

SURFACE CHARACTERISTICS OF KAOLINITIC CLAYS AND CLAY–HUMIC ACID COMPLEXES BY POTENTIOMETRIC AND CONDUCTOMETRIC TITRATIONS

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Abstract—Acid and non-acid forms of kaolinite clays were found by potentiometric and conductometric titrations to possess a weak acid species, the concentration of which was increased by acidic preparation conditions and by the presence of soil organic matter bound to the clay. A stronger acid species was also found in untreated and in organic-free, HCl-treated samples (washed free of excess acid). The end points for organic-free and/or ion-exchanged samples were used to predict the end points for untreated samples. A surface-chemical model involving MOH_2^+ , MOH , and MO^- species (where $\text{M} = \text{Al}$ and/or Fe) was fitted to the titration data and to the cation-exchange capacities. MOH_2^+ is the stronger acid and MOH the weaker acid; exchange of Na^+ counterions by H^+ converts $\text{MO}^- \text{Na}^+$ sites to MOH sites. Humic acid was probably complexed or chelated to some hydroxylated Al/Fe sites through COOH and phenolic OH groups. The COOH groups contributed supplementary stronger acid species which were not exchangeable, whereas the OH groups contributed supplementary weaker acid species and also increased the CEC relative to that for organic-free samples.

Key Words—Conductometric titration, Humic acid, Kaolinite, Potentiometric titration, Surface properties.

INTRODUCTION

Clay dispersions are common by-products of the processing of many ores. Coal washing, phosphate rock processing, diamond mining, tar sands extraction, and sand washing are examples of industrial operations that produce large quantities of aqueous clay rejects. Such suspensions settle slowly and only to a limited extent under gravity, giving rise to liquid sediments that are difficult to dewater and consolidate. The settling process itself and further compaction and dewatering depend on interactions between clay particles and between clay particles and water molecules. These reactions in turn depend on the surface and colloidal properties of the particles in suspension. In the aqueous clay rejects from one sand-washing operation near Melbourne, Australia, the clay particles appear to be complexed with soil humic acid, and the settled sediment (18% solids) exhibits a pH of 2–4. Such a system lends itself to investigation by potentiometric and/or conductometric titration to characterize the particle surfaces and to understand the dispersion/flocculation mechanisms of the system.

Past interpretations of potentiometric and conductometric titrations of clay suspensions have been highly controversial (see Marshall, 1964), so much so, that many investigators have avoided using these techniques altogether. Most of the earlier work was carried out on nonkaolinitic clays, whereas the clay in the sand-washing rejects noted above is kaolinite. Furthermore, current knowledge of clay–humic acid interactions (Schnitzer and Khan, 1972; Greenland and Hayes, 1978; Theng, 1979) has been developed mainly with

nonkaolinitic clays, primarily montmorillonite. Past titration studies have also, unfortunately, been concerned almost exclusively with 'acid' clays (i.e., the exchange cations were nominally hydrogen ions), because 'acid' clays are the only 'natural' candidates for reaction with alkali.

This paper presents data on the potentiometric and conductometric titration of the hydrogen and sodium forms of kaolinitic clay rejects with and without organic matter complexed to the clay. The results are compared with those obtained on a reference kaolinite to test the generality of the interpretations.

SAMPLE PREPARATION

Source

The starting material was the 'reject' clay dispersion from the sand-washing plant of Monier Sands at Clayton, Victoria, Australia. Two batches derived from different parts of the deposits were provided by G. J. Sparrow of the CSIRO Division of Mineral Chemistry. More than 80% of the particles in both batches were $<1 \mu\text{m}$ in size, kaolinite being by far the dominant mineral, with minor amounts of quartz (nearly all $>10 \mu\text{m}$), and traces of mica, gibbsite, and pyrite (Sparrow, 1978). The dispersions were dark brown due to organic matter carried over from the original sand.

Physical and chemical tests

Centrifuging and redispersing the settled suspensions several times with distilled or deionized water, or dialysis in cellophane membrane tubing, both of which extract excess electrolyte, did not remove the acidity,

nor did they alter the color or the state of coagulation of the clay. The solvents ethanol, acetone, and ether also failed to extract organic material. Optical and scanning electron microscopy showed no significant chemical differences among individual particles. Thus, the organic matter appears to be bound chemically to the clay, rather than being physically mixed with it. The dry clays gave exothermic differential thermal analysis (DTA) peaks and showed weight losses on heating in air to 400°C of 6.0% (batch A) and 6.2% (batch B) with a color change from dark brown to orange-red. The proportion of organic matter thus seems to be about 6%, and the residual color possibly indicates the presence of oxidized iron. Reduction with sodium dithionite lightened the dark brown color of the aqueous clay rejects only slightly and gave a pale yellow supernatant liquid. This behavior suggests that most of the iron is in the clay structure itself.

NaOH treatment of the clay rejects at $\text{pH} \geq 13$ extracted 5–6% by weight as a blood-red solution. This is probably an iron–fulvic/humic acid complex, because ferric derivatives of monobasic carboxylic acids are blood-red in color (Sidgwick, 1950). After neutralization with acid the solution was yellow, indicating that a fulvic acid fraction of the extracted organic matter remained soluble. The residual solids from the NaOH extraction were gray-brown and are likely to be a clay-humin complex.

Hydrogen peroxide reacted vigorously with the clay rejects to give an off-white product resembling 'normal' kaolinite in appearance. This product no longer gave an acid pH; it exhibited no exothermic DTA peak, and lost <1% up to 400°C. The untreated and peroxide-treated clays (after washing and drying) differed in their infrared spectra (KBr discs) in that the weak absorption peaks at 2920 and 2860 cm^{-1} and a broad band from 1330 to 1480 cm^{-1} were considerably reduced in intensity in the treated sample. A sample of humic acid (Toyo Kasei H161) run under the same conditions gave weak absorptions at 2925 and 2850 cm^{-1} and a broad band between 1350 and 1470 cm^{-1} . Thus, the organic material appears to be soil humic acid that can be removed by hydrogen peroxide, presumably via oxidation to CO_2 and H_2O .

Surface analysis by X-ray photoelectron spectroscopy (ESCA) confirmed that most of the iron at the clay particle surfaces remained after the peroxide treatment. Unfortunately, ESCA did not *prove* the presence and removal of the organic matter, because even a pure reference kaolinite gave a carbon signal, presumably due to organic molecules (from the pump oil?) at the strongly adsorbent surfaces of the clay particles. Even so, an ESCA signal from sodium in the reference Na-kaolinite (Na ~0.12%, see below) was clearly visible. Thus, the lack of a distinguishable ESCA C_{1s} signal for as much as 6% of organic matter suggests that the clay–organic complex involves edge surfaces of the clay

platelets, rather than face surfaces which make up most of the surface area.

Sample preparation

Several starting materials were prepared. Following each chemical treatment listed below, the crude aqueous rejects were repeatedly centrifuged and redispersed with conductivity water until the sediments and the supernatants both showed approximately constant conductivities, indicating that all excess electrolyte had been removed.

1. Untreated samples: no chemical treatment.
2. NaCl samples: two treatments with 0.33 M NaCl solution. The dark brown color did not change, so that all of the organic material remained, although the exchangeable cations were replaced by Na and the pH was no longer acid.
3. HCl/ H_2O_2 samples: reaction with peroxide followed by two treatments with 0.33 M HCl for ~0.5 hr at room temperature. The organic material was removed, and the exchangeable cations became H or, more likely, an H-Al species.
4. NaCl/ H_2O samples: reaction with peroxide followed by two treatments with 0.33 M NaCl solution. Organic material was removed, and the exchangeable cations became Na.
5. HCl samples: two treatments with 0.33 M HCl. The supernatant liquids were yellow (instead of colorless as in all of the other preparations), suggesting some decomposition.
6. NH_4Ac samples: two treatments with 0.33 M ammonium acetate solution to replace the exchangeable cations by NH_4 .
7. $\text{NH}_4\text{Ac}/\text{H}_2\text{O}_2$ samples: reaction with peroxide followed by two treatments with 0.33 M ammonium acetate solution.

Samples 6 and 7 were used only to obtain the cation-exchange capacity (CEC) via release of the ammonia on boiling with strong alkali. The CEC values are approximately equivalent to the Na contents of samples 2 and 4, respectively. In all the preparations special care was taken to ensure uniform procedures. All samples reached a minimum, approximately constant, conductivity after five or six washings. The sediments from all final centrifugations were 40–50% solids and were immediately dried in vacuo to avoid the slow decomposition of clay that occurs in acidic aqueous dispersions (Coleman and Craig, 1961).

The NaCl (2) and NH_4Ac (6) samples became peptized after four washings. Indeed, a 1% dispersion of the NaCl sample in distilled water did not settle appreciably in 24 hr, whereas the untreated sample reached 12% solids in 8 hr. Peptization is due to net charges of the same sign on faces and edges of clay particles, thus inhibiting edge-to-face association. The organic material (after cation exchange) appeared to act similarly to

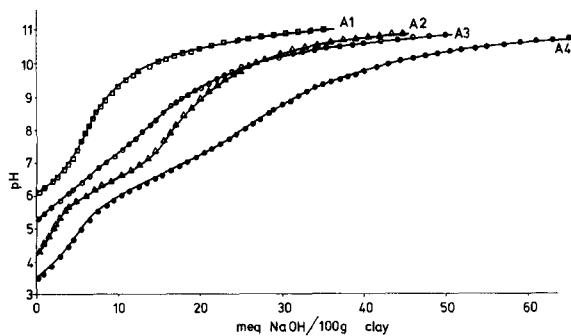


Figure 1. pH vs. alkali added for batch A: A1 = NaCl/H₂O₂, A2 = HCl/H₂O₂, A3 = NaCl, A4 = untreated.

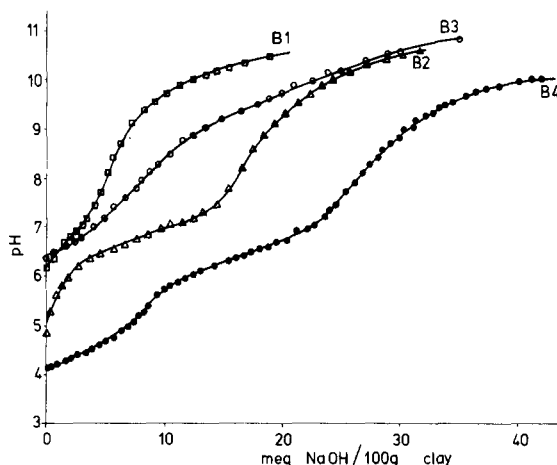


Figure 2. pH vs. alkali added for batch B: B1 = NaCl/H₂O₂, B2 = HCl/H₂O₂, B3 = NaCl, B4 = untreated.

peptising anions, such as fluoride, phosphate, and tannate (Van Olphen, 1977), which complex with the edge surfaces of clays. This was confirmed by the action of sodium fluoride or sodium hexametaphosphate (Calgon) on the untreated sample. Peptization occurred along with some loss of color into the liquid phase, indicating a partial displacement of organic material by these edge-adsorbing anions.

Finally, the <2- μ m fraction of British Drug Houses kaolin (Society of Leather Trades Specification) was also treated with HCl and with NaCl to provide reference samples comparable to the HCl/H₂O₂- and NaCl/H₂O₂-treated reject samples. The CEC of this reference kaolinite was also determined via NH₄Ac exchange.

EXPERIMENTAL METHODS

Potentiometric measurements were made with a Leeds and Northrup 7410 pH Meter calibrated with two buffer solutions at pH 4 and 9. Conductometric measurements were made with a Wayne-Kerr B221 Universal Bridge. In both cases 0.2 g of dry sample was mixed with 20 g of conductivity water in a sealed 50-ml plastic beaker on which the appropriate electrodes were mounted. Each clay was dispersed by magnetic stirring to achieve a constant (maximum) conductivity or constant (minimum) pH value. Each dispersion was then titrated with 0.01 M NaOH solution; the sample was stirred after each addition until the reading was approximately constant (± 0.01 pH unit/min). The maximum pH reached in the titrations could not have been >12 (the pH of 0.01 M NaOH), whereas displacement of organic matter only occurs (see above) at pH ≥ 13 . Therefore the observed titration reactions did not correspond to a significant replacement of the organic species by OH⁻. The pH and conductivity values observed during the titrations were corrected for the dilution factor. The pH correction was small, and neither correction altered the positions of the end points (see below) within the errors involved, though the end points did become slightly sharper.

RESULTS AND ANALYSIS

The pH titrations are presented in Figure 1 for batch A of the clay rejects, Figure 2 for batch B, and Figure 3 for the 'reference' kaolinite samples. The untreated and HCl/H₂O₂ samples were initially acidic and exhibited two reactions with the alkali. Indeed, the pH curves are very similar to those for the titration of a mixture of a strong and a weak acid with a strong alkali. The NaCl and NaCl/H₂O₂ samples were initially near neutral and exhibited one reaction with the alkali. This reaction, at higher pH, was common to all samples, and the range of pH over which it occurred decreased from

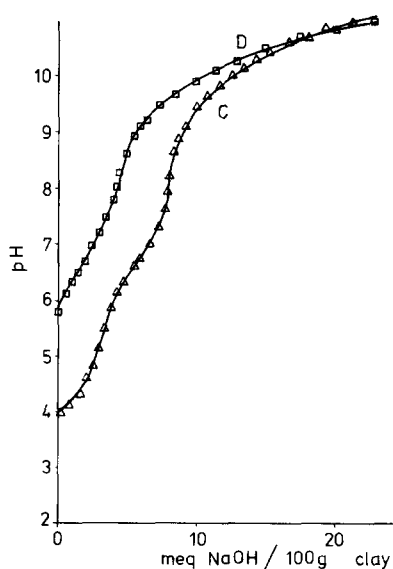


Figure 3. pH vs. alkali added for reference kaolinite: C = HCl, D = NaCl.

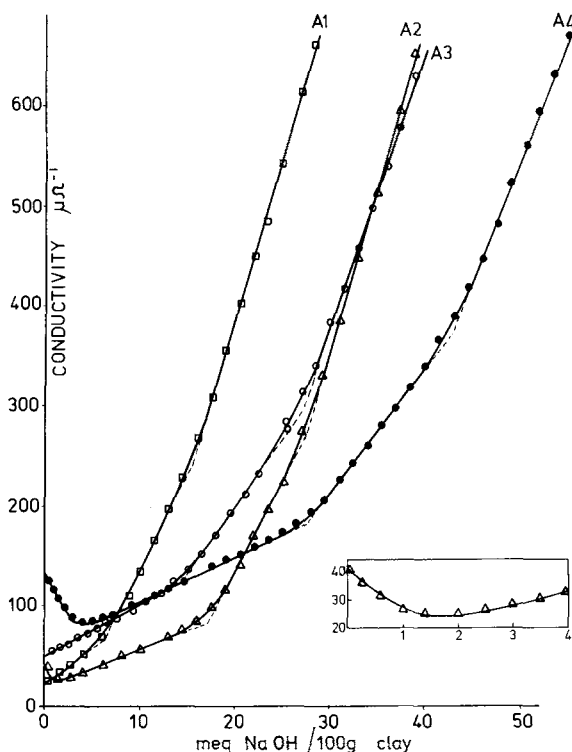


Figure 4. Conductivity vs. alkali added for batch A: A1 = NaCl/H₂O₂, A2 = HCl/H₂O₂, A3 = NaCl, A4 = untreated. Inset shows initial portion of A2 titration on a larger scale.

the untreated to the NaCl/H₂O₂ samples, with batch B always giving a narrower pH range than batch A. The pH range for batch B was close to that found for the 'reference' kaolinites.

The conductivity titrations for batch A are presented in Figure 4, for batch B in Figure 5, and for the 'reference' kaolinite samples in Figure 6. These curves also resemble those for a mixture of a strong and a weak acid titrated with a strong alkali. The untreated and HCl/H₂O₂ samples showed an initial decrease in conductivity not seen in the NaCl and NaCl/H₂O₂ samples, indicating that hydrogen ions in the former samples were removed as water and were replaced by less mobile Na ions from the alkali. After this reaction a gentle rise in conductivity was recorded, followed by a steeper rise when by a rapid increase in conductivity due to excess alkali.

The HCl samples gave pH and conductivity titration curves of practically the same shape as the untreated samples shown in Figures 1, 2, 4, and 5, proving that the 'untreated' samples were already 'acid treated.' However the curves for the HCl samples were compressed by about 20% along the NaOH axis, reflecting the loss of reactive material when relatively concentrated acid was used. The results for these HCl samples are omitted from the illustrations to avoid overlapping with the other samples.

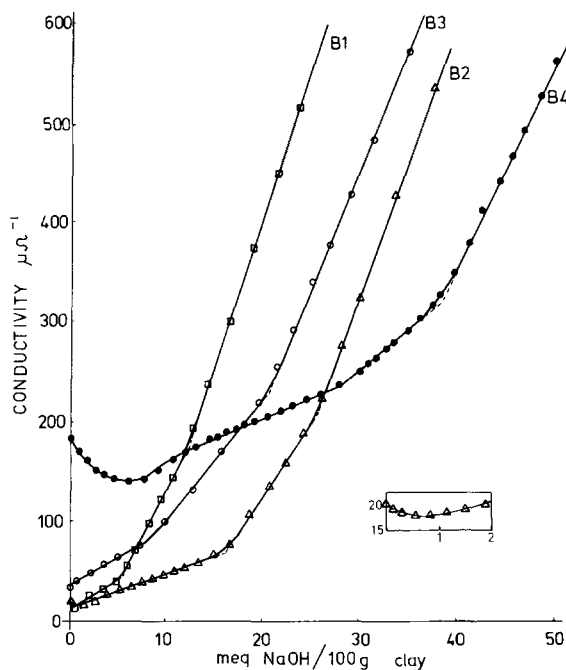


Figure 5. Conductivity vs. alkali added for batch B: B1 = NaCl/H₂O₂, B2 = HCl/H₂O₂, B3 = NaCl, B4 = untreated. Inset shows initial portion of B2 titration on a larger scale.

The end points of the titrations in Figures 1–6 were quantitatively determined as shown schematically in Figure 7. The pH end points (marked by crosses) are midway between the intersections of the extrapolations marked by asterisks. The 'dissociation constant' or pK value is the value of the pH when an amount of alkali equal to half the end point has been added, or in the case of two end points, at half the first end point and halfway between the first and second end points. The first reaction is sometimes incompletely defined in the pH curves, so that the end-point parameters are estimates only. In addition, the breadth of the second reaction in the pH curves of batch A may result in a significant error in determining the end point. Therefore the pH end points were also obtained independently by the first derivative method. These two well-established procedures gave end points differing by less than 5%; the average values are quoted in the tables and discussion following. The conductivity end points are located at the extrapolated intersections of the regions of different slopes; reproducibility in duplicate runs was about 2%. The end point C₁ corresponds approximately to the end point pH₁, and C₂ to pH₂, but the third end point, C₃ has no counterpart in the pH curves. Presumably the process responsible for the end point C₃ does not involve H⁺ and OH⁻ ions, at least not directly.

Table 1 lists the end points in meq alkali/100 g dry clay; each end point is subtracted from the succeeding one so as to give the amount of alkali needed for each

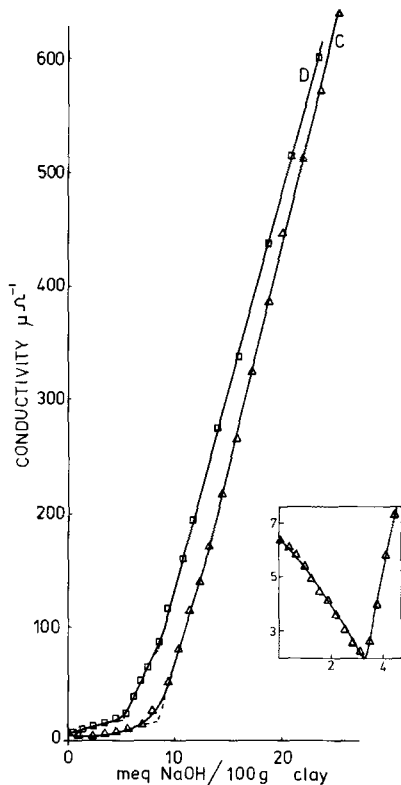


Figure 6. Conductivity vs. alkali added for reference kaolinite: C = HCl, D = NaCl. Inset shows initial portion of C titration on a larger scale.

reaction. The appropriate pH and pK values are also recorded, and the CECs are entered in the rows for the NaCl and NaCl/H₂O₂ samples. These data strongly suggest that the pH and conductivity techniques yield approximately the same end points, unlike much of the

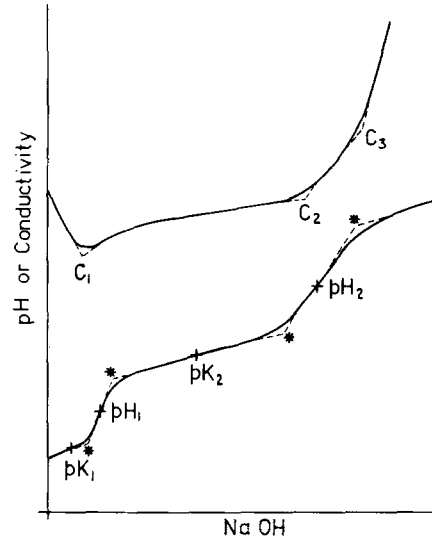


Figure 7. Diagrammatic representation of the end points and the pH/pK values.

earlier work on other clays (Marshall, 1964), and also that the reactions involved are much the same for the different samples. For the HCl-samples not shown in Figures 1, 2, 4, and 5 the pH and pK values were not significantly different from those for the untreated samples (e.g., batch A HCl-sample, pH₁ = 4.77 and pH₂ = 8.26). The 'untreated' samples are indeed acid treated.

The results in Table 1 may be analyzed without identifying the reactions and the reacting species. The first end-point values for the HCl/H₂O₂ samples represent the relatively strong acid component of these 'acid clays,' while the differences between these values and the corresponding values for the untreated samples rep-

Table 1. Data from conductivity and pH titration curves.

Sample ¹	Initial conductivity (μΩ ⁻¹)	Conductivity end points					Initial pH	pH end points			pH at end point		pK values		CEC via NH ₄ Ac (meq/100 g)
		1	2	3	2 - 1	3 - 2		1	2	2 - 1	1	2	1	2	
Batch A															
Untreated	136.5	3.4	27.8	43.0	24.4	15.2	3.47	4.6	27.7	23.1	4.67	8.37	3.92	6.73	21.7
NaCl	52.0		14.4	27.1	14.4	12.7	5.12		14.0	14.0		8.16		6.70	
HCl/H ₂ O ₂	40.7	1.4	17.2	27.6	15.8	10.4	4.10	1.9	17.4	15.5	4.87	8.18	4.47	6.50	
NaCl/H ₂ O ₂	22.4		6.3	15.7	6.3	9.4	5.98		6.2	6.2		8.03		6.72	
Batch B															
Untreated	185.2	6.5	28.1	38.4	21.6	10.3	4.11	8.0	26.1	18.1	5.22	7.91	4.52	6.48	17.4
NaCl	34.5		8.4	20.8	8.4	12.4	6.38		7.9	7.9		7.88		6.97	
HCl/H ₂ O ₂	20.0	0.7	16.3	25.7	15.6	9.4	4.82	0.8	17.0	16.2	5.50	8.32	~5.2?	6.85	
NaCl/H ₂ O ₂	20.2		5.4	12.2	5.4	6.8	6.18		5.5	5.5		8.27		6.95	
Reference kaolinite															
NaCl	4.87		5.2	8.6	5.2	3.4	5.81		4.4	4.4		8.22		6.77	5.1
HCl	6.42	3.3	8.3	12.8	5.0	4.5	4.00	3.1	8.2	5.1	5.28	8.28	4.34	6.63	

¹ See text for preparation procedures.

represent the stronger acid component of the organic matter. Similarly, the entries in the 2 - 1 columns represent the weaker acid components for which the minimum concentration occurs in the NaCl/H₂O₂ samples. The difference 14.0 - 6.2 (batch A, pH), for example, represents the weak acid contribution of the organic matter, which was also present in the untreated sample but not in the HCl/H₂O₂ sample. The difference 15.5 - 6.2 represents supplemental weak acid associated with the clay itself when the preparation was carried out under acidic conditions; it applies to the HCl/H₂O₂ and untreated samples, but not to the NaCl samples. Thus, for the untreated sample a minimum value of 6.2 meq/100 g should be supplemented by 7.8 meq/100 g due to the organic matter and 9.3 meq/100 g due to the acidic environment. The *predicted* total is thus 23.3 meq/100 g, which compares very well with the actual total of 23.1 meq/100 g in Table 1. The conductivity for batch A gives 23.9 meq/100 g (predicted) and 24.4 meq/100 g (found), while for batch B the pH and conductivity predictions both total 18.6 meq/100 g, and the observed values are 18.1 and 21.6 meq/100 g, respectively.

It is interesting to note that the difference in CECs in the last column of Table 1 is equivalent to the weak acid contribution of the organic matter. This is true for both batches, despite the quite different proportions of stronger and weaker acid sites associated with the organic matter. Other tests on additional batches of clay rejects (not reported here) suggest that batch A is more representative of the clay-organic complexation in the sand deposits than batch B.

For the reference kaolinites the concentration of the stronger acid component (3.1-3.3 meq/100 g) is comparable to that of the weaker acid component (4.4-5.2 meq/100 g) rather than being only a fraction of the latter as in batches A and B. In addition, very little supplementary weak acid appeared under acidic preparation conditions; indeed, it is difficult to estimate this extra weak acid because the errors become crucial when two relatively large and nearly equal numbers are subtracted to get a small difference. Nonetheless, Figures 3 and 6 are basically the same as Figures 1, 2, 4, and 5, and the pH and pK values are similar (Table I), while the smaller end-point values are reflected in smaller CEC values. Thus, the empirical analysis is consistent for two kaolins of quite different origins and properties.

DISCUSSION AND THEORETICAL MODELS

The foregoing empirical analysis, while useful, is limited in that the stronger and weaker acid species are not defined (cf. Garrels and Christ, 1956). Some clues as to the nature of these species can be obtained from the literature on kaolinite clays, particularly that dealing with the acid form of the clay and that pertaining to interactions with soil organic matter. A permanent negative charge at face surfaces, arising from ionic substitution in the structure by cations of lower valency and

which is compensated by exchangeable cations, is characteristic of most clay systems. Despite some controversy (Ferris and Jepson, 1975) general opinion is that such a constant-charge surface exists in kaolinite and gives rise to a pH-independent CEC (Van Olphen, 1977; Williams and Williams, 1978). An additional, pH-dependent charge in kaolinite arises from the interaction of H⁺/OH⁻ potential-determining ions with oxide and/or hydroxide surface groups (Van Olphen, 1977; Williams and Williams, 1978), particularly at the edge surfaces where the silica and alumina sheets are disrupted. Whether this is an 'intrinsic' charge associated directly with (amphoteric) Si-OH and/or Al-OH groups in the clay structure (Bolland *et al.*, 1976; Williams and Williams, 1978), or an 'extrinsic' charge associated with aluminosilicate species dissolved from and then reabsorbed by the clay surfaces (Ferris and Jepson, 1975; Greenland and Hayes, 1978) is debatable. For example, the high pH value of the edge isoelectric point (Rand and Melton, 1977), which is typical of alumina and not typical of silica, has been accounted for (Van Olphen, 1977) by preferential breaking of bonds in the silica sheets at places where Al substitutes for Si (an intrinsic mechanism) or by uptake of Al ions at the exposed silica sheets (an extrinsic mechanism).

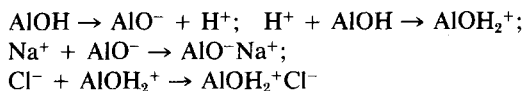
Chemical changes resulting in 'extrinsic' surface charges are a feature of *acid* clays. The untreated clay sample in this paper became acidic through natural weathering and environmental factors. In the laboratory acid clays have been prepared by electro dialysis, strong acid washing, or treatment with an H⁺ ion-exchange resin, the latter being the least damaging (Marshall, 1964). Such H-saturated clays are unstable and change with time to different surface compositions having extractable forms of Al (and Mg) in exchange positions (Van Olphen, 1977; James and Parks, 1981). The rate of breakdown of the moist clay depends strongly on temperature, pH, and the type of clay. Kaolinite is the most resistant of the common clays towards acids (Coleman and Craig, 1961; Marshall, 1964, pp. 112, 295) and is not attacked appreciably by dilute HCl at ambient temperatures (Worrall, 1975, p. 107). Nonetheless, Al is apparently leached (and in preference to Si) at a measureable rate at pH < 6.5 (Bolland *et al.*, 1976; Buchanan and Oppenheim, 1968). The aluminum is possibly reabsorbed as nonexchangeable species, such as Al(OH)₃ and polymerized hydroxy-Al (Coleman and Thomas, 1967; Thomas, 1977; Greenland and Hayes, 1978), or as exchangeable species, such as Al(H₂O)_n³⁺, Al(OH)₂²⁺, and Al(OH)₂⁺ (Marshall, 1964; Conley and Althoff, 1971), or both.

Extrinsic or intrinsic, and exchangeable or nonexchangeable, all of the above Al species should be titratable with alkali, with the more strongly acidic species (reflecting more weakly bound hydrogen ions) titrating first. Continuous recording of the pH of montmorillonite clays (Volk and Jackson, 1963) in the

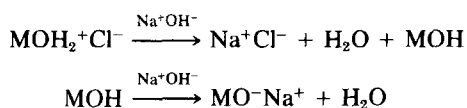
presence of background electrolyte, as a function of alkali added, revealed five distinguishable reactions involving: (1) exchangeable H^+/H_3O^+ , (2) exchangeable $Al^{3+}/Al(H_2O)_6^{3+}$, (3) and (4) hydroxy-alumina 'neutralization,' and (5) aluminosilicate dissolution. Conventional titrations (Low, 1955) allowed a little time to reach equilibrium, and stages 2-4 and probably 5 merged. The initial inflexion, representing completion of the exchangeable H^+ reaction and commencement of the exchangeable Al reaction, remained distinguishable, as in the present results.

Titrateable Al species (probably supplemented by titrateable iron species for all of the present samples except the reference kaolinites) thus seem to be responsible for the higher pH, weaker acid reaction that was a feature of all samples. The concentration of this weak acid species must increase under acidic preparation conditions and when organic matter is present, without changing its chemical nature significantly. Soil acids do complex or chelate strongly with (polyhydroxylated) multivalent cations, such as Al and Fe (Schnitzer and Khan, 1972; Greenland and Hayes, 1978; Theng, 1979), and indeed have their acid strengths determined by the hydroxylated Fe and Al (Thomas, 1977). It is therefore appropriate to devise a surface chemical model based on amphoteric (pH-dependent) Al-OH (and Fe-OH) groups, with provision for cation exchange, in order to explain the present results.

A recent analysis of the surface chemistry and electric double layer structure in aqueous colloids (James and Parks, 1981) described the amphoteric function of AlOH groups and the ion-binding reactions for colloidal alumina in the presence of NaCl electrolyte as follows:



The present author has adopted this scheme, allowing Fe to supplement the Al. In the following analysis M represents Al and/or Fe. Consider the organic-free pair of samples NaCl/H₂O₂ and HCl/H₂O₂. Let the concentration of weaker acid sites in the NaCl/H₂O₂ sample be $MOH_2^+Cl^- = a$ meq/100 g; $MOH = b$; $MO^-Na^+ = c$. Three possibilities then exist for the HCl/H₂O₂ sample: $MOH_2^+Cl^- = a$, $MOH = b + c$; or $MOH_2^+Cl^- = a + b$, $MOH = c$; or $MOH_2^+Cl^- = a + b + c$, $MOH = 0$. In titrating with alkali, the reaction steps are:



The titration values in the 2 - 1 columns of Table 1 could represent the first step alone, or both steps together. Taking batch A as the example and averaging

Table 2. Concentrations of possible reacting species.¹

	Batch A ²		Batch B ²		Reference kaolinite ²	
	NaCl/H ₂ O ₂	HCl/H ₂ O ₂	NaCl/H ₂ O ₂	HCl/H ₂ O ₂	NaCl	HCl
Weaker acid (one step)						
MOH ₂ ⁺ Cl ⁻	6.25	15.65	5.45	15.9	4.8	5.05
MOH	0	0	0	0	0	0
MO ⁻ Na ⁺	9.4	0	10.45	0	0.25	0
Weaker acid (two steps)						
MOH ₂ ⁺ Cl ⁻	3.13	1.65	2.73	2.73	1.2	2.4
MOH	0	12.35	3.95	10.45	0	1.2
MO ⁻ Na ⁺	9.4	0	10.45	0	0.25	0
Stronger acid						
Clay ⁻ Na ⁺	1.65	1.65	0.75	0.75	3.2	3.2
Clay ⁻ MOH ₂ ⁺						

¹ Values in meq/100 g dry clay are derived from the average of the pH and conductivity results in Table 1 in the manner described in the text. The organic matter contributes an extra 2.35 and 7.95 meq/100 g stronger and weaker acid sites respectively for batch A with 6.5 and 2.7 meq/100 g stronger and weaker acid sites respectively for batch B.

² Values in brackets are the most probable solution.

the pH and conductivity end points in Table 1, the two-step reaction is: $2a + b = 6.25$ and (1) $2a + b + c$ or (2) $2a + 2b + c$ or (3) $2a + 2b + 2c = 15.65$. The one-step reaction is: $a = 6.25$ and (4) a or (5) $a + b$ or (6) $a + b + c = 15.65$. Case 4 is clearly impossible. One further constraint applies—that c (i.e., $\text{MO}^- \text{Na}^+$) be close to the required CEC value, which in this example is about 11.9 meq/100 g (13.6 meq/100 g minus the exchangeable species represented by the stronger acid end point of 1.4–1.9 meq/100 g). This 11.9 meq/100 g may be a little too high, because the total NH_4^+ uptake may include two small contributions which are not reflected in the end point for the NaCl sample, namely absorbed neutral NH_3 (like water of hydration) and NH_4^+ co-ions (rather than counter-ions). The actual maximum value of c (9.4 meq/100 g) occurs for case 1, and also for case 6 provided $b = 0$. Cases 2–5 can be safely rejected because c is between 0 and 4.7 meq/100 g. Thus, two general solutions, 1 and 6, exist, though 1 can be fitted to any pair of values satisfying $2a + b = 6.25$. Table 2 lists calculated values for batches A, B, and the 'reference' kaolinites which span the possible range; in each case equations 1 and 6 have been applied to the average of the 2-1 columns of the pH and conductivity in Table 1.

The *stronger* acid component represented by the first end point in Table 1 would at first sight be attributable to free hydrogen ions from the acid clays and from the humic acid. However, a reaction $\text{H-clay} + \text{NaOH} \rightarrow \text{Na-clay} + \text{H}_2\text{O}$ involves replacement of H^+ by the 7-times less mobile Na^+ . This is incompatible with the shallow decrease in conductivity towards the first end point for the $\text{HCl}/\text{H}_2\text{O}_2$ samples and for the HCl kaolinites and also with the ratio of starting conductivities for both the $\text{HCl}/\text{H}_2\text{O}_2$ and the $\text{NaCl}/\text{H}_2\text{O}_2$ samples and the two 'reference' kaolinites. Thus, the 'stronger acid' species is strong *relative* to the weak MOH species and is *not* comparable to conventional strong acids. This relativity is confirmed by the pK_a values for the first end points, by the approximate superposition of the contribution from the organic acid and by the detailed conductivity-concentration data reported in the accompanying paper. A further significant conclusion (from Table 1) is that subtracting the first end point (column 1) from the second end point (column 2 – 1) for the untreated, $\text{HCl}/\text{H}_2\text{O}_2$, and HCl kaolinite samples always gives the CEC value in the last column. The *first* end point therefore seems to be due to hydrogen ions, bound within an MOH_2^+ species, reacting to produce MOH which then contributes to the second end point. The last row of Table 2 lists the concentrations of this *relatively* strong acid MOH_2^+ corresponding to the average of the pH and conductivity data; this species is exchangeable for Na^+ .

The samples containing humic acids probably have carboxylic COOH and phenolic OH groups complexed

or chelated at some hydroxylated Al/Fe sites. Referring to the results for batch A in Table 1, the COOH contributes 2.35 meq/100 g of stronger acid sites (the average of 3.4–1.4 and 4.6–1.9) while the phenolic OH contributes 7.95 meq/100 g of weaker acid sites (the average of 14.4–6.3 and 14.0–6.2). The corresponding values for batch B are 6.5 and 2.7 meq/100 g. The extra stronger acid sites disappeared after NaCl treatment, which suggests the formation of an Na-carboxylate salt and consequently an increased CEC. However, the enhancements in CEC in Table 1 are in fact wholly accounted for by the weaker acid species, which implies that phenolic MOH groups became phenolic $\text{MO}^- \text{Na}^+$ groups after NaCl treatment. Yet such groups are no longer titratable, which is inconsistent with the second end points for the NaCl samples compared to the NaCl/ H_2O_2 samples. Thus, more information will be needed to state precisely how the surface chemical description illustrated in Table 2 extends to the samples which contain organic matter. The literature does not seem to provide specific details of the bonding arrangement between clays and humic acids nor of the reaction mechanism with alkali.

The analysis so far has relied solely on titration end points. Some (or all!) of the possibilities in Table 2 could be eliminated by comparing the predicted and the actual values of the conductivity and/or of the pH. Complete titration curves can be examined using theoretical models (James and Parks, 1981), but it is simpler to analyze the pH or conductivity of the samples alone, without any titrant added. The sample concentration is then the important variable. As it is difficult to measure pH reliably as a function of concentration, the conductivity has been studied (Lockhart, 1981) at different concentrations of the clay dispersions. This work ruled out all possibilities except $\text{MOH}_2^+ \text{Cl}^- \leq 1.65$ meq/100 g for batch A, ≤ 0.75 meq/100 g for batch B, and ≤ 1.2 meq/100 g for the reference kaolinites. $\text{MOH}_2^+ \text{Cl}^- = 0$ is the only consistent solution in view of the fact that when $\text{MO}^- \text{Na}^+$ species is treated with HCl it should produce MOH or MOH_2^+ species but not both, i.e., MOH_2^+ is only involved in the stronger acid reaction, whereupon it is converted to MOH species and then contributes to the weaker acid reaction.

The present surface chemical model and the calculations based on it is not necessarily unique. The present paper shows that detailed quantitative analysis of titration data is possible, particularly when acid and nonacid forms of clays are examined together.

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Резюме—Обнаружено путём потенциметрического и кондуктометрического титрования, что кислотные и некислотные формы каолиновых глин имели слабые кислотные вещества, концентрация которых увеличивалась по мере кислотных условий приготовления и присутствия почвенных органических веществ, связанных с глинами. Более сильные кислотные вещества были обнаружены в необработанных, а также в свободных от органических субстанций HCl-обработанных образцов (промытых от избытка кислоты). Граничные точки для органически свободных и/или ионообменных образцов были использованы, чтобы определить граничные точки для необработанных образцов. Поверхностнохимическая модель, включающая вещества MOH_2^+ , MOH , и MO^- (где M = Al и/или Fe), была приспособлена к данным по титрованию и к катионообменным способностям. MOH_2^+ является более сильной кислотой, а MOH —более слабой; обмен противоионов Na^+ ионами H^+ трансформирует места MO^-Na^+ в места MOH . Гуминовая кислота подвергалась, вероятно, комплексообразованию или хелатации с некоторыми гидроксильными местами Al/Fe через группы COOH и феноловые OH . Группы COOH внесли добавочные более сильные кислотные вещества, которые были необмениваемыми, в то время как группы OH внесли добавочные более слабые кислотные вещества, а также увеличили катионообменную способность относительно величине, принадлежащей к органически свободным образцам. [E.C.]

Resümee—Potentiometrische und konduktometrische Titration zeigte, daß saure und nicht saure Formen von Tonen eine schwach saure Spezies aufweisen, deren Konzentration durch saure Präparationsbedingungen und durch die Gegenwart von an den Ton gebundenen organischen Bodensubstanzen erhöht wurde. Eine stärker saure Spezies wurde ebenfalls in unbehandelten Proben und in HCl-behandelten Proben, die frei von organischen Substanzen waren, beobachtet (überflüssige Säure wurde ausgewaschen). Die Endpunkte der Titration der Proben, die frei von organischen Substanzen waren, und/oder der Ionen-ausgetauschten Proben wurden verwendet, um die Endpunkte der unbehandelten Proben vorauszusagen. Ein Modell für die Oberflächenchemie, das MOH_2^+ , MOH , und MO^- Spezies (wobei M = Al und/oder Fe) berücksichtigt, wurde den Titrationsdaten und den Kationenaustauschkapazitäten (CEC) angepaßt. MOH_2^+ ist die stärkere Säure und MOH die schwächere. Der Austausch von Na^+ -Gegenionen durch H^+ wandelt die MO^-Na^+ -Plätze in MOH -Plätze um. Huminsäure wurde wahrscheinlich an einige hydratisierte Al/Fe-Plätze durch COOH - und phenolische OH -Gruppen als Komplexe oder Chelate gebunden. Die COOH -Gruppen lieferten entsprechend stärker saure Spezies, die nicht austauschbar waren, während die OH -Gruppen entsprechend schwächer saure Spezies lieferten und die CEC im Vergleich zu der CEC der Proben frei von organischen Substanzen erhöhten. [U.W.]

Résumé—On a trouvé par titrations potentiométriques et conductométriques que des formes acides et non-acides d'argiles kaolinitiques possédaient une espèce acide faible, dont la concentration était augmentée par des conditions de préparation acide et par la présence de matière organique liée à l'argile. Une espèce acide plus forte a aussi été trouvée dans des échantillons non traités et sans matière organique, lavés à l'HCl (lavés d'acide en excès). Les points extrêmes pour les échantillons sans matière organique et/ou à ions échangés ont été employés pour prédire les points extrêmes pour les échantillons non traités. Un modèle de surface chimique impliquant les espèces MOH_2^+ , MOH , et MO^- (où $M = \text{Al}$ et/ou Fe) a été ajusté aux données de titration et aux capacités d'échange de cations. MOH_2^+ est l'acide le plus fort, et MOH le plus faible; l'échange de contre-ions Na^+ par H^+ convertit les sites MONa^+ à des sites MOH . L'acide humique a probablement été complexé ou chélaté à quelques sites hydroxylatés Al/Fe par les groupes COOH et les groupes OH phénoliques. Les groupes COOH ont contribué des espèces d'acide plus fort supplémentaires, qui n'étaient pas échangeables, tandis que les groupes OH ont contribué des espèces d'acide plus faible supplémentaires et ont aussi augmenté la CEC relativement aux échantillons sans matière organique. [D.J.]