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Influence of powder characteristics on the rheological behaviour of hydroxyapatite slurries

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A study of the influence of several dispersants (nature and concentration), of the calcination temperature and of the concentration of hydroxyapatite (HAP), on the rheological behaviour of HAP slurries, made it possible to obtain low viscosity slurries containing 73 wt% HAP and 3.5 wt% dispersant. The calcination of the HAP powder affected both the morphology and the chemical nature of the surface of particles. This last effect was clearly shown by the decrease of the zeta potential with increasing calcination temperature. The optimal calcination temperature was chosen beyond 800 °C. Parts sintered at 1200 °C for 30 min were obtained with a density higher than 96% of theoretical by casting optimized suspensions.

1. Introduction

Many studies devoted to the *in vivo* and *in vitro* behaviour of hydroxyapatite (HAP) have shown excellent biocompatibility when used as bone substitute [1–3].

The demand for porous parts for filling or reconstruction has increased in the last few years. These porous pieces can be obtained by various routes: by duplicating a coral skeleton [4], by producing porosity during the drying of a slurry [5, 6] or during the elaboration of a glass [7, 8], and by impregnating a porous polymeric mould which is subsequently pyrolysed [9–11]. This latter method allows generation of complex shapes, but requires a good knowledge of the rheological behaviour of concentrated HAP suspensions. The characteristics of the powder (particle shape and size, and chemical composition) which depend on the parameters of the powder synthesis, greatly influence the rheological behaviour.

The objective of this study was to investigate the influence of the calcination temperature and powder concentration of HAP powder on the rheological behaviour of HAP suspensions.

2. Experimental procedures

2.1. Powder preparation

The HAP powder was obtained by precipitation between $Ca(NO_3)_2$ and $(NH_4)_2HPO_4$ at 100 °C and pH = 8. The precipitate was then treated at temperatures varying from 100 °C to 1180 °C, leading to different specific surface area.

2.2. Slurries preparation

HAP powders were dispersed, with the help of a dispersant, by agitation in an alumina jar with porcelain balls. Slurries were prepared with powder concentrations varying from 60 to 75 wt%, and with various specific surface area powders. To reach high concentration the addition of powder to the slurry was done in several steps.

2.3. Dispersant

The nature and the optimized amount of dispersant were determined in terms of viscosity behaviour. The dispersant screening was performed using suspensions containing 63 wt% HAP (specific surface area: $18\ m^2\ g^{-1}$) and 3 wt% dispersant.

2.4. Characterization of the suspensions

Dispersant screening and rheological investigations were performed at 20 °C using a rotating automatic viscometer (Haake RV 20). Viscosity was measured for a shear rate range from 0 to $100\ s^{-1}$. Each curve corresponds to a mean value of three experiments.

Four methods of determination of particle size (agglomerates, grains, crystallites) were used. Agglomerate size distribution was performed using an X-ray granulometer (Micromeritics Sédigraph 5000) with a lower detection limit of 0.1 μm. Elementary grain size was determined by specific surface area measurement (BET method with a Micromeritics 2205 apparatus). Values of both agglomerate size and grain size were confirmed by scanning electronic microscopy (Hitachi S2500). Elementary crystallite size was evaluated by treatment of profiles of X-ray diffraction peaks, on the 0 0 2 peak (intensity 40%), after deconvolution of the 2 0 1 peak.

Zeta potential was measured using a laser zetameter (Pen Kem-501). Each electrophoretic mobility was calculated from the average of four measurements on suspensions containing 400 mg l^{-1} of HAP.

The relative density was determined by measuring the geometrical dimensions of polished plots.

3. Results and discussion

3.1. Choice of dispersant

Among the 34 dispersants which were tested, many were not efficient, in particular sodium silicate and non-ionic surfactants. The most efficient one, for HAP powder, was an anionic polyelectrolyte. This dispersant allowed the achievement of slurries containing 70 wt% HAP with a viscosity of 75 mPa s at a shear rate of 128 s^{-1}. According to the variation of the viscosity versus the amount of dispersant (Fig. 1), a concentration of 3.5 wt% was retained for this study.

3.2. Influence of powder concentration

Powder concentration greatly influences the rheological behaviour of a slurry. There is an extensive literature concerning the rheological behaviour of suspensions of clays, alumina, barium titanate and other fine ceramics [14–17], but few studies concern HAP. Nordström *et al.* [18] reached a concentration of 63 wt% for a mixture of TCP and $Ca(OH)_2$, and Galassi *et al.* [19] prepared suspensions with 80 wt% of HAP calcined at 1000 °C. Similar results were recently obtained by Simoes *et al.* [20], and more recently Toriyama *et al.* succeeded in the realization of slurries containing 20 vol% HAP with 3% polyacrylate dispersant [21].

The viscosity of slurries containing 60, 65, 70, 73 and 75 wt% HAP powder (18 $m^2 g^{-1}$) was measured (Fig. 2).

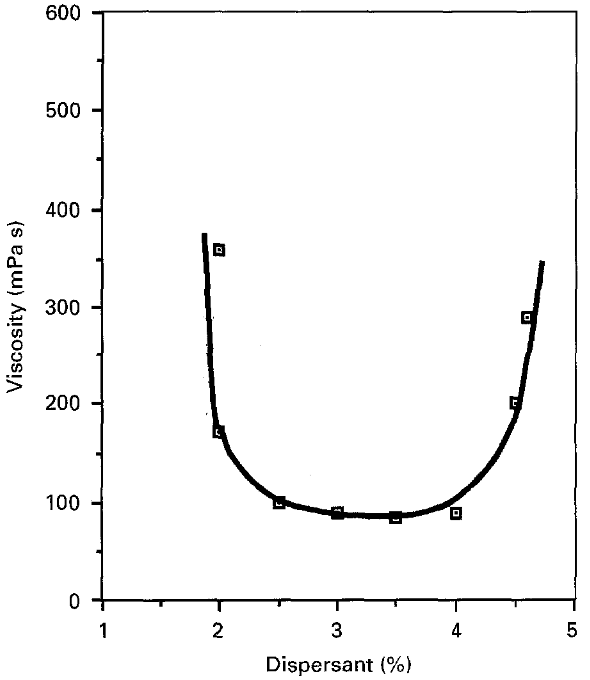

Figure 1 Influence of dispersant concentration on viscosity of an HAP slurry (powder concentration 60 wt%).

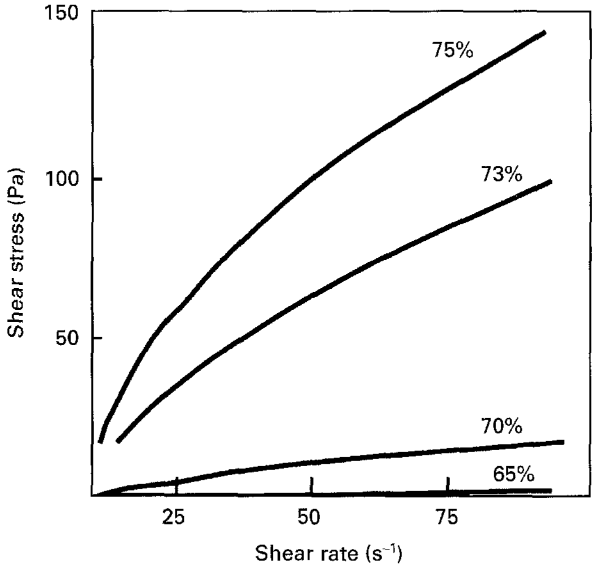

Figure 2 Rheological curves for slurries containing different amounts (wt%) of HAP powder (dispersant concentration 3.5 wt%).

TABLE I Rheological behaviour of HAP (18.2 $m^2 g^{-1}$) slurries containing various powder concentrations, with 3.5 wt% dispersant

HAP concentration (wt%)	Model	Correlation coefficient	Equation	Coefficients
60	Newton	1	$\tau = \eta D$	$\eta = 0.02$
65	Newton	1	$\tau = \eta D$	$\eta = 0.04$
70	Ostwald	0.99	$\tau = \eta D^n$	$\eta = 688$ $n = 0.73$
73	Ostwald	1	$\tau = \eta D^n$	$\eta = 6.2$ $n = 0.61$
75	Ostwald	1	$\tau = \eta D^n$	$\eta = 11.5$ $n = 0.56$

For low powder concentrations, i.e. lower than 70 wt%, slurries exhibited a Newtonian behaviour, whereas for higher powder concentrations the slurries were shear thinning. Table I confirms these behaviours: the linear (Newtonian) and the power law (shear thinning) are in agreement with experimental data for HAP concentrations lower and higher than 70 wt%, respectively.

The transition of Newtonian to shear thinning behaviour can be attributed to an increasing difficulty for particles to orientate in the direction of the shear stress as the powder concentration, and then the viscosity, increase. At a shear rate of 75 s^{-1}, the viscosity drastically increased at concentrations above 70 wt% HAP: from 200 mPa s for 70 wt% HAP to 1800 mPa s for 75 wt% HAP (Fig. 3).

The green density of samples cast in plaster moulds increased as the powder concentration in the slurry increased. The density of samples dried and sintered at 1200 °C for 30 min also increased with powder concentration (Table II).

The green density increased from 48 to 51% of theoretical density (3.15 g cm^{-3}) and the sintered density from 94 to 96% as HAP concentration increased from 60 to 75 wt%. High fired density requires high powder loading, and good casting characteristics

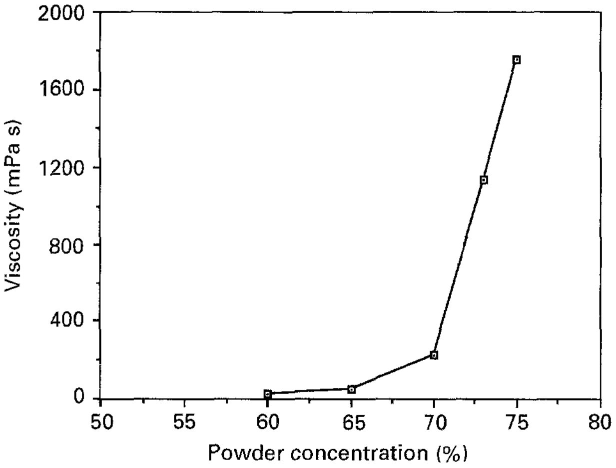

Figure 3 Increase of slurry viscosity with powder concentration (dispersant concentration 3.5 wt%, shear rate 75 s^{-1}).

TABLE II Green and sintered (1200 °C; 30 min) densities of samples cast with slurries containing various HAP concentrations (theoretical density = 3.15 $g\,cm^{-3}$)

HAP concentration (wt%)	60	65	70	73	75
Green density (%)	48	49	50	51	51
Fired density (%)	94	95	95	96	96

require low viscosity and hence, low powder loading. An HAP concentration of 73 wt% seems to be a good compromise between these two requirements.

This optimum concentration was determined using an HAP powder calcined at 750 °C, leading to a specific surface area of 18.2 $m^2\,g^{-1}$. The temperature of calcination of the HAP powder greatly influences the specific surface area and thus the rheological behaviour of slurries.

3.3. Influence of specific surface area

HAP powders were calcined at temperatures from 90 to 1180 °C, without any plateau. Whatever the temperature of calcination, X-ray diffraction patterns show well-crystallized stoichiometric apatite with a Ca/P ratio which remains equal to 1.66 (no peak for CaO or β-TCP, and a negative reaction with phenolphtaleine). The specific surface area decreased from 60 $m^2\,g^{-1}$ (for the dried cake) to 0.68 $m^2\,g^{-1}$ as the calcination temperature increased up to 1180 °C (Fig. 4).

Agglomerate, grain and crystallite sizes are given in Table III.

Whatever the calcination temperature, SEM observations show dense particles (Fig. 5).

The powder morphology is greatly modified above a calcination temperature of 750 °C, with agglomerates ranging in size from 3 to 20 µm constituted of 0.5 to 2 µm grains. A direct consequence of this large increase in particle size (grains and agglomerates) was sedimentation of slurries prepared with powders calcined above 1180 °C.

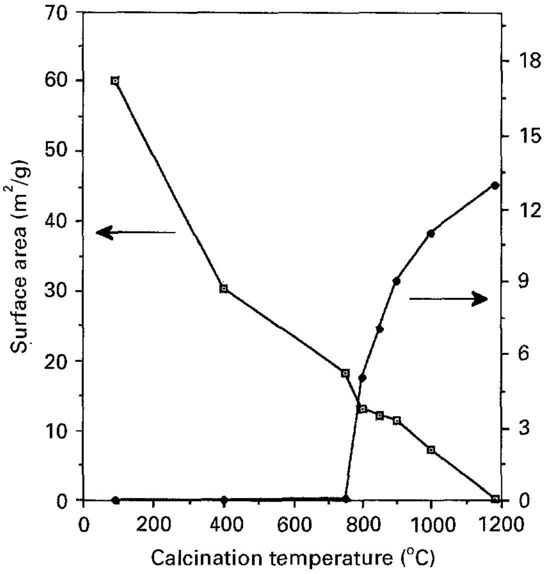

Figure 4 Influence of calcination temperature on the surface area and mean grain diameter of HAP.

TABLE III Size of agglomerates, grains and crystallites of HAP powders calcined at 90, 750 and 1180 °C

Method for measuring *r* (µm)	Temperature (°C)		
	90	750	1180
Sedimentation	< 0.3	< 0.3	13
BET	–	0.05	2.79
S.E.M.	0.04	0.05	Agglomerates a few µm
XRD	0.045	0.045	0.085

The morphology and nature of the surface of HAP particles (depending on the calcination temperature) influenced the rheological behaviour of the slurries (Fig. 6).

Slurries containing 73 wt% HAP exhibited shear thinning behaviour for high specific surface area powders (higher than 7.5 $m^2\,g^{-1}$, calcination temperature < 1000 °C), with a yield value for a calcination temperature of 1000 °C. The slurry prepared with a very low specific surface area powder, calcined at 1180 °C, exhibited Newtonian behaviour (Table IV).

Using rheological laws given in Table IV, the viscosity values, at 50 s^{-1}, of slurries containing 73 wt% HAP were calculated. Calculated viscosities were reported versus the specific surface area and hence, the temperature of calcination, in Fig. 7.

A drop in viscosity appears above a specific surface area of 12 $m^2\,g^{-1}$, corresponding to a calcination temperature of 800 °C.

Fig. 1 shows that the viscosity of a slurry prepared with powder with a specific surface area of 18.2 $m^2\,g^{-1}$ increases for a dispersant concentration higher than 4 wt%, corresponding to a surface concentration of 2.2 $mg\,m^{-2}$. The electric double layer was compressed by too high an electrolyte concentration and the electrostatic repulsion was less effective. If the temperature of calcination does not affect the

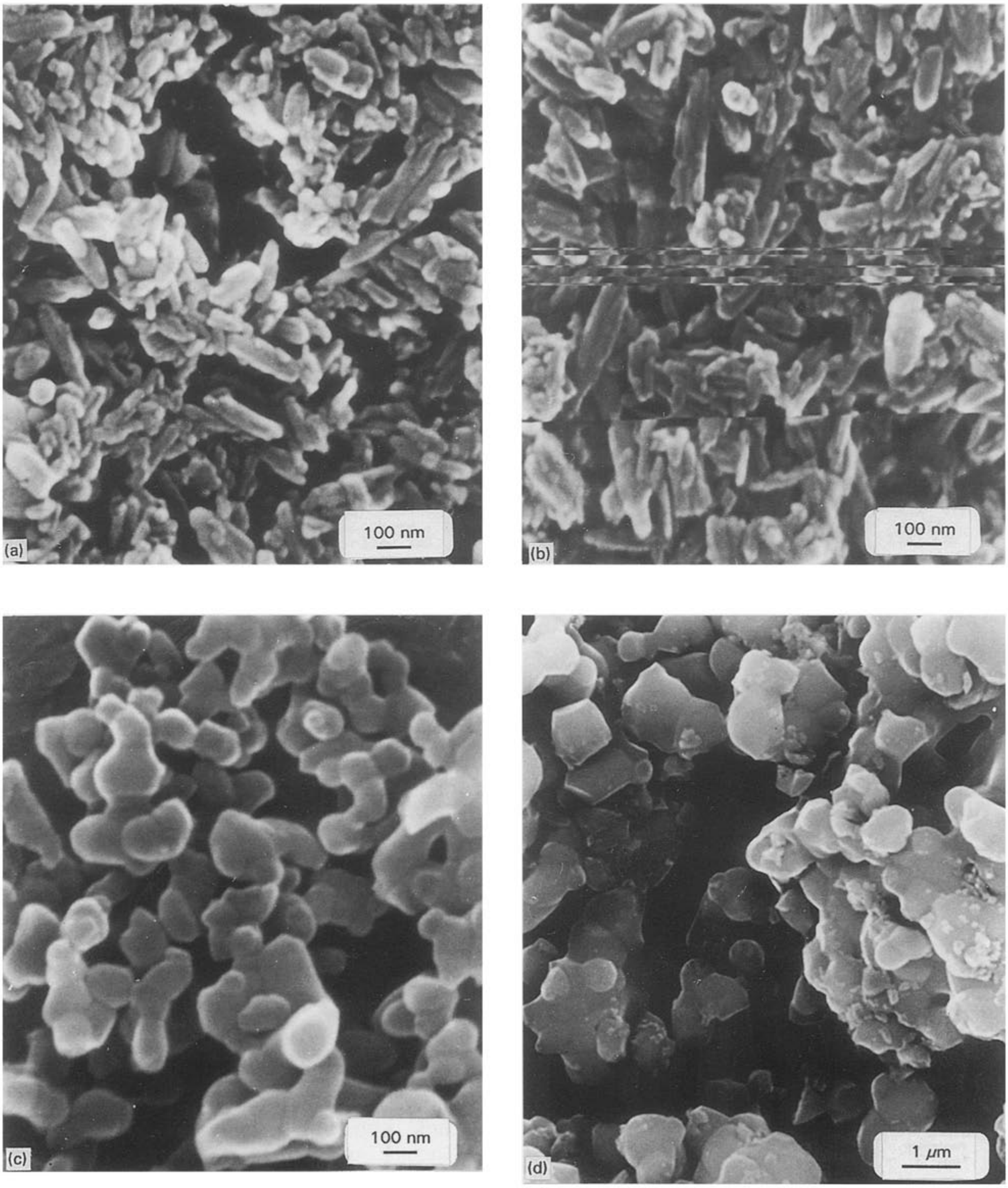

Figure 5 Scanning electron micrograph of HAP calcined at different temperatures: (a) 90 °C, (b) 400 °C, (c) 900 °C, (d) 1180 °C.

chemical nature of the particle surface, the viscosity of a suspension containing 3.5 wt% of dispersant should increase for powders having a specific surface area lower than 16 $m^2 g^{-1}$, corresponding to a surface concentration higher than 2.2 $mg m^{-2}$. Then, for calcination temperatures higher than 750–800 °C, the viscosity of slurries containing 3.5 wt% of dispersant should increase, which is not in agreement with our results. We can conclude that the thermal treatment affected the chemical nature of the surface of the particles and that the electric charges developed at the surface in presence of the dispersant were changed with the calcination temperature.

Zeta potential, which is representative of the state of dispersion, was measured for powders calcined at various temperatures. The value of zeta potential rapidly decreased for calcination temperatures higher than 800 °C (Fig. 8).

Whereas the specific surface area continuously decreased as the temperature increased, the viscosity and zeta potential were greatly affected only above a critical temperature of 800 °C. This temperature also corresponded to the beginning of densification.

Green and fired (1200 °C for 30 min) densities of samples elaborated by slip casting of slurries containing 3.5 wt% dispersant and 73 wt% powder

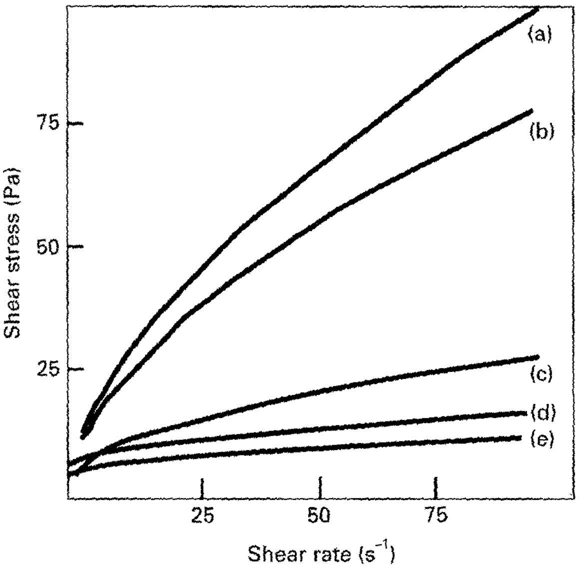

Figure 6 Rheological curves for slurries containing powders calcined at different temperatures (3.5 wt% dispersant): (a) 750 °C, (b) 800 °C, (c) 900 °C, (d) 950 °C, (e) 1000 °C.

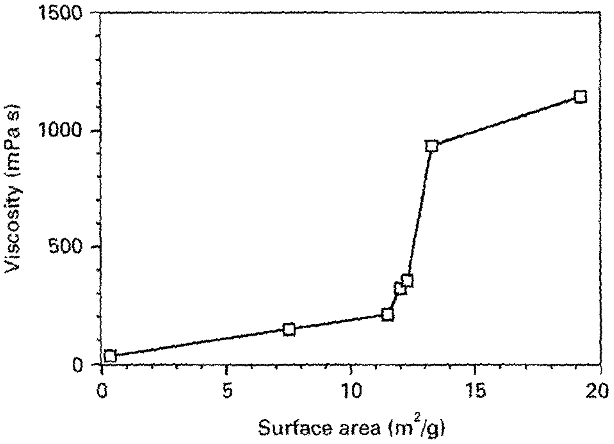

Figure 7 Influence of the surface area of the starting powder on the viscosity of HAP slurries (shear rate 50 s^{-1}).

with various specific surface areas were plotted in Fig. 9.

Higher fired densities did not correspond to higher green densities. Low specific surface area powders exhibited a better grain arrangement but were less reactive. The densification rate varied with the elementary grain radius r, as r^{-3} or r^{-4}. An increase of calcination temperature from 750 to 1180 °C resulted in an elementary grain size increase from 0.05 to 2.8 μm, and hence a reduction of the densification rate of a factor 6×10^5 or 31×10^6 for volume diffusion or grain boundary diffusion controlling mechanisms, respectively.

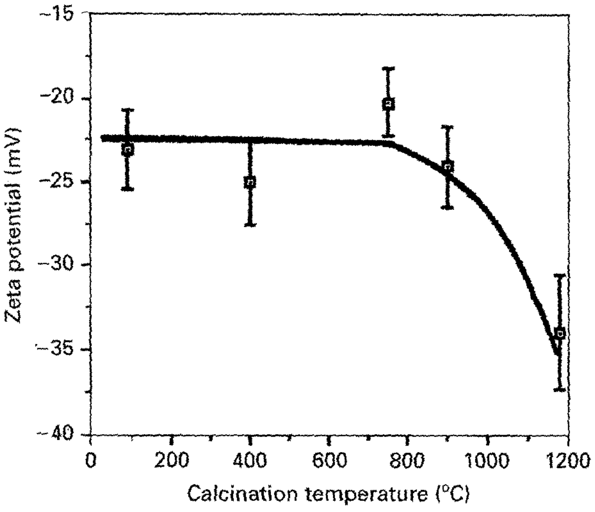

Figure 8 Evolution of HAP zeta potential versus calcination temperature.

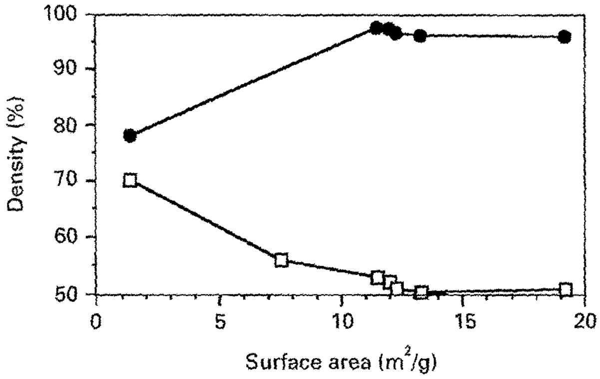

Figure 9 Green (-□-) and fired (-●-) density (1200 °C, 30 min) for samples obtained by slip casting.

TABLE IV Rheological behaviour of slurries containing 73 wt% HAP calcined at various temperatures, with 3.5 wt% dispersant

T (°C)	S_{BET} (m^2 g^{-1})	Model	Correlation	Equation	Coefficients
750	18.2	Ostwald	1	$\tau = \eta D^n$	$\eta = 6.17$ $n = 0.61$
800	13.3	Ostwald	1	$\tau = \eta D^n$	$\eta = 5.52$ $n = 0.59$
850	12.3	Ostwald	1	$\tau = \eta D^n$	$\eta = 2.9$ $n = 0.50$
900	12	Ostwald	1	$\tau = \eta D^n$	$\eta = 2.81$ $n = 0.50$
1000	7.5	Bulkley	0.95	$\tau = \tau_0 + \eta D^n$	$\eta = 0.57$ $\tau_0 = 2.96$ $n = 0.62$
1180	0.3	Newton	1	$\tau = \eta D$	$\eta = 0.026$

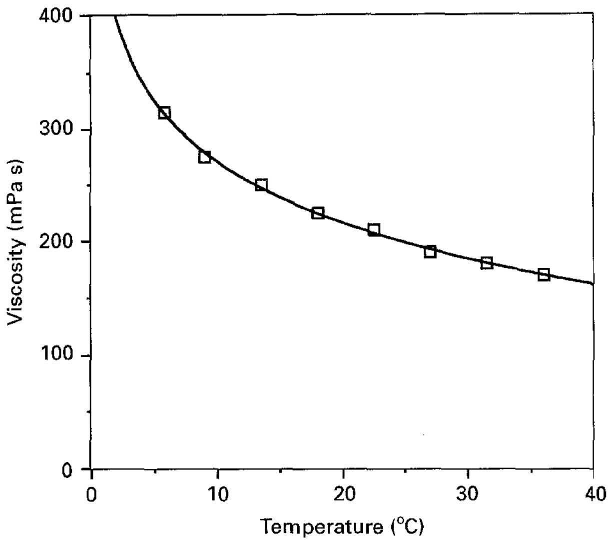

Figure 10 Dependence of the viscosity of an HAP slurry on the temperature (73 wt% HAP of surface area: $11.5\,m^2\,g^{-1}$ with 3.5 wt% dispersant at a shear rate of $100\,s^{-1}$).

3.4. Influence of slurry temperature

The evolution of viscosity with temperature of a slurry containing 73 wt% HAP calcined at 950 °C (specific surface area $11.5\,m^2\,g^{-1}$) and 3.5 wt% is plotted in Fig. 10.

A classical decrease of viscosity (η) is observed with temperature (T); the viscosity can be expressed by

$$\eta = 443.5 - 75.79 \ln T.$$

4. Conclusion

This work has shown that the conditions of elaboration of HAP powders play a prominent role in the rheological behaviour of slurries. The influence of the temperature of calcination was studied. Calcination of the HAP powder affected both the morphology and chemical nature of the surface of particles. It was not possible to achieve suspensions with a high powder loading for HAP calcined below 500 °C, due to acicular particles and high specific surface area ($> 26\,m^2\,g^{-1}$). Too high a temperature of calcination (> 1000 °C) led to large particles which settle out. A good compromise is in the 500–900 °C range.

Using an anionic polyelectrolyte dispersant, it was possible to prepare suspensions with an HAP concentration of 73 wt% and to obtain parts with a sintered density (at 1200 °C) higher than 96%. A further task will be to improve the sintering cycle in order to try to increase the fired density.

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