

Effect of sodium hexametaphosphate and ageing on the rheological behaviour of kaolin dispersions

F. Andreola^a, E. Castellini^{b,*}, J.M.F. Ferreira^c, S. Olhero^c, M. Romagnoli^a

^a Department of Material Engineering, University of Modena and Reggio Emilia, Via Vignolese 905, 41100 Modena, Italy

^b Department of Chemistry, University of Modena and Reggio Emilia, Via Campi 183, 41100 Modena, Italy

^c Department of Ceramics and Glass Engineering, CICECO, University of Aveiro, 3810-193 Aveiro, Portugal

Received 3 December 2004; received in revised form 22 July 2005; accepted 4 August 2005

Available online 7 November 2005

Abstract

Concentrated dispersions (35% v, v) of ceramic grade kaolin dispersed with sodium hexametaphosphate (NaHMP) were prepared at three different experimental conditions: in distilled water at 30 and 60 °C, and in a 5×10^{-3} M $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ solution, at 30 °C. The dispersions were kept at constant temperatures for different ageing times (2, 4, 6, 18, 24, 48 h). After each ageing period they were submitted to rheological measurements and centrifuged to measure the concentration of HMP^- ion in the supernatant solution by ICP.

Measurements of the electrophoretic mobility in dispersions containing $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ and KCl as background electrolyte were also performed both in the presence and in absence of NaHMP.

The results allow a better understanding of the roles played by calcium ions and ageing of kaolin dispersions in the presence of NaHMP. They also shed light on the deflocculating mechanism of NaHMP. Correlations between rheological parameters and chemical properties of the dispersions could be established.

© 2005 Elsevier B.V. All rights reserved.

Keywords: Kaolin; Sodium hexametaphosphate; Deflocculation mechanism; Calcium; Temperature; Ageing-time

1. Introduction

Kaolin is the most important raw material used in whiteware ceramic industry. The term “kaolin” refers to a rock whose percentage of the mineral kaolinite ($\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$) is higher than 50% (Dombrowsky, 2000); in kaolin, kaolinite is often found in association with other minerals such as quartz, feldspar and micaceous which account for the percentage of impurity and contribute to the amounts of salts and cations found in kaolinitic rocks.

Ceramic raw materials are frequently handled as dispersions in some steps of industrial processing. They are dispersed or milled in water and the suspensions are stored and transported, spray dried into granules, or partially dehydrated for working in the plastic state or consolidated directly through casting technique (Galassi et al., 2001). The flow properties of the dispersions and their compaction behaviour are strongly influenced by phenomena occurring at the solid–liquid interface and by interactions which govern the aggregation of the dispersed phase. In particular, the repulsive interparticle forces due to the addition of a deflocculant, i.e. an additive employed to reduce the viscosity of the dispersions, are crucial to control their flow behaviour.

* Corresponding author. Fax: +39 059 373543.

E-mail address: castellini.elena@unimore.it (E. Castellini).

Among common deflocculants, sodium hexameta-phosphate (NaPO_3)₆ (NaHMP), is known to show good performance on dispersing natural raw materials in ceramic processing. NaHMP accomplishes its deflocculating action through a concerted mechanism: (i) by increasing the overall negative surface charge, being adsorbed as an anion especially at the edges of the clay mineral particles; (ii) by complexing the dissolved flocculant alkaline earth cations and replacing them by Na^+ cations, therefore increasing the thickness of the electrical double layer (Andreola et al., 2004). However, many points concerning the details of this dispersion mechanism still remain obscure and need to be further investigated. Some literature reports (Kronberg et al., 1986; Choi et al., 1993), aiming at improving the flotation technique of kaolinite, have focused on competitive adsorption of the HMP^- species with some flotation collectors, but the nature of the surface complex formed by adsorption of the deflocculant anion onto kaolinite edges at Al^{3+} sites was not described.

It is known that HMP^- forms a strong 1:1 complex with Ca^{2+} , whose thermodynamic stability constant is very high ($K=10^{6.9}$) (Kura and Ohashi, 1974). The interaction ability of several cations with the surfaces of clay minerals like kaolinite is also well known (Grim, 1968; Tarasevich and Klimova, 1999, 2001; Mpofu et al., 2003; Adebowale et al., 2005). However, a complete description of the concomitant mutual interactions occurring in a dispersion containing kaolinite, HMP^- and Ca^{2+} is rather lacking in the literature.

Therefore, one part of this paper will focus on the role played by flocculant Ca^{2+} ions, which interact both with the surface of kaolinite particles and with the deflocculant anions. Dissolved Ca^{2+} ions have deleterious effects on dispersing clay materials by: (i) adsorbing onto the kaolinite surface, reducing the thickness of the electrical double layer; (ii) decreasing the amount of HMP^- available to be adsorbed on kaolinite edges through soluble complex formation. The influence of the two phenomena and if synergetic effects occur are still not clear.

The purpose of this work is to attempt a correlation between rheological properties of kaolin dispersions under proper operative conditions, electrophoretic and adsorption measurements. This kind of investigation is particularly useful for application purposes, since industrial water usually contains soluble salts, which are deleterious for the stability of the dispersions, Ca^{2+} being one of the most common ions. Moreover, adding NaHMP to an aqueous industrial kaolin dispersion enhances the release of Ca^{2+} ions to the solution

(Andreola et al., 2004), a phenomenon worthy of investigation.

Since both complexation and adsorption processes involve the establishment of equilibrium conditions, they should be temperature-dependent. However, no efforts have been reported in the literature in order to evaluate how temperature affects the above referred equilibrium conditions. Therefore, another part of the present work aims at determining how and why the deflocculating efficiency is affected at the relatively high temperatures reached during industrial milling processes.

2. Materials and methods

2.1. Materials

A ceramic-grade kaolin (hereafter C.G.K.) was used. The sampling procedure as well as a complete characterization of C.G.K. was reported in Andreola et al., 2004.

General properties of C.G.K. are as follows: density $d=2.683\pm 0.054$ g/ml (liquid pycnometry); specific surface area $S_{\text{BET}}=15.01$ m²/g (Brunauer–Emmett–Teller method, Micromeritics Gemini 2630); average particle size $d_{50}=4.08$ μm (laser particle-sizer analysis, Fritsch Analyzette 22); chemical composition in weight percentage of respective oxides: SiO_2 47.1%, Al_2O_3 36.1%, CaO 0.40%, MgO 0.27%, Na_2O 0.59%, K_2O 1.06%, Fe_2O_3 0.75%, TiO_2 0.24%, LOI 12.49%; cation exchange capacity 3.7 meq/100 g. X-ray powder diffraction technique (Philips PW3710) using $\text{CuK}\alpha$ radiation and a step scanning technique of $0.02^\circ/\text{s}$, in the $5\text{--}70^\circ$ 2θ angle range, revealed that the main mineralogical components are kaolinite (91%), illite, quartz and a small amount of feldspar.

Standard kaolinite KGa-1b was purchased from the Clay Minerals Society (The Clay Minerals Society, Source Clays Repository, University of Missouri, Columbia, MO); general properties were reported by Andreola et al., 2004.

The deflocculant was sodium hexametaphosphate (NaHMP) (Carlo Erba, RE grade).

Potassium chloride and calcium nitrate tetra hydrate were purchased from Carlo Erba, RPE grade.

2.2. Methods

2.2.1. Electrophoretic measurements

The electrophoretic mobility of the kaolin particles was determined at 30 °C using a Doppler electrophoretic light scattering analyzer (Delsa 440SX, Coulter, UK). The measurements were performed under $5\cdot 10^{-3}$ M of two different background electrolytes, KCl and $\text{Ca}(\text{NO}_3)_2\cdot 4\text{H}_2\text{O}$, both in the absence and in the presence of NaHMP ($2.12\cdot 10^{-2}$ M). Stock dispersions containing 5% w, w kaolin in deionised water (corresponding to a kaolin volume fraction of 1.9%), in absence and in presence of NaHMP, were first prepared and let

to equilibrate for 24 h. Before starting the electrophoretic measurements, each stock dispersion was first ultrasonicated for 10 min to destroy the agglomerates. Then, aliquots of 0.4 ml of the stock dispersion were added to 200 ml of each electrolyte solution kept at 30 °C. Each diluted dispersion was divided in two equal portions, one for decreasing pH runs and the other for increasing pH runs and the electrophoretic mobility as a function of pH was measured at least four times in each point. The standard deviation values varied from one point to another but within the range of 3% to 6%, being the higher ones mostly observed in the acidic pH range. The pH values were adjusted using 0.1 M KOH or HCl solutions in the case of KCl electrolyte and NH_4OH or HNO_3 in the case of $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ electrolyte.

2.2.2. Rheological and ICP measurements

A preliminary series of rheological tests, performed in absence of deflocculant (the C.G.K. content was therefore limited to 15% v, v) aimed at evaluating the effect of $[\text{Ca}^{2+}]$ on the rheological characteristics of the dispersions by adding increasing concentrations of $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ ($4 \cdot 10^{-4}$, $8 \cdot 10^{-4}$, $1.5 \cdot 10^{-3}$, $5 \cdot 10^{-3}$, $6 \cdot 10^{-3}$, 10^{-2} and 10^{-1} M). The C.G.K. dispersions were prepared in a laboratory ball mill. The kaolin and the proper solution were blended and dispersed in a laboratory ball mill (300 ml) with 10 alumina grinding balls ($\phi=1$ cm) for 10 min at 400 rpm; B.E.T. measurements performed on kaolin before and after this dispersing procedure did not show appreciable differences, attesting that this step does not affect the BET surface. The rheological measurements were carried out immediately after milling.

Other more highly concentrated C.G.K. dispersions (35% v, v) were prepared in the presence of the optimal amount ($2.12 \cdot 10^{-2}$ M) of NaHMP to disperse the C.G.K., according to an established procedure (Andreola et al., 2004). The kaolin and the deflocculant solution were blended and dispersed as reported above; also in this case, B.E.T. measurements performed on kaolin before and after this dispersing procedure did not show appreciable differences, confirming that this step does not affect the BET surface. After milling, the dispersions were transferred to sealed plastic vessels (PET) and kept at a constant temperature (30 or 60 °C) in a thermostatic bath (Memmert WB/WB) for different ageing times (2, 4, 6, 18, 24, 48 h). One series of C.G.K. dispersions was prepared in the NaHMP solution and aged at 30 °C in the presence of $5 \cdot 10^{-3}$ M $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ (≈ 200 ppm), since this corresponds to a typical Ca^{2+} concentration found in industrial milling water. Two other series of C.G.K. dispersions were prepared in the NaHMP solution, aged at 30 and 60 °C. For comparison purposes, a series of dispersions of the standard kaolinite KGa-1b was also prepared in the NaHMP solution and aged at 30 °C.

After ageing, the dispersions were divided into two equal parts, one was shaken in rollers for 10 min and then used for rheological measurements; the other was centrifuged using a multi-speed centrifuge (ALC multi-

speed centrifuge PK 121) and the phosphorus concentration in the supernatant liquid was analysed by ICP (ICP Plasma Varian mod. Liberty 200).

The rheological measurements were performed using a Searle Control Rate Haake viscosimeter (VT 550), equipped with coaxial cylinder measuring sensor (MV1) in isothermal conditions at 30 °C. All samples were measured using a four-step cycle: 1 min at a shear rate of 500 s^{-1} and 1 min at rest to exclude the effects of the sample preparation, followed by a shear rate increase from 0 to 500 s^{-1} in 10 min and a shear rate decrease from 500 to 0 s^{-1} in 10 min. From the complete flow curves yield stress, apparent viscosity and other rheological parameters could be calculated using suitable rheological models.

3. Results

3.1. Electrophoretic measurements

Fig. 1 reports electrophoretic mobility values of C.G.K. particles dispersed in both background electrolytes KCl and $\text{Ca}(\text{NO}_3)_2$ as a function of pH. The electrophoretic mobility values measured in the same electrolytes but in the presence of $2.12 \cdot 10^{-2}$ M NaHMP are also plotted.

In all cases, electrophoretic mobility values are negative and no apparent isoelectric point (IEP) was detected. This can be understood since the basal surfaces of plate-like kaolinite, which represent the most significant part of the overall surface of the particles, present a negative charge within the whole pH range (Diz and Rand, 1989; Rand and Melton, 1977).

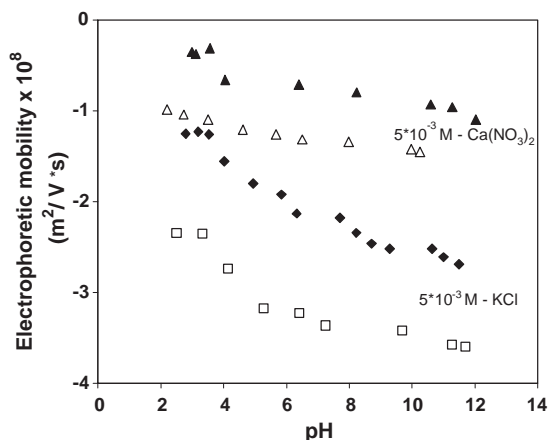


Fig. 1. Electrophoretic mobility of C.G.K. particles as a function of pH, measured in $5 \cdot 10^{-3}$ M solutions of different electrolytes, KCl and $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$, in the absence (full symbols) and in the presence of NaHMP $2.12 \cdot 10^{-2}$ M (open symbols).

3.1.1. Electrophoretic mobility in KCl solutions

The electrophoretic mobility (hereafter considered only in its absolute value) obtained in absence of deflocculant for pH values higher than 4 show a clear pH-dependence, with electrophoretic mobility increasing as pH increases. This behaviour can be attributed to the progressive deprotonation of surface edge sites. A similar pH dependence in 10×10^{-3} M solution of KNO_3 has been observed by Galassi et al. (2001) for a kaolinite-rich ball clay. This is also in agreement with the model in which the edge surfaces behave like oxides, with a pH-dependent potential, reversing in sign at the isoelectric point (Diz and Rand, 1989).

An inflexion point is apparent at about pH 5–5.5, which can be due to the vicinity to the IEP of particle edges (Diz and Rand, 1989). This value is somewhat lower than those found in literature for homoionic kaolinite samples (Diz and Rand, 1989) which vary from 5.6 to 8.8, probably due to the different mineralogical composition of C.G.K. with respect to Cornish China Clay employed in literature (Diz and Rand, 1989; Rand and Melton, 1977). Considering that quartz exhibits a IEP at pH ≈ 2 (Huang and Fuerstenau, 2001), very similar to that of illite (Qing et al., 1997) and that IEP of kaolin can be considered a sort of average weighted value of the minerals present, the apparent shift of IEP in C.G.K. kaolin might be attributed to the presence of a not negligible amount of quartz, provided that a size fraction of dimensions $< 10 \mu\text{m}$ is present (Galassi et al., 2001); the observed shift cannot be analogously attributed to the presence of illite, since this mineral is found both in C.G.K. and in Cornish China Clay (Rand and Melton, 1977).

The values of electrophoretic mobility increase significantly in the presence of NaHMP, as a direct consequence of the specific adsorption of HMP^- anions. In fact, the chemisorption effects are also observed for pH values higher than apparent IEP of the edges, confirming that the driving force for adsorption of HMP^- on kaolin is essentially chemical and not simply electrostatic. A similar behaviour has been observed by Beattie and Djerdjev (Beattie and Djerdjev, 2000) who found that the anion of poly(methacrylic acid) was adsorbed on to alumina at pH values higher than the IEP of alumina (pH=8.7). Accordingly, another consequence of HMP^- adsorption is a shift of the apparent IEP of the edges to pH ≈ 4.5 . It is suggested that HMP^- anions interact with Al^{3+} at the edges of the kaolinite particles replacing the already existing hydroxyl groups (ligand exchange) (Van Olphen, 1963; Lagaly, 1989, 1993; Ioannou and Dimirkou, 1997; Penner and Lagaly, 2001).

3.1.2. Electrophoretic mobility in $\text{Ca}(\text{NO}_3)_2$ solutions

The electrophoretic mobility in $\text{Ca}(\text{NO}_3)_2$ is significantly smaller, and the same applies concerning its variability as a function of pH, either in the absence and in the presence of deflocculant. This trend is according to the enrichment of Ca^{2+} ions in the Stern-layer, leading to lower electrophoretic mobility values with respect to K^+ cations. The increase of electrophoretic mobility values as a function of pH is more accentuated at around pH 4, followed by a slightly increasing trend, similarly to that observed by Galassi (Galassi et al., 2001) for a kaolinite-rich ball clay dispersed in twice the concentration (10^{-2} M) of the same electrolyte; only for pH values higher than 8 they obtained a plateau, instead of a slightly increasing pH dependence observed in the present work. The reduced pH dependence in comparison to the case of KCl could be explained assuming that deprotonation of the kaolinite edge surface sites as pH increases might be balanced by the adsorption of Ca^{2+} cations in the electric double layer (edl) of clay mineral particles.

Adding NaHMP increases the electrophoretic mobility, confirming that even in the presence of high concentrations of Ca^{2+} , HMP^- is chemisorbed onto kaolinite surface. This experimental observation could be explained based on two plausible hypothesis: (i) the Ca^{2+} ions in the edl do not affect the deflocculant adsorption, however, their adsorption in the Stern-layer is more effective in reducing the electrophoretic mobility than K^+ ions; (ii) the Ca^{2+} ions inhibit the HMP^- adsorption since they form a soluble complex with the deflocculant: as a consequence, the efficiency of HMP^- in increasing electrophoretic mobility value is lowered. The slight pH dependence experimentally observed both in the absence and in the presence of deflocculant is the consequence of the calcium cations adsorption and suggests the former hypothesis as the most probable one.

3.2. Rheological measurements

3.2.1. Effect of Ca^{2+} ions on rheological behaviour of kaolin dispersions

Fig. 2 reports the flow curves of C.G.K. dispersions at different values of $[\text{Ca}^{2+}]$. Both plots of shear stress versus shear rate and of apparent viscosity as a function of $[\text{Ca}^{2+}]$ (Fig. 3) show a strong dependence on $[\text{Ca}^{2+}]$ in the range 0.0004–0.01 M, followed by a very attenuated dependence, tending to constant values at higher concentrations. This evolution is in close agreement with the electrophoretic results and can be attributed to a progressive Stern-layer adsorption of the

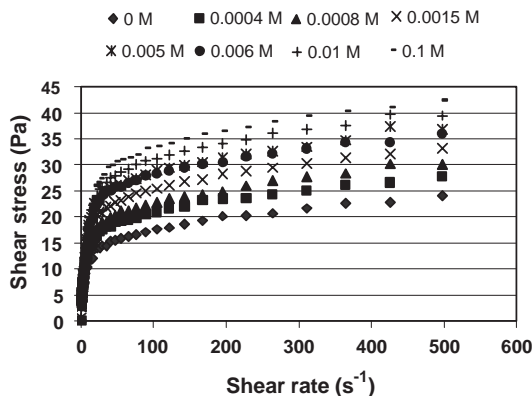


Fig. 2. Flow curves of 15% v, v C.G.K. dispersions realized with calcium concentrations: $4 \cdot 10^{-4}$, $8 \cdot 10^{-4}$, $1.5 \cdot 10^{-3}$, $5 \cdot 10^{-3}$, $6 \cdot 10^{-3}$, 10^{-2} and 10^{-1} M.

Ca^{2+} ions and therefore to a decrease of the magnitude of the electrostatic repulsive forces. The loss of the dependence of apparent viscosity on calcium concentration corresponds to the saturation of the clay surface by the Ca^{2+} ions.

3.2.2. Effect of ageing on C.G.K. dispersions in the presence of NaHMP at 30 °C

The effect of ageing on rheology of C.G.K. dispersions in $2.12 \cdot 10^{-2}$ M NaHMP, kept at 30 °C for different periods (2–48 h) is reported in Fig. 4. The shear stresses required for making the dispersions to flow at given values of shear rate always increase with increasing ageing time.

Concentrated (35% v, v) C.G.K. dispersions in NaHMP show a more complex rheological behaviour in comparison to the diluted dispersions (15% v, v) in the absence of the deflocculant: they show shear thinning at low shear rates and then change to shear thickening. Therefore, the flow curves have been fitted using the Casson model at low shear rates ($< 50 \text{ s}^{-1}$) to determine

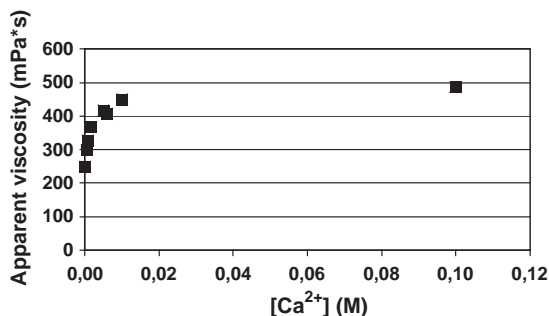


Fig. 3. Apparent viscosity (recorded at 65 s^{-1}) as a function of calcium concentration for 15% v, v C.G.K. dispersions.

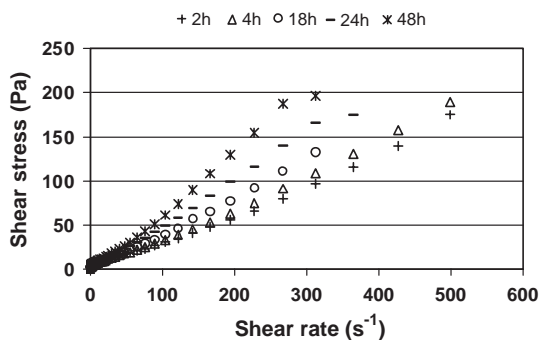


Fig. 4. Flow curves of 35% v, v C.G.K. dispersions in $2.12 \cdot 10^{-2}$ M NaHMP and kept at 30 °C for different time periods.

the yield stress values, and the Herschel Bulkley model at high shear rates ($> 50 \text{ s}^{-1}$) to determine both the flow index and consistency.

The resulting values of apparent viscosity, yield stress, flow index and consistency are reported in Table 1. As many of the curves obtained at 60 °C were interrupted at relatively low shear rates due to maximum torque exceeded, viscosity values of all the series were reported at 65 s^{-1} for comparison purposes. All rheological parameters experienced small changes within the first 6 h followed by a more accentuated increasing trend, except the flow index that shows a certain tendency to decrease in the explored time range. The changes observed with time suggest that the ageing process is still far from reaching a steady state situation.

3.2.3. Effect of ageing on C.G.K. dispersions in the presence of NaHMP and Ca^{2+} ions at 30 °C

The flow curves in the presence of $5 \cdot 10^{-3}$ M Ca^{2+} (Fig. 5) are similar to those observed in absence of Ca^{2+} (Fig. 4); however, all values of apparent viscosity, yield stress and consistency, obtained as previously described in 3.2.2, are higher (Table 2). Even in the presence of NaHMP the Stern-layer adsorption of Ca^{2+} ions is pronounced and/or the adsorbed amount of HMP^{-}

Table 1
Rheological parameters for 35% v, v C.G.K. dispersions in $2.12 \cdot 10^{-2}$ M NaHMP, kept at 30 °C for different time periods

t (h)	η ($\dot{\gamma}=65 \text{ s}^{-1}$) (mPa s)	τ_0 , Casson (Pa)	n , Herschel Bulkley	k , Herschel Bulkley (Pa s^n)
2	320	1.21	1.16	0.14
4	338	1.22	1.15	0.15
6	334	1.23	1.11	0.16
18	388	1.29	1.13	0.20
24	464	1.36	1.08	0.25
48	547	1.38	1.04	0.45

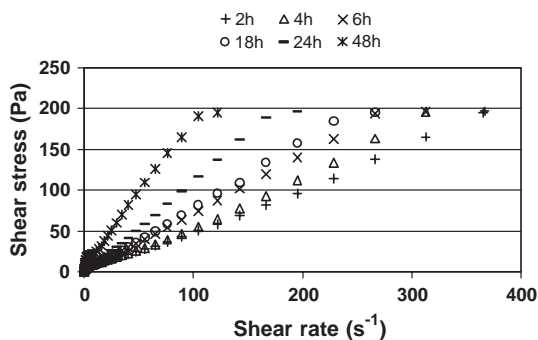


Fig. 5. Flow curves of 35% v/v C.G.K. dispersions in $2.12 \cdot 10^{-2}$ M NaHMP in the presence of $5 \cdot 10^{-3}$ M $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ and kept at 30 °C for different time periods.

anions is reduced due to the complex formation with Ca^{2+} ions. In any case, the used HMP^- concentration is not enough to sequester all the Ca^{2+} ions present in solution.

The comparison between Figs. 4 and 5 shows that the effect of ageing on rheology is enhanced in the presence of Ca^{2+} . These observations are in good agreement with the above reported electrophoretic results.

3.2.4. Effect of ageing on C.G.K. dispersions in the presence of NaHMP at 60 °C

Like in the other two series, the values of apparent viscosity, yield stress and consistency increase with ageing, but the effect is more pronounced at 60 °C (Tables 1–3, Figs. 4–6). At 60 °C the apparent viscosity and yield stress increase strongly with ageing time, especially in the first 18 h. Also consistency strongly increases within the first 18 h, and then tends to reach a constant value after 24 h. The flow index values obtained from the Herschel–Bulkley model are almost unaffected. The more pronounced ageing effects observed at 60 °C may be related to different cooperative phenomena: (i) a change in adsorption of NaHMP induced by the higher temperature: in fact, the

Table 2
Rheological parameters for 35% v/v C.G.K. dispersions in $2.12 \cdot 10^{-2}$ M NaHMP in the presence of $5 \cdot 10^{-3}$ M $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$, kept at 30 °C for different time periods

t (h)	η ($\dot{\gamma}=65 \text{ s}^{-1}$) (mPa s)	τ_0 , Casson (Pa)	n , Herschel Bulkley	k , Herschel Bulkley (Pa s^n)
2	489	1.65	1.18	0.20
4	520	1.68	1.12	0.22
6	714	1.77	1.08	0.23
18	764	1.81	1.13	0.56
24	1070	2.43	1.11	0.64
48	1940	3.67	1.12	1.25

Table 3
Rheological parameters for 35% v/v C.G.K. dispersions in $2.12 \cdot 10^{-2}$ M NaHMP, aged at 60 °C for different time periods

t (h)	η ($\dot{\gamma}=65 \text{ s}^{-1}$) (mPa s)	τ_0 , Casson (Pa)	n , Herschel Bulkley	k , Herschel Bulkley (Pa s^n)
2	586	0.83	1.15	0.27
4	904	2.95	1.21	0.51
6	1460	5.20	1.04	0.93
18	2540	6.16	1.10	1.21
24	3110	8.44	1.11	1.59
48	3111	9.22	1.01	1.60

temperature dependence of the adsorption constant of HMP on kaolinite shows a decreasing trend with raised temperature, suggesting the exothermic nature of this process (Castellini et al., in press); the observed decrease in the adsorption ability of HMP at increasing temperature accords with the lowering deflocculation efficiency exhibited at high temperatures; (ii) a temperature-driven accelerated hydrolysis (inactivation) of the deflocculant: it consists of the cleavage of HMP ring to give a linear hexaphosphate which then degrades

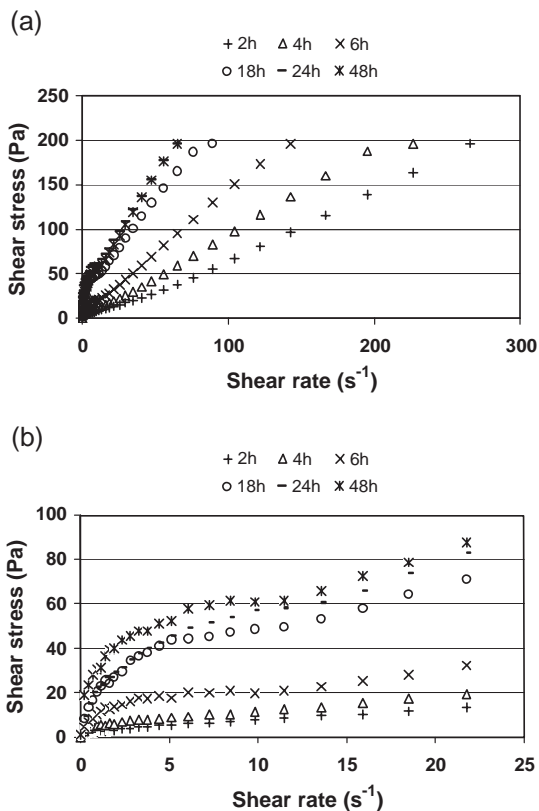


Fig. 6. (a) Flow curves of 35% v/v C.G.K. dispersions in $2.12 \cdot 10^{-2}$ M NaHMP, aged at 60 °C for different time periods; (b) the same of (a), but the data are plotted only for $\dot{\gamma} < 25 \text{ s}^{-1}$.

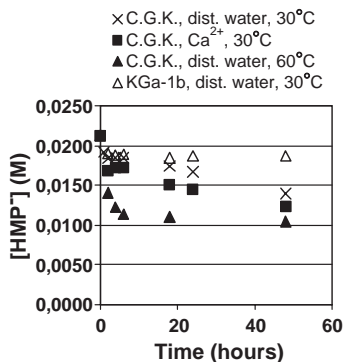


Fig. 7. Molar concentration of HMP⁻ still remaining in solution as a function of ageing time (hours).

into lower phosphates (Thilo, 1965); (iii) an increase of the kinetic energy of colliding particles, which might be enough to overcome the energy barrier arising from the overlapping of attractive and repulsive interactions forces, according to the DLVO theory (Derjaguin and Landau, 1941; Verwey and Overbeek, 1948).

3.3. ICP measurements

Fig. 7 reports the molar concentration of HMP⁻ still remaining in solution as a function of the contact time under different experimental conditions for the C.G.K. kaolin and for the standard kaolinite KGa-1b.

In all cases, the concentration of HMP⁻ in solution decreases with increasing ageing time. However, substantial differences can be found among the different experimental conditions, especially at 30 and 60 °C.

When a solution of HMP⁻ in distilled water at 30 °C is used on C.G.K., its concentration first decreases to an apparent plateau within 2–6 h, followed by a gradual decreasing trend for longer ageing periods. The

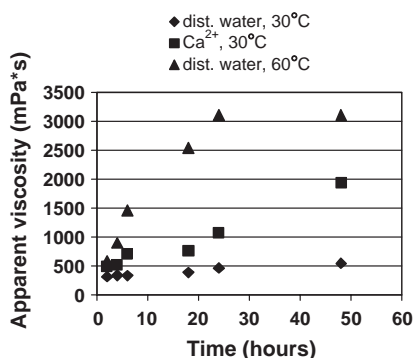


Fig. 8. Apparent viscosity (mPa*s, recorded at 65 s⁻¹) of the C.G.K. dispersions as a function of the ageing time (hours) under different experimental conditions.

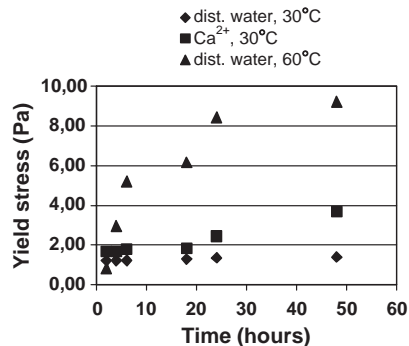


Fig. 9. Yield stress (Pa) of the C.G.K. dispersions as a function of ageing time (hours) under different experimental conditions.

adsorption measurements performed under the same conditions with the standard kaolinite KGa-1b, also reported in Fig. 7, show that a clear steady-state plateau is soon reached, suggesting that the decreasing trend observed for C.G.K. might be attributed to time-dependent alterations involving accessory minerals other than kaolinite.

A similar trend is observed on ageing the C.G.K. dispersions added with NaHMP in the presence of Ca²⁺ ions at 30 °C, but the amount of HMP⁻ still remaining in solution is lower, probably due to the adsorption, in some extent, of the Ca-HMP complex. This means that the total amount of adsorbed species derived from the deflocculant does not necessarily account for the deflocculation efficiency. In fact, even though deflocculant adsorption increases, the rheological measurements performed in the presence of Ca²⁺ ions show an increase of apparent viscosity. As a matter of fact, the presence of Ca²⁺ could not hinder the adsorption of the deflocculating species and the obtained electrophoretic mobility values, lower than those found in the presence of KCl, could be only due to

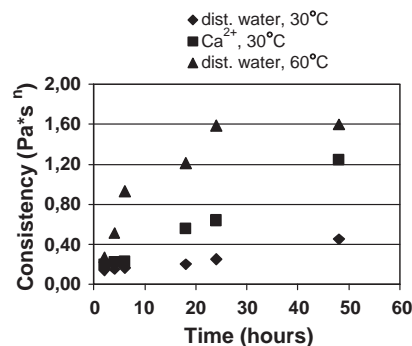


Fig. 10. Consistency (Pa*sⁿ) of the C.G.K. dispersions as a function of ageing time (hours) under different experimental conditions.

the higher screening effect of the surface charge by the adsorbed Ca^{2+} ions.

As mentioned above, the ageing process is much faster at 60 °C. The distinctive features of the plot of $[\text{HMP}^-]$ versus time are the absence of the steady state at short times and a very sharp decrease of $[\text{HMP}^-]$ with time up to reaching a nearly constant value for ageing periods ≥ 6 h. The sharp decrease of $[\text{HMP}^-]$ observed for short ageing times suggests that besides adsorption, other possible phenomena might have occurred under these experimental conditions, such as inactivation of deflocculating species due to hydrolysis (Thilo, 1965).

4. Discussion: interpretation of viscosimetric data

Fig. 8 clearly shows that the changes of apparent viscosity with ageing time strongly depend on the experimental conditions. A sharp increase is observed at 60 °C, especially for short ageing periods, while at 30 °C the changes are smaller and accomplished after longer ageing times. Similar trends were observed for the yield stress (Fig. 9) and consistency (Fig. 10).

It is interesting to note that the more accentuated changes in the rheological parameters occurred for ageing times at which the most relevant changes in the concentration of NaHMP species remaining in solution were observed (Fig. 7). The disappearance of NaHMP species from solution can be due to an increase of the amounts adsorbed at the surface of the clay particles or to degradation by hydrolysis, this is still an open question. Since a steady-state plateau of the concentration of NaHMP species remaining in solution is soon reached for the standard kaolinite KGa-1b at 30 °C, it seems that the observed changes would involve interactions with other accessory clay minerals (Andreola et al., 2004). In any case, the contemporary increasing trend of apparent viscosity, yield stress and consistency indicates stronger attractive interaction forces between the clay particles during ageing. The resulting dispersion structure resists to higher shear stress before starting to deform, and the mutual streaming of the particles also requires higher values of shear stress.

Adding NaHMP to C.G.K. dispersions overcomes the strong attractive forces (mostly face-edge type interactions) existing among the clay particles and allows to significantly increase the solid content from 15% to 35% v. v. Adsorption of HMP^- species at the positive sites of the edges increases the repulsive interactions, decreasing the values of yield stress, apparent viscosity and consistency. The obtained results (Figs. 7 and 9) are in agreement with the hypothesis (Diz

and Rand, 1989) that the adsorption process of HMP^- is mainly responsible for the decrease of yield stress. Complex formation between dissolved HMP^- and Ca^{2+} species also accounts for the stability and rheological behaviour of the dispersions, which in turn strongly depend on temperature and ageing time. The results presented in this work show that all these phenomena have to be considered when preparing ceramic slips, since industrial milling waters usually contain soluble divalent cation salts and temperature during milling can increase for a few tens of °C, limiting the time period along which the dispersions can be handled in further processing steps.

5. Conclusions

In the absence of deflocculant, calcium cations exert a prominent effect on the rheological curves of kaolin dispersions, even though a critical concentration above which the activity of the cation remains nearly constant is observed.

Electrokinetic measurements confirm that HMP^- is adsorbed onto the surface of the kaolin particles.

ICP measurements prove that the adsorption process of HMP^- onto the surface of kaolin particles in presence of calcium cations is not hindered; contrarily, it is slightly enhanced.

Electrophoretic mobility measurements also showed that, in the presence of NaHMP, calcium ions keep a remarkable activity towards kaolin surface, significantly decreasing the absolute values of the electrophoretic mobility due to their strong Stern-layer adsorption.

Acknowledgments

The authors are grateful to Professor Gerhard Lagaly for helpful comments and suggestions.

References

- Adebowale, K.O., Unuabonah, I.E., Olu-Owolabi, B.I., 2005. Adsorption of some heavy metal ions on sulphate- and phosphate-modified kaolin. *Applied Clay Science* 29, 145–148.
- Andreola, F., Castellini, E., Manfredini, T., Romagnoli, M., 2004. The role of sodium hexametaphosphate in the dissolution process of kaolinite and kaolin. *Journal of the European Ceramic Society* 24, 2113–2124.
- Beattie, J.K., Djerdjev, A., 2000. Rapid electroacoustic method for monitoring dispersion: zeta potential titration of alumina with ammoniumpoly(methacrylate). *Journal of American Ceramic Society* 83 (10), 2360–2362.
- Castellini, E., Lusvardi, G., Malavasi, G., Menabue, L., in press. Thermodynamic aspects of the adsorption of hexametaphosphate

- on kaolinite. *Journal of Colloid and Interface Science* (available online 18 July 2005).
- Choi, J.K., Wen, W.W., Smith, R.W., 1993. Technical note: the effect of a long chain phosphate on the adsorption of collectors on kaolinite. *Minerals Engineering* 6, 1191–1197.
- Derjaguin, B.V., Landau, L.D., 1941. Theory of stability of highly charged lyophobic sols and adhesion of highly charged particles in solutions of electrolytes. *Acta Physico-Chemica URSS* 633–662.
- Diz, H.M.M., Rand, B., 1989. The variable nature of the isoelectric point of the edge surface of kaolinite. *British Ceramic Transactions* 88, 162–166.
- Dombrowsky, T., 2000. The origins of kaolinite—implication for utilization. In: Carty, W. (Ed.), *Science of Whiteware*. The American Ceramic Society, Westerville, OH, pp. 3–12.
- Galassi, C., Costa, A.L., Pozzi, P., 2001. Influence of ionic environment and pH on the electrokinetic properties of ball clays. *Clays and Clay Minerals* 49, 263–269.
- Grim, R.E., 1968. *Clay Mineralogy*, 2nd edition. McGraw Hill, New York.
- Huang, P., Fuerstenau, D.W., 2001. The effect of the adsorption of lead and cadmium ions on the interfacial behavior of quartz and talc. *Colloids and Surfaces. A, Physicochemical and Engineering Aspects* 177, 147–156.
- Ioannou, A., Dimirkou, A., 1997. Phosphate adsorption on hematite, kaolinite, and kaolinite–hematite systems as described by a constant capacitance model. *Journal of Colloid and Interface Science* 192, 119–128.
- Kronberg, B., Kuortti, J., Stenius, P., 1986. Competitive and cooperative adsorption of polymers and surfactants on kaolinite surface. *Colloids and Surfaces* 18, 411–425.
- Kura, G., Ohashi, S., 1974. Complex formation of cyclic phosphate anions with bivalent cations. *Journal of Inorganic and Nuclear Chemistry* 36, 1605–1609.
- Lagaly, G., 1989. Principles of flow of kaolin and bentonite dispersions. *Applied Clay Science* 4, 105–123.
- Lagaly, G., 1993. From clay minerals to colloidal clay mineral dispersions. In: Dobias, B. (Ed.), *Coagulation and Flocculation. Theory and Applications*. Marcel Dekker, New York, pp. 427–494.
- Mpofu, P., Addai-Mensah, J., Ralston, J., 2003. Influence of hydrolysable metal ions on the interfacial chemistry, particle interactions, and dewatering behavior of kaolinite dispersions. *Journal of Colloid and Interface Science* 261, 349–359.
- Penner, D., Lagaly, G., 2001. Influence of anions on the rheological properties of clay mineral dispersions. *Applied Clay Science* 19, 131–142.
- Qing, D., Zhongxi, S., Willis, F., Hongxiao, T., 1997. Acid–base properties of aqueous illite surfaces. *Journal of Colloids and Interface Science* 187 (1), 221–231.
- Rand, B., Melton, I.E., 1977. Particle interactions in aqueous kaolinite suspensions: I. Effect of pH and electrolyte upon the mode of particle interaction in homoionic sodium kaolinite suspensions. *Journal of Colloid and Interface Science* 60, 308–320.
- Tarasevich, Y.I., Klimova, G.M., 1999. Complexing sorbents based on dispersed minerals for recovery of heavy metal ions from aqueous solutions. *Theoretical and Experimental Chemistry* 35 (3), 158–161.
- Tarasevich, Y.I., Klimova, G.M., 2001. Complex-forming adsorbents based on kaolinite, aluminium oxide and polyphosphates for the extraction and concentration of heavy metal ions from water solutions. *Applied Clay Science* 19, 95–101.
- Thilo, E., 1965. The structural chemistry of condensed inorganic phosphates. *Angewandte Chemie. International Edition* 4 (12), 1061–1071.
- Van Olphen, H., 1963. Peptization of clay suspensions. In: Van Olphen, H. (Ed.), *An Introduction to Clay Colloid Chemistry*. Interscience, New York, pp. 112–113.
- Verwey, E.J.W., Overbeek, J.T.G., 1948. *Theory of the Stability of Lyophobic Colloids*. Elsevier, Amsterdam.