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HYDROLYSIS AND DECOMPOSITION OF HECTORITE IN DILUTE SALT SOLUTIONS[1]

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Abstract—The hydrolysis and decomposition of M-hectorite (M being Na, Li, Mg, or Ca) in dilute solutions of M-chlorides were studied by recording the changes in electrical conductivity (EC) of the clay suspensions with time, and by chemical analyses of the interclay solutions and resulting solid phases. The rate of hydrolysis of the hectorites in suspension, as evaluated by the change of EC with time, was found to decrease with increase in salt concentration (to zero for Na-hectorite in NaCl concentration of 47 meq/liter), and to decrease with increase in the valency of the adsorbed cation (the rate of hydrolysis of Ca-hectorite was one sixth of that of Na-hectorite). The rate of Na-hectorite hydrolysis was determined by the concentration of protons at the clay surface as calculated from the diffuse double layer theory.

Conversely, in suspensions of Al-hectorite saturated with Na, the hydrolysis rates were not dependent on the electrolyte concentrations. This result can be explained by assuming that the hydroxy-Al polymers at the clay surface determine the proton concentration at the clay surface. Hectorites saturated with structural cations (such as Mg and Li) are chemically more stable than those saturated with Na and Ca. The presence of Li and Mg at the clay surface slowed down the diffusion release of these octahedral ions to the clay surface, compared with Na and Ca hectorite, respectively.

Key Words—Electrical conductivity, Hectorite, Hydrolysis, Hydroxy-Al polymers, Salt solution.

INTRODUCTION

The instability of Na-saturated montmorillonite and its transformation into Al- or Mg-saturated products upon leaching with distilled water has been described by Kelley (1951), Barshad (1960), and Bar-On and Shainberg (1970). Recently, Brown and Miller (1971), Shainberg (1973), Frenkel and Suarez (1977), and Llorca and Cruz-Romero (1977) reported that Na-smectites are not stable in dilute salt solutions even when the hydrolysis products are not removed. Shainberg (1973) found that the specific conductance, K, of Na-montmorillonite from Wyoming in suspension increased linearly with the square root of time, namely:

$$K - K_0 = S\sqrt{t}, \qquad (1)$$

where K_0 is the initial specific conductivity, t is the time, and S is an empirical constant which determines the slope of the line. The value of S increased with increasing clay concentration, amount of substitution in the octahedral layer, and temperature. Shainberg *et al.* (1974) showed that the change in specific conductance of the suspensions was a criterion of the degree of advancement of the decomposition of the clay and was related to the amount of Na released to the interclay solution.

To explain this empirical rate law, Shainberg (1973) proposed a mechanism consisting of two consecutive independent reactions, namely, the exchange between adsorbed Na^+ and H^+ from the solution (Donnan hydrolysis) and the penetration of adsorbed protons into the structure to displace octahedral Mg^{2+} and Al^{3+}. The first reaction was assumed to occur rapidly, whereas the second was assumed to occur slowly and to be the rate-determining one.

The latter reaction was found to be first order with respect to the H^+ concentration at the clay surface (Barshad and Foscolos, 1970; Shainberg, 1973) or in the equilibrium solution (Osthaus, 1956) and to involve an interdiffusion of H^+ with octahedral cations (Eeckman and Laudelout, 1961). Kamil and Shainberg (1968) showed that in a montmorillonite suspension of low electrolyte concentration, Donnan exchange equations were determined by the concentration of H^+ at the clay surface. The concentration of H^+ at the clay surface (H_s) explains the instability of M^+-saturated clay in dilute salt solution, and accounts for the driving force for

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the M^+-clay decomposition (Shainberg, 1973). The concentration of H^+ at the clay surface was calculated using Gouy-Chapman theory (Kamil and Shainberg, 1968) which can be modified to include the selectivity coefficient of the H^+–M^+-exchange reaction.

This mechanism was applied successfully to explain the hydrolysis and dissolution of Na-montmorillonite (Shainberg, 1973; Shainberg *et al.*, 1974) and Na-illite (Feigenbaum and Shainberg, 1975). However, some deviations from the mechanism were reported for dioctahedral smectites: Shainberg *et al.* (1974) observed that the rate of hydrolysis was independent of the initial salt concentration between 0.1 and 6.0 meq/liter, and consequently of the H^+_s concentration predicted by Donnan exchange. Frenkel and Suarez (1977) observed a similar hydrolysis rate for Na- and Ca-montmorillonites. They suggested, following Kamil and Shainberg (1968), that the H^+_s concentration of dioctahedral smectites was buffered by the presence of hydroxy-Al-polymers according to the following reaction:

$$[Al(H_2O)_5OH]^{2+} + H_3O^+ = [Al(H_2O)_6]^{3+} + H_2O \quad (2)$$

The pK of the reverse of this reaction in solution, which is the pK of hydrolysis of $[Al(H_2O)_6]^{3+}$, is 5 (Jackson, 1963). This dehydroxylation results in buffering the H_s concentration between 10^{-5} and 10^{-6} mole/liter, depending upon the actual pK of the dehydroxylation reaction. It was postulated that the rate of clay decomposition was proportional to the proton concentration at the clay surface. Thus, the presence of hydroxy-Al polymers, which prevent high concentration of H^+_s at the surface, control the decomposition process at a uniform rate.

The objectives of the present work were to study (1) the chemical stability of a nearly Al-free smectite, hectorite, in dilute salt solutions, (2) the effect of the exchangeable cation on the chemical stability of the clay, and (3) the effect of artificially introduced Al on these reactions. The information obtained will enable the proposed mechanism to be tested and its validity to be extended over a wide range of experimental conditions, as well as the effect of hydroxy-Al on the dissolution rate of clays, to be determined.

MATERIALS AND METHODS

Hectorite from Hector, California (A.P.I. No. 34a) was used in this study. The structural formula of this clay is $(Mg_{5.42},Li_{0.68},Al_{0.016})^{VI}(Si_8)^{IV}O_{20}(F,OH)_4Na_{0.66}$ (American Petroleum Institute, 1951). The clay was hand-ground and then stirred continuously in a 1.0 N NaCl solution. To remove carbonate impurities, 0.1 N HCl solution was added slowly to the suspension, which was maintained at pH $\geq$ 5. Carbonate was assumed to be absent when the pH stabilized at pH 5 for a two-hour period.

The hectorite was subsequently Na-saturated by three washings with 1.0 N NaCl (clay/solution ratio of 1/15), excess salt was removed by washing twice with distilled water, and the clay was then resuspended for size fractionation in distilled water (2%). The <2-μm fraction was siphoned out of the suspension and concentrated in 1.0 N NaCl. The cation-exchange capacity (CEC) of the clay fraction, as measured by the ammonium acetate method (Black, 1965), was 80 meq/100 g. The clay was then saturated with Na, Ca, Mg, and Li cations by four successive washings with 1.0 N chloride solutions of the respective cations (clay/solution ratio of 1/15). Part of the hectorite clay was also Al-saturated by five washings with a 1.0 N $AlCl_3$ solution. Following the procedure of Frink and Peech (1963), the excess salt was removed and the Al-hectorite was equilibrated for one week in a 0.1 N NaCl solution containing $Mg(HCO_3)_2$ (62 meq/100 g of clay). This hectorite fraction was subsequently Na-, Ca-, Mg-, and Li-saturated as described above. The M-hectorite clays (M = Li, Na, Ca, Mg) in 1.0 N chloride solutions were washed once or twice with 10^{-3} M chloride solution. For the lower initial salt concentration an additional washing with 10^{-4} M chloride solution was carried out. The range of initial salt concentrations investigated was from 10^{-4} N to 0.06 N. The clay concentration in the suspension was 2 or 1.2% (w/v).

Plastic vials containing the suspensions were sealed hermetically and shaken continuously in a water bath at 30°C for two weeks. Specific conductance and pH were measured periodically. For some of the Na-clay suspensions, changes in the chemical composition of the interclay solution were also followed. At the end of the experiments, the clays and the interclay solutions were separated by centrifugation, and each phase was analyzed for its chemical composition. The exchangeable cations and CEC were analyzed by the ammonium acetate method. Li and Na concentrations were measured by flame photometry, Ca, Mg, and Al by atomic absorption spectroscopy, Cl by titration with $AgNO_3$ using a chloridometer, and Si by the ammonium molybdate colorimetric method (Black, 1965). Following the two weeks of shaking, centrifugation, and removal of the supernatant solution, some of the hectorite suspensions were resuspended in fresh solutions of the same initial salt concentration. The clay suspensions were shaken and their pH and EC recorded. As many as four shaking cycles were performed with some of the samples.

RESULTS AND DISCUSSION

The specific conductance, K, of Na-hectorite suspensions (Figure 1) and the corresponding ionic concentrations of the interclay solution (Figure 2) both increased linearly with the square root of time. The slope of the EC line, S, depended on the initial salt concentration, and dissolution of structural cations followed

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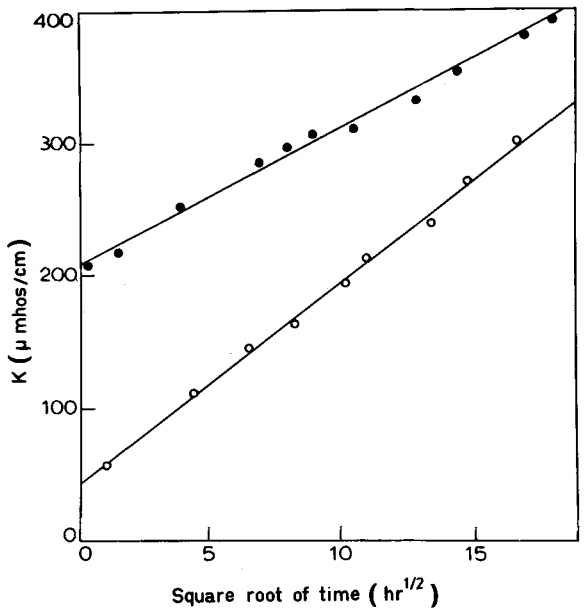


Figure 1. Electrical conductivity of 1.2% (w/v) Na-hectorite suspensions (in 0.1 and 2.2 meq/liter NaCl solutions) as a function of the square root of time. The symbols ○ and ● denote 0.1 and 2.2 meq/liter NaCl, respectively.

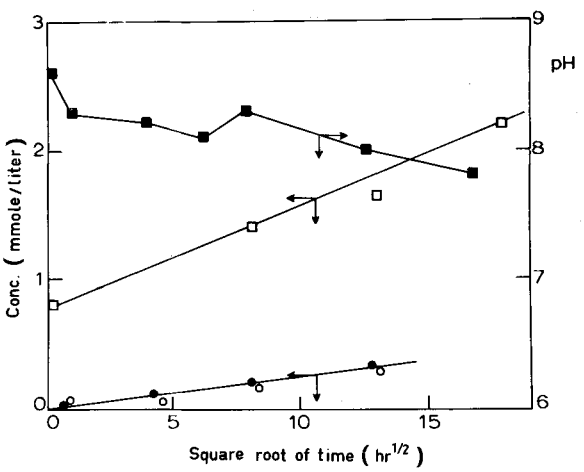


Figure 2. Changes in the chemical composition of the interclay solutions with the square root of time (□ = Na; ○ = Mg × 10; ● = SiO_2; ■ = pH).

a rate law similar to that which described the release of the exchangeable cations. The slope of the K lines for hectorite suspensions with various initial salt concentrations and various exchangeable cations, and during the successive shaking cycles, are presented in Table 1. The slope values of the Ca-, Mg-, and Li-hectorite suspensions were adjusted with respect to the EC of the Na-hectorite system by considering the equivalent conductance of the various cations in dilute solutions. These adjusted slope values are also presented in Table 1 as is the chemical composition of the supernatant solutions extracted at the end of the shaking treatments. By comparing the EC of the suspensions with the chemical data of the supernatant, it is evident that the increase of the M^+ and M^{2+} concentration in the interclay solution was the main cationic contribution to the EC changes.

The linear change in EC of the hectorite suspensions is expressed by Eq. (1) and is similar to that obtained by Shainberg *et al.* (1974) for various dioctahedral montmorillonites. One would therefore expect, *a priori,* that hectorite follows the same reaction mechanism as that proposed for dioctahedral smectites (Shainberg, 1973; Shainberg *et al.*, 1974). From the data in Table 1, the following effects are apparent:

Effect of salt concentration

That the rate of hydrolysis decreased with the increase in initial salt concentration is clearly illustrated by the results obtained with 1.2% Na-hectorite suspensions. Here a gradual decrease in the hydrolysis rate, down to zero, was obtained for NaCl concentrations increasing from 0.1 to 47 meq/liter. Kamil and Shainberg (1968) postulated that the driving force of the hydrolysis reaction is the H^+ concentration at the clay surface, H^+_s. This concentration may be estimated, for various Cl^- concentrations, using the Boltzmann equation:

$$H^+_s = H^+_0 \exp(e\psi_s/kT) \qquad (3)$$

where H^+_0 is the H^+ concentration in the interclay solution, e is the electronic charge, ψ_s represents the electrical potential at the clay surface in e.s.u. units, k is the Boltzmann constant, and T is the absolute temperature. The term ψ_s can be calculated from diffuse double layer theory (Van Olphen, 1963). The H^+_s value computed in this way for the various Na-clay suspensions are also presented in Table 1. These data show that increasing the salt concentration in the suspension resulted in a decrease in the proton concentration at the clay surface, and consequently in a decrease in the dissolution rate of Na-hectorite. As postulated by Shainberg (1973), the rate-limiting step of the reaction was the penetration of adsorbed H^+ into the lattice with the release of octahedral cations, which depended linearly on the H^+_s concentration.

Effect of the exchangeable cation

Ca-hectorite. The rate of hydrolysis of Ca-hectorite was about one-sixth of that measured for Na-hectorite when the other parameters (clay and salt concentration) were held constant. According to the diffuse double layer theory, the value of H^+_s in Eq. (3) for a clay saturated with divalent cation is half that for one saturated with a monovalent cation when the electrolyte concen-

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Table 1. Rates of dissolution of Na-, Ca-, Mg-, and Li-hectorite suspensions, chemical composition of supernatant solutions, and computed H^+_s values.

Exchange cation	Clay conc. (%) (w/v)	Cl^- conc. (meq/liter)	Slope (μmho/cm/hr$^{1/2}$)	Slope adjusted (μmho/cm/hr$^{1/2}$)	H^+_s [(eq/liter) $\times 10^6$]	M (meq/liter)	SiO_2 (mmole/liter)	Mg (meq/liter)	pH
				First shaking cycle					
Na	1.2	47.4	0.0	—	2.012	47.4	0.13	0.007	8.1
	1.2	7.9	4.8	—	9.44	10.1	0.31	0.04	8.1
	1.2	2.2	8.4	—	19.47	4.9	0.30	0.037	8.1
	1.2	1.6	10.4	—	63.9	2.98	0.77	0.165	7.8
	1.2	1.2	12.6	—	87.3	2.18	0.12	0.117	7.8
	1.2	0.1	15.1	—	87.3	2.18	0.71	0.535	7.8
	2.0	4.6	5.9	—	4.95	6.1	0.1	0.116	8.6
	2.0	3.5	6.7	—	6.56	4.6	0.1	—	8.6
Mg	2.0	2.34	0.67	0.65	2.21	2.46	0.026	2.46	7.5
	2.0	1.85	1.8	1.75	1.85	2.21	0.031	2.21	7.0
Ca	2.0	2.88	1.1	1.0	0.17	3.02	0.024	0.29	8.55
	2.0	1.34	3.1	2.82	0.08	1.69	0.014	0.17	9.8
Li	2.0	6.25	3.9	4.44	24.5	6.92	0.100	—	7.85
	2.0	4.4	3.0	3.42	24.66	4.87	0.105	—	8.0
	2.0	1.5	3.2	3.65	41.27	2.06	0.100	—	8.15
				Second shaking cycle					
Na	1.2	5.6	2.8	—	8.6	6.99	0.145	0.286	8.3
	1.2	1.2	5.1	—	38.85	1.95	0.23	0.444	8.2
	1.2	0.35	9.3	—	100.1	1.51	0.218	0.260	7.9
				Third shaking cycle					
Na	1.2	1.2	4.2	—	24.46	2.46	0.422	0.275	8.3
	1.2	0.48	6.1	—	165.2	1.45	0.567	0.259	7.7

tration in the suspension is kept equal. Accordingly, a lower surface concentration of H^+ is expected for a clay saturated with divalent cation than for one saturated with monovalent cation. It is evident from Table 1 that the H^+_s concentrations for Ca-hectorite suspensions are about two orders of magnitude lower than those for Na-clay suspensions. The low H^+ concentration at the surface of Ca-hectorite clay explains the low hydrolysis rate of this clay. However, the real concentrations of adsorbed H^+ in Ca-hectorite were probably higher than those presented in Table 1. In the Gouy calculation it was usually assumed that the platelets are far apart. However, in Ca-montmorillonite, tactoids or quasi-crystals are formed with extensive overlapping of the diffuse double layers (the d(001) spacing between the platelets in a Ca-tactoid is 18.9 Å). As a result of the overlapping, the electrical potential at the clay surface increases (Van Olphen, 1963), and the concentration of adsorbed H^+ increases.

The suspension pHs recorded for Ca-hectorite were higher than those observed for the other M-hectorite suspensions (Table 1). Moreover, the pH values, at the end of the shaking (when the system tends to equilibrate with atmospheric CO_2), were close to the computed values for a system where the pH is controlled by a calcite phase:

$$pH + 1.2 \log(Ca^{2+}) = 4.92 - \tfrac{1}{2}pCO_2 \qquad (4)$$

It is postulated that a Ca-hectorite suspension was transformed spontaneously into a hectorite-calcite-solution system and that the presence of calcite accounted for the higher suspension pH and lower H^+_s concentration and, hence, for the higher stability of the Ca-saturated clay.

Mg-hectorite. The rate of hydrolysis of the Mg-saturated clay (Table 1) was lower than that found for Ca-hectorite. The difference between Ca- and Mg-hectorite becomes more significant if the difference in the pH of the suspension (7.5 and 8.5–9.0 for Mg- and Ca-suspensions, respectively) is considered. The lower pH of Mg-clay suspensions renders the computed H^+_s concentrations much higher for the Mg-clay than for the Ca-hectorite. Thus, exchangeable Mg must exert a specific rate-reducing effect on the hectorite-hydrolysis. It is possible that Mg, also an octahedral cation in the hectorite structure, stabilized the clay by slowing down the diffusion of structural Mg towards the clay surface. The presence of a high concentration of Mg at the clay surface would slow down the release and diffusion of the octahedral Mg out of the framework and hence reduce the overall reaction rate.

Li-hectorite. The hydrolysis rates of the Li-hectorite suspensions were lower than those found for the Na-clay suspensions at the same concentrations of clay and

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salt in the suspensions (Table 1). The H^+_s concentrations, estimated for both Li- and Na-clays, however, were of the same magnitude. It thus appears that exchangeable Li also exerts a specific effect on the rate of hydrolysis, and that this effect is superimposed on the relationship between the H^+_s concentration and the reaction rate. A similar effect was obtained for Mg-hectorite. It should be remembered that both cations are about the same size (0.65 and 0.60 Å for Mg^{2+} and Li^+, respectively) and that both fit into the octahedral sheet. Moreover, both constitute part of the hectorite structure. Thus, the specific effect of Li may be explained by a mechanism similar to that of Mg, namely, slowing down of the interdiffusion of the octahedral cation into the exchange phase by reducing the driving force for the diffusion. It is also possible that the specific effect exerted by Li and Mg is of a more general nature, namely, that the presence of a cation which may occupy the octahedral sites reduces the rate of clay decomposition.

Effect of clay concentration

From the results obtained in this study it is not possible to determine the influence of clay concentration on the hydrolysis rate, due to the simultaneous variation of other parameters (pH and salt concentration). Nevertheless, the data on dioctahedral montmorillonite obtained by Shainberg (1973) and by Shainberg *et al.* (1974) suggest that the rate of EC increase, S, is linearly related to the square root of the clay concentration in the suspension. This relationship was also predicted by the reaction model proposed by Shainberg (1973). A similar trend was observed in this study with hectorite clay suspensions.

Effect of shaking cycle

Table 1 shows that when clay and salt concentrations were held constant the rate of Na-hectorite hydrolysis decreased gradually from one shaking cycle to the next. For example, in suspensions with 1.2 meq/liter of NaCl the S values were 10.4, 5.1, and 4 mho/cm/$hr^{1/2}$ for three successive shaking cycles. One explanation of this phenomenon is that as the hydrolysis proceeded, the concentration of negative sites saturated with Na and available for further hydrolysis decreased from one batch to the next. Since the rate of EC increase is linearly related to the square root of the clay (or exchange sites) concentration in the suspension, it is expected that a decrease in adsorbed Na will be accompanied by a decrease in the decomposition rate. However, in suspensions with 1.2 meq/liter NaCl, only 20% and 8% of the exchangeable Na were released during the first and second cycles, respectively. It is thus obvious that the decrease in concentration of Na-saturated sites alone cannot account for the considerable changes in the reaction rates observed, and that an additional explanation is needed.

Considering the reaction mechanism of Shainberg (1973), it is expected that during decomposition, exchangeable Na will be replaced by octahedral Mg and that the proportion of exchange sites saturated with Mg cations will therefore increase in successive shaking cycles. Since exchangeable Mg slows down the hydrolysis rate and increases the chemical stability of the clay, it is likely that the progressive decrease in hydrolysis rate obtained when subjecting the clay to successive shaking cycles was due mainly to the increase in Mg concentration at the clay surface. Our data indicate that when 20% and 28% of the exchange sites are Mg-saturated the reaction rate is reduced, respectively, to 50% and 40% of the rate of decomposition of homoionic Na-clay suspensions. Complete Mg-saturation of the exchange sites (Table 1) reduced the hydrolysis rate to about 10% of that of the Na-clay suspension.

Effect of Al presence on the clay

Increasing the salt concentration (from 0.1 to 6 meq/liter) in a Na-saturated dioctahedral smectite suspension had no influence on the rate of the dissolution reaction (Shainberg *et al.*, 1974). Similarly, Frenkel and Suarez (1977) observed a similar hydrolysis rate for both Ca- and Na-saturated montmorillonite suspensions. Conversely, with hectorite, a clay mineral with very little structural Al, the hydrolysis rate was found to depend on both the salt concentration and the exchangeable cation, and this dependence could be predicted on the basis of the concentration of H^+ at the clay surface. The difference between hectorite and the other smectites may be explained by the presence of Al and hydroxy-Al polymers in the dioctahedral smectite suspensions. This hypothesis was tested in the following way: Hectorite clay was artificially saturated with hydroxy-Al polymers using the procedure described by Frink and Peech (1963). The Al-hectorite was subsequently saturated with Na, Ca, Mg, and Li, and its chemical stability in low salt solution was studied. As a result of the treatment, the CEC of the clay dropped from 80 to 52.6 meq/100 g. According to Frink and Peech (1963), clay dissolution occurring during the Al-saturation process accounted for a CEC reduction of 10 meq/100 g. The remaining 17.4 meq/100 g drop was caused by the fixation of Al polymers and by charge blocking. When Al-hectorite was submitted to $NaNO_3$ treatment for 6 hr (Frink, 1965), 21.7 moles of nonexchangeable Al was extracted per 100 grams of clay. Frink and Peech (1963) concluded that the Al-coating treatment resulted in the deposit of hydroxy-Al polymers with an OH/Al molar ratio of about 2.20. This value is in agreement with those usually reported for such polymers (Barnishel, 1977).

The EC of the various M^+- and M^{2+}-Al-hectorite suspensions also increased linearly with the square root of time. The slopes and the adjusted slopes (accounting

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Table 2. Rate of dissolution of Al-coated, Na-, Ca-, Mg-, and Li-hectorite suspensions and chemical composition of the supernatant solutions.

Exchangeable cation	Clay conc. (%) (w/v)	Cl (meq/liter)	Slope (μmho/cm/hr$^{1/2}$)	Adjusted slope[1] (μmho/cm/hr$^{1/2}$)	H^+_s (eq/liter $\times 10^5$)	Chemical analysis of interclay solution			
						Cation (meq/liter)	SiO_2 (mmole/liter)	Mg (meq/liter)	pH
Na	2	12.20	4.4	—	1.342	12.64	0.082	0.0181	5.85
		2.37	4.0	—	2.172	2.47	0.049	—	6.35
		2.00	4.8	—	1.768	2.41	0.039	—	6.45
		0.95	3.6	—	2.198	1.54	0.0313	—	6.55
Ca	2	0.36	5.2	4.73	0.003	1.18	0.009	0.029	7.6
		0.14	5.0	4.55	0.008	0.46	0.013	0.066	7.3
Mg	2	0.46	0.83	0.81	0.174	0.50	0.013	0.50	5.95
		0.26	0.77	0.75	0.155	0.25	0.0186	0.25	6.15
Li	2	2.6	2.0	2.28	2.090	2.88	0.063	—	6.3
	2	1.8	1.54	1.75	1.972	2.16	0.052	—	6.45

[1] Accounting for the equivalent conductivities of the various cations (in comparison to Na).

for the equivalent conductivity of the various cations) of the EC lines and the chemical composition of the interclay solutions extracted at the end of the shaking experiments are recorded in Table 2. It is evident that for Al-clay, the rate of hydrolysis was unaffected by the initial salt concentration. In addition, a similar hydrolysis rate was obtained for both Na- and Ca-hectorite suspensions. No relationship was found between the rate of exchangeable-cation release and the computed H^+_s concentration (Table 2). For instance, similar reaction rates were noted for the Na- and Ca-hectorites, in spite of a three orders of magnitude difference in the computed H^+_s concentrations. Thus, the presence of Al-polymers at the clay surface must control the surface concentration of H^+, and subsequently the rate of hydrolysis and dissolution of the clay is independent of both the salt concentration in the interclay solution and the valence of the exchangeable cation. The slopes obtained for Na- and Ca-saturated, Al-coated hectorite were similar to those obtained for Na-hectorite in about 5 meq/liter solutions (Table 1). H^+_s of the Na-hectorite suspension at this solution concentration was estimated at 10^{-5} N (Table 1); thus, if the H^+_s concentration determined the rate of hydrolysis, the concentration of H^+_s at the surface of Al-coated clay is also 10^{-5} N, irrespective of the salt concentration and the type of exchangeable ion. A similar value for H^+_s was suggested by Kamil and Shainberg (1968) that is within the second buffer range observed by Schwertmann and Jackson (1964) by titrating partially neutralized Al-hydroxy-solutions. It should be emphasized that for Na-hectorite suspended in dilute NaCl solutions (less than 5 meq/liter), a deposit of Al-polymers on the clay surface has the effect of controlling the H^+_s concentration at levels lower than those expected from double layer theory. Thus, in this case, the presence of Al-polymers acts as a stabilizing factor for the clay. The reverse is true for Ca-saturated clay, in which Al has the effect of controlling the H^+_s concentration at a level which is higher than that predicted from double layer theory, and thus appears to promote instability in the clay.

Mg- and Li-saturated, Al-coated hectorites hydro-

Table 3. Clay dissolutioin as a result of hydrolysis.

Treatment	Exchangeable cations released (meq/100 g clay)	Mg released (meq/100 g)	Si released (mmole/100 g)	CEC reduction (meq/100 g)
Na-clay				
1 cycle in 10^{-3} N solution	5.46	4.44	0.46	2.90
1 cycle in 10^{-3} N solution	7.44	7.57	0.63	4.05
3 cycles in 10^{-4} N solution	44.0	41.35	9.2	31.9
Ca-clay				
1 cycle in 10^{-3} N solution	2.43	7.13	0.08	3.76
1 cycle in 10^{-4} N solution	6.29	10.94	0.13	2.9
Li-clay				
1 cycle in 10^{-4} N solution	3.36	10.68	0.5	0

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lyze much more slowly than the other M-saturated clay (Table 2). The specific effect of these structural cations on the reaction rate is evident in Al-coated clays as well.

Suspension pH. For both untreated and Al-hectorite, the pH of the suspension measured at the beginning of the shaking experiment was higher than that predicted by assuming equilibrium with atmospheric CO_2. This was also observed for dioctahedral smectites (Llorca and Cruz-Romero, 1977). At the end of the shaking experiments, however, the pH of the hectorite suspension coincided with the calculated equilibrium value, whereas the pH of the Na-saturated, Al-clay suspension was significantly lower than the equilibrium pH value. This suspension acidification, reported by Llorca and Cruz-Romero (1977) for dioctahedral smectites, was also obtained with Al-hectorite, suggesting that the presence of Al and hydrolysis in the system are responsible for the phenomenon postulated by these authors.

Clay dissolution

The amounts of exchangeable cations, octahedral Mg, and tetrahedral Si released by the clay during the shaking treatments are presented in Table 3. For Na-hectorite, the amounts of Mg and Si released from the clay were proportional to the amount of exchangeable Na that had been removed. For Na-hectorite, at least, this relation is stochiometric, and one equivalent of octahedral Mg (most of which remains on the exchange sites) is released for each equivalent of exchangeable Na removed. The same relationship was not evident for Ca- and Li-saturated hectorites, where the amount of Mg released from the framework was greater than the amount of adsorbed cations released.

The hydrolysis reaction proceeded also with the tetrahedral sheet dissolution although more slowly than that of the octahedral sheet (Table 3). The extent of hectorite dissolution accompanying exchangeable cation release is thus highly unexpected. The CEC values of the clays dropped slightly during the hydrolysis reaction (Table 3), indicating that the rate of dissolution of the octahedral sheet, where the charge originated, was more rapid than that of the tetrahedral sheet. Thus, as a result of dissolution the weight of the clay diminished, but more slowly than the charge. The differences in the rates of octahedral and tetrahedral dissolution were especially pronounced in Na-hectorite subjected to three cycles of shaking. In this case, the amount of Mg released was 41.35 meq/100 g and that of Si was only 9.2 mmole/100 g, leading to a change in CEC of 31.9 meq/100 g.

CONCLUSIONS

Al-free hectorite appears to be a good model for studying the mechanism of M^+-smectite hydrolysis in dilute salt solution proposed by Shainberg (1973). Any modifications which result according to double layer theory, in a decrease in the proton concentration at the clay surface, such as increasing the salt concentration or saturating the clay with a divalent cation, reduce the hydrolysis rate. This observation supports the hypothesis that the rate-limiting step of the overall hydrolysis reaction is the protonic dissolution of the octahedral sheet and that the reaction rate depends on the proton concentration at the clay surface.

The rate of hydrolysis of the clay saturated with octahedral cations (Li or Mg) was lower than that of either the Na- or Ca-saturated clay. The slow rate of dissolution can be explained in terms of the diminished driving force for the octahedral cation to interdiffuse towards the adsorbed phase. An Al-hectorite behaves like the dioctahedral smectites investigated previously. The same deviations from the model occur, i.e., the reaction rate is independent of the solution concentration and the valency of exchangeable cation (Na vs. Ca). Comparison between a pure untreated and an Al-hectorite shows that the presence of hydroxy-aluminum polymers buffers the H^+ concentration at the clay surface, and is thus the dominant factor in determining the rate of the clay dissolution. Al is a constituent of most of the clay minerals and under natural conditions is present at the clay surface of these minerals. The buffer effect of hydroxy-Al polymers is, therefore, a common phenomenon in nature.

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Резюме—Исследовались гидролиз и реакция разложения М-гекторита (где М то Na, Li, Mg, или Ca) в разбавленных растворах М-хлоридов путем регистрации изменений по времени электрической проводимости (ЭП) глиновых суспензии и путем химического анализа межглиновых растворов и получающихся твердых тел. Скорость гидролиза гекторита в суспензии, получаемая путем изменений ЭП по времени, уменьшалась с увеличением концентрации соли (полностью исчезая для Na-гекторита при концентрации NaCl равной 47 мэкв/литр), а также с увеличением валентности адсорбированного катиона (скорость гидролиза Ca-гекторита составляла одну шестую величины для Na-гекторита). Скорость кидролиза Na-гекторита определялась по концентрации протонов на поверхности глины как это вычисляется по теории диффузионного двойного слоя.

В противоположность, в суспензиях Al-гекторита, насыщенного Na, скорости гидролиза были независимы от концентрации электролита. Этот результат можно объяснить принимая, что гидрокси-алюминиевые полимеры на поверхности глины определяют концентрацию протонов на поверхности глины. Гекториты, насыщенные структурными катионами (такими как Mg и Li), являются химически более стабильными, чем гекториты, насыщенные Na и Ca. Присутствие Li и Mg на поверхности глины замедляло диффузионное освобождение этих октаэдрических ионов на поверхности глины по сравнению с Na- и Ca-гекторитами, соответственно. [E.C.]

Resümee—Es wurde die Hydrolyse und Zersetzung von M-Hektorit (M = Na, Li, Mg, oder Ca) in verdünnten Lösungen von M-Chloriden untersucht. Dazu wurde die Änderung der elektrischen Leitfähigkeit (EC) der Tonsuspensionen im Laufe der Zeit verfolgt, und die Lösungen in den Zwischenschichten sowie die neugebildeten Festphasen chemisch analysiert. Wie aus der Veränderung der EC im Laufe der Zeit hervorgeht, nimmt die Hydrolysegeschwindigkeit der Hektorite in der Suspension mit zunehmender Salzkonzentration ab (bis auf 0 für Na-Hektorit bei einer NaCl-Konzentration von 47 mÄq/Liter), sowie bei zunehmender Wertigkeit der adsorbierten Kationen (e.g., die Hydrolysegeschwindigkeit von Ca-Hektorit war nur $^1/_6$ von der des Na-Hektorits). Die Hydrolysegeschwindigkeit von Na-Hektorit wurde mittels der Protonenkonzentration auf der Tonoberfläche bestimmt, die mit der Theorie der diffusen Doppelschicht berechnet wurde.

Im Gegensatz dazu war die Hydrolysegeschwindigkeit von Al-Hektorit in mit Na gesättigten Suspensionen nicht von den Elektrolytkonzentrationen abhängig. Dieses Ergebnis kann durch die Annahme erklärt werden, daß die Aluminium-Hydroxy-Polymere an den Tonoberflächen die Protonenkonzentration an der Tonoberfläche bestimmen. Hektorite, die mit Struktur-Kationen gesättigt sind (wie Mg oder Li) sind chemisch stabiler als Hektorite, die mit Na oder Ca gesättigt sind. Das Vorhandensein von Li und Mg an der Tonoberfläche verzögert die Diffusion der Oktaederkationen an die Tonoberfläche im Vergleich zu Na- bzw. Ca-Hektorit. [U.W.]

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Résumé—L'hydrolyse et la décomposition d'hectorite-M (M étant Na, Li, Mg, ou Ca) dans des solutions diluées de chlorides-M ont été étudiées en enregistrant les changements de la conductivité électrique (EC) des solutions argileuses avec le temps, et par des analyses chimiques des solutions interargile et des phases solides résultantes. On a trouvé que le taux d'hydrolyse des hectorites en suspension, évalué d'après le changement d'EC avec le temps, décroissait avec une augmentation de la concentration en sel (zéro pour l'hectorite-Na dans une concentration NaCl de 47 meq/litre), et décroissait avec une augmentation de la valence du cation adsorbé (le taux d'hydrolyse de l'hectorite-Ca était un sixième de celui de l'hectorite-Na). Le taux d'hydrolyse de l'hectorite-Na a été déterminé par la concentration de protons à la surface de l'argile, calculé à partir de la théorie de la couche double diffuse.

Réciproquement, dans des suspensions d'hectorite-Al saturées de Na, les taux d'hydrolyse n'étaient pas dépendants des concentrations sur l'électrolyte. Ce résultat peut être expliqué en assumant que les polymères hydroxy aluminium à la surface de l'argile déterminent la concentration de protons à la surface de l'argile. Les hectorites saturées de cations structuraux (tels que Mg et Li) sont chimiquement plus stables que celles saturées de Na et Ca. La présence de Li et Mg à la surface de l'argile a ralenti le déchargement par diffusion de ces ions octaèdraux à la surface de l'argile en comparaison avec les hectorites-Na et -Ca, respectivement. [D.J.]

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