

DEGRADATION OF HECTORITE BY HYDROGEN ION

By

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ABSTRACT

Hydrogen hectorite-water sol was prepared using mixed-bed ion-exchange resins. At 25° C, the rate of change of concentration with respect to time was determined for (a) strong- and weak-acid hydrogen ions; (b) low molecular weight, unassociated silicates; and (c) soluble, unassociated magnesium ion.

The experimental data indicate that two consecutive first-order reactions are occurring: (1) strong acid is undergoing a rapid, spontaneous reaction to yield weak acid, and (2) the resulting weak acid is undergoing a slow, spontaneous reaction to yield a neutral clay. The equivalent weight of the strong acid is apparently one-half that of the weak acid. For each milliequivalent of strong-acid hydrogen ion undergoing reaction, one milliequivalent of magnesium ion is released from the crystal lattice. Thus, the acid clay is eventually converted to magnesium clay. In addition, for each milliequivalent of weak-acid hydrogen ion undergoing reaction, one millimole of silica is released from the lattice. Since the release of magnesium ion precedes the release of silica, proton attack is probably occurring at the edges of the crystals. The exact nature of the weak acid is unknown and detailed study would probably be difficult in view of its transitory existence.

Freshly prepared acid hectorite contains approximately 40 meq of hydrogen ion per 100 g clay. Therefore, only 3 percent of the total magnesium is released from the lattice. The lattice structure of the resulting magnesium clay is identical with that of natural hectorite as shown by x-ray diffraction.

INTRODUCTION

It has long been recognized and established by a number of workers that clay acids are not simple hydrogen-ion systems (Paver and Marshall, 1934; Chatterjee and Paul, 1942; Mukherjee, Chatterjee, and Gaswanni, 1942). Slabaugh (1952) prepared acid Wyoming bentonite by means of ion-exchange resins. Titration curves of freshly prepared and aged samples showed the fresh material to be predominantly strong acid in character, whereas the aged clay is essentially a weak acid. The recent reports of Coleman and Harward (1953) and Low (1955) show that strong-acid behavior is due solely to hydrogen ion, and the weak-acid properties are attributable to the presence of free aluminum ion.

Osthaus (1954), in extending the work of Brindley and Youell (1951), demonstrated that aluminum, iron, and magnesium in montmorillonite and nontronite are removed by excess acid following a first-order reaction with respect to clay concentration.

In view of these findings, there can be no doubt that acids or hydrogen ion attack the lattices of most clays, particularly montmorillonites, resulting in the release of cations. However, no effort has yet been made to determine the mechanism of proton attack. In the present work sufficient experimental rate data were obtained to propose a tentative mechanism for the attack of hydrogen ion on the lattice of hectorite, a member of the montmorillonite group.

EXPERIMENTAL

An impure colloidal dispersion of 3.5 percent hectorite in water was obtained by vigorous and constant stirring for 36 hours to effect hydration. The dispersion was then twice passed through a Sharples supercentrifuge to remove the major portions of calcite and silica.

Ross and Hendricks (1945) conclude, on the basis of chemical analyses, that hectorite has no tetrahedral substitution for silicon. Hectorite is characterized by containing practically no aluminum or iron, but is essentially a magnesium silicate with isomorphous substitution of lithium for magnesium.

Preparation and Storage of Acid Hectorite

A 3 percent dispersion of hectorite was diluted with ion-free water to yield a 0.95 percent sol. Over a 0.5-hr. period, 1 liter of sol was passed through a 2-inch diameter column containing a 6-inch bed-depth of an intimate mixture of equal volumes of Amberlites IR-120 (hydrogen form) and IRA-400 (hydroxyl form). Work in this laboratory demonstrated that the anion-exchanger removes sulfate ion from the clay, probably present as gypsum. Nitrogen pressure of 5 to 10 psi impressed on the column facilitated flow of sol through the resins.

The first 125-ml portion of the effluent was used immediately for titration and for silica and magnesium analyses as described below. These data were assumed to represent the acid-clay properties at zero time. When one-half of the remaining sol was columned, an electric timer was started. The effluent was stored in a constant temperature bath at $25.00 \pm 0.03^\circ \text{C}$. Appropriate samples were removed periodically from the bath for titration and analysis. The corresponding time, as noted on the timer, was recorded.

Potentiometric Titrations

Twenty-five-gram samples ($25.0 \pm 0.1 \text{ g}$) were titrated with 0.1000 *N* sodium hydroxide solution using a micro-burette graduated to the nearest 0.05 ml. A model H-2 Beckman pH-meter was employed using a glass electrode and a shielded calomel electrode. Agitation was effected with a glass-encased magnetic stirrer. From the titration data the acidity of the clay could be calculated with a precision of ± 2 meq hydrogen ion per 100 g clay.

Analytical Methods

The concentrations of low molecular-weight unassociated silicates were determined spectrophotometrically using the silicomolybdic acid method. The procedure was essentially the same as that reported by Alexander (1953). Free magnesium ion was determined by the versenate method as described by Cheng, Kurtz and Bray (1952). Magnesium ion and calcium ion are determined as a sum. Calcium ion is determined separately and magnesium ion is then calculated by difference; any error in the calcium analysis thus appears as an error in magnesium.

The validity of the analytical methods was demonstrated by the use of pure hectorite sols to which were added known concentrations of sodium metasilicate

and magnesium nitrate. The sols were purified by passage through a mixed-bed ion-exchange column consisting of a cation exchanger in the ammonium form, and anion exchanger in the hydroxyl form. Sols thus prepared were shown to be free of water-soluble magnesium ion and low molecular-weight silicates.

The standard and unknown sol samples were prepared for analysis by the addition of Analytical Reagent Grade sodium chloride followed by batch centrifuging. The clear supernatant liquid was taken for analysis. The use of standard sol samples indicated that the analyses were accurate to approximately ± 5 percent.

RESULTS AND DISCUSSION

Typical titration curves are shown in Figure 1. These curves indicate that freshly prepared clay is essentially a strong acid whereas aged samples consist of both strong and weak acids. Furthermore, the total acidity of the clay decreases with time.

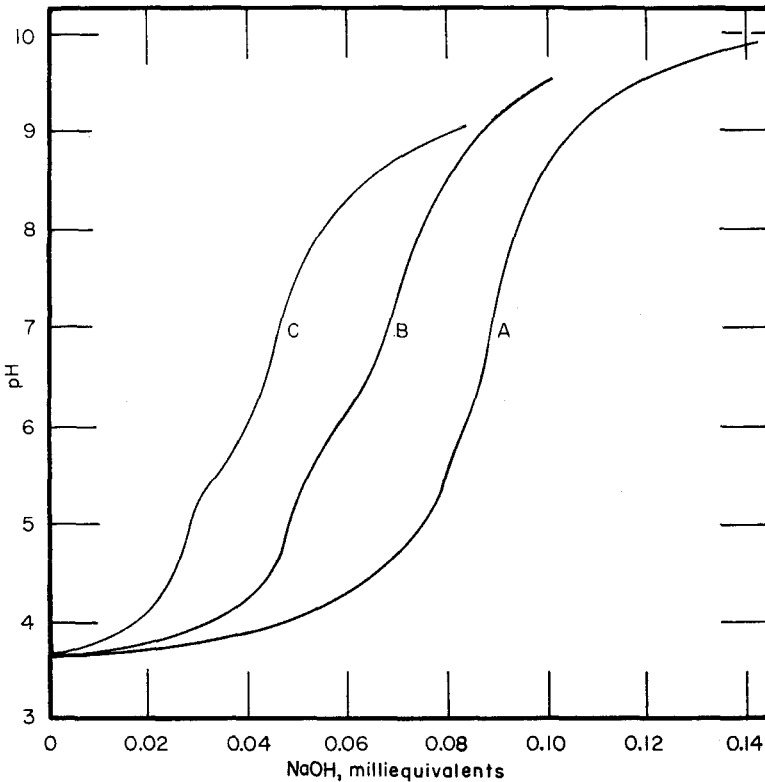


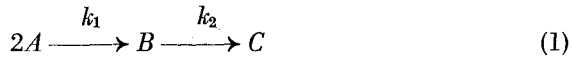
FIGURE 1. — Typical potentiometric titration curves of 25.0-ml samples of 0.95 percent acid hectorite: *A*, fresh sample; *B*, aged 60 minutes; *C*, aged 120 minutes.

In Figure 2 the acid concentrations are plotted logarithmically as a function of time. It will be noted that the total- and strong-acid concentrations closely follow straight lines. The values at zero time deviate somewhat from the lines. This is probably caused by the difficulty of obtaining a true zero-time sample since the columning operation is time consuming. These samples had probably aged 5 to 10 minutes.

The significance of the data presented in Figure 2 can be summarized as follows:

- (a) At zero time, hydrogen hectorite is exclusively a strong acid.
- (b) The strong acid is undergoing a relatively rapid spontaneous first-order reaction to yield a weak acid.
- (c) The weak acid is undergoing a relatively slow spontaneous first-order reaction to yield a nonacidic clay.
- (d) The reaction of strong acid to yield weak acid results in a loss of titratable hydrogen ion.

As shown below, two strong-acid hydrogen ions apparently result in the formation of one weak-acid hydrogen ion. These changes can be expressed mathematically:



Where: A represents strong acid
 B represents weak acid
 C represents nonacidic clay
 Let: a = conc of A at zero time
 x = conc of B formed at time t
 y = conc of C formed at time t
 k_1 = specific reaction-rate constant
 for conversion of A to B
 k_2 = specific reaction-rate constant
 for conversion of B to C

Then: $a - 2x$ = conc A present at time t
 $x - y$ = conc B present at time t
 $a - x - y$ = conc $A + B$ present at time t (total acid)

$$\text{Hence: } -\frac{d[a - 2x]}{dt} = k_1 [a - 2x] \quad (2)$$

$$\text{On integration of (2): } a - 2x = ae^{-k_1 t} \quad (3)$$

$$\text{or } x = \frac{a(1 - e^{-k_1 t})}{2}$$

$$\frac{dy}{dt} = k_2 [x - y] = k_2 \left[\frac{a(1 - e^{-k_1 t})}{2} - y \right] \quad (4)$$

$$\text{On integration of (4): } x - y = \frac{ak_1(e^{-k_1 t} - e^{-k_2 t})}{2(k_2 - k_1)} \quad (5)$$

$$\text{and: } y = \frac{a[k_2(1 - e^{-k_1 t}) - k_1(1 - e^{-k_2 t})]}{2(k_2 - k_1)} \quad (6)$$

$$a - x - y = \frac{2ak_2e^{-k_1 t} - ak_1(e^{-k_1 t} - e^{-k_2 t})}{2(k_2 - k_1)} \quad (7)$$

$$\text{If } k_1 = 2k_2: a - x - y = ae^{-k_2 t} \quad (8)$$

Equations (3) and (8) state that both strong-acid and total-acid concentrations, expressed logarithmically as a function of time, should plot a straight line for the case where $k_1 = 2k_2$. The logarithmic plot of weak-acid concentration versus time, however, should give a curved line as shown by Equation (5).

The curves presented in Figure 2 are based on the theoretical values as calculated from Equations (3), (5) and (8), where:

$$\begin{aligned} a &= 45 \text{ meq H}^+ / 100 \text{ g clay} \\ k_1 &= 1.12 \times 10^{-2} / \text{min} \\ k_2 &= 0.56 \times 10^{-2} / \text{min} \end{aligned}$$

The experimental values agree with the calculated values within the experimental error of the titration, except for zero-time samples (discussed above).

In Figure 3, the upper curve is plotted from Equation (3) and the lower curve from Equation (6). In addition, the concentrations of magnesium ion and free silica are plotted in Figure 3. The zero-time sample was found to contain 1.4 millimoles of silica and 7.4 milliatoms of magnesium ion per 100 g of clay. The subsequent concentrations were reduced accordingly. Thus, the values plotted can be regarded as "corrected" values. Very probably these corrections are too high, since, as previously pointed out, the zero-time sample is actually of finite age. Nevertheless, these data indicate that the release of magnesium ion proceeds simultaneously with the rate of formation of weak acid. Obviously, then, the magnesium-ion release occurs simultaneously with the reaction of strong acid. Moreover, the release of silica from the lattice occurs simultaneously with the reaction of weak acid. In view of these facts, it seems highly improbable that proton attack occurs on the silicate surfaces of the clay. Therefore, it is concluded that attack is initiated at the edges of the crystals.

The following tentative mechanism is proposed: The magnesium and silicon atoms at the crystal edge are each monohydroxylated. The rate-determining step in the first reaction series consists of a proton attacking the magnesium-hydroxyl resulting in the formation of water. The magnesium ion is instantly released from the lattice and a second proton becomes quickly attached to the highly nucleophilic silicon-oxygen system. The resulting dihydroxylated silicon is assumed to be a monobasic weak acid. This acid then undergoes a relatively slow first-order hydrolysis, or depolymerization, to be released from the edge of the lattice as a low molecular-weight silicate or silicic acid. Thus, exchangeable cation in the clay is ultimately magnesium ion. Upon release of magnesium and silica, the freshly exposed crystal edge is identical with the crystal edge before attack. That is, the new terminal magnesium ion and silicon atom are each monohydroxylated.

Magnesium hectorite, prepared in this laboratory by ion-exchange tech-

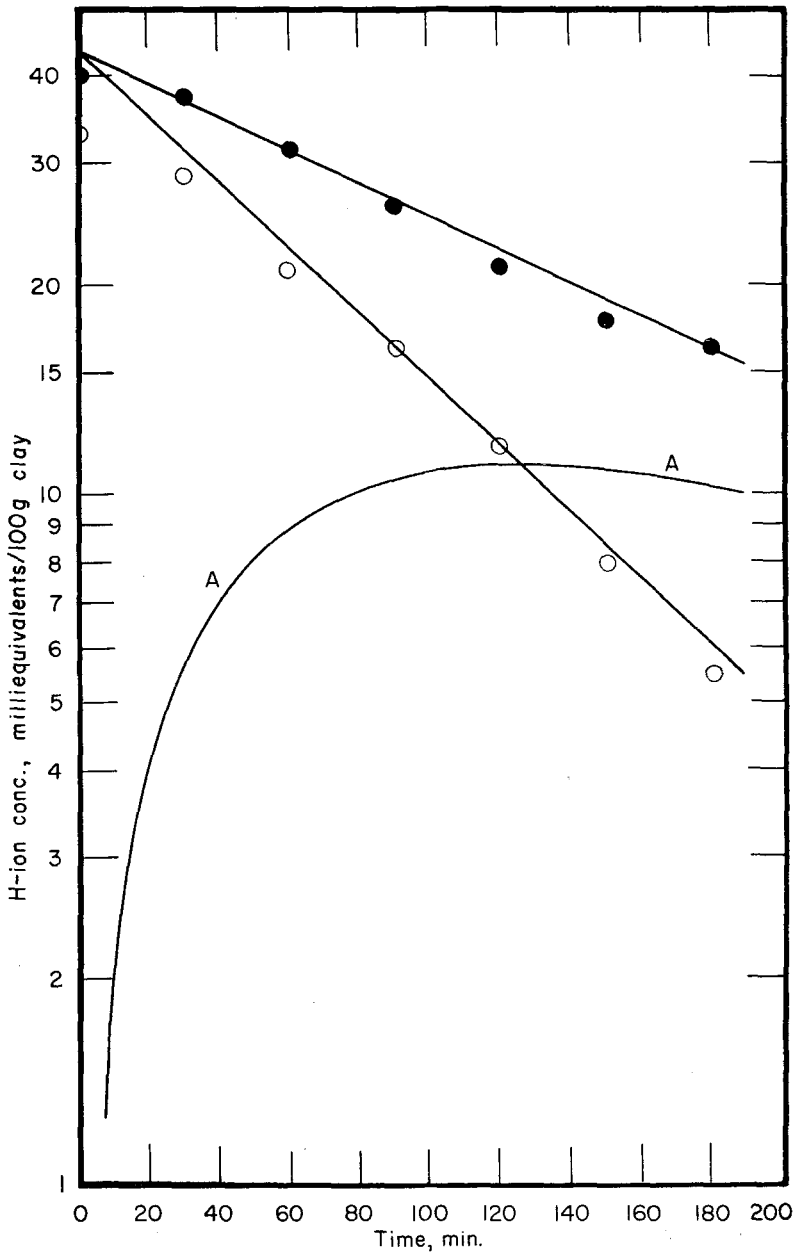


FIGURE 2.—Hydrogen-ion concentrations of acid hectorite versus time: solid circles, total H⁺ concentration; open circles, H⁺ concentration contributed by strong acid; curve A, H⁺ concentration contributed by weak acid (by difference).

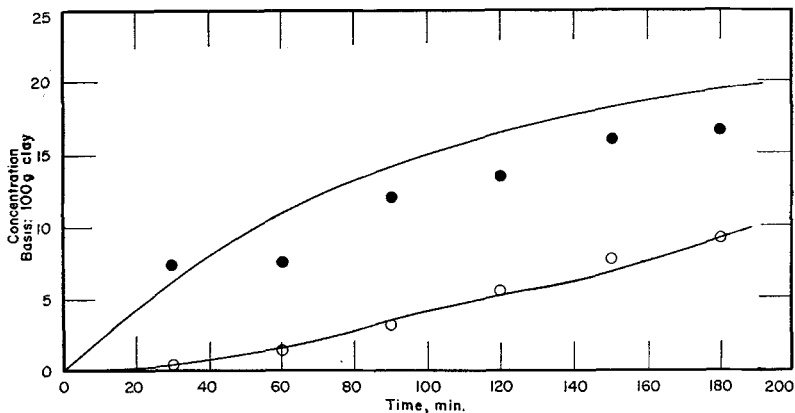


FIGURE 3. — Hydrogen-ion, magnesium-ion, and free-silica concentrations in acid hectorite versus time: solid circles, Mg^{2+} (milliatoms); open circles, free SiO_2 (millimoles); upper curve, total weak acid H^+ formed (milliequivalents); lower curve, weak acid H^+ reacted (milliequivalents).

nique, was found to be nontitratable with sodium hydroxide. Likewise, metasilicic acid, also prepared by ion exchange using sodium metasilicate, was nontitratable. These findings are in agreement with the mechanism.

When the reaction is completed 45 meq or 22.5 milliatoms of magnesium ion are released, compared with approximately 700 milliatoms of magnesium actually present in 100 g of clay. Hence, only a small fraction of the clay lattice is attacked. X-ray diffraction powder pictures demonstrated that the hectorite crystal lattice is intact in aged acid clay.

Previous research (Osthaus, 1954) and the results of the work herein reported suggest that the rate of reaction of protons with clay is actually dependent on the concentration of clay as well as acid. In the present work, the clay concentration is nearly constant compared with the decrease in proton concentration. In the work of Osthaus, the clay concentration was quite small and a large excess of acid was used.

Knowledge concerning the weak acid is inadequate. Because of the transitory existence of this acid, more detailed information of its nature would probably be difficult to obtain. Until such knowledge is acquired any proposed mechanism will be speculative.

An exploratory investigation of the behavior of acid Wyoming bentonite indicated that the rate of reaction at $70^\circ C$ is essentially second-order with respect to hydrogen-ion concentration. Shortly after the beginning of reaction, the rate constant appears to decrease. A complete study of this reaction would be complicated by two factors: (1) in Wyoming bentonite, aluminum ion is proxied for silicon in the tetrahedral layer; and (2) the released aluminum ion gives rise to the existence of a permanent weak acid which might mask the presence of a temporary weak acid.

CONCLUSIONS

Experimental kinetic data have been obtained for the attack of hydrogen ion on the crystal lattice of hectorite at 25° C. Highly dissociated protons in the acid clay attack the lattice following a first-order reaction with a specific reaction-rate constant of 1.12×10^{-2} per minute. The reaction is accompanied by the simultaneous release of magnesium ion and the formation of a weak acid. The equivalent weight of the weak acid appears to be twice that of the strong acid, which suggests that two highly dissociated protons are involved in the initial attack to result in the formation of a monobasic weak acid. The weak acid also reacts following first-order kinetics with a rate constant of 0.56×10^{-2} per minute. The products of this reaction, nonacidic clay and free silica, are formed at the same rate. Consequently, the weak acid appears to be a form of silicic acid which is part of the lattice structure.

Since the release of magnesium ion precedes the release of silica, proton attack is most probably occurring at the lattice edge rather than at the silicate surface. A complete understanding of this reaction awaits more detailed knowledge of the nature of the weak acid. The present data indicate that the clay is ultimately converted to magnesium clay, and for low hydrogen-ion concentrations only a portion of the lattice is attacked. The remainder of the clay is unaltered hectorite and the newly exposed edges are identical with the edge structure prior to attack.

The relative simplicity of its structure makes hectorite an obvious choice for kinetic study. The absence of tetrahedral substitution and the nonacidic nature of the magnesium clay considerably simplify the interpretation of the experimental data. However, an exploratory investigation of a more complicated clay, Wyoming bentonite, suggests that the techniques presented here might be applicable to a variety of clays.

REFERENCES

- Alexander, G. B., 1953, The reaction of low molecular weight silicic acids with molybdc acid: *J. Amer. Chem. Soc.*, v. 75, p. 5655-5657.
- Brindley, G. W., and Youell, R. F., 1951, A chemical determination of the tetrahedral and octahedral aluminum ions in a silicate: *Acta Cryst.*, v. 4, p. 495-497.
- Chatterjee, B., and Paul, M., 1942, Interaction between hydrogen clays and neutral salts: *Indian J. Agr. Sci.*, v. 12, p. 113-120.
- Cheng, K. L., Kurtz, T., and Bray, R. H., 1952, Determination of calcium, magnesium, and iron in limestone: *Anal. Chem.*, v. 24, p. 1640-1641.
- Coleman, N. T., and Harward, M. E., 1953, The heats of neutralization of acid clays and cation exchange resins: *J. Amer. Chem. Soc.*, v. 75, p. 6045-6046.
- Low, P. F., 1955, The role of aluminum in the titration of bentonite: *Soil Sci. Soc. Amer. Proc.*, v. 19, p. 135-139.
- Mukherjee, J. N., Chatterjee, B., and Gaswami, P. C., 1942, Limiting exchange of aluminum ions from hydrogen clays on the addition of neutral salts: *J. Ind. Chem. Soc.*, v. 19, p. 40-407.
- Osthaus, B. B., 1954, Chemical determination of tetrahedral ions in nontronite and montmorillonite: in *Clays and clay minerals*, Natl. Acad. Sci.—Natl. Res. Council Pub. 327, p. 404-417.
- Paver, H., and Marshall, C. E., 1934, The role of aluminum in the reaction of the clays: *J. Soc. Chem. Ind. (London)*, v. 53, p. 750-760.
- Ross, C. S., and Hendricks, S. B., 1945, Minerals of the montmorillonite group, their origin and relation to soils and clays: *U. S. Geol. Survey Prof. Paper 205-B*, p. 23-79.
- Slabaugh, W. H., 1952, The heat of neutralization of hydrogen-bentonite: *J. Amer. Chem. Soc.*, v. 74, p. 4462-4464.