COMPARATIVE STUDY OF DEFLOCCULATION MECHANISMS IN COLLOIDAL CLAY SUSPENSIONS

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ABSTRACT

The present work analyses the alterations in the rheological properties of colloidal clay suspensions caused by introducing deflocculating substances, with a view to understanding the deflocculation mechanisms through which each of these substances acts. In a first stage, five clays used in Brazilian and Italian ceramic companies were selected. The clays were characterised by chemical and mineralogical analysis, determining their densities in the presence of water, cation exchange capacity, specific surface areas, particle size distributions, zeta potential and pH on dispersion in water. In the second stage of the work, the changes arising in certain clay suspension properties caused by the addition of three different types of deflocculating substances was studied. That is, the study addressed clay suspension deflocculation mechanisms. Each type of deflocculant acted according to a preferential deflocculation mechanism. The deflocculants used were sodium tripolyphosphate to study the electrostatic stabilisation mechanism, sodium phosphonate for the cation capture mechanism and sodium polyacrylate for the stabilisation mechanism by steric hindrance. The deflocculants were added to the clay suspensions, analysing the change in particle zeta potential, pH and apparent viscosities of the suspensions (rheological tests) as a function of the addition of each type of deflocculant. It was found that each type of deflocculant had a similar, specific effect on clay suspensions, which also exhibited similar physical and chemical properties.

KEY WORDS: Rheology, mechanisms, deflocculation, suspensions, clays.

1 - INTRODUCTION

At present, in the ceramic tile industry, world clay consumption is of the order of two dozen million tons / year[1]. Considering the importance of these minerals, their industrial use should be analysed, jointly addressing technological and economic aspects.

From a technological viewpoint, much of the ceramic production sector works with a technology based on unit operations that use these raw materials in aqueous suspension[1]. From an economic viewpoint, such suspensions should be prepared with a high solids concentration associated with excellent flowability. On having a suspension with these characteristics, the specific energy costs of the milling and spray drying stages of the ceramic body are significantly reduced[1,2,3].

With regard to the economic aspects, there is a conflicting feature, since increasing solids content in a clay suspension significantly reduces its flowability[2,3,6]. The clay particles are in colloidal suspension, and hence subject to mutual attraction interactions that increase considerably with the rise in solids content. Such an effect negatively affects suspension flowability, as the formation of "contacts" between particles hinders liquid flow as a whole[2,3,6].

The optimisation of a ceramic suspension therefore depends on introducing substances that eliminate interparticle attraction interactions as far as possible, i.e. which have a diluting effect on the suspension[2,4,5]. These substances are chemical additives known as deflocculants. Some alkaline metal salts (e.g.: silicate, sodium tripolyphosphate and polyacrylate) are the most frequently found types of chemical compounds used as deflocculants[2,4,5]. A deflocculant can act on a clay suspension through three deflocculation mechanisms: by electrostatic action; steric hindrance and cation capture[2,3]. Each type of deflocculant exhibits a preferential action mechanism.

The addition of an alkaline salt to a clay suspension can produce deflocculation. A monovalent salt, with alkaline metal ions of the type Na^+ and Li^+, raises the zeta potential of the suspended clay particles[9,10]. The Na^+ ions, which are large, have a small charge and are highly hydratable, remain 'tenuously" adsorbed to the clay particle, forming a very thick electric double layer. Thus, the repellent forces between the particles have quite a wide field of action and appear at a distance where the attraction forces are negligible (DLVO theory)[14]. The introduction of these ions directly raises suspension pH and hence formation of a negative charge on the edges of the clay particles, which further encourages deflocculation of the system[11,12]. Sodium polyphosphates are one of the most widely used deflocculants in colloidal clay suspension stabilisation[13]. In this case, these types of deflocculant are said to act preferentially by an electrostatic stabilisation mechanism, since suspension stabilisation is produced by alterations of the effective electric potential of the particles.

Sodium phosphonate ($HPO(ONa)_2$) is a deflocculant that acts primarily by cation capture[2,3]. This clay suspension stabilisation mechanism involves capturing flocculating cations from the liquid or from the clay mineral structure[2,3]. There are certain types of substances, the "chelants", which have the capacity to capture cations through the formation of metallic complexes (chelates)[7]. A complex is formed by a metal and certain ions or molecules, called 'ligands", held to it. Each ligand is linked to the metal by superimposition on the orbital hole of the metal (cation) of a filled orbital of the same metal. The bonds are therefore covalent with a variable ionic character[7]. Capture is selective for the polyvalent cations, which are the problematic cations with regard to clay suspension flocculation. The introduction of those substances in a suspension acts directly by removing the flocculating cations present in the clay particle double layer, i.e., increasing its zeta potential. In aqueous solution, sodium phosphonate decomposes and releases the $HPO(O^-)_2$ ion, which is a nucleophile and therefore has a chelating property[7].

The introduction in the dispersing medium of polymers that cover the particles and impede their coalescence defines the deflocculation mechanism by steric hindrance[11,15]. When organic polymeric molecules are adsorbed on the surface of colloidal particles, a new type of repulsion force arises between them, caused by steric hindrance[8,11,14]. This hindrance is due to two types of contribution[8,14,15]: i) one caused by an osmotic effect, since a larger polymer concentration exists in the overlapping region, and when the particles approach each other, they need to expel the liquid between them. This produces an osmotic pressure by introducing liquid between the particles, to keep a concentration equilibrium between the overlapping area and the liquid medium; ii) and volume restriction, caused by the decreasing possibilities of polymeric chain formation in the restricted space between the particles as they approach each other. The two effects predominate at different interaction distances. The osmotic effect is activated by overlapping layers of adsorbed polymers, i.e., at a distance twice the thickness of the layer. The restrictive volume effect predominates at distances between the particles smaller than that of the layer of adsorbed polymer[15]. The intensity of the steric repulsion forces is influenced by the type of polymer that covers the particles, by the type of polymer-liquid interaction and by the degree of surface coverage[11,15]. The most widely used deflocculants in this case are the sodium polyacrylates, which are really bi-functional, i.e., they act through ion exchange and the steric hindrance mechanism, the latter being much more pronounced[2]. An important factor, when a deflocculant of this type is to be selected, is its molecular weight[15]. Polymers with an excessively long chain can produce polymeric bridge formation between the dispersed particles, completely neutralising the deflocculating effect of these substances[11]. The same result is noticed with excessive addition of a short-chain polymer. In these two cases over-deflocculation occurs, i.e., the addition of the deflocculant raises the apparent viscosity of the suspension. Therefore, molecular weight and polymer concentration control the efficiency of the steric stabilisation process[15].

The effectiveness of the deflocculation process of a colloidal suspension can be measured by the alteration of its rheological behaviour, caused by the introduction of deflocculating substances[2,3,6]. However, the types of clay minerals found in nature differ, and the deflocculating action of these substances depends on the properties of each mineral. Therefore, deflocculant type and the physical and chemical properties of the clay determine the optimum condition of the deflocculation process of a colloidal clay suspension.

2 – EXPERIMENTAL PROCEDURE

Five clays from ceramic tile companies were selected. The mineralogical composition of the clays was determined by X-ray diffraction (XRD) and chemical analysis by X-ray fluorescence (XRF). Sample preparation for the analyses was done by manual milling of 1g of each raw material in an agate receptacle, after drying in an oven at 110°C.

Particle size analysis of all the clays was carried out by laser diffraction in a granulometer. A sample of 1g clay was dispersed in 30ml distilled water and part of this suspension was introduced in the instrument for measurement. The specific surface area measurements of the studied clays were carried out using the BET method. Three samples of each clay were treated at 100°C, on a flow of N_2, for 2h, subsequently conducting the measurements.

The quantities of water that each type of clay adsorbed/absorbed until its saturation were determined. For this, samples of the clay were prepared, after oven drying at 110°C, by fast milling in a laboratory mill for 10min. (standard condition). Subsequently, 5g of clay was added to a receptacle with 100ml distilled water and the suspension was allowed to stand for 24h. The suspensions were then vacuum filtered to withdraw the excess water. A sample of 100mg of clay, still wet (saturated in water), was subjected to thermogravimetric analysis in a thermal analysis system, with a heating rate of 5°C/min., to a temperature of 400°C.

The densities of the clays were also determined in contact with water. The method used was pycnometry, where 5 samples of 3g clay were placed in 10ml volume test flasks (volume calibrated with water), part of the test flask volume being filled with distilled water. Subsequently, ultrasonics was applied for 30min, then filling the test flask. The volume of each sample was calculated by the difference between the volume of the test flask and the mass (volume) of added water. As part of the added water was adsorbed and/or absorbed by the clay, a corrected density was determined as follows: i) the quantity of the water retained by the clay was incorporated into the mass of the sample; ii) the same quantity of retained water was incorporated into the volume of the sample.

The cation exchange capacity was measured (CEC) of each clay. The method used involved a receptacle with 100ml solution (twice distilled water) of a substance that acted as a cation donor, to which 10g clay was added, stirring the dispersion for 24h. The quantity of ions exchanged between the clay mineral and the solution was then measured. For this, chemical analysis was performed using plasma (ICP) of the elements Na, K, Ca, Mg, Ba, Fe and Al present in the previously filtered solution. Solutions were used of $BaCl_2$ (0.5N), LiCl (1N) and HCl (0.1N) as cation donors.

The zeta potential values of the studied clay particles were measured in a Zeta Plus instrument. The preparation of the samples was carried out as follows: i) preparation of a clay suspension in distilled water with concentration of 25% solids by volume; ii) suspension pH measurement; iii) withdrawal of a sample of 2ml suspension, diluting to 10ml; iv) centrifuging of the sample for 10min at 1000rpm; v) withdrawal of 1ml of the supernatant liquid, again diluting to 10ml; vi) re-centrifuging; vii) and finally a sample of the liquid was subjected to measurement.

Rheological tests were carried out using a rotational viscometer with computer control of the strain rate. Each rheological test was run in three stages: i) application of a strain rate of $500s^{-1}$ for 30s; ii) sample rest for 2min; and iii) application of an up strain rate from 0 to $500s^{-1}$ in 10min. The samples of 150ml suspension, with a 25 vol% concentration of clay in distilled water were homogenised in a fast laboratory mill for 5min. The effect of the deflocculant addition on the rheological properties of the suspensions was determined by adding four concentrations (by weight) of deflocculant to the clay suspensions. Sodium tripolyphosphate PA ($Na_5P_3O_{10}$) was used as the deflocculant for the study of electrostatic stabilisation; sodium polyacrylate ($(C_3H_5\text{-}COONa)_n$) of low molecular weight (2100 g/gmol) for the steric effect; and sodium phosphonate ($HPO(ONa)_2$), diluted in distilled water to 33% by weight, for the mechanism by flocculating cation capture. The pH and particle zeta potential measurements of each suspension were carried out by the methods set out above.

3 - RESULTS AND DISCUSSION

Table I details the chemical analysis data (in wt%) and loss on ignition (L.O.I.) of the studied clays.

Raw material	SiO_2	Al_2O_3	CaO	MgO	Na_2O	K_2O	Fe_2O_3	TiO_2	L.O.I.
Kaolin SP	47.15	36.6	0.12	0.3	0.07	1.65	0.7	0.11	13.19
Kaolin C 201	50.47	34.33	0.09	0.26	0.09	1.36	0.69	0.17	12.49
Clay APR 1	50.07	29.67	1.66	1.87	0.09	0.33	1.52	1.92	12.82
Clay TSMA	62.18	24.19	0.68	0.87	0.06	0.75	1.62	0.63	8.97
Clay UKR	63.98	23.12	0.36	0.57	0.42	2.21	1.15	1.24	6.9

Table I: Chemical analysis data of the studied clays.

The X-ray diffraction results are shown in Figure I. Analysing the results shows that Kaolin SP, Kaolin C201 and clay APR1 basically consist of kaolinite ($Al_2Si_2O_5(OH)_4$), confirmed by the presence of the peaks at 7.16, 3.58 and 1.62Å in their X-ray diffraction. The high ignition loss of the group of kaolinitic clays (see Table I) is related to the loss of the hydroxyls (OH^-) of the kaolinite phase in their composition. In clay TSMA there is a mixed composition of kaolinite and montmorillonite. The kaolinite presents differentiated crystallisation, since its X-ray peaks are at 7.24, 3.58 and 2.50Å. Another phase in its composition is sodium calcium montmorillonite of 15Å ($Na_xCa_y(Al,Mg)_2Si_4O_{10}(OH)_2\ zH_2O$), since it exhibits peaks at 15.6, 4.50 and 3.04Å. Clay UKR presents X-ray peaks at 7.18, 3.58 and 2.50Å which confirm the presence of the kaolinite phase in its composition. The existence of peaks located at 1.98, 10.06 and 5.01Å shows that illite ($KAl_2(Si_3AlO_{10})(OH)_2$) is one of the phases in clay UKR. The ignition loss of these last two raw materials is relatively small, compared with the values of the kaolinitic clays. This is because kaolinite has a relative mol quantity of OH^- exceeding that of montmorillonite and illite. Analysis using the database of the diffractometer involved, taking into account the chemical analysis of the clays, shows that quartz (peaks at 3.34, 1.82 and 2.46Å) is the main impurity in the raw materials.

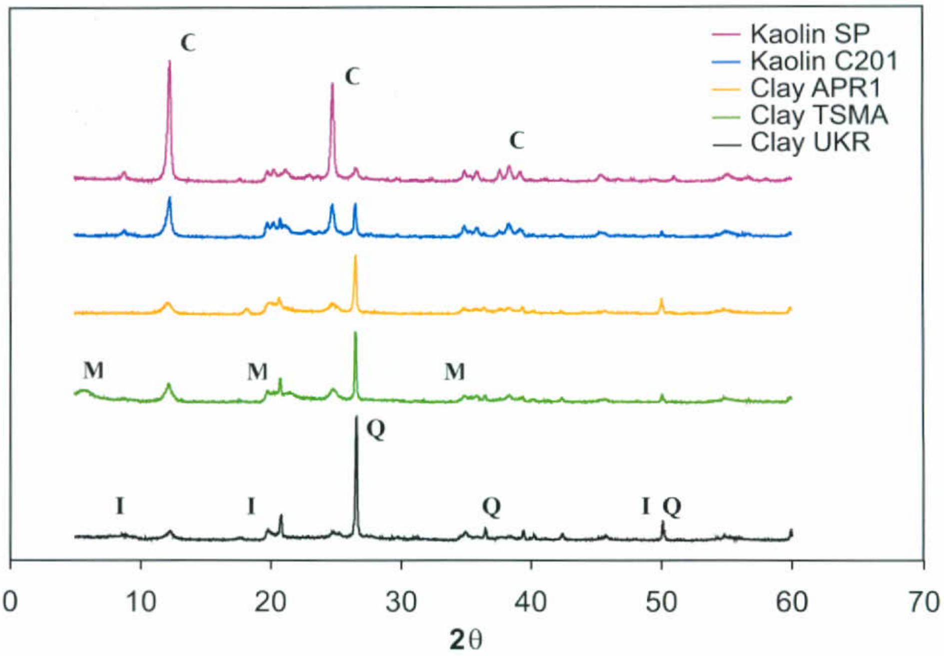

Figure I: Diffractograms of the studied clays: C(Kaolinite), M(Montmorillonite), I(Illite), Q(Quartz).

Figure II shows the results of the particle size analysis of the clays studied in the form of their cumulative distribution curves (% by volume). The results indicate that in spite of being milled under the same conditions for the same time, the clays presented different particle size distributions. The maximum particle diameters in the distributions respectively range from 10 to 50μm for Kaolin C201 and clay TSMA. The mean distribution diameters range from 2.6 to 3.9μm.

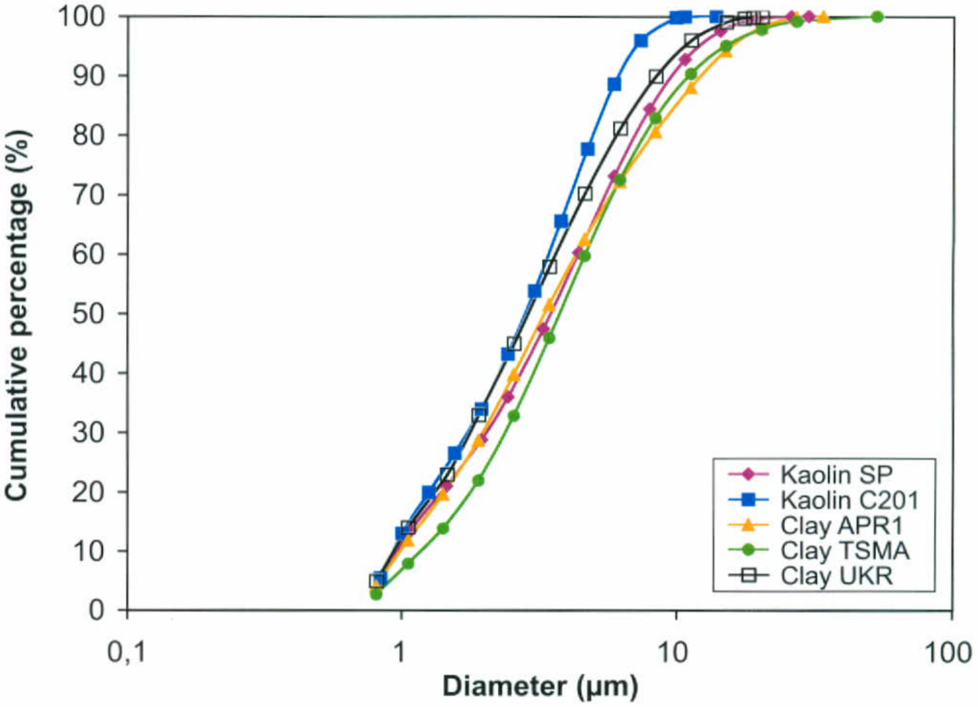

Figure II: Cumulative particle size distribution of the clays.

Table II gives the specific surface area data of the clays, with the standard deviation found for the three measurements. Comparison between the results of the particle size analysis (see Figure II) and surface area data shows no direct correlation, i.e., clays that have quite fine particles (Kaolin C201) present small surface area values. Two important factors should be taken into account on analysing the surface area data. The first one relates to the shape or surface appearance of the particle, as solid particles with a very irregular shape and surface possess a high surface area. This can explain the high surface area values found for clay APR1, since it is a clay with relatively coarse particles. The other factor to be remembered is that, because of their crystalline structure, some clay minerals have bigger surface areas than others. This is the case of montmorillonite (clay TSMA), which has a high surface area (existence of interlaminar gaps) and kaolinite (Kaolins) characterised by having a lower value.

Raw Material	Surface Area (m^2/g)	Standard Deviation
Kaolin SP	13.9	+/- 0.1
Kaolin C 201	19.8	+/- 0.7
Clay APR 1	41.4	+/- 0.6
Clay TSMA	37.0	+/- 1.8
Clay UKR	27.4	+/- 1.4

Table II: Raw materials specific surface area data.

The quantities of water adsorbed (100-200°C) and absorbed (110-200°C) and the total value of the water incorporated per gram of each clay is shown in Table III. Analysis of the results set out in Table III indicates that the clays can be divided into two groups: low water retention (g H_2O/g clay <0.10) and high water retention (g H_2O/g clay> 0.10). Practically all the water retained by the clays is water of the adsorbed type. Furthermore, water adsorption is directly dependent on the specific surface area of the clay (see Table II) and on the effective quantity of impurities in the composition (see Table I and Figure I). Using the example of clay UKR, it can be observed that in spite of presenting a high surface area its adsorbed water content is small, since this clay has a large quantity of quartz in the composition. The quantities of absorbed water of the clays are directly linked to the type of clay mineral phases present in the composition. These quantities are always shown to be very small when compared to the adsorbed water, because all the clays are made up of mineralogical phases that do not tend to incorporate water into their structure. The quantity of absorbed water is only representative for the case where the clay contains montmorillonite in its composition (clay TSMA).

	Weight Loss (%)			
Raw material	**100-200°C**	**100-110°C**	**110-200°C**	**g H_2O / g clay**
Kaolin SP	8,7	8,5	0,2	0,12
Kaolin C 201	5,1	4,6	0,5	0,07
Clay APR 1	12,2	11,4	0,8	0,19
Clay TSMA	9,2	7,3	1,9	0,15
Clay UKR	2,7	2,0	0,7	0,04

Table III: Weight loss values found in thermogravimetric analysis.

The mean corrected density values, together with the mean uncorrected density values (pycnometer), of each clay, are presented in Table IV.

	Density (g/cm^3)	
Raw Material	**Pycnometric**	**Corrected**
Kaolin SP	2.48	2.15
Kaolin C 201	2.44	2.23
Clay APR 1	2.65	2.11
Clay TSMA	2.49	2.15
Clay UKR	2.57	2.45

Table IV: Corrected and pycnometric density values of the clays.

The results of Table IV show that in general, the clays with a higher pycnometric density value are those that also possess high water retention values and hence smaller corrected density values. This because, on introducing water into the pycnometer for the measurement, the clay retains a certain quantity, for this reason giving the impression of having a higher density than is actually the case. Thus, in the direct density measurement there is a upward error that increases as the clay water retention value rises. An exception exists in the case of clay UKR, since in spite of the drop in water retention, it presents a high pycnometric density value. However, the chemical composition of the clay contributed considerably to its density value. This value can be due to the quantity of quartz (density 2.7g/cm^3) in its composition.

The total quantities in meq / 100g clay of the exchanged cations (CEC) for each raw material, with the exchange cation solutions (H^+, Li^+ and Ba^{+2}), are set out Table V.

	CEC (meq/100g)		
Raw material	**H^+**	**Li^+**	**Ba^{+2}**
Kaolin SP	2.0	2.0	2.0
Kaolin C 201	2.0	1.0	1.0
Clay APR 1	3.0	1.5	1.5
Clay TSMA	3.5	6.5	6.0
Clay UKR	5.0	5.0	5.0

Table V: Results of CEC of the clays for each type of exchange cation.

The CEC results confirm the data found in the literature[2]. Kaolinite has a small CEC and the montmorillonites are the clay minerals that present the greatest exchange capacities. In fact, the results divide the clays sharply into their groups of mineralogical composition: i) the kaolinitic clays exhibit the smallest CEC values; ii) the kaolinitic-montmorillonitic clay exhibits the largest value; and iii) and the kaolinitic-illitic clay has an intermediate value, because the illite phase is characterised by having a lower CEC to that of montmorillonite. Another factor to be remembered, in the analysis of the results of Table V, is that the type and charge of the exchange cation (H^+, Li^+ and Ba^{+2}) cause small alterations in the CEC results of the studied clays. The CEC results for the exchange ions Li^+ and Ba^{+2} are very similar, in spite of these two cations having quite a different charge/ion radius ratio.

The results of suspended clay particle zeta potential in distilled water, and of the pH of the suspensions mentioned, are detailed in Table VI.

Raw material	Zeta Potential (mV)	Natural pH
Kaolin SP	-18	4.3
Kaolin C 201	-18	4.4
Clay APR 1	-16	4.6
Clay TSMA	-10	4.6
Clay UKR	-34	7.4

Table VI: Results of particle zeta potential and suspension pH.

The values in Table VI show that the zeta potential of the clay particles is directly dependent on two factors: i) pH of the suspension; ii) and state of particle break-up. The pH of a clay suspension acts directly on the type and magnitude of the electric charge generated on the edges of the suspended particles. In acid pH, the charge that forms is positive and decreases the zeta potential of these particles. In alkaline pH the effect is the opposite, because the charge generated on the edges is negative. The results of clay UKR show that, on being the most alkaline, it has the largest zeta potential. The state of particle break-up directly affects the relationship between the total area of the edge region and the total area of the particle flat faces. The higher the ratio between these areas, the greater will be the influence of the charge generated on the particle edges on the particle zeta potential value. The results obtained for clay APR1 confirm this hypothesis, because, despite having a pH value exceeding that of the kaolins, it exhibits a smaller zeta potential. However, it is this clay that has the largest specific surface area of the three (see Table II).

Deflocculants are added to clay suspensions to alter their rheological behaviour. A fully deflocculated suspension should present Newtonian behaviour. The deflocculant eliminates interparticle interactions responsible for the departure from the ideal behaviour of the suspension.

The deflocculant used in this work to study the electrostatic stabilisation mechanism was sodium tripolyphosphate (TFP). Figure III shows the variation of apparent viscosity of the suspensions of studied clays (with a 25 vol% concentration), as a function of the deflocculant addition. The viscosities were determined at a strain rate of 500 s^{-1}. The mass of added deflocculant was calculated in relation to the mass of dry clay, i.e., all the suspensions were prepared with the same relative quantity of this substance.

The results of Figure III show the efficiency of sodium tripolyphosphate in reducing the apparent viscosity of the clay suspensions. After adding 0.7% deflocculant, most of the suspensions, with the exception of clays UKR and TSMA, present an apparent viscosity in the range 3 to 5 mPa.s. This indicates that on eliminating the interparticle interactions, the suspensions tend to have the same viscosity, which in this case becomes solely dependent on the solids volume concentration. Moreover, TFP is observed to be more efficient in some cases than in others. The Kaolin SP suspension, is already "fully deflocculated" after just adding 0.1% deflocculant, while that of clay APR1 only undergoes a small variation in viscosity. In the case of clays UKR and TSMA, the deflocculant has not been able to provide a change in behaviour similar to that of the other clays. Clay suspension UKR has undergone deflocculation, but the level of final apparent viscosity is higher (+/-20 mPa.s). In the case of clay TSMA a deflocculation process has practically not taken place, with a minimum viscosity (90 mPa.s) at 0.5% deflocculant.

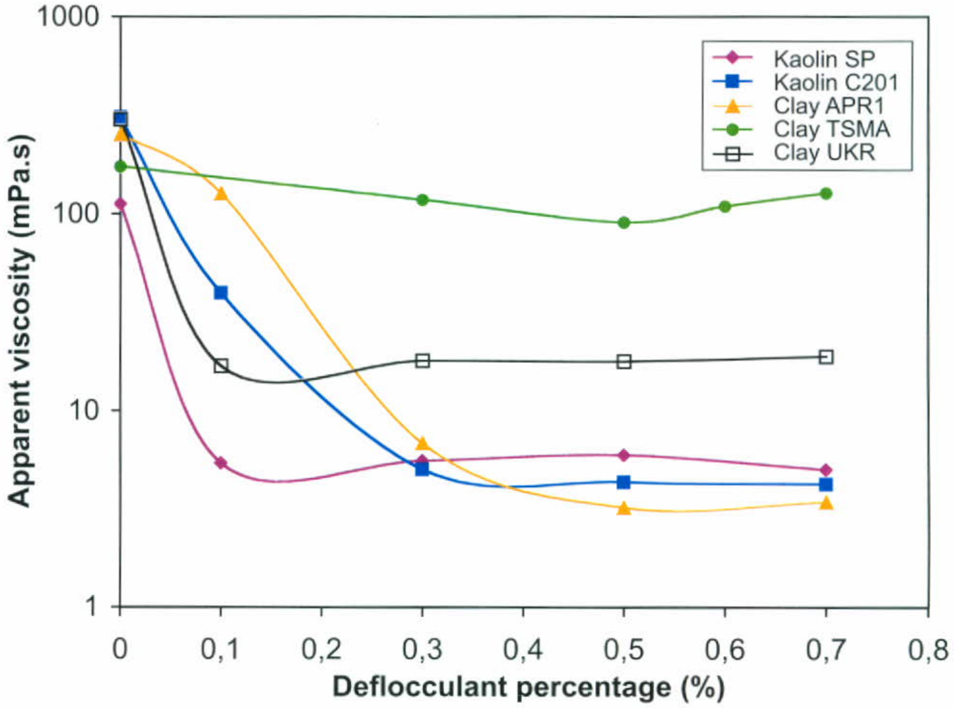

Figure III: Apparent viscosity of the clay suspensions as a function of the TPF percentage.

TFP efficiency in the deflocculation process of the studied clay suspensions was shown to be variable. To understand the electrostatic deflocculation mechanism, the alteration that occurs with the deflocculant addition in some properties of the liquid and solid phases in the suspension needs to be analysed. Adding sodium tripolyphosphate to an aqueous medium, as a salt with an alkaline character, provides an increase of solution pH. In fact, the introduction of this deflocculant in the clay suspensions causes an alteration in the pH of its liquid phase, as shown in Figure IV.

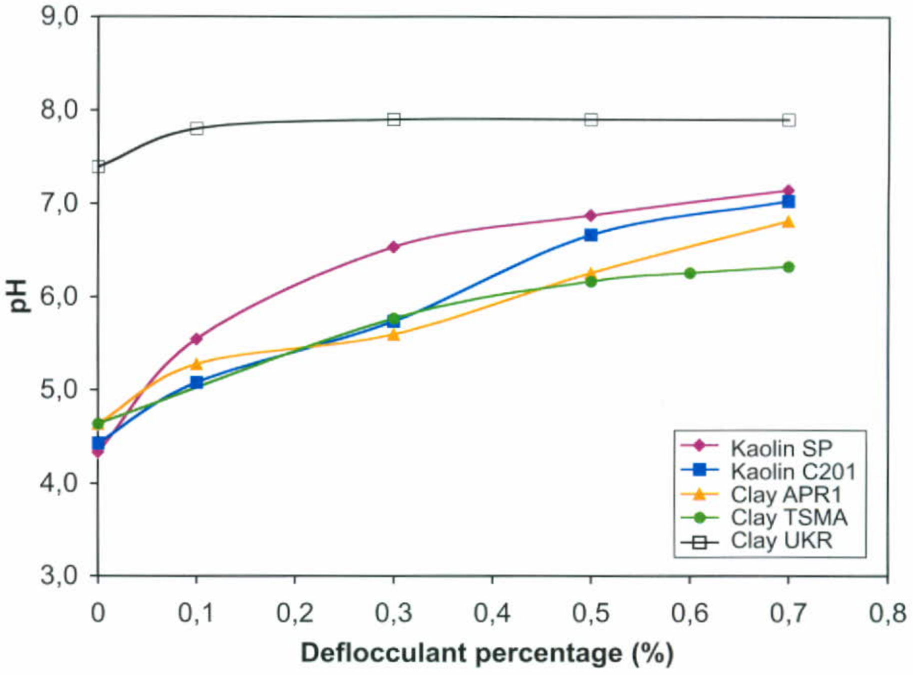

Figure IV: Variation of clay suspension pH as a function of the TPF percentage.

Comparison between the results of Figures III and IV clearly shows that the reduction of apparent viscosity in the suspensions is linked to the increase of its pH, provided by the deflocculant addition. The behaviour for the case of clay UKR, for example, shows that when suspension pH stops rising, the variation of its apparent viscosity also ceases. Furthermore, TFP efficiency is more evident for the clay suspensions that present a natural pH in the range between 4 and 5. For the clay having a natural pH over 7, the deflocculant has not been able to alter its pH significantly and, hence the apparent viscosity of the suspension. In the case of clay TSMA, the pH rise with the TFP addition has not been very marked either.

At this point it is worth remembering that clay suspension pH is one of the factors that determines the zeta potential of its particles. This property is also known to have a pronounced effect on the rheological properties of the suspension. Therefore, analysis of the evolution of zeta potential of the suspended particles as a function of the deflocculant addition is of fundamental importance in understanding the electrostatic deflocculation mechanism. Figure V presents these results. The figure does not show the results for the case of Kaolin C201, since it was considered that those of Kaolin SP and clay APR1 would suffice to illustrate the behaviour of the kaolinitic clays.

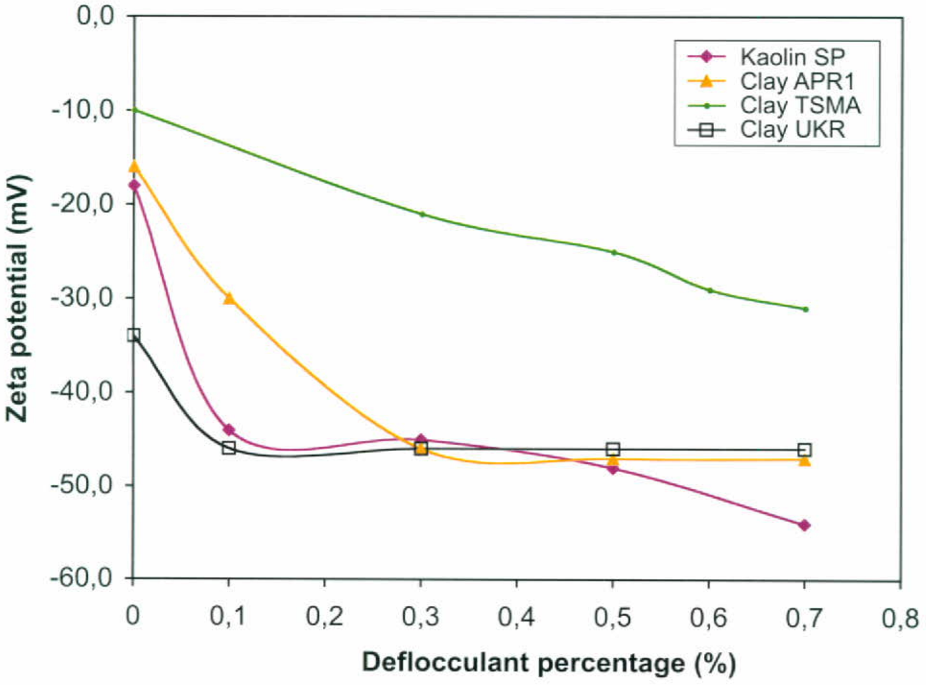

Figure V: Zeta potential of the clay particles as a function of the TPF addition.

The TFP addition produces a significant alteration in the zeta potential of the particles of the kaolins and of clay APR1. The pH alteration caused by this addition (Figure IV) acts directly on the magnitude and type of electric charge formed in the edge region of particles of this type of clay. The results obtained for Kaolin SP and for clay APR1 are a good example of this phenomenon. In acid pH, the amphoteric character of the alumina causes a positive electric charge to form on the clay particle edges. As TFP is added to the suspension, the value of the positive charge in the edge area drops, and hence the zeta potential of the particle. For values of pH in the range 6 to 7, the edge charge is zero, no change is noticed in the zeta potential value. For pH values over 7, the charge that forms is negative and particle potential grows again (results of Kaolin SP in

Figure V). The results of clay UKR show that the pH limit for the deflocculant to be effective is around 8, i.e., as TFP is not a strong base, it is not able to take the pH of the suspensions to much higher values than this. For this reason, the alteration in the zeta potential of these clay particles exhibits the behaviour shown in Figure V. The potential increases and halts when the pH stops changing. The results obtained with clay TSMA show another important contribution to the understanding of the mechanism of TFP action on clay particle zeta potential. In the case of this clay, the alteration of the electric charge formed on the particle edges has less effect on the value of its zeta potential than in the case of the kaolinitic clays. The crystalline structure of montmorillonite consists of two quartz layers to one alumina layer, while in the kaolinite the structure is 1:1. Therefore, the overall contribution of the charge formed on the alumina layer is smaller. Thus, as can be observed, the zeta potential of the TSMA clay particles undergoes a much less pronounced increase, despite the increase in suspension pH.

Another TFP action mechanism can be explained by the effect of cation exchange. Clay suspension TSMA is poorly deflocculated by the electrostatic mechanism, basically due to the high cation exchange capacity of this clay. A clay suspension with high CEC value has a liquid phase with a high ionic strength. When the clay is put in suspension, the cations adsorbed to its structure migrate to the liquid, raising the ion concentration in the vicinity of the particles. A high clay CEC value also indicates that the clay has a high electric surface potential, since this value is an indication of the number of isomorphic substitutions present in the structure of the clay. The combination of these two factors gives these clays particles a high surface potential, associated with a thin electric double layer. Thus, the interparticle interaction energy curve of this type of clay (DLVO theory) presents a high repulsion energy value associated with a characteristic distance to the point of minimum attraction. The practical result of all the foregoing is that the clay particles have a small zeta potential, and when they approach each other, at the moment of collision, they are still subject to attraction forces, because the particles can position themselves with small interparticle separation distances. At these distances, the attraction forces are greater, since the van der Waals forces are inversely proportional to distance to the sixth power.

The behaviour shown in Figure III for clay TSMA describes the mechanism of the TPF effect well on the apparent viscosity of montmorillonitic clay suspensions. Initially, the introduction of the deflocculant in the suspensions causes apparent viscosity to fall. From 0.5% TPF on, the addition raises viscosity, characterising the phenomenon of over-deflocculation. Adding TPF raises zeta potential and the maximum repulsion between the suspended particles. Furthermore, the addition of excess deflocculant causes the thickness of the electric double layer surrounding the particles to decrease. The apparent viscosity values of the suspensions depend on these two deflocculant action components. Initially, the zeta potential-raising component predominates and suspension apparent viscosity decreases. The flocculating cations that surround the particles are replaced by the Na^+ ions of the deflocculant, raising particle electric double layer thickness. This increase is progressive and becomes less and less marked. From 0.5% TPF on, an excess of cations is found around the particles. Now the deflocculant addition still promotes cation exchange, however with a shrinkage in volume of the electric double layer.

On the other hand, the electrostatic deflocculation mechanism acts in quite an efficient way on the suspensions of Kaolins and clay APR1. These clays have a small cation exchange capacity and a small zeta potential (see Tables V and VI). Thus, the interparticle interaction energy curve of these clay suspensions is characterised by presenting a small maximum repulsion value. However, as they have a small natural pH value, the possibility exists of interaction between the negative faces of one particle with the positive edge of another. Adding sodium tripolyphosphate decreases the apparent viscosity of these suspensions, since: i) it causes an increase of the zeta potential of their particles, through the mechanism of pH moving; ii) it eliminates the positive electric charge in the particle edge region; and iii) as the concentration of ions around the particles is small (small CEC), on introducing TPF in the suspensions, the Na^+ ions of the deflocculant form a very thick double layer. The TPF addition makes the interparticle interaction energy curves have a progressively higher maximum repulsion value. The possibility is also eliminated of attraction between particle faces and edges in the suspensions. Kaolin SP, after the addition of 0.1% TPF, presents a zeta potential value of -44 mV (-54 mV at 0.7% TPF), while in clay TSMA the value does not exceed -31 mV, even with the introduction of 0.7% of this deflocculant. It is worth highlighting that none of the kaolin suspensions (or of clay APR1) underwent over-deflocculation processes. As these clays present small CEC values, the addition of the deflocculant quantities involved was not enough to establish a cation excess around the particles in the suspensions. The only case that can be considered an exception was that of clay UKR. In spite of this clay suspension undergoing deflocculation, the final value of its apparent viscosity exceeds that of the other clays. However, the value of the natural pH of this clay is high when compared with those of the others and the deflocculant was unable to increase the zeta potential value of its particles. In this clay there is also a high CEC value and its particles are quite fine (Figure II).

Figure VI shows the evolution of clay suspension apparent viscosity as a function of the sodium phosphonate (FOS) addition. The results confirm the poor efficiency of the deflocculant in the stabilisation of the clay suspensions. The deflocculant has only been able to significantly reduce the apparent viscosity of the suspensions of Kaolin SP and clay APR1.

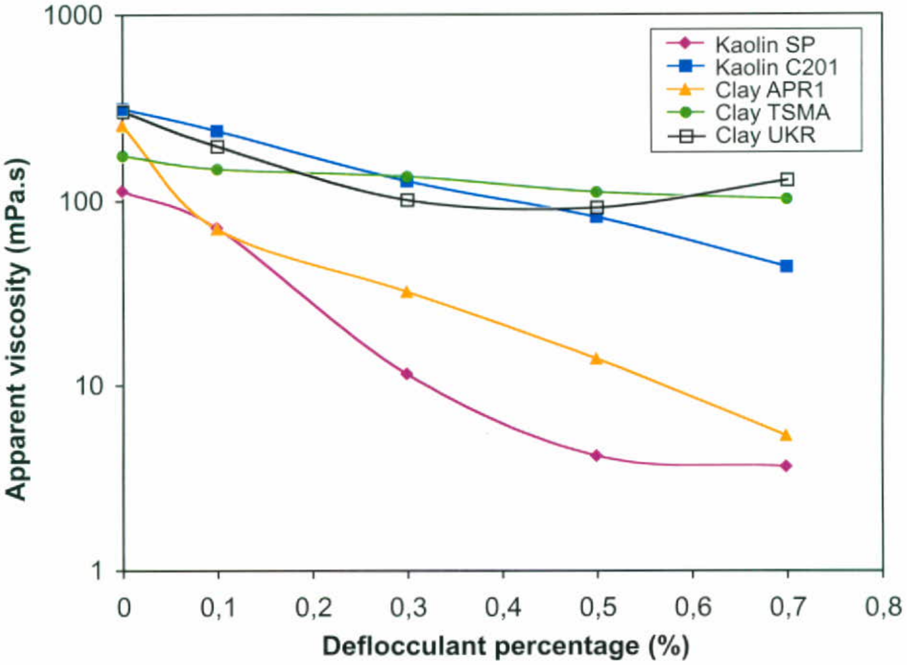

Figure VI: Variation of clay suspension apparent viscosity as a function of the FOS percentage.

The alteration caused by the addition of sodium phosphonate on the zeta potential of the clay particles in the suspensions is shown in Figure VII.

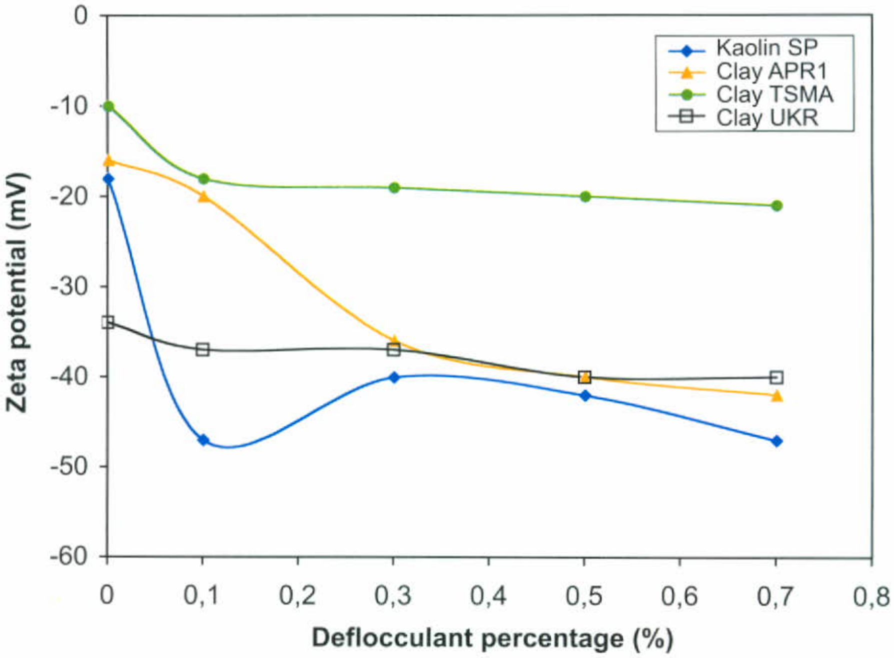

Figure VII: Zeta potential of the clay particles as a function of the FOS addition.

The variation of clay particle zeta potential by the cation capture mechanism depends on factors that involve the chelation reaction process of the flocculating cations. The cation removal capacity will be bigger: i) with a larger deflocculant concentration; ii) with a smaller attraction force between the cation and the negative surface of the particle; and iii) with a smaller cation concentration around the particle. A particle with a high surface charge holds the cations in its electric double layer strongly bound to it. Thus, the activation energy of the cation capture reaction will be high. The formation of the metallic complex, which is the reaction product, depends on the cluster of sequestering ions around the flocculating cations. The greater the cation concentration in the electric double layer of a particle, the greater will be the steric hindrance reaction.

The results of Figure VII confirm the above, as they show that the largest gains in zeta potential with the deflocculant addition were found in the suspensions of Kaolin SP and clay APR1. These clays possess a small CEC (Table V) and a small initial zeta potential (Table VI). These characteristics indicate that such clay particles have a small surface charge, associated with a small cation concentration in their vicinities. The results of clay TSMA are intermediate. This clay presents a small initial zeta potential, however its cation exchange capacity is high. The smallest potential gain value was observed for clay UKR. This clay exhibited the largest initial zeta potential value and a high CEC.

Thus, the results found for the variation of apparent viscosity of the suspensions as a function of the deflocculant addition are now clear, because sodium phosphonate was shown not to be very effective in raising the zeta potential of the clay particles. The reduction in apparent viscosity of the suspensions can be directly associated with the change in zeta potential of its particles (see Figures III and IV). The deflocculant addition increases the maximum interparticle repulsion value and the characteristic minimum attraction distance (DLVO theory). The value of the interparticle attraction forces therefore become steadily smaller, decreasing the electroviscous effect produced by the particles, and reducing suspension apparent viscosity.

To conclude the section on the analysis of the results of this study, it is still necessary to evaluate the alterations that occurred in the rheological properties of the clay suspensions with the introduction of a deflocculant that acts primarily through the steric hindrance mechanism. Figure VIII presents the deflocculation curves of the clay suspensions on adding sodium polyacrylate (PAC)..

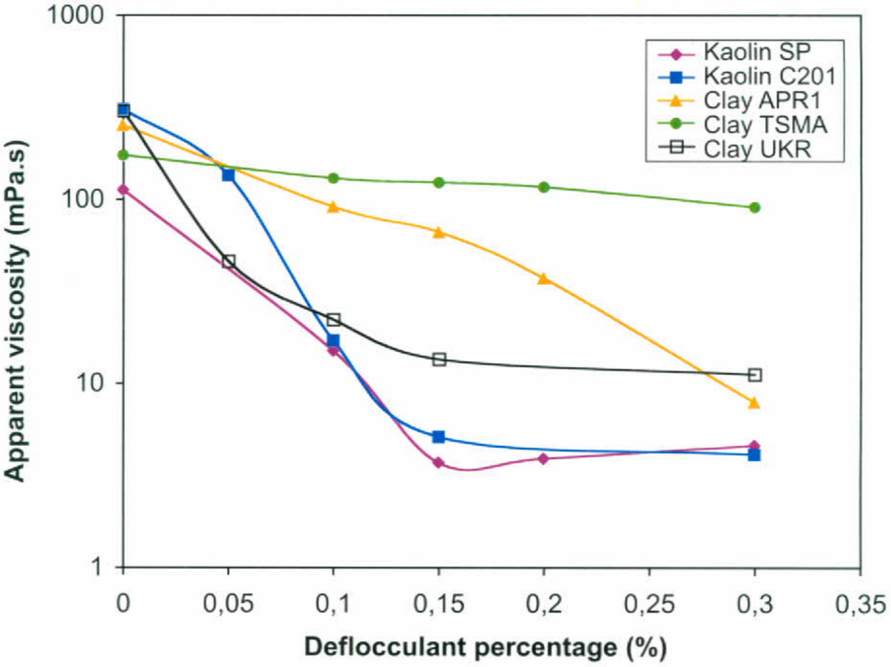

Figure VIII: Apparent viscosity of the clay suspensions as a function of the PAC percentage.

First, observing the results of the above figure, sodium polyacrylate can be said to behave differently with regard to the reduction of suspension apparent viscosity. The deflocculant was shown be quite efficient in the case of some suspensions, since significant reductions of viscosity were observed with the addition of just 0.3% of this substance. In fact, sodium polyacrylate is able to act according to two deflocculation mechanisms. The polymeric chains of the dissolved polyacrylate ions can cover the particles in the suspensions and the deflocculant proceeds to act by steric hindrance. The Na^+ ions, due to their alkaline character, are able to alter suspension pH. A pH increase raises the zeta potential of the particles, and the deflocculant acts by an electrostatic stabilisation mechanism. The efficiency of this deflocculant depends on its capacity to increase suspension pH. Figure IX plots the variation of clay suspension pH with PAC percentage.

There was hardly a significant alteration in pH in the case of the Kaolin SP suspensions. PAC is an organic salt with a relatively low alkaline character and for this reason has not been able to alter the pH of the other suspensions. The relative molar quantity of Na^+ cations present in a PAC molecule is less than the quantity in a TPF molecule. Kaolin SP is characterised by having a small CEC, and hence the quantity of cations from its structure, present in the liquid phase, are small. For this reason, the action of the alkaline Na^+ ions of the deflocculant on the increase in suspension pH is easier. The presence of flocculating cations (Ca^{+2}, Al^{+3}, etc.) in the liquid phase of a suspension hinders the effect of the deflocculant, since these cations possesses a character of greater acidity than that of the cations of the alkaline earth metals. It can be observed that the change in pH of clay suspensions with a high CEC is less pronounced. The clay suspensions with a high natural pH also underwent a less noticeable increase of this variable.

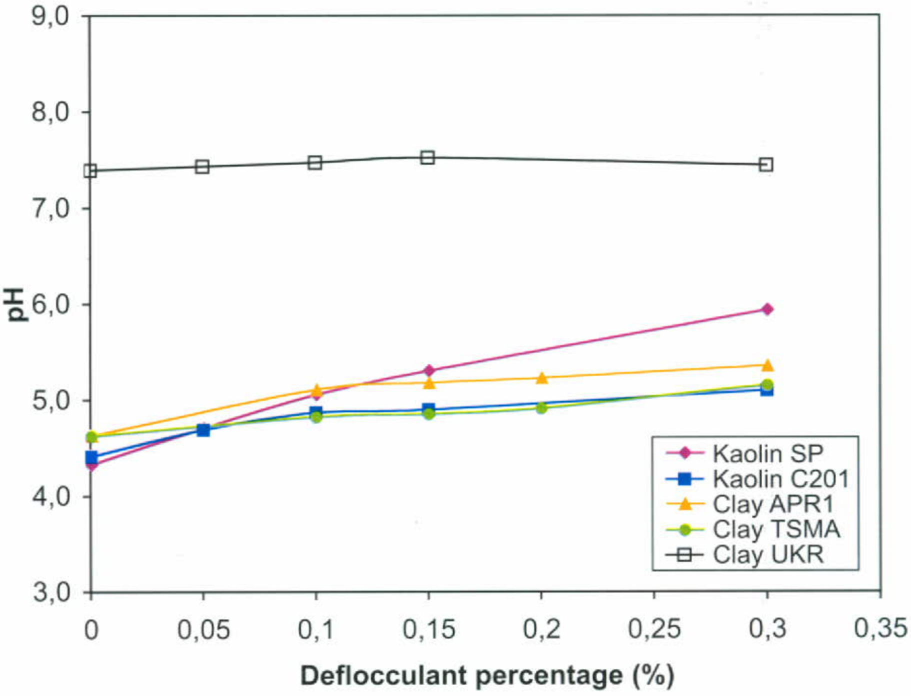

Figure IX: Variation of clay suspension pH as a function of the PAC percentage.

The increase in suspension pH indicates the efficiency of the deflocculant in increasing particle zeta potential. Thus, the only suspension in which PAC has acted effectively through the electrostatic stabilisation mechanism has been that of Kaolin SP. In the others, the reduction in apparent viscosity has been mainly the result of the action of the deflocculant by the steric hindrance mechanism.

The efficiency of a deflocculant that acts by steric hindrance depends on the degree of polymeric coverage of the particles in the suspension, provided by the deflocculant addition. The degree of coverage, in turn, depends on the polymer-surface affinity and total area to be covered. With regard to the affinity of the polymer that produces the adsorption of the polymeric chains on the particle surface, in the case of the clays this can be considered a factor of minor importance. Owing to the very similar characteristics of the clay particle surfaces, independently of their mineralogical composition, the polymeric chains can be considered to have the same adsorption conditions. The main factor that controls the degree of particle coverage is the specific surface area of the suspended clay.

Comparing the results of Figure VIII with the surface area values of Table II shows that sodium polyacrylate has more effectively reduced the apparent viscosity of the suspensions of the clays with a smaller specific surface area. In these cases, the area to be covered is smaller and complete particle coverage is achieved with a smaller deflocculant concentration. The suspension of Kaolin SP has been the one in which the deflocculant was most effective, since this clay has the smallest surface area value. Clay APR1 has the largest surface area value in the group of kaolinitic clays. For this reason, it is difficult for the deflocculant to reduce the viscosity of the suspension. As the polyacrylate is added, the polymeric film on the particles becomes more and more continuous and homogeneous. The larger the polymer concentration on the particle surface, the greater will be the osmotic and volume restricting effects that give rise to steric hindrance. When the concentration increases, the gain in repulsion energy of steric origin also increases and the apparent viscosity of the suspension decreases. It deserves pointing out that with the addition of a larger quantity of deflocculant, the suspension should reach a similar viscosity value to the one obtained for Kaolin SP (in the range 3 to 5 mPa.s). Clay TSMA has a high surface area and the effect of the deflocculant on suspension viscosity was much less effective.

The results found for clay UKR justify the following observation. Despite the suspension of the clay undergoing deflocculation, the final apparent viscosity value found exceeds the others (11 mPa.s). This fact already occurred when sodium tripolyphosphate was used. This suggests some error, at least with regard to the measurement of the quantities of water adsorbed and absorbed by this clay. An indication of this error is the fact that the clay has presented a smaller value of water incorporation than all the others. If this error occurred, the calculation of its density in water would then provide a larger value than the real one, and all the suspensions of this clay would have a larger volume fraction than the one specified.

4 – CONCLUSIONS

The efficiency of the electrostatic deflocculation mechanism, in the process of reducing the apparent viscosity of the suspensions of studied clays, is directly linked to the capacity of the deflocculant (TPF) to raise suspension pH and hence the zeta potential of the clay particles, and also depends on the cation exchange capacity of the clays. The electrostatic mechanism acts in quite an efficient way in clay suspensions with a small cation exchange capacity and low values for zeta potential and natural pH.

The deflocculation mechanism by cation capture was not found to be very efficient in the stabilisation of the clay suspensions. The deflocculant did not reduce apparent viscosity significantly in most of the clay suspensions, while the suspensions did not reach the levels of viscosity obtained with TPF. The poor efficiency of FOS, in reducing suspension apparent viscosity is due to the deflocculant not being very effective in raising the zeta potential of the clay particles. For all the suspensions, the potential alteration provided by FOS was less than that produced with TPF. The largest gains in zeta potential were found in the clay suspensions with a small cation exchange capacity.

The efficiency of the deflocculation mechanism by steric hindrance in reducing clay suspension apparent viscosity depends directly on the degree of polymeric coverage of the particles in the suspension. The degree of coverage, in turn, is inversely proportional to the total area to be covered, i.e., the primary factor that controls the degree of particle coverage is the specific surface area of the suspended clay. PAC most effectively reduced the apparent viscosity of suspensions of clays with the smallest specific surface area.

5 – ACKNOWLEDGEMENTS

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