

EFFECTS OF IRON AND ALUMINIUM OXIDES ON THE COLLOIDAL AND SURFACE PROPERTIES OF KAOLIN

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Abstract—The association between clay silicates, and iron and aluminium oxides has a major influence on the chemical and physical properties of soils. In this work the interaction of a kaolin substrate with iron and aluminium oxides and/or hydroxides obtained by basification of solutions of the metal ions was compared to that of quartz. Both precipitates were obtained in the presence of the substrates.

The aluminium precipitates had higher crystallinity, and thus led to smaller increases in specific surface area than those of iron, and were more effective modifiers of the surface electrical properties of the kaolin-oxide mixtures. At concentrations as low as 0.43% Al (g/100 g of substrate) the point of zero charge (PZC) of the components with variable charge was measurable, while Fe required 2.23% and gave lower PZCs than those of corresponding concentrations of Al. In both cases the PZCs shifted to higher pH as metal concentration was increased, as did the flocculation interval of colloidal suspensions of kaolin, which were close to the PZCs (where these were evaluated).

The Al and Fe oxides precipitated on quartz had higher crystallinities. Both metals increased the specific surface area to a similar extent, with an almost linear relationship to metal concentration. Samples containing ca. 6.5% Fe or Al had similar or slightly higher PZCs than corresponding kaolin samples.

The results were interpreted by assuming, in the case of kaolin, the union of the metal precipitate with the basal faces of the substrate, so decreasing the negative charge at this surface; and in the case of quartz, the formation of a hydroxide coating that neutralizes the negative charge on the silica surface. The difference between the results obtained for each metal was attributed to the different morphologies of their oxide precipitates.

Key Words—Aluminium oxides, Colloidal stability, Iron oxides, Kaolinite, PZC.

INTRODUCTION

Knowledge of the interactions between clay silicates and iron and aluminium oxides is important for understanding the physical and chemical properties of soils, particularly the highly weathered soils of which they are the major components. Although most research has centred on the influence of these interactions on soil aggregation (Blackmore 1973, Arduino *et al* 1989, Colombo and Torrent 1991) and related physical properties, such as hydraulic conductivity, porosity, friability and the state of flocculation/dispersion (Deshpande *et al* 1968, El-Rayah and Rowell 1973, El-Swaify and Emerson 1975, El-Swaify 1976, Shanmuganathan and Oades 1982), they also have significant effects on ion adsorption and exchange (Chao *et al* 1964, Sakurai *et al* 1989).

The iron oxides present in the clay fraction of red soils have been reported to exist as small granular discrete particles having little effect on the soil physical properties (Greenland *et al* 1968, Deshpande *et al* 1968). Robert *et al* (1987) consider that it is crystalline iron oxides that are commonly found as discrete particles, while compounds of low crystallinity more commonly occur as small spheres on the surface of the clay silicates. Physical mixing of kaolinite and a crystalline oxide (e.g., goethite or haematite) in the laboratory barely produces association, while with a poorly crys-

talline oxide association is significant (Schahabi and Schwertmann 1970, Golden and Dixon 1985). Studies of laboratory synthesized complexes of ferrihydrite and kaolinite (Saleh and Jones 1984) have shown that at pH 3 the oxide apparently associates with the basal surfaces of the kaolinite crystals; that at pH 6 this association is less pronounced; and that at pH 9 the ferrihydrite and kaolinite do not associate. Nevertheless, associations formed at pH 3 have been shown to be stable up to ca. pH 10 (Yong and Ohtsubo 1987). The most likely interaction holding the two materials together is coulombic attraction between the positive charges of the oxide and the negative charges on the basal surfaces of the kaolinite (Follett 1965). Increasing the pH of the medium should only affect the charges on the oxide which are not neutralized by interaction with the kaolinite, which means the association remains intact. It seems that the most stable links are obtained when the oxide is precipitated in the presence of the clay surface, allowing contact between this latter and the initial hydrolysis products (Blackmore 1973); under these conditions chemisorption of the oxide may also be occurring.

As in the case of iron, several laboratory studies of the association of kaolinite with Al hydroxide or with hydroxy-Al-polymers, and of the modifications of the surface properties of the kaolinite produced by this

coating, have been described (Bundy and Murray 1973, El-Swaify and Emerson 1975, El-Swaify 1976, Goldberg and Glaubig 1987, Robert *et al* 1983, Oades 1984, Sakurai *et al* 1989).

Iron coatings on quartz grains are widespread in soils and sediments (Jones and Uehara 1973, Barral and Guitián 1991), but, as far as we know, natural Al hydroxide coatings on quartz have not been reported in the literature. In laboratory experiments, Follett (1965) has obtained stable complexes of iron colloids and quartz particles, and Scheidegger *et al* (1993) have coated silica sand (quartz and cristobalite) with haematite or goethite by mixing the sand with an aqueous suspension of the oxide and carefully adjusting the pH and ionic strength. In the latter work, the extent of the coating reaction increased with pH, but abruptly decreased at pH values above the PZC of goethite. This behaviour could be explained by a simply electrostatic model; however, on the basis of X-ray photoelectron spectroscopy, Scheidegger *et al* (1993) suggested that formation of Fe-O-Si bonds might also be responsible for the stability of the coating.

We have previously observed that the addition of synthetic oxides of iron and aluminium to kaolin substrates appreciably modified the particle size distribution of the latter, favouring their aggregation (Arias *et al* 1992a, 1992b and 1992c). Amorphous precipitates of Al were more effective aggregants than those of Fe, while crystalline Al hydroxide barely affected aggregation. It is noteworthy that, at the same time as the proportion of sand-sized aggregates increased with Al concentration, some redispersion of the clay occurred when the samples richest in Al were suspended in water. This has been attributed to charge inversion resulting from coating of the kaolinite by Al hydroxide. We observed no redispersion of the Fe samples within the range of concentrations studied.

In the present work the colloidal and surface properties (area and electrical charge) of kaolin associated with increasing amounts of Fe or Al hydroxides of differing crystallinities were examined. In order to promote formation of stable associations, the hydroxides were precipitated from Fe or Al solutions in the presence of the substrate. A quartz substrate was included for the purpose of comparison. Knowledge of the surface properties of these associations should shed light on the mechanisms of the kaolin-hydroxide interaction and the way Fe and Al hydroxides affect clay flocculation and dispersion.

MATERIALS

Substrates

Commercial grade kaolin supplied by E.C.E.S.A came from deposits in Burela (Lugo, Spain) produced by the weathering of volcanic rocks which had undergone hydrothermal autometamorphism. This kaolin has been

Table 1. Physico-chemical characteristics of A. the kaolin and B. the quartz substrate.

A	
Clay (% w/w)	61.6
Silt (% w/w)	38.1
Sand (% w/w)	0.3
pH (H ₂ O)	5.5
pH (KCl)	4.2
S _{EGME} (m ² g ⁻¹)	46.7
C.E.C.* (cmol ₍₊₎ kg ⁻¹)	7.0
Exchangeable Na (cmol ₍₊₎ kg ⁻¹)	0.13
Exchangeable K (cmol ₍₊₎ kg ⁻¹)	0.04
Exchangeable Mg (cmol ₍₊₎ kg ⁻¹)	0.09
Exchangeable Ca (cmol ₍₊₎ kg ⁻¹)	0.06
B	
Clay (% w/w)	9.0
Silt (% w/w)	72.6
Sand (% w/w)	18.4
pH (H ₂ O)	5.6
pH (KCl)	4.5
S _{EGME} (m ² g ⁻¹)	3.1

* Ammonium acetate (pH 7).

studied in detail by Galán and Martín (1975) and by Conde-Pumpido (1986), among others. It is 95% (w/w) kaolinite of high Hincley index (1.28) and 5% (w/w) micas. For the purpose of comparison we carried out some experiments with a ground sample of quartz material from a dike at Pico Sacro (La Coruña, Spain). In both cases the <100 µm particle size fraction was used. The most important physico-chemical characteristics of these substrates are given in Table 1.

Oxides

Non-aged precipitates. The iron precipitates (kFe_n on kaolinite, qFe_n on quartz) were obtained as follows: 0 (blank), 10, 25, 50, 100 or 150 ml of a 0.4 M solution of Fe(NO₃)₃ were added to 50 g of substrate and made up to 200 ml with distilled water. Each suspension was agitated intermittently for 30 min to encourage contact between the kaolin and the initial products of the Fe and Al hydrolysis, and then 30% ammonia solution was added until the pH of the suspension reached 7.5. The solids were separated and washed with distilled water until the washings showed a negative response to Nessler's reagent. The aluminium precipitates (kAl_n on kaolinite, qAl_n on quartz) were prepared from 0.8 M AlCl₃ and 0.5 M NaOH solutions by the same procedure, but using the AgNO₃ test in the washing stage. Finally, both groups of samples were oven-dried at 40°C. The proportions used are roughly equivalent to the addition of 0.5, 1.0, 2.0, 4.5 and 6.5 g of Fe or Al per 100 g of substrate.

Aged precipitates (kAl_a, qAl_a, kFe_a, qFe_a). The procedures used were identical to those for non-aged precipitates, except that following washing the samples were suspended in 500 ml of water and maintained at 70°C for 17 days before oven-drying at 40°C.

Table 2. Crystallinities of aged and non-aged iron hydroxide precipitated in the presence of kaolin or quartz substrates (see text), as indicated by the ratio of Fe extracted by oxalic acid-ammonium oxalate (Fe_o) to Fe extracted by dithionite-citrate-bicarbonate (Fe_d). Values of Fe_o/Fe_d close to 1 indicate low crystallinity.

Fe*	Days of aging	Fe_o/Fe_d	
		Quartz	Kaolin
0.45	0	0.97	0.96
	17	0.86	1
1.12	0	1	0.96
	17	0.75	0.96
2.23	0	0.93	0.86
	17	0.73	0.86
4.45	0	1	1
	17	0.69	1
6.68	0	0.95	0.96
	17	0.58	0.94

* g/100 g substrate.

METHODS

Crystallinity and mineralogy of the precipitates

The degree of crystallinity and mineral composition of the precipitates were studied by X-ray diffraction and selective dissolution. The differential solubilities of the iron precipitates in oxalic acid-ammonium oxalate (Fe_o) and dithionite-citrate-bicarbonate (Fe_d) (Schwertmann 1964, Mehra and Jackson 1960) allowed evaluation of sample crystallinities from their ratio (Fe_o/Fe_d), which lies close to 1 for amorphous materials and falls as crystallinity increases. The crystallinities of the Al-precipitates were similarly deduced from their solubilities in oxalic acid-ammonium oxalate (Al_o) (considered to dissolve only amorphous Al) compared to 0.5 M NaOH (Al_s) (capable of dissolving all Al outside the network of crystalline silicates) (Borggaard 1985).

Specific surface area

This was measured by the ethylene glycol monoethyl ether (EGME) adsorption method (Heilman *et al* 1965).

Point of zero charge (PZC)

The procedure followed was based on the method proposed by Sakurai *et al* (1988), which can be considered a potentiometric titration at a very low salt concentration. The sample (0.2 g) was added to calculated volumes of distilled water which were then made up to 20 ml with the required amount of HCl or NaOH to give the desired range of pHs (from 3 to 9). These mixtures were equilibrated for 48 h, following which their pHs were measured (pH_1). Next, 0.5 ml of 2 N NaCl was added to each of the samples, which were then stirred for 3 h before their pHs were measured a second time (pH_2). Water and 0.0488 N NaCl

blanks were also titrated, and the amount of H^+ or OH^- ion adsorbed by the samples at each pH was calculated. By plotting the amount of ion adsorbed against pH_1 and pH_2 , two titration curves are obtained whose cross-over point is taken as the PZC, the pH at which the adsorption of H^+ or OH^- ions by the components with variable charge is at equilibrium and the net charge is zero. The net adsorption capacity for H^+ or OH^- ions at the PZC (σ_p) allows estimation of the permanent charge of the system (which will have the opposite sign to σ_p). Measurements were reproducible to within ± 0.1 pH units for PZC and ± 0.2 $cmol\ kg^{-1}$ for σ_p .

Colloidal stability

The procedure followed was similar to that of El-Swaify (1976). The sample (0.2 g) was suspended in 38 ml of distilled water in a 50 ml beaker and the pH was adjusted to a value between 2 and 12 by addition of HCl or NaOH. The volume was made up to 40 ml, and the sample was sonicated for 20 s and then left to stand for 2 h. At the end of this period the upper 2.5 cm of the suspension were syphoned off and the pH of the remaining solution was immediately measured. The separated samples were placed in cuvettes and their absorbance at 615 nm was measured. Deionized water was used as 0 absorbance blank. Readings are reported in absorbance units on a scale from -2 to $+4$.

RESULTS

Characteristics of the precipitates

The observed Fe_o/Fe_d ratios (Table 2) show that only amorphous Fe-precipitates were obtained with the kaolinite substrate, even after aging. However, in the case of quartz, the aged oxides had increased crystallinity, particularly for the samples with high iron concentration, whose X-ray diffraction diagrams, in keeping with their red colour (hue 2.5 YR), showed low-intensity reflections at 2.69 and 2.51 Å suggesting the presence of haematite.

The Al-precipitates rapidly developed high crystallinity in both aged and non-aged samples as was deduced from their low Al_o/Al_s ratios (Table 3). X-ray diffraction of aged samples containing high levels of Al indicated the presence of gibbsite.

Specific surface area S

The specific surface area of the kaolinite blanks ranged between 54 and 58 m^2g^{-1} . In the case of the non-aged Al-precipitates on kaolin (kAl_n), the value of S increased almost linearly with addition of Al. However, the aged samples (kAl_a) showed irregular behaviour, with a value of S lower than that of the blank for 0.43% Al, a subsequent linear increase as Al concentration increased to 4.32%, and a final drop with 6.48% Al. For the Fe-kaolinite systems (kFe_n and kFe_a), the spe-

cific surface areas were always greater than for corresponding concentrations of Al. Like their crystallinity, the values of *S* of Fe-precipitates was only slightly affected by aging.

As expected, the quartz, comprising predominantly silt-sized grains with no internal surfaces, had a very small value of *S* ($3 \text{ m}^2\text{g}^{-1}$). The non-aged quartz-Al mixtures (qAl_n) showed an almost linear relationship between *S* and the concentration of Al hydroxide. The surface area of the more crystalline aged samples (qAl_a) was smaller than that of the corresponding non-aged samples and increased non-linearly with Al, tending to level off at Al concentrations greater than 2.16%. The values of *S* for the non-aged Fe-precipitates on quartz (qFe_n) were similar to those for qAl_n , as were those for the aged samples (qFe_a) up to 2.23% Fe, beyond which concentration the increasing crystallinity of these samples becomes significant and leads to smaller increases in *S* on addition of Fe.

PZC

The titration curves for the kaolinite substrate in the absence of Al or Fe had very steep gradients below ca. pH 4.5, possibly due to a high capacity for H^+ adsorption at permanently negatively charged sites or at sites with variable charge which, as a result of adsorption of this ion, bear a positive charge. Dissolution of the kaolinite may also contribute to this consumption of H^+ , as is suggested by both the steep gradients observed and the fact that the titration curves coincided below pH 4. The long contact time in the method of PZC determination probably facilitated dissolution. Above a pH of approximately 4.5 the titration curves level off, reflecting a reduced capacity for ion adsorption at sites of variable charge. The curves for pH₁ and pH₂ lie very close to each other up to approximately pH 6.5, at which point they diverge, with a greater net adsorption of OH^- ions in NaCl solution. The point of divergence may correspond to the PZC of the sites of variable charge along the edges of the kaolinite particles, which according to viscosity measurements should lie between pHs 5.8 and 7.3 (Rand and Melton 1977).

In the presence of Al hydroxide, the slopes of the titration curves increase in the basic region, reflecting increased adsorption of OH^- ions. Below about pH 4.5 the curves are also steep and tend to converge, which is attributed to dissolution of the Al hydroxide: determination of Al in equilibrated solutions of kAl_a samples (4.32% Al) at pH 4.4 showed that $1.8 \text{ mmol liter}^{-1}$ Al were present in solution. Above 0.43% Al, the two curves show a point of intersection enabling estimation of the PZC, which shifts towards higher pHs as the concentration of Al is increased. This shift is pronounced and almost linear with respect to Al concentration up to 2.16% (Figures 1 and 2), at which point it begins to level off, suggesting that some saturation

Table 3. Crystallinities of aged and non-aged aluminium hydroxide precipitated in the presence of kaolin or quartz substrates (see text), as indicated by the ratio of Al extracted by oxalic acid-oxalate (Al_o) to Al extracted by 0.5 M NaOH (Al_e). Values of Al_o/Al_e close to 1 indicate low crystallinity.

Al*	Days of aging	Al_o/Al_e	
		Quartz	Kaolin
0.43	0	0.74	0.82
	17	0.23	0.52
1.08	0	0.47	0.65
	17	0.35	0.39
2.16	0	0.65	0.60
	17	0.30	0.34
4.32	0	0.99	0.83
	17	0.26	0.27
6.48	0	0.91	0.97
	17	0.27	0.31

* g/100 g substrate.

limit is being approached. The maximum observed PZC was 7.5, for 6.48% Al. There are no notable differences between the PZCs of samples containing aged and non-aged precipitates, in spite of their different crystallinities. The value of σ_p (Table 5) was also modified by the addition of Al hydroxide: between 0.43 and 6.48% Al it ranged from +2 to -31 cmol kg^{-1} for kAl_n and from +3 to -32.2 cmol kg^{-1} for kAl_a .

In the *kFe* samples the two potentiometric curves only intersect cleanly above 2.23% Fe (Figure 3). The PZC increases with Fe concentration, but is generally lower than for corresponding *kAl* samples. Between

Table 4. Specific surface area (*S*) of A. aged (17 days at 70°C) and non-aged aluminium hydroxide (Al_a and Al_n , respectively), and B. aged (17 days at 70°C) and non-aged iron hydroxide (Fe_a and Fe_n , respectively) precipitated in the presence of quartz (q) or kaolin (k) substrates (see text).

Al*	<i>S</i> ($\text{m}^2 \text{g}^{-1}$)			
	kAl_n	kAl_a	qAl_n	qAl_a
0	54	58	3	3
0.43	60	49	12	3
1.08	64	65	19	10
2.16	69	73	29	23
4.32	90	96	52	29
6.48	110	89	66	32

Fe*	<i>S</i> ($\text{m}^2 \text{g}^{-1}$)			
	kFe_n	kFe_a	qFe_n	qFe_a
0	58	58	3	3
0.45	70	nd**	5	8
1.12	77	nd**	14	16
2.23	93	91	29	24
4.45	119	121	50	28
6.68	138	141	71	51

* g/100 g substrate. ** not determined.

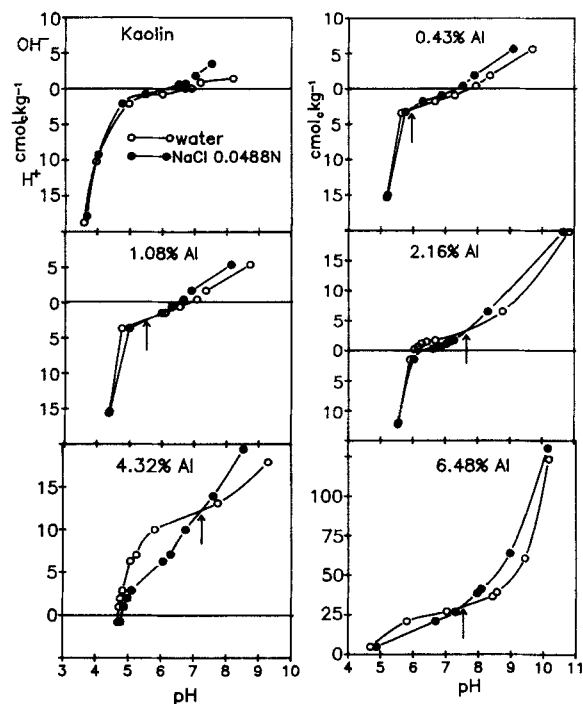


Figure 1. Net adsorption of H^+ or OH^- ions by non-aged kaolinite and kAl_n samples (see text) in water (○) or 0.0488 N NaCl solution (●) at various pH values. Arrows show PZCs, where identifiable.

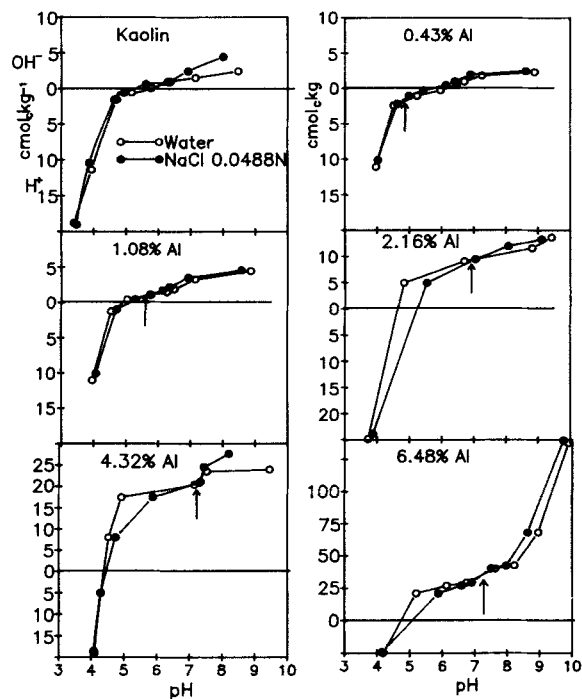


Figure 2. Net adsorption of H^+ or OH^- ions by aged kaolinite and kAl_n samples (see text) in water (○) or 0.0488 N NaCl solution (●) at various pH values. Arrows show PZCs, where identifiable.

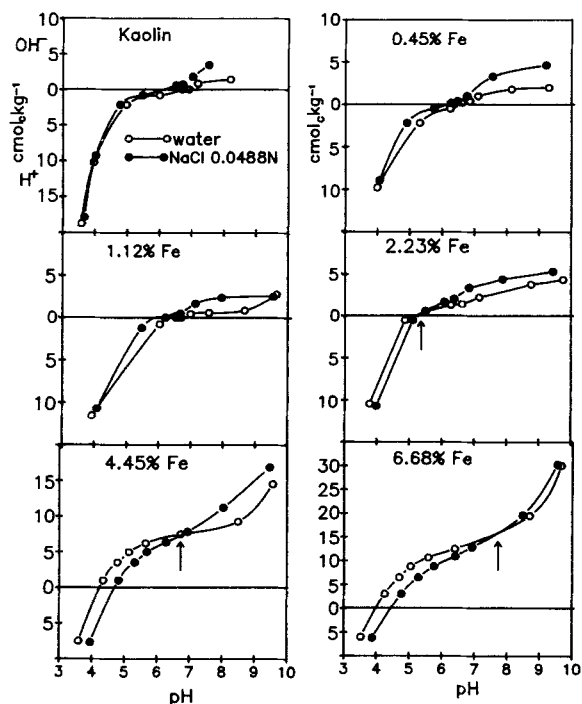


Figure 3. Net adsorption of H^+ or OH^- ions by non-aged kaolinite and kFe_n samples (see text) in water (○) or 0.0485 N NaCl solution (●) at various pH values. Arrows show PZCs, where identifiable.

2.0 and 6.5% Fe, the value of σ_p fell from -0.5 to -16.5 $cmol\ kg^{-1}$.

In the studies with a quartz substrate the PZC and σ_p were only evaluated for the samples with greatest Fe or Al concentration (Figure 4). These values and those obtained with kaolin at the corresponding metal concentrations were very similar, suggesting that the electrical characteristics of the mixtures are determined by the precipitate at high metal concentration, possibly because it coats the entire surface of the substrates and, in the case of quartz, because of the small number of charged sites on the substrate surface. As with kAl , the titration curves for qAl mixtures steepen and converge or coincide below pH 4.5 which is again due to dissolution of the Al hydroxide ($1.1\ mmol\ liter^{-1}$ Al were

Table 5. σ_p of aged and non-aged aluminium hydroxide (Al_n and Al_n , respectively) and non-aged iron oxide (Fe_n) precipitated in the presence of kaolin (k).

Al or Fe*	$\sigma_p (cmol\ kg^{-1})$		
	k Al_n	k Al_n	k Fe_n
0.5	+3.0	+2.0	—
1.0	+1.8	-1.0	—
2.0	-4.0	-9.5	-0.5
4.5	-12.5	-22.0	-7.5
6.5	-31.0	-32.2	-16.5

* Approximate concentrations of metal (g/100 g substrate).

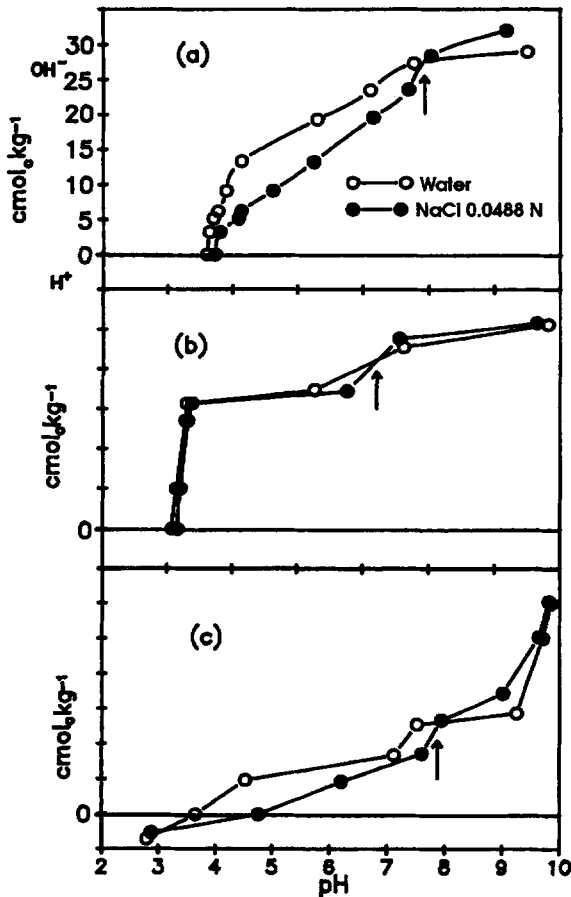


Figure 4. Net adsorption of H⁺ or OH⁻ ions by (a) 6.48% Al precipitated on quartz non-aged, (b) 6.48% Al precipitated on quartz aged and (c) 6.68% Fe precipitated on quartz, non-aged (see text) in water (O) or 0.0488 N NaCl solution (●) at various pH values. Arrows show PZCs, where identifiable.

measured in the qAl_n suspension equilibrated at pH 4.2).

Colloidal stability

Figure 5 shows the absorbance of kAl and kFe suspensions at 615 nm as a function of pH. High absorbance is indicative of high stability, and vice versa. For both metals the flocculation intervals contained the PZCs of the samples for which PZC had been evaluated, and generally broadened and shifted to higher pH as the metal concentration was increased.

On the basic side of the flocculation interval of kAl_n mixtures (Figure 5a) redispersion always occurred, while for kAl_s (Figure 5b), beyond a certain Al hydroxide concentration (somewhere between 2.16 and 4.32%), it did not. For the kFe mixtures (Figure 5c), the flocculation interval was at slightly more acidic pH than that of the kAl mixtures and, although redispersion occurred at alkaline pHs, samples also appeared to flocculate below pH 3.

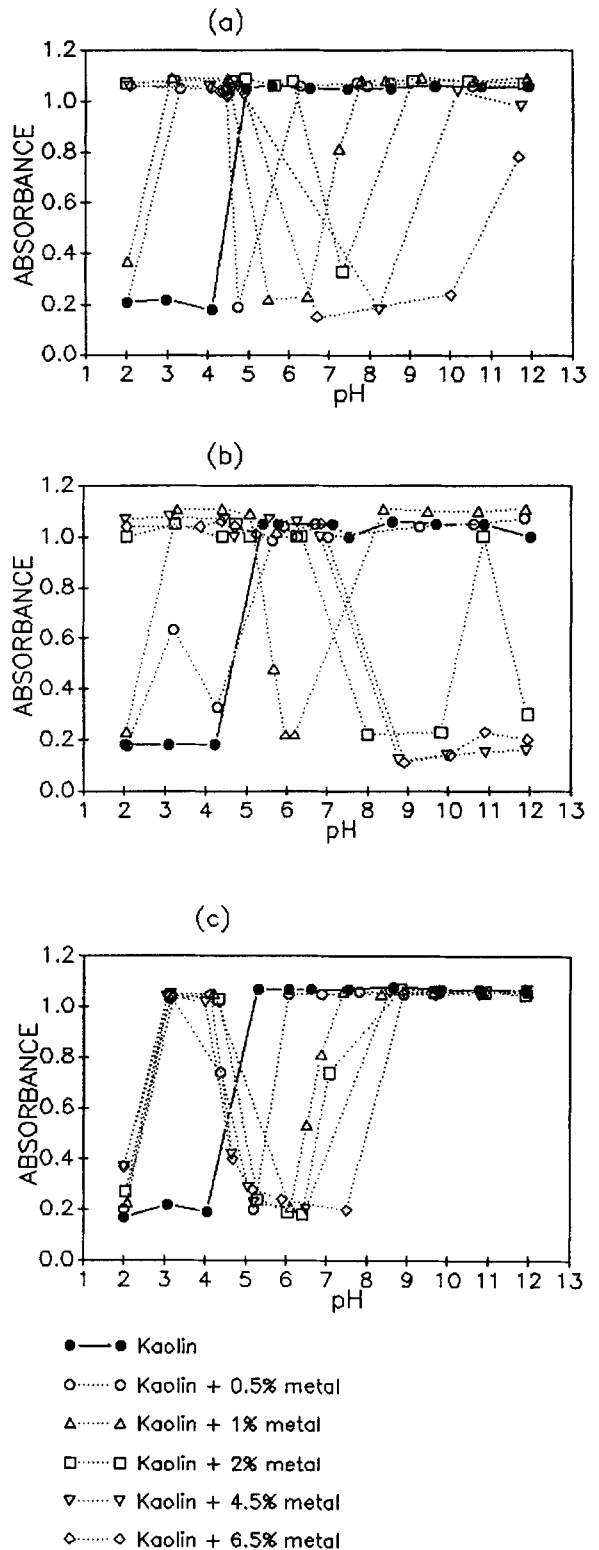


Figure 5. Absorbance at 615 nm as a measure of colloidal stability between pHs 2 and 12 of (a) kAl_n samples; (b) kAl_s samples; (c) kFe_n samples (see text).

Table 6. Al and Si in dithionite-citrate-bicarbonate extracts (Al_d and Si_d , respectively).

Sample	Si_d ($mg\ kg^{-1}$ substrate)	Al_d	Si:Fe*	Al:Fe*	Si:Al*
Kaolin untreated	550	3390	—	—	—
KFe_n (6.68% Fe)	480	3310	0.015	0.109	—
KFe_a (6.68% Fe)	570	3510	0.018	0.115	—
KAl_n (6.48% Al)	250	—	—	—	0.004
KAl_a (6.48% Al)	250	—	—	—	0.004

* Atomic ratios.

DISCUSSION

The rapid formation of an ordered structure by Al-precipitates, even in the presence of kaolin, which has been observed previously by other workers (Hsu and Bates 1964, Hsu 1966, Hsu 1989), contrasts with the low crystallinity, even after aging, of the Fe precipitates. Other researchers (Greenland and Oades 1968, El-Swaify and Emerson 1975, and Sakurai *et al* 1990) have also remarked on the low crystallinity of Fe precipitated in the presence of clays.

One possible explanation for the low crystallinity of the Fe-precipitates in this work is that Al and Si were released from the kaolin—particularly during the period prior to oxide precipitation, when it was exposed to acidic solutions—and were subsequently adsorbed onto the oxide. Dissolved Si and Al have previously been observed to inhibit or retard iron oxide crystallization (Schwertmann and Thalmann 1976, Schwertmann 1988), while, according to the results of Wada and Kubo (1975), Al oxides precipitated in the presence of Si show a greater propensity to crystallize. Determination of the Al and Si in dithionite-citrate-bicarbonate extracts (Al_d and Si_d , respectively) of both Fe- and Al-rich samples revealed the levels of these to be similar or even lower than for untreated kaolin (Table 6). Thus exposure to the acidic solutions of Fe and Al did not cause appreciable dissolution of the kaolin and, moreover, the Si_d and Al_d values for the kaolin-oxide samples may well include a contribution due to Si and Al derived from the kaolin itself. If we assume, however, that Al_d and Si_d derive only from the oxide precipitate, the ratios of Si to Fe atoms in the aged and non-aged Fe-precipitates are 0.015 and 0.018, respectively, and thus approach the value of 0.02, which is the minimum ratio for which Anderson and Benjamin (1985) observed inhibition of iron oxide crystallization. The corresponding Al/Fe ratios for KFe_n and KFe_a were 0.109 and 0.115, respectively; the values reported by Schwertmann *et al* (1979) to inhibit Fe oxide crystallization were all >0.2 .

An alternative explanation is that adsorption of the precipitate on the silicate surface affects its transformation into more crystalline oxides. This would explain how the quartz limits the crystallinity of Fe oxides

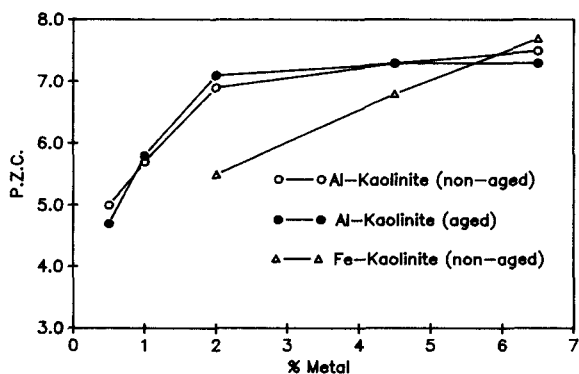


Figure 6. PZC as a function of the amount of metal (g/100 g of substrate) in suspensions of non-aged Al hydroxide with kaolinite (○—○), aged Al hydroxide with kaolinite (●—●), and non-aged Fe hydroxide with kaolinite ---- (see text).

to a lesser extent than kaolinite, which has a more reactive surface, but does not account for the smaller effects observed with Al. Here, the important factor may be that both hydroxy-Al polymers and gibbsite have planar structures so that adsorption of the former onto kaolinite does not create significant steric impediments to its transformation into the latter.

The results of the specific surface area studies (Table 4) suggest that Fe- and Al-precipitates interact with quartz through similar mechanisms, since in both cases S increased almost linearly with metal concentration and at similar rates. On kaolinite, however, the specific area of Fe-precipitates increased much faster with metal concentration than that of Al precipitates. This confirms previous studies, in some of which S remained constant, or even fell, upon addition of Al (Rengasamy and Oades 1977, Oades 1984, Sakurai *et al* 1989). The Fe hydroxides in these studies were observed as discrete particles on the surface of the kaolinite; deposition of such particles would allow surface area to increase independently of the underlying mineral. Al-polyocations (Oades 1984) and Al hydroxide (Sakurai *et al* 1989), on the other hand, are thought to be adsorbed directly onto the kaolinite in chains or layers, so producing little net increase in surface area.

The oxides (in the widest possible sense) of Fe and Al are substances of variable charge. The reported PZC of synthetic iron oxides ranges from 7 to 9 (Parks 1965, Schwertmann and Taylor 1989), while that of gibbsite is 9.8 (Kavanagh *et al* 1975). Thus these compounds possess a net positive charge at normal soil pH. Kaolinite particles exhibit variable charges along their edges and a small permanent negative charge on the basal faces (according to the results of Weiss and Russov 1963, mainly those corresponding to the tetrahedral layer; see also Follett 1965). The PZC of kaolinite particles lies between 2.8 and 4.8 (Tschapek *et al* 1974), so that at higher pHs a small net negative

charge is exhibited. However, along the edges of the particle positive charges still predominate until the slightly higher PZC of the edge sites is reached. Hence we would expect Fe and Al oxides to adsorb only at the basal faces, principally those showing the tetrahedral Si-O layer (Follett 1965). This type of association has been observed by many authors (Robert *et al* 1987, Yong and Ohtsubo 1987, Saleh and Jones 1984), and produces, amongst other effects, a reduction in the number of negative charges on the kaolinite (Greenland 1975). In our own experiments, addition of Fe or Al hydroxide clearly changed the surface electrical properties of the samples: above 0.43% Al and 2.23% Fe the behaviour of these samples is dominated by the variable charge nature of the oxides, giving rise to a clear PZC at a pH that increased with metal concentration.

The PZCs of kAl were generally higher than those of kFe, changing markedly upon the addition of only small quantities of Al (as did σ_p) at levels below 2.16% Al (above which the effects began to diminish), while for kFe the PZC was only identifiable above this concentration threshold (Figure 6). These observations suggest that Al hydroxide is a more effective modifier of the surface electrical properties of kaolinite than Fe: Oades (1984) has suggested that Al-polycations neutralize the negative charges of clays better than those of Fe, which he ascribed to the higher charge and planar morphology of the Al-polycations. Iron hydroxide particles, although capable of reducing the net negative charge of the clay, seem limited in their capacity to block its negatively charged sites. Electron microscopy of ferrihydrite (Fh) adsorbed onto the faces of kaolinite has shown it to be non-uniformly distributed (Jones and Saleh 1987). At concentrations of 1–2% Fh it formed small disperse aggregates, presumably adsorbing to negatively charged sites, which coalesced as concentration was increased until, at 8% Fh or more, an apparently continuous layer was formed. For this reason it has been considered incorrect to apply the term “coating” to the actually discontinuous layer of Fe oxide that is frequently observed in amorphous Fe oxide-kaolinite associations (Robert *et al* 1987).

In those samples for which the PZC was identifiable, the value of σ_p was slightly more negative in Al samples, and for both Al and Fe varied almost linearly with metal concentration. The reduction in the positive value of σ_p upon first addition of metal may be attributed simply to the masking of the negative charges on the basal faces of the kaolinite by metal hydroxide. Its subsequent shifting towards negative values may be due to the formation of OH-deficient non-stoichiometric precipitates carrying a net positive charge. Negative values of σ_p have been reported previously for hydroxide-coated kaolinite, but no explanation was given for this behaviour (Sakurai *et al* 1990). Permanent positive charges (negative σ_p) have also been re-

ported in natural soil samples rich in goethite and gibbsite (Gillman and Uehara 1980), and in the B2 horizon of an Acrohumox (van Raij and Peech 1972). In naturally occurring oxides this charge is usually attributed to replacement of Fe³⁺ or Al³⁺ by tetravalent ions such as titanium, which cannot be the case in our synthetic systems.

The changes in the surface electrical properties of the kaolinite-hydroxide mixtures were, as expected, accompanied by changes in the stability of their colloidal suspensions, which is also influenced both by the pH, the ionic strength and ionic composition of the medium. Thus pure kaolin flocculates at pHs below 5, which is attributed to face-edge association between the kaolin particles (Schofield and Samson 1954). Addition of Fe or Al prevented flocculation at pH between ca. 2 and 6, doubtless by increasing the overall positive charge on all surfaces of the kaolinite. Flocculation at pH 2, which was more evident in kFe samples, can be attributed to double layer compression due to the high concentration of the HCl electrolyte (El-Swaify 1976, Gregory 1989). Similar behaviour was not observed at alkaline pH, probably because the NaOH electrolyte has a dispersive effect due to the large hydrated radius of the sodium ion. Colloidal stability of all the samples was low in a pH interval of variable width around the PZC, which may be attributed to minimal coulombic repulsion between the hydroxide-coated kaolinite particles. Redispersion at higher pHs was no doubt due to repulsion between the increasingly negatively charged particles. As reported previously for gibbsite (El-Swaify 1976), no redispersion occurred above the PZC in Al-rich aged samples, in which this mineral was identified.

Since our samples were dried, the question arises whether the stability experiments might not have been affected by the presence of cemented aggregates, rather than reflecting only the charge properties of the suspended particles. However, our results are similar to those obtained by El-Swaify (1976) with mixtures of Al- or Fe-hydroxides and kaolinite which, in order to prevent cementation, were not dried prior to stability measurements. This similarity suggests that any cementation that may have occurred when our samples were dried did not affect the colloidal stability results, either because the sedimentation of aggregates removed them from the suspension layer that was syphoned off for absorbance measurements, or because the ultrasound treatment successfully dispersed any cemented aggregates into single particles or aggregates small enough to behave as such.

The variation of colloidal stability with pH and the concentration and nature of the oxide in this work corroborates El-Swaify's (1976) conclusion that Al- and Fe-oxides may behave as either flocculants or dispersants of soil particles, depending on the above variables and the type of clay with which they interact. Robert *et al* (1983) have stated that only Al and Fe forms with

low degrees of polymerization generally behave as flocculants, while the polymerized forms have no effect or favour dispersion (especially in the case of Al); and have suggested that this might explain the migration of clays from planosols or washed and degraded soils (due to the presence of Al) and from washed fersialitic soils (due to the presence of Fe).

In previous experiments, which examined the particle size distribution of these samples (Arias *et al* 1992b), we found that in small quantities Al had a flocculant effect on kaolinite, but at $\geq 4.32\%$ Al some redispersion of the clay in water occurred; while Fe oxides caused flocculation of the clay in water with no redispersion occurring in the range studied (up to 6.68% Fe). This behaviour is in keeping with the results of the present work: the pH of the aqueous kaolinite/metal hydroxide suspensions in the previous work (ca. 5) is less than the PZC found in this work (so that the net variable charge of the particles was positive at that pH), and lies in an interval in which Figures 5a and 5b show dispersion of the kAl suspensions while Figure 5c shows flocculation of the kFe suspensions. The explanation for this differing behaviour may again be that, unlike the Al-precipitates, the Fe-precipitates formed a discontinuous coat on the surface of the kaolinite particles, thus allowing exposed negative charges on the basal faces to interact with positive charges on the edges or oxide coating of other particles.

In the work reported here, the effects of Al- and Fe-oxides on the colloidal stability of the clay seemed to be independent of the formation of stable aggregates in water, which always increased in percentage (w/w) as metal concentration was increased. Thus although flocculation of the colloid favours aggregation, the two phenomena do not necessarily go together; other processes, such as chemisorption and additive interactions such as Van der Waals forces (thought to be important in cementation) are also active in the formation of stable links between the particles.

CONCLUSIONS

Fe-precipitates obtained in the presence of kaolin are of low crystallinity, even after aging. Al-precipitates formed under the same conditions rapidly develop high degrees of crystallinity.

The specific surface area of Fe-kaolinite mixtures increases more rapidly upon addition of metal than that of Al-kaolinite mixtures, and in all cases falls as the crystallinity of the precipitate increases. In quartz mixtures, specific surface area depends linearly on metal concentration, with little observable difference between the Fe and Al systems.

The surface electrical properties of Fe and Al oxide-kaolin mixtures markedly differ from those of pure kaolin. Above 0.43% Al and 2.23% Fe, the point of zero charge (PZC) of the species with variable charge

can be determined; as metal concentration increases, it shifts to higher pH, reaching values above 7. The PZC is generally higher for samples containing Al than for the same concentration of Fe. The residual charge at the PZC varies in magnitude and sign with metal concentration, taking a negative value in the samples richest in metal (-31 cmol kg^{-1} for $k\text{Al}_n$, -32.2 for $k\text{Al}_a$ and -16.5 for $k\text{Fe}_n$), which thus bear a net positive charge.

The colloidal stability of aqueous suspensions of the kaolin samples is affected by the changes in surface electrical properties. The metal-kaolin mixtures exhibit low colloidal stability in a pH region of variable width which contains the PZC and, like the PZC, shifts to higher pH as metal concentration is increased. Both Fe and amorphous Al sample show ampholytic behaviour, remaining disperse on the low and high pH sides of the region of low colloidal stability, while, above ca. 2.5% Al, those with crystalline Al do not redispense on the basic side.

As pointed out by other authors, these phenomena suggest marked differences between the interactions of Fe and Al with kaolinite. These differences probably arise from morphological differences between the precipitates. The Al hydroxide has a greater capacity for intimate coating, resulting in smaller increases in surface area and more effective masking of the negative charges of the kaolinite. This results in a higher PZC, and flocculation at more basic pHs, than in samples containing Fe hydroxide.

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