

# THE EFFECT OF ACID AND HEAT TREATMENT ON MONTMORILLONIDS

A. C. MATHERS, S. B. WEED, AND N. T. COLEMAN  
North Carolina State College

## ABSTRACT

H-montmorillonite, -beidellite, and -nontronite were found to change spontaneously into Al-clays. Rates of conversion of H- to Al-clay were slow at 0° C, but at temperatures of around 100° C, moist H-montmorillonite changed to Al-saturated montmorillonite within 24 hours. It appeared that Al-ions moved from lattice positions to exchange positions, with octahedral Al moving more rapidly than tetrahedral Al.

Treatment of montmorillonoids with HCl solutions at 80° C resulted in the removal of large quantities of Fe, Mg, and Al. The residue after hot acid treatment appeared to be a mixture of essentially unaltered montmorillonoid and SiO<sub>2</sub>, rather than a new mineral.

On heat treatment, H- and Al-montmorillonites became largely non-expanding of 300° C, and lost the bulk of the CEC which could be attributed to permanent lattice charge. H- and Al-nontronite and -beidellite, on the other hand, did not suffer irreversible dehydration and loss of CEC until heated to sufficiently high temperatures to cause the expulsion of lattice OH. Montmorillonites with largely octahedral charge had smaller CEC's after heating to 500° C than did montmorillonites with appreciable tetrahedral charge.

## INTRODUCTION

The natures and reactions of acid-treated clays, particularly the montmorillonoids, are of interest to workers in many fields. Although several extensive studies of the result of mineral acid treatment on the compositions and reactions of clays have been made, a number of the effects of acid treatment remain obscure. The objective of the present work was three-fold:

1. To measure the changes in the composition and to study possible changes in the structures of clays caused by treatment with mineral acids;
2. To study the cation exchange properties of acid-treated clays; and
3. To investigate the effect of dry heating on the CEC and the lattice expansion of acid-treated montmorillonoids.

## EXPERIMENTAL

The clays used were montmorillonites from Plymouth, Utah, Clay Spur, Wyoming, Polkville, Mississippi, and Little Rock, Arkansas; nontronite from Garfield, Washington; and hectorite from Hector, California. Except for the Plymouth montmorillonite, all of the clay samples were API (Kerr, *et al.*, 1952, pp. 34, 37, 38, 42, 43) reference minerals.

*Acid Treatment*

The clays were first treated with cold dilute HCl to dissolve free carbonates and then were leached with a *N* NaCl solution to replace the exchangeable ions with Na. Five gm. portions of each clay were then treated with 100 ml. of various concentrations of HCl for different lengths of time, both at room temperature and at 80° C. After the HCl treatment, the clays were transferred to Buchner funnels, filtered, and washed first with cold *N* HCl and then with water. The filtrate was analyzed for Al, Fe, Mg, and Si by standard methods.

Table I shows the proportions of the total Al, Fe, and Mg removed from the clays by certain acid treatments. As expected from other work (Thomas, *et al.*, 1950, p. 868), the quantities of the metals removed from the clays depended on the acid concentration, the time of contact, and the digestion temperature. Ten percent HCl at 80° C removed large proportions of the Al, Fe, and Mg from all of the clays. Nontronite and hectorite were completely decomposed, while the Plymouth montmorillonite was attacked to a greater extent than were the other montmorillonites. Smaller quantities of the metal ions were removed by 3 percent HCl at 80° C, but the losses were still appreciable, particularly for hectorite and nontronite. As has been found before (Thomas, *et al.*, 1950, p. 868), cold dilute mineral acid dissolved only minor amounts of the lattice ions from the clays, and it seems that the cold 3 percent HCl treatment had little effect other than to achieve H-saturation of the clays. No appreciable concentrations of Si were found in any of the filtrates.

For all of the acid treatments, the percentages of the Al, of the Fe, and of the Mg removed from a particular mineral were much the same. It appears that extra-lattice forms of these metals were removed by the HCl-NaCl pre-treatment, and that each of the three ions was dissolved from the clay lattice at about the same rate. This was also observed by Glasser (1946, p. 1241) and by Thomas, *et al.*, (1950, p. 868). This indicates that the process resulting in the appearance of the metal ions in solution was the

TABLE I. — PERCENTAGE OF THE TOTAL AL, FE, AND MG REMOVED FROM MONTMORILLONOIDS BY 2-HOUR CONTACT WITH HCl

Clay	10% HCl, 80° C				3% HCl, 80° C				3% HCl, 30° C			
	Al	Fe	Mg	CEC <sup>1</sup>	Al	Fe	Mg	CEC <sup>1</sup>	Al	Fe	Mg	CEC <sup>1</sup>
	%	%	%	me./gm.	%	%	%	me./gm.	%	%	%	me./gm.
Ply.	56	58	62	0.57	24	26	30	0.84	2.4	3.7	3.3	0.98
C.S.	18	22	18	0.71	10	14	15	0.80	1.8	2.4	3.2	0.89
Polk.	28	31	32	0.95	12	12	14	1.11	2.2	2.9	3.2	1.25
L.R.	24	26	25	0.67	11	13	12	0.84	2.1	2.4	3.8	0.94
Nontronite	91	100	100	0.14	30	31	33	0.46	3.1	5.2	4.7	0.83
Hectorite	—	100	100	—	—	83	86	—	—	5.4	6.3	—

<sup>1</sup> Based on samples dried at 105° C.

dissolution of a part of the clay in the sample rather than the migration of metal ions from lattice positions to exchange positions, followed by their appearance in solution. If this were so, a silica residue which would readily dissolve in alkaline solution should remain. To investigate this, samples of the clays which had been treated with hot HCl were digested in 5 percent  $\text{Na}_2\text{CO}_3$  solution for 1 hour at  $80^\circ\text{C}$ . The quantities of silica removed by the alkaline digestion were approximately equivalent to the amounts of Al, Fe, and Mg which had been removed by the prior acid treatment. Because of the solution of lattice silica in alkaline solutions, only qualitative agreement could be expected.

The X-ray diffraction patterns given by the acid-treated samples of montmorillonite are typified by those for the Clay Spur montmorillonite, shown in Figure 1. After acid treatment, the clay was Ca-saturated by leaching with  $N$   $\text{CaCl}_2$ , and a 100 mgm. sample was then ground in a mortar with water and two drops of glycerol. Drops of the resulting suspensions were placed on microscope slides and allowed to dry slowly, yielding oriented specimens. Diffraction patterns were obtained with a North American Phillips X-ray spectrometer, using  $\text{FeK}_\alpha$  radiation.

Very distinct series of 00l reflections were obtained for the acid-treated clays. The first five orders appear distinctly. The more drastic HCl treatments resulted in diminution of the intensity of the various reflections, but did not affect their positions or their intensities relative to one another.

Also of interest are the cation exchange capacities of the acid-treated clays. The CEC's were determined by leaching 1 gm. samples of these with 250 ml. of  $N$  KCl solution and determining the acidity of the leachate by titration with NaOH. CEC determined in this way is analogous to the "permanent lattice charge" as defined by Schofield (1939, p. 2), and probably is close to the lattice charge resulting from isomorphous substitution. It is always less, sometimes considerably so, than the CEC determined at some alkaline reaction. The exchange acidity determined in this way is analogous to the values obtained by Grenall (1949, p. 1486), who titrated clays in salt solutions.

The CEC's of all of the montmorillonoids decreased with increases in the severity of the acid treatment. This is shown in Table I. Values obtained for cold 3 percent HCl-treated montmorillonites varied from 0.89 to 1.25 me. per gm., while the range of CEC's after treatment with 10 percent HCl at  $80^\circ\text{C}$  was from 0.57 to 0.95 me. per gm. The decreases in CEC were correlated with the losses of metals from the lattice, again indicating the decomposition of a part of the clay.

#### *The Conversion of H- to Al-Clay*

It has been shown (Coleman and Harward, 1953, p. 6045) that acid clays prepared by electro dialysis or by leaching with very dilute (less than about 0.1*N*) mineral acids contain trivalent Al rather than H as the exchangeable cations. However, nearly complete H-saturation can be achieved by the

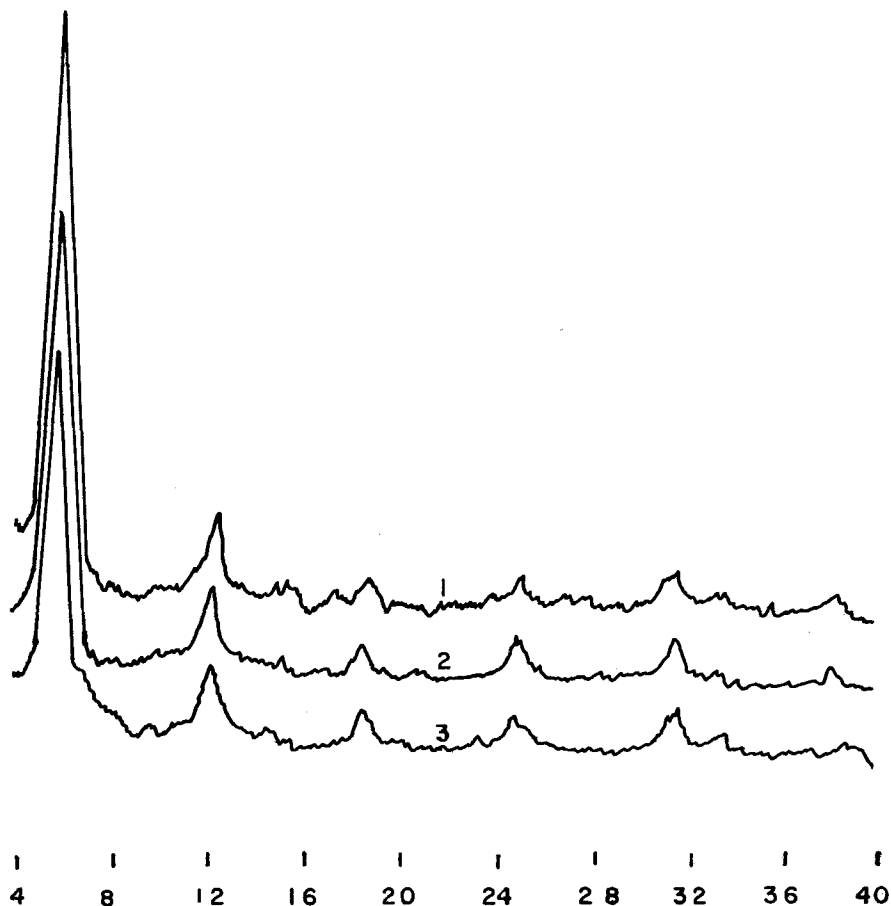


FIGURE 1.—X-ray diffraction patterns of HCl-treated C. S. montmorillonite. (1) 3% HCl, 30° C. (2) 3% HCl, 80° C. (3) 10% HCl, 80° C. Fe K $\alpha$  radiation.

treatment of clays with large volumes of more concentrated acids (Harward and Coleman, 1954, p. 181):

The clays which had been treated with cold 3 percent HCl were from 80 to 90 percent H-saturated when freshly prepared, the remainder of the permanent lattice charge being neutralized by Al (and possibly some Mg). This was measured by leaching samples of clay with *N* CaCl<sub>2</sub> solution and determining H and Al in the leachate by a two endpoint titration with NaOH. However, the H-clays did not remain as such, but changed spontaneously into Al-clays on moist storage.

The rate of the H-Al conversion was studied in some detail with the Plymouth montmorillonite. The results of this experiment are summarized

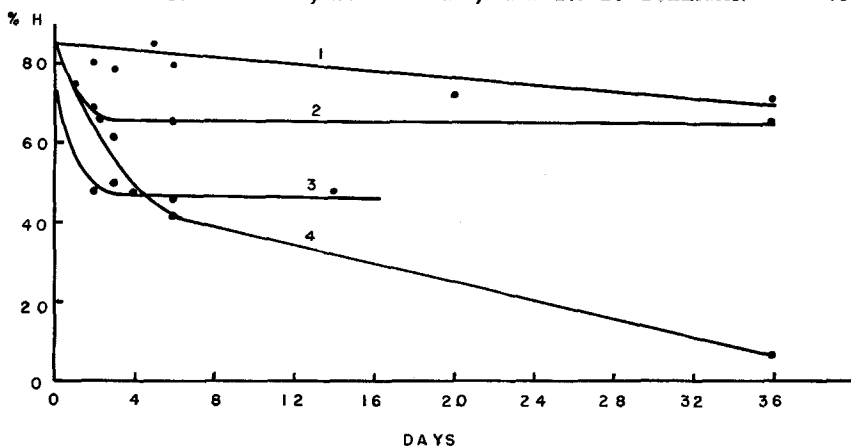


FIGURE 2.—Rate of conversion of H- to Al-clay under the following storage conditions: (4) Moist, 30° C. (1) Moist, 4-7° C. (2) Dry, 30° C. (3) Dry, 185° C.

in Figure 2. The rate of spontaneous conversion of H- to Al-montmorillonite depended both on the storage temperature and the moisture content of the sample. H-clay, stored with 100 percent water at 30° C (Curve 4), changed rapidly into Al-clay, while that stored at the same moisture content at 3-5° C (Curve 1) lost little of its exchangeable H over a period of 36 days. Curve 2 was obtained with a sample of H-clay which was stored in a vacuum desiccator over  $\text{CaCl}_2$  at 30° C. The H-saturation of this sample fell rapidly over the first two days, but after the clay was dry, no further change occurred. Curve 3 shows the same behavior for H-clay that was dried in an oven at 105° C and was left at this temperature for 14 days. There was a large immediate loss of exchangeable H, with a concurrent increase in exchangeable Al. Presumably this change occurred during the drying process. Thereafter, the H-saturation did not change appreciably during the course of the experiment.

The Plymouth montmorillonite lost exchangeable H and gained exchangeable Al on moist storage considerably faster than did the other clays which were studied. Table II shows the H- and Al-saturations of various cold

TABLE II.—H- AND AL-SATURATION OF HCl-TREATED MONTMORILLONIDS AFTER TWO PERIODS OF MOIST STORAGE

Clay	Stored 2 days			Stored 7 days		
	H mc./gm.	Al mc./gm.	% H	H mc./gm.	Al mc./gm.	% H
Ply.	0.69	0.30	70	0.42	0.60	41
C.S.	0.68	0.22	76	0.52	0.35	60
Polk.	0.99	0.28	78	0.80	0.44	64
L.R.	0.70	0.25	74	0.52	0.41	56
Nont.	0.61	0.24	72	0.45	0.36	56

HCl-treated clays after 2 and 7 days of moist storage. The nontronite and all of the montmorillonites lost exchangeable H and gained exchangeable Al during this period, with reaction being most rapid in the case of the Plymouth clay.

### *The Effect of Heating Acid Montmorillonoids*

Since the ion exchange studies described in the last section indicated that Al-ions may move from lattice positions to exchange positions, it was deemed of interest to investigate the influence of dry heating on the lattice expansion and the CEC of H- and Al-clays. Both H and Al are small ions, and one might expect the same effects with these that were observed by Greene-Kelley (1952, p. 222) for Li and Mg. That is, dioctahedral montmorillonoids with octahedral lattice charge saturated with H or Al might become nonexpanding and lose the bulk of their permanent charge on heating to 200° C-300° C, while clays with tetrahedral charge would not.

To investigate this, samples of cold 3 percent HCl-treated Plymouth montmorillonite and nontronite and samples of these same clays which had been Al-saturated by leaching with  $AlCl_3$  were heated in a furnace for 12 hours at temperatures from 100° C-400° C. After removal from the furnace the clays were rehydrated for 24 hours in an atmosphere saturated with water vapor.

Samples of the heat-treated clays were leached with *N* CaCl<sub>2</sub> to replace exchangeable H and Al, and these were determined by titration of the leachate with NaOH. Oriented specimens of the resulting Ca-clays were prepared for X-ray examination as noted earlier. Other samples of the Ca-clays were placed in a desiccator over saturated CaCl<sub>2</sub> (relative pressure  $\approx$  0.32) at 25° C. The sorbed water was determined gravimetrically after a one week equilibration period.

The results of this experiment are summarized in Table III. Data obtained with Li-montmorillonite are included for comparison. Heating H- or Al-montmorillonite at 100° C or 200° C for 12 hours caused considerable reductions in the amounts of exchange acidity, but did not reduce water sorption or the 001 lattice spacing. The Li-montmorillonite, on the other hand, suffered almost complete loss of CEC and became non-expanding on heating to 200° C. Heating at 300° C for 12 hours caused a large loss in CEC and produced irreversible dehydration of both H- and Al-montmorillonites. This was evidenced by the water sorption and the 001 spacing. The H- and Al-nontronite, however, remained expanding and retained its lattice charge at 300° C. At 400° C, lattice hydroxyls had been expelled from the nontronite, though some regularity in the C-direction persisted.

The fact that H- and Al-montmorillonites suffered irreversible dehydration and almost complete loss of lattice charge on heating to 300° C is of interest, since the acidic properties of calcined clays used as petroleum cracking catalysts have been stressed (Thomas, *et al.*, 1950, p. 868). They found the quantities of KOH consumed by acid-treated and calcined mont-

TABLE III. — PROPERTIES OF HEAT-TREATED MONTMORILLONITE AND NONTRONITE

T° C	Al-Utah		H-Utah		Al-nont.		H-nont.		Li-Utah	
	CEC <sup>1</sup>	% H <sub>2</sub> O <sup>2</sup>	CEC <sup>1</sup>	% H <sub>2</sub> O <sup>2</sup>	CEC <sup>1</sup>	% H <sub>2</sub> O <sup>2</sup>	CEC <sup>1</sup>	% H <sub>2</sub> O <sup>2</sup>	CEC <sup>1</sup>	% H <sub>2</sub> O <sup>2</sup>
25	1.11	16.8	0.94	18.0	0.97	14.8	0.82	14.0	—	14.9
100	0.74	15.8	—	17.4	0.99	15.0	—	13.9	—	13.6
200	0.62	15.0	0.49	14.6	0.97	14.0	0.82	14.6	0.11	4.3
300	0.20	8.0	0.20	6.0	0.90	14.1	0.75	13.6	0.10	3.6
400	0.10	4.4	0.15	4.3	0.27	7.4	0.07	3.6	—	—

<sup>1</sup> Me. of NaOH to neutralize KCl leachate from 1 gm. dry clay.<sup>2</sup> Percent H<sub>2</sub>O sorbed at a relative pressure of 0.32.

morillonite samples to be large (0.5 to 1.0 me. per gm.) and to increase with the intensity of the acid pretreatment. In contrast to this, the data given above shows that the permanent charge contribution to the CEC of acid Plymouth montmorillonite which had been heated to 400° C was only 0.10-0.15 me. per gm. Since part of this charge was balanced by Al, the quantity of H-ions electrostatically bonded to this particular calcined clay was very small.

To investigate the effect of heat-treatment on montmorillonites having different proportions of octahedral and tetrahedral charge, the acid-treated samples considered in Table I were calcined at 500° C for 2 hours. Exchange acidities were determined as before by leaching with *N* CaCl<sub>2</sub>, and oriented specimens of glycerol-Ca-clay complexes were prepared for X-ray study.

In Table IV are listed the CEC's, measured as exchange acidity, and the 001 spacings of the acid- and heat-treated clays. The X-ray diffraction patterns of selected samples are shown in Figure 3. According to the analyses of Earley, *et al.*, (1953, p. 712), the proportions of octahedral charge for the four montmorillonites are: Ply., 81; C.S., 62; Polk., 56; and L.R., 44. It appears from the data in Table IV that montmorillonites with largely octahedral charge may be changed more profoundly by heat treatment than are those with a large proportion of tetrahedral charge. The Little Rock sample, with 56 percent of its charge in the tetrahedral layer showed a pronounced 17.7 Å spacing after heat treatment, and had a much larger CEC than did the other minerals. So far as CEC is concerned, this clay behaved like the clays studied by Grenall (1949, p. 1486). The intensity of the acid pre-treatment had little effect on the CEC or the lattice expansion of the several clays.

### SUMMARY

Treatment of montmorillonoids with mineral acids resulted in the loss of lattice Al, Fe, and Mg, the amounts removed depending on the acid concentration, the temperature, and the time of contact. The three metal ions were removed in the same proportion that they occurred in the minerals, indicating that acid treatment resulted in the complete decomposition of a

TABLE IV.—CEC AND FIRST STRONG 001 REFLECTION OF ACID- AND HEAT-TREATED MONTMORILLONITES

Clay	10% HCl, 80° C		3% HCl, 80° C		3% HCl, 30° C	
	CEC me./gm.	001	CEC me./gm.	001	CEC me./gm.	001
Ply.	0.11	10.1	0.12	10.1	0.14	10.1
C.S.	0.07	9.4	0.13	9.4	0.12	9.4
Polk.	0.10	10.1	0.11	10.1	0.10	10.1
L.R.	0.18	17.7	0.22	17.7	0.24	17.7

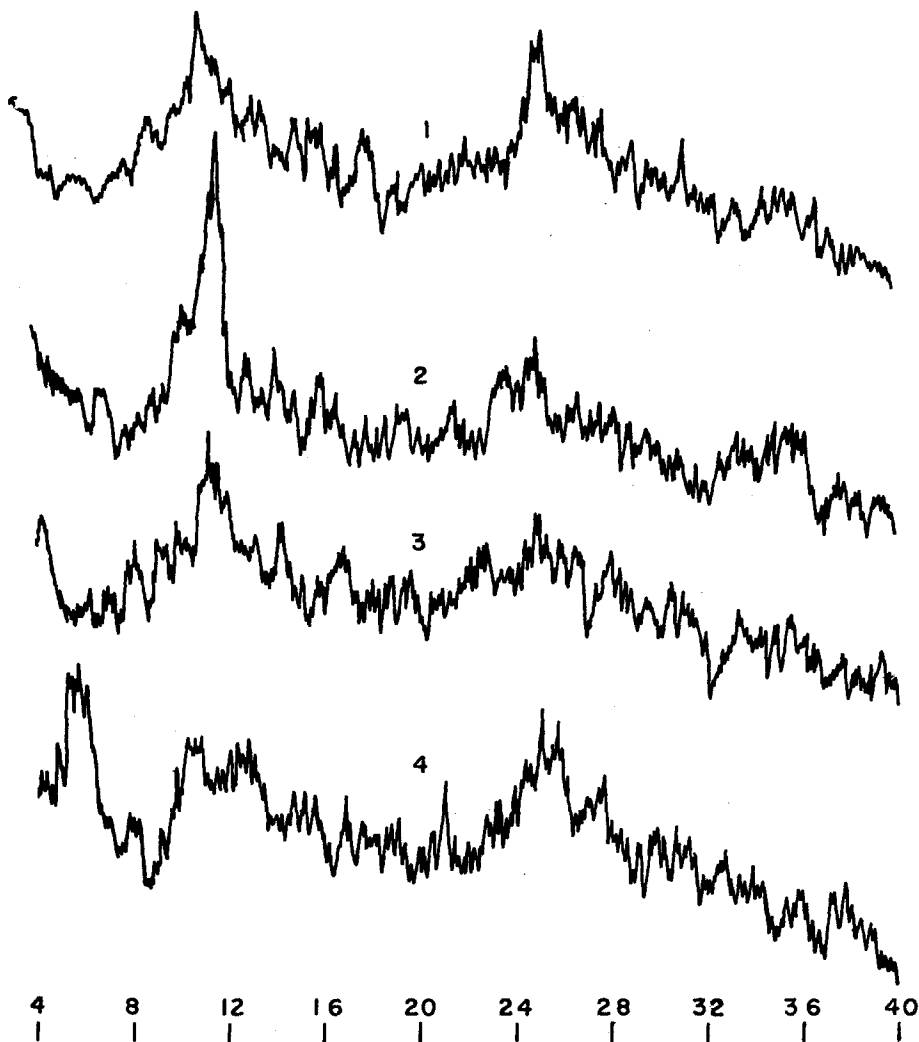


FIGURE 3.—X-ray diffraction patterns of acid-treated montmorillonites which had been heated at 500° C for 2 hours. (1) Ply. (2) C. S. (3) Polk. (4) L. R. Fe  $K\alpha$  radiation.

part of the clay. Si was not removed by acid treatment, though quantities of alkali-soluble silica roughly equivalent to the Al, Fe, and Mg dissolved could be extracted from the acid-treated clays. Acid treatments which removed up to 50 percent of the Al, Fe, and Mg of the clay had no effect on the X-ray patterns obtained with oriented specimens, other than to cause a diminution in the intensities of the 001 spacings.

Montmorillonites treated with moderately concentrated solutions of mineral acids were largely H-saturated when freshly prepared. On moist storage, however, exchangeable H was lost and exchangeable Al appeared in its place. The rate at which H-clays were spontaneously changed into Al-clays depended on the temperature and the moisture content of the sample. At low temperatures or low moisture contents, H-clays appeared to be fairly stable.

When H- and Al-montmorillonites were heated at temperatures between 200° C and 300° C for 12 hours, irreversible dehydration occurred. This was manifested by large losses in CEC and in surface as measured by water sorption, and by the failure of such clays to form glycerol complexes. H- and Al-nontronite, however, was not drastically altered by dry heating except at temperatures corresponding to the loss of lattice hydroxyls. The Little Rock clay, with a large proportion of tetrahedral charge, had a larger CEC after acid- and heat-treatment than did the other montmorillonites. In addition, this mineral formed a 2-layer glycerol complex even after being acid-treated and calcined at 500° C.

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