THE CHARACTERISATION OF CLAY SLURRIES USING POLARIZATION RESISTANCE MEASUREMENTS

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SUMARY

The deflocculation of water slurries is usually characterised by the measurement of classical rheological parameters like viscosity, shear stress, etc. The quality of slips depends on the powder surface charges (usually determined by the zeta potential) and on the characteristics (ionic force, dissolved gases) of the liquid.

The interactions between liquid and solid surface can also be related to electrochemical parameters among which polarisation curve and polarisation resistance (Rp).

This paper describes the relation between polarisation resistance and surface agent behaviour and the use of Rp to optimise the deflocculation. Some practical examples of industrial applications are given to show how to control sanitary slurries ageing using such a measurement and to prepare slips by mixing fresh suspensions with used ones and scraps.

INTRODUCTION

The main problem in the process of ceramic slip casting is to achieve a perfect control of the slurry. Indeed, this last has to exhibit the following characteristics :

- to be homogeneous;
- to be stable a long time enough to be processed;
- to have the highest dried matter content to reduce the energetic costs during drying stage and to give a maximal green density of the cast body;
- to have a high fluidity to pour easily all the parts of complex shape moulds.
- to be easily removed from the mould without any apparition of green defects.

The main defects met during pouring can be summarised as :

- a too slow pouring of the mould, difficulties to pump the slip;
- sedimentation of the slip, bubbles;
- a too great thickness of the green wall with a too high water content and deformability;
- a too quick drying of the green part, which become brittle.

These problems, well known by the ceramists, result from bad rheological properties : too high or too low viscosity, too high or too low thixotropy.

To solve them, ceramists usually add deflocculants in the slurry to modify its rheological characteristics. In that way, the particle surface charges are modified by increasing or decreasing the Coulombian repulsion forces. To assess the influence of the double layer around the particles, the zeta potential can be measured.

In this paper, we show how the deflocculation of a slurry can be better controlled using polarisation resistance (Rp) which allow to emphasise the importance of dissolved oxygen in the aqueous suspensions. Indeed, the adsorbed oxygen on the particles are perhydroxyl groups which are responsible for the suspensions ageing.

2. EXPERIMENTAL DEVICES

2.1. RHEOLOGICAL MEASUREMENTS

The apparent viscosity measurements are carried out at 90 sec^{-1} using a viscosimeter with coaxial cylinders (type Searle)[1].

2.2. ZETA POTENCIAL

The zeta potential determinations are made by electrophoretic technique using E.M.T.A. (Electrophoretic Mass Transport Analysis)[2]. The electrophoretic velocity calculation results from the weight variation of a pycnometer containing the slurry under an electric field. This apparatus is able to assess actual industrial slurries. The zeta potential value is calculated by the Smoluchovsky's equation.

2.3. POLARISATION CURVE AND POLARIZATION RESISTANCE

The experimental device described at figure 1 includes a saturated calomel reference electrode, a large dimensions platinum electrode (28 cm^2) and a Pt working electrode. The surface of the latter is 0.00509 cm2 for the potentio-dynamic curve measurement and 1 cm2 for the determination of the polarisation resistance (Rp).

The three electrodes (reference, large and working) are related to polarisation measurement devices (see figure 1). A system allows to record the studied phenomenon.

To realise the polarisation curves, a variable tension is applied, between the reference electrode and the working one, with a linear increase or decrease of 5 mV/s. The tension-current density curve

[1] *Haa Rotovisco RV III (NI).*

[2] *Micromeritics (USA)*

is recorded between the anodic oxygen release and the cathodic hydrogen release (resulting from the water electrolysis).

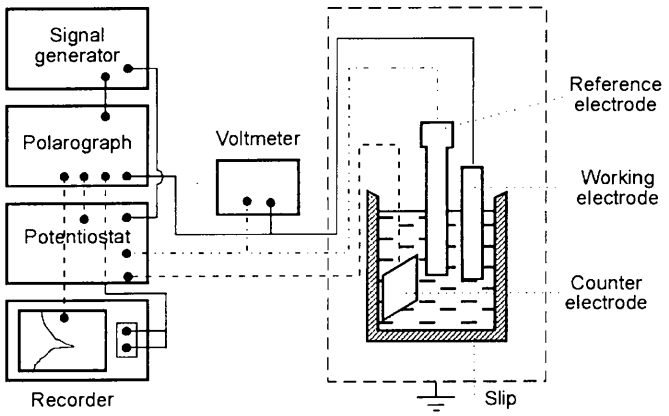

Figure 1.

The polarisation resistance (Rp) is the opposite of the polarisation curve slope at the origin of the curve. The polarisation resistance is measured by recording the polarisation curve slope, ± 10 mV around the free potential where the current is null.

2.4. RAW MATERIALS

Various industrial mixtures were used. They are described in the corresponding paragraphs. Sodium silicate contains 35.4 % of silicate and a SiO_2/Na_2O ratio of 3.4. Sodium carbonate is pro analysis.[3]

3. EXPERIMENTAL RESULTS AND DISCUSSION

3.1. POLARISATION MEASUREMENTS

3.1.1. Polarisation curves

It has been shown (1,2,3) that the polarisation curve of a clay slurry can be schematised as in figure 2. For anodic part, before oxygen releasing, a plateau can be detected. This plateau is attributed to the organic matter adsorbed on particle surface oxidation.

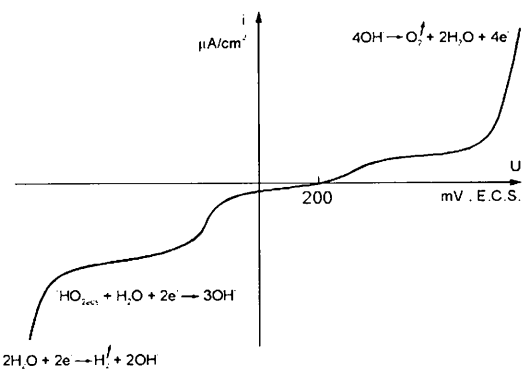

Figure 2. Polarisation curve of ceramic slip on platinum electrode

[3] *Merck (Germany)*

For cathodic part, a plateau is always present around 450 mV/ECS. It is attributed to oxygen adsorbed on the particle surface, transformed in perhydroxyl species. Indeed, such a behaviour is in accordance with the following reactions :

$$O_{2dissolved} + H^+ + 2\ e^-(lattice) \rightarrow -HO_{2\text{-}ads}$$

or, in basic conditions:

$$O_2 + H_2O + 2\ e^- (lattice) \rightarrow -HO_2^- + OH^-$$

This reaction implies a decreasing of zeta potential, which provides the electrons needed for the electrochemical reaction (the particles are negatively charged).

Therefore, the electrochemical reaction explaining the observed plateau becomes:

$$-HO_{2\ ads}^- + H_2O + 2e^- \rightarrow 3OH^- \text{ (in basic middle)}$$

3.1.2. Polarisation resistance

The polarisation resistance is defined as the derivative of the overvoltage by the current density when these two values are closed to zero. When the cathodic reaction is limited by the diffusion of the reactant component to the electrode, the theory shows that the diffusion polarisation resistance is inversely proportional to the diffusion current density and then to the reactive species concentration.

$$R_d = -\frac{RT}{zF}\sum_\gamma \frac{V_\gamma}{i_{d,\gamma}}$$

and

$$R_D = \frac{RT}{z^2F^2}\sum_\gamma \frac{v^2{}_\gamma d}{D_\gamma c_\gamma}$$

where,

R,T and F represent perfect gas constant, temperature and Faraday, respectively;
z is the number of exchanged electrons;
v_γ is the stoichiometric coefficient of the γ component;
D_γ is the diffusion coefficient of the γ component;
d is the thickness of the diffusion layer;
$i_{d,\gamma}$ is the diffusion current density of the γ component;
c_γ is the γ compound concentration in solution.

As shown in figure 3, the polarisation resistance measurement, and therefore in this case the diffusion resistance, can be related with the ceramic slurries deflocculation. Thus, (figure 3) when the increase of the charge is due to pH or to specific adsorption of a low steric effect molecule, the real access for oxygen to the particle surface increases in the same way as deflocculation. The perhydroxyl species concentration is higher and the polarisation resistance decreases.

The maximum of deflocculation corresponds to the minimum of polarisation resistance.

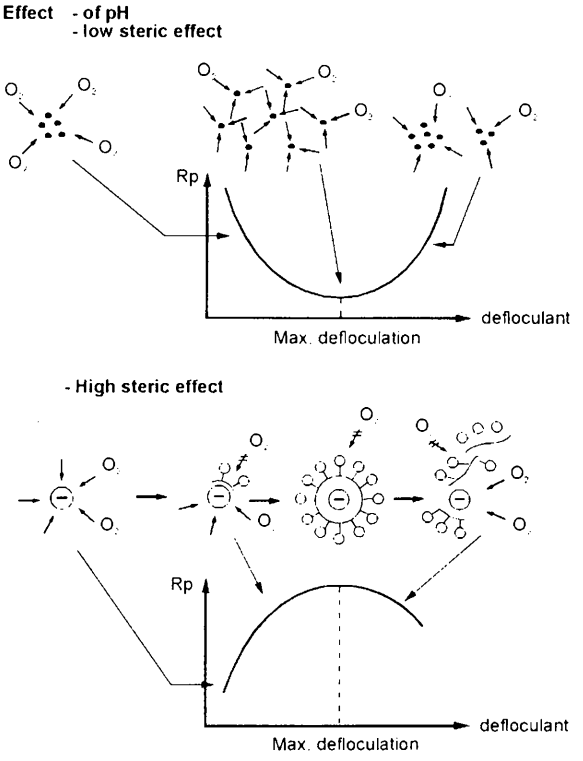

Figure 3. Relation polariation resistance/deflocculation

In the case of adsorption of a large steric effect molecule the behaviour will be the opposite. Indeed, the large molecule, attached on the surface, limits more and more the access of the dissolved oxygen molecules; therefore, the polarisation resistance increases with the deflocculation increase. An excess of deflocculant leads to a decrease of Rp due to a too large covering of the particle.

The maximum of deflocculation is obtained in such a case for the maximum polarisation resistance value.

3.2. BEST DEFLOCCULATION CONDITIONS

The process used consists first to optimise the sodium silicate concentration in the slurry. The dry matter concentration is slightly lower (68 %) in the purpose to obtain highly under-deflocculated suspensions. The adjustment to the standard concentration (73%) is simply obtained by a rule of three. The suspension used for these experiments is a classical china composition containing clays, kaolin and calcium carbonate (0.5%).

Figure 4 shows the polarisation resistance as a function of sodium silicate content. This slurry was 24 hours aged to allow ionic exchange between the solution, deflocculant and particles to occur. The polarisation resistance is maximum for the following composition: 0.05 percent of silicate. This value is closely related to the maximum of deflocculation as we can see in the zeta potential curve (figure 5) which shows a minimum for the same value of sodium silicate. The apparent viscosity curve (figure 6) also shows a minimum for this value. The silicate anion changes the surface charge because it adsorbs and then prevents oxygen particles to reach particle surface.

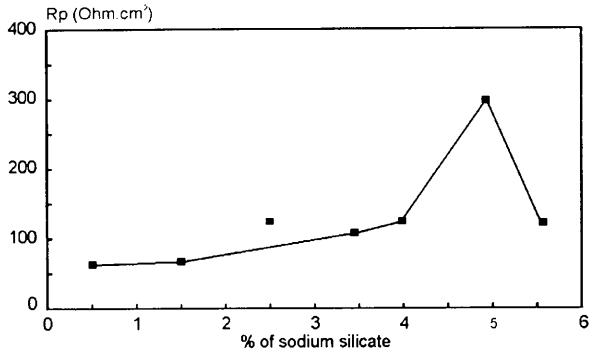

Figure 4. Evolution of the polarisation resistance as a function of the sodium silicate concentration

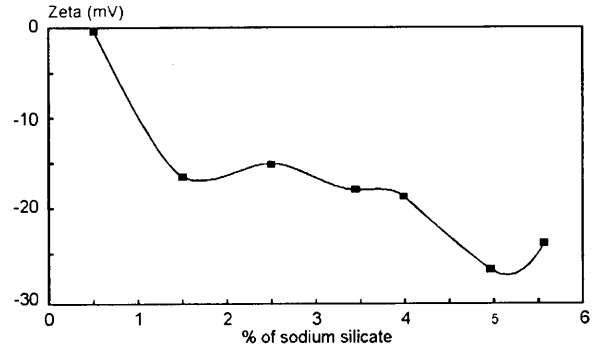

Figure 5. Evolution of the zeta potencial of the slurries as a function of the sodium silicate concentration

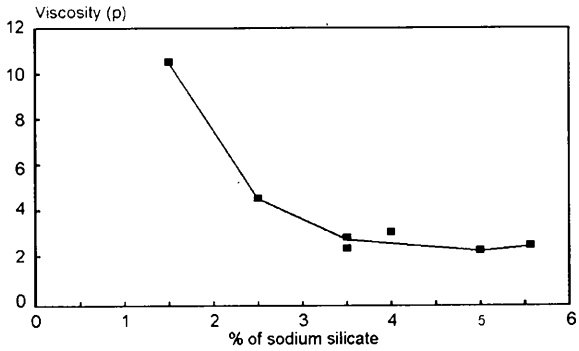

Figure 6. Evolution of the viscosity as a function of the sodium silicate concentration

In the same way, the Na2CO3 concentration is determined from small volumes of suspension preserved from air access during 24 hours, also to allow the exchange between the different concentrations of carbonate and the slurry to occur. Figure 7 shows a polarisation resistance minimum as a consequence of sodium carbonate action. This is due to the increasing of pH from 9.30 to 10.40; this pH is in favour of deflocculation, leading to a reduction of H+ ions amount adsorbed in the Helmholtz layer. This particles separation causes a better access of oxygen to the surface and then, as explained before, a decrease of polarisation resistance. The maximum of deflocculation is obtained for 0.2 percent, value confirmed by zeta potential data presented in
figure 8.

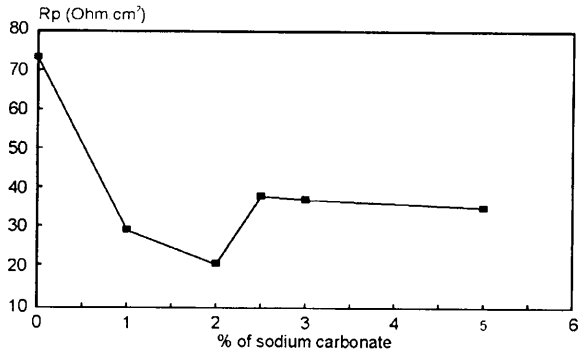

Figure 7. Evolution of the polarisation resistance as a function of sodium carbonate concentration

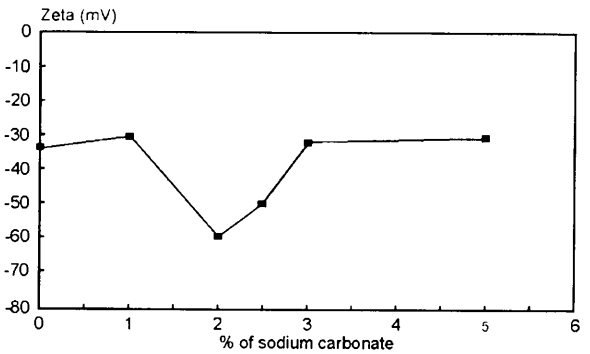

Figure 8. Evolution of the zeta potencial as a function of the sodium carbonate concentration

3.3. ATMOSPHERE EFFECT

The experiments were carried out on kaolin suspensions. The slurry has been deoxygenated by nitrogen bubbling or oxygenated by oxygen bubbling. The results (figure 9) can be compared with the same slurry kept sheltered from air.

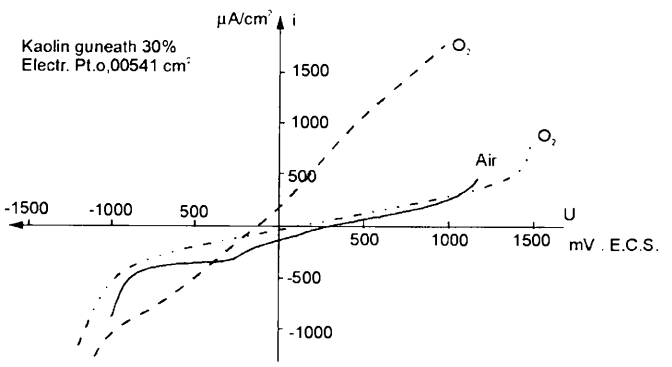

Figure 9. Effect of the atmosphere nature on the polarisation

3.3.1. Rest potential (Ur)

It decreases with the nitrogen or oxygen bubbling down to a value slightly negative (-120 mV/ECS), independently of the injected gas. At the same time, slurry pH value increases from 4.6 to 5.

The nitrogen bubbling changes out dissolved CO_2 and then increases pH value. Therefore, the rest potential decreases (U = cste-0.03 pH). To confirm this hypothesis, CO_2 was bubbled in the kaolin slurry. An acidification of the suspension was recorded and a rest potential increase was observed as shown in the following table:

CO_2 bubbling time	pH	Ur (mV/ECS)
0	5.29	+170
5 h 30	4.59	+220

3.3.2. Cathodic curves

The adsorbed oxygen reduction currents decrease logically in the sequence oxygen, air, nitrogen.

3.3.3. Anodic curves

Even though air and nitrogen show similar polarisation currents , the oxygen bubbling leads to a large increase of anodic current densities. Taking into account that oxygen is not oxidizable, such an anodic current increase is surprising. It can however been explained by a dispersed electrode phenomenon with platinum reacting in the O_2/H_2O system.

Indeed, with a dispersed electrode, the electrochemical reaction becomes preponderant with the concentration increase of particles inducing this reaction. In this case, if the number of the kaolin particles does not change, the perhydroxyl adsorbed radicals concentration increases with oxygen bubbling; thus the $-HO_2^-$ species oxidation implies anodic currents :

$$-HO_{2\,ads}^{-} \rightarrow H^+ + O_2 + 2e^-$$

3.4. AFEING INFLUENCE

The slurry used here is a sanitary ware composition containing 73 % of dried matter : 32 % of Guneath kaolin , 30 % of Hycast clay, 20 % of Mol sand and 18 % of nepheline syenite. The deflocculation was realised with sodium carbonate and sodium silicate (0.1 and 0.27 percent). The suspension ageing was followed during seven days, the first day being the preparation one. The results are represented at figures 10, 11 and 12 which represent viscosity, zeta potential, dissolved oxygen concentration, cathodic limit current (image of the adsorbed perhydroxyl radicals concentration), and polarisation resistance as a function of time.

The apparent viscosity decreases until the second day, probably because of the kinetic of deflocculation, which is not yet completely achieved; then, it increases as much as the slurry is aged. All the tests were carried out without any evaporation.

The zeta potential increases, in absolute value, between the first and the second day which justifies the recorded viscosity decrease. After that, it decreases continuously, proving the slurry progressive degradation during ageing.

The cathodic limit current density and the dissolved oxygen concentration vary in the same way leading to an asymptotic value. For the oxygen, this latter is the limit of oxygen dissolution for such ionic force (corresponding to 2.11 mg/l). For the cathodic limit current, this value means that all the perhydroxyl radicals occupy the free sites on the particles surface. The increase of the two curves is due to a rapid adsorption at the first time; the adsorption consuming dissolved oxygen.

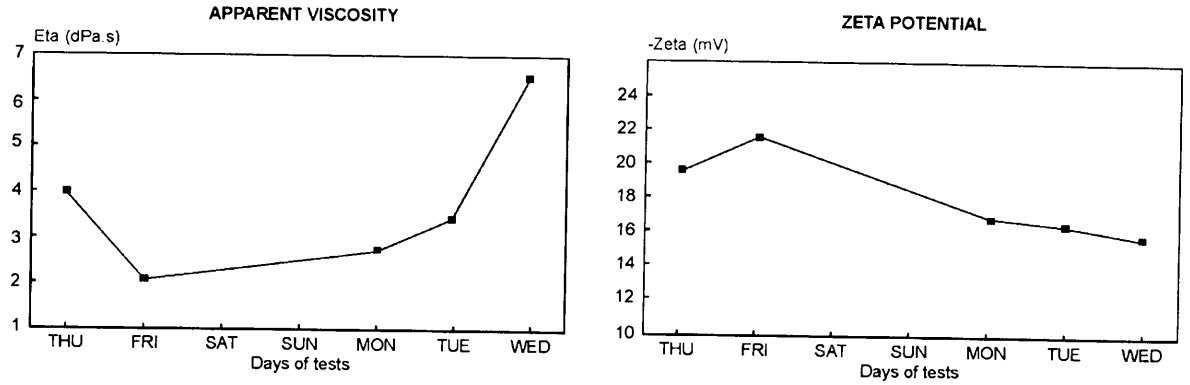

Figure 10. *Ageing effect on a sanitary slip*

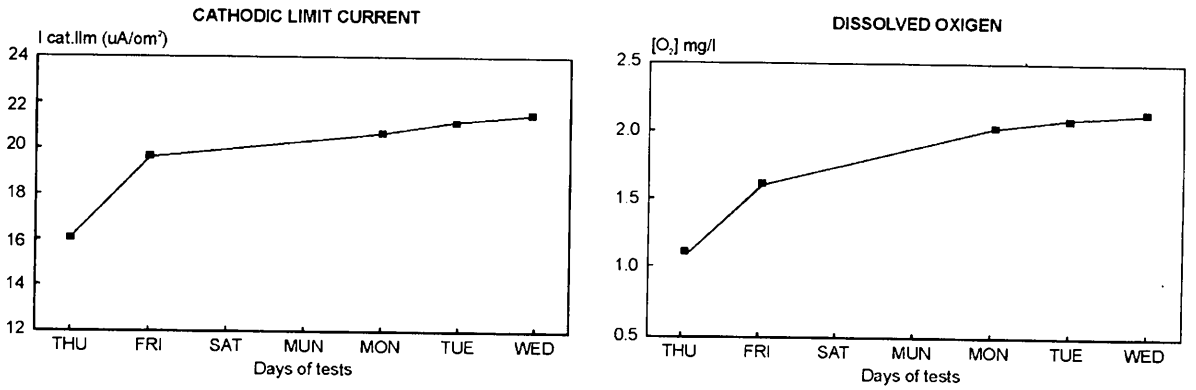

Figure 11. *Ageing effect on a sanitary slip*

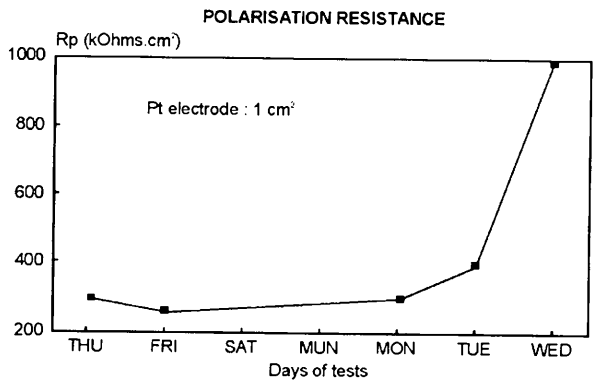

Figure 12. *Ageing effect on a sanitary slip*

After, as a consequence of the sites occupation, the adsorption rate decreases and a lower consumption of dissolved oxygen follows and thus, the recorded concentration increases.

The polarisation resistance decreases from the first to the second day and increases afterwards; at the seventh day a large increase is observed. The decrease of the polarisation resistance between the first and the second day is ascribable to the best deflocculation of the suspension. After, even if the cathodic limit current does not change, the increase of the polarisation resistance can be explained by the diminution of the particle charge, which will contribute to limit the particle charges transfer. As a consequence of the viscosity increase, both γ value (Equation 2) and polarisation resistance increase.

3.5. MIXING OF FRESH SLURRIES AND SCRABS

The slurries used for these experiments are not deflocculated. The classical process consists in clays and flux mixing in humid atmosphere, followed by filter pressing the past. Large amounts of pasts coming from unfired scraps, bad pieces, ... are then added to the fresh slurry.

A mixing of 20 % of fresh slurry and 80 % of old ones was studied as a function of time. The results of all the measurements are shown in figures 13, 14, 15 and 16 (viscosity, zeta potential, specific conductivity, polarisation resistance) after 2, 5 and 24 hours.

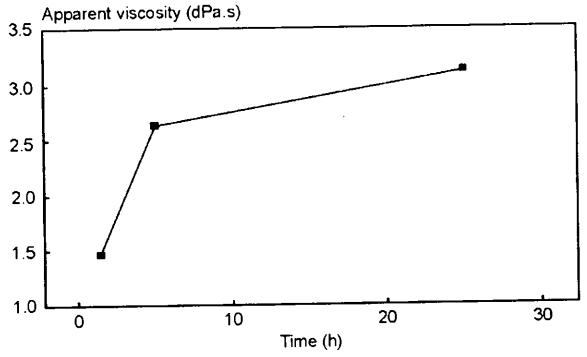

Figure 13. *Evolution of the apparent viscosity in function of time*

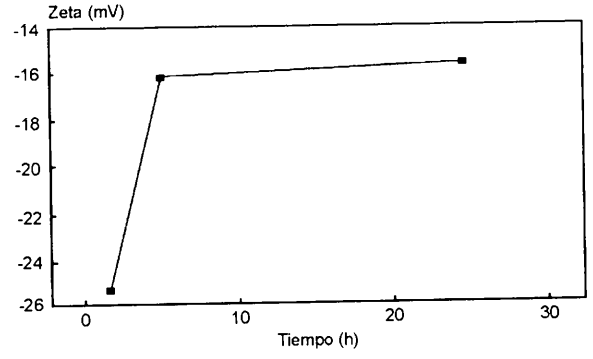

Figure 14. *Evolution of the zeta potencial in function of time*

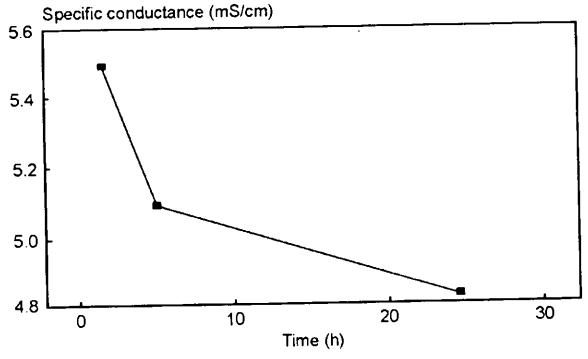

Figure 15. *Evolution of the specific conductivity in function of time*

As it can be seen in the figures, the specific conductivity decrease shows that the homogeneity is not yet completely achieved : an ionic exchange between particles takes place with a probable adsorption within the Hemholtz layer of counter-ions, because of a zeta potential decrease (in absolute value) and of an apparent viscosity increase.

The flocculation of the system involves an increase of the polarisation resistance as shown in paragraph 3.2. The explanation is the same.

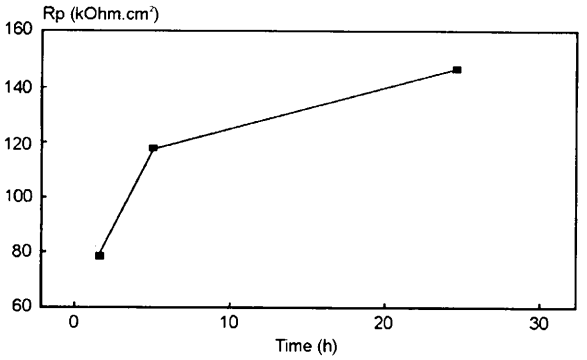

Figure 16. *Evolution of the polarisation resistance in function of time*

4. CONCLUSION

Classical electrochemical techniques can be used to determine the best deflocculation conditions of a ceramic slurry. The polarisation resistance emphasises the exchanges between particle surface and dissolved oxygen.

Dissolved oxygen, adsorbed on the particle surface as perhydroxyl species, is responsible of the suspension ageing and of its rheological properties degradation.

The study of slurry ageing also shows that the polarisation resistance variation results from two phenomenons:

- the variation of perhydroxyl species concentration as a function of deflocculant concentration
- the difficulty to achieve the charge transfer for limited concentration variations.

ACKNOWLEDGEMENT

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