

STABILITY OF MIXED IRON AND ALUMINUM HYDROUS OXIDES ON MONTMORILLONITE*

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Abstract—Montmorillonite clay samples were coated with 16 m-equiv/g of clay or iron plus aluminum as hydrous oxides and aged 1 yr, in suspensions of pH 6 or 8. The magnesium exchange capacity (MgEC) decreased linearly with the amount of non-crystalline aluminum hydrous oxide associated with the clay. Eight to 16 m-equiv of iron per g of clay reduced the MgEC by 20 m-equiv/100 g at pH 6, but did not affect the MgEC at pH 8. The quantity of non-crystalline aluminum associated with the clay depended on the suspension pH and aging time, and was unaffected by the coprecipitation of 8–16 m-equiv of iron hydrous oxide/g clay. The crystalline form of aluminum hydrous oxide depended on the suspension pH and was shown by X-ray diffraction to be gibbsite at pH 6 and bayerite at pH 8. Gibbsite and bayerite formed rapidly with a rate dependent on the suspension pH when excess non-crystalline aluminum hydrous oxides were present. The quantity of non-crystalline aluminum hydrous oxides remaining after one year in suspensions of iron hydrous oxides and montmorillonite varied from 2.3 m-equiv/g of montmorillonite at pH 8–4.0 m-equiv/g of montmorillonite at pH 6. Differential thermal analysis and MgEC measurements indicated some regular organization of the iron hydrous oxides, however, crystalline iron minerals were not detected by X-ray diffraction.

INTRODUCTION

Iron and aluminum are common in soils as the weathering product of soil-forming minerals. Iron may occur as coatings on silicate clay minerals (Davidtz and Sumner, 1965; Roth *et al.*, 1968) or as discrete particles on the surfaces of clay minerals (Greenland *et al.*, 1968). Hydrous oxides of iron and aluminum can significantly influence the physico-chemical properties of clay minerals (Tweneboah *et al.*, 1967; Roth *et al.*, 1968; Davey and Low, 1971). For example the cation exchange capacity (CEC) of vermiculites was increased up to 30 per cent by removing a positively charged iron and aluminum hydrous oxide coating (Roth *et al.*, 1968) and the CEC of various soil clays increased by 10–40 m-equiv/100 g following the removal of aluminum from the clay surfaces (Frink, 1965). The magnitude of CEC reduction resulting from iron and aluminum should be determined by the nature of the interaction between hydrous oxides and the clay mineral. This work reports the effects of iron and aluminum hydrous oxides on the measured cation exchange capacity of a montmorillonite and the resultant stable products that are formed during the equilibration under slightly acidic or slightly alkaline conditions.

MATERIALS AND METHODS

Montmorillonite from Upton, Wyoming (A.P.I. 25, Wards Scientific Establishment, Rochester, New York) was sodium saturated by washing with NaCl solution.

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The excess NaCl was removed by washing with deionized water followed by dialysis until a negative chloride test (AgNO_3) was obtained in the wash solution. The dispersed suspension was allowed to stand quietly and the less than $2 \mu\text{m}$ fraction was removed for use in this study. Aliquants of the suspension containing 2.5 g of montmorillonite were placed in a polyethylene beaker and titrated to $\text{pH } 2.50 \pm 0.01$ with dilute nitric acid. Forty m-equiv (16 m-equiv/g clay) of iron plus aluminum was added as freshly prepared 1.0 N $\text{Fe}(\text{NO}_3)_3$ and 1.0 N $\text{Al}(\text{NO}_3)_3$ solutions to the rapidly stirred acidified suspension (Table 1). The mixed acidic suspensions containing ferric iron, aluminum, and montmorillonite were titrated with freshly prepared 0.2 N NaOH to $\text{pH } 6.00 \pm 0.01$ or 8.00 ± 0.01 . The suspensions were washed three times with deionized water to remove the excess salts and then diluted to 500 ml with water. The mixed iron–aluminum–montmorillonite suspensions were stored in polyethylene bottles at room temperature ($24 \pm 2^\circ\text{C}$). The suspension pH decreased slightly with aging. Additions of freshly prepared 0.2 N NaOH were made bi-weekly for the first month, then monthly to maintain a 6.00 ± 0.01 or 8.00 ± 0.01 throughout this study period.

The magnesium exchange capacity (MgEC) was determined by washing 50 mg of montmorillonite clay three times with 0.5 N $\text{Mg}(\text{NO}_3)_2$ followed by five washings with 0.01 N $\text{Mg}(\text{NO}_3)_2$. The magnesium of the exchange complex was replaced by washing five times with 0.2 N CaCl_2 and the magnesium determined by atomic absorption spectrophotometry (Roth *et al.*, 1969). The MgEC values were reported on a montmorillonite clay weight basis regardless of the amount of hydrous oxides present.

Table 1. Amount of iron and aluminum salts added to the acidified montmorillonite and subsequently precipitated as hydrous oxide coating plus the resulting cation exchange capacities

Treatment No.	pH	M-equiv added/g clay		Aging time					
				1 week	1 month	4 month	6 month	1 yr	
		Fe	Al		CEC (m-equiv/100 g)				
1	6	4	12	34	51	73	77	83	
2	6	8	8	36	40	57	56	61	
3	6	9.6	6.4	36	38	52	53	60	
4	6	11.2	4.8	40	44	50	50	58	
5	6	12.8	3.2	48	51	59	56	62	
6	6	14.4	1.6	65	69	72	71	76	
7	6	16.0	0	72	74	81	80	86	
8	6	Control		94	96	97	95	99	
1	8	4	12	69	81	96	93	90	
2	8	8	8	69	83	87	86	83	
3	8	9.6	6.4	66	77	86	83	79	
4	8	11.2	4.8	68	81	84	83	75	
5	8	12.8	3.2	76	85	84	78	85	
6	8	14.4	1.6	82	91	92	87	94	
7	8	16.0	0	93	99	100	100	103	
8	8	Control		95	99	99	97	104	

Potassium saturated samples were prepared for thermal gravimetric analysis (TGA), differential thermal gravimetric analysis (DTGA), differential thermal analysis (DTA) and X-ray diffraction (XRD) by washing three times with 1 N KCl, followed by three washings with deionized water to remove the excess salts. The potassium saturated clay was air dried on a glass plate and lightly ground in an agate mortar for TGA, DTGA and DTA. Fifteen to twenty mg of the dried and ground sample was placed in a platinum sample boat inside a quartz tube for TGA and DTGA. The quartz tube was evacuated to 0.1 atm to minimize thermal convection currents and the furnace surrounding the tube was heated at a constant rate of 10°C/min from room temperature to 800°C. Sample weight (TGA), measured with an electrobalance, and the rate of change of the sample mass (DTGA), computed with a time derivative computer, were recorded on the Y-axes of a X₁ Y₂ recorder. Sample temperature, recorded on the X-axis of the same recorder, was measured with a Pt, Pt-10 per cent Rh thermocouple positioned inside the evacuated chamber approx. 4 mm below the sample. Instrumental calibration for crystalline Al(OH)₃ was accomplished by preparing a standard curve of weight loss versus the quantity of gibbsite present.

Twenty to twenty-four mg of dried potassium-saturated clay, was gently packed in the platinum sample holder of a DuPont 900 Differential Thermal Analyzer for differential thermal analysis (DTA). The reference sample holder was packed with an equivalent amount of calcined aluminum oxide (Al₂O₃). Sample and differential temperature were measured with Pt, Pt-13 per cent Rh thermocouples in contact with the platinum foil sample holder while the surrounding furnace was heated at 10°C/min from 25-800°C. All DTA investigations were conducted at atmospheric pressure in static air.

Potassium-saturated clay (5 mg) was dried as an approx. oriented film on a glass slide and the X-ray powder diffraction pattern was obtained with a filtered diffractometer, CuK_α radiation. Sensitivity for full scale deflection was set at 2000 counts/sec from 2-10 degrees 2θ and increased to 500 counts/sec from 12-32 degrees 2θ.

RESULTS AND DISCUSSION

Thermal analysis of gibbsite

Pure samples of gibbsite lost 34.6 ± 1.0 per cent of their weight when heated from room temperature to 800°C. The theoretical weight loss for the conversion of gibbsite, Al(OH)₃, to alumina, Al₂O₃, is 34.64 per cent. The maximum rate of weight loss from gibbsite, heated at 10°C per minute and weighed at a pressure of 0.1 atmosphere, occurred between 260 and 270°C depending on the sample size. This is 30-40°C less than the dehydroxylation temperature of 300°C reported for gibbsite at atmospheric pressure (Mackenzie, 1957). Examination of the TGA data revealed that 83.2 ± 2.0 per cent of the theoretical weight loss from gibbsite occurred in a temperature span of 30°C above to 30°C below the temperature of which the rate of dehydroxylation was a maximum. The weight loss over this 60°C temperature span was used for the quantitative determination of both gibbsite and bayerite since the TGA and DTGA curves for both were essentially alike and the chemical composition was identical.

Thermal weight loss of Fe and Al hydrous oxides

The total weight lost by a heterogeneous coating of iron and aluminum hydrous oxides on the surface of montmorillonite between room temperature and 500°C depended on the aging time and composition of the sample. Most of the weight loss resulting from

dehydration of non-crystalline iron and aluminum hydrous oxides occurred at less than 200°C under the experimental conditions of this study. Dehydroxylation of crystalline $\text{Al}(\text{OH})_3$ occurred mainly in the temperature range between 230 and 300°C. Thermal gravimetric analysis of many Fe–Al hydrous oxide coated montmorillonite samples containing no crystalline $\text{Al}(\text{OH})_3$ revealed a small but essentially constant weight loss (0.5 per cent or 0.10 mg for 20 mg samples) between 230 and 300°C. This weight loss was attributed to partial loss of hydroxyls from the montmorillonite which occurs at this low temperature because the clay layers are separated by the Fe–Al hydrous oxide coatings.

The quantity of crystalline $\text{Al}(\text{OH})_3$ present in the Fe–Al hydrous oxide coated montmorillonite samples could be determined in the following manner. The total weight loss over a 60°C temperature span, centered at the temperature where the rate of dehydroxylation was a maximum, was determined by TGA. The weight loss attributed to partial dehydroxylation of montmorillonite in this temperature range was subtracted from the total weight loss, giving the weight loss attributed to dehydroxylation of crystalline $\text{Al}(\text{OH})_3$. Since gibbsite or bayerite lost 83.2 ± 2.0 per cent of their theoretical weight loss in this 60°C temperature span, the amount of crystalline $\text{Al}(\text{OH})_3$ present in the sample was determined. This amount of crystalline $\text{Al}(\text{OH})_3$ divided by the weight of montmorillonite, determined by assuming the iron and aluminum were present only as the oxides (Fe_2O_3 and Al_2O_3) at 800°C and using an experimentally determined factor of 1.10 to correct for complete dehydroxylation, gave the quantity of crystalline $\text{Al}(\text{OH})_3/\text{g}$ of oven dry (110°C) montmorillonite.

Non-crystalline aluminum present in the sample was calculated by subtracting the crystalline $\text{Al}(\text{OH})_3$, determined by TGA, from the total aluminum added to the sample. This was possible because very little aluminum was lost when the freshly precipitated Al–Fe hydrous oxide coated montmorillonite samples were washed. Therefore, the weight lost over a 60°C temperature span of a sample containing montmorillonite, iron and aluminum hydrous oxides, and crystalline $\text{Al}(\text{OH})_3$, represents the difference between crystalline and non-crystalline aluminum hydrous oxides.

Magnesium exchange capacity

The magnesium exchange capacity (MgEC) of montmorillonite coated with hydrous oxides of iron and aluminum ranged from 34–104 m-equiv/100 g of clay depending on the quantity of added hydrous oxides and aging time (Table 1). The MgEC was linearly related to the non-crystalline aluminum associated with the montmorillonite clay (Fig. 1). The slope of the regression line shows that the exchange capacity satisfied by a given amount of non-crystalline aluminum associated with the clay surface is slightly more in the more acid environment. The exchange capacity reduction is a direct result of the interaction between the hydrous oxide coating and the montmorillonite since

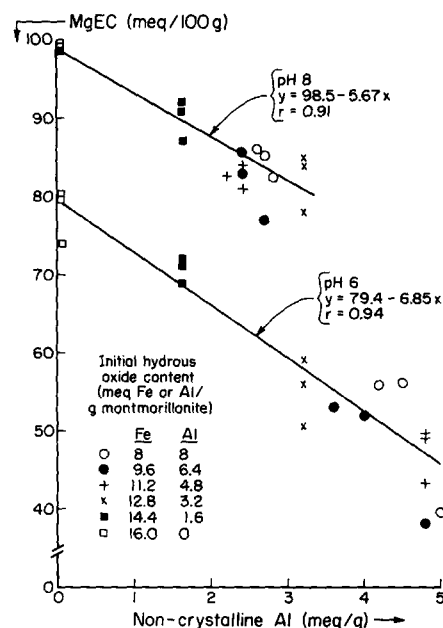


Fig. 1. Relation between MgEC and non-crystalline Al in montmorillonites coated with 0.8 m-equiv Al and 8–16 m-equiv Fe hydrous oxides/g clay and aged 1–6 months.

the exchange capacities were based on the amount of montmorillonite present.

Other investigators have shown that the reduction in exchange capacity by aluminum hydrous oxide coatings on montmorillonite depends on the method of sample preparation and the time of equilibration (Shen and Rich, 1962; Carstea, 1968; Barnhisel, 1969; Kidder and Reed, 1972). Although some of the variability between studies can be attributed to ion selectivity (Dolcater *et al.*, 1968), the net positive charge/aluminum, which is greater when the suspension is slightly acid, may reduce the cation exchange capacity (CEC). Large variation in the exchange capacity blocked/aluminum would be expected if both crystalline and non-crystalline aluminum are present and are collectively used to calculate the net positive charge/mole of aluminum. Crystalline aluminum, if included as a portion of the total aluminum hydrous oxide, would not reduce the exchange capacity of the clay because of the net negative charge of crystalline $\text{Al}(\text{OH})_3$ above pH 4.8 (van Schuylenborgh, 1950).

Freshly precipitated aluminum hydroxy material forms charged hydroxy aluminum cations that polymerize to positively charged six membered rings by hydroxide bridging of aluminum ions (Hsu and Bates, 1964). Crystallization of the polymers to either gibbsite or bayerite brings about a reduction of the isoelectric point by nearly four pH units (Jackson, 1963). Thus, the crystallization of $\text{Al}(\text{OH})_3$ results in the loss of the positively charged polymer and the formation of $\text{Al}(\text{OH})_3$ crystals which exhibit a small negative charge at the pH used in this study. The negatively charged crystalline $\text{Al}(\text{OH})_3$ would be repelled from the region of the similarly charged montmorillonite surface, therefore, the MgEC would increase proportional to

the quality of crystalline aluminum formed. Determination of crystalline $\text{Al}(\text{OH})_3$ by TGA and calculating the quantity of the non-crystalline aluminum by difference, reveals that the reduction in MgEC is related to the amount of non-crystalline aluminum hydroxides associated with the montmorillonite. The non-crystalline aluminum is assumed to exist as a non-exchangeable cation.

Reduction of the MgEC of montmorillonite by iron hydroxides depends entirely on the pH of the suspension (Table 1). The slopes of the regression lines in Fig. 1 show a slightly more positive charge per unit aluminum at pH 6 than at pH 8 and no detectable change in exchange capacity with 8–16 m-equiv of iron hydroxides per gram of montmorillonite. Iron hydroxides at pH 8 did not significantly reduce the MgEC of montmorillonite during the 1 yr of this study. However, at pH 6 the MgEC was reduced approximately 20 m-equiv/100 g of montmorillonite and was invariant with 8–16 m-equiv of iron/g clay. The iso-electric point of fresh ferric hydroxide is near pH 8 (van Schuylenborgh, 1950). Freshly precipitated iron hydroxides should be electrically neutral at pH 8 and should not influence the MgEC. At pH 6 the iron hydroxide is positively charged and should reduce the exchange capacity. The decrease in MgEC resulting from the interaction of iron hydroxide with montmorillonite at pH 6 is shown by the distance separating the regression lines for pH 6 and 8 in Fig. 1 because this separation is essentially constant throughout the range of non-crystalline aluminum.

A slight increase in the MgEC was observed as the iron hydroxide-coated montmorillonite aged from 1–6 months. This MgEC increase is interpreted as some regular organization of the iron polymers resulting in a decreased positive charge, or iso-electric point/unit of iron, at constant pH.

Gibbsite and bayerite formation

The quantity of crystalline $\text{Al}(\text{OH})_3$ formed depended on the amount of added aluminum and the pH of the suspension when a total of 16 m-equiv of iron plus aluminum/g clay was coprecipitated in montmorillonite suspensions. Crystalline $\text{Al}(\text{OH})_3$ formed at a rate proportional to the quantity of non-crystalline aluminum present. At pH 6, gibbsite formation during 1 yr reduced the amount of non-crystalline aluminum from the 4.8–12 m-equiv originally precipitated to approximately 3.7 m-equiv/g clay. This quantity of non-crystalline aluminum was not significantly affected by the presence of 4–11.2 m-equiv iron hydroxide/g montmorillonite (Table 2). Bayerite formation at pH 8 reduced the non-crystalline aluminum to approximately 2.6 m-equiv/g clay (Table 2). However, the montmorillonites coated with the larger amounts of aluminum, and consequently with the smaller amounts of iron, retain more non-crystalline aluminum at pH 8 than those with less aluminum and more iron. Substitution of aluminum in iron structure

Table 2. Aluminum remaining as non-crystalline aluminum in a hydroxide-coated montmorillonite suspension aged 1 yr

Treatment* No.	(m-equiv Al/g montmorillonite)	
	Al initially added	Non-crystalline Al after aging
		pH 6 pH 8
6	1.6	1.6 1.6
5	3.2	3.2 3.2
4	4.8	3.7 2.3
3	6.4	3.6 2.4
2	8.0	4.0 2.7
1	12.0	3.6 3.1

* Treatment number from Table 1.

has been reported (Norrish and Taylor, 1961; Gastuche *et al.*, 1964) and could account for the apparent increase in non-crystalline aluminum as the Al/Fe increased.

Broadening of the DTA crystalline $\text{Al}(\text{OH})_3$ dehydroxylation peak with iron substitution in gibbsite (Gastuche *et al.*, 1964) was not observed. This indicates minimum contamination of the crystalline $\text{Al}(\text{OH})_3$ with iron. The quantity of non-crystalline aluminum/g clay was greater in the presence of iron hydroxides than that previously reported (Barnhisel and Rich, 1963) for montmorillonite with only aluminum hydroxides. This suggests that a mixed, positively charged, iron and aluminum polymer may be present in the montmorillonite exchange complex.

In the absence of montmorillonite and iron hydroxides, the neutralization of aluminum salts forms crystalline $\text{Al}(\text{OH})_3$ within one hour (Hsu, 1966; Hem, 1968) and gibbsite was essentially the only aluminum hydroxide present after two months aging. The first order diffraction spacing of 10 Å, after K saturation and oven drying, and the complete restoration of the CEC of an aluminum hydroxide coated montmorillonite following 6 months of aging (Barnhisel and Rich, 1963) suggests that polymeric aluminum cations, under the conditions of this study, remain on the exchange complex of montmorillonite less than 6 months.

In this study the MgEC of montmorillonite coated with hydroxides of iron and aluminum was not restored to its original value after aging one year. The crystalline $\text{Al}(\text{OH})_3$ determined by thermal gravimetry did not account for all the aluminum added at pH 6 or 8. Therefore, in the presence of iron hydroxide some aluminum remained as a polymeric cation on the montmorillonite. The inclusion of iron hydroxides might impose an activation energy barrier that prevents complete crystallization of the aluminum hydroxide. A positively charged copolymer, formed from mixed iron and aluminum hydroxides aged in montmorillonite suspensions, is compatible with the reported data in this study and is suggested by the work of Gastuche *et al.* (1964).

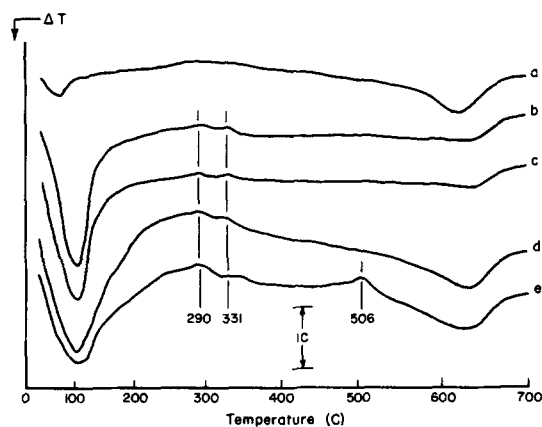


Fig. 2. Differential thermal analysis curves of (a) montmorillonite control and (b–e) iron hydrous oxide coated montmorillonite containing 16 m-equiv Fe/g clay, (b) aged 6 months at pH 6, (c) aged 6 months at pH 8, (d) aged 1 yr at pH 6, and (e) aged 1 yr at pH 8.

Differential thermal analysis

Differential thermal analysis of montmorillonites coated with more than 11.2 m-equiv of iron hydrous oxides/g clay and aged at least 4 months showed exothermic reactions at 290 and 330°C (Figs. 2b, c, d and e). The exotherms were present with samples containing up to 4.8 m-equiv of aluminum hydrous oxides/g clay. With more aluminum, and the subsequent formation of crystalline $\text{Al}(\text{OH})_3$, the exotherms were not observed, presumably due to the strong endothermic peak for crystalline $\text{Al}(\text{OH})_3$ dehydroxylation at approximately the same temperature.

Iron hydrous oxide-coated montmorillonite, aged one year at pH 8 in the absence of aluminum, shows two small exothermic peaks near 300°C, plus one strong exothermic peak at 506°C (Fig. 2e). Freshly precipitated iron hydrous oxide forms ferrihydrite, a protohematite which give an exothermic peak near 300°C (Chukhrov *et al.*, 1972). With aging, two exothermic peaks appear near 300°C, possibly due to either larger crystal size or increased strength of the water bonds as the material partially dehydrates (*ibid.*, 1972). The exothermic peaks at 300 and 500°C are quite specific for maghemite (Gheith, 1952). Iron hydrous oxides in montmorillonite suspensions aged 4–6 months at pH 6 or 8 apparently form a ferrihydrite-type structure. Since ferrihydrite forms rapidly in the absence of montmorillonite, the four-month lag time could be a result of the iron hydrous oxides being attached to the montmorillonite surfaces. This is supported by the observation of increased bond rigidity of iron hydrous oxides precipitated on montmorillonite (Yassoglou and Peterson, 1969). Differential thermal analysis data suggests both ferrihydrite and maghemite are formed in montmorillonite suspensions after aging one year at pH 8.

X-ray diffraction

Crystalline aluminum hydroxides were identified as gibbsite with basal spacings of 4.89 and 4.34 Å at pH 6

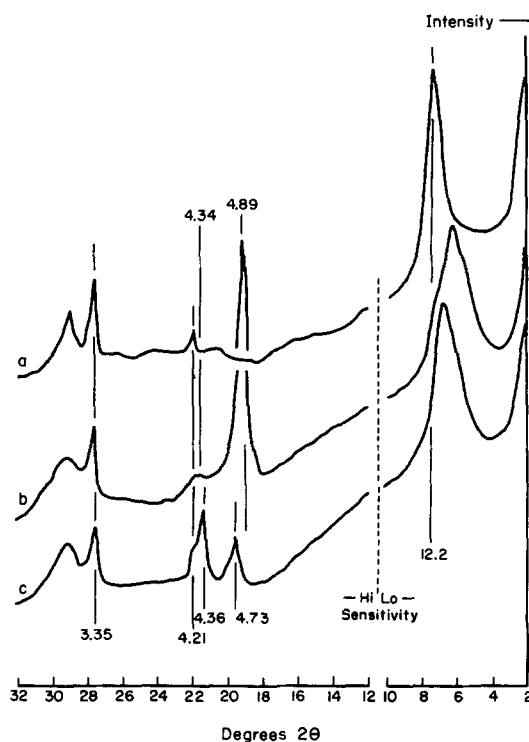


Fig. 3. X-ray diffraction patterns of potassium saturated, air-dried (a) montmorillonite control and aluminum-iron hydrous oxide coated montmorillonite (12 m-equiv Al plus 4 m-equiv Fe/g clay) aged 6 months at (b) pH 6 and (c) pH 8.

and bayerite with basal spacing of 4.73 and 4.36 Å at pH 8 (Fig. 3). These spacings of crystalline aluminum hydroxy materials were not observed in the control montmorillonite samples. Increased aluminum interlayering was indicated by the larger basal spacings for the montmorillonite first order peak of the aluminum-coated montmorillonite aged at pH 6 as compared to those aged at pH 8 (Fig. 3). Thermal gravimetric analysis showed less crystalline $\text{Al}(\text{OH})_3$ at pH 6. Therefore, more non-crystalline (interlayered) aluminum remained on the montmorillonite at pH 6 than at pH 8. This is in agreement with the conclusion of Rich (1968) that aluminum interlayer formation is favored by reducing the pH of the suspension. Heating the samples to 300°C eliminated the diffraction spacings associated with crystalline $\text{Al}(\text{OH})_3$, but the non-crystalline hydrous oxides remained interstratified between the montmorillonite layers (Fig. 4). The broad 10–14 Å first-order diffraction spacing indicates random interstratification of the hydroxy-aluminum-iron interlayers.

Crystalline iron compounds were not detected by X-ray powder diffraction analysis. Some regular order in the iron hydrous oxides was indicated by both DTA and CEC measurements. Therefore, the problem appears to be one of detection by X-ray diffraction techniques. Because careful X-ray powder diffraction analysis with either CuK_α or CoK_α (unpublished data)

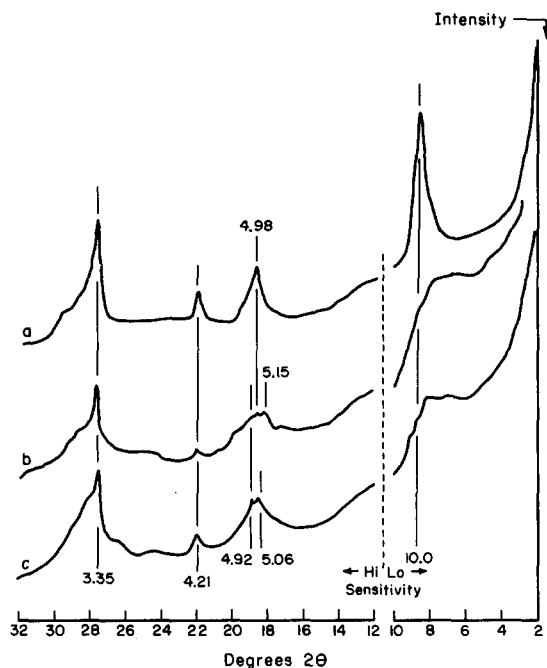


Fig. 4. X-ray powder diffraction patterns of potassium-saturated heated, 300°C for 2 hr, (a) montmorillonite control and aluminum-iron hydrous oxide coated montmorillonite (12 m-equiv Al plus 4 m-equiv Fe/g clay) aged 6 months at (b) pH 6 and (c) pH 8.

radiation did not reveal crystalline iron oxides before or after heat treatment, the iron oxide particles formed were of insufficient size or quantity to be detected.

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