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RHEOLOGICAL STUDY OF CLAY-KAOLIN AQUEOUS SUSPENSIONS

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Translation of "Studio Reologico di Sospensioni Acquose di Argilla/Caolino", Ceramurgia, Volume 11, Number 2, 1981, pp. 57-61.

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16. Abstract

Reological characteristics of clay-kaolin aqueous suspensions were studied by a rotational viscometer to correlate their behavicr with the properties of ceramic slips for casting containing quartz, feldspars, and other nonplastic materials. In particular, the effects of the different amounts of dry materials and deflocculant (mixture 1:1 of Na_2CO_3 and Na_2SiO_3) and of temperatures on the shear-time-dependent properties of suspensions were examined.

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RHEOLOGICAL STUDY OF CLAY-KAOLIN AQUEOUS SUSPENSIONS

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1. Introduction

The property of clay to give colloidal aqueous suspensions is   /57*
widely used by the ceramic industry. These suspensions to which kaolin,
fluxes and finely crushed quartz as well as deflocculants are added are
placed in suitable gypsum molds so as to obtain, after hardening and
drying, the object of desired shape.

The rheological properties of such slips, which are deeply affected
by the dose of the different components, influence considerably the
casting speed. On the other hand, possible changes in their composition,
meant for accelerating this phase of the production process, may alter
the drying speed and some characteristics of the objects such as, for
example, the crude mechanical resistance in the crude slate and the
appearance of the surfaces.

In general the slips are non-Newtonian inasmuch as the viscosity
depends on the speed gradient to which the material is exposed and on
the rheological history of the material itself. Consequently it is nec-
essary to know their characteristics depending on shear and time and the
parameters affecting them.

This is extremely useful in planning and determining the dimensions
of the spray dryer, unless drastic simplifications are adopted such as
that of disregarding the losses of load inside the centrifugal nozzles
or resorting to empirical types of relationships whose applications are
difficult to suspend suspensions with different contents of dry mater-
ial and deflocculant. Finally the paper industry which uses kaolin as

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*Numbers in the margin indicate pagination in the foreign text.

"filler" applied by means of a wet process is involved in very similar problems.

All these considerations lead us to implementing a program of research concerning the rheological behavior of suspensions containing kaolin and clay; also because a literature search of the study convinced us that in spite of the fact that there has been considerable scientific activity in the sector, many investigators used instruments which did not make it possible to characterize completely, from the rheological point of view, the systems examined or they used disputable procedures such as those of hysteresis loop or finally they confined themselves to investigations of suspensions at very low concentrations of solid material.

2. Materials and Experimental Procedures

The starting material used in our experiments consisted of a mixture containing 52.5 % kaolin and 47.5 % of a crushed French clay of the GSG type furnished by the Petra Company. The two components were characterized from the chemical, mineralogical and granulometric point of view by the traditional techniques (chemical weight analysis and by atomic absorption, RX diffractometry, sedimentometric balance). The results are given in Table 1. The deflocculant used is the classic mixture with a weight proportion 1 to 1 of sodium carbonate and silicate, the percentages added, calculated with regard to dry material, varied between 0.1 and 1 %.

The suspensions prepared by this method (altogether 1 kilogram) were homogenized in a ball grinder with a capacity of 1.4 liter and with a speed of rotation of 82 rpm.

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Table 1. Chemical Composition and Granulometric Distribution of the Materials Used

	Chemical composition (weight percentage)			Granulometric Distribution (weight percentage)		
	clay	kaolin		$d(\varnothing)$	clay	kaolin
l.i.(*)	11.6	12.3		> 9.6	6.6	1.6
SiO_2	50.6	46.0				
Al_2O_3	33.7	39.3				
Fe_2O_3	1.5	0.8		$9.6 \div 3.0$	6.7	10.1
TiO_2	1.4	---				
K_2O	0.7	0.4		$3.0 \div 1.6$	6.7	31.1
Na_2O	0.1	0.4				
CaO	0.3	0.1		< 1.6	80.0	57.2
MgO	0.1	0.1				

*firing loss; $(\varnothing)$ equivalent diameter in μm.

The experimental tests were carried out with a rotational viscosimeter of the type Rotovisko Haake, RV2, in the velocity gradient range between 10 and 2,000 s^{-1}. The measurement system used is of the type with coaxial cylinders (diameter ratio = 0.96). The experimental procedure adopted consisted of the application of the sequence of constant velocity gradients; each gradient was applied until a stationary value of the shear force was obtained. The tests were conducted at 25 $\pm$ 0.1° C.

3. Results and Discussion

At high concentrations of solids and low concentrations of the deflocculant, the experimental procedure makes it possible to reveal a considerable thixotropic behavior, that is considerable variations of the shear force in time with constant velocity gradient. These variations of the shear force in time are the result of processes of structural destruction or reconstruction taking place within the material through the effect of variations of the kinematic conditions imposed.

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Various approaches may be followed to describe the thixotropic behavior and to give a theoretical interpretation. In previous publications [1, 2] some examples were given of application of the approaches of Cheng [3] and Camina [4] to the thixotropic behavior of suspensions of kaolin and clay.

As regards the shear-dependent properties which are the subject of this study, all the systems show a similar behavior in the range of velocity gradients studied. This behavior depends to a considerable extent, in quantitative terms, on the concentration of solids and deflocculant.

Figures 1, 2 and 3 give the curves of the equilibrium flux of the systems at three different concentrations of solid considered. The above mentioned similarity of rheological behavior and the drastic reduction of viscosity resulting from the addition of deflocculant is apparent.
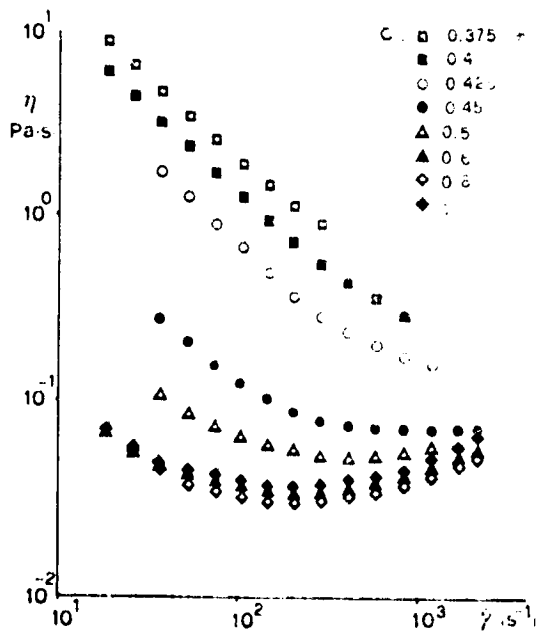
Figure 1: Viscosity η against velocity gradient $\dot{\gamma}$ for the systems with concentration of solid C_S equal to 61 %.
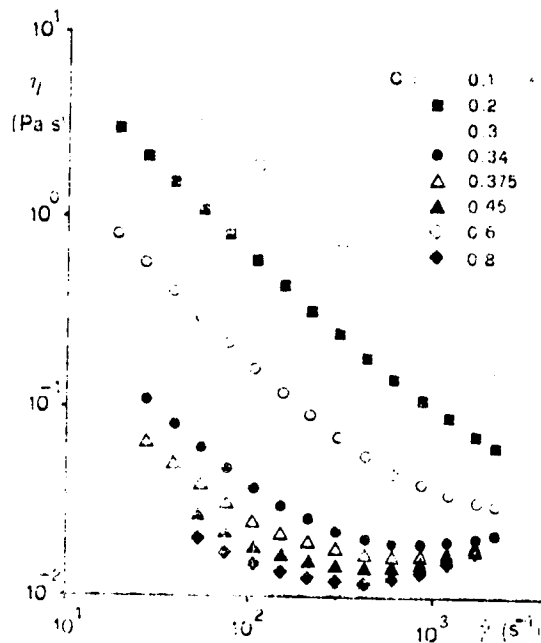
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Figure 2: Viscosity η against velocity gradient $\dot{\gamma}$ for the systems with solid concentration C_S equal to 50 %.
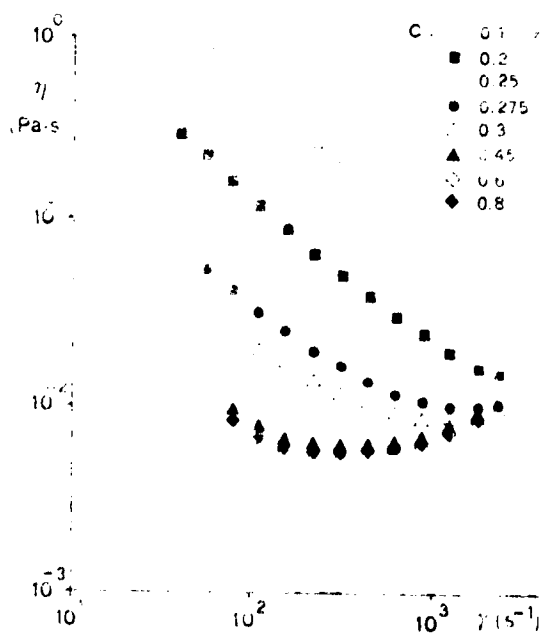

Figure 3: Viscosity η against velocity gradient $\dot{\gamma}$ for the systems with solid concentrations C_S equal to 40 %.

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The similarities of the curves of flux makes it possible to give a compact representation of the shear-dependent behavior of all the systems considered, according to a procedure of superimposition by translation of the curve [2,5]. The flux curve of a system (in the present case the system with concentrations of solid C_S - 61 %, and concentration of deflocculants equal to 0.375 %) is taken as reference curve. The flux curves of all the other systems are translated over the reference curve. The components of the translation vector determine the translation factors a and a_γ. The curve of the reference system may be taken as characteristic curve of the family of systems (master curve) in a diagram $\log \eta_R$ - $\log \dot\gamma_R$ in which η_R and $\dot\gamma_R$ are reduced variables defined by $\eta_R = \eta/a \; ; \; \dot\gamma_R = \dot\gamma/a$
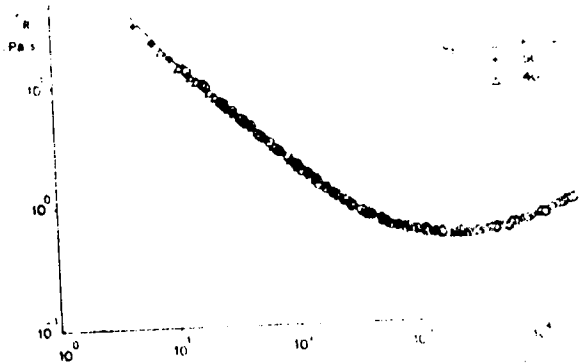

Figure 4: Characteristic flux curve (master curve) in terms of reduced viscosity η_R against reduced velocity gradient $\dot\gamma_R$.

Therefore the first result which is obtained with this procedure is the plotting of the characteristic curve shown in Figure 4 in a diagram $\log \eta_R$ - $\log \dot\gamma_R$. Another advantage deriving from the application of such a procedure is that in this way it is easy to obtain the characteristic rheological parameters of this sytem. As regards these parameters it is observed primarily that for each system it is possible to determine both directly and/or through the above mentioned procedure a critical velocity gradient $\dot\gamma_c$ below which the shear-dependent behavior is plastic and may be described satisfactorily with the Bingham model.

Above $\dot\gamma_c$ the behavior becomes dilating. Figure 4 shows the flux curve described by the Bingham model and obtained through the fitting

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of all the experimental points concerning the field of velocity gradients less than $\dot{\gamma}_c$.

Therefore the shear-dependent rheological behavior of each system is characterized by three parameters: the limit of slipping τ_B, the plastic viscosity η_P and the critical velocity gradient $\dot{\gamma}_c$. The effect of the concentration of the solid and the deflocculant on the shear-dependent rheological properties of the suspensions may therefore be described by the variations of such parameters.

Figure 5: Limit of slipping τ_B against concentration of deflocculants C.

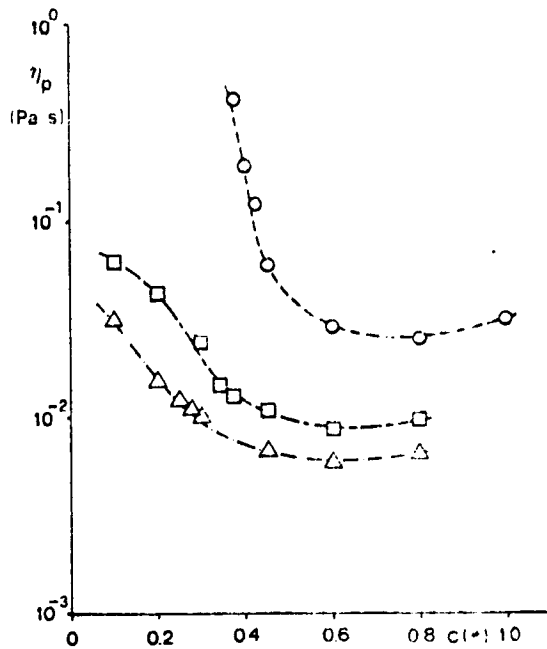($\bigcirc$: C = 61%; $\square$: C = 50%; $\triangle$: C = 40%)

Figure 6: Plastic viscosity η_p against concentration of deflocculant C.

$(\bigcirc : C_v = 61\%;\ \square : C_v = 50\%;\ \triangle : C_v = 40\%)$.

Figure 7: Critical velocity gradient $\dot{\gamma}_c$ against concentration of defloccu-lant C.

$(\bigcirc : C\ 61\%;\ \square : C\ 50\%;\ \triangle\ C\ 40\%)$

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Figures 5, 6 and 7 give the variations of τ_B, η_P and $\dot{\gamma}_C$ with the variation of the concentration of deflocculant. The progressive addition of deflocculant causes a drastic reduction of the parameters, a reduction which is maximum in case of saturation conditions. This condition is achieved for different values of concentration at the three levels of solid concentration studied. Beyond these conditions, subsequent conditions of deflocculant do not cause considerable effects of overdoping. Figures 8, 9 and 10 show the effects of the variation of the solid concentration on τ_B, η_P and $\dot{\gamma}_C$, evaluated in accordance with three different values of concentration of deflocculant.
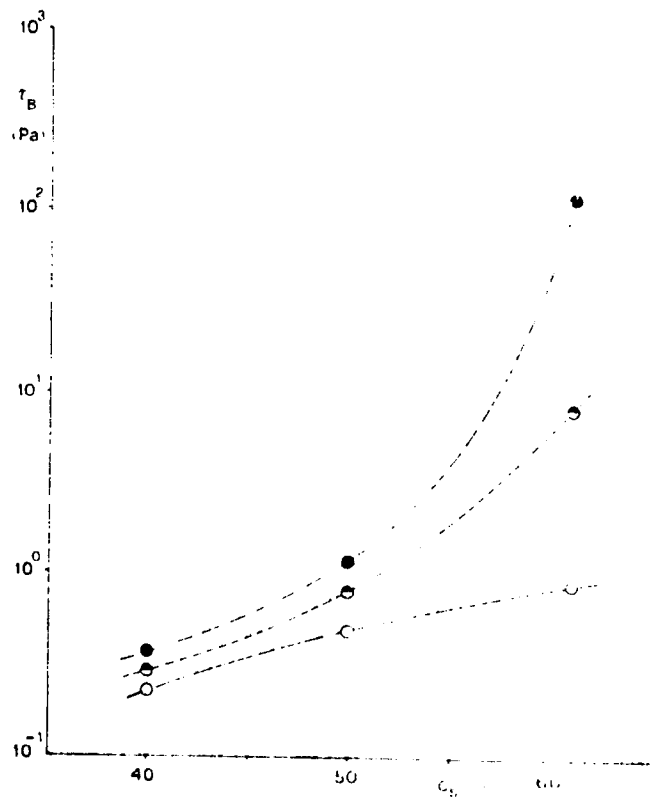

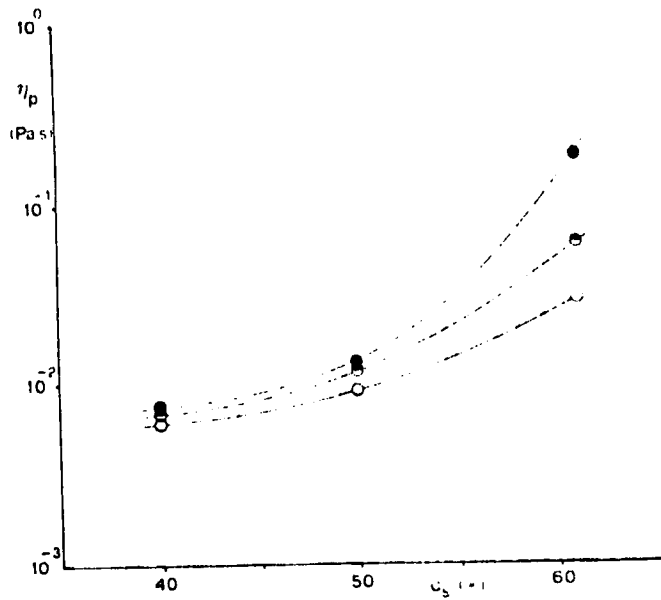Figure 8: Limit of slipping τ_B against solid concentration C_s (● : C = .4%; ◓ : C = .45%; ○ : C = .6%).

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Figure 9: Plastic viscosity η_p against solid concentration C_S.
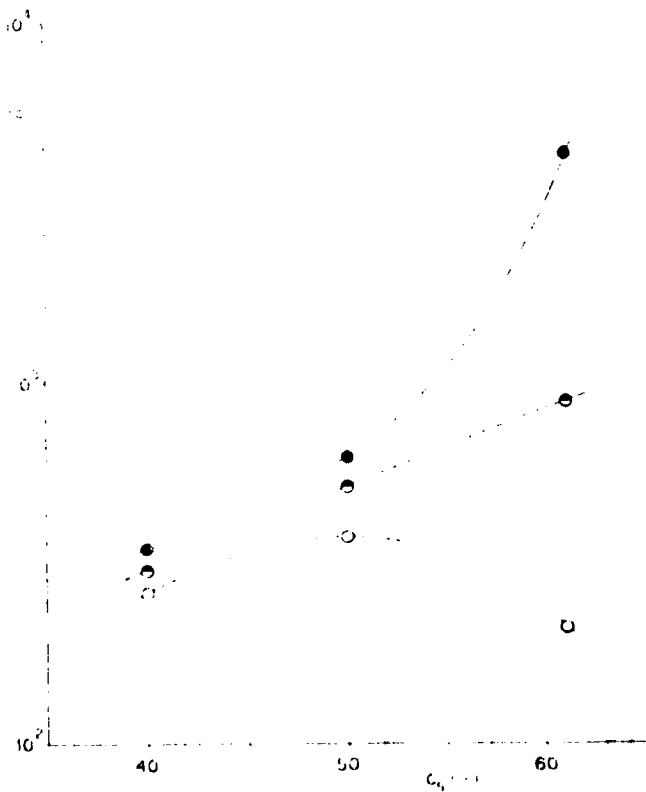
($\ominus$: C = .4% ; $\spadesuit$: C = .45% ; $\bigcirc$: C .6%).

Figure 10: Critical velocity gradient $\dot{\gamma}_c$ against solid concentration C_S.

($\bullet$: C .4% ; $\spadesuit$: C .45% ; $\bigcirc$: C .6%).

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The variation of the parameters with the concentration of deflocculants is derived from the variations of the state of aggregation of the particles obtained from the absorption of deflocculant and the variation of potential. Actually the adsorption and the development of the double layer are the main mechanisms by means of which we explain the effect of the deflocculant used which frees by hydrolysis Na^+ cations and colloidal silica.

The high concentrations of solids and the considerable variations inside the family of systems studied, of the conditions of aggregation of the dispersed phase makes it difficult to apply extensively the analyses and models proposed by various authors [6-12] to interpret the rheological behavior of suspensions of kaolin, clay and similar materials. At the present time it was considered suitable to reexamine some interpretations proposed by Firth and Hunter [9] concerning the flow properties of colloidal suspensions to evaluate the possibility of extending them to the systems in question.

According to those authors and according to what was already indicated by Thomas [8], it is possible to obtain from the data on plastic viscosity, an estimate of the effective value of the concentration of the dispersed phase and its variation with the variation of the concentration of deflocculants.

From the value of the relative viscosity η_R (defined by the ratio η_p/η_S with η_S the viscosity of the dispersing medium) and from the equation of Thomas [13], valid for suspensions of spherical particles without mutual interaction:

$$\eta_R = 1 + 2.5 \, \Phi + 10.05 \, \Phi^2 + 2.73 \times 10^{-3} \exp (16.6 \, \Phi)$$

it is possible to obtain the value of the effective volumetric fraction of the dispersed phase assuming the flux units present in conditions of high velocity gradients as spherical.

The ratio $C_{FP} = \phi_{Eff}/\phi_P$, in which ϕ_{Eff} is the effective volumetric fraction calculated by this means and ϕ_P is the nominal volumetric fraction, gives a measure of the increase of volume of the dispersed phase resulting from the aggregation of particles. Table 2 gives the values of C_{FP} for three different concentrations of solids (C_S = solid concentration, C = concentration of deflocculant. It is apparent that according to the conditions of maximum reduction of the plastic viscosity of the systems, the deflocculation of the dispersed phase is not complete, the minimum values of C_{FP} being equal to 1.99, 1.62 and 1.43 for the three different concentrations of solids considered.

Table 2: Values of C_{FP} calculated on the basis of equations of Thomas

$c_s = 40$		$c_s = 50$		$c_s = 61$	
c (%)	C_{FP}	c (%)	C_{FP}	c (%)	C_{FP}
1	2.73	1	2.16	.375	1.91
.2	2.44	.2	2.06	.4	1.78
.25	2.36	.3	1.92	.425	1.70
.275	2.31	.34	1.78	.45	1.59
.3	2.26	.375	1.74	.5	1.54
.45	2.07	.45	1.68	.6	1.46
.6	1.99	.6	1.62	.8	1.43
.8	2.03	.8	1.65	1.0	1.48

As regards the dependence of τ_B on C_{FP}, the linear correlation given by Hunter and Frayne [12] may be considered valid only in the first approximation. The decrease of $\dot{\gamma}_c$ with the addition of deflocculation means that in conditions of greater deflocculation, the expansive behavior of the kaolin/clay suspensions is manifested at lower velocity gradients. We refer to the article by Beazley [14] for a possible interpretation.

From an examination conducted on a restricted series of systems within the range from 20 to 30°C, it was found that the variations of viscosity with temperature are more marked at high velocity gradients. As regards the characteristic rheological parameters, this is manifested in a considerable variation of the plastic viscosity η_P, while the

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limit of slipping τ_B remains approximately constant in the cases
studied. If we analyze the data in terms of relative viscosity,
it is observed that under this aspect too no considerable varia-
tions are observed with the temperature, and the conclusion must
therefore be drawn that in the range of temperature considered
and for the systems studied, the decrease of the viscosity of
the suspensions with the temperature is derived substantially
from the decrease of viscosity of the dispersing agent.

4. Conclusions

a) At high solid concentrations and low concentrations of
deflocculant, a substantial thixotropic behavior may be noted
experimentally. In a subsequent study we will present the results
of a detailed investigation of the effect of the temperature on
the rheological properties of the suspension in question.

b) All the systems studied show a similar shear-dependence
behavior which may be described synthetically through a character-
istic flux curve (master curve).

c) It is possible to determine a critical velocity gradient
$\dot{\gamma}_C$ and consequently to differentiate two regions of different
shear-dependent behavior (plastic for gradients less than $\dot{\gamma}_C$,
expanding at higher gradients). The plastic behavior may be
described with the Bingham behavior.

d) Three rheological parameters (τ_B, η_P and $\dot{\gamma}_C$) are suf-
ficient to characterize the shear-dependence of the systems studied
and to describe the effects of the variations of the contents of
solid and deflocculant.

e) For the three levels of solid contents studied, values
of concentrations of deflocculant were determined beyond which
further additions of deflocculant do not cause perceptible varia-
tions of the rheological behavior.

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f) It is possible to extend partly to the systems examined the interpretations suggested by Firth et al. for similar systems with low solid concentration.

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