

# CATION EXCHANGE IN KAOLINITE-IRON OXIDE SYSTEMS\*

*by*

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## ABSTRACT

Kaolinite, to which iron oxides had been added by heating with  $\text{FeCl}_3$  solution, was studied with regard to its cation exchange capacity. It was observed that net cations held (cations less anions) varied directly with pH. Cations and anions are removed in equivalent amounts when the clays are washed with water. Removal of exchangeable cations proceeds as the last anions are removed. As a consequence, the negative sites may become saturated with non-exchangeable hydroxy-aluminum ions. To obtain the true CEC of a kaolinite-iron oxide system, it is necessary to estimate the amount of non-exchangeable hydroxy-aluminum by conductometric titration.

## INTRODUCTION

Cation exchange in acidic kaolinite-iron oxide systems is complicated by the adsorption of anions as well as cations (Ayres and Hagihara, 1953; Thomas, 1960A). The exchange equation for the reaction of  $\text{KCl}$  with such a system then becomes



where the hydrogen ions arise from the hydrolysis of exchangeable and/or hydroxy-aluminum, and the hydroxide ions are found associated with iron and aluminum coatings on the clay. Equation (1) implies that both  $\text{K}^+$  and  $\text{Cl}^-$  disappear from the solution phase as the reaction moves towards the right and that  $\text{OH}^-$  and  $\text{H}^+$  ions are replaced, forming water. If the reaction is reversed, hydrolysis occurs with the attendant replacement of both  $\text{K}^+$  and  $\text{Cl}^-$ .

The exchange system shown above strongly influences the nutrient status in such soils. For example, soil solution concentrations are generally quite low (Mehlich, 1952) and anion (and therefore, cation) movement is relatively slow (Berg and Thomas, 1959). Because the iron and aluminum oxide coatings practically assure the maintenance of an acid system, even a Na-saturated Fe-kaolinite preparation does not disperse upon prolonged washing with water (cf. Schofield and Samson, 1954). Since at low pH

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values  $\text{Cl}^-$  is held in about the same quantity as the added cation, removal of all  $\text{Cl}^-$  to determine a "net" cation exchange capacity (cations less anions) leads to a small value. This net value becomes smaller as the amount of chloride adsorbed increases. Chloride adsorption has been shown to increase approximately linearly with decreasing pH (Toth, 1939). Thus, an apparent pH-dependent CEC at all pH values will result. Such an effect is seen with the Cecil soil in Fig 1. Schofield (1949), however, has suggested that there is a true "permanent" charge due to isomorphous substitution within the clay lattice and that the CEC does not change below about pH 6. Such idealized behavior in a kaolin is shown by the Kamec halloysite curve in Fig. 1.

It appears that the presence of iron in a kaolinite system markedly affects the cation exchange properties of the clay. This comes about because of the interaction of anions with iron-coated clays. The purpose of this paper is to point out the differences in cation exchange in an Fe-kaolinite preparation as compared to an idealized cation exchange system such as Wyoming Bentonite.

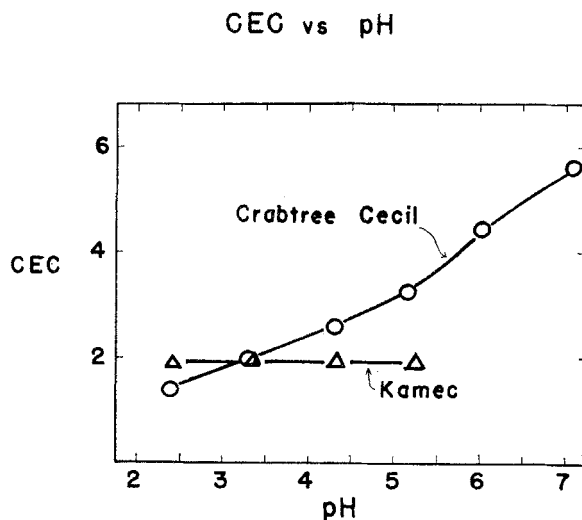


FIGURE 1.—The "net" cation exchange capacity ( $\text{K}^+$  less  $\text{Cl}^-$ ) of Cecil soil and Kamec clay vs. the pH of saturating KCl.

### MATERIALS AND METHODS

The general method of study used consisted of equilibrating various clays with N solutions of a chloride salt. Washing then proceeded by thoroughly mixing the clay and added water with an electric stirrer, centrifuging and saving the supernatant for analysis of the cation and chloride. Calcium and  $\text{K}^+$  were determined on the Beckman DU Flame spectrophotometer and

Cl<sup>-</sup> was estimated by titration with AgNO<sub>3</sub> using a Ag-AgCl electrode with a calomel reference electrode in conjunction with a Beckman model G pH meter.

Addition of iron oxides to Georgia (Pioneer) kaolinite was accomplished by heating the clay at about 80°C in a solution of FeCl<sub>3</sub> for several days. From time to time the supernatant liquid was poured off and fresh FeCl<sub>3</sub> solution added. This removed excess HCl and added additional Fe which in turn hydrolyzed. The apparent reaction is



Conductometric titration of clay was carried out in a closed glass bottle with a volume of about 100 ml. The titrating solution was 0.1 N NaOH and the conductometric titration apparatus is Model RC16B, as supplied by Industrial Instruments.

In addition to Georgia Kaolinite, Kamec halloysite from Spruce Pine, N.C., and Cecil soils from Raleigh, N.C., and Dixie, Va., were used in this study. With similar amounts of Fe, their properties become remarkably similar.

## RESULTS AND DISCUSSION

If an acid Fe-kaolin is equilibrated with N KCl and washed with increments of water, the K<sup>+</sup> and Cl<sup>-</sup> contents will decrease rapidly at first and then level off, suggesting that the last bit of Cl<sup>-</sup> is very difficult to remove. Figure 2 shows such a plot for the Dixie Cecil soil. Throughout the curve K<sup>+</sup> is equivalent to Cl<sup>-</sup> as predicted by eq. (1). If these same data are plotted as log of the Cl<sup>-</sup> remaining vs. the volume of wash water (which is proportional to time) a straight line indicates a first order reaction. The actual plot for the Cecil is shown in Fig. 3. It suggests that there are two separate first-order reactions involved in the removal of Cl<sup>-</sup> from Fe-kaolinite systems. The first curve apparently is an indication of chloride removal by simple washing. The second, much slower reaction, is presumably due to hydrolysis and the subsequent replacement of the exchangeable metal ion by H<sup>+</sup> and the anion by OH<sup>-</sup> ions. If the second (hydrolysis) curve is extrapolated to the ordinate, the intercept should give the amount of Cl<sup>-</sup> actually adsorbed by the clay before any washing occurs. In Fig. 3, this value is 6.2 meg per 100 gg. This intercept moves up the ordinate as pH is lowered and/or Fe is added to kaolinite as shown in Table 1. The data in Table 1 suggest that the intercept is at least proportional to the amount of Cl<sup>-</sup> adsorbed since it varies as would be expected. If the second curve is subtracted from the first curve in Fig. 3 the true curve for the first reaction is obtained. This can be used to find the number of washes after which very little free Cl<sup>-</sup> is present in the system. This appears to be about 75 ml for the 5g sample shown.

The first step in determining a true CEC for an Fe-kaolinite preparation is to remove the excess (non-adsorbed) Cl<sup>-</sup>. This point is reached where the total Cl<sup>-</sup> in the system is equal to the value of the intercept. Any washing

K, Cl Removal By H<sub>2</sub>O

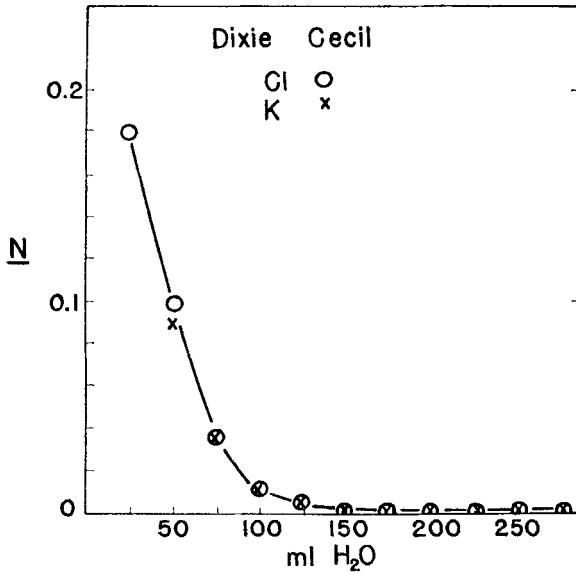


FIGURE 2.—The concentration of K<sup>+</sup> and Cl<sup>-</sup> in wash water from 5 gg of Cecil soil.

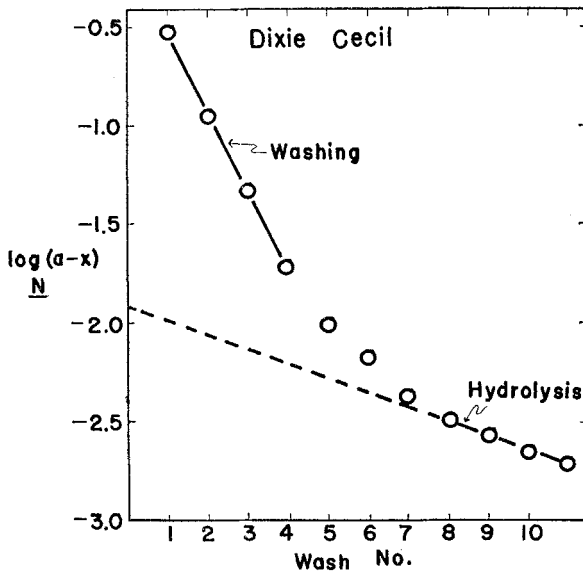


FIGURE 3.—Log of remaining Cl<sup>-</sup> in Cecil soil vs. wash number. (Each wash was 25 ml).

TABLE 1.—THE EFFECT OF FE AMOUNT AND SATURATING CATION ON THE Cl RETAINED  
(Estimated from the ordinate intercept on a first-order plot).

% Fe on Kaolin	Cl Retained, meq/100 g	
	HCl-Saturated	CaCl <sub>2</sub> -Saturated
0.15	1.38	0.64
1.65	2.57	0.83
4.55	6.60	2.21

beyond this point hydrolyzes both cations ( $K^+$ ) and anions ( $Cl^-$ ). When  $H^+$  ions arrive on the exchange surfaces they meet not only the clay itself but also complex hydroxy-aluminum ions (Rich and Obenshain, 1955; Thomas, 1960B). The  $H^+$  ions tend to neutralize some of the  $OH^-$  on the hydroxy aluminum ions, increasing their positive charge. The net effect, since the hydroxy-Al ions are not exchangeable, is to reduce the number of negative sites available to added cations. In some soil clays this has proceeded to such an extent that very little effective CEC remains.

Thomas (1960B) observed that the equivalents of hydroxy-Al ions could be estimated by means of conductometric titration even though they are not replaceable by  $N NaCl$ . It would be expected that, if the charge below pH 6 really is invariant, the amount of "titratable" Al and H should increase as the  $K^+$  or other basic cation is hydrolyzed. With this assumption in mind,  $CaCl_2$  and  $KCl$ -saturated Georgia kaolinite samples with approximately 2.5 per cent added Fe were washed with different amounts of water, and the  $Cl^-$ ,  $K^+$  or  $Ca^{2+}$  and on a duplicate sample the titratable H and Al were determined. The  $Cl^-$  merely served as a check on the amount of hydrolysis which had occurred since in all cases there was less  $Cl^-$  than the value of the intercept.

Table 2 shows the results of the summation of H, Al and Ca or K and calculated "permanent" charge which results. The results appear to be almost free of any effects of cation used or amount of washing. These observations suggest that a truly invariant CEC below pH 6 does exist even in Fe-kaolinite systems, but that under ordinary methods of CEC determination this fact is masked by the interaction of anions.

Thus, it appears that as long as there is less  $Cl^-$  (or other anion) on the clay than the amount determined by extrapolating the second curve in a first order plot, the determination of the total exchangeable cations present and estimation of H-Al by conductometric titration of a duplicate sample will give a true value for charge due to lattice isomorphous substitution. This value appears to be invariant with regard to pH, degree of hydrolysis and nature of cation used.

TABLE 2.—CALCULATED CEC'S FOR FE-GEORGIA KAOLIN SATURATED WITH KCl OR CaCl<sub>2</sub> AND WASHED WITH VARYING AMOUNTS OF WATER

Cl <sup>-</sup> Remaining	K <sup>+</sup>	H <sup>+</sup>	Al	CEC K <sup>+</sup> + H <sup>+</sup> + Al
3.58	4.81	0.12	0.12	5.05
2.60	4.50	0.24	0.48	5.22
2.34	4.19	0.24	0.77	5.20
	Ca <sup>2+</sup>			
3.81	4.78	0.24	0.29	5.31
2.41	4.41	0.37	0.55	5.33

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