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Characterisation of Alumina Pastes for Plastic Moulding

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Abstract

A better understanding of the parameters controlling the interactions between particle surfaces and water solution would allow an improvement of highly concentrated ceramic paste behaviour for use in the extrusion process, as well as a dramatic decrease of the organic additive concentration needed to reach satisfactory plasticity. Therefore, the heat treatment step would also become easier and quicker.

Alumina was selected as a model ceramic powder, and rheological and electrochemical measurements were performed using increasing dry matter content. It was shown that, at natural pH, an optimal range of dry matter content exists, corresponding to a minimum water content, which can be determined from plasticity data and from electrochemical measurements. © 1996 Elsevier Science Limited.

Une meilleure compréhension des paramètres régissant l'interaction entre la surface des particules et les solutions aqueuses devrait permettre un contrôle amélioré du comportement plastique des masses céramiques mises en forme par extrusion, ainsi qu'une diminution de la teneur en additifs organiques nécessaires à l'obtention d'une plasticité optimale. Cela réduirait les inconvénients des traitements thermiques qui sont de longue durée et coûteux.

L'alumine a été choisie comme modéle de poudre céramique pour cette étude et ses caractérristiques ont été déterminées en fonction de la teneur en matiére séche. On a pu montrer qu'à pH naturel, il existait un domaine de teneur en matiere seche qui peut être déterminé à la fois par les mesures rhéologiques et électrochimiques et qui correspond à une zone de plasticité optimale.

Introduction

The parameters influencing powder dispersion, both in the advanced ceramics' and in the clays' fields have been largely studied. These researches allowed successful preparation of suspensions with 75 wt% dry matter concentration. The slip casting method is now well developed and largely industrially applied. However, although this technique is appropriate to form pieces with very complicated shapes, for elongated products presenting a symmetrical form, other shaping methods like extrusion or isostatic pressing should be envisaged. In particular, in the absence of clays or other plastic inorganic raw materials, the extrusion technique requires large quantities of organic additives. The use of these additives involves not only a necessary long debinding step with possible flaw formation, but also precautionary measures to avoid environmental pollution due to organic degradation and release to atmosphere and, consequently, a cost increase of the components fabricated by this process. Therefore, it is economically interesting to develop an extrusion process which can reduce all these disadvantages.

The use of water as dispersing medium and a careful study of the ceramic paste's rheological behaviour is the route that we have chosen. Indeed, a better understanding of the parameters influencing the interactions between particle surfaces and aqueous solution would allow an improved control of the highly concentrated ceramic paste's behaviour, a decrease of the organic additives needed to obtain adequate plasticity and would also increase the quality of the sintered materials.

The aim of this study is thus to correlate the physicochemical properties of the ceramic powder

Table 1. Chemical analysis of the A16SG alumina powder

Oxide	*Weight%*
Al_2O_3	99·5
Na_2O	0·08
SiO_2	0·08
Fe_2O_3	0·015

surface and the behaviour of the ceramic paste to be shaped. Alumina powder was selected as a model ceramic because its behaviour in water in the range of dry matter content for slip casting (75%) is well known.[1] The study was carried out according to the hypothesis that pastes can be considered as the highest concentrated slurries, which means that a continuum exists between slurries and pastes and that the behaviour of these last can be understood on the basis of particle surface properties like surface charge or adsorbed ions' nature and content.

Experimental Procedures

Alumina powder characterisation

The alumina powder was the grade A16SG from Alcoa (USA), synthesised by the Bayer process and 99·5% pure. Table 1 presents the chemical analysis given by the supplier.

The surface area was measured by the BET method.

The particle size distribution curves were obtained by the sedimentation method with a Micromeritics Inc. (Type 5000) Sedigraph. The agglomerate size was determined as a function of pH. Before measurement, the powder was dispersed by mechanical stirring in aqueous suspensions of different pH values obtained with HCl for the acid range and NH_4OH for the basic one. The distribution obtained is a weight distribution which shows the agglomerate size distribution. The mean diameter (d_a) is the diameter corresponding to 50% of the Sedigraph curve.

Preparation for pastes and samples

The rheological and electrochemical properties development of the alumina pastes, prepared with various water contents (see Fig. 4), was studied at natural pH (≅10) using increasing dry matter content. Each paste composition was prepared by mixing manually the alumina.

For the rheological measurements, small cylinders (diameter: 8 mm, length: 50 mm) were shaped by paste extrusion (Netzsch extrusion machine 250·05 Type V5).

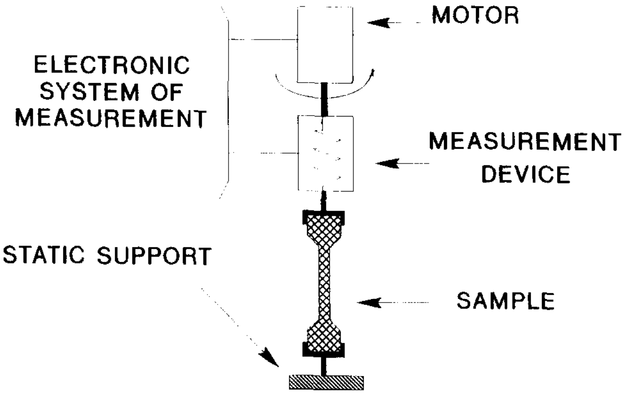


Fig. 1. Measurement system of the paste plasticity.

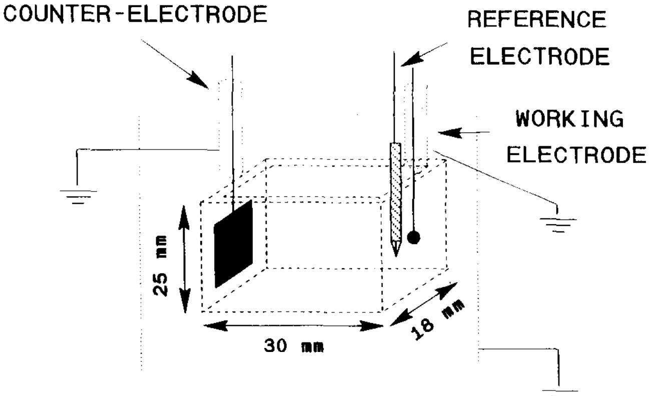


Fig. 2. Schema of the electrolytic paste cell.

Rheological measurements

Rheological measurements were performed using a Haake (Germany) viscometer, modified in order to allow the determination of torsion resistance of solid samples, which simulates best the stresses applied on the paste during the extrusion step (Fig. 1).

The alumina paste cylinder to be characterised is held between two grips. The lower part is fixed and the higher is directly attached to the measuring spring coupled to the drive unit. As for suspension viscosity measurements, the observed resistance of the spring deformation to the imposed stress is recorded as a function of the time. The rotation rate is constant and can be fixed from 0·1 to 10 r.p.m.

To verify the reproducibility of this method, some preliminary tests were carried out using clay cylinders. The strength–deformation curves obtained showed that the work optimal conditions correspond to a rotation rate of 0·8 r.p.m.

Electrochemical measurements

A special electrochemical cell was developed in order to adapt the shape, the dimensions and the nature of the electrodes to ceramic pastes study (Fig. 2).

In order to obtain a simple arrangement of the current lines between the electrodes, the cell shape selected was a parallelepiped. Small dimensions were chosen for two reasons: first to reduce the ohmic loss between the electrodes as the charge transport is strongly slowed down in concentrated pastes; second to allow the conductivity measurements.

The cell was made of polymethylmethacrylate because this material is an electrical insulator and is chemically resistant to most of plasticiser agents that can eventually be added. The transparency of the polymer allowed also external verification of the quality of the paste packing and the correct position of the electrodes.

The working electrode was made of platinum, with area as small as possible to obtain the highest current densities and thus optimal electrochemical data. A section of a wire with a diameter of 0·6 mm was chosen.

The platinum counter-electrode had an area of 4 cm^2 and was fixed on the opposite face. Contrary to the working electrode, it had the largest surface possible within the cell dimensions to prevent any measurement disturbance due to parasite reactions. In order to avoid a parasite capacity formation, the two electrode wires were earthed.

A reference electrode was also used. It was a calomel-saturated classical electrode with a sharp extremity, designed especially to favour an easy penetration into the paste.

The three electrodes were connected to the polarographic equipment (Tacussel PJT 35-2 polarograph with IMT-1 interface, France). The voltammetric curves were directly corrected from the pre-measured ohm loss.

The electrochemical measurements were carried out according to procedures described elsewhere.[2,3]

Results and Discussion

The alumina surface area is 7·5 m^2/g.

Table 2 presents the mean diameter evolution as a function of pH values. It can be seen that a good dispersion can only be obtained at acidic pH or at pH above 12. Such results are in good agreement with the value of the null point of charge of alumina (pH ≈ 8·5).

Rheological measurements

A classical plasticity curve measured on a paste is shown in Fig. 3.[4] LE is the yield strength, LM the maximal strength and LR the rupture strength.

The larger the LE-LR zone is, the more the sample has to be considered as plastic because it supports a larger deformation before the rupture occurs. Consequently, this part of the curve may be considered as the characteristic of the plasticity.

Table 2. Agglomerates mean diameter as a function of pH

pH	d_a(*μm*)
2·8	0·20
3·9	0·34
4·8	0·36
6	0·58
7	8·00
7·9	1·00
9·9	10·5
11	9·20
12	0·90

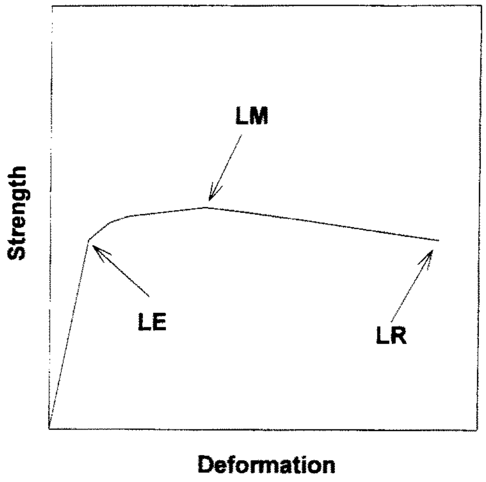


Fig. 3. Classical strength–deformation curve of a paste.

The mean plasticity curves obtained for different dry matter contents are shown in Fig. 4. The best plastic properties (corresponding to the larger LE-LR zone) are obtained for 81·7% of dry matter concentration.

The corresponding yield strength (LE), maximal strength (LM) and rupture strength (LR) are also shown as a function of the dry matter content in Fig. 5.

The curves variations are similar: they present an inflexion point corresponding to about 82·5% of dry matter content.

Electrochemical measurements

Electrochemical properties (conductivity, rest potential, polarisation curves and polarisation resistance) were determined using the electrochemical cell specially adapted to paste study.

Each test was carried out 24 h after paste preparation to allow it to homogenise and also to develop exchanges between the particle surfaces and the water.

Conductivity

The specific conductivity measurements (carried out at 2000 Hz) are shown as a function of the dry matter concentration in Fig. 6.

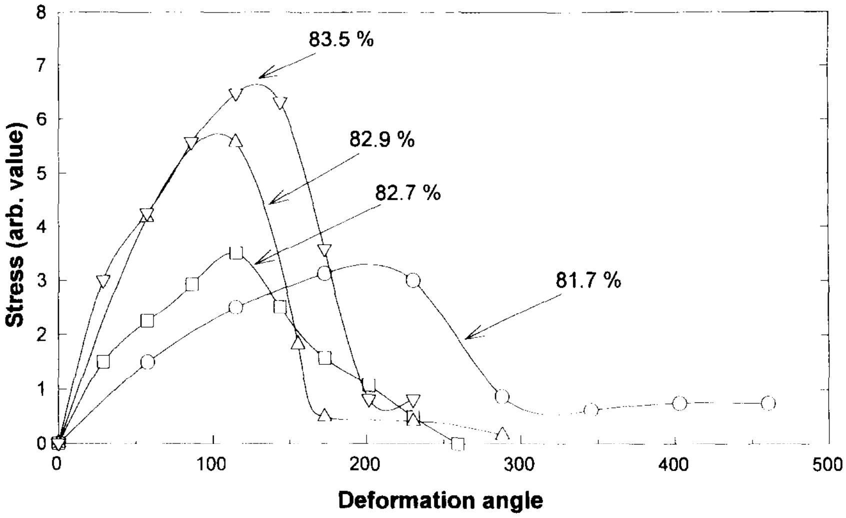


Fig. 4. Mean plasticity curves of Al_2O_3 pastes.

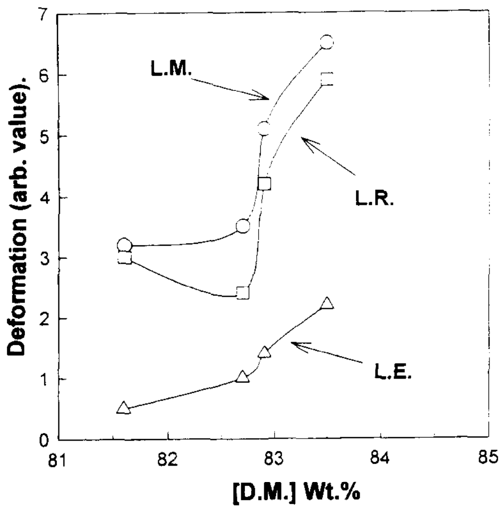


Fig. 5. LE, LM and LR as a function of the dry matter content.

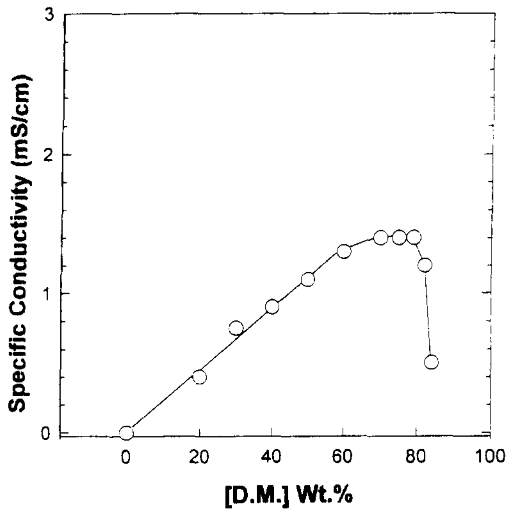


Fig. 6. Specific conductivity of Al_2O_3 pastes as a function of the dry matter content.

It can be seen that the conductivity increases linearly up to 60% of dry matter content. For higher contents, a plateau is reached between 70% and 78%. Finally, for drier pastes, a dramatic conductivity decrease is observed.

The conductivity may be considered as the sum of:

1. the equilibrium solution conductivity;
2. the interface conductivity, which represents the surface conductivity and the double layer conductivity; and
3. the particle conductivity.

Alumina being an insulator, the third part may be neglected.

The first constituent of the global conductivity is essentially, at pH ≅ 10, attributed to, of course, the OH^- but also the Na^+ and the small amount of AlO_2^- ions dissolved from the surface of the alumina powder. The pH value is constant, thus the OH^- quantity does not change. This conductivity value should proportionally increase with the content of Na^+ and, consequently, with the dry matter concentration. Moreover, in the diffuse layer, the conductivity is essentially cationic because the surface is negatively charged, and is proportional to the cation charges in the double layer and also to their mobility.

Previous chemical analysis showed that all the Na_2O which is present in the alumina powder and that can be dissolved, is detected in the solution after 24 hours;[5] so, at constant pH 10, the cations responsible for the conductivity variation are the Na^+.

With the increase of dry matter content, the quantity of intermicellar liquid progressively decreases, the charge transport coming from the free ions disappears and the conductivity becomes dependent only on the ions of the double layer. At the same time, the double layer compresses, progressively reducing the cation mobility.

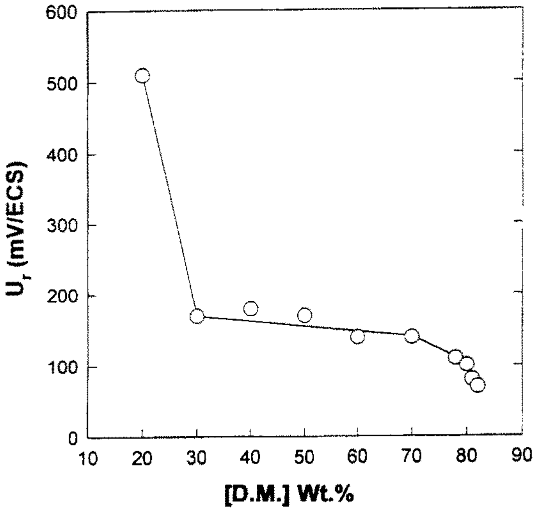


Fig. 7. Effect of the dry matter content on the rest potential of Al_2O_3 paste.

At 70% of dry matter, the suspension can be considered as a paste. Therefore, the cations cannot migrate within the free water and the conductivity values stay unchanged up to 80%.

For higher concentrations the conductivity decreases dramatically, because, simultaneously both diffuse layer and water molecules disappear.

Rest potential

The rest potential linearly decreases from 20 to 70% of dry matter content (Fig. 7); beyond this concentration, it presents very low values.

In aqueous solution, for the platinum–water interface and without any other oxidation–reduction couple, the rest potential represents the H_2O/O_2 equilibrium, given by the Nernst equation:

$$U = U_0 + \frac{RT}{2F} \ln \frac{p_{O_2}}{a\mathrm{HO_2^-} \cdot a\mathrm{OH^-}}$$

with: R, T, F: usual meanings, a: activity, p_{O_2}: fugacity of dissolved oxygen, U_0: standard potential, and corresponding to the following equation at basic pH:

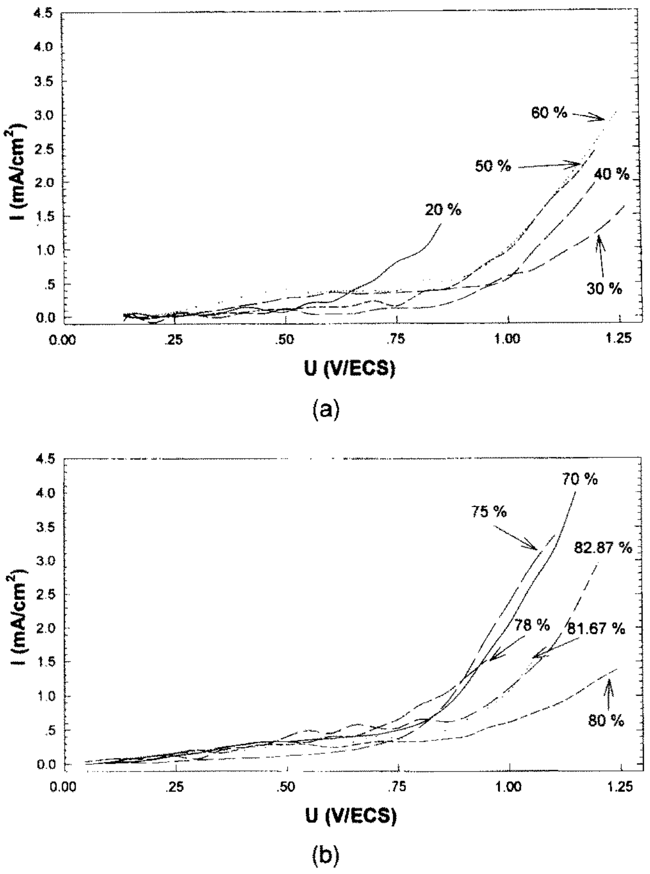
$$\mathrm{HO_2^- + OH^- \leftrightarrow O_2 + H_2O + 2e^-} \qquad (1)$$

Then, the rest potential depends upon the perhydroxyl ions presence, following the reaction:

$$U = U_O + 0{\cdot}029\,[14 - \mathrm{pH} + \log p_{O_2}/a\,\mathrm{HO_2}] \text{ at } 20^\circ\mathrm{C}$$

For given pressure and temperature, the pH (fixed at 10 by Na_2O present in the alumina) and the p_{O_2} may be considered as constant. Consequently, an increase of HO_2^- will correspond to a potential decrease.

The HO_2^- ion activity is dependent on the dissolved oxygen content (see eqn (1)) and on the amount of perhydroxyl ions adsorbed on the particle area. These ion formations (following eqn (1)) appears naturally on the particle surface, because of the negative charges present in excess on the particle surface.



(a)

(b)

Fig. 8. Anodic polarisation curves of Al_2O_3.

The slip of 20% of dry matter is flocculated and, consequently, the measured rest potential is that of the water in the suspension.

Above 30%, as the slurry presents a good homogeneity, the measurements are significant.

The larger rest potential decrease observed above 70% may be explained by a higher perhydroxyl ion concentration in the paste. Indeed, between 70 and 82%, the oxygen dissolves directly on the particle surface and no more in water and the HO_2^- adsorbed formation becomes more and more effective.

Finally, for the two last measurements carried out for 82·7 and 83·5%, respectively, the water concentration is no longer enough to assure oxygen dissolution and, consequently, the HO_2^- ion concentration decreases, which also corresponds to a bad plastic behaviour.

Polarisation curves

The anodic polarisation curves are shown in Figs 8a and b. It can be seen that they are independent of the dry matter concentration. Indeed, the current densities are within the same range of value from 20 to 82·9% of dry matter content.

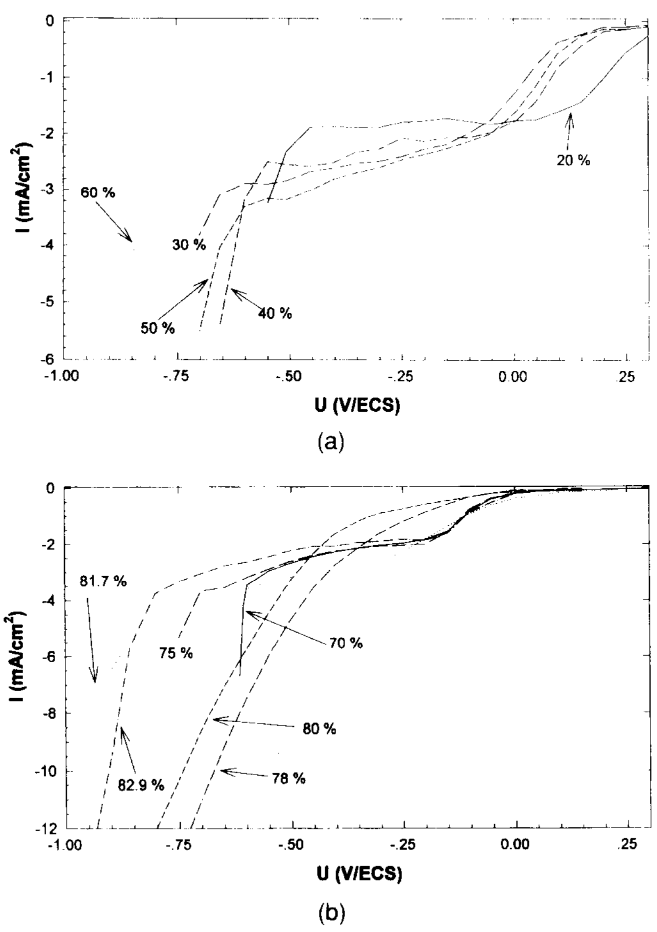


Fig. 9. Cathodic polarisation curves of Al_2O_3.

In such a case, the decrease of water concentration influence is insignificant and the charge transport is caused by the particles. The presence of a zone between 78 and 80% with high reduction currents, which corresponds to the maximum plasticity, can be identified for the cathodic polarisation curves presented in Figs 9a and b.

The cathodic curves correspond to the following surface reaction:[1]

$$HO_2^-{}_{ads} + H_2O + 2e^- \rightarrow 3\ OH^-{}_{ads}$$

The current densities increase and, moreover, for 78 and 80% their exponential shape, corresponding to a simple charge transfer reaction, without any diffusion limitation of the adsorbed HO_2^- ions, confirms the presence of a larger amount of perhydroxyl ions adsorbed at the alumina surface which react at the electrode.

For 82 and 83%, the observed lower current values are attributed, as for the rest potential data discussed above, to a too low water content to allow an optimum O_2 dissolution and perhydroxyl ion formation. Indeed, the high ionic force impedes dissolution of large quantities of O_2.

The structure of water molecules should have a major effect on the charge transport. The optimum range of water concentration seems to be between the 'free water' disappearance and that of the diffuse layer. The diffuse layer, with its high ion concentration, acts as a continuous medium for the current, whereas the 'free water' shows a high resistivity and therefore limits the diffusion.

Conclusions

This paper relates to the rheological behaviour of highly concentrated pastes studied using electrochemical techniques. A model ceramic powder (alumina) was chosen.

It was shown that, at natural pH, an optimal range of dry matter content exists, which can be determined using both plasticity data and conductivity measurements. This range of powder concentration (≅ 80 wt%) corresponds also to the minimum water content necessary to preserve a good paste workability.

The results are in agreement with Michaël and Bolger's theory.[6] Indeed for the optimal water value, the paste structure is perfectly coherent; under this value, the water content is not sufficient to develop the surface charge. On the other hand, for higher liquid contents, the particles being too far from each other, the structure becomes unstable.

The presence of a zone with large reduction currents corresponding to the maximal plasticity is shown by polarisation curve data. For this range, free water seems to be absent and only a diffuse layer interpenetrating could explain the current increase. According to the current evolution we conclude that dissolved oxygen is adsorbed as perhydroxyl ions stabilised by the surface negative charge. As a function of the dry matter concentration, this dissolution will appear in the 'free water' or in the water of the diffuse layer. The formation of perhydroxyl ions directly in the diffuse layer explains the higher current densities observed. Moreover, in such a case, the adsorption occurs at the expense of the surface charges with consequently a structure strengthening and a positive contribution to the plasticity.

According to the results obtained, alumina small cylinders were shaped by extrusion, without the use of any organic additives.

Acknowledgements

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