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Fe^{2+}-Fe^{3+} TRANSFORMATIONS IN CLAY AND RESIN ION-EXCHANGE SYSTEMS

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Abstract—The pH, Eh, electrical conductivity (EC), and the amounts and valency of replaceable iron were measured periodically on Fe^{2+}- and Fe^{3+}-saturated montmorillonite and cation-exchange resin at three temperatures. Differences in the pattern of change of pH, Eh, and EC with time appear to be related more to the histories and modes of preparation of the systems than to intrinsic differences in the hydrolysis of the iron in them. Electron transfer reactions involving crystal components of the clay can cause oxidation of adsorbed Fe^{2+} ions; the activation energy (Ea) for oxidation on the clay's surface was 6 kcal/mole, less than a third of the activation energy reported for Fe^{2+} oxidation in solution. In the Fe^{2+}-resin, where Ea = 10.7 kcal/mole, perturbed surface-water molecules may act as electron acceptors enhancing Fe^{2+} oxidation.

Polymerization and precipitation of the adsorbed iron is affected by the necessity to maintain electroneutrality, the ability of the iron-hydroxy ions and small polymers to move about in the voids of the ion exchanger, and the steric hindrance posed by the matrix of the ion exchanger to the formation of large polymers. In resin, little or no iron precipitates, probably due both to steric hindrance and the inability of the resin to release ionic components to maintain electroneutrality. In clays, steric hindrance is small, and Al and Mg are released from the crystal to maintain electroneutrality, thus the precipitation of iron is abundant and is controlled by the rate of release of Al and Mg from the crystal.

Key Words—Adsorption, Electron transfer, Ion-exchange resin, Iron, Oxidation, Smectite.

INTRODUCTION

The chemistry of iron in solution is complex, and in clay suspensions it is even more complex due to several reactions which take place simultaneously or consecutively and which affect the partition of iron between the various dissolved and crystalline species. Numerous works on the behavior of iron in soils and clays have dealt primarily with interlayer formation, the formation of crystalline materials, or changes in structural iron (e.g., Carstea, 1968; Carstea *et al.*, 1970; Herrera and Peech, 1970; Rozenson and Heller-Kallai, 1976, 1978). With the exception of several works (Turner, 1965; Thomas and Coleman, 1964; Whittig and Page, 1961; Kawaguchi and Kawachi, 1969; Fordham, 1969a, 1969b), the behavior of iron as an adsorbed-exchangeable cation has received little attention, and ferrous iron has been nearly completely ignored. The importance of iron as an exchangeable cation in both the ferric or ferrous state, has been described by Brinkman (1970) who proposed the name *ferrolysis* for the disintegration and dissolution of minerals in water by a process based upon the alternate reduction and oxidation of iron. To the best of the present authors' knowledge, no study of the oxidation of Fe^{2+} as an exchangeable cation in clays has been conducted. In the present paper experimental results on the behavior of Fe^{2+} adsorbed on montmorillonite clay and on an ion-exchange resin are discussed in relation to the hydrolysis, oxidation, and polymerization-precipitation reactions of iron.

MATERIALS AND METHODS

Materials

Analytical grade $FeCl_2$ and $FeCl_3$ were used in preparing all iron solutions. Amberlite IR-120 cation-exchange resin having a nominal cation-exchange capacity (CEC) of 4.3–5.0 meq/g and 8% cross linking (Helfferich, 1962) was used along with Wyoming bentonite (B-235) from Fisher Scientific Inc. The CEC of the bentonite is 83–95 meq/100 g, depending on the method of preparation and the adsorbed ion (Table 1).

Methods

Preparation of Fe^{2+}-resin. Freshly prepared H^+-resin was placed in a glass column and leached with $FeCl_2$ solution for 24 hr. N_2 gas was bubbled through the solution while preparing the Fe^{2+}-resin to prevent oxidation. The resin was then washed with deionized water until the electrical conductivity of the percolating solution was that of deionized water. The amount of exchangeable Fe^{2+} on the resin after preparation was 4.3 meq/g as determined by the procedure below.

Preparation of Fe^{3+}-clay. Five parts (volume) of acidified (pH $\simeq$ 2.5) 1 N $FeCl_3$ were added to one part (weight) of the crude clay. The resulting suspension was shaken on a mechanical shaker for 30 min after which it was centrifuged at 2000 R.C.F. (relative centrifugal force) for 20 min. The supernatant liquid was

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decanted, and the clay was redispersed in a fresh portion of the $FeCl_3$ solution. This process was repeated four times with either the second or third shaking period lasting 12 hr to ensure complete exchange. Excess salts were removed by repeatedly washing and centrifuging with deionized water until the electrical conductivity of the supernatant solution remained constant at about 40 μmho/cm; about five such washings were necessary. The CEC as measured immediately after preparation by the method described below was 83 meq/100 g (Table 1).

Preparation of Ca^{2+}- and Fe^{2+}-clays. Ca^{2+}- and Fe^{2+}-clays were prepared by the quantitative ion-exchange process described by Banin (1973). This method entails titrating a mixture of freshly prepared H^+-montmorillonite and OH^--saturated anion-exchange resin with the chloride salt of the desired cation. The added cation replaces H^+ from the clay surface while the Cl^- exchanges with OH^- from the resin; OH^- and H^+ then neutralize each other. The titration is completed at approximately pH 5.5 or lower if there is any possibility of the cation precipitating. At this point the electrical conductivity (EC) is at a minimum between 10 and 100 μmho/cm. The reaction can be summarized as:

$$H^+\text{-clay} + R\text{–}OH + MCL \rightleftharpoons M^+\text{-clay} + R\text{–}Cl + H_2O \quad (1)$$

During the preparation of the Fe^{2+}-clay, air was replaced by N_2 in the titration vessel. The CEC obtained by this method was 96 meq/100 g.

Attempts to prepare an Fe^{3+}-clay by this method were unsuccessful due to the hydrolysis and precipitation of the ferric iron at pHs above ~3.0 which obscured the endpoint of the titrations.

Kinetics of the conversion. The freshly prepared resin was dispersed in distilled water to give a slurry of 6 g dry resin/liter (~28 meq of CEC/liter), and the clay was kept as a 2% suspension. All materials studied were stored in sealed plastic containers in the absence of light, held at various temperatures (5°C, 25°C (30°C for the clay), and 50°C ± 1°C), and shaken intermittently. Electrical conductivity, pH, and Eh were determined periodically on the resin and clay slurries. Eh was measured using a combined Pt electrode calibrated by the method of Light (1972). Iron was fractionated into soluble, exchangeable, and acid-extractable fractions according to the following scheme. Twenty milliliters of the well-mixed clay suspension and resin slurry were sampled, and the solids were separated from their respective supernatant liquid by centrifugation and gravitational sedimentation, respectively. The clear supernatant liquid was decanted, and the ions found in it were termed the "soluble fraction." The solids were then redispersed in 20 ml of 1 N $CaCl_2$ (pH 6.5) and shaken for 30 min, and the supernatant liquid was again separated by the appropriate method. These extractions were repeated four times, and the collected leachates were brought to volume with deionized water. The ions found in this extract were termed the "exchangeable fraction." The "acid-extractable" fraction was then obtained similarly by repeated extractions of the solid phases with 0.5 N HCl.

Table 1. Properties of the various clay suspensions studied.

	Fe^{2+}-clay	Fe^{3+}-clay	Ca^{2+}-clay
Concentration (wt. %)	1.72	1.55	1.84
Plates/tactoid	2.8	12.2	3.1
Treatment temperature (°C)	5, 30, 50	5, 30, 50	30
Soluble Fe	0.3	0.2	—
Exchangeable Fe^{2+}	38.6	1.4	—
Exchangeable Fe^{3+}	0.0	14.8	—
Acid-extractable Fe^{2+}	5.6	1.6	—
Acid-extractable Fe^{3+}	2.6	10.8	—
Total (mmole/100 g)	47.1	28.8	—
Total (meq/100 g)	96.2	83.2	—

Iron in the solutions and the extracts from the resins and clays was determined by two methods. Total Fe in each sample was determined using a Perkin-Elmer Model 303 Atomic Absorption Spectrophotometer. Fe^{2+} and Fe^{3+} were determined by the colorimetric procedure of Fortune and Mellon (1938) which was slightly modified as follows:

An appropriate aliquot, giving not more than 5 ppm Fe upon dilution to 50 ml, was added to each of two 50-ml volumetric flasks, and deionized water was added to bring the volume to about 25 ml. For acid-extractable aliquots, 4 ml of 1 N Na-citrate reagent per 10 ml aliquot was added to each of the flasks. One milliliter of 1% hydroquinone solution was added to one of the duplicate samples only, whereas 1 ml of 0.2% 1,10-phenantroline solution (in 50% ethanol) was added to both duplicates. The flasks were shaken and then completed to volume. After 20–30 min the color development was complete, and the optical density was read at 510 nm. Iron content was read from a calibration curve prepared with standard iron solutions (ferrous ammonium sulfate) with hydroquinone to assure that all of the iron was in the ferrous state. The flasks containing hydroquinone yielded the total iron concentration, whereas those without hydroquinone gave only Fe^{2+} concentration. Fe^{3+} was obtained by difference. Preliminary work showed that solutions containing only Fe^{3+} gave no appreciable readings when checked by this method. In all three fractions of the clay suspensions, Si, Al, and Mg were determined by atomic adsorption spectroscopy.

Several clay samples were given extra washings with 0.5 N HCl, and Fe, Si, Mg, and Al in the extracts were determined to evaluate the crystal stability. Other clay samples were treated for the removal of sesquioxides by the method of Mehra and Jackson (1960).

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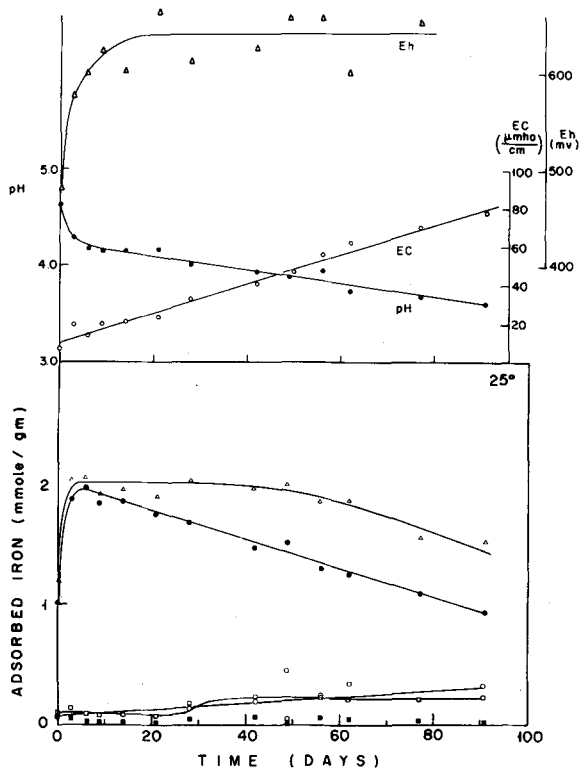


Figure 1. Changes in the pH, electrical conductivity and Eh (upper diagram) and the fractionation of adsorbed iron (lower diagram) in the Fe^{2+}-resin slurry held at 25°C. Legend for iron fractionation: △—total extractable iron, ●—exchangeable Fe^{2+}, ■—acid extractable Fe^{2+}, ○—exchangeable Fe^{3+}, □—acid extractable Fe^{3+}, ▲—soluble.

At less frequent intervals, aliquots of the clay suspensions were diluted to concentrations of 250 ppm of clay and scanned in a Cary 15 UV-VIS spectrophotometer from 800 to 200 nm to determine their optical density. The relative tactoid size was calculated from the ratio of the optical density at 700 nm to that of a similar Li-montmorillonite suspension in which it was assumed that the clay was completely dispersed (Banin and Lahav, 1968).

Data analysis. The order of reaction was determined by plotting the iron content data according to the integrated form of several general rate expressions, with the best fit determined by linear regression methods. The plot with the highest correlation coefficient was then assumed to give the reaction order, and the rate constant was determined from the slope of this plot. In nearly all cases a first order plot gave the highest correlation coefficient (see Table 2) although in several cases zero on second order plots also gave high correlation coefficients (0.90–0.95). For the sake of consistency first order data were used throughout. The activation energy was obtained from the Arrhenius plot of the log of the rate constants against the reciprocal of the absolute temperature.

Table 2. Comparison of the initial and final total content and partition of iron among various fractions in Fe^{2+}-resin, and the kinetic data for the oxidation of the adsorbed Fe^{2+} at three temperatures.

Temperature (°C)	Treatment duration (days)	Exchangeable (meq/g)	Acid extractable (meq/g)	Total (meq/g)	K[1] ($days^{-1}$)	Linear regression coefficient[1] (r)
5	6	4.00	0.10	4.10	0.0014	0.965
5	91	3.38	0.36	3.75		
25	6	3.94	0.23	4.17	0.0072	0.997
25	91	2.80	0.75	3.45		
50	6	3.74	0.28	4.06	0.0204	0.997
50	91	2.71	0.72	3.43		

Activation energy = 10.7 kcal/mole.

[1] Rate constant (K) and coefficient of linear regression (r) of the reaction data plotted according to first order kinetics.

RESULTS

Fe^{2+}-resin

Changes in pH, Eh, EC, and chemical fractionation with time are presented in Figure 1 for the resin held at 25°C. Similar curves were obtained at the other temperatures, but are not given here for the sake of brevity. The initial extraction of the resin gave unusually low results for the exchangeable Fe^{2+} which are most likely due to experimental error; thus the data from the second extraction (2 days) were taken to represent the resin's initial state.

After 3 months pH and EC were still changing at all temperatures indicating that equilibrium had not been obtained. Calculation of the pH from conductivity data yielded values within 0.2 pH units of the measured pH, indicating that hydrogen ion was mostly responsible for the increased EC. Eh was constant after about 20 days. No iron was found in the soluble fraction, and slight amounts of ferric iron were detected in the acid-extractable fraction. The exchangeable Fe^{2+} content tended to decrease with time while the exchangeable Fe^{3+} content increased with time. Although the total extractable iron in the Fe^{2+}-resin decreased somewhat with time (Table 2), mostly due to the decrease in the exchangeable fraction, it is shown below that these decreases were small compared to the decreases in extractability of the iron in the Fe^{2+}-clay.

First order kinetics was found to fit the data closely. However, as pointed out previously, zero and second order kinetics also correlated well with the data so that use of first order kinetic data does not imply any specific mechanism.

Fe^{2+}-montmorillonite

Figure 2 shows the effect of time upon the pH, EC, and Eh of the clay suspension held at 30°C. Similar

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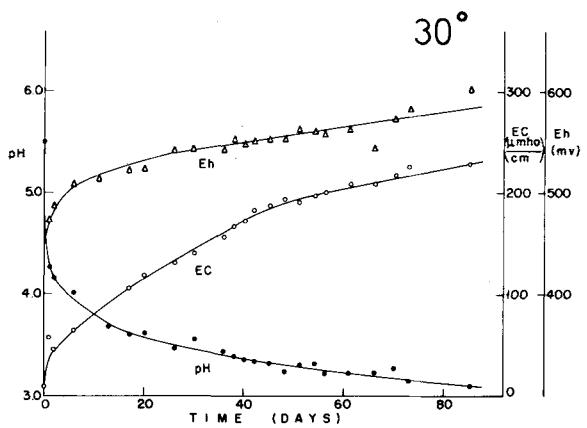


Figure 2. Changes in pH, electrical conductivity, and Eh of Fe^{2+}-clay suspensions held at 30°C.

trends were found for the suspensions held at other temperatures. However, at 50°C the system reached equilibrium within 2 weeks, attaining a final pH of 2.9, an EC of 400 μmho/cm, and an Eh of 680 mV. At 30°C, it was still undergoing changes after 82 days. At 5°C only small changes occurred with time, and the final pH was 4.05, the EC was 40 μmho/cm, and the Eh was 450 mV. The initial rapid decrease in pH at all three temperatures is characteristic of suspensions prepared by the quantitative ion-exchange method. (Cf. the Ca-clay data in Figure 5.) pH values calculated from EC data fall fairly close to the actual measured pH values as was the case for the resin, again indicating that most of the changes in EC result from changes in the H^+-ion concentration.

Detailed results of the iron fractionation for the treatments are shown in Figure 3. The general decrease in exchangeable Fe^{2+} is readily apparent. At 5°C the decrease in exchangeable Fe^{2+} is not accompanied by an appreciable increase in any other fraction, whereas at 30°C an appreciable amount of acid-extractable Fe^{3+} was detected. Both exchangeable and acid-extractable Fe^{3+} appear early at 50°C and subsequently disappear. At no temperature was a sizeable amount of acid-extractable Fe^{2+} detected, nor was iron detected in the soluble fraction.

To facilitate comparison of the temperature treatments, the variation of the total extractable Fe^{3+} and Fe^{2+} (exchangeable and acid-extractable fractions) with time is given in Figure 4. The temperature dependence of the rate of conversion of sorbed Fe^{2+} to Fe^{3+} and the subsequent transformations of the Fe^{3+} to non-extractable forms is clearly visible. Additional washings with 0.5 N HCl failed to remove additional iron from the samples; however, periodic determinations of the dithionite-extractable iron revealed that the "missing" iron can be recovered and that the sum of the total extractable iron plus the dithionite-extractable fraction

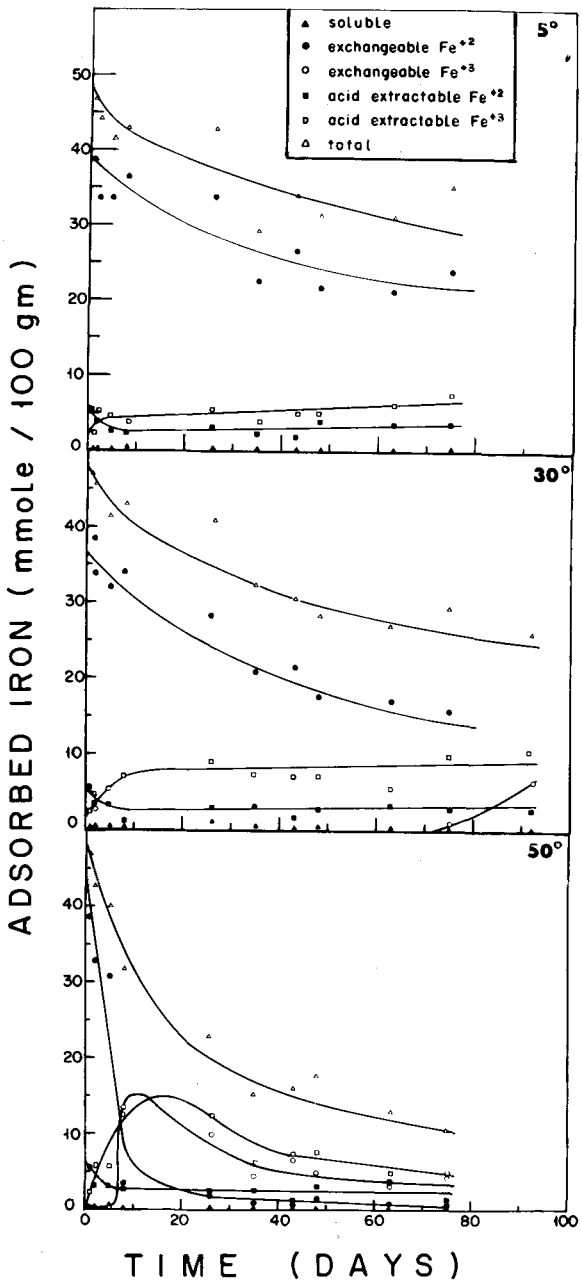


Figure 3. Concentration changes of the various fractions of adsorbed iron in Fe^{2+}-montmorillonite at 5°, 30°, and 50°C.

is nearly constant and very nearly equal to the CEC of the clay (Table 3).

Fe^{3+}-montmorillonite

Figure 5 shows the effect of time upon the pH, Eh, and EC of the Fe^{3+}-clay suspension at 30°C. The results at 5°C and 50°C are similar, namely little or no change in the pH (note expanded scale) or Eh, and only a slight increase in the EC. Figure 6 shows that the exchange-

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Table 3. Partition of iron among the various fractions in Fe^{2+}- and Fe^{3+}-montmorillonite and kinetic data for the oxidation of Fe^{2+} on the Fe^{2+}-clay.

Time (days)	5°C			30°C			50°C		
	A[1]	B[2]	A + B	A	B	A + B	A	B	A + B
				Fe^{2+}-clay					
7	—	—	—	—	—	—	23.2	15.6	38.8
39	—	—	—	—	—	—	17.2	23.7	40.9
43	34.3	4.3	38.6	31.0	9.7	40.7	16.2	24.6	40.8
75	—	—	—	30.1	11.5	41.6	10.6	28.9	39.5
K ($days^{-1}$)		0.028			0.035			0.135	
r^3		0.992			0.998			0.999	
Activation energy = 5.99 kcal/mole									
				Fe^{3+}-clay					
0	28.7	3.9	32.6	28.7	3.9	32.6	28.7	3.9	32.6
2	25.1	3.8	28.9	25.5	3.3	28.8	25.7	3.7	28.4
51	23.6	4.0	27.6	25.1	3.9	28.0	24.5	7.4	31.9
66	21.2	4.4	25.6	22.1	7.1	29.2	19.7	13.0	32.7
85	24.5	3.8	28.3	23.8	4.7	28.5	20.7	13.1	33.8
98	23.7	3.9	27.6	23.2	6.3	29.5	20.0	20.5	40.3

[1] A = soluble + exchangeable + acid extractable (mmole/100 g).
[2] B = dithionite extractable (mmole/100 g).
[3] Coefficient of linear regression of the reaction data plotted according to first order kinetics.

able Fe^{3+} fraction initially decreases with time. The soluble fraction and acid-extractable Fe^{2+} make up only a minor portion of the total Fe in each case, while acid-extractable Fe^{3+} comprises over one third of the iron at all temperatures. The exchangeable Fe^{2+} exhibits a surprising increase at all temperatures, but at 30°C and 50°C it eventually decreases to nearly zero.

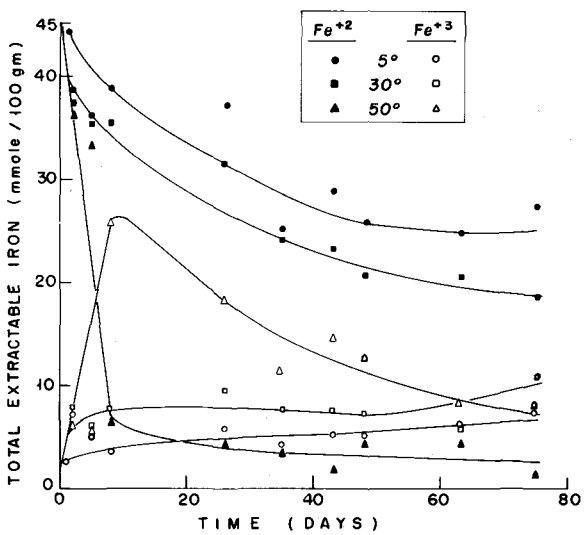


Figure 4. Total extractable (exchangeable + acid) Fe^{2+} and Fe^{3+} from Fe^{2+}-montmorillonite suspensions as a function of time and temperature.

Extractions with dithionite achieved full recovery of the iron (Table 3). With the exception of the 50°C treatment after more than two months of aging, the dithionite-extractable iron constitutes a constant, and not insignificant, fraction of the total iron extracted. The dithionite-extractable fraction is generally small compared to the acid-extractable Fe^{3+}. Whereas the acid extraction will remove only slightly crystallized forms of iron (Carstea *et al.*, 1970), the dithionite treatment removes all forms of highly crystallized iron oxides and hydroxides except for magnetite and ilmenite (Jackson, 1956). It is assumed, therefore, that stable interlayers

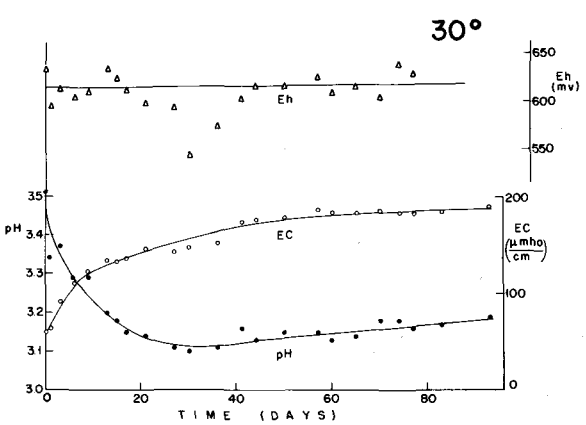


Figure 5. Changes in pH, electrical conductivity and Eh of the Fe^{3+}-clay suspensions kept at 30°C.

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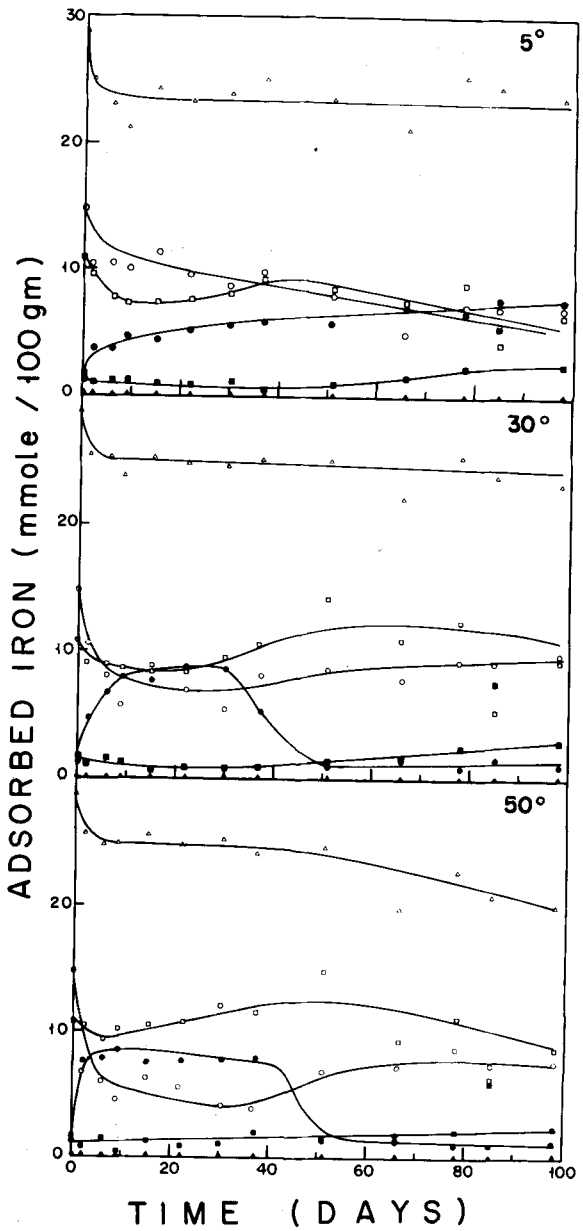


Figure 6. Concentration changes of the various fractions of adsorbed iron in Fe^{3+}-montmorillonite at 5°, 30°, and 50°C (Legend as in Figure 1).

have not yet formed and that Fe^{3+} is likely present as small polymers of hydroxy-iron ions.

Ca-montmorillonite

A Ca-saturated clay was also prepared by the quantitative ion-exchange method in order to compare its changes in pH, EC, degree of dissolution, and particle size in suspension with those of the Fe^{2+}-montmorillonite prepared in this manner. The variation of pH and

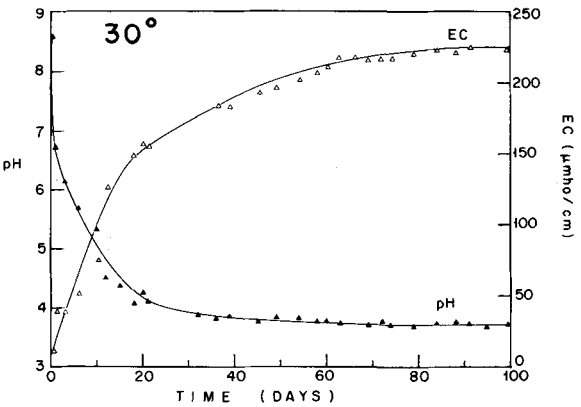


Figure 7. Changes in the pH and electrical conductivity for Ca-clay suspensions at 30°C.

EC with time for the Ca-montmorillonite suspension is shown in Figure 7; the tactoid size is shown in Table 1. The suspension pH of Ca-montmorillonite prepared by the batch method is usually 6–7, with 8–12 plates/tactoid (Banin and Lahav, 1968). In the present study only 3 plates/tactoid were found, differences which are due to the unique method of preparation of this clay.

DISCUSSION

Hydrolysis reactions

The decrease in pH with time for the Fe^{2+} systems indicates that hydrolysis reactions are taking place. Since Fe^{2+} hydrolyzes less than 0.1% at pH $\leq$ 6, it is unlikely that Fe^{2+} hydrolysis *per se* can be responsible for the observed decrease in pH. For the Fe^{2+}-resin the increased H^+ concentration is related to the oxidation of Fe^{2+}. This is in agreement with the mechanism proposed by Hudis and Dodson (1955) which suggests that in solution hydrated $Fe(H_2O)_6^{2+}$ oxidizes to $Fe(H_2O)_5OH^{2+} + H_3O^+$, or that, alternatively, in the reaction sequence $Fe(H_2O)_6^{2+} \rightarrow Fe(H_2O)_6^{3+} \rightarrow Fe(H_2O)_5OH^{2+} + H_3O^+$, the second reaction is instantaneous. Either of these mechanisms will result in a decreased pH as noted for the Fe^{2+}-resin. The reaction will continue in the resin as long as Fe^{2+} oxidizes to Fe^{3+} resulting in a continuing decrease in pH.

In the clay systems, other mechanisms play a role as well. For example, the Ca-montmorillonite studied here exhibited a pH-time curve similar to that of the Fe^{2+}-clay, yet Ca^{2+} does not hydrolyze at all under the conditions of the experiment. It is likely that, in part, this pH decrease is a property of the clay system resulting from its preparation process. This preparation entailed a relatively intense leaching with 0.5 N HCl followed by salt titration in the presence of OH^--resin, which was terminated at a pH of 5 (*vide supra*). At this stage the system seemed to be slowly approaching an equilibrium pH of about 3.0–4.0. It is possible that dur-

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ing the acid wash, contaminating insoluble salts and hydroxides in the crude material, which regularly were capable of controlling and buffering the pH of the suspension at high values, were dissolved. Upon completion of the titration, at pH 5.5, the hydrolysis of edge Al exerted a buffering capacity on the suspension, bringing the system to about pH 4. This explanation is further supported by the results of Gerstl (1974) who found that for an H-montmorillonite (in which excess H^+ was removed by mixing with OH^--resin) the pH increased from 2.7–2.9 to 3.1. The reaction causing the increase in pH involved edge Al and the spontaneous decomposition of the clay resulting in the eventual formation of an Al-clay which has an equilibrium pH of 3.5–4.0 (Low, 1955; Banin and Ravikovitch, 1966) regardless of the direction of approach to this equilibrium. In the presence of Fe^{2+} the pH of the clay system will continue to decrease as a result of iron oxidation in a mechanism similar to that mentioned above for the resin system. The decrease, however, will be checked in part due to the buffering exerted by the edge Al. This is evident if the rate and extent of iron oxidation are compared to the effective rate of pH decrease in the clay system.

Oxidation reactions

The oxidation of Fe^{2+} solutions is dependent on both the pH and partial pressure of oxygen (Stumm and Morgan, 1970). In the present study the pH was not constant but changed during the course of the reactions, similar to the changes expected in natural systems (Brinkman, 1970). However, a time-weighted average pH can be calculated for the period of iron oxidation by integration of the area under the pH-time curve, allowing rates to be compared with those of systems at constant pH (Stumm and Morgan, 1970). For the clay kept at 30°C this value is pH 4.0 for a period of 0–10 days, and the rate constant for the clay suspension at 25° (adjusted from 30°C by use of activation energy) is 0.03/day. Stumm and Morgan (1970) reported for the oxidation of Fe^{2+} solutions at 25°C, pH 4, and a partial pressure of oxygen of 0.2 atm, a value of 6.3×10^{-4}/day. It is obvious that the oxidation reaction proceeds much more quickly in the clay suspension than in solution.

While it is possible that oxygen diffused through the walls of the containers, it is unlikely that this was the main cause of Fe^{2+} oxidation. If one assumes an extreme case where the solution is in equilibrium with the external atmosphere, the oxidation rate constant should be similar to that observed for Fe^{2+} solutions with a partial pressure of oxygen of 0.2, yet a difference of nearly two orders of magnitude was found between the clay suspension and the Fe^{2+} solutions. Moreover, since the suspensions were prepared under nitrogen and the reaction vessels were immersed in water, the partial pressure of oxygen in them was probably much less than 0.2 atm, so that this extreme case is unlikely to occur.

The literature is replete with examples of how the crystal components of montmorillonite can participate in electron transfer reactions causing either oxidation or reduction of sorbed species under non-extreme conditions (Barshad and Kishk, 1970; Ismail, 1970; Raman and Jackson, 1966; Solomon, 1968; Theng, 1971; Theng and Walker, 1970). In addition, Meisal *et al.* (1971) reported that Fe^{3+} in mordenite can be reduced to Fe^{2+} by electron transfer from perturbed water molecules on the surface or by reaction with edge AlO_4 groups. Thus a crystal's ability to participate in electron transfer reactions can explain the oxidation of sorbed Fe^{2+}. One possibility is that the electron transferred into the crystal reduces octahedral Fe^{3+} to Fe^{2+}, consequently increasing the clay's exchange capacity to accommodate the larger charge of the newly oxidized Fe^{3+}. Such a mechanism has been proposed by Rozenson and Heller-Kallai (1976) for the reduction of structural Fe^{3+} in montmorillonite, and by Stucki and Roth (1977) for nontronite. Alternatively, lattice OH^- can deprotonate producing O^{2-} and thereby compensating for the increased charges on the surface (Roth *et al.*, 1968, 1969). The observed activation energy of the sorbed Fe^{2+} oxidation process of 6 kcal/mole is considerably lower than the 23 kcal/mole reported for the same reaction in solution (Chen and Davidson, 1955). This lower activation energy most probably results from the clay's crystal participating as a catalyst in the oxidation process by acting as an electron acceptor.

In contrast to the clay, the resin matrix structure is such that it is unable to participate in oxidation-reduction reactions as do the clay's crystal components. Although the IR-120 resin used is reported to be extremely stable to reduction (Bio-Rad Laboratories, 1969), oxidation of Fe^{2+} did occur in the Fe^{2+}-resin system but at a slower rate than in the clay system. The clay's enhancement of the reaction results from its electron transfer ability. The only property of the resin which can accelerate the reaction rate, compared to that in solution, appears to be related to surface effects. Chen and Davidson (1955) reported that glass wool (specific surface area = 2300 cm^2/g) enhances the rate of Fe^{2+} oxidation; the resin may produce the same effect by the formation of perturbed or excited water molecules which may act as electron acceptors (Meisal *et al.*, 1971). It is also possible that the resin and clay surfaces adsorbed the dissolved oxygen, thereby raising its effective concentration near the surface and thus increasing the reaction rate of the sorbed iron species.

Polymerization reactions

The total extractable iron of the Fe^{2+}-montmorillonite decreased rather rapidly with time. The iron which

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was resistant to extraction with 0.5 N HCl in Fe^{2+}-montmorillonite was fully recovered by citrate-dithionite extraction. Most likely, this iron was in hydroxide-polymeric form on the clay surface, which produces material resistant to acid attack (Carstea *et al.*, 1970). The present results show that this process occurs on those clays where the ferric iron results from the oxidation of Fe^{2+}. On clays initially saturated with Fe^{3+}, however, it occurs to a much lesser extent (see Table 3). Hsu (1973) and Hsu and Ragone (1972) indicated that the rate and nature of polymerization of Fe^{3+} in solution depends upon the degree of supersaturation of the solution with respect to $Fe(OH)_3$ and the number of polymerization nuclei relative to the concentration of monoionic species. It is assumed that relatively small polymers will be formed when a large number of polymerization nuclei are present, resulting in a turbid, relatively stable sol. When only a few such nuclei are available, the polymers that eventually form are large in size, tend to precipitate, and leave a clear solution. Similar to what occurs in solutions it is suggested that in the Fe^{2+}-clay, the hydrolysis of Fe^{3+}, which can be assumed to be instantaneous (Hudis and Dodson, 1955; Stumm and Morgan, 1970), depends on the rate of Fe^{3+} formation from the oxidation of Fe^{2+}, resulting in relatively few large-size polymerization nuclei. In the Fe^{3+}-clay the numerous washings with distilled water to remove excess Fe^{3+} results in rapid hydrolysis of the Fe^{3+} and the production of a large number of smaller nuclei. Thus, in the Fe^{2+}-clay more precipitation occurs than in the Fe^{3+}-clay. Precipitation will also be easier on the Fe^{2+}-clay, as opposed to the Fe^{3+}-clay, since the number of platelets/tactoid is much smaller (Table 1), allowing the nuclei and monoionic species greater mobility. In addition, reduction in charge of the Fe^{3+} resulting from hydrolysis and polymerization requires the addition of other cations to the system to maintain electroneutrality. As seen in Table 4, the total extractable (Fe^{3+} + Mg^{2+} + Al^{3+}) in the Fe^{2+}-clay system is nearly constant, indicating that the release of cationic components from the clay's crystal structure may be coupled to and possibly drive the process by which Fe^{3+} disappears. In the Fe^{3+}-clay system dissolution of the lattice is slower as fewer H^+ ions are formed, crystal cationic components are not released, and the precipitation of iron is prevented due to the need to maintain electroneutrality.

The iron precipitate formed is ferrihydrite, as can be seen from Figure 8, in which the Eh and pH values fall on a line parallel to the Fe^{2+}–ferrihydrite conversion line. Several papers (e.g., Gotoh and Patrick, 1974; Ponnamperuma *et al.*, 1967) showed that the Fe^{2+}–$Fe(OH)_3$ (ferrihydrite) couple governs iron behavior in submerged soils. In the Fe^{2+}-resin system the main equilibrium is between Fe^{2+} and $Fe(OH)^{2+}$ as seen from Figure 9. This is in accord with the proposed oxidation

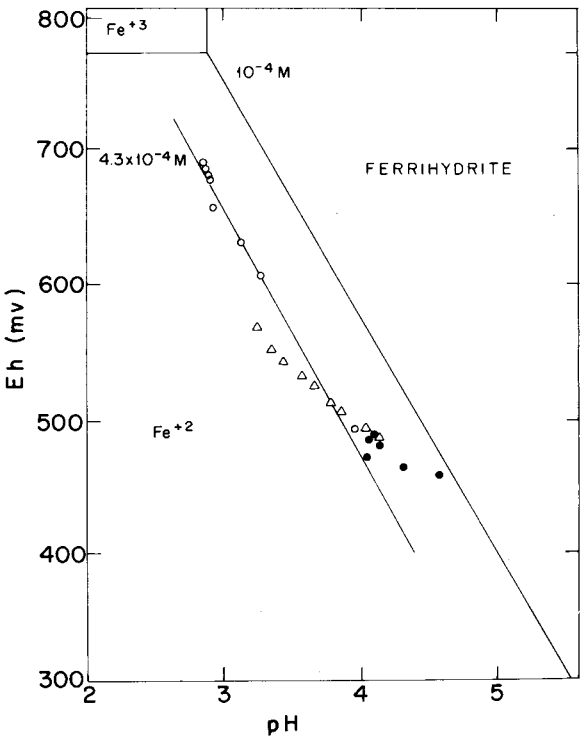


Figure 8. Eh-pH data for the Fe^{2+}-montmorillonite systems held at 5°C (●), 30°C (△), and 50°C (○). Time progresses from the lower right data points to the upper left data points.

mechanism and the results of Brownlow (1962) and Mackey and Collins (1967) who found that Fe^{3+} in resins was mainly in the form of mono- and di-hydroxy-ions. In such a case the excess charge resulting from oxidation and hydrolysis should permit condensation of ferrihydrite; however, unlike the Fe^{2+}-clay system where the small tactoid size and the clay's ability to expand allows for any reconfiguration necessary, the resins structure is rigid and nonexpanding. Kunin and Myers (1950) showed that for the type of resin employed in the present study less than 40% of the resin's exchange capacity is available to ions of ionic diameter greater than 15 Å. Hsu (1973) and Murphy *et al.* (1975)

Table 4. Release of Al and Mg from the Fe^{2+}-montmorillonite held at 50°C.

Time (days)	Total extractable iron (meq/100 g)	Al + Mg (meq/100 g)	Total (meq/100 g)
8	78	10	88
26	56	20	76
43	38	44	82
48	39	38	78
75	26	67	93

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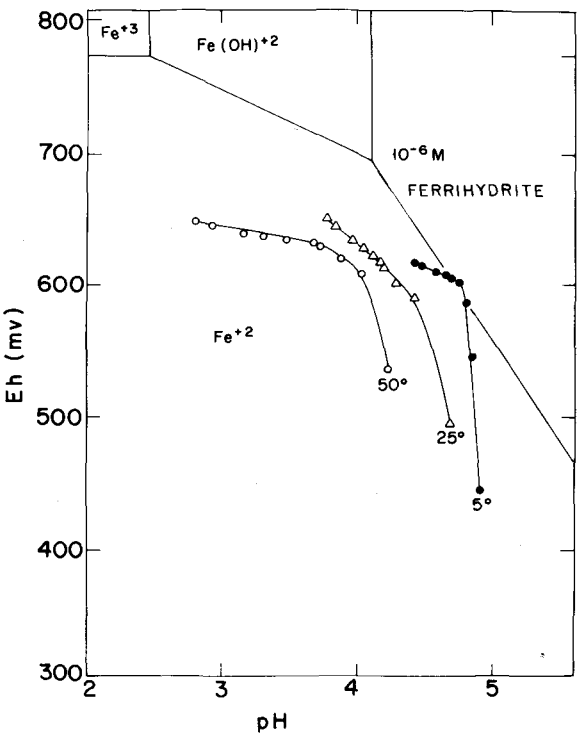


Figure 9. Eh-pH data for the Fe^{2+}-resin systems held at 5°C, 25°C, and 50°C. Time progresses from the lower right data points to the upper left data points.

reported that in the initial stages of Fe^{3+} precipitation, species of 10–15 Å diameter are formed, thus, the small pore diameter of the resin may restrict movement of sorbed iron so that polymerization is slowed down.

These results are summarized in Figure 10, where the percentage of change from the original amount of exchangeable iron is plotted for the various systems as a function of time. In the Fe^{3+} systems no noticeable change occurs. In the Fe^{2+} systems, the clay exhibits rapid changes as a result of surface polymerization of the adsorbed and oxidized iron, whereas in the resin, only a very slow change takes place.

SUMMARY

Adsorbed Fe^{2+} on clays appears to undergo the following sequence of reactions and transformations: Fe^{2+} on montmorillonite is oxidized to Fe^{3+} which hydrolyzes, forming hydroxy-ions that polymerize and that may eventually precipitate as a neutral iron compound. H^+ ions resulting from the hydrolysis reactions attack the clay crystal and release Al and Mg ions which take the place of the iron as exchangeable ions. This sequence is similar to that of ferrolysis which occurs in natural systems and which has been proposed as a hydromorphic soil-forming process.

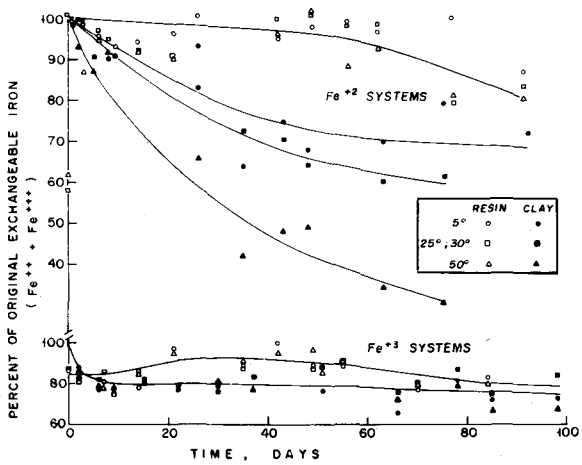


Figure 10. Relative change in extractable iron in the clay and resin systems.

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Резюме—Периодически замерялись pH, Eh, электрическая проводимость (ЭП), и количества и валентность замещаемого железа монтмориллонита и катионно-обменной смолы, насыщенных Fe^{2+} и Fe^{3+} при трех температурах. Различия в картине изменения pH, Eh, и ЭП в времени, по видимому, более связаны с предисториями и способами приготовления систем, чем с присущими различиями гидролиза железа в них. Реакции переноса электронов, включающие кристаллические компоненты глины, могут вызывать окисление адсорбированных ионов Fe^{2+}; энергия активизации (ЭА) для окисления на поверхности глины равнялась 6 ккал/мол, меньше трети энергии активации, потребной для окисления Fe^{2+} в растворе. В Fe^{2+}-смоле, где ЭА = 10,7 ккал/мол, возмущенные поверхностные молекулы воды могут действовать как электронные акценторы, помогая окислению Fe^{2+}.

Полимеризация и осаждение адсорбированного железа находится под воздействием необходимости поддерживать электронную нейтральность, способность гидрокси-железных ионов и небольших полимеров передвигаться в полостях ионо-обменника, и пространственного препятствия, вызываемого кристаллической решеткой ионо-обменника, образованию больших полимеров. В смоле мало или вообще нет железных осадков, вероятно из-за пространственного препятствия и неспособности смолы высвобождать ионные компоненты для поддержания электронной нейтральности. В глинах пространственное препятствие незначительно, и Al и Mg высвобождаются из кристалла для поддержания электронной нейтральности; в результате железо осаждается в изобилии и контролируется степенью высвобождения Al и Mg из кристалла. [N.R.]

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Resümee—Der pH, Eh, die elektrische Leitfähigkeit (EC), sowie die Mengen und Leitfähigkeit ersetzbaren Eisens wurde in gleichen Abständen an Fe^{2+}- und Fe^{3+}-gesättigten Montmorilloniten und an Kationenaustauschharzen gemessen. Unterschiede in der Art, wie sich pH, Eh, und EC im Laufe der Zeit ändern, scheinen mehr davon abzuhängen, wie die Systeme präpariert wurden, als von wirklichen Unterschieden bei der Hydrolyse des enthaltenen Eisens. Elektronenübergangsreaktionen, die Kristallbestandteile des Tons betreffen, können die Oxidation des adsorbierten Fe^{2+} verursachen; die Aktivierungsenergie (Ea) für die Oxidation an der Tonoberfläche betrug 6 Kcal/Mol, weniger als ein Drittel der Aktivierungsenergie, die für die Oxidation von Fe^{2+} in Lösung angegeben wird. Im Fe^{2+}-Ionenaustauschharz, mit einer Ea von 10,7 Kcal/Mol, Können gestörte Oberflächenwassermoleküle als Elektronenakzeptor wirken und die Oxidation von Fe^{2+} verstärken.

Die Polymerisation und Ausfällung des adsorbierten Eisens wird von folgenden Faktoren beeinflußt: von der notwendigen Erhaltung der Elektroneutralität, von der Fähigkeit der Eisenhydroxyionen und kleiner Polymere, in den Hohlräumen des Ionenaustauschers umherzuwandern und von sterischen Widerständen der Matrix des Ionenaustauschers gegen die Bildung großer Polymere. Im Ionenaustauschharz fällt wenig oder kein Eisen aus, wahrscheinlich sowohl wegen sterischer Widerstände als auch weil das Ionenaustauschharz keine Ionen abgeben kann, die die Elektroneutralität Aufrechterhielten. In Tonen ist der sterische Widerstand gering, und Al und Mg werden vom Kristall abgegeben, um die Elektroneutralität zu erhalten, sodaß die Eisenausfällung stark ist. Sie wird durch die Geschwindigkeit bestimmt, mit der Al und Mg vom Kristall abgegeben werden. [U.W.]

Résumé—Les pH, Eh, conductivité électrique (EC), et les quantités et la valence de fer remplaçeable ont été périodiquement mesurés sur une montmorillonite saturée en Fe^{2+} et Fe^{3+} et une résine à cation-échangeable à trois températures. Les différences dans le dessin de changements de pH, Eh, et EC avec le temps semblent être plus apparentées aux histoires et aux modes de préparation des systèmes qu'à des différences intrinsèques à l'hydrolyse du fer qu'ils contiennent. Les réactions de transfert d'électrons impliquant les composés cristaux de l'argile peuvent causer l'oxidation d'ions Fe^{2+} adsorbés; l'energie d'activation (Ea) pour l'oxidation à la surface de l'argile était 6 kcal/mole, moins qu'un tiers de l'énergie d'activation rapportée pour l'oxidation de Fe^{2+} en solution. Dans la résine-Fe^{2+}, où Ea = 10.7 kcal/mole, des molécules d'eau de surface perturbées peuvent se comporter comme des acceptantes d'électrons favorisant l'oxidation de Fe^{2+}.

La polymérisation et la précipitation du fer adsorbé sont affectées par la nécessité de maintenir l'électroneutralité, l'abilité des ions hydroxy-fer et des petits polymères de se mouvoir dans les vides de l'échangeur d'ions, et l'obstacle stérique posé par la matrice de l'échangeur d'ions à la formation de larges polymères. Dans la résine, peu ou pas de fer ne précipite, probablement à la fois à cause d'un obstacle stérique et de l'inabilité de la résine à lâcher des composés ioniques pour maintenir l'électroneutralité. Dans les argiles, l'obstacle stérique est petit, et Al et Mg sont lâchés du cristal pour maintenir l'électroneutralité, ainsi, la précipitation du fer est abondante et est contrôlée par l'allure de dégagement d'Al et de Mg du cristal. [D.J.]

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