INFLUENCE OF SILICATE- AND MAGNESIUM-SPECIFIC ADSORPTION AND PARTICLE SHAPE ON THE RHEOLOGICAL BEHAVIOR OF MIXED SERPENTINE-GOETHITE SUSPENSIONS

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Abstract—The influence of dissolved species and particle morphology on the electrokinetic behavior and the initial yield stress values of Cuban lateritic aqueous suspensions was studied. The lateritic samples were mixtures of serpentine and goethite in different relative proportions. The addition of silicate and Mg ionic species, which are normally found in natural waters used in industrial processes, affected the electrokinetic and flow behavior of the lateritic suspensions. Specific adsorption of these species on particle surfaces was shown by a shift of the isoelectric point and the maximum of the initial yield stress to more acidic pH (Si ionic species adsorption) and more basic pH (Mg ionic species adsorption), when compared to suspensions containing only non-adsorbing electrolytes. The initial yield-stress values determined in samples consisting entirely of goethite varied from sample to sample. A detailed crystallochemical characterization revealed that these changes were associated with the axial ratio (*i.e.* ratio of particle length to width) of the mineral particles. Goethite samples with larger particle size (smaller number of particles for a given solid concentration) and greater axial ratios presented initial yield-stress values greater than those goethites with smaller particle size and lower axial ratio.

Key Words—Electrokinetic Characterization, Goethite, Lateritic Suspensions, Serpentine, Specific Adsorption, Yield Stress.

INTRODUCTION

Lateritic soils are found in the tropical and sub-tropical regions of Cuba, Brazil, The Philippines, Indonesia and southern China (Kuhnel *et al.*, 1975; Ramanaidou *et al.*, 1996). These soils have attracted considerable attention, due to their high Ni and Co contents (Avotins, 1979; Avramidis and Turian, 1991). During the extraction process of these elements, many problems associated with the variability of the flow behavior in different batches have been encountered (Cerpa *et al.*, 1996). Therefore, the Ni and Co recovery process requires an adequate study of the stability and flow properties of the suspensions. These properties are influenced by many factors, such as surface chemistry, particle density, concentration and size, and shape of the suspended particles (Padmanabhan and Mermut, 1995).

For lateritic suspensions, some factors are not easily controlled and the influence of these is not understood well (Avramidis and Turian, 1991). Cerpa *et al.* (1996, 1999) showed that the stability of lateritic suspensions depends strongly on the serpentine/goethite ratio of the colloidal fraction as it represents ~70% of the solids components in the bulk sample. They also reported that the suspensions present either plastic or Newtonian flow behavior depending on pH, solid concentration and sample composition.

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Considering the heterogeneity of lateritic sediments there is need for more information about the other factors that may influence the flow behavior of lateritic suspensions. One of the main mineral components of the Cuban lateritic soils is goethite (Cerpa *et al.*, 1996), which normally grows in acicular form (Cornell *et al.*, 1983). A general feature of suspensions composed of elongated particles is that packing densities are low when the particle aspect ratios (length/width ratio) are high. For example, sediment densities of rod-like colloids are considerably lower than the random packing density for spheres (Philipse, 1996). This factor could play an important role in the flow behavior of the Cuban laterite suspensions. On the other hand, serpentine weathering generates silicate and Mg ionic species (the exact nature of which depends on pH) in the natural waters used in the industrial process (Vera, 1979; Cerpa *et al.*, 1996). These species adsorbed on particles could strongly affect the flow properties of suspensions. Therefore, the aim of this work was to determine how the particle shape and the presence of silicate and Mg ionic species could affect the electrokinetic and flow behavior of aqueous lateritic suspensions.

MATERIALS AND METHODS

Sample origin and characterization

Four mineral samples (SG, GS, G1 and G2) from lateritic deposits in Cuba were used for their crystallo-

Table 1. Mineral compositions (relative wt.% between samples) determined by XRD for the lateritic samples. Data for samples SG and GS were taken from Cerpa *et al.* (1999). Intensity factors reported by Schultz (1964) were used for the quantification.

Sample	Goethite	Serpentine	Maghemite	Gibbsite	Quartz	Serpentine/goethite ratio
SG	50	43	4	3	–	0.9
GS	79	15	3	tr	3	0.2
G1	100	–	–	–	–	0
G2	100	–	–	–	–	0

–: not detected

chemical, electrokinetic and rheological characterization. The colloidal fraction obtained by sedimentation was selected because the flow behavior of lateritic samples is dominated by this fraction (Cerpa *et al.*, 1999). A detailed characterization of samples SG and GS has been reported elsewhere (Cerpa *et al.*, 1999). X-ray diffraction (XRD, Philips PW1130 diffractometer) patterns obtained from samples G1 and G2 showed the presence of goethite only. Details of the mineral compositions obtained from XRD random-powder patterns are given in Table 1.

Cell parameters of samples were determined by a least-squares fit of the XRD data using Si as the internal reference standard. To determine the positions of the diffraction peaks, single-peak fittings using a pseudo-Voigt profile were performed. Samples diluted in a KBr matrix were characterized by infrared (IR) spectroscopy (Nicolet 20SXC spectrophotometer). Thermogravimetric (TG) analyses (Netsch STA 781) were conducted in dynamic air at a heating rate of $10°C$ min^{-1}.

The contents of Fe, Al, Si, Ni, Cr and Mn in the goethite samples were determined by X-ray fluorescence (XRF) spectrometry on glass disks using rock standards for calibration. The $K\alpha$ lines were measured with a Siemens SRS300 sequential spectrometer (Rh end-window tube). Analytical uncertainties were <1% for Fe and 5% for Cr, Al, Si, Ni and Mn.

A transmission electron microscope (TEM, Jeol 2000 FX2) equipped with an energy-dispersive spectrometry (EDX) analyzer (LINK QX2000) was used to determine the shape, size and chemical composition of single particles.

Electrokinetic and rheological characterization of suspensions

The isoelectric points (IEP) of laterite samples were determined by measuring the electrophoretic mobility of aqueous dispersions as a function of pH in a Delsa Coulter 440 device. 15 mg of sample were dispersed in 100 cm^3 of an aqueous suspension containing NaCl as an electrolyte, and the pH was adjusted with either NaOH or HCl. The IEP values determined at different NaCl concentrations (10^{-1}, 10^{-2} and 10^{-3} M) showed no variation which proves that there is no specific adsorption of either Na^+ or Cl^- ions (Hunter, 1981). To check for the effect of silicate and Mg ionic species on the laterite/water
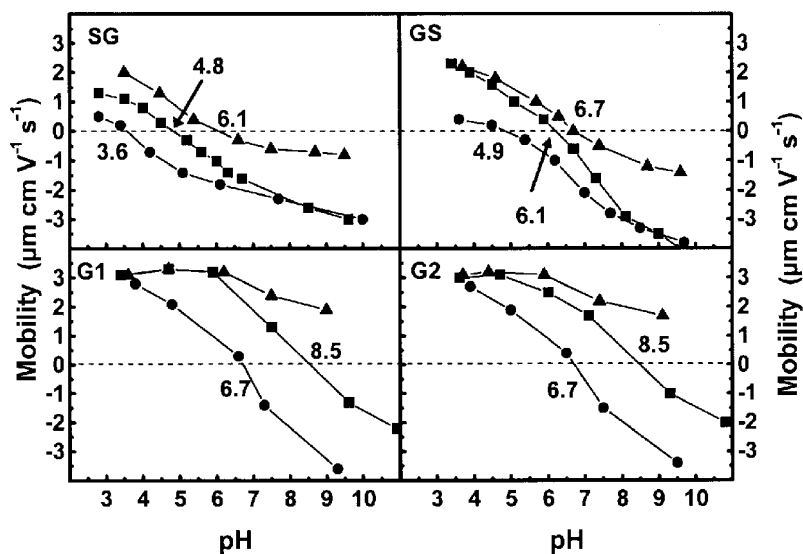

Figure 1. Electrophoretic mobility values as a function of pH and the nature of the electrolyte for the four samples studied. NaCl is represented by ■, Na_2SiO_3 by ● and $MgCl_2$ by ▲. The ionic strength was kept equivalent to that of a 10^{-2} M NaCl solution.
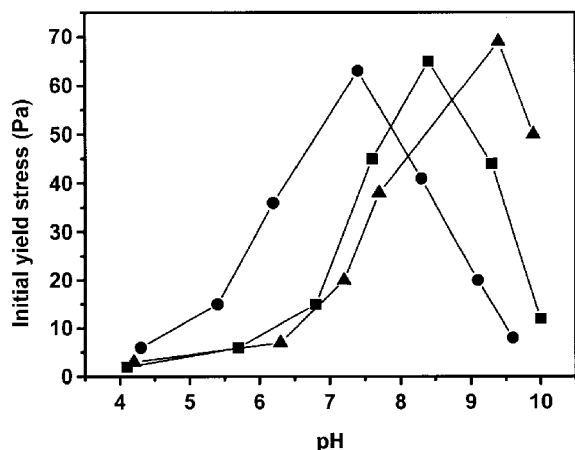
Figure 2. Initial yield stress values as a function of pH and the nature of the electrolyte for sample G1. The symbols are as in Figure 1. The ionic strength was kept equivalent to that of a 10^{-2} M NaCl solution.

Figure 3. Initial yield-stress values as a function of pH in 10^{-2} M NaCl aqueous suspensions for samples G1 (■) and G2 (●).

electrical interface, Na_2SiO_3 (10^{-3} M) and $MgCl_2$ (10^{-3} M) were also used as electrolytes, adding the appropriate amount of NaCl to keep the ionic strength equivalent to that of a 10^{-2} M NaCl aqueous solution. Larger amounts of silicate anions cannot be added to the system, as they will precipitate (Lindsay, 1979). The electrophoretic mobility curves of aqueous suspensions containing $MgCl_2$ were not registered at pH >10. At this pH, the number of Mg species in solution would exceed the solubility product of the common Mg hydroxides (Pugh and Bergström, 1988).

Flow properties of suspensions with a solid content of 15 wt.% were measured in a Haake Rotovisco RV20 concentric cylinder viscosimeter as a function of pH. This equipment allows direct determination of the initial yield-stress (Schramm, 1994). Experiments were carried out in aqueous suspensions containing 10^{-2} M NaCl, and also either Na_2SiO_3 (10^{-3} M) or $MgCl_2$ (10^{-3} M) plus the necessary amount of NaCl to keep the ionic strength equal to that of a 10^{-2} M NaCl aqueous solution.

RESULTS AND DISCUSSION

The influence of silicate and Mg ionic species on the electrokinetic and flow behavior of suspensions

The IEP of the four lateritic samples in the presence of NaCl is a function of the serpentine/goethite ratio
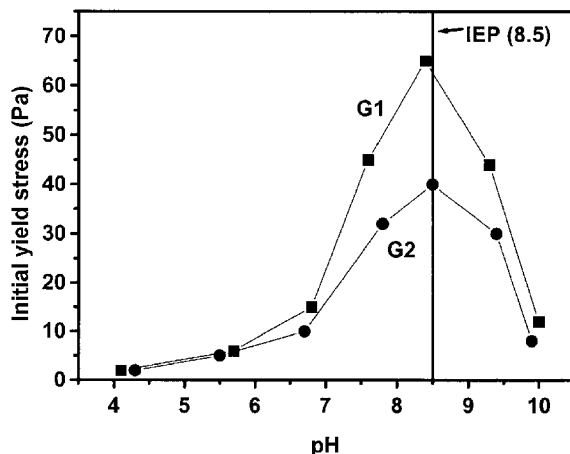
(Figure 1) as previously observed by Cerpa *et al.* (1999). Samples G1 and G2 present the same IEP value of 8.5. This value is similar to that of pure goethite reported by Parks (1965). On the other hand, samples GS and SG have IEP values of 6.1 and 4.8, respectively. The observed decrease in IEP, as the serpentine content increases, has been associated with the pronounced weathering of the lateritic soils (Luce *et al.*, 1972; Bales and Morgan, 1985; Tartaj *et al.*, 2000).

The effect of adding Na_2SiO_3 on the electrokinetic behavior of suspensions is illustrated in Figure 1. For each sample, a shift of the IEP to more acidic values was detected when compared to the suspensions prepared with only NaCl. This is due to the adsorption of silicate anions on the particle surfaces. In sample SG the IEP shifted to 3.6 whilst in sample GS the new IEP value was 4.9. Samples G1 and G2 showed similar shifts reaching an IEP value, in both cases, of 6.7. The fact that the more pronounced changes in mobility are detected in the more acidic pH region is not surprising. In this region, the particle surfaces are more positively charged and therefore adsorption of silicate anions is more likely to occur. This is also probably the reason why the more pronounced changes in mobility values are detected for the samples with the highest IEP (G1 and G2).

Specific adsorption of silicate anions in Fe oxides was reported by others authors (Hingston *et al.*, 1972; Sigg and Stumm, 1981; Barrow and Bowden, 1987; Bruun-Hansen *et al.*, 1994). The specific adsorption

Table 2. Chemical analyses (wt.%) performed by XRF for samples G1 and G2.

Sample	Fe_2O_3	SiO_2	Al_2O_3	NiO	Cr_2O_3	MnO	H_2O[1]	Total
G1	74.8	4.0	4.5	2.1	1.8	1.2	12	100.4
G2	73.9	3.5	4.9	1.9	1.9	1.1	12	99.2

[1] Water content determined by thermogravimetric analysis. The value comes from a contribution of the adsorbed water and the dehydroxylation of goethite.

depends on pH, ionic strength, and the number of surface sites available on samples (Bruun-Hansen *et al.*, 1994). In particular, Hingston *et al.* (1972) reported a similar shift of the IEP values in synthetic goethite samples to the ones detected here for samples G1 and G2.

It is noteworthy that significant adsorption of silicic acid ionic species is detected at pH values >IEP (*i.e.* where the particle surfaces are strongly negatively charged). In this region the decrease in the surface electric potential should decrease silicate adsorption. However, as suggested by Barrow and Bowden (1987), at basic pH values, the amount of monovalent silicic anions decreases in favor of divalent ones. Therefore, the decrease in the surface electric potential is compensated by an increase in the silicate adsorption strength (*i.e.* increase in divalent anions with respect to monovalent ones).

The adsorption of Mg ionic species after the addition of $MgCl_2$ promoted a shift of the mobility to more positive values (Figure 1), which was more significant for the pH range where particles are more negatively charged. For samples SG and GS, shifts of the IEP to 6.1 and 6.7 were registered, respectively. For samples G1 and G2, the adsorption of Mg ionic species generated the reverse of the surface charge from negative to positive values in the basic pH.

To illustrate the effect of addition of Na_2SiO_3 and $MgCl_2$ on the rheological behavior of suspensions, we have measured the initial yield-stress values as a function of pH and type of electrolyte for sample G1 (Figure 2). In essence, we observed the same features as displayed in the electrokinetic behavior curves (Figure 1). The maximum in initial yield-stress values are shifted to lower pH after adding Na_2SiO_3, and to higher pH after adding $MgCl_2$. Samples SG, GS and G2 showed analogous behavior.
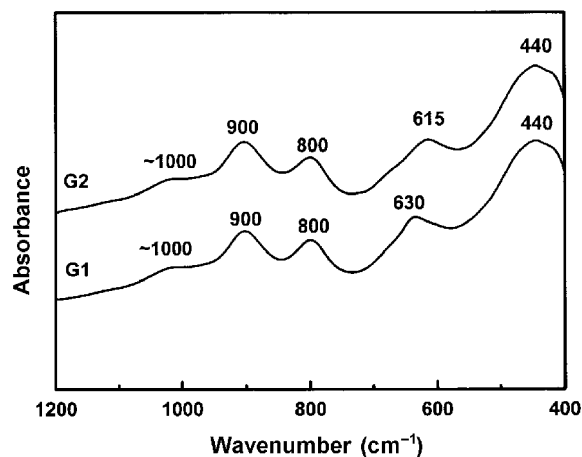
Flow behavior of suspensions containing G1 and G2 samples

It is interesting to compare the values of the initial yield-stress (Figure 3) for 10^{-2} M NaCl aqueous suspensions containing the samples G1 and G2 near the IEP (~8.5). At the IEP, only van der Waals attractive forces govern the interaction between the particles in the solution, which provides maximum values of initial yield-stress. Even though samples G1 and G2 are composed of goethite (Table 1), they had different initial yield-stress values. While sample G1 presents a value of 65 Pa, G2 gives a value of 40 Pa. A detailed crystallo-chemical characterization was performed to explain the difference.

The chemical composition of G1 and G2 was similar (Table 2). The samples were composed mainly of Fe oxide with minor amounts of SiO_2, Al_2O_3, MnO, Cr_2O_3 and NiO (Table 2). These constituents can be found within the goethite structure forming solid solutions (Cornell and Schwertmann, 1996). This result suggests that samples G1 and G2 were not only similar in mineralogy but also chemically equivalent. In agreement, the goethite cell parameter values and the IR spectra of both samples were similar (Table 3, Figure 4). The only significant difference in the IR spectra was the position of the vibration mode at ~625 cm^{-1}, which appeared at 630 cm^{-1} in sample G1 and at 615 cm^{-1} in sample G2. According to Cornell and Schwertmann (1996), as the axial ratio of the acicular goethite particles increases, a shift of this mode to higher frequencies is observed. Therefore, we can expect that the axial ratio of particles in sample G1 must be greater than that of the particles in sample G2.

The spectra also displayed a small intensity band at ~1000 cm^{-1}, the position of which is within the frequency range expected for Si in tetrahedral coordination (Moenke, 1974). This result is in agreement with the small amount of Si detected by XRF (Table 2). Its position, together with the absence of bands at 1100 and 1200 cm^{-1}, seem to suggest that this band is not associated with quartz (Wong *et al.*, 1986). This result is in agreement with XRD (Table 1), by which no quartz was detected for samples G1 and G2.

The TEM studies showed the presence of typical acicular crystals of goethite (Figure 5). Both samples had a very similar mean particle width (50±20 nm) but their particle length was different. In particular, for sample G1 the mean particle length was ~400±150 nm,

Figure 4. IR spectra for the G1 and G2 samples.

Table 3. Lattice parameters (nm) and unit-cell volumes, V (nm^3), for goethites (samples G1 and G2) from Cuba.

Sample	a	b	c	V
G1	0.4606 (2)	0.9943 (3)	0.3010 (2)	0.1379 (2)
G2	0.4603 (2)	0.9945 (4)	0.3009 (1)	0.1377 (2)

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