

# Preventing ageing on Al<sub>2</sub>O<sub>3</sub> casting slips dispersed with polyelectrolytes

C. A. GUTIÉRREZ, R. MORENO

*Instituto de Cerámica y Vidrio, CSIC, 28500, Arganda del Rey, Madrid, Spain*

Slip casting process needs a highly stabilized and well-characterized suspension, which involves not only the traditional rheological measurements, but an estimation of the colloidal stability in terms of interaction potentials between particles. For electrosterically stabilized ceramic suspensions the calculation of the steric contribution is not well described in the available theories because they are developed for ideal conditions where many variables affecting the stability of concentrated suspensions are neglected. In this work, alumina suspensions were prepared at 75 wt% solids and characterized considering the potential energy curves and the rheological behaviour. The main objective is to select the proper dispersing conditions in order to prevent ageing of the slips, which is an important problem in any manufacturing cycle. For the polyacrylate dispersant used it was shown that a concentration of 0.8 wt% provided the lowest viscosity, allowed ageing prevention and resulted in higher green and sintered densities. © 2000 Kluwer Academic Publishers

## 1. Introduction

In colloidal shaping of ceramics, an essential requirement for scaling-up to industrial processes is to assure the constancy of slip properties with time. The ageing effect can promote important differences in the final properties of the product (e.g. density and microstructure) because a variation in the colloidal state of the slip leads to a different particle packing. The packing behaviour is a function of the capability of the particles to remain separated from each other. This repulsion is enhanced by the action of a dispersant, but changes in the particle surface/dispersant interaction can occur with time. The adsorption of polyelectrolytes onto particles surfaces is a dynamic process that needs a certain amount of time to reach saturation, but at longer times the adsorption state can also change (desorption, interpenetration of adsorbed layers, settling of particles, etc) promoting different interactions among particles, which directly influence the rheological properties of slips.

The electrosteric stabilization mechanism is widely used in slip forming processes. This mechanism basically depends on the adsorption of a surfactant or a polymer to prevent coagulation. These polymer molecules have an organic chain that attaches to the particle surface thus impeding particle contact and therefore avoiding the primary minimum in the pair potential curve. In addition, they have a charged end that contributes to stabilization by means of an electrostatic mechanism.

As particles approach each other, the adsorbed layers start to overlap and this results in an osmotic pressure that pushes particles apart. In addition, the presence of charges in the polymer chains provides a high potential

energy at large distances. In the simplest interpretation, the particle behaves as a charged particle whose radius is increased by the thickness of the adsorbed layer.

If the slip is stable, very little interpenetration of the layer occurs and the simplest approximation is to assume a collision diameter  $d$ , as  $d = 2(a + \delta)$ ,  $a$  being the particle radius and  $\delta$  the thickness of the adsorbed layer.

In this work it is assumed that particles are covered by a monolayer of adsorbed molecules. From the dispersant molecular weight and structure, the length of the chains has been estimated to be  $\delta = 9$  nm.

The aim of this work is to study the time stability of aqueous Al<sub>2</sub>O<sub>3</sub> concentrated casting slips dispersed with a polyacrylic acid based polyelectrolyte. In a first step, the dispersing conditions are controlled in order to improve slip homogeneity and in order to compare the rheological properties with the particle potential curves of the slips at different dispersant concentrations in fresh suspensions. Subsequently, the ageing behaviour was studied by means of rheological measurements. The green and sintered characteristics of the cast bodies are related to the rheology in both the fresh and the aged slips. By controlling the proper dispersing conditions, ageing can be prevented, allowing a low viscosity to be maintained with time, as well as a high green density.

## 2. Experimental procedure

A high purity alumina powder (>99.99%  $\alpha$ -Al<sub>2</sub>O<sub>3</sub>, Condea HPA 0.5, USA) was used in the formulated slips. It had a mean diameter size of 0.3  $\mu$ m as measured

with a laser particle size analyser (Mastersizer, Malvern instruments, U.K.), and a BET surface area of 8 m<sup>2</sup>/g. Deflocculation was carried out using an ammonium salt of a polyacrylic acid (Duramax, D-3005, 35 wt% active matter, Rohm and Haas, USA, molecular weight of 2400 daltons). The dispersing liquid was deionized water. The milling process was carried out using batch sizes of 300 g of slurry, milled with Al<sub>2</sub>O<sub>3</sub> jar and balls. Slips were prepared by first mixing the dispersant and water and stirring for 10 minutes. The powder was slowly added while maintaining stirring at 200 rpm for 20 minutes and then the mixture was ball milled. The milling time was 6 h for all the batches, in order to promote good homogenisation and particle deagglomeration.

The as-prepared slips were characterized by means of zeta potential and viscosity measurements. These slips were maintained at low speed agitation in a closed flask in order to check the evolution of the rheological behaviour with ageing time, up to 48 h. The solid loading of all fresh and aged slips was 75 wt% (43 vol%).

Electrophoretic mobility measurements were carried out using a mass transport analyser (Micromeritics, USA). The  $\zeta$ -potential values were calculated from electrophoretic mobility values determined on slurries containing different dispersant concentrations after diluting to a solid content of 20 wt%. The pH values were measured prior to the mobility determinations, using a pH-meter (Metrohm AG, Switzerland). Rheological properties were determined using a controlled rate and controlled stress rheometer (R50, Haake, Germany) with a plate - double cone measuring system (35 mm diameter) and a closing lid to prevent evaporation and possible variations in composition. Deflocculation curves were determined by changing the dispersant content from 0.5 to 1.5 wt% (referred to dry solids). The different slips (fresh and aged) were cast on plaster of Paris moulds to form solid disks 2 cm in diameter. Green casts were left in air 48 h for drying before measuring the green density by Hg immersion. Samples were sintered at 1550°C/2 h in order to evaluate the effect of ageing on the final density and to select the most efficient dispersing conditions in the slip for preventing ageing damage in the sintered compacts.

### 3. Results and discussion

#### 3.1. Stabilization of the slips

It is well known that steric hindrance operates at short separation distances between particles. This is useful to prevent direct contact between particles surfaces in suspensions with high solids concentration. The main problem for an effective control of the total interaction arises from the actual difficulties to determine the pair potential curve of those suspensions, as it depends on a large number of variables [1].

On the other hand, electrostatic stabilization provides a long-ranged repulsive effect that has been well described by the DLVO theory. According to this theory it is possible to estimate the pair potential curve as a function of separation distance [2, 3] as the sum of an attractive van der Waals term and a repulsive

electrostatic term. In the case of slips dispersed with polyelectrolytes, at short distances the steric hindrance impedes the particles from touching each other. For long distances, and considering the shortness of the attached polyelectrolyte chains, the total potential will be dominated by electrostatic repulsion [4]. According to Buscall *et al.* [5], when the zeta-potential is large enough (higher than ~40 mV) and the factor  $kd > 10$  the corresponding repulsive potential is given by the DLVO theory, according to Equation 1.

$$V_R = \pi \epsilon \epsilon_0 d \psi_0^2 \ln\{1 + \exp[-k(R - 2a)]\} \quad (1)$$

$k$  being the reciprocal of the Debye length,  $a$  the particle radius,  $\epsilon$  the medium dielectric constant,  $\epsilon_0$  the dielectric permittivity in vacuum and  $\psi_0$  the surface potential. Since surface potential cannot be experimentally measured it was replaced by the zeta potential obtained for the suspensions prepared with each dispersant concentration.

On other hand, the attractive potential (van der Waals) depends, principally, on  $H = R - 2a$  (the surface-to-surface particle separation) and the Hamaker constant ( $A$ ), according to Equation 2.

$$V_A = -\left(\frac{Aa}{12(R - 2a)}\right) \quad (2)$$

As reported in the literature,  $A$  can be estimated by means of optical measurements [6]. The value used for the calculus of the attractive van der Waals potential, was that proposed by Horn [7] for alumina particles interacting in an aqueous media ( $A = 6.2 \times 10^{-20}$  J). The isoelectric point of the starting powder occurs at pH ~ 8.5. When adding dispersant the natural pH of the slip does not change significantly, but the anion adsorbs at the particle surface producing a repulsive surface charge. The higher is the repulsive surface charge the higher is the zeta potential, hence slip stability increases. Fig. 1 shows the zeta potential of slurries containing different dispersant concentrations. A maximum zeta potential is reached after an addition of

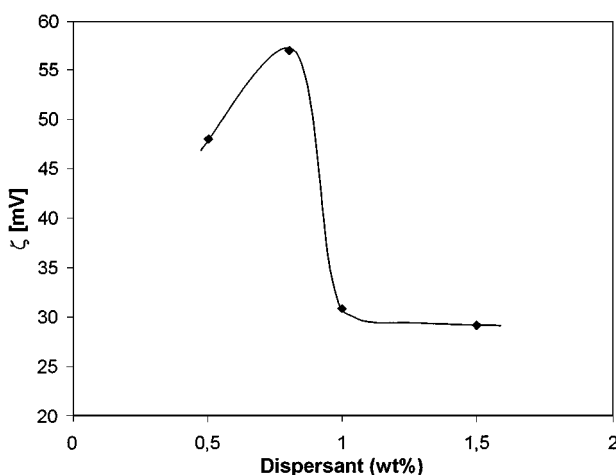


Figure 1 Zeta potential measurements as a function of dispersant concentration for fresh suspensions.

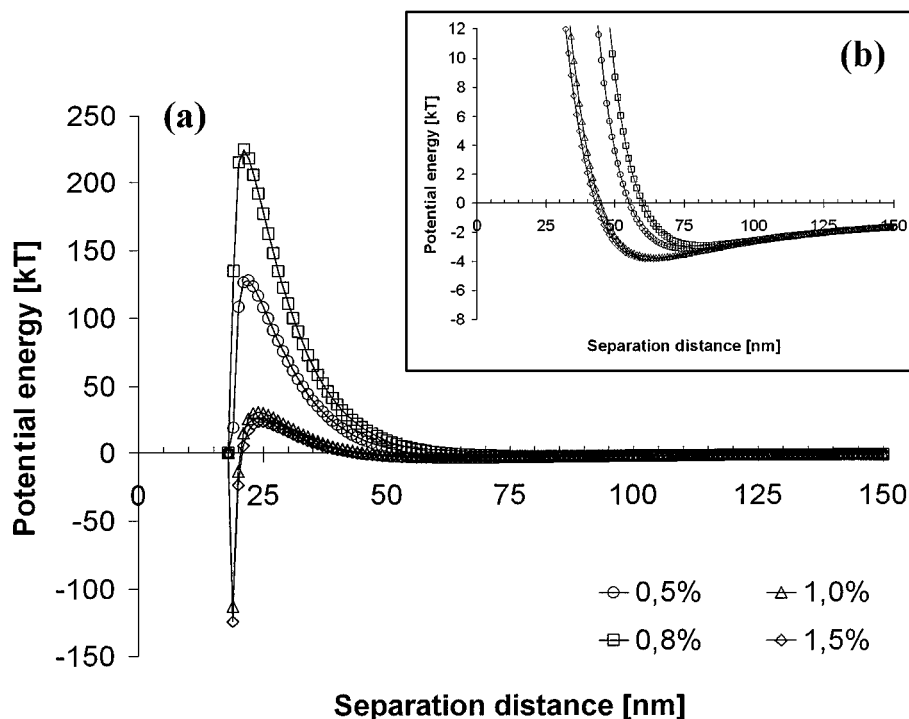


Figure 2 a) Particle pair potential curve for fresh slips at different dispersant concentration, b) Detail of the secondary minimum for each dispersant concentration.

0.8 wt% dispersant. From this curve and having in mind the above considerations, it is possible to represent the interaction as a function of the particle separation distance. Fig. 2 shows the calculated interaction potential curves for the dispersant concentrations considered in Fig. 1. As observed in the figure, a small secondary minimum appears as separation distance reduces below 60 nm, this meaning that slips can weakly flocculate, as expected generally in electrosterically stabilized suspensions. As particles approach the total potential starts to increase reaching a maximum at  $\sim 20$  nm, corresponding to the potential barrier due to the electrostatic repulsive forces developed between the particles surrounded by the adsorbed polymer layers. It is assumed that when the polymer is added the particle radius is increased in a quantity defined by the chain length, but without changing the hard sphere behaviour. Theoretically, it is expected that the maximum should occur at a separation distance of  $2 \times 9$  nm, which is in very good agreement with the values in the curves plotted in Fig. 2. Considering that only the electrostatic contribution to the total interparticle potential is being calculated a primary minimum appears in the potential energy curves. However, as the polyelectrolyte adsorbs onto the particle surface, the steric effect contribution provide a short-distance repulsive potential that is not included in the calculations from DLVO theory. However, these results provide a qualitative guide to the behaviour of the slips.

It can be seen from both representations that stabilization increases with an addition of 0.5 wt% to 0.8 wt%, but a further addition promotes destabilization. This could be related to some bridging phenomenon occurring as a consequence of the excess of polymer in suspension and the increased ionic strength [8, 9].

The interaction potential developed between particles in the slip have a marked influence in the rheology of the system during forming and determine the homogeneity and properties of the final sintered body. Zeta potential measurements (and thus, calculated potential energy curves) are restricted by the limited solid content of the slurries used for the measurements. But for castable slips as concentrated as 43 vol%, the rheology is the only technique that can provide the needed characterization. For these concentrations of particles in suspension, double layers or adsorbed polymer layers can interpenetrate and this effect cannot be observed in zeta potential measurements due to the low solid content required for these measurements. The rheological behaviour of the slips as well as the ageing effects are reported below.

### 3.2. Rheological properties

The rheological characterization of slips is suitable for optimising slip forming performance. According to this, the behaviour predicted by the potential energy curves can be confirmed by rheological measurements. As shown in Fig. 2 the slips prepared at 0.8 wt% of dispersant reduces the depth of the secondary minimum. The strong influence of dispersant concentration on the rheological behavior of 75 wt% slips can be seen in Fig. 3. This figure shows the variation of viscosity (at a shear rate of  $50 \text{ s}^{-1}$ ) and mean particle size with dispersant concentration. Viscosity decreases at 0.8 wt%, and then increases again. This is in good agreement with electrokinetic data. On the other hand, mean particle size also decreases at 0.8 wt%, but it doesn't change any more. Small changes in the surface state produce important variations in the viscosity due to the high solid loading [10].

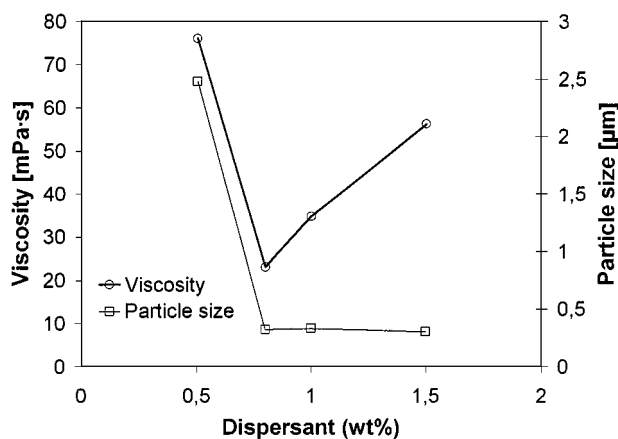


Figure 3 Viscosity (at  $50 \text{ s}^{-1}$ ) and mean particle size variation with dispersant concentration.

Both zeta potential and particle size measurements are performed with much lower powder concentrations, so that possible bridging effects cannot be detected. The pH of the slips is maintained between 9.2–9.3, which enables full dissociation of the dispersant [8]. The conductivity linearly increases with dispersant concentration between 1.2 and 3.2 mS/cm.

The rheological behavior of the 75 wt% slips can be observed in Fig. 4. Fig. 4a shows the flow curves, confirming the above observations. Fig. 4b plots a double logarithmic representation of strain versus shear stress, measured in controlled stress operation mode. Regarding to the flow curves, they can be best fit to a Casson model. Table I summarizes the rheological properties of the slips including the fitting parameters. Suspensions obtained for 0.8 wt% dispersant shows a very low yield point and very low pseudoplasticity; this is desirable for slip casting operations. A lower concentration (0.5 wt%) is insufficient to provide the required stability and the slip behaves as a plastic with a yield point. An excess of deflocculant produces also an increase of viscosity and yield value.

### 3.3. Ageing behavior

An essential consideration in any industrial production process is reliability. In the case of slip processing of ceramics, handling of the slip should be easy and must allow storage without settling. Therefore, the optimum dispersing concentration should be properly

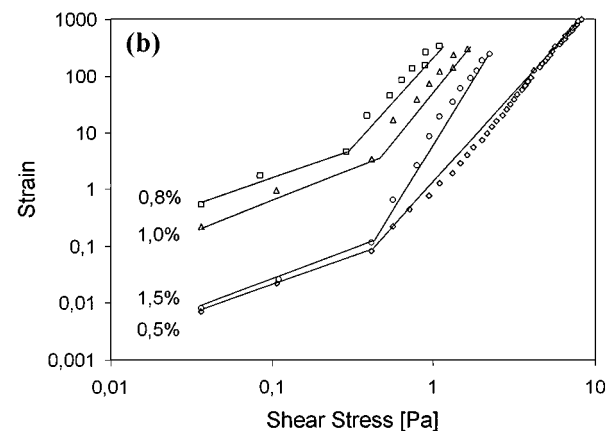
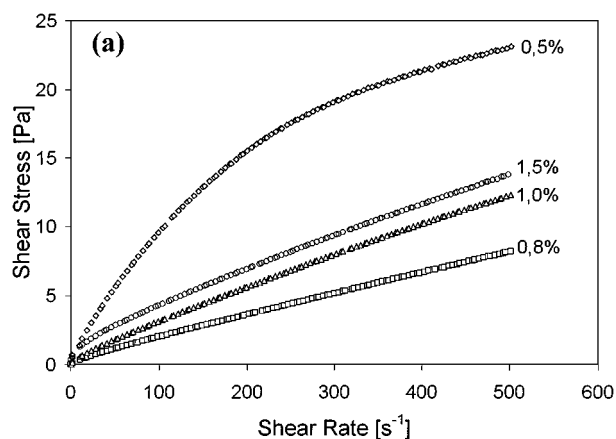


Figure 4 (a) Flow curves of fresh slips at different dispersant concentration measured in controlled rate mode, (b) Logarithmic representation of controlled stress mode of slips.

determined, to assure the constancy of properties few days before use.

According to this, the flow curves of the four slips have been measured as prepared and after 12, 24 and 48 hours. The results are plotted in Fig. 5, where it can be clearly seen that the slips with 0.8 wt% do not present any changes in the rheological behavior with time. This demonstrates the high stability of the slips in which flocculation is prevented. Furthermore the evolution of the yield point of the slips with ageing time are plotted in Fig. 6. These data demonstrate that the slips with 0.8 wt% dispersant are better dispersed as expected from zeta potential and potential energy curves. Slips prepared at dispersant concentration below 0.8 wt% are

TABLE I Rheological fitting results of fresh suspensions

Dispersant (%)	Flow curve segment	Viscosity [mPa·s]	Thixotropy [Pa/s]	Fitting parameters		
				Best fitting	$\tau_o$ [Pa]	$\eta_{lim}$ [Pa·s]
0.5	(↑)	76.1	-359.3	Bingham	2.626	0.02969
	(↓)			Casson	1.556	0.01726
0.8	(↑)	23.0	4.32	Casson	0.054	0.0138
	(↓)			Casson	0.054	0.0138
1.0	(↑)	34.7	19.98	Ostwald	$n = 0.8374^*$	$K = 0.6539^*$
	(↓)			Bingham	0.889	0.0217
1.5	(↑)	56.2	-0.916	Casson	0.632	0.01539
	(↓)			Casson	0.755	0.0139

\*Pseudo-plastic Ostwald-de-Waele model Parameters.

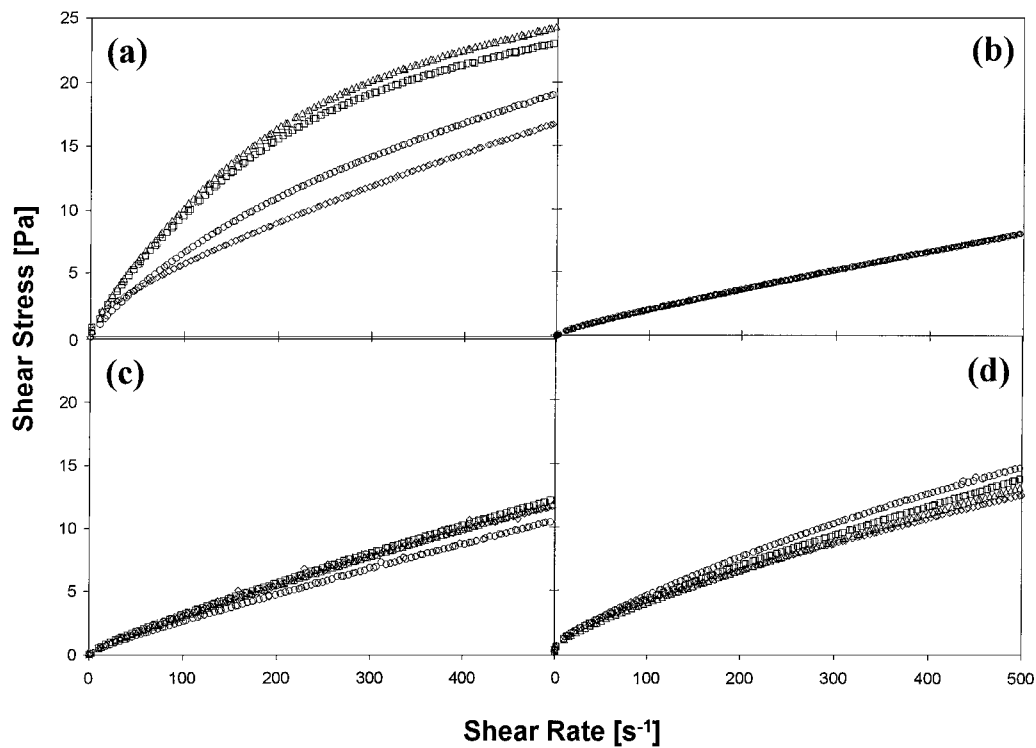


Figure 5 Ageing effect of slips;  $\triangle$ , 0 h;  $\circ$ , 12 h;  $\diamond$ , 24 h; and  $\square$ , 48 h. Dispersant concentrations of, (a) 0.5 wt%, (b) 0.8 wt%, (c) 1.0 wt%, (d) 1.5 wt%.

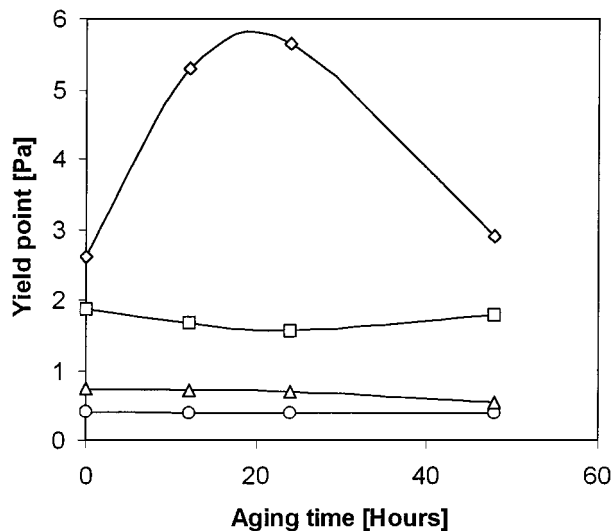


Figure 6 Effect of ageing time on slips yield point with different dispersant concentration.

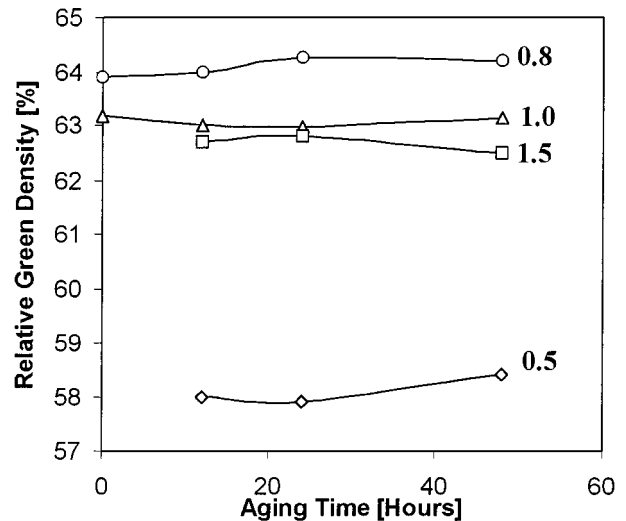


Figure 7 Influence of dispersant concentration and ageing time on green density of cast disks.

highly unstable and shows a different flow behavior in increasing shear rate segment and decreasing one. Upper dispersant concentrations shows low viscosity, but high yield point and thixotropy, that can produce lower green properties in cast bodies.

### 3.4. Slip casting

In accordance with the reported results, ageing time can be prevented by means of a proper addition of dispersant with a controlled homogenization time and procedure. The well dispersed slips maintain stability for a few days. The adsorbed dispersant chains prevent coagulation, which would occur when electrostatic repulsion was the only stabilizing mechanism. Obviously, this must influence the packing structure developed dur-

ing consolidation, as well as the uniformity of the microstructure of the sintered material [11].

To prove the influence of slip ageing on the green properties, the fresh and the aged slips with different dispersant concentrations were slip cast on plaster of Paris moulds. The green density of the cylindrical casts is shown in Fig. 7 as a function of ageing time. Slips with 0.8 wt% dispersant shows the highest green density (64% theoretical) with no changes with ageing. An insufficient quantity of dispersant makes the viscosity to be higher, resulting in a poor packing density. An excess of dispersant results also in less efficient packing of particles. This suggests again that free polymer in excess can lead to bridging between chains adsorbed in a particle surface or, at solid loading increases, between the adsorbed layers of two different particles.

TABLE II Relative density results of sintering test

Dispersant concentration (wt%)	Relative density of sintered bodies	
	0 h	48 h
0.5	98.1	95.4
0.8	99.3	99.1
1.0	98.2	99.2
1.5	98.9	98.8

The packing lowers as a consequence of the increasing separation distance between particles.

Sintering tests were performed for samples obtained after casting the fresh and the 48 h-aged slips. The results reveal that the aged slip is not stable and density is lower than that obtained for the better concentration of dispersant. This is reflected in Table II where the density values for bodies obtained from suspensions at 0.8% dispersant gives the highest density values that keep constant with ageing time.

#### 4. Conclusions

In this work, aqueous alumina suspensions were stabilised by means of electrosteric mechanism. The particle pair potential curve obtained considering only the electrostatic mechanism is in good agreement with rheological measurements. Suspension with 0.8 wt% of dispersant was more stable than with other dispersant concentrations and gives a very low yield values that assures good green properties. For this optimum

concentration the slip does not show ageing effect and only minor changes could be detected in rheological behaviour. The optimum dispersant concentration selected from the pair potential curve and the rheological measurements give the maximum green and sintered density. Again, under these optimized conditions the characteristics of the cast bodies were not affected by ageing.

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