

## Hydrolysis and Decomposition of Calcium Montmorillonite<sup>1</sup>

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### ABSTRACT

The extent to which exchangeable calcium hydrolysis occurs during the preparation of homoionic calcium montmorillonite clay and the rate of the reaction in distilled water at various suspension concentrations and levels of CO<sub>2</sub> was determined at 25°C. The rate and extent of hydrolysis was found to be comparable to that reported for sodium montmorillonite and increased with CO<sub>2</sub> concentration. CEC was appreciably reduced during washing of residual salts while preparing calcium montmorillonite. The mechanism of hydrolysis is discussed.

**Additional Index Words:** leaching, clay, cation exchange capacity, electrical conductivity.

HYDROGEN CLAYS are unstable and transform readily into aluminum-saturated clays (Coleman and Craig, 1961; Eckman and Loudelout, 1961; Barshad and Foscolos, 1970). Sodium clays are also unstable in dilute salt solutions. Kelley (1951) reported that leaching Na-saturated soil with distilled water yielded a concentrated sodium carbonate leachate in the presence of atmospheric CO<sub>2</sub>; in the absence of CO<sub>2</sub>, an equivalent concentration of NaOH was obtained. Barshad (1960) found that upon leaching a number of Na-clays with distilled water, about 50% of the adsorbed Na<sup>+</sup> was replaced by Mg<sup>2+</sup> and Al<sup>3+</sup> derived from the lattice. Bar-On and Shainberg (1970) obtained similar results upon leaching Na-montmorillonite with distilled water. The concentration of Na<sup>+</sup> in the effluent was constant at a value of  $1.1 \times 10^{-4}$  mole/liter until all exchangeable Na<sup>+</sup> was replaced by Mg<sup>2+</sup>, Al<sup>3+</sup> and H<sup>+</sup> ions. At the end of their experiment, the exchange capacity had decreased and 15% of the clay had dissolved. Shainberg (1973) found that Na-montmorillonite was quite stable as long as the electrolyte concentration was above 0.03*N* NaCl. When the electrolyte concentration dropped below 0.001*N*, the clay decomposition rate became appreciable.

Hydrolysis and decomposition rates depended on the temperature and clay concentration and were proportional to the square root of time. The proportionality constant was also linearly related to the degree of isomorphous substitution in the octahedral layer (Shainberg et al., 1974). Shainberg (1973) proposed that sodium montmorillonite is chemically transformed by two consecutive reactions: (i) exchange between adsorbed Na<sup>+</sup> and H<sup>+</sup> in solution, and (ii) penetration of adsorbed H<sup>+</sup> into the crystal to displace octahedral Mg<sup>2+</sup> and Al<sup>3+</sup>. Shainberg (1973) reported that reaction 1 occurred rapidly and reaction 2 occurred slowly and was the rate-determining step.

The objective of this study was to examine the extent of hydrolysis of calcium montmorillonite and to determine its dependence on clay concentration and P<sub>CO<sub>2</sub></sub>. This reaction affects the preparation of homoionic clays and the stability of clays in soil environments during leaching with low electrolyte waters.

### PROCEDURE

The clay-size fraction, < 2 μm, of Wyoming montmorillonite was obtained by allowing coarser fractions to settle in aqueous suspension. Calcium-saturated montmorillonitic clays were prepared by reacting the clay fraction samples three times with 1*N* reagent grade CaCl<sub>2</sub>.

"Partially washed" clays were prepared by washing the clay three times with distilled water (1.0% clay suspensions). "Completely washed" clays were prepared by successively washing with distilled water until the supernatant was almost free of chloride (approximately  $5 \times 10^{-6}$  *M* as estimated using the AgNO<sub>3</sub> detection test). The resulting clays were freeze-dried and kept in a desiccator over CaCl<sub>2</sub>. Aqueous suspensions (50 ml) containing 0.25, 0.5, 1.0, and 2.5% clay by weight were prepared and placed in polypropylene tubes in a shaker for up to 830 hours at 25° C. Electrical conductivity (EC) and pH of the suspensions were measured periodically. Also, pH, EC, Ca, Mg, and Cl were determined in the final solutions. Ca and Mg were determined by atomic absorption and Cl was determined with an American Instrument<sup>3</sup> chloride titrator. This procedure was repeated three times for each sample of "partially washed" clay and twice for "completely washed" clay. After this, the clays were freeze-dried and cation exchange capacity was determined using the sodium acetate method (U.S. Salinity Lab. Staff, 1954).

In another set of experiments, the effect of different partial pressures of CO<sub>2</sub> on the rate of hydrolysis was studied. Aqueous suspensions (0.25%) of partially washed clay were continuously stirred for 200 hours in closed systems. One was initially open to the atmosphere and subsequently closed after the addition of the clay. The other suspensions were bubbled with a 5% CO<sub>2</sub> gas mixture which was previously bubbled through distilled water to saturate the gas with water. EC and pH were continuously monitored in both sets of experiments. The final solutions were analyzed as described previously.

### RESULTS AND DISCUSSION

The solution compositions for completely washed clays obtained in each reaction with distilled water are given in Table 1. The data show that adsorbed Ca was hydrolyzed from montmorillonite. The EC of the suspensions increased with time and with the amount of clay present. The EC did not increase linearly with the clay content. As the clay content increased, conductivity increased and proportionally less hydrolysis occurred. This is demonstrated by the values given for the percent Ca hydrolyzed calculated from Ca in solution and corrected for residual CaCl<sub>2</sub>. The more dilute suspensions with lower EC values underwent greater percent hydrolysis as determined by Ca release and final CEC values. One would expect this since the degree of hydrolysis and decomposition should decrease with increasing solution concentration. The data obtained with the second equilibration demonstrate that the clay has the capacity to undergo further hydrolysis upon re-exposure to distilled water. The EC's obtained after the second equilibration were about 75% of those obtained with the first equilibration. The appearance of soluble Mg in solution suggests that adsorbed H replaces structural Mg and Al, which migrates to the clay surface.

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<sup>3</sup>The company name is included for the benefit of the reader and does not imply any endorsement or preferential treatment of the product listed by the U.S. Dept. of Agriculture.

Table 1—Electrical conductivity and solution compositions obtained during the hydrolysis of completely washed Ca montmorillonite in distilled water.

Clay concentration % wt/vol	Solution composition										% Ca <sup>2+</sup> hydrolyzed
	Suspension				EC	pH	Concentration × 10 <sup>5</sup> N				
	pH	EC	EC	EC			Cl	Ca	Mg		
	μmho/cm										
	First equilibration with distilled water										
	After 24 hours	After 360 hours	After 530 hours			After 530 hours					
0.25	9.4	35.2	58.8	59.7	59.6	7.7	2.5	50.0	1.8	20.3	
0.5	9.3	40.4	66.5	71.0	66.7	7.8	2.5	57.0	1.9	11.7	
1.0	9.2	51.4	82.2	91.2	82.1	7.9	2.7	77.0	2.5	7.9	
2.5	8.8	79.4	126.0	136.0	111.0	8.0	3.2	102.0	2.9	4.3	
	Second equilibration with distilled water										
	After 19 hours	After 350 hours	After 830 hours			After 830 hours					
0.25	9.3	40.7	48.2	51.5	47.7	7.8	0.8	44.6	1.9	18.8	
0.5	9.3	42.0	49.7	58.1	53.3	7.9	0.8	49.9	2.0	10.5	
1.0	9.2	46.5	59.2	69.8	62.2	7.9	1.2	57.8	2.3	6.1	
2.5	9.0	60.7	81.7	94.6	77.6	8.0	1.0	71.0	2.1	3.0	

Figure 1 shows the EC vs.  $t^{1/2}$  relationship obtained for the first equilibration period of the completely washed clays. As was found by Shainberg et al. (1974) for Na-montmorillonite, the linear relationship,  $K = K_0 + St^{1/2}$ , where  $K$  is measured specific conductance in  $\mu\text{mhos cm}^{-1}$ ,  $K_0$  is the extrapolated conductance at  $t = 0$ ,  $t$  is time in hours, and  $S$  is the rate constant in  $\mu\text{mhos cm}^{-1} \text{ hr}^{-1/2}$  was found to describe the hydrolysis of Ca montmorillonite ( $r^2$  of 0.96 to 0.99). Each point in Fig. 1 is the average of five replicates. The values of  $S$  found in this set of equilibrations were 2.11, 1.81, 2.22, and 3.07 for the 0.25, 0.5, 1, and 2.5% suspensions, respectively. These values are similar to values of 0.8, 1.4, 1.9, and 3.8 obtained by Shainberg et al. (1974) for Na montmorillonite for the same suspension concentrations (and same method of preparation and equilibration).

The solution compositions for partially washed clays, obtained after each reaction with distilled water, are given in Table 2. As can be seen in Fig. 2, the hydrolysis of the partially washed clays also yielded straight line relationships

between EC and  $t^{1/2}$ . The slopes of the reaction rates obtained (0.88, 1.44, 1.99, and 2.86) for the partially washed suspensions are only slightly smaller than those obtained for the completely washed clays, due to the higher initial electrolyte concentration (which suppresses hydrolysis). Based on the rate constants and the final EC values, it is apparent that Ca hydrolysis is appreciable and at about the same level as Na hydrolysis. Concentrations of Ca found in solution (when corrected for residual  $\text{CaCl}_2$ ) correspond to the levels obtained with completely washed samples (see Table 1). Amounts of hydrolysis were similar in both completely and partially washed treatments, even though the electrolyte concentration was higher in the latter treatment. This indicates that significant hydrolysis occurs during preparation of salt-free clay. Partially washed clay should have a greater capacity for hydrolysis (since it has undergone less hydrolysis during preparation), thus compensating for its higher electrolyte level. By the second washing, the residual salts are negligible and the solution EC and Ca from the partially

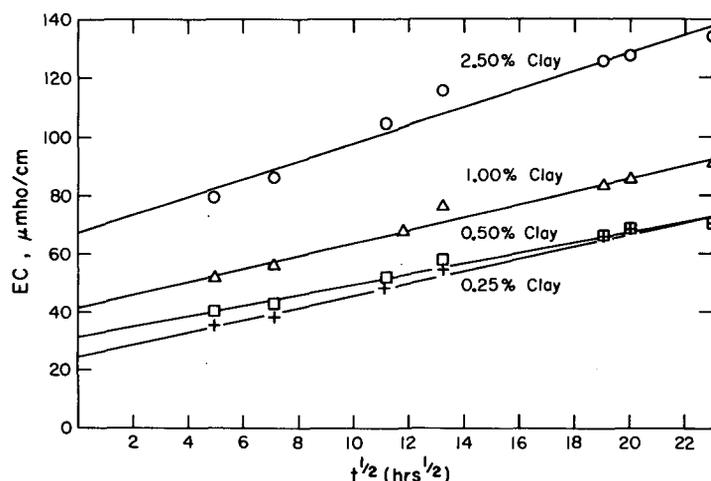


Fig. 1—Electrical conductivity (EC) vs. square root of time ( $\text{hours}^{1/2}$ ) for completely washed clays of 0.25, 0.50, 1.00, and 2.50% w/vol in distilled water. Each point is the mean of five determinations.

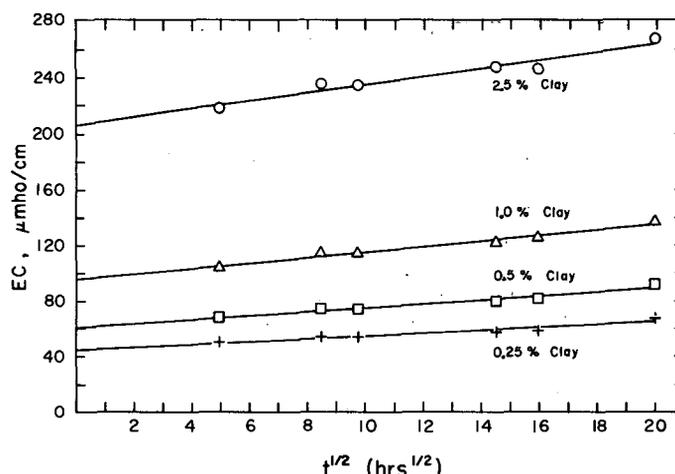


Fig. 2—Electrical conductivity (EC) vs. square root of time ( $\text{hours}^{1/2}$ ) for partially washed clays of 0.25, 0.50, 1.00, and 2.50% w/vol in distilled water. Each point is the mean of five determinations.

Table 2—Electrical conductivity and solution compositions obtained during the hydrolysis of partially washed Ca montmorillonite in distilled water.

Clay concentration % wt/vol	Suspensions				$\Delta$ EC $\mu$ mho/cm	Solution composition					% Ca <sup>2+</sup> hydrolyzed
	EC $\mu$ mho/cm	pH	EC $\mu$ mho/cm	pH		Concentration $\times 10^5$ N			Mg		
						Cl	Ca				
First equilibration with distilled water											
	After 24 hours		After 400 hours			After 400 hours					
0.25	49.5	9.35	67.3	9.05	17.9	65.7	7.72	9.4	56.1	0.9	20
0.5	67.6	9.4	91.3	8.85	23.7	86.6	7.59	19.0	75.2	0.8	12.1
1.0	104.0	9.3	136.0	8.5	32.6	132.0	7.68	37.0	103.0	1.1	7.1
2.5	218.0	8.9	267.0	8.1	48.7	228.0	7.87	84.3	185.0	1.6	4.3
Second equilibration with distilled water											
	After 28 hours		After 364 hours			After 364 hours					
0.25	27.0	9.25	30.2	8.2	5.28	28.3	7.48	0.6	29.9	0.9	12.6
0.5	38.9	9.4	52.6	9.1	13.7	49.1	7.85	1.5	46.3	0.7	9.6
1.0	42.9	9.25	62.6	8.9	19.7	57.0	8.03	2.3	58.1	0.8	6.0
2.5	63.4	8.85	94.6	8.65	31.2	76.6	7.9	4.7	72.0	0.6	2.9
Third equilibration with distilled water											
	After 14 hours		After 422 hours			After 422 hours					
0.25	5.48	7.29	13.2	6.79	7.72	12.5	6.73	0.5	12.8	2.8	5.3
0.5	33.0	9.64	37.3	7.64	43.5	43.5	7.29	0.6	37.5	2.9	7.9
1.0	41.1	9.61	62.1	8.36	70.5	70.5	7.72	0.5	60.2	1.9	6.4
2.5	57.9	9.32	85.2	8.57	81.8	81.8	7.67	0.5	66.9	1.5	2.8

washed clays are higher than in the second wash solution of the washed clay, since partially washed clay has undergone less total hydrolysis.

The exchangeable cations on the completely washed clays at the conclusion of the experiment are given in Table 3. The values shown in this Table are approximately 45 to 75% of the sum of the % hydrolyzed values for the two equilibrations calculated in Table 1. This discrepancy may be the result of the input of Ca from sources other than the exchange sites. Impurities of Ca silicate or CaCO<sub>3</sub> could produce these results; recently, Llorca and Cruz-Romero (1977) detected the presence of CaCO<sub>3</sub> in Wyoming bentonite.

Although impurities would result in higher Ca values in solution than present by hydrolysis of Ca from the exchange sites alone, they would tend to stabilize the Ca-clay (by increasing Ca in solution and raising the pH). Ca-bearing impurities would thus reduce the hydrolysis of Ca clay and result in lower decreases in exchangeable cations. The reductions in CEC in Table 3 would, thus, be less than expected for a pure system. For Na-saturated clays, CaCO<sub>3</sub> would enhance Na hydrolysis, as pointed out by Llorca and Cruz-Romero (1977).

In order to insure that our clay was not contaminated with CaCO<sub>3</sub>, an additional experiment was undertaken. A

Table 3—Exchangeable cations as determined by the NH<sub>4</sub>OAc method.

Clay†	Ca	Mg	$\Sigma$ CEC	Reduction in CEC —%—
	meq/100 g			
Original=Ca clay			93.2	—
Hydrolyzed-Clay from				
0.25% Suspension	65.2	2.25	67.4	28.9
0.5% Suspension	76.8	2.28	79.0	16.2
1.0% Suspension	85.4	2.13	87.5	6.81
2.5% Suspension	88.1	1.91	90.0	3.8

† Ca montmorillonite, chloride-free.

Na-saturated clay was equilibrated with 1N NaCl and 1 atm CO<sub>2</sub>. Repeated equilibrations of the clay were made with the 1N NaCl until Ca levels in solution were below 0.02 meq/liter. The clay was then equilibrated three times with 1N CaCl<sub>2</sub>. The clay was subsequently washed 5 times with distilled water and freeze-dried. Suspensions were prepared as described above and reacted with distilled water. After 169 hours the suspensions EC's were 56.0, 74.7, and 137.5 for 0.5, 1.0, and 2.5%, respectively. These values are very similar (at equivalent times) to those shown in Fig. 1. The slopes of the EC vs.  $t^{1/2}$  curves were also similar to those in Fig. 1. Despite the preparation procedure used, the discrepancy between Ca loss from the clay and Ca in solution was very similar to that found in the data of Table 1 and Table 3. Apparently, a source of Ca (silicate) exists that results in very slow release of Ca (not a CaCO<sub>3</sub> phase). This release results in less hydrolysis from the clay (smaller percent reduction in CEC) but the absolute level of Ca in solution was controlled by the hydrolysis reaction.

In the equilibrations with variable CO<sub>2</sub>, the low CO<sub>2</sub> treatment (initially atmospheric and subsequently closed, so CO<sub>2</sub> decreased as hydrolysis occurred and pH rose) resulted in a much slower rate of hydrolysis (or rise in EC) than did the 5% CO<sub>2</sub> treatment (see Fig. 3). The EC data shown were corrected for KCl leakage from the pH electrode. As shown in Fig. 4, the low CO<sub>2</sub> treatment produced a very sharp rise in pH and then a gradual drop (presumably because CO<sub>2</sub> diffused into the reaction flask). The reaction in the 5% CO<sub>2</sub> treatment produced a relatively small rise in pH, which thereafter remained essentially constant. Undoubtedly the hydrolysis reaction,  $2\text{H}_2\text{O} + \text{Ca}^{2+}_{\text{ex}} = 2\text{H}^{+}_{\text{ex}} + \text{Ca}^{2+} + 2\text{OH}^{-}$ , was inhibited in the low CO<sub>2</sub> treatment by the high pH in solution. Less H in solution resulted in less Ca exchange on the clay surface and, hence, a slower replacement of Al by H. At 5% CO<sub>2</sub>, the greater abundance of H in solution produces more Ca exchange, a lower surface pH, and, thus, faster replacement of Al by H. Our EC vs. time

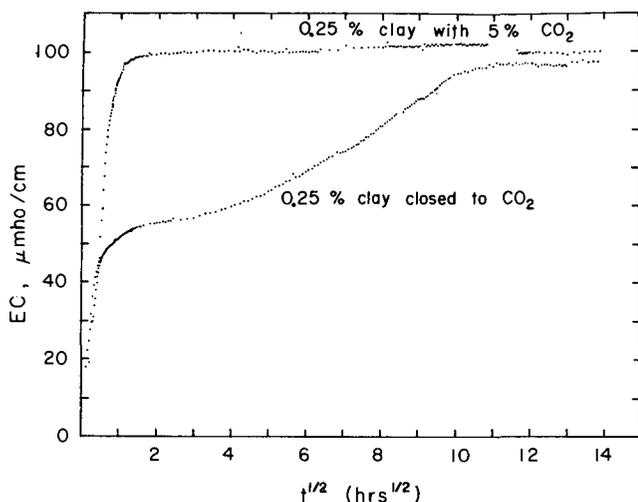


Fig. 3—Electrical conductivity (EC) vs square root of time (hours<sup>1/2</sup>) for 0.25% w/vol partially washed clay in distilled water at 5% CO<sub>2</sub> and in a closed flask (initially atmospheric CO<sub>2</sub>).

relationship is consistent with H-Ca exchange rates given by Banin (1960), indicating that H-Ca exchange rates are not faster than the overall reaction in our study. The rate-limiting step at 5% CO<sub>2</sub> may thus be the exchange of Ca by H. Under both high and low CO<sub>2</sub>, the final EC values obtained were very similar.

The similarity in final EC values for pH = 6 and pH = 8 shown in Fig. 3 may indicate that, at intermediate pH values, surface H concentration is independently controlled by aluminum species, as suggested by Kamil and Shainberg (1968). That Ca montmorillonite hydrolysis has been shown comparable to Na montmorillonite hydrolysis is also consistent with Al control of surface pH. Donnan hydrolysis would predict higher surface pH's for Ca and, thus, less Ca hydrolysis as compared to Na hydrolysis.

As can be readily seen, the data shown in Fig. 3 cannot be represented by a straight-line relationship. The overall reaction rate is governed by different processes during subsequent phases of the experiment and apparently different rate-limiting steps. When the data were fitted to first- and second-order equations, the results were still nonlinear, as were the individual sections of the curves. Under low CO<sub>2</sub> conditions, a plot of conductance vs. hours<sup>1/2</sup> adequately represents the data only during the intermediate phases of the reaction. This section of the curve is analogous to the curves presented in Fig. 1 and 2. The data indicate that the EC vs. hours<sup>1/2</sup> relationship found for Na montmorillonite hydrolysis, and believed to be the result of a diffusion-controlled reaction in the crystal lattice, can also be found for Ca montmorillonite under similar conditions. Changes in P<sub>CO<sub>2</sub></sub> and intensity of mixing for Ca montmorillonite change not only rates but the shapes of the curves as well.

It is not believed that CaCO<sub>3</sub> was significant in either of these treatments. Dissolution of CaCO<sub>3</sub> would have resulted in substantially larger EC values for the high CO<sub>2</sub> treatment than for the low CO<sub>2</sub> treatment; this was not observed. A determination of Ca and alkalinity revealed undersaturation with respect to calcite.

The EC values shown in Fig. 3 are considerably higher than those found in the earlier portion of the study at equiva-

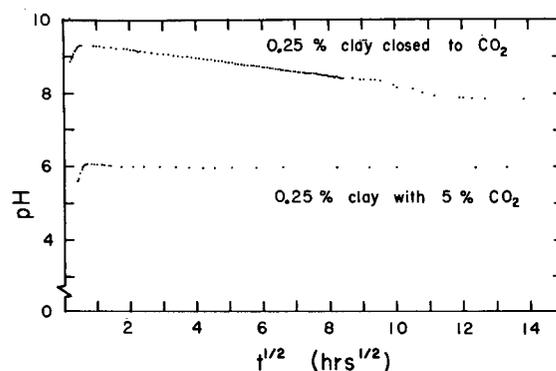


Fig. 4—Square root of time (hours<sup>1/2</sup>) vs pH for 0.25% w/vol partially washed clay in distilled water at 5% CO<sub>2</sub> and in a closed flask (initially atmospheric CO<sub>2</sub>).

lent times (see 0.25% clay data shown in Fig. 2). This may be a result of the more rigorous stirring procedure employed with the latter experiments. If the reaction is dependent on mixing, the more intensely mixed samples should attain equilibrium more rapidly. This is confirmed by the leveling of the EC data at approximately 100 hours for the low CO<sub>2</sub> treatment. Under similar conditions, the atmospheric CO<sub>2</sub> treatment (Fig. 2) would be expected to result in a faster equilibration than the low CO<sub>2</sub> treatment. The effect of the milder stirring in the earlier treatment can be seen in Fig. 2, where equilibrium has not yet been achieved after 400 hours.

## CONCLUSIONS

Our data indicate that substantial hydrolysis of Ca and decomposition of Ca montmorillonite occurs upon reaction with distilled water. The extent and rates of reaction are comparable to those previously reported for Na montmorillonite with the same procedure.

The variation in published CEC values for any of the well-characterized clays (e.g., Wyoming montmorillonite) might be explained by hydrolysis dependent on the number of washings and time of reaction during preparation.

The rate of reaction was found to be highly dependent on P<sub>CO<sub>2</sub></sub> and mixing procedure. With 5% CO<sub>2</sub>, the rate-limiting step may be Ca-H exchange.

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