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# The Influence of Solid Type and Content on the Rheological Behaviour of Coagulated Slurries and Their Bearing on the Consolidation by Pressure Filtration

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***Abstract***

*The present work is part of a model study aimed at upgrading the technique of creating porosity within a ceramic body via the incorporation of organic particles, used in traditional ceramics, exploring at the same time the colloidal processing from coagulated slurries. The method described by Lange et al., based on the manipulation of short-range repulsive (lubricating) hydration force and long-range attractive van der Waals force, was used to pack to a high density a bimodal mixture of submicron ceramic particles (matrix) and larger organic particles (inclusions) during consolidation by pressure filtration of dispersed suspensions coagulated by added electrolyte. The results reported show how the rheological behaviour of dispersed ceramic slurries changes through coagulation by added electrolyte, the role played by added organic particles and how they affect the coagulation state, bearing on the conceptual relation between interparticle potential and the observed rheological behaviour. © 1996 Elsevier Science Limited.*

## Background

Other than counteracting the mechanisms that favour densification, the obvious alternative to create 'artificial' porosity within a ceramic body is the introduction of an expendable constituent in the ceramic mixture. Whereas in traditional ceramics high levels of macro porosity are usually obtained via the incorporation of particulate organic compounds, the majority of engineering (structural) foams, are produced by the replica technique, using a foamed polymer as a precursor. This technique essentially consists of dipping the polymer foam into a slurry containing an appropriate binder and ceramic phases, followed by pressureless sintering at elevated temperatures. However, the cellular ceramics thus produced contain varied microstructural flaws, mostly due to processing, and present comparatively low strength and fracture toughness.[1]

The present work is part of a model study aimed at upgrading the technique of creating porosity via the incorporation of organic particles, used in traditional ceramics, exploring at the same time the colloidal processing from coagulated slurries. The ceramic material chosen was a submicron high-alumina composition,[2] known to sinter at 1400°C for 4 h, from dry-pressed powder compacts, reaching ~97% relative density and a cold modulus of rupture of ~280 MPa. As for the pore precursor, emulsion PVC was used, readily available as roughly spherical particles of ~2 μm average diameter.

## Introduction

The colloidal treatment of ceramic powders minimizes the occurrence of microstructural inhomogeneities through the manipulation and control of the interparticle forces. The nature of these forces was elucidated in the works of Derjaguin and Landau, and Verwey and Overbeek, which have become the cornerstone of colloid science and known as the DLVO theory. To take full advantage from the colloidal methods, the consolidated body should be formed directly from the suspension, for example by pressure filtration. To do this, the suspension should, ideally, be stable and easy to manipulate, with a high volume fraction of solids, viscous enough to prevent mass segregation, and produce a high particle packing density in the consolidated body.

In spite of the high particle packing density achieved from dispersed suspensions, the latter have a narrow stability range. However dispersed suspensions can be stabilized via coagulation, as shown by Lange *et al.*[3,4] in their work on the colloidal consolidation of aqueous alumina slurries without the use of binders. Their results demonstrate the existence of a short-range repulsive hydration potential between the alumina particles in suspension at low pH and high electrolyte concentration. In other words, the viscosity of the alumina dispersed suspensions can be significantly augmented by the addition of suitable counterions which screen the repulsive interparticle electrostatic potential. Coagulated slurries are unique in that their rheological behaviour is similar to that of flocced slurries but, unlike flocced slurries, they can be packed at lower pressures to densities similar to those achieved with dispersed slurries. Thus, the high packing density in the consolidated body is not affected due to the strong repulsive hydration layer build up, which also explains the liquid-like rheology of the resulting saturated consolidated body.

Despite the extensive work carried out by Lange *et al.*[3,4] little is known about the effect of added organic particles on the rheological behaviour of coagulated ceramic slurries. Previous work has shown[5] that the introduction of much bigger PVC particles (suspension PVC, average diameter ≈80 μm) alters the rheology of coagulated slurries containing the same ceramic solids only inasmuch as the average particle size increases, decreasing the viscosity of the slurry, and a denser packing of particles is produced in the consolidated body. The introduction of organic particles, to create artificial porosity, together with the colloidal processing of coagulated slurries of ceramic powders, was shown to be a reliable and reproducible technique to produce porous ceramic bodies with controlled porosity, adequate for engineering applications. The purpose of this work was to investigate further whether the addition of particles of widely different nature but comparable sizes altered the rheological behaviour of the slurries and its implications on the slurries' consolidation by pressure filtration.

## Experimental Procedure

The selected ceramic composition[2] was prepared from submicron Alcoa CT3000SG alumina (96 wt%) and equal amounts of Merck titanium and manganese oxides. Aqueous slurries containing 20 vol% solids were produced by mixing the fixed ceramic composition, alone or with variable volume proportions of emulsion PVC (Companhia Industrial de Resinas Sintéticas S. A., 3861 Estarreja, Portugal) (≈2 μm average diameter), with distilled water, dispersed at pH≈4 and coagulated with $NH_4Cl$.

The zeta potential and the electrophoretic mobility of the various powders and their mixtures, as a function of pH, were first determined using a MALVERN Zetasizer 4, series 7032 multiangle correlator apparatus, to access the respective pH dispersion range.

Steady-state viscosity measurements, as a function of shear rate, were carried out using a Carri-Med CSL rheometer, cone and plate type (cone angle 1° 59', cone diameter 2.0 cm), starting from dispersed slurries (pH≈4) to which increasing amounts of $NH_4Cl$ were added, to determine the critical coagulation concentration. Each sample was presheared to 5 Pa for 15 s, followed by 1 min equilibration time (rest); the viscosity was then measured by first raising the shear stress up to the maximum of 20 Pa (2 min), hold for 15 s, and lowering it back to close to zero (2 min). The whole procedure was automatically repeated three times and an average viscosity versus shear rate curve was produced.

## Results and Discussion

Figure 1 shows scanning electron micrographs of the alumina (the major constituent of the ceramic mixture) and the PVC particles. Their morphology and size can thus be compared.

The measurement of the zeta potential and the electrophoretic mobility of the various ceramic powders and their mixture, as a function of pH (Fig. 2), showed that, although titanium and manganese oxides have isoelectric points in the pH range from 4 to 5, the isoelectric point of the ceramic mixture was very near to that of alumina alone, and the corresponding slurry was fully dispersed at pH<4.

The prevalence of the repulsive particle network causes the viscosity of the dispersed slurry containing the mixture of ceramic particles only (Fig. 3) to be low and relatively independent of the shear rate, showing a nearly Newtonian behaviour. For pH values near the isoelectric point of the ceramic mixture, a strong attractive network of particles is formed, with high yield strength, and the flocced slurry exhibits a strong shear-thinning behaviour and very high viscosity.

With salt addition to the dispersed slurry, a weakly attractive network is initiated, with

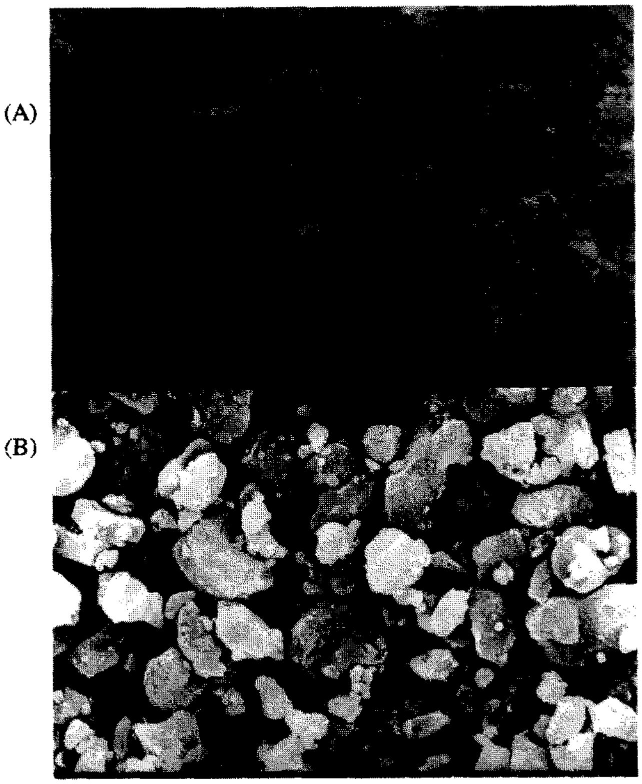

**Fig. 1.** Scanning electron micographs of (A) PVC and (B) alumina particles (bar=2 μm).

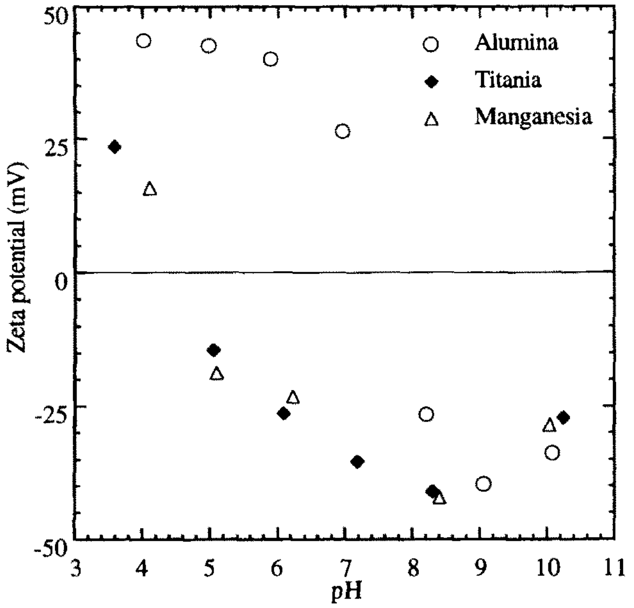

**Fig. 2.** Zeta potential as a function of pH for the various ceramic particles.

increasing yield strength and viscosity, until an electrolyte concentration is reached, the critical coagulation concentration, above which no significant effect on the slurry rheology was observed. Again, the slurry viscosity became strongly dependent on the shear rate, showing a shear-thinning behaviour, but the attractive particle networks produced by adding salt are much weaker than that of the flocced slurry.

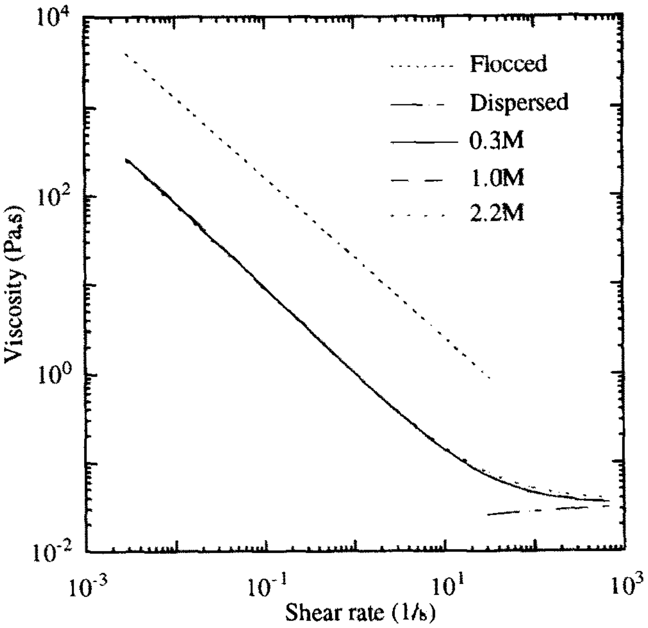

**Fig. 3.** Effect of shear rate on the viscosity of slurries containing 20 vol% solids, ceramics only, dispersed, flocced and with varied contents of added $NH_4Cl$.

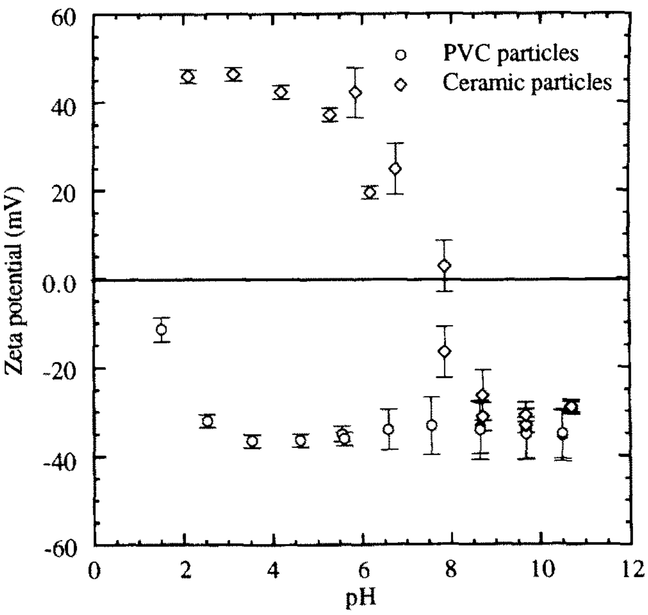

**Fig. 4.** Zeta potential as a function of pH for ceramic particles and PVC particles.

It was observed that the zeta potential of the mixture of ceramic powders alone (Fig. 4) is positive at low pH, decreases to zero (the isoelectric point) at a pH near 8, and then becomes negative; on the other hand (Fig. 4), the zeta potential of the PVC particles alone is hardly ever positive, with an isoelectric point at a pH below 2. Given that the isoelectric point of the PVC particles and the ideal dispersion pH for the ceramic slurries are in the same range, when the organic particles are added to the ceramics dispersed slurry a significant fraction of PVC particles might indeed be flocced. As a consequence, instantaneous flocculation can be observed, with a sharp increase in viscosity.

It is envisaged that this particular combination of opposite natures lends extra importance to the screening ability of the hydration layer produced by coagulation, particularly below the critical coagulation concentration and for higher PVC contents. All slurries containing PVC particles besides ceramics, with or without added salt, show high viscosities and shear-thinning behaviour. The immediate effect of the added electrolyte is to decrease the viscosity and the yield strength of the slurry (Figs 5 and 6). It can be hypothesized that strong, albeit smaller, mixed agglomerates form when the organic particles first come into contact with the formerly dispersed ceramic particles, leading to flocculation. The effect will grow stronger with increasing fraction of PVC in the solids, as shown in Fig. 6. The role of the added salt will first be to break those agglomerates. In other words, while the electrolyte transforms a repulsive particle network into a weakly attractive network when only ceramic particles are present, a similar network is produced from a strongly attractive one when both types of particles are present. It is possible that under partial coagulation conditions a misleading rheological behaviour can be observed, and the measured viscosity might be comparable to that of fully coagulated slurries. Further work is being carried out and it is expected that the analysis of shear stress versus shear rate curves and the measurement of the change in the electrical conductivity of the slurries might further the understanding of the rheological behaviour of coagulated slurries.

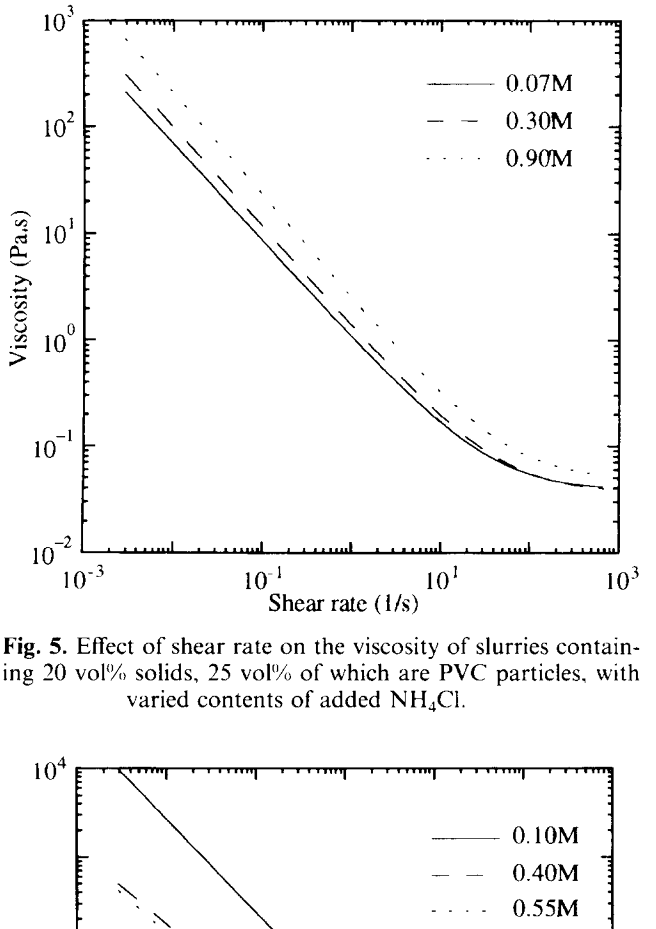

**Fig. 5.** Effect of shear rate on the viscosity of slurries containing 20 vol% solids, 25 vol% of which are PVC particles, with varied contents of added $NH_4Cl$.

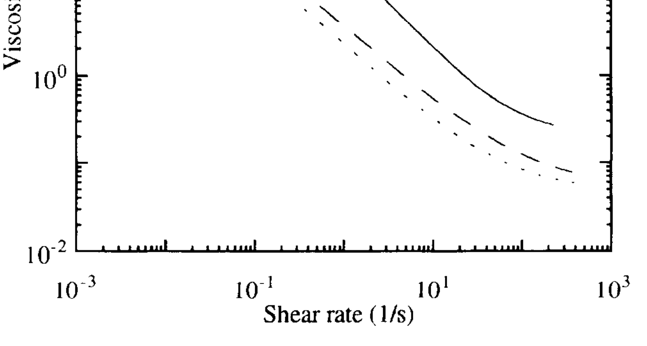

**Fig. 6.** Effect of shear rate on the viscosity of slurries containing 20 vol% solids, 50 vol% of which are PVC particles, with varied contents of added $NH_4Cl$.

## Conclusions

The present work shows how the rheological behaviour of dispersed ceramic slurries changes through coagulation by added electrolyte, the role played by added organic particles of slightly larger size, and how they affect the coagulation state. Previous work had shown[5] that the introduction of much bigger organic particles altered the rheology of coagulated slurries containing the same ceramic solids only inasmuch as the average particle size increased, decreasing the viscosity of the slurry, and producing a denser packing of particles in the consolidated body. The results reported might bear on the conceptual relation between interparticle potential and particle packing and the observed behaviour will affect the consolidation process by pressure filtration and rheology of the consolidated body.

## Acknowledgements

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