graduated cylinder. The cylinder was covered with flexible film (to prevent solvent evaporation) and the particles in suspension were allowed to settle until the sediment height no longer changed with time. The sedimentation bulk volume was determined directly from sediment height in the graduated cylinder. The weight of Al_2O_3 in the sediment volume was determined by multiplying the known weight of suspension in the cylinder times the known weight percentage of Al_2O_3 in the suspension.

The suspension was then cast in $60 \times 60 \times 6$ mm plaster moulds. After 2 h the cast solid was removed from the moulds and dried at room temperature for 1 day, and then at 110°C for 1 day. The green density was measured using Archimedes' principle. Before determination of the weight in water, the green bodies were immersed in paraffine to close the pores.

4. Results and discussion

4.1. Powder characterization

In order to obtain particle-size distributions of Al_2O_3 powder using the laser granulometer technique, it is necessary to disperse the powders in a suitable liquid. The preliminary experiments indicated that distilled water and ethanol could be used. The particle-size distribution and specific surface area of various commercial Al_2O_3 powders are shown in Fig. 2. It is interesting to observe that the Al_2O_3 powder B (A17) shows a plateau in the equivalent spherical diameter between 1 and $4 \mu\text{m}$. This powder has 53% particles (cumulative mass per cent) below $1.0 \mu\text{m}$ range and 47% particles have 4 to $10 \mu\text{m}$ range. The particle packing is based on the concept of filling the voids in a bed of large spheres with smaller size spheres. The remaining pores between the smaller spheres are then filled with still smaller spheres, etc. to give good particle packing [17]. The remaining Al_2O_3 powders show a majority of small particles (powder A) or a majority of large particles (powders C and D).

Scanning electron microscopy (Fig. 3b) of Al_2O_3 powder B (A17) shows the small and large particles,

while the other powders show agglomerates of finer particles (Fig. 3a). The presence of agglomerates gives microstructural defects in the fired bodies and is detrimental to mechanical properties of the material. For these reasons, Al_2O_3 powder B (A17) should be good for slip casting. The BET specific surface areas of Al_2O_3 powder are determined by a nitrogen adsorption isotherm and are given in Fig. 2.

4.2. Preliminary tests

The state of the particulate dispersion is affected mainly by the suspension solid loading (i.e. the solid/liquid ratio). The viscosity of the suspensions increases drastically and abruptly, when the weight per cent of the solid in the suspensions is increased beyond a critical value. The present study shows the variation of viscosity with shear rate for aqueous (distilled water) and nonaqueous (ethanol), Al_2O_3 (A17) suspensions prepared with various solid loadings. The aqueous and nonaqueous suspension with 80 wt % Al_2O_3 solid has a low viscosity and Newtonian flow behaviour. Above this weight per cent of Al_2O_3 the slip has a high viscosity and pseudoplastic behaviour. The results of Newtonian flow behaviour are characteristic of suspensions in which particle-particle electrostatic repulsive forces are large [18].

Generally the best deflocculants for slip casting are those based on specific adsorption and must have a high dipole moment. One end of the dipole must be preferentially adsorbed in the surface. The other end of the molecule then presents a charged layer to the surrounding liquid and other particles. In the present study, Dolapix CE 64 is used as a deflocculant. To determine the variation of the viscosity of slips as a function of the amount of Dolapix CE 64 deflocculant, the solid content was kept constant (80 wt % Al_2O_3 (A17) powder). From the plots, an optimum deflocculant concentration (0.2 wt % for Al_2O_3) can be determined corresponding to the minimum value of viscosity. For lower amounts of deflocculant, the electrical charges are present at the surface of the particles and the repulsive forces are ineffective. On the other hand, when the deflocculant

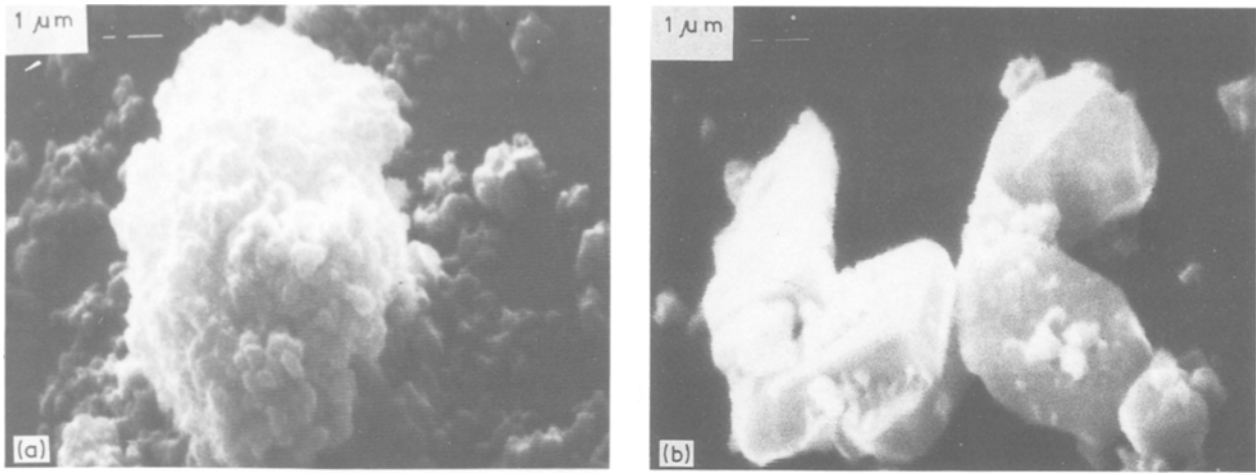


Figure 3 Scanning electron micrographs of Al_2O_3 powder, (a) 3000 SG, (b) A17.

concentration becomes too high, the ionic strength increases and the electrostatic repulsion energy decreases, as a result flocculation takes place again [19].

4.3. Rheological properties

To study the rheological properties, the slips were prepared in the following way:

- (i) 80 wt % Al_2O_3 (A17) and 20 wt % distilled water or ethanol,
- (ii) 80 wt % Al_2O_3 , 20 wt % distilled water or ethanol with 0.20 wt % Dolapix CE 64 deflocculant.

After homogeneous mixing of the slip, the pH was adjusted to various levels and the viscosity at each level was measured. The results are given in Table I. In the present study, the pH is lowered by using small additions (2 to 3 drops) of concentrated HCl and raised by using small additions of concentrated tetramethyl ammonium hydroxide solution. It has been reported in the literature [5] that the addition of

NaOH or NH_4OH in order to control the pH has two separate effects on the double layer. OH^- ions increase the surface potential and the zeta potential. At the same time Na^+ or NH_4^+ ions act as counter ions or produce a surface layer reaction to compress the diffuse layer and reduce the zeta-potential. In acid slips, the Cl^- ion does not act as a counter ion and hence would not effect the diffuse double layer. This system gives rise to repulsive forces between particles and, under proper conditions, deflocculation results.

Figs 4a and b show the rheological behaviour (i.e. viscosity–shear rate) at several pH values for Al_2O_3 –water, with and without a deflocculant system. Figs 5a and b give the viscosity dependence of various pH values at constant shear rate ($D = 825 \text{ sec}^{-1}$). At neutral pH the viscosity shows a maximum value, while for acidic or basic range of pH, the viscosity shows a minimum value. The given data for slips with and without deflocculant show a minimum viscosity at $\text{pH} = 9.0$ and rheological behaviour is Newtonian, i.e. viscosity is independent of shear rate. These results indicate that at $\text{pH} = 9.0$, the particles are well dispersed and show a high sedimentation density (Fig. 5b). Obviously high sedimentation density and low viscosity values tend to form good green bodies. At the remaining pH (see Figs 5b and 8), the viscosity is high and the slip has pseudoplastic behaviour, i.e. the viscosity decreases significantly as the shear rate increases. This behaviour gives a highly flocculated

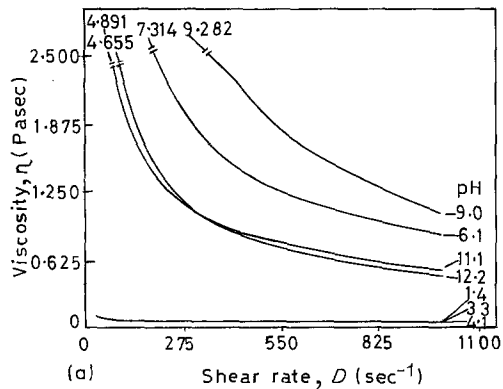
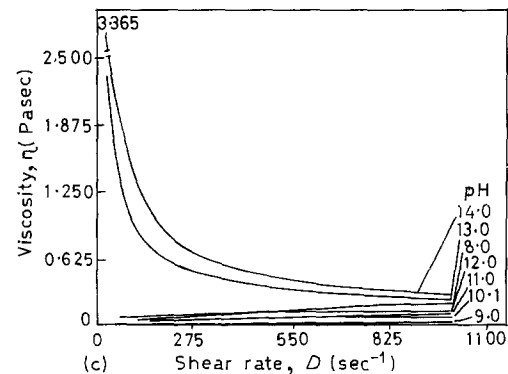
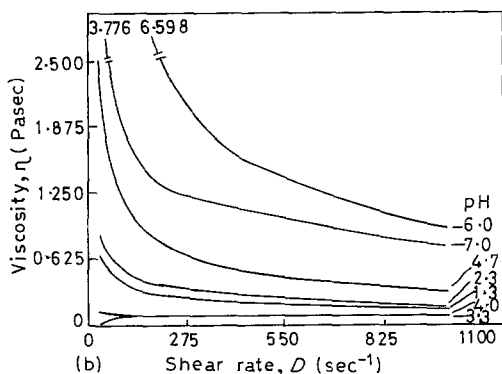


Figure 4 Plots of viscosity against shear rate for suspensions (80 wt % solids content) with pH values indicated. (a) Al_2O_3 –water system; (b, c) Al_2O_3 –water–deflocculant system.



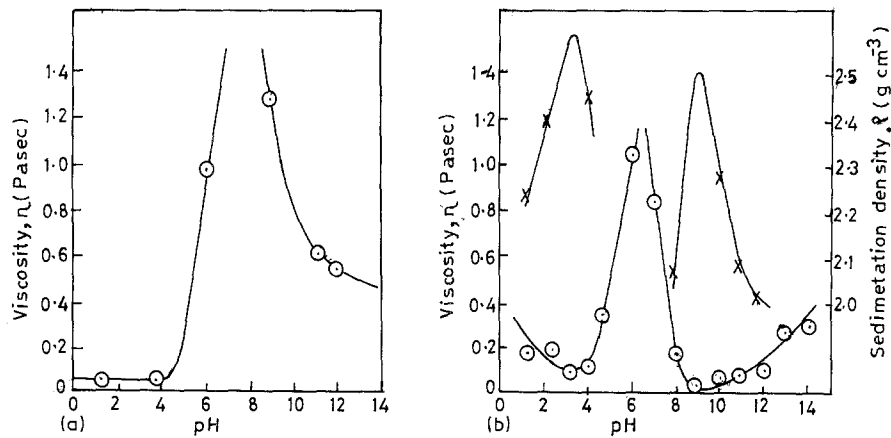


Figure 5 Plots of viscosity against several pH values (at constant shear rate $D = 825 \text{ sec}^{-1}$); (a) Al_2O_3 -water system, (b) Al_2O_3 -water-deflocculant system.

TABLE I Rheological properties of Al_2O_3 slips at several pH values

(a) 80 wt % Al_2O_3 + 20 wt % H_2O				
pH	Viscosity behaviour	slip density (g cm^{-3})	Sedimentation density (g cm^{-3})	Remarks
1.38	Pseudoplastic	2.44	2.67	Not thixotropic
3.35	Newtonian	2.46	2.78	Not thixotropic
4.05	Newtonian	2.43	2.56	Not thixotropic
6.12	Pseudoplastic	2.46	-	Not thixotropic
9.00	Pseudoplastic	2.44	-	Thixotropic
11.14	Pseudoplastic	2.46	-	Thixotropic
12.15	Pseudoplastic	2.45	-	Thixotropic
(b) 80 wt % Al_2O_3 + 20 wt % H_2O + 0.20 wt % Dolapix CE 64				
1.30	Pseudoplastic	2.47	2.29	Not thixotropic
2.30	Pseudoplastic	2.48	2.40	Thixotropic
3.30	Newtonian	2.45	2.52	Not thixotropic
4.02	Newtonian	2.45	2.29	Thixotropic
4.70	Pseudoplastic	2.43	-	Thixotropic
6.03	Pseudoplastic	2.43	-	Thixotropic
7.00	Pseudoplastic	2.46	-	Thixotropic
8.00	Newtonian	2.48	2.18	Thixotropic
9.00	Newtonian	2.47	2.47	Not thixotropic
10.00	Newtonian	2.47	2.05	Not thixotropic
11.01	Newtonian	2.48	2.19	Not thixotropic
12.02	Newtonian	2.44	2.14	Thixotropic
13.00	Pseudoplastic	2.46	-	Thixotropic
14.00	Pseudoplastic	2.45	-	Not thixotropic
(c) 80 wt % Al_2O_3 + 20 wt % ethanol				
1.18	Pseudoplastic	2.24	-	Thixotropic
3.27	Near Newtonian	2.26	2.33	Not thixotropic
4.05	Pseudoplastic	2.26	-	Not thixotropic
6.10	Pseudoplastic	2.24	-	Not thixotropic
8.04	Pseudoplastic	2.27	-	Not thixotropic
9.20	Pseudoplastic	2.25	-	Not thixotropic
10.02	Pseudoplastic	2.23	-	Not thixotropic
(d) 80 wt % Al_2O_3 + 20 wt % ethanol + 0.20 wt % Dolapix CE 64				
1.16	Pseudoplastic	2.23	-	Thixotropic
2.33	Pseudoplastic	2.26	-	Thixotropic
3.28	Pseudoplastic	2.27	-	Thixotropic
4.07	Pseudoplastic	2.27	-	Thixotropic
5.02	Pseudoplastic	2.25	-	Thixotropic
6.08	Pseudoplastic	2.25	-	Thixotropic
7.02	Pseudoplastic	2.26	-	Thixotropic
8.06	Pseudoplastic	2.24	-	Thixotropic
9.08	Newtonian	2.23	2.35	Thixotropic
10.01	Pseudoplastic	2.23	2.15	Thixotropic
11.09	Pseudoplastic	2.24	-	Thixotropic
12.11	Pseudoplastic	2.27	-	Thixotropic
13.10	Pseudoplastic	2.25	-	Thixotropic

suspension. In a thixotropic system the viscosity will decrease if the system is held under a constant shear rate. Thus thixotropy is a time-dependent effect. It can strongly influence the homogeneity of cast solid samples. Observations of the thixotropic effect at several pH values are given in Table I.

Figs 6a and b show the rheological behaviour at several pH values for the Al_2O_3 -ethanol system with and without deflocculant. Figs 7a and b give the viscosity dependence of various pH values at constant shear rate ($D = 825 \text{ sec}^{-1}$). The minimum viscosity is observed at $\text{pH} = 9$ for Al_2O_3 -ethanol with deflocculant system. At these minimum viscosity levels the slips show Newtonian behaviour. In the Al_2O_3 -ethanol system the viscosity remains constant at several pH values. The rheological properties of these slips show pseudoplastic behaviour, i.e. a highly flocculated suspension. The behaviour of particles in polar organic liquid, such as ethanol, is similar to that in water. The preliminary difference in repulsive force of the electrical double layer is due to the dielectric constant ($\epsilon_{\text{H}_2\text{O}} = 80$ and $\epsilon_{\text{ethanol}} = 24$) of the liquid. The thickness of the diffuse double layer is proportional to the square root of the dielectric constant. Because most organic liquids have lower dielectric constants than water, flocculation occurs at lower counter-ion concentrations than that in water.

A comparison between viscosity and green density of the cast bodies with pH values is given in Fig. 8 for the Al_2O_3 -water-deflocculant system. The viscosity values have been determined at a constant shear rate of $D = 90 \text{ sec}^{-1}$. In this system the highest green density was 71% theoretical at a pH of 10.

In the Al_2O_3 -ethanol systems the viscosity was higher than in the Al_2O_3 -water system and, because of problems with the casting of these slips, only a few specimens could be obtained. The maximum green density was 60% theoretical.

4.4. Deterioration of the mould

Because little shrinkage ($\sim 1.6\%$) occurs in the mould, an absolutely smooth surface is necessary to permit removal of the cast solid piece from the mould. Any action of the slip that tends to roughen the mould surface will quickly render the mould unsatisfactory for further investigations.

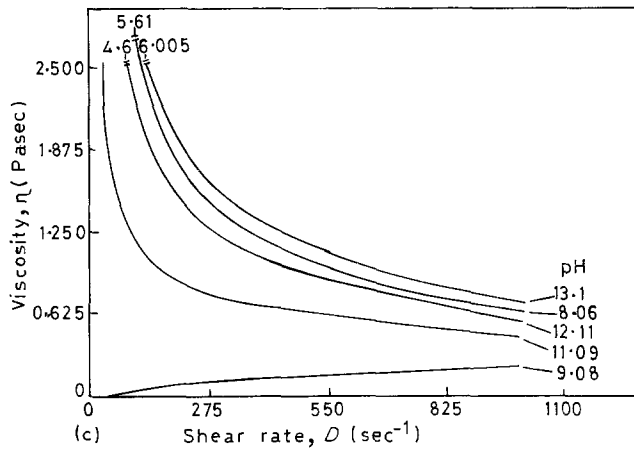
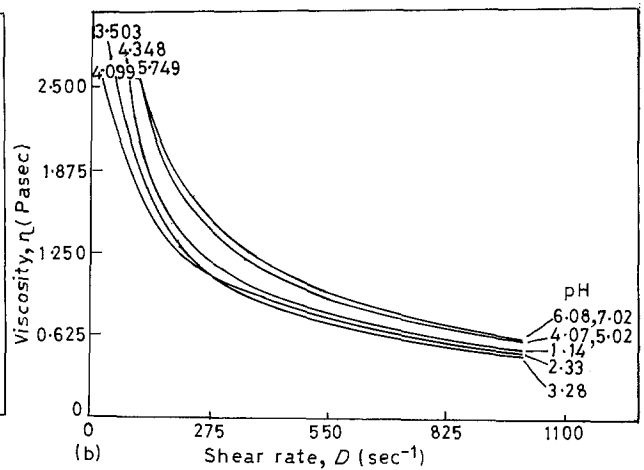
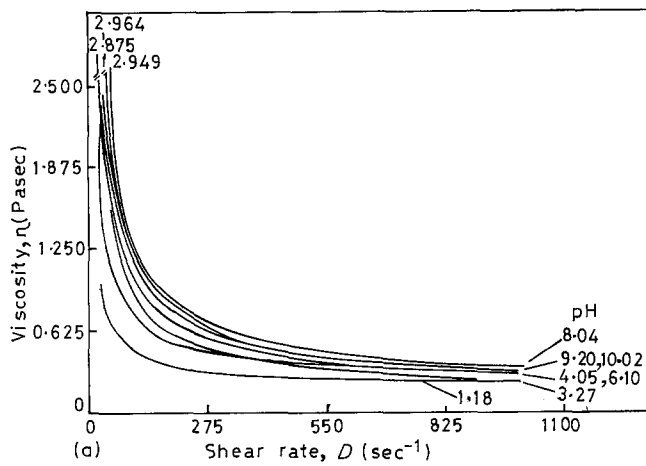


Figure 6 Plots of viscosity against shear rate for suspensions (80 wt % solid content) with pH values indicated; (a) Al_2O_3 -ethanol system; (b, c) Al_2O_3 -ethanol-deflocculant system.

Acidic slips are found to be detrimental to the moulds, causing the formation of minute pits or holes on the mould surface after casting. Basic slips, however, have a much less harmful effect on the mould surface, in the form of a general roughening of the surface rather than of pitting. This is believed to have been caused by the abrasive nature of the particles rather than by chemical attack. The Al_2O_3 -water-deflocculant gives a good solid casting behaviour compared to Al_2O_3 -water and Al_2O_3 -ethanol-deflocculant systems. The solid castings obtained from the Al_2O_3 -ethanol-deflocculant system are brittle in nature.

5. Conclusions

1. Particle-size distribution, scanning electron

microscopy and BET specific surface area measurements show that Al_2O_3 powder B (A17) is good for slip casting.

2. Preliminary tests of the rheological behaviour show 80 wt % Al_2O_3 (A17) powder, 20 wt % distilled water or ethanol and 0.20 wt % Dolapix CE 64 gives minimum viscosity and Newtonian flow behaviour.

3. Satisfactory castable slips can be obtained by deflocculation of the treated Al_2O_3 powder with HCl and $\text{C}_4\text{H}_{13}\text{NO}$ (tetramethyl ammonium hydroxide).

4. Rheological tests show minimum viscosity for the system Al_2O_3 -water at pH 1 to 4, Al_2O_3 -water-deflocculant at pH 3 to 4 and pH 9 to 11 and Al_2O_3 -ethanol-deflocculant at pH 9.

5. 80 wt % Al_2O_3 (A17) powder, 20 wt % distilled water, 0.20 wt % Dolapix CE 64 and pH 9 to 10 is recommended as a good castable slip, leading to bodies with a green density of more than 70% theoretical.

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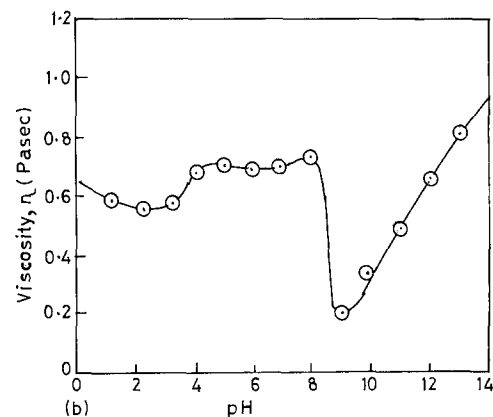
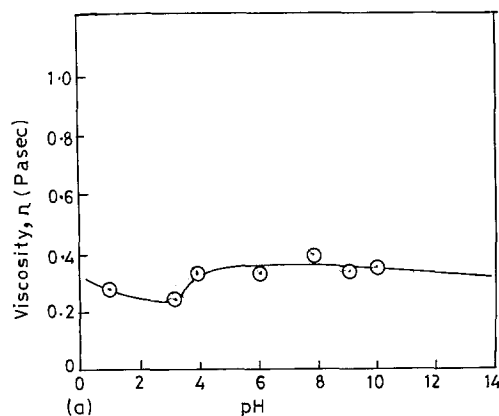


Figure 7 Plots of viscosity against several pH values (at constant shear rate $D = 825 \text{ sec}^{-1}$): (a) Al_2O_3 -ethanol system; (b) Al_2O_3 -ethanol-deflocculant system.

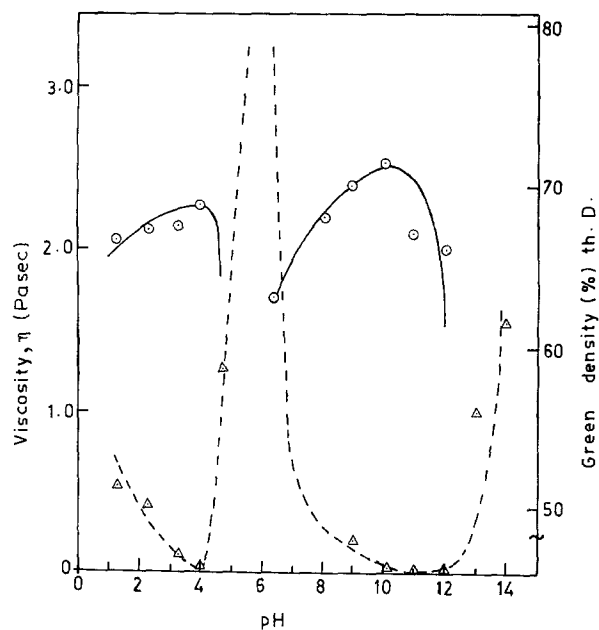


Figure 8 Plots of viscosity and green density against pH values for the Al_2O_3 -water-deflocculant system at constant shear rate $D = 90 \text{ sec}^{-1}$.

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