Slip casting of partially stabilized zirconia

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Casting behaviour and rheological properties are studied in order to define the appropriate conditions under which to prepare slips for the production of high-temperature ceramics. Various commercial powders have been used, which were characterized with respect to morphology, particle size distribution and specific surface area. Zirconia slips with 75 wt% solid content were prepared with distilled water and ethanol as dispersing agent, with and without deflocculant. Hydrochloric acid and tetramethylammonium hydroxide were used to control 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 densities were measured.

1. Introduction

Partially stabilized zirconia is considered today to be an advanced ceramic material because of its high values of strength and fracture toughness [1–5], which are related to the stress-induced phase transformation [6–8].

The rheological and casting parameters of yttria-stabilized tetragonal zirconia polycrystalline powder obtained by a wet-chemical coprecipitation route have been reported [9]. Moreno *et al.* also studied the colloidal stability through zeta potential measurements. Taguchi *et al.* [10, 11] reported the slip-casting of yttria-partially stabilized zirconia emphasizing the effect of solids content on relative density and firing shirnkage. These authors also studied the effect of milling on these properties.

The laboratory techniques of slip casting have been reported for nonplastic materials such as Al_2O_3, CaF_2, CaO-stabilized ZrO_2, MgO, β-alumina, silicon, etc. [12–15]. According to Whiteway *et al.* [12], the use of small particle sized MgO (50% < 1 μm) is essential to obtain low porosity in the finished specimens, and ethanol-based suspensions have good MgO casting properties. They also discussed the variation of slip density and firing temperature. Masson *et al.* [13] reported the preparation of specimens of CaO-stabilized ZrO_2 by slip casting from ethanol-based suspensions. The slip casting of alumina–zirconia composites has been reported [16, 17], and the dispersion states of aqueous composite Al_2O_3/ZrO_2 colloidal suspensions have been studied by measuring particle-size distribution as a function of pH [18]. The stability of the suspensions in non-aqueous media has been investigated by various workers [19, 20]. Studies using more polar liquids have been reported [21, 22].

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.

To obtain defect-free bodies, the slips are required to be concentrated stable suspensions with low viscosity. The shape of a flow curve (shear stress against shear rate) provides information about the effectivity of the 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 the particle surfaces [23–27]. 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 partially stabilized ZrO_2 in polar solvent (e.g. water and ethanol) were used at different pH values. The rheological behaviour, slip, green and sedimentation bulk densities were also studied. Interest has recently been shown in the influence of pH on rheological properties of Al_2O_3 slips [28].

2. Experimental procedure

Commercial powder of different zirconium oxide (ZrO_2) were used. The as-received powders were analysed by X-ray powder diffractometry (phases present in the powder), scanning electron microscopy (particle size), laser granulometry (particle-size distribution) and the BET method (surface area). A polycrystalline tetragonal zirconia powder containing 5 mol% yttria powder B (3-YS$^+$) was used as starting material for

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the investigation of the slip behaviour. This powder has a composition (wt %) of ZrO_2 94.6, Y_2O_3 5.27, Na_2O 0.001 and an ignition loss of 0.10%. The average particle size was ~ 0.5 μm. The specific surface area (N_2 adsorption; BET method) was 6.8 $m^2 g^{-1}$ for powder B. Water, as well as ethanol, was used as a dispersion medium. Suspensions containing 75 wt % powder, 25 wt % distilled water or ethanol plus 0.4 wt % Dolapix CE 64 (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 homogeneity of the 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, $(CH_3)_4NOH$, 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, τ, and viscosity, η with shear rate, D) were determined at room temperature with a Rotation Viscosimeter (Physica, Viscolab LC 10). The measuring device was a bob/cup system Z3 DIN, the shear rate range 0–1000 s^{-1}. The rheological flows were computed by using a basic program RHEO-LOGIC VS 100 for rotational tests "program $\tau = f(D)$".

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 ZrO_2 in the sediment volume was determined by multiplying the known weight of suspension in the cylinder by the known weight of percentage of ZrO_2 in the suspension.

The suspension was then cast in 60 mm × 60 mm × 6 mm plaster moulds (made with a 75/100 water-to-plaster ratio by weight to form solid-cast pieces). 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 paraffin to close the pores.

3. Results and discussion

3.1. Powder characterization

The phases present in the partially stabilized ZrO_2 powder were determined by X-ray powder diffractometry using Ni-filtered CuK_α radiation. The (tetragonal + cubic)/monoclinic ratio was estimated from (1 1 1) tetragonal and ($\bar{1}$ 1 1) peak intensities by using the Garvie–Nicholson equation [29]. X-ray estimation indicated that both tetragonal and monoclinic phases were present in the powder B (3-YS$^+$) with 80/20 tetragonal-to-monoclinic ratio. The other powder of ZrO_2 (3-Y) showed a 70/30 tetragonal-to-monoclinic ratio (powder A). The partially stabilized zirconia containing metastable tetragonal ZrO_2 appears to have the greatest toughening and other desirable properties [4, 30]. For these reasons ZrO_2 powder B (3-YS$^+$) should be better for slip casting.

In order to obtain the particle-size distribution of partially stabilized ZrO_2 powder using laser granulometry 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 of two commercial partially stabilized ZrO_2 powders (A and B) are shown in the Fig. 1. ZrO_2-quality powder was obtained by spray drying and contained agglomerates of hard particles. The particle-size distribution shows the agglomerates to be > 7 μm and the dispersed fine particles to be < 1 μm. It is interesting to observe that the ZrO_2 powder B (3-YS$^+$) shows a plateau in the equivalent spherical diameter between 1 and 4 μm. This powder has 60% particles (cumulative mass per cent) below the 1.0 μm range and 40% particle in the 4–10 μm range. The particle packing is based on the concept of filling the voids in a bed of large spheres with smaller sized spheres. The remaining pores between the smaller spheres are then filled with still smaller spheres, etc., to give good particle packing [31]. The other ZrO_2 (3-Y) powder shows a majority of small particles (Powder A).

Scanning electron microscopy (Fig. 2) of partially stabilized ZrO_2 powder B (3-YS$^+$) shows the small and large particles, while the other powder shows agglomerates of finer particle crystals. The presence of agglomerates produces microstructural defects in the fired bodies and is detrimental to mechanical properties of the material. For these reasons the ZrO_2 powder B (3-YS$^+$) should be good for slip casting. The BET specific surface areas of ZrO_2 powder were determined from the nitrogen adsorption isotherm and were found to be 6.8 $m^2 g^{-1}$ for powder B (3-YS$^+$) and 17.3 $m^2 g^{-1}$ for powder A (3-Y).

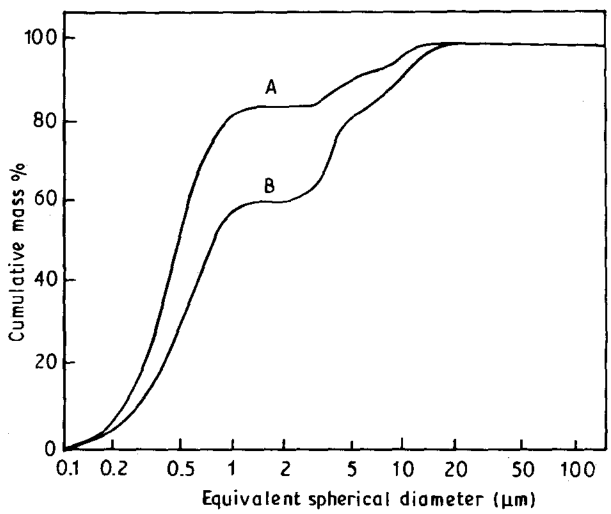


Figure 1 Particle size distribution and specific surface area of ZrO_2 powder A TZ-3Y, and powder TZ-3YS$^+$.

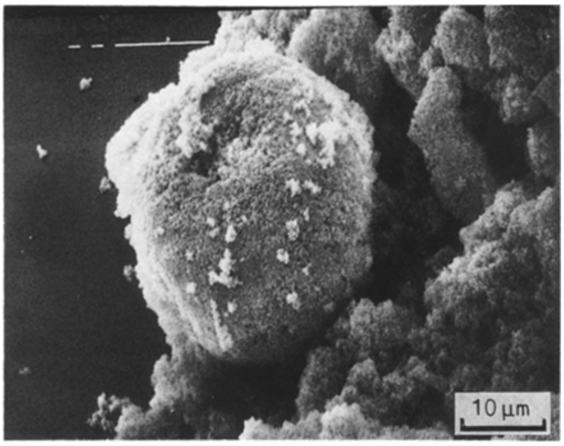


Figure 2 Scanning electron micrograph of ZrO_2 powder B (3-YS$^+$).

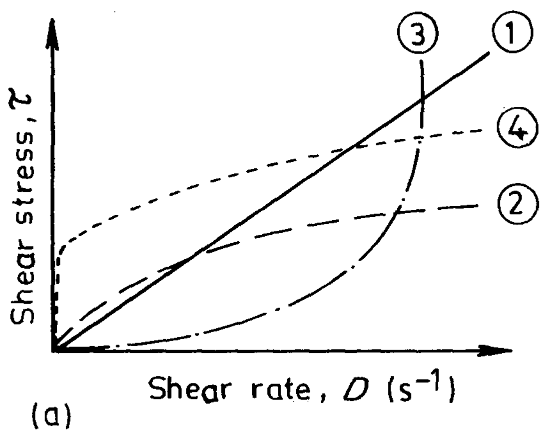
3.2. Preliminary tests

Measurement of rheological properties is one of the most useful methods for studying slip-casting systems. Rheological properties can be measured with any of the viscometers which permit variation in shear rates. The viscosity of a slip can be used to determine the optimum concentrations of the potential-determining ion and the counter ion. The flow properties of slips are usually illustrated by graphs (Fig. 3a–c) showing shear stress and viscosity as a function of shear rate. The viscosity of a Newtonian system is constant and independent of the shear rate. A pseudo-plastic system is one which has a decrease in viscosity with increasing shear rate. A plastic system has a yield point, below which no flow occurs. Above the yield point the plastic would have a decreasing viscosity with increasing shear rate. Dilatancy is the opposite of pseudoplasticity. In a dilatant system the viscosity increases with increasing shear rate. A highly dilatant slip cannot be poured, nor will it fill small details of a mould.

Thixotropy is a time-dependent effect. In a thixotropic system the viscosity will decrease if the system is held under a constant shear rate (see Fig. 3c). It can strongly influence the homogeneity of cast solid samples.

The state of 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 solid in the suspension is increased beyond a critical value. The present study shows the viscosity versus shear rate for aqueous (distilled water) and nonaqueous (ethanol), ZrO_2 (3-YS$^+$) suspensions prepared with various solid loadings (solid/liquid ratios of 75/25, 80/20, and 85/15 by weight and 0.4 wt % Dolapix CE 64 deflocculant). The aqueous and nonaqueous suspension with 75 wt % ZrO_2 solid has a low viscosity and Newtonian flow behaviour. Above this weight per cent of ZrO_2, 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 [32].

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 (0.1–0.8 wt % deflocculant concentration), the solid content was kept constant (75 wt % ZrO_2 (3-YS$^+$) powder). From the plots, an optimum deflocculant concentration (0.40 wt % for ZrO_2) can be determined corresponding to the minimum viscosity. For lower amounts of deflocculant, electrical charges are present at the surface of the particles and the



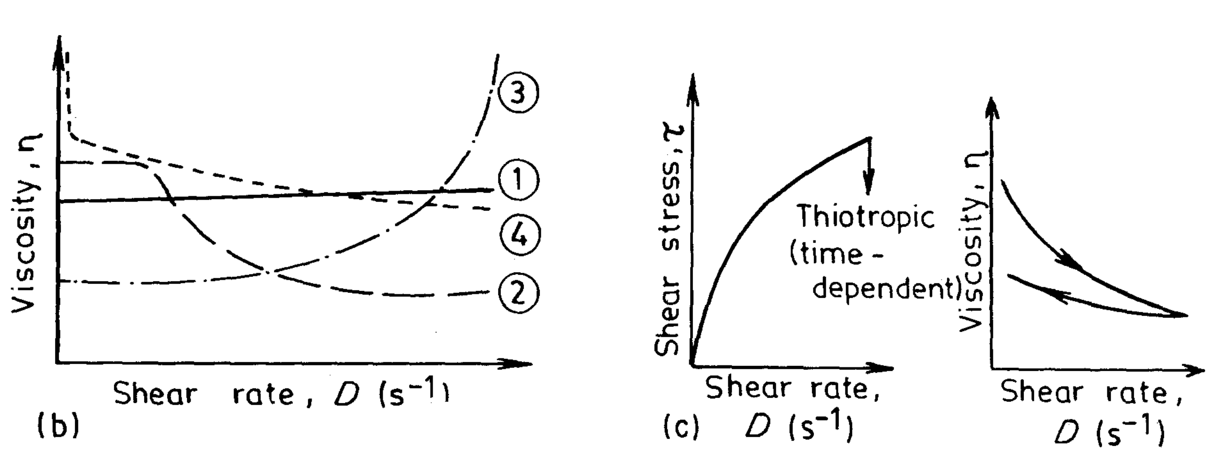


Figure 3 Typical flow curves encountered in slip casting. (a) Flow curve, (b) viscosity curve, (c) thixotropic substance. Flow: 1, Newtonian; 2, pseudoplastic; 3, dilatant; 4, plastic.

repulsive forces are ineffective. On the other hand, when the deflocculant concentration becomes too high, the ionic strength increases, the electrostatic repulsion energy decreases, and as a result flocculation takes place again [33].

The suspension containing 75 wt % ZrO_2 powder B (3-YS$^+$) and 25 wt % distilled water or ethanol was placed in a polyethylene bottle with alumina balls, and milled for 24 h to achieve a good homogeneous dispersion. After dispersion, the suspension was then placed in plaster moulds. The cast specimens were removed from the moulds and dried at 110 °C for 1 day. X-ray powder diffractionometry shows that cast specimens contain tetragonal, cubic and monoclinic ZrO_2. The starting material (powder B, 3-YS$^+$) contains ~ 20% monoclinic ZrO_2. The amount of monoclinic ZrO_2 of this powder was slightly increased and had a value of 25% at 24 h milling. Longer milling was not attempted, in order to avoid a high degree of contamination from the milling media. The particle-size distribution of both starting material and the cast specimens did not show any significant change in the particle size. These results suggest that the crystallite size of ZrO_2 does not decrease with milling times up to 24 h. It has been reported that the particle-size distribution of tetragonal ZrO_2 shows that particles larger than 2 μm did not break up significantly in short milling times (< 24 h). The crystallite size of tetragonal + cubic and monoclinic ZrO_2 is independent of milling time. The relative density of the cast specimen does not depend on the amount of tetragonal or monoclinic ZrO_2, but depends on the dispersion of the suspension [11, 18].

3.3. Rheological properties

To understand clearly the results obtained and the reasons for the behaviour of the slips, it is advisable to consider briefly the theory pertaining to the zirconia–water system developed in connection with this investigation. The theory is based on the diffuse double layer theory that has been so successfully applied to clay system [28, 34]. Essentially it may be considered that each particle of Zirconia of colloidal size holds an attached water layer, and a net charge or potential exists at the outer edge of this layer owing to the presence of preferentially adsorbed ions on the surface of the particle and a swarm of counter charges (or counter ions) in the fixed and moveable medium surrounding the particle. In the acidic slip the preferentially adsorbed ions are hydrogen ions and the chloride ions act as countercharges. In the basic slip, the hydroxyl ions may be considered to be preferentially adsorbed and the tetramethylammonium ions acts as the counter ions. This system gives rise to repulsion forces between particles and, under the proper conditions, deflocculation results.

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

(i) 75 wt % ZrO_2 (3-YS$^+$) and 25 wt % distilled water or ethanol,

(ii) 75 wt % ZrO_2, 25 wt % distilled water or ethanol with 0.40 wt % Dolapiz CE 64 deflocculant.

After homogeneous mixing of the slip (~ 24 h), the pH was adjusted to various levels and the viscosity at each of these levels was measured. The results are given in Table I. In the present study, the pH was lowered by using small additions (2–3 drops) of

TABLE I Rheological properties of ZrO_2 slips at several pH values

System	pH	Viscosity behaviour	Slip density ($g\,cm^{-3}$)	Sedimentation density ($g\,cm^{-3}$)	Remarks
75 wt % ZrO_2	1.30	Pseudoplastic	2.90	–	Thixotropic
+ 25 wt % H_2O	2.33	Newtonian	2.89	2.69	Not thixotropic
	5.00	Near Newtonian	2.91	2.52	Thixotropic
	6.38	Pseudoplastic	2.94	–	Thixotropic
	10.05	Pseudoplastic	2.94	–	Not thixotropic
75 wt % ZrO_2	1.10	Pseudoplastic	2.90	–	Not thixotropic
+ 25 wt % H_2O	3.05	Pseudoplastic	2.89	–	Not thixotropic
+ 0.40 wt %	5.05	Pseudoplastic	2.91	–	Not thixotropic
Dolapix CE 64	7.10	Pseudoplastic	2.89	–	Thixotropic
	9.04	Newtonian	2.92	2.78	Not thixotropic
	10.10	Newtonian	2.93	2.86	Not thixotropic
	11.09	Newtonian	2.90	2.86	Not thixotropic
	12.03	Pseudoplastic	2.94	–	Not thixotropic
	13.00	Pseudoplastic	2.90	–	Thixotropic
	14.00	Pseudoplastic	2.93	–	Thixotropic
75 wt % ZrO_2	1.20	Pseudoplastic	2.65	–	Thixotropic
+ 25 wt % ethanol	4.00	Pseudoplastic	2.63	–	Thixotropic
	7.00	Pseudoplastic	2.66	–	Thixotropic
	10.00	Pseudoplastic	2.64	–	Thixotropic
	12.25	Pseudoplastic	2.65	–	Thixotropic
75 wt % ZrO_2	3.35	Pseudoplastic	2.65	–	Thixotropic
+ 25 wt % ethanol	5.00	Pseudoplastic	2.63	–	Thixotropic
+ 0.40 wt %	8.15	Pseudoplastic	2.65	–	Thixotropic
Dolapix CE 64	10.30	Pseudoplastic	2.64	–	Thixotropic
	12.10	Pseudoplastic	2.63	–	Thixotropic

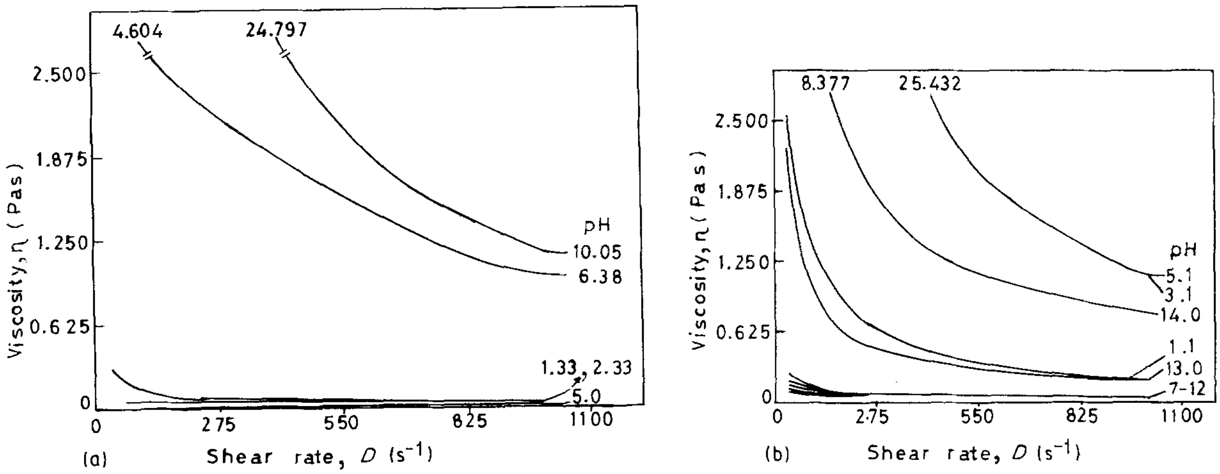


Figure 4 Plots of viscosity against shear rate for suspensions (75 wt % solids content) with pH values indicated. (a) ZrO_2–water system, (b) ZrO_2–water–deflocculant system.

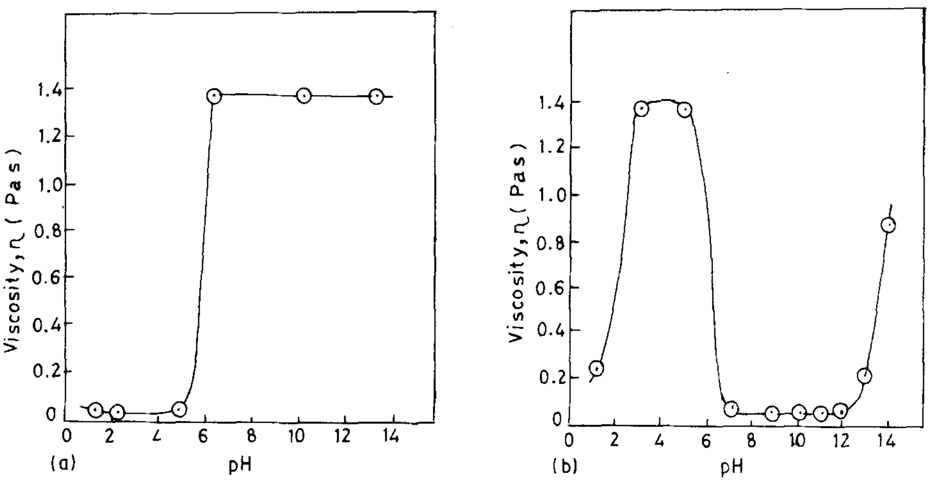


Figure 5 Plots of viscosity against several pH values (at constant shear rate $D = 825\ s^{-1}$); (a) ZrO_2–water system; (b) ZrO_2–water–deflocculant system.

reagent grade concentrated HCl and raised by using additions of concentrated tetramethyl ammonium hydroxide solution.

It has been reported [23] 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^- ions 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.

Fig. 4a and b show the rheological behaviour (i.e. viscosity–shear rate) at several pH values for ZrO_2–water system, with and without deflocculant. Fig. 5a and b give the viscosity dependence of various pH values at constant shear rate ($D = 825\ s^{-1}$). In the ZrO_2–water system (Fig. 5a) the viscosity shows a minimum value at pH = 2–5 and then viscosity rises steeply to a plateau for pH = 6–14. In the ZrO_2–water–deflocculant system (Fig. 5b), the viscosity shows a maximum value at pH = 2–6, and then it decreases to a minimum value at pH = 7–12. At these minimum viscosity values, the rheological behaviour is Newtonian, i.e. viscosity is independent of shear rate. These results indicate that at pH = 2.33 (in the ZrO_2–water system) and at pH = 10.01 and 11.09 (in the ZrO_2–water–deflocculant system), the particles are well dispersed, and show a high sedimentation density. Obviously high sedimentation density and low viscosity values tend to form good green bodies. Usually, basic suspensions are preferred to prevent the rapid formation of a strong bond between the concentrated particulate suspension and the mould during the casting process [35]. At the remaining pH values (see Figs 5b and 7), the viscosity is high and the slip has pseudoplastic behaviour, i.e. the viscosity decreases significantly as the shear rate increases. This behaviour gives highly flocculated suspensions.

In the present study the "RHEO-LOGIC VS 100" computer program was used for the study of rheological properties. In a thixotropic system the viscosity will decrease if the system is held under a constant shear rate ($D = 1000\ s^{-1}$) for 1 min. If the shear rate is removed and the system allowed to remain at rest for some time, the original flow curve cannot be observed,

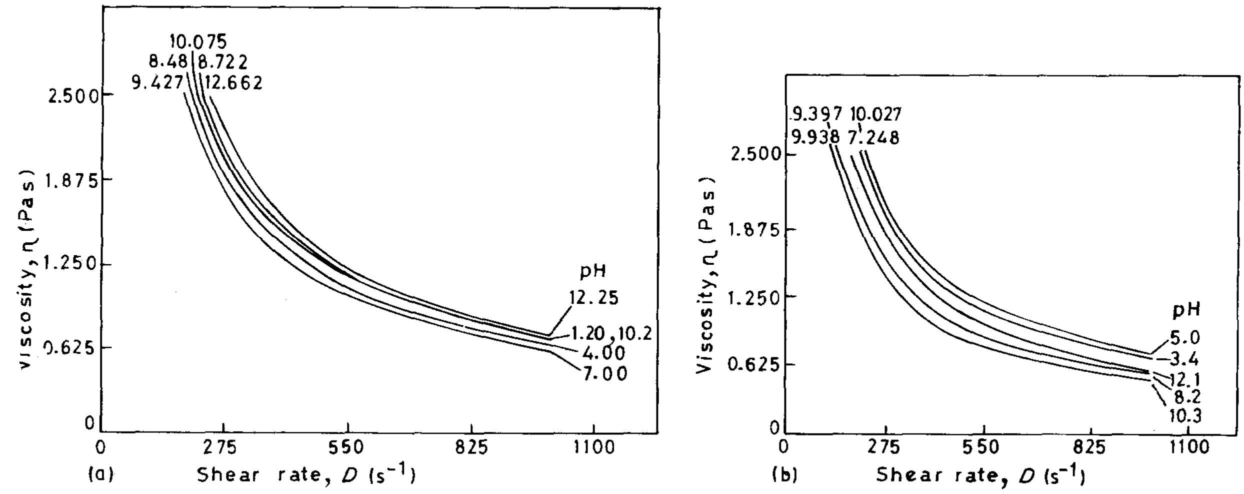


Figure 6 Plots of viscosity against shear rate for suspensions (75 wt % solids content) with pH values indicated; (a) ZrO_2–ethanol system; (b) ZrO_2–ethanol–deflocculant system.

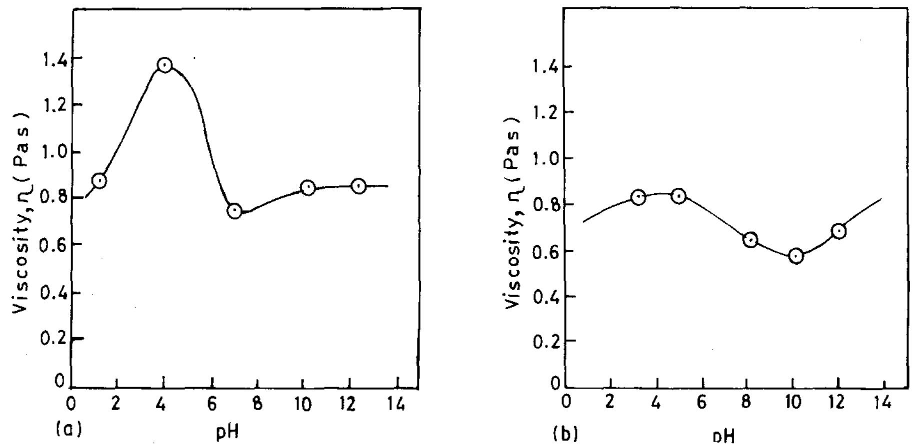


Figure 7 Plots of viscosity against several pH values (at constant shear rate $D = 825\,s^{-1}$); (a) ZrO_2–ethanol system; (b) ZrO_2–ethanol–deflocculant system.

i.e. hysteresis type. This is called thixotropy while the original flow curve can be repeated, then it is non-thixotropy. The nature of the thixotropy graph is shown in Fig. 3c. Observations of thixotropic effect, slip and sedimentation density at several pH values are given in Table I.

Fig. 6a and b show the rheological behaviour at several pH values for the ZrO_2–ethanol system with and without deflocculant. Fig. 7a and b give the viscosity dependence of various pH values at constant shear rate ($D = 825\,s^{-1}$). In both systems the viscosity is nearly 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 a polar organic liquid, such as ethanol, is similar to that in water. The preliminary difference in the repulsion force of the electrical double layer is due to the dielectric constant ($\varepsilon_{H_2O} = 80$ and $\varepsilon_{ethanol} = 24$) of the liquid. The thickness of the diffuse double layer is proportional to the square root of dielectric constant. Because most organic liquids have lower dielectric constants than water, flocculation occurs at lower counter-ion concentration 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 ZrO_2–water–deflocculant system. The viscosity values have been determined at a constant shear rate of $D = 100\,s^{-1}$. In this system the highest green density was 48% theoretical at pH 10. The theoretical density of a 80% tetragonal ZrO_2 and 20% monoclinic ZrO_2 mixture is $6.09\,g\,cm^{-3}$.

In the ZrO_2–ethanol systems the viscosity was very high; therefore no usable specimens could be cast.

3.4. Deterioration of the mould

When a slip poured into a plaster mould, liquid is drawn in to its pores by capillary action. The casting rate of a slip is partially determined by mould permeability. This affected by such variables as the plaster/water ratio in the initial mix and the amount of water in the mould from previous use. Initially, the casting rate is slow but soon becomes faster because of the dissolving action of water on gypsum which increases the permeability. Deflocculating agents in the slip cause deterioration of the mould by chemical corrosion, therefore the mould was dried between

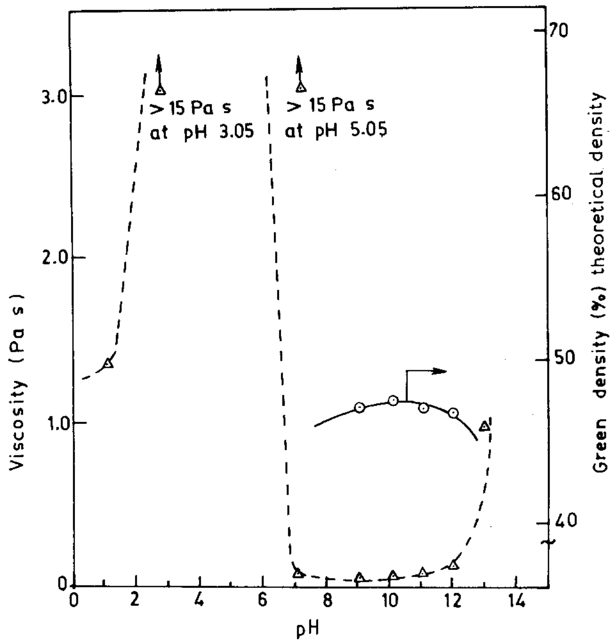


Figure 8 Plots of viscosity and green density against pH values for the ZrO_2–water–deflocculant system at constant shear rate $D = 100\ s^{-1}$.

castings, and the entire mould had to be removed after about four castings because the pores became plugged.

The suspension was cast in a 60 mm × 60 mm × 6 mm plaster mould, and after 2 h the cast solid was removed from the mould and dried at room temperature for 1 day, and then at 110 °C for 1 day. Because little shrinkage (~ 1.7%) occurs in the mould, an absolutely smooth surface is necessary to permit removal of the cast solid piece from the mould. Acidic slips (in the ZrO_2–water system) are found to be detrimental to the moulds, causing the formation of minute pits or holes on the mould surface after casting. Basic slips (in the ZrO_2–water–deflocculant system), 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. ZrO_2–water–deflocculant gives good solid casting behaviour compared to ZrO_2–water and ZrO_2–ethanol–deflocculant systems. In the ZrO_2–water–deflocculant system the highest green density was observed at pH 10 (see Fig. 8). This is generally due to the increase in the green densities with decreasing casting rate constant [36].

4. Conclusions

1. X-ray diffractometry, particle size distribution, scanning electron microscopy and BET specific surface area measurements show that ZrO_2 powder B (3-YS$^+$) is good for slip casting.

2. Preliminary tests on the rheological behaviour show 75 wt % ZrO_2 (3-YS$^+$) powder, 25 wt % distilled water or ethanol and 0.40 wt % Dolapix CE 64 gives minimum viscosity and Newtonian flow behaviour.

3. Satisfactory castable slip can be obtained by deflocculation of the treated ZrO_2 powder with HCl and tetramethyl ammonium hydroxide.

4. Rheological properties show minimum viscosity for the system ZrO_2–water at pH 2–5, ZrO_2–water–deflocculant at pH 7–12, while ZrO_2–ethanol and ZrO_2–ethanol–deflocculant systems do not show a minimum viscosity.

5. 75 wt % ZrO_2 (3-YS$^+$) powder, 25 wt % distilled water, 0.40 wt % Dolapix CE64 and at pH = 10.01 and 11.09 is recommended as a good castable slip.

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