Influence of deflocculants on the characteristics of alumina bodies obtained by slip casting

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Conformation of alumina bodies with differential porosities was carried out using a slip-casting technique. Preliminary results, showing the relationship between changes of rheological properties of the suspensions caused by pH variation and wall characteristics of the bodies, have been reported previously. The research was continued in order to establish the dependence of the structure of flow units in suspension on type and amount of deflocculants and its influence on the porosity of the walls obtained by slip casting. Rheometry, sedimentometry and electrophoresis were used to characterize the suspensions. Mercury porosimetry enabled the determination of porous structure. Results show a strong correlation between the properties of the suspensions and the characteristics of the presintered bodies and corroborate the possibility of fabrication of articles with differential porosities.

1. Introduction

The main objective of this investigation was the obtention, by slip casting, of alumina bodies with differential porosities, so that impregnation with molten metal can be carried out. It was therefore necessary to study the factors that influence the porosity of cast walls, namely, degree of deflocculation of the starting suspension, water/plaster ratio and casting time. The first factor to be studied was the degree of deflocculation of alumina suspension.

Previous work [1] has been carried out on bodies obtained from suspensions where the degree of flocculation was varied by modifying the pH of suspensions. Results obtained showed that flow unit structure in suspension influences the porosity of the cast wall: voluminous, low-density flocs lead to more porous walls; dense flocs lead to less porous walls. The conclusion was that the structure in suspension is a determining factor of the samples obtained by slip casting.

In the present work it was decided to evaluate how deflocculants acted on alumina-particle aggregation in aqueous suspensions.

2. Basic principles

Oxide particles in aqueous suspension carry a charge which is dependent on the pH of the suspension and the adsorption of ions. This charge results in the formation of an electrical double layer around the particles and an isoelectric point may be defined at a certain pH value [2]. Interaction between the particles in suspension is dependent on the nature and thickness of the electrical double layers associated with them. When the ionic strength of the suspending medium is low, particles with similar electrical double layers repel each other. Thus, at pH values away from the isoelectric point, there is no structure in suspension. At the isoelectric point, there is no repulsion between the particles. Van der Waals forces bring them together and flocculation occurs.

There have been ample efforts to study and optimize the choice of various dispersants [3]. By adsorption onto the surface of alumina particles these dispersants will impart either electrostatic repulsion or steric hindrance to deflocculate the suspension [4]. When the dispersant is a polymer or polyelectrolyte, a steric barrier can be obtained between the particles, through adsorption of a polymer layer on the particles surfaces [5]. 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 [6]. If the polymer is charged, the particle charge will decrease or increase, depending on the charge of the polyelectrolyte.

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 [7].

Most previous studies in various dispersants are mainly concerned with their efficiency [8].

The characteristics of the flocs in suspension are determined, among other factors, by the energy of the links between the particles [9]. They are voluminous, porous and of low density, when particle attraction is strong and dense when particle attraction is weak.

Chou and Senna [10] attempted to correlate densities of cast bodies with the "bulkiness" of the flocs formed in suspension. Chou and Lee [11] used alumina powder as a model to study the effects of different dispersants on the rheological and casting behaviour of concentrated suspensions. Previous results [1] allow us to explain the dependence of the Bingham yield stress and the plastic viscosity of alumina suspensions on the pH of the suspending medium, in terms of variations on the surface potential of particles and variation of flow unit size and concentration, respectively. The dependence of flow unit size with pH was explained in terms of the elastic floc model and related to the particle–particle interactions. We also concluded that flow unit structure in suspension influences the porosity of the cast wall: voluminous, low-density flocs lead to more porous walls, whilst dense flocs lead to less porous walls.

3. Experimental procedure

3.1. Material

The starting material was an alumina powder (Reynolds, RC 172 DBM) which has already been characterized [12]. Hydrochloric acid, sodium hydroxide, Dolapix PC67, Dolaflux B and Dolaflux SP were used to vary the degree of flocculation/deflocculation of the particles in suspension.

3.2. Equipment and procedure

Rheological properties of aqueous suspensions with a 90 wt % concentration were measured with a Ferranti–Shirley cone and plate viscometer reaching a maximum speed of 1000 r.p.m., following stirring in a mechanical agitator for a period of 30 min.

Particle-size analysis for the determination of flow properties was carried out in dilute suspensions (0.01 wt %) using a sedimentograph (Lumosed-RETCH).

Electrophoretic mobilities were determined in dilute suspensions (0.01 wt %) using a Rank Brothers microelectrophoresis apparatus and flat cells. All dispersions that were used in the electrophoresis experiments were prepared in 10^{-3} mol dm^{-3} KCl solution, in order to maintain a constant electrical double-layer thickness.

The conformation was carried out pouring the slips into plaster moulds with a plaster:water ratio of 1.4:1. Cylindrical pellets with differential porosities were obtained by pouring first a flocculated suspension into the mould followed by a deflocculated one. Moulds were filled with suspensions and drainage of excess of suspension was carried out after formation of the wall.

After mould release, the samples were dried at 40 °C for 2 h and then at 110 °C to constant weight.

Pre-sintering at 1450 °C for 3 h was carried out followed by cutting of the samples and analysis by mercury porosimetry.

4. Results and discussion

4.1. Effect of pH

Previous work [1] has shown that the structure in suspension is a determining factor of the structure of samples obtained by slip casting.

The effect of pH, as modified by 10^{-1} M HCl and 10^{-1} M NaOH solutions, upon the Bingham yield value and upon the plastic viscosity of 90 wt % suspensions is shown in Figs 1 and 2, respectively. From these graphs it can be seen how rheological properties of alumina suspensions vary with pH. These results indicate an isoelectric point around pH = 8.0. This conclusion is in agreement with other authors [13].

From sedimentation measurements we also found that when the pH varies, the maximum diameter and percentage of flow units in suspension allowed us to correlate the last two properties with the structure in suspension, as can be seen from Figs 3 and 4.

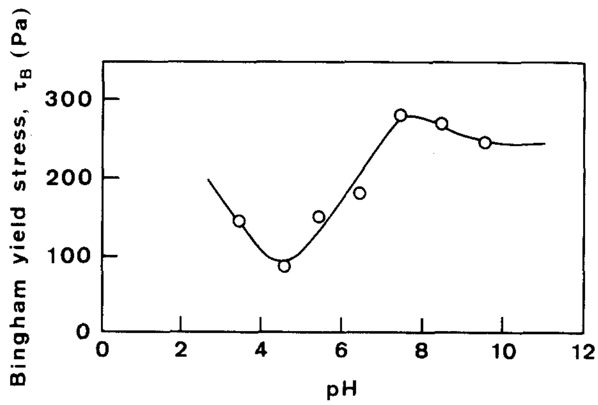

Figure 1 Variation of Bingham yield stress with pH of suspensions (90 wt % solids).

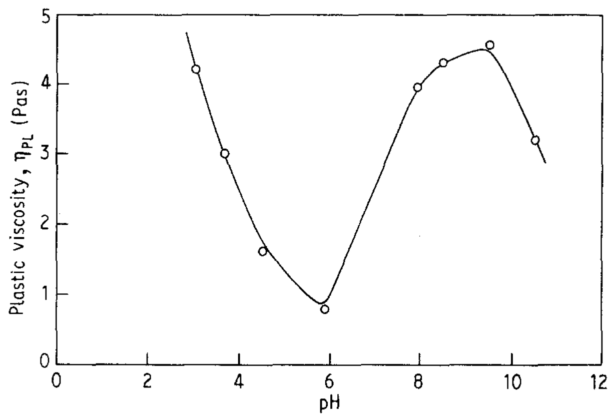

Figure 2 Variation of plastic viscosity with pH of suspensions (90 wt % solids).

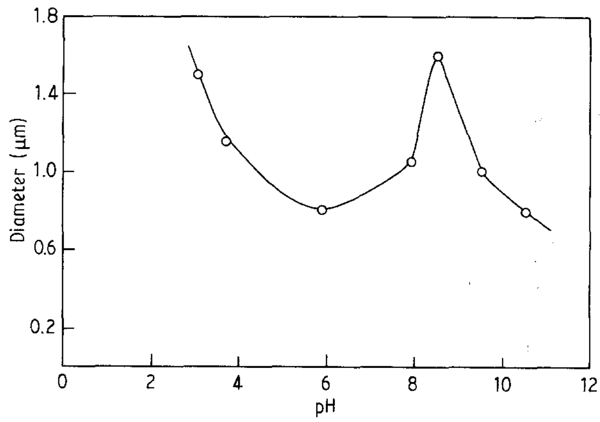

Figure 3 Variation of flow unit maximum diameter with pH of suspensions (0.01 wt % solids).

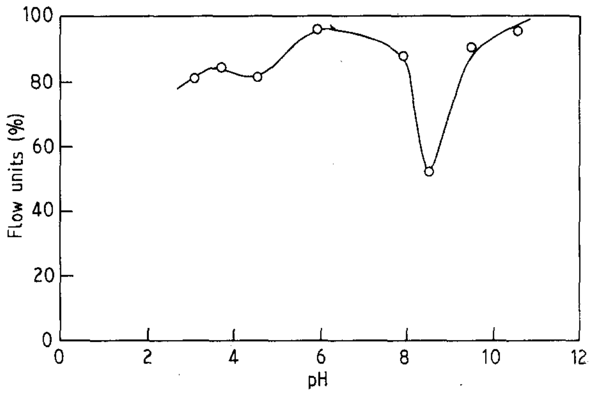

Figure 4 Variation of percentage of flow units below 0.8 μm with pH of suspensions (0.01 wt % solids).

4.2. Effect of deflocculants

The effect of Dolapix PC67, Dolaflux B and Dolaflux SP upon the same suspensions is shown in Fig. 5. The following conclusions can be drawn.

1. With Dolapix PC67 we can observe a strong decrease of Bingham yield value, followed by a very slight increase, as over flocculation occurs.

2. A similar trend is observed with Dolaflux B, although a higher concentration of deflocculant is necessary to obtain the same effect.

3. This also applies to Dolaflux SP, although the strong over deflocculation that occurs when present in excess does not recommend its use.

Comparing these graphs with that showing variation of Bingham yield stress with pH (Fig. 1), we can conclude that the addition of deflocculant is much more effective in promoting dispersion than the simple variation of pH of the suspension. This conclusion is in agreement with other authors [14]. Thus the adsorption of polyelectrolytes modify more strongly the characteristics of electrical double layers of the particles and the interaction between them.

The results showed that Dolapix PC67 was the best deflocculant. Results obtained from sedimentometry cannot be used because the degree of deflocculation is too high, therefore particles are well separated and sediment quickly, and there are no flocs in suspension. The interaction between alumina particles in suspension in the presence of Dolapix was then studied indirectly by electrophoresis. This study was conducted at different temperatures, so that results could be applied to shop-floor conditions.

4.3. Electrophoretic mobility results

Fig. 6 shows the variation of electrophoretic mobility for suspensions without deflocculants at 25, 30, 35 and 40 °C. From these graphs it can be concluded that an increase in temperature has two effects:

(a) to decrease the isoelectric point from a pH value around 8 to 6;

(b) to increase mobility of the ions (particularly of H^+ ions) from a value of about two units of mobility to a value around 6.

So, it can be said that an increase in temperature of suspension favours the liberation of H^+ ions from the surface, as is indicated by published results [15]. This effect is very important because it shows that it is possible to act over the slip-casting process just by varying the temperature.

To study the effect of the amount of deflocculant upon electrophoretic mobility three concentrations were chosen: two of them close to its maximum effect as deflocculant (0.01% and 0.02%) and one in the region of over deflocculation (0.05%). The results are shown in Figs 7–9.

Comparing these results with results obtained without deflocculant, we can see two main things: a decrease in the isoelectric point; and an increase in the electrophoretic mobility at high pH values. In addition we can conclude that increasing the temperature results in a decreasing isoelectric point, as was observed for suspensions without deflocculant. An increase in the amount of Dolapix to 0.02% results in

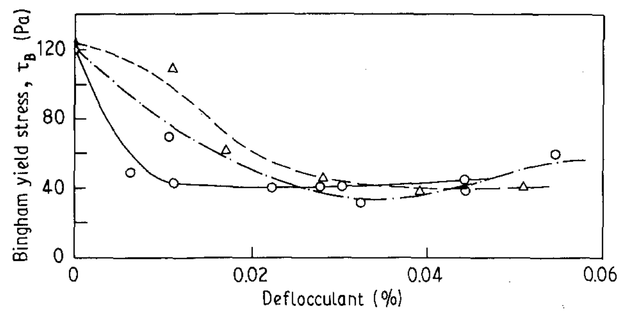

Figure 5 Variation of Bingham yield stress of suspensions (90 wt % solids) with the concentration of deflocculant (referred to dried solid weight). (○) Dolapix PC67, (△) Dolaflux B, (□) Dolaflux SP.

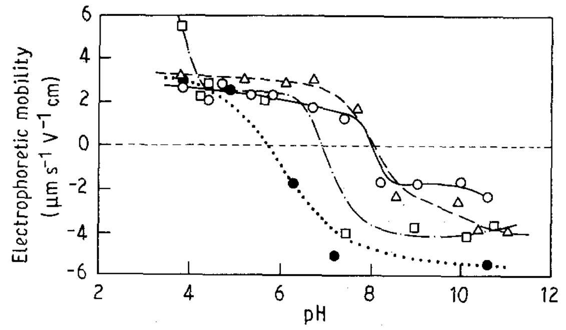

Figure 6 Variation of electrophoretic mobility with pH of suspensions (0.1 wt % solids) at (○) 25, (△) 30, (□) 35 and (●) 40 °C. Ionic strength = 10^{-3} mol dm^{-3}.

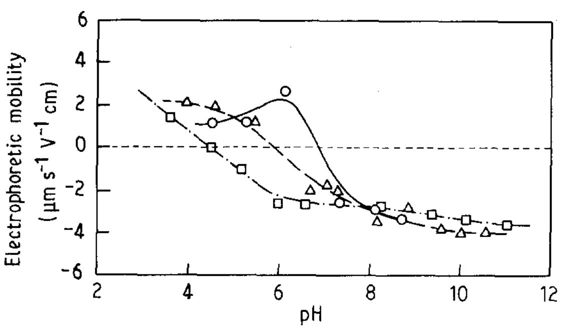

Figure 7 Variation of electrophoretic mobility with pH of suspensions (0.1 wt % solids; 0.01 wt % Dolapix PC67, referred to dried solid weight) at (○) 25, (△) 30 and (□) 35 °C. Ionic strength = 10^{-3} mol dm^{-3}.

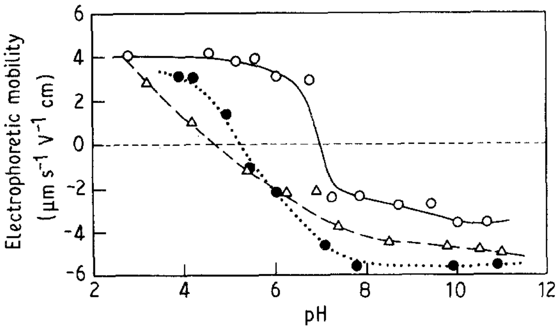

Figure 8 Variation of electrophoretic mobility with pH of suspensions (0.1 wt % solids; 0.02 wt % Dolapix PC67, referred to dried solid weight) at (○) 25, (△) 30 and (●) 40 °C. Ionic strength $= 10^{-3}$ mol dm^{-3}.

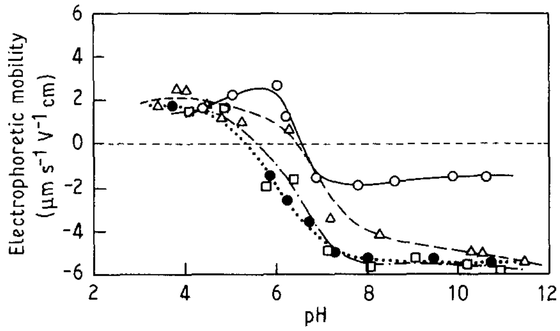

Figure 9 Variation of electrophoretic mobility with pH of suspensions (0.1 wt % solids; 0.05 wt % Dolapix PC67, referred to dried solid weight) at (○) 25, (△) 30, (□) 35 and (●) 40 °C. Ionic strength $= 10^{-3}$ mol dm^{-3}.

the same effect and higher mobilities, as can be seen from Fig. 8. On continuing to increase the amount of Dolapix to 0.05%, the effect is less pronounced, as can be seen from the graphs in Fig. 9.

These results show that changes in pH, deflocculant concentration and temperature of the suspension induce modification of the electrophoretic mobilities of the particles in suspension. This reflects different characteristics of electrical double layers which, in turn, result in different kinds of interaction between the particles, and thus different degrees of deflocculation and different types of flocs.

4.4. Porosity measurements

In order to confirm previous results with suspensions where the degree of deflocculation was modified just by varying the pH [1], it was decided to pre-sinter some samples and carry out porosity measurements. Figs 10 and 11 show the variation of specific surface area and the porosity of pre-sintered alumina pellets obtained by slip casting of a suspension with different pH values.

It can be seen that both curves are similar to those which relate Bingham yield value and plastic viscosity with pH (Figs 1 and 2). They are also similar to those which show the variation of floc size in suspension with pH (Figs 3 and 4).

Using Dolapix PC67 as a deflocculant it can be seen from Figs 12 and 13 that specific surface area and

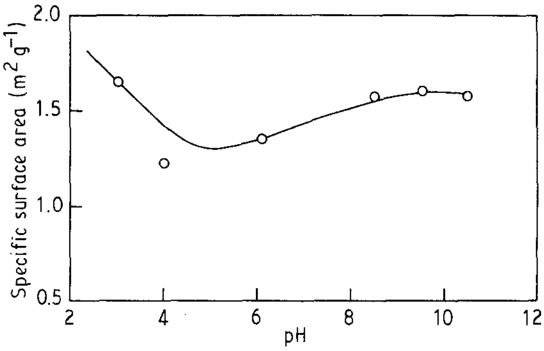

Figure 10 Variation of specific surface area of sintered pellets with pH of suspensions (90 wt % solids).

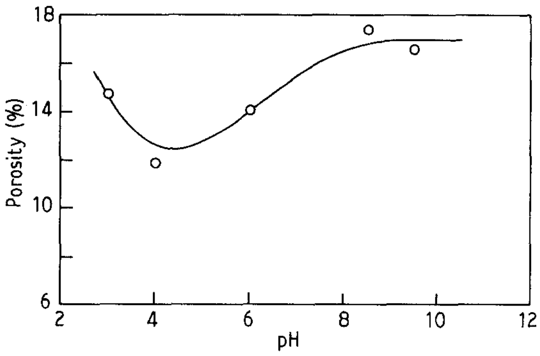

Figure 11 Variation of porosity of sintered pellets with pH of suspensions (90 wt % solids).

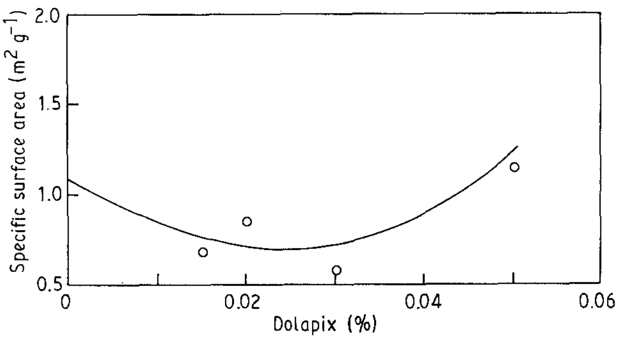

Figure 12 Variation of specific surface area of sintered pellets (suspensions 90 wt % solids) with the concentration of Dolapix (referred to dried solid weight).

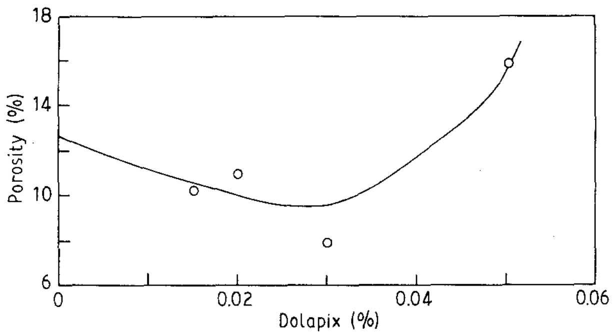

Figure 13 Variation of porosity of sintered pellets (suspensions 90 wt % solids) with the concentration of Dolapix (referred to dried solid weight).

porosity of pre-sintered pellets follow a close relation to the degree of deflocculation, i.e. floc characteristics.

From these figures the following conclusions can be drawn.

1. For suspensions without Dolapix, a greater degree of deflocculation leads to pre-sintered bodies with a small porosity and specific area, as expected.

2. A similar result is obtained for suspensions with Dolapix (better deflocculation implies less pores and a smaller specific area).

3. Comparison of results for bodies obtained from suspensions with and without addition of Dolapix allow the conclusion that this deflocculant is much more effective than the pH in separating particles, as could be concluded by the analysis of yield-stress variation.

5. Conclusions

From the present investigation the following conclusions can be derived.

1. There are various ways in which we can control structure in suspension, namely, pH, deflocculant (type and amount) and temperature.

2. The control of the structure in suspension enables the control of the structure obtained by slip casting.

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