

# MODIFICATION OF Ca-MONTMORILLONITE BY LOW-TEMPERATURE HEAT TREATMENT\*

by

CLARA HO and R. L. HANDY  
Iowa State University, Ames, Iowa

## ABSTRACT

THE OBJECTIVES of this investigation were to measure the effects of moderate heat treatments, below the dehydroxylation temperature, on physical and chemical properties of a calcium-montmorillonite clay. Previous workers have noted the reductions in cation exchange capacity and swelling property after heating in the range 200°–400°C, and have suggested several possible explanations, such as hysteresis effect, increased interlayer attractions owing to removal of interlayer water, or changes in the disposition of interlayer or layer-surface ions.

The liquid limits of Ca-montmorillonite steadily decreased with increased treatment temperature, until they reached a constant level at 450° to 500°C. The plastic limit decreased slightly up to 350°C. Above this temperature samples could no longer be rolled into threads. The gradual change is in contrast with sudden major changes noted for weight loss (maximum rates of change at 100°C and 500°C), glycol retention surface area (maximum change at 520°C), and changes of peak intensity and breadth character after glycolation of the first diffraction maximum (530°C). Other properties showing more gradual reductions with heat treatment were: cation exchange capacity by  $\text{NH}_4\text{Ac}$  method,  $d_{001}$  intensity (21 Å spacing) after storing at 100 per cent r.h. one month and re-wetting with water, and amount of calcium exchangeable without water soaking. Previous water soaking allowed much greater release of fixed  $\text{Ca}^{++}$  up to 450°C. Similar results were obtained with cation exchange capacities when samples were treated with 1N  $\text{CaCl}_2$  solution.

The 21.0 Å peak intensity curve showed close similarity to the liquid limit and plastic index curves in the low temperature range, and an explanation is suggested.

## INTRODUCTION

HEAT treatment, a rather obvious means for stabilizing soils, probably dates to prehistoric times. A road built in India about 800 B.C. appears to be soil burnt *in situ*. In 1908, a heat stabilization method was tried on buckshot or gumbo clay soil near Tallula, La. According to the *Times-Picayune* newspaper (Slack, 1908), ditches spaced 4–5 ft apart were cut across the road to act as flues; wood was piled on the road, covered with soil from the ditches to a depth of 2 or 3 ft and ignited with crude oil. After being burned, the soil

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was found to be stabilized to a depth of about 2 ft. The road was finished by rolling.

Another example of use of heat treatment is reported by Hogentogler (1937): A self-propelled, slow-moving downdraft furnace using wood as fuel was used to treat Australian black soil. The rate of movement was 10 ft per hr; the depth of treatment was about 6 in. After treatment the clods were broken, and a clay binder was added and mixed in. The 6-ft wide machine produced about 500 ft of 18-ft roadway per week.

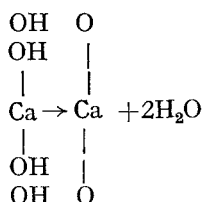
Because of the high fuel consumption and low production rate, thermal stabilization is now little more than a historical curiosity. Engineers often assume that the treatment must be carried, as for ceramic products, to sintering temperatures to be effective. However, moderate heat treatment, below the clay dehydroxylation temperature, brings about marked changes in the character of clayey soils. Wintermyer (1925) observed a reduction in plasticity when what appears to be a kaolinitic clay soil was heated to 300°C. A similar change in kaolinite was found by Holdridge and Moore (1953), who cited the temperature of change as between 250° and 270°C. Oven drying generally causes a change in plasticity of clay soils and is therefore not used for routine tests (Casagrande, 1932).

A common explanation for the reduction in plasticity after moderate heating is (Grim, 1962): Drying causes shrinkage, and the resulting closer proximity of clay particles or layers brings into play larger attractive forces, so that the shrinkage is irreversible. Since the clay will not accept as much water on re-wetting, the plastic limit is lowered.

Hoffman and Endell, and Hoffman and Klemen report (cited by Grim, 1953) that heat reduces the cation exchange capacity of montmorillonite before the swelling property is lost. The reduction is large for montmorillonite saturated with  $\text{Li}^+$  and  $\text{Ca}^{++}$ , but it is small when saturated with  $\text{Na}^+$ . Hoffman and Endell (Grim, 1953) suggest that when the clay is heated the exchangeable cations tend to move inside the montmorillonite lattice; the small  $\text{Li}^+$  probably fits easily into vacancies in the octahedral layer and consequently only a low temperature is required for the shift into the structure. The large  $\text{Na}^+$  ion would fit into the structure with difficulty, and a high temperature would be required for the move.

González García (cited by Greene-Kelly, 1953) showed that Li- and Mg-montmorillonite gave an irreversible loss of surface after heating to 200° and 300°C respectively, while Sr- and Ba montmorillonite showed little change in properties after being heated to 400°C. He suggested that this loss of surface was a function of the ability of the exchange ion to polarize molecules, i.e. the small ions of high charge are more effective in promoting irreversible change of surface than other ions. Greene-Kelly (1953) attributed the unusual behavior of Li-montmorillonite to the migration of the small  $\text{Li}^+$  ions into the vacant octahedral position with a consequent neutralization of the charges originating in that layer. The mineral was then assumed to have a pyrophyllite-type structure with a consequent loss of expanding properties.

Méring (1946) suggested that the loss of internal surface in Ca-montmorillonite between 350°–400°C resulted from partial elimination of OH groups, leading to oxide links in which the divalent exchangeable cation was supposed to link adjacent silicate sheets as diagrammed below:



To summarize, several hypotheses have been suggested to explain the changes in properties of montmorillonite when heated to temperatures from 200°–400°C. These include permanently increased attractions owing to removal of adsorbed water; entry of exchangeable ions into the clay crystal structure, neutralizing the layer charge; polarization of clay surfaces; and partial dehydroxylation.

The objectives of our present investigation were to measure the effects of low temperature heat treatments on properties of calcium-montmorillonite clay, such as abounds in Iowa soils, and to explore the reaction mechanism in more detail, with a view toward increasing its usefulness.

## MATERIALS AND METHODS

### *Heat Treatment*

A hundred grams of natural Ca-saturated Panther Creek bentonite (American Colloid Co.) was divided in ten small crucibles, 10 g in each, and heated at various constant temperatures for 24 hr. After cooling in a desiccator, the weight loss of each sample was recorded and was expressed as the percentage of the dry weight at the temperature to which it had been heated. The various heated samples were analyzed as follows:

### *X-ray Diffraction*

A small amount of each sample was mixed with a few drops of ethylene glycol and smoothed into a Bakelite holder by using a glass slide. The glycolated sample was then equilibrated overnight and X-rayed with a GE XRD-5 diffractometer using Cu  $K\alpha$  radiation, 1° beam slit, MR soller slit, 0.2° detector slit, and 3 sec time constant.

Other samples were saturated with water in Bakelite holders and equilibrated for one month in a closed vessel at 100 per cent relative humidity. At the end of equilibration each sample was again moistened and smoothed with a glass slide before being X-rayed.

The  $d_{001}$  peak intensities at 17.7 Å spacing for the glycolated samples and at 21 Å spacing for the rehydrated samples were measured with a polar planimeter.

#### *Exchange Properties*

*Cation exchange capacity.* Two methods were used for comparison: the conventional  $\text{NH}_4\text{Ac}$  method and the  $\text{CaCl}_2$  method. In the first, a 0.2-g sample in a 50-ml. Erlenmeyer flask was shaken with 25-ml. 1N  $\text{NH}_4\text{Ac}$  for 1 hr and then set overnight. The suspension was filtered in a small Gooch crucible followed by further leaching with 20-ml. 1N  $\text{NH}_4\text{Ac}$  solution to assure  $\text{NH}_4^+$  saturation. Excess  $\text{NH}_4\text{Ac}$  was removed by washing four to five times with 75 per cent methyl alcohol in water. The  $\text{NH}_4^+$  adsorbed was steam-distilled with a microsteam distillation apparatus in the presence of  $\text{NaOH}$  and  $\text{MgO}$  (Ho and Handy, 1963).

In the  $\text{CaCl}_2$  method, a 0.2-g sample was shaken with 25-ml. 1N  $\text{CaCl}_2$  solution and equilibrated as above. The sample was washed four to five times with 75 per cent methyl alcohol and then with water until no  $\text{Cl}^-$  ions were indicated by  $\text{AgNO}_3$  test. The  $\text{Ca}^{++}$  adsorbed was displaced with 30-ml. 1N  $\text{KCl}$  by slow leaching, and titrated with standard EDTA (Cheng and Bray, 1951).

*Exchangeable calcium.* Exchangeable calcium was displaced with 1N  $\text{KCl}$  by two methods. First, a 0.2-g sample was weighed into a 50-ml. Erlenmeyer flask, shaken with 25-ml. 1N  $\text{KCl}$  solution for 1 hr, and allowed to set overnight. The suspension was filtered and washed twice with distilled water, and the  $\text{Ca}^{++}$  displaced was titrated with EDTA. A second 0.2-g sample was soaked in 12.5-ml. distilled water for 3 days; then 12.5 ml. of 2 N  $\text{KCl}$  solution was added to extract the exchangeable  $\text{Ca}^{++}$  as described.

#### *Atterberg Limits*

The Atterberg limits were determined according to standard procedures (ASTM, 1964).

#### *Surface Adsorption*

Surface adsorption studies were made by both glycol (Bower and Goertzen, 1959) and water retention methods. A modified arrangement was used in the glycol method: 0.3 g of sample was accurately weighed into a small weighing bottle, further dried at 110°C overnight and again weighed. The dried sample was immediately moistened with 0.8 ml. or less of ethylene glycol, and covered for equilibration overnight. The glycol- $\text{CaCl}_2$  solvate prepared according to Bower's procedure was placed in the bottom of a 6-in. vacuum desiccator, and over this was placed a perforated plate to hold the sample containers. With this arrangement, as many as 14 samples could be treated each time.

The water-retention studies were performed the same way except that 98 per cent relative humidity was maintained by a saturated  $\text{Pb}(\text{NO}_3)_2$  solution. An aspirator was used for evacuation before equilibrating.

## RESULTS

*Effect of Heat Treatment on Weight Loss and Surface Area*

Changes in weight-loss and surface area with temperature are shown in Fig. 1. In addition to two sharp reductions in weight, at 25°–150°C (11.8 per cent) and 450°–600°C (5 per cent), relating to the loss of adsorbed water and clay structural hydroxyl groups, a small gradual weight loss (<0.7 per cent)

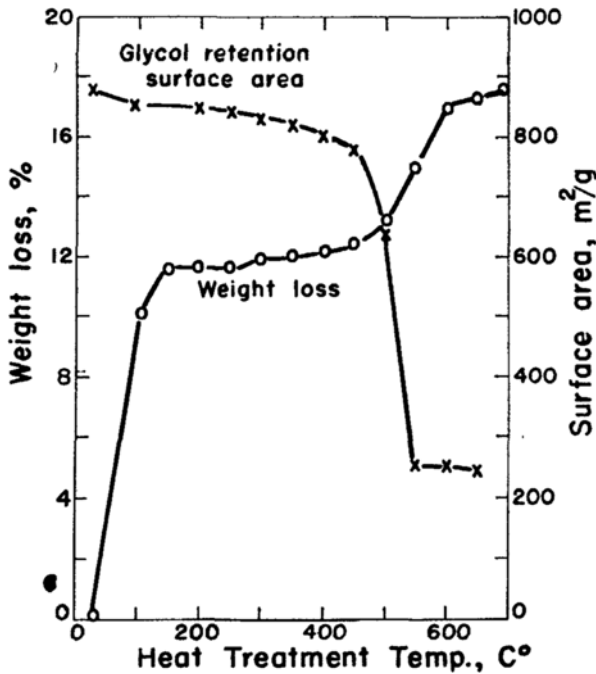


FIG. 1. Relationship of weight-loss and surface area to heat treatment of Ca-montmorillonite.

occurred at 250°–300°C. Drastic reduction in surface area (from 780 to 250 m<sup>2</sup> per g) occurred in a small temperature range of 450°–550°C, coinciding with the dehydroxylation weight loss. Below 450°C and above 550°C the surface area decreased only slightly.

*Exchange Properties*

*Exchangeable Ca<sup>++</sup>.* As shown in Fig. 2, without previous water soaking, the amount of Ca<sup>++</sup> ions displaced by 1 N KCl decreased rapidly depending on low temperature heat treatment, and remained almost constant between

350°–500°C. Further heating up to 650°C resulted in a small increase in KCl extractable  $\text{Ca}^{++}$ , followed by a drop at 700°C.

A different trend is shown in exchangeable  $\text{Ca}^{++}$  extracted by 1N KCl after heating and 3 days water soaking; soaking apparently allowed a much larger release of  $\text{Ca}^{++}$  in the range of heat treatment up to 450°C.

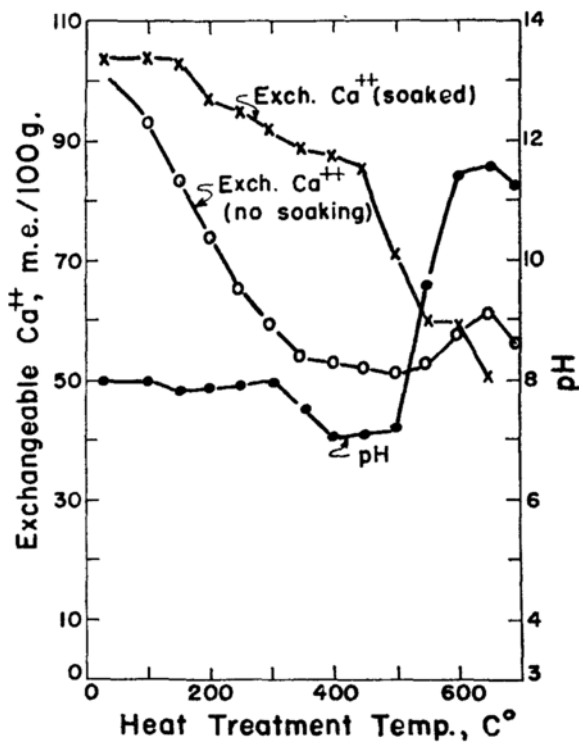


FIG. 2. Exchangeable  $\text{Ca}^{++}$  and pH of heat-treated Ca-montmorillonite.

*pH.* The corresponding pH of unsoaked samples remained (Fig. 2) near 8 for samples heated below 300°C, then decreased to 7 in the temperature range 300°–400°C and remained constant from 400°–500°C. The pH increased abruptly from around the dehydroxylation temperature, 500°–600°C.

*Exchange capacity.* The cation exchange capacity measured by  $\text{NH}_4\text{Ac}$  method ( $\text{CEC}_{\text{NH}_4\text{Ac}}$ ) is distinctly different from that measured by the  $\text{CaCl}_2$  method ( $\text{CEC}_{\text{CaCl}_2}$ ) (Fig. 3), the former being much lower through the entire range of heat treatments. The differences ranged from 20, at 25°C, to 50 me/100 g at around 400°C. The  $\text{CEC}_{\text{NH}_4\text{Ac}}$  decreased slightly in the temperature range 100°–250°C, then dropped continuously in the temperature range

250°–700°C. The  $\text{CEC}_{\text{CaCl}_2}$  decreased slightly over a much larger temperature range, 100°–450°C, then dropped rapidly in the narrow dehydroxylation temperature range of 450°–550°C. Thus the general trends of the  $\text{CEC}_{\text{CaCl}_2}$ , the water-soaked exchangeable  $\text{Ca}^{++}$ , and the surface area curves (Fig. 1) are the same.

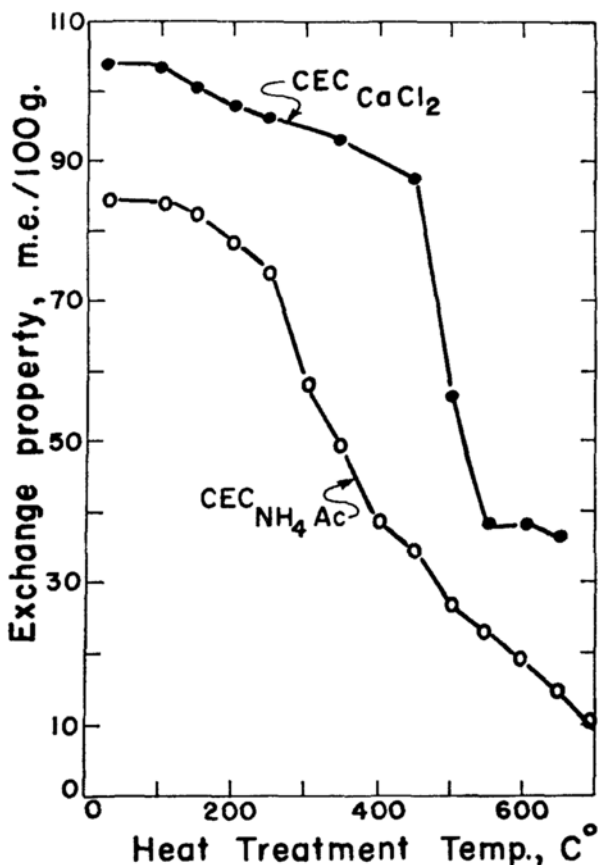


FIG. 3. Cation exchange capacities of heat-treated Ca-montmorillonite.

#### *X-ray Diffraction Data*

Water- and glycol-saturated samples were made to test the changes in expansive properties of heated Ca-montmorillonites. The  $d_{001}$  spacings of the glycolated samples re-expanded to 17.7 Å after heat treatment as high as 600°C (Fig. 4). The intensity of this peak remained almost constant up to 450°C, then decreased rapidly to zero at 650°C. Expansion of the  $d_{001}$  spacings of the water-saturated samples to 21 Å was inhibited at the much lower

temperature of 450°C. The intensity of the 21 Å peak remained constant up to 150°C, decreased 50 per cent at 300°C and reached zero at 500°C. The peak breadth of the 21 Å peaks at half-maximum intensity was also measured (Fig. 4) and shows a slight and gradual increase up to 350°C followed by larger increases at higher temperature. The corresponding broadening for the 17.7 Å peak was comparatively slight.

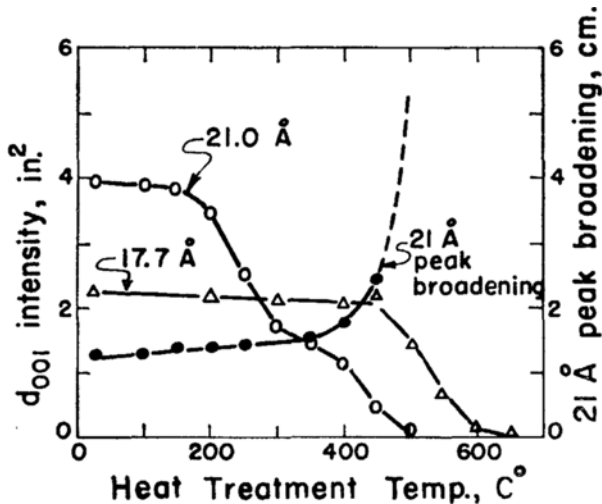


FIG. 4. X-ray diffraction  $d_{001}$  peak intensities and broadening (21 Å) of heat-treated Ca-montmorillonite after re-expanding with water (21.0 Å peak) or ethylene glycol (17.7 Å peak).

#### *Change in Atterberg Limits with Temperature*

As shown in Fig. 5, plastic limits decreased slightly but remained relatively little changed in samples heated up to 350°C, above which samples could no longer be rolled into threads. This was primarily because of the pronounced decrease in liquid limit. The difference between the two limits, defined as the plasticity index, is markedly reduced. When the plasticity index approaches zero, the soil is nonplastic and behaves as a clean silt or sand.

Some of the moistened samples were equilibrated under 100 per cent r.h. for 3 days before the Atterberg limits were determined. As might be expected, the Atterberg limits in general were higher than the corresponding values determined without equilibration. An interesting feature of the liquid limit curve is its similarity to the curve of  $d_{001}$  peak intensity at 21 Å spacing.

#### *Water Retention*

Water retention by the clay at 98 per cent r.h. remained almost constant after heat treatment in the range 25°–300°C, then decreased; the decrease



was most rapid in the temperature range of 450°–550°C (Fig. 6). Heating above 550°C resulted in little change in water retention. The water retention follows a pattern similar to that shown by the glycol-retention surface-area curve in Fig. 1.

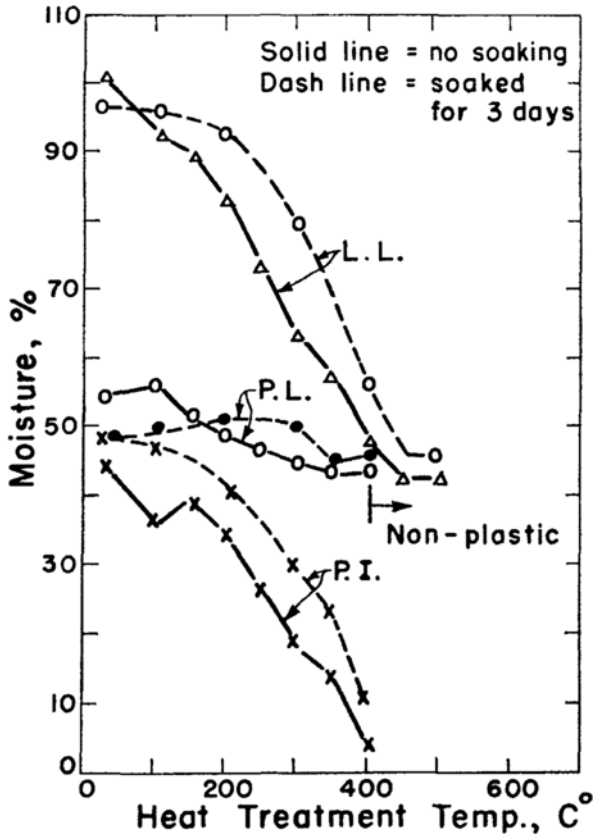


FIG. 5. Plastic limits and liquid limits of heat-treated Ca-montmorillonite.

## DISCUSSION

### *Immobilization of Ca<sup>++</sup>*

Exchangeable calcium data show that moderate heat treatment below 350°C immobilizes some of the adsorbed Ca<sup>++</sup> ions as they become non-exchangeable with KCl. However, some of the exchange sites remain blocked, indicated by the reduction in CEC measured by the NH<sub>4</sub>Ac method. Immobilization of Ca<sup>++</sup> is not associated with loss in internal surface measured by

glycol retention or by X-ray diffraction, since the collapsed  $d_{001}$  spacings re-expand to 17.7 Å with glycol or to 21 Å with H<sub>2</sub>O (Fig. 4). However, immobilization of Ca<sup>++</sup> and blocking of exchange sites apparently are not of a permanent nature, since most of the blocked exchange sites and the associated immobilized Ca<sup>++</sup> can be recovered either by using a salt solution containing small polyvalent cations or by soaking the samples with water for a few days, if a salt solution containing large monovalent cations like K<sup>+</sup> is used for cation exchange.

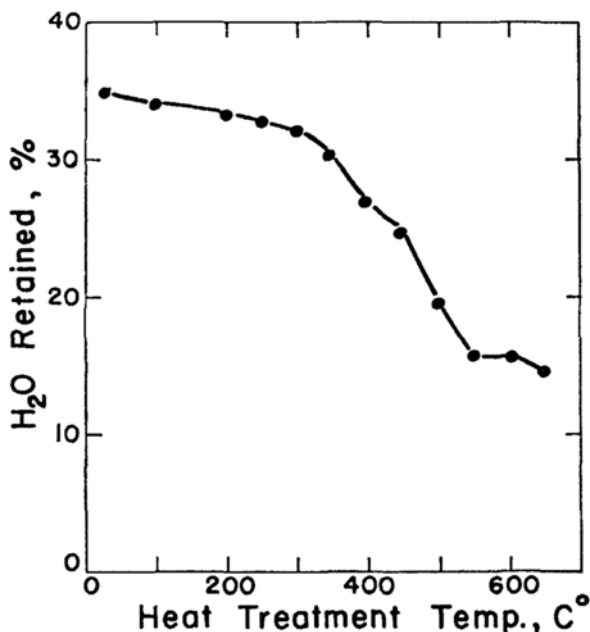


FIG. 6. Retention of water by heat-treated Ca-montmorillonite.

The discrepancy in exchangeable Ca<sup>++</sup> measured with and without previous water soaking becomes more pronounced with temperature up to 450°C, indicating that previous water treatment facilitated cation exchange between K<sup>+</sup> and the immobilized Ca<sup>++</sup>. The difference in CEC<sub>CaCl<sub>2</sub></sub> and CEC<sub>NH<sub>4</sub>Ac</sub> showed a similar trend.

This brings up the question of the location of the fixed Ca<sup>++</sup> ions. The nature of the Ca<sup>++</sup> immobilization is distinctly different from that of Li<sup>+</sup> immobilization reported by Greene-Kelly (1953). As previously mentioned, Li<sup>+</sup>, with a radius of 0.60 Å, is believed to enter the octahedral layer and neutralize the lattice charge, creating a pyrophyllite-like structure with loss of expansive properties. Ca<sup>++</sup> is probably too large to fit in an octahedral layer and does not cause loss in expandibility.

The suggestion of Méring (1946) that exchangeable  $\text{Ca}^{++}$  is immobilized by formation of  $-\text{O}-\text{Ca}-\text{O}-$  linkages between adjacent silicate sheets is untenable for two reasons: dehydroxylation is required, and probably does not occur at the temperatures at which  $\text{Ca}^{++}$  fixation begins; and such bonding would probably bring about an irreversible collapse of the  $d_{001}$  spacing. In the present study, irreversible collapse with respect to glycolation was observed only after heating to  $650^\circ\text{C}$ , where weight loss and DTA data indicate that dehydroxylation is essentially complete.

The present results suggest another possible explanation. When the clay is heated above  $150^\circ\text{C}$ , some of the exchangeable  $\text{Ca}^{++}$  ions become dehydrated and attach tightly or sink into the hexagonal holes in the surface of the Si-tetrahedral layer, allowing compensation of the exchange sites in the octahedral layer as revealed by the corresponding reduction in  $\text{CEC}_{\text{NH}_4\text{Ac}}$ . That the fixed  $\text{Ca}^{++}$  becomes nonexchangeable with respect to  $\text{K}^+$  and  $\text{NH}_4^+$  could be due to the large sizes of these cations and to clogging action. The latter might even prevent the penetration of water molecules and thus the hydration of the immobilized  $\text{Ca}^{++}$  between the layers.

This hypothesis may be supported as follows: First, most of the fixed  $\text{Ca}^{++}$  became exchangeable with KCl after the samples had been water-soaked, suggesting that the  $\text{Ca}^{++}$  ions probably underwent slow hydration with resulting expansion of the collapsed layer, as shown by the X-ray diffraction pattern. Second, the clogging action of  $\text{K}^+$  ions was further evidenced by the finding that the heated samples treated directly with 1N KCl did not swell or re-expand to any sharp peak in the time interval tested, as did those samples treated with water or  $\text{CaCl}_2$  alone. The 1N  $\text{CaCl}_2$ -treated samples clearly showed swelling properties and re-expanded to  $21 \text{ \AA}$  after heat treatment up to  $400^\circ\text{C}$ . It appears that upon treating with  $\text{CaCl}_2$ , the small  $\text{Ca}^{++}$  ions probably enter the interlayer through edges, leading to partial expansion, followed by gradual penetration of water molecules into the layer. This in turn could introduce gradual hydration and migration of the immobilized  $\text{Ca}^{++}$  ions to the surface.

Above  $450^\circ\text{C}$  the drastic decreases in surface area,  $\text{CEC}_{\text{CaCl}_2}$ ,  $\text{Ca}^{++}$  exchangeable after water soaking,  $17.7 \text{ \AA}$  peak intensity, and the sudden increases in weight-loss and pH were probably all associated with dehydroxylation and destruction of the original clay structure.

#### *Effect of Heat Treatment on Atterberg Limits*

Moderate heat treatment between  $200^\circ\text{C}$ – $450^\circ\text{C}$  greatly decreased the liquid limit and plastic index. The partial recovery after three days curing further indicates a slow rehydration of the interlayer cations. Nevertheless, the fact that curing did not cause the liquid limits and plastic indexes to recover to the same extent as did the exchangeable  $\text{Ca}^{++}$  (with previous water soaking) and  $\text{CEC}_{\text{CaCl}_2}$  suggests that the exchangeable  $\text{Ca}^{++}$  and charges may not be the only factors causing reduction of liquid limits and plastic indexes. These

limits neither correlate with the glycol surface area nor with the water-retention data, yet their trend does show similarity to the 21 Å peak intensity curve.

The sudden decrease in the 21 Å peak intensity around 250°C could be due to particle orientation and/or break down of the large particles rather than destruction of clay structure, since there is small change in peak broadening. The particle orientation could result from the change in particle shape after moderate heat treatment.

## CONCLUSIONS

1. Moderate heat treatment of Ca-montmorillonite immobilizes some of the exchangeable  $\text{Ca}^{++}$  ions and blocks some of the exchange sites without causing a significant loss of internal surface or irreversible collapse of the  $d_{001}$  spacing. Most of the immobilized  $\text{Ca}^{++}$  ions become re-exchangeable after soaking in water, and the blocked exchange sites are recovered.

2. The mechanism of  $\text{Ca}^{++}$  immobilization apparently relates to dehydration of the  $\text{Ca}^{++}$  ions and tighter bonding to the tetrahedral layer, perhaps by sinking into the hexagonal holes. When the clay is soaked with water or with a salt solution containing small polyvalent cations, most of the  $\text{Ca}^{++}$  ions become gradually rehydrated and exchangeable.

3. Heating this clay above 450°C resulted in dehydroxylation with associated drastic reduction in water retention, internal surface, swelling, exchange properties and an increase in pH.

4. Heating caused reduction in liquid limits and plastic indexes at temperatures below the dehydroxylation temperature, brought about by changes in bonding of the interlayer  $\text{Ca}^{++}$  ion and probably by changes in clay particle shape and/or nature of particle surface other than surface area.

## ACKNOWLEDGMENTS

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## REFERENCES

- ASTM Standards, Part II, Soils* (1964) American Society for Testing and Materials, Philadelphia, Pa.
- BOWER, C. A., and GOERTZEN, J. O. (1959) Surface area of soils and clays as determined by an equilibrium ethylene glycol method, *Soil Sci.* **87**, 289-92.
- CASAGRANDE, A. (1932) Research on Atterberg limits of soils, *Public Roads* **13**, No. 136.
- CHENG, K. L., and BRAY, R. H. (1951) Determination of calcium and magnesium in soil and plant material, *Soil Sci.* **72**, 449-58.
- GREENE-KELLY, R. (1953) Irreversible dehydration in montmorillonite, Part II, *Clay Minerals Bull.* **2**, 52-6.

- GRIM, R. E. (1953) *Clay Mineralogy*, McGraw-Hill, New York.
- GRIM, R. E. (1962) *Applied Clay Mineralogy*, McGraw-Hill, New York.
- HO, C., and HANDY, R. L. (1963) Characteristics of lime retention by montmorillonite clays, Presented at the 42nd Annual Meeting of the Highway Research Board, NAS-NRC, Washington D.C.
- HOGENTGLER, C. A. (1937) *Engineering Properties of Soils*, McGraw-Hill, New York.
- HOLDRIDGE, D. A., and MOORE, F. (1953) Clay-water relationships in ceramics, *Clay Minerals Bull.* **2**, 26–8.
- MÉRING, J. (1946) On the hydration of montmorillonite, *Trans. Faraday Soc.* **42B**, 205–19.
- SLACK, A. L. (1908) New way of making roads, [New Orleans] *Times Picayune*, July 11.
- WINTERMYER, A. M. (1925) Percentage of water freezable in soil, *Public Roads* **5**, No. 12.