Special Report

MODIFICATION OF CA-MONTMORILLONITE
BY
LOW-TEMPERATURE HEAT TREATMENT

by

Clara Ho, Research Associate and
Richard L. Handy, Professor of Civil Engineering,
Iowa Engineering Experiment Station,
Iowa State University of Science and Technology,
Ames, Iowa

IOWA
ENGINEERING
EXPERIMENT
STATION

Project 531-S

IOWA STATE UNIVERSITY
of Science and Technology / **Ames, Iowa**

MODIFICATION OF CA-MONTMORILLONITE
BY
LOW TEMPERATURE HEAT TREATMENT[1]

by

Clara Ho and R. L. Handy[2]

ABSTRACT

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 reduction in cation exchange capacity and swelling property after heating in the range 200 to 400°C, and have suggested several possible explanations, such as hysteresis effect, increased inter-layer attractions due to removal of inter-layer water, or changes in the disposition of inter-layer or layer surface ions.

The liquid limits of Ca-montmorillonite were steadily decreased with increased temperature of treatment, levelling at about 450°C. The plastic limit decreased slightly up to 350°C, above which 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 (520°C), and d_{001} diffraction peak intensity (17.7 Å spacing) and breadth after glycolation (530°C). Other properties showing more gradual reductions

with heat treatment were amount of exchangeable calcium (without water soaking), cation exchange capacity by NH_4AC method, and d_{001} intensity (21 Å spacing) after storing at 100% r.h. one month and re-wetting with water. Previous water soaking allowed much greater release of fixed Ca^{++} up to 450°C. Similar results were obtained with cation exchange capacities when samples were treated with N $CaCl_2$ 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 local newspaper (Slack, 1908), ditches spaced 4 to 5 feet 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 feet, and ignited with crude oil. After being burned, the soil was found to be stabilized to a depth of about 2 feet. The road was finished by rolling.

Another example of use of heat treatment is from an Australian source (Hogentogler, 1937): A self-propelled, slow-moving downdraft furnace using wood as fuel was used to treat the Australian "black soil". The rate of movement was 10 feet per hour; the depth of treatment was about 6 inches. After treatment the clods were broken, and a clay

binder was added and mixed in. The 6-foot wide machine produced

only about 500 feet of 18-foot roadway per week.

Because of the high fuel consumption and low production rate,

thermal stabilization is now little more than a historic 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 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 more closely

defined the temperature of change between 250 and 270°C. Oven

drying generally causes a change in plasticity properties of clay soils,

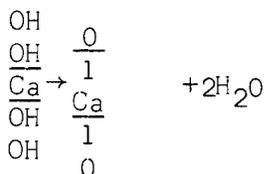and is therefore not used for routine tests (Casagrande, 1932).

A common explanation for plasticity reduction after moderate

heating is as follows (Grim, 1962): Drying causes shrinkage, and the

resulting closer proximity of clay particles or layers brings into

play larger attractive forces, such that the shrinkage is irreversible.

Since the clay will not accept as much water on re-wetting the plastic

limits is in effect lowered.

Hoffman and Endell and Hoffman and Klemen report (cited by

Grim, 1953) that heat reduces the cation exchange capacity of mont-

morillonite before the swelling property is lost. The amount of

reduction is large for montmorillonite saturated with Li^+ and Ca^{++},

but it is small when saturated with Na^+. Hoffman and Endell (Grim,

1953), suggest that the exchangeable cations when heated tend to move inside the montmorillonite lattice; the small 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 Na^+ ion would fit into the structure with difficulty, and a high temperature would be required for the move.

Gonzalez Garcia (Greene-Kelley, 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. The unusual property of Li-montmorillonite was explained by Greene-Kelley (1953) as due to the migration of the small Li^+ ions into vacant octahedral position with a consequent neutralization of the charges originating in that layer. The mineral is then assumed to have a pyrophyllite-type structure with a consequent loss of expanding properties.

Mering (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.

$$\begin{array}{c} OH \\ \underline{OH} \\ \underline{Ca} \\ \underline{OH} \\ OH \end{array} \rightarrow \begin{array}{c} \underline{O} \\ 1 \\ \underline{Ca} \\ 1 \\ O \end{array} \quad + 2H_2O$$

To summarize, several hypotheses have been sugested to explain
the changes in montmorillonite properties when heated to temperatures
from 200 to 400°C. These include permanently increased attractions
due to removal of adsorbed water; entry of exchangeable ions into the
clay crystal structure, neutralizing the 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 towards increasing
its usefulness.

MATERIALS AND METHODS

Heat Treatment

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

X-Ray Diffraction

A small amount of a sample was mixed with a few drops of
ethylene glycol and smoothed in a Bakelite holder by means of a
glass slide. The glycolated sample was then equilibrated overnight

and X-rayed with a GE XRD-5 diffractometer using Cu Kα beam, 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 desiccator modified for 100% 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 NH_4AC method and the $CaCl_2$ method. In the former an
0.2g sample in 50 ml. Erlenmeyer flask was shaken with 25 ml. N NH_4AC
for one hour and then set overnight. The suspension was filtered in
a small Gooch crucible followed by further leaching with 20 ml. N NH_4AC
solution to assure NH_4^+ saturation. Excess NH_4AC was washed 4 to 5
times with 75% methyl alcohol in water. The NH_4^+ adsorbed was steam
distilled with a micro-steam distillation apparatus in presence of
NaOH and MgO (Ho and Handy, 1963).

In the $CaCl_2$ method, an 0.2g sample was shaken with 25 ml.
N $CaCl_2$ solution and equilibrated as above. The sample was washed
4 to 5 times with 75% methyl alcohol and then with water until no Cl^-
ions were indicated by $AgNO_3$ test. The Ca^{++} adsorbed was displaced
with 30 ml. N KCl by slow leaching, and titrated with standard EDTA
(Cheng and Bray, 1951).

Exchangeable calcium: Exchangeable calcium was displaced with N KCl by two methods. First, 0.2g sample was weighed into a 50 ml. Erlenmeyer flask, shaken with 25 ml. N KCl solution for 1 hour, and allowed to set overnight. The suspension was filtered and washed twice with distilled water, and the Ca^{++} displaced titrated with EDTA. A second 0.2g sample was soaked in 12.5 ml. distilled water for 3 days; then 12.5 ml. 2 N KCl solution was added to extract the exchangeable 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: 0.3g 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-$CaCl_2$ solvate prepared according to Bower's procedure was placed in the bottom of a 6-inch vacuum desiccator, and on top of this a perforated plate was placed 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% relative humidity was maintained by a saturated $Pb(NO_3)_2$ 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%) and 450-600°C (5%), relating to the loss of adsorbed water and clay structural hydroxyl groups, a small gradual weight loss (<0.7%) occurred at 250-300°C. Drastic reduction in surface area (780 to 250 m^2/g) occurred in a small temperature range of 450 to 550°C, coinciding with the dehydroxylation weight loss. Below 450°C and above 550°C surface area decreased only slightly.

Exchange Properties

Exchangeable Ca^{++}: As shown in Fig. 2, without previous water soaking the amount of Ca^{++} ions displaced by N KCl decreased rapidly depending on low temperature heat treatment, and remained almost constant between 350 to 500°C. Further heating up to 650°C resulted in a small increase in KCl extractable Ca^{++}, followed by a drop at 700°C.

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

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 to 400°C and remained constant from 400 to 500°C. The pH increased abruptly from around the dehydroxylation temperature, 500 to 600°C.

Exchange capacity: The cation exchange capacity measured by NH_4AC method (CEC_{NH_4AC}) is distinctly different from that measured by the $CaCl_2$ method (CEC_{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/100g at around 400°C. The CEC_{NH_4AC} decreased slightly in the temperature range 100 to 250°C, then dropped continuously in the temperature range 250° to 700°C. The CEC_{CaCl_2} decreased slightly over a much larger temperature range, 100 to 450°C, then dropped rapidly in the narrow dehydroxylation temperature range of 450 to 550°C. It may be noted that the general trends of the CEC_{CaCl_2}, the water-soaked exchangeable Ca^{++}, and the surface area curves (Fig. 1) are the same.

X-Ray Diffraction Data

Water and glycol saturated samples were made to test the changes in expansive properties of heated Ca-montmorillonites (Fig. 4). The d_{001} spacings of the glycolated samples re-expanded to 17.7 Å after heat treatment as high as 600°C. 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 much lower temperature 450°C. The intensity of the 21 Å peak remained constant up to 150°C, decreased 50% 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.

Change in Atterberg Limits with Temperature

As shown in Fig. 5, plastic limits decreased slightly but remained relatively little changed in heated samples 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 is defined as the plasticity index, and is markedly reduced. When the plasticity index approaches zero, the soil is non-plastic and behaves as a clean silt or sand.

Some of the moistened samples were equilibrated under 100% 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% r.h. remained almost constant after heat treatment in the range 25 to 300°C, then decreased; the decrease was most rapid in the temperature range 450 to 550°C (Fig. 6). Heating above 550°C resulted in little change in water retention. It can be noticed that the water retention follows a similar pattern as that shown by the glycol retention surface area

curve in Fig. 1.

DISCUSSION

Immobilization of Ca^{++}

Exchangeable calcium data show that moderate heat treatment below 350°C immobilizes some of the adsorbed Ca^{++} ions as they become non-exchangeable with KCl. However, some of the exchange sites remain blocked, indicated by the reduction in CEC measured by NH_4AC method. Immobilization of Ca^{++} 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_2O (Fig. 4). However immobilization of Ca^{++} and blocking of exchange sites apparently are not of a permanent nature; since most of the blocked exchange sites and the associated immobilized Ca^{++} can be recovered by either 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 mono-valent cations like K^+ is used for cation exchange.

The discrepancy in exchangeable Ca^{++} 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^+ and the immobilized Ca^{++}. The difference in CEC_{CaCl_2} and CEC_{NH_4AC} showed a similar trend.

This brings up the question as to the location of the fixed Ca^{++} ions. The nature of the Ca^{++} immobilization is distinctly different from that of Li^+ immobilization reported by Greene-Kelley (1953).

As previously mentioned, Li^+, with a radius of 0.60 Å is believed
to enter the octahedral layer and neutralize the lattice charge,
creating a pyrophyllite-type structure with loss of expansive
properties. Ca^{++} is probably too large to fit, and does not cause
loss in expandibility.

The suggestion of Mering (1946) that exchangeable Ca^{++} is
immobilized by formation of -0-Ca-0 linkages between adjacent
silicate sheets is untenable for two reasons: dehydroxylation is
required, and probably does not occur at the temperatures where Ca^{++}
fixation begins; and such bonding would probably bring about an
irreversible collapse of the d_{001} spacing. In the present study,
irreversible collapse was observed (by glycol) only after heating to
650°C, where weight loss data and DTA curve indicate that dehydroxyla-
tion is essentially complete.

The present results suggest another possible explanation.
When heated to higher than 150°C, some of the exchangeable Ca^{++}
become dehydrated and attach tightly or sink into the hexagonal holes
in the surface of the Si-tetrahedral layer, allowing compensation of
these exchange sites in the octahedral layer as revealed by the
corresponding reduction in CEC_{NH_4AC}. That the fixed Ca^{++} become
non-exchangeable with respect to K^+ and NH_4^+ could be due to the
large sizes of these cations and to clogging action. The clogging
action might even prevent penetration of water molecules and thus
the hydration of the immobilized Ca^{++} between the layers.

The above hypothesis may be supported as follows: First,
most of the fixed Ca^{++} became exchangeable with KCl when samples

were previously soaked with H_2O, suggesting that the Ca^{++} ions probably underwent slow hydration with resulting expansion of the collapsed layer, shown by X-ray diffraction pattern. Secondly, the clogging action of K^+ ions was further evidenced by the finding that the heated samples treated directly with N KCl did neither swell nor re-expand to any sharp peak as did those observed in samples treated with water or $CaCl_2$ alone in the time interval tested. The N $CaCl_2$ treated samples showed clearly swelling properties and re-expanded peak at 21 Å up to 400°C. It appears that upon treating with $CaCl_2$ the small 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 Ca^{++} ions to the surface.

Above 450°C the drastic decreases in surface area, CEC_{CaCl_2} exchangeable Ca^{++} after water soaking, 17.7 Å 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 to 450°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 bring liquid limits and plastic indexes back to the same extent as the exchangeable Ca^{++} (with previous water soaking) and CEC_{CaCl_2} suggests that the exchangeable 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 $\overset{\circ}{\mathrm{A}}$ peak intensity curve.

The sudden decrease in the 21 $\overset{\circ}{\mathrm{A}}$ 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 as shown by the 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 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 Ca^{++} ions become re-exchangeable by soaking in water, and the blocked exchange sites are recovered.

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

3. Heating 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 lower than the dehydroxylation temperature, brought about by changes in bonding of the inter-layer Ca^{++} ion and probably changes in clay particle shape and/or nature of particle surface other than surface area.

ACKNOWLEDGEMENTS

REFERENCES

American Society for Testing and Materials. (1964). Book of ASTM Standards. Part 11; soils.

Bower, C. A. and J. O. Goertzen (1959). Surface area of soils and clays as determined by an equilibrium ethylene glycol method. Soil Sci. V. 87, pp. 289-292.

Casagrande, A. (1932). Research on Atterberg limits of soils. Public Roads V. 13, No. 136.

Cheng, K. L. and R. H. Bray (1951). Determination of calcium and magnesium in soil and plant material. Soil Sci. V. 72, pp. 449-458.

Greene-Kelley, R. (1953). Irreversible dehydration in motnmorillonite. Part II. Clay Mineral Bull. V. 2, No. 9 pp. 52-56.

Grim, R. E. (1962). Applied Clay Mineralogy. McGraw-Hill Co., Inc.
New York. 422 pp.

Grim, R. E. (1953). Clay Mineralogy. McGraw-Hill Book Co., Inc.
New York. 384 pp.

Ho, C. and R. L. Handy (1963). Characteristics of lime retention by
montmorillonite clays. Presented at the 42nd Annual Meeting
of the Highway Res. Board, NAS-NRC, Washington 25, D. C.

Hogentogler, C. A. (1937). Engineering properties of soils. McGraw-
Hill Book Co., Inc. New York. 283 pp.

Holdridge, D. A. and F. Moore (1953). Clay-water relationships in
ceramics. Clay Mineral Bull. V. 2, pp. 26-28.

Mering, J. (1946). On the hydration of montmorillonite. Trans.
Faraday Soc. 42B. pp. 205-219.

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, V. 5, No. 12.
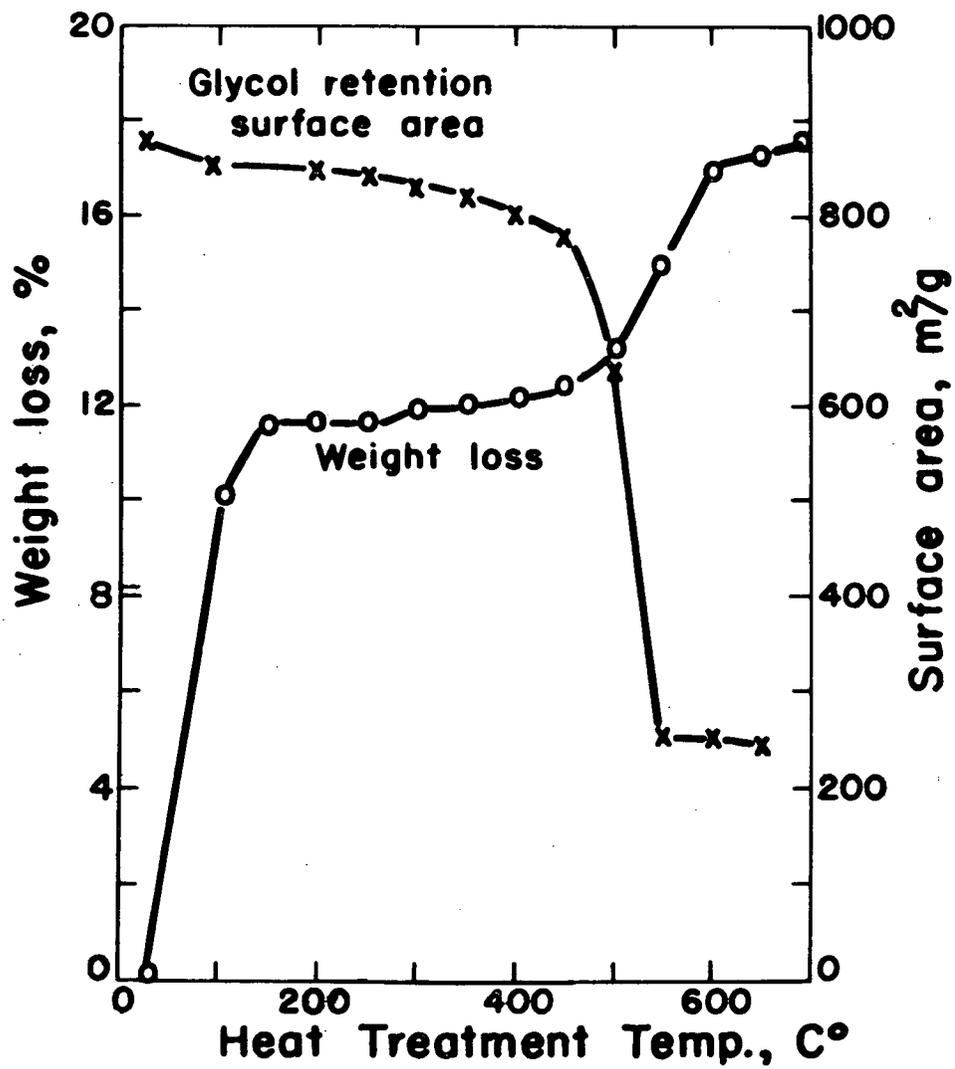
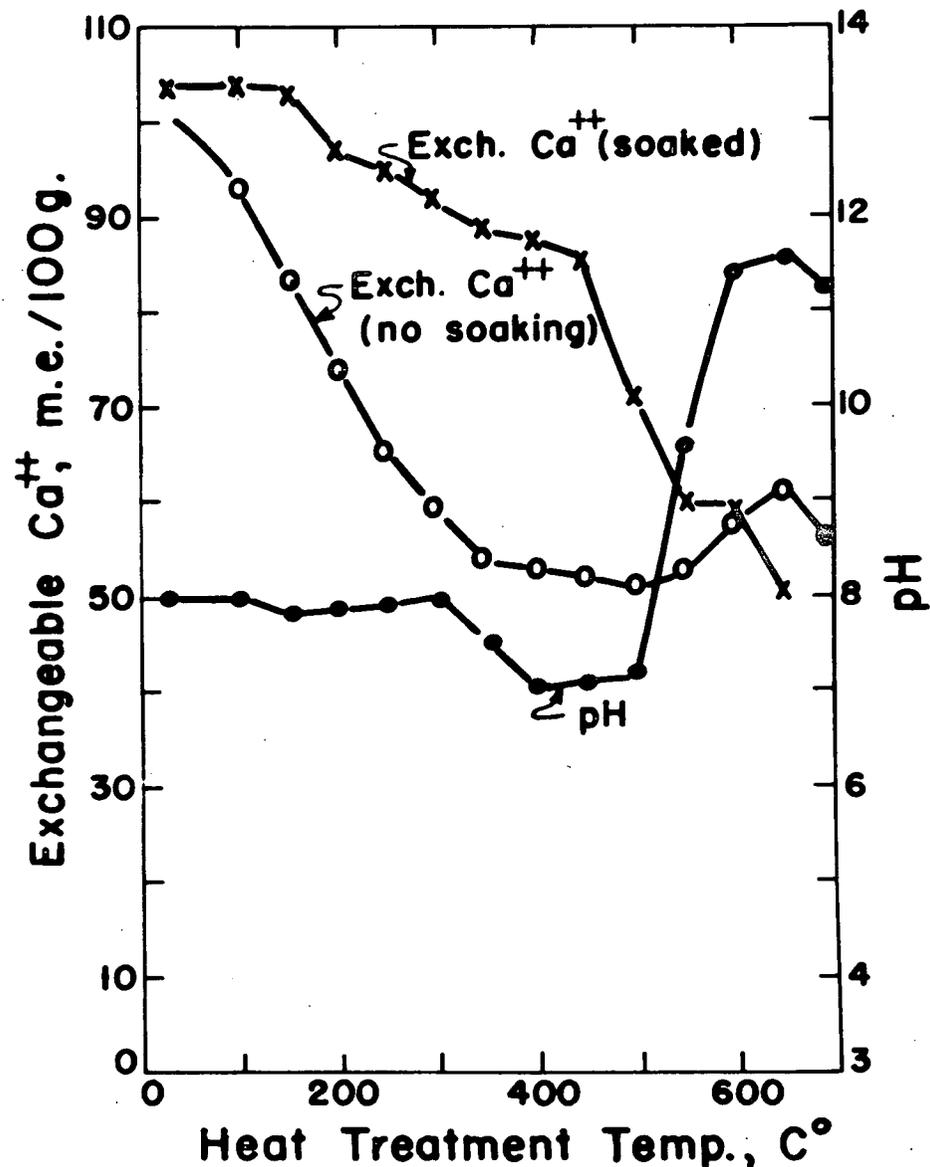Fig. 1. Relationship of weight loss and surface area to heat-treatment of Ca-montmorillonite

Fig. 2. Exchangeable Ca^{++} and pH of heat-treated Ca-montmorillonite
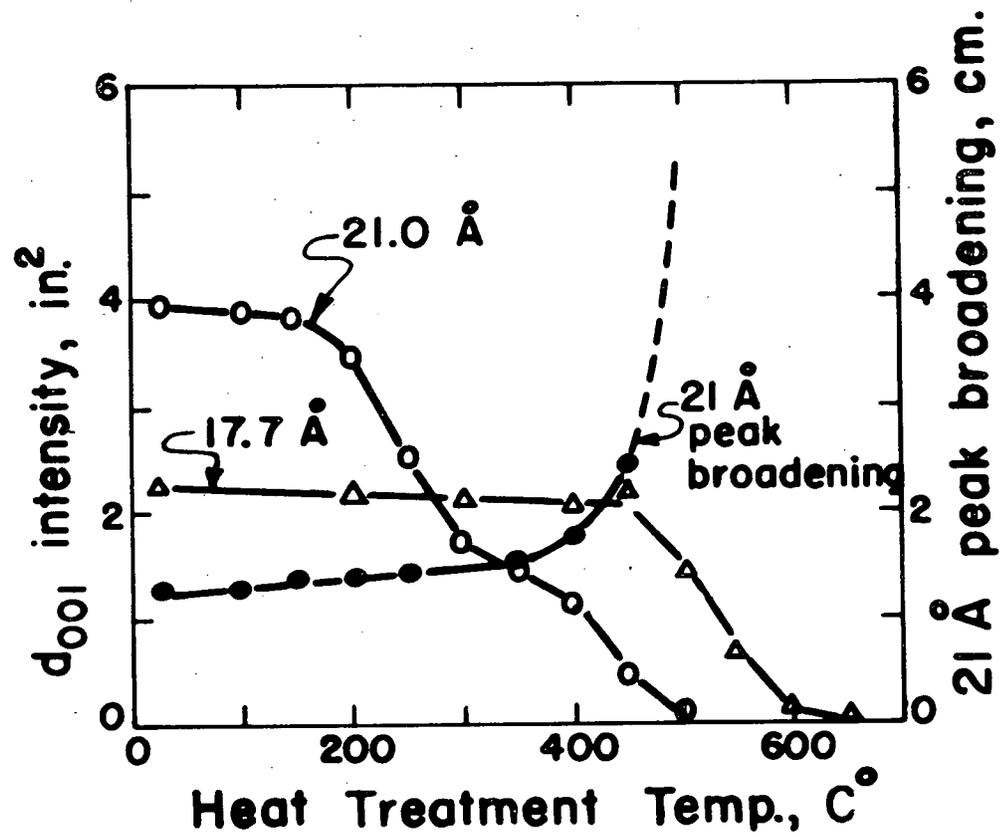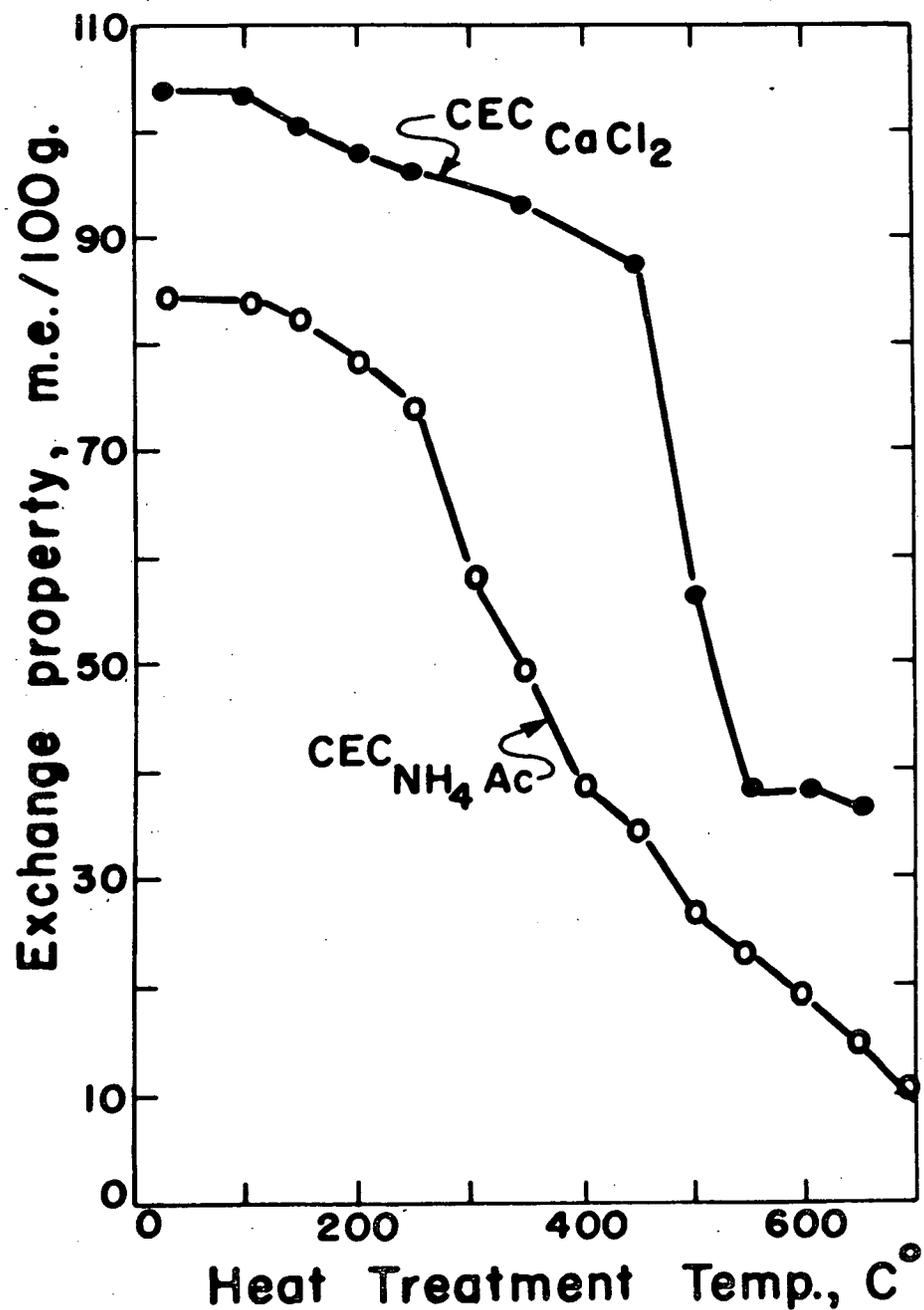
Fig. 3, at left. Cation exchange capacities of heat-treated Ca-montmorillonite

Fig. 4, above. 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)
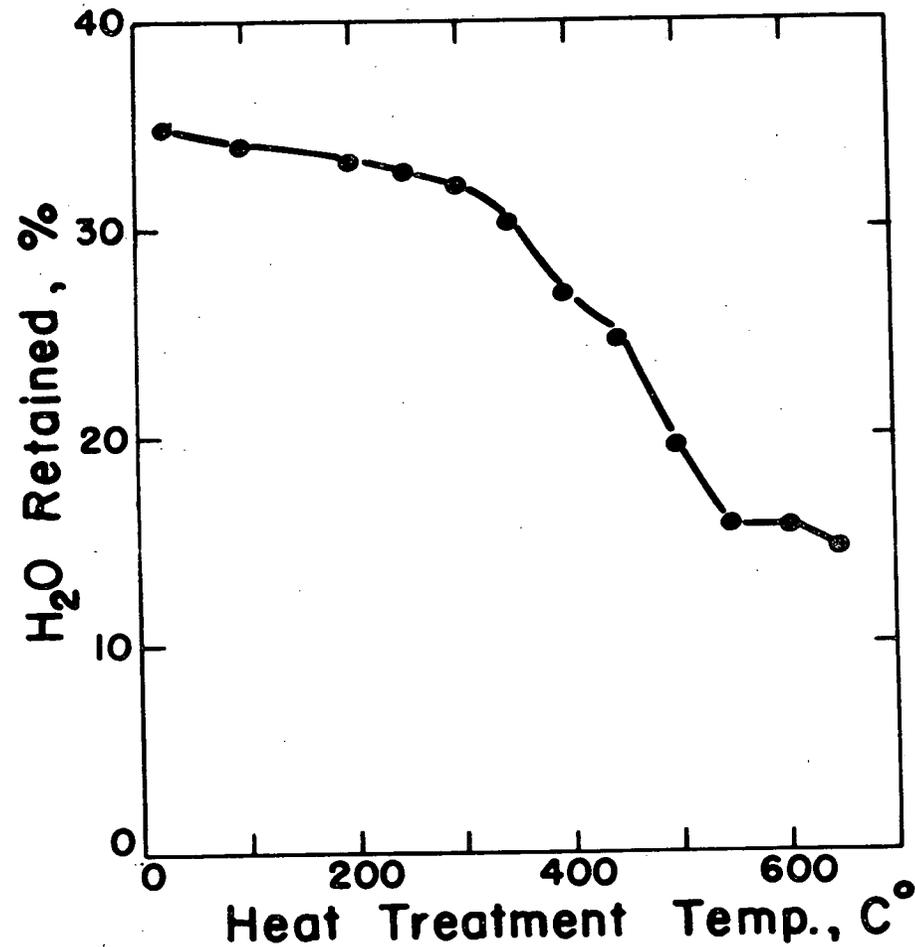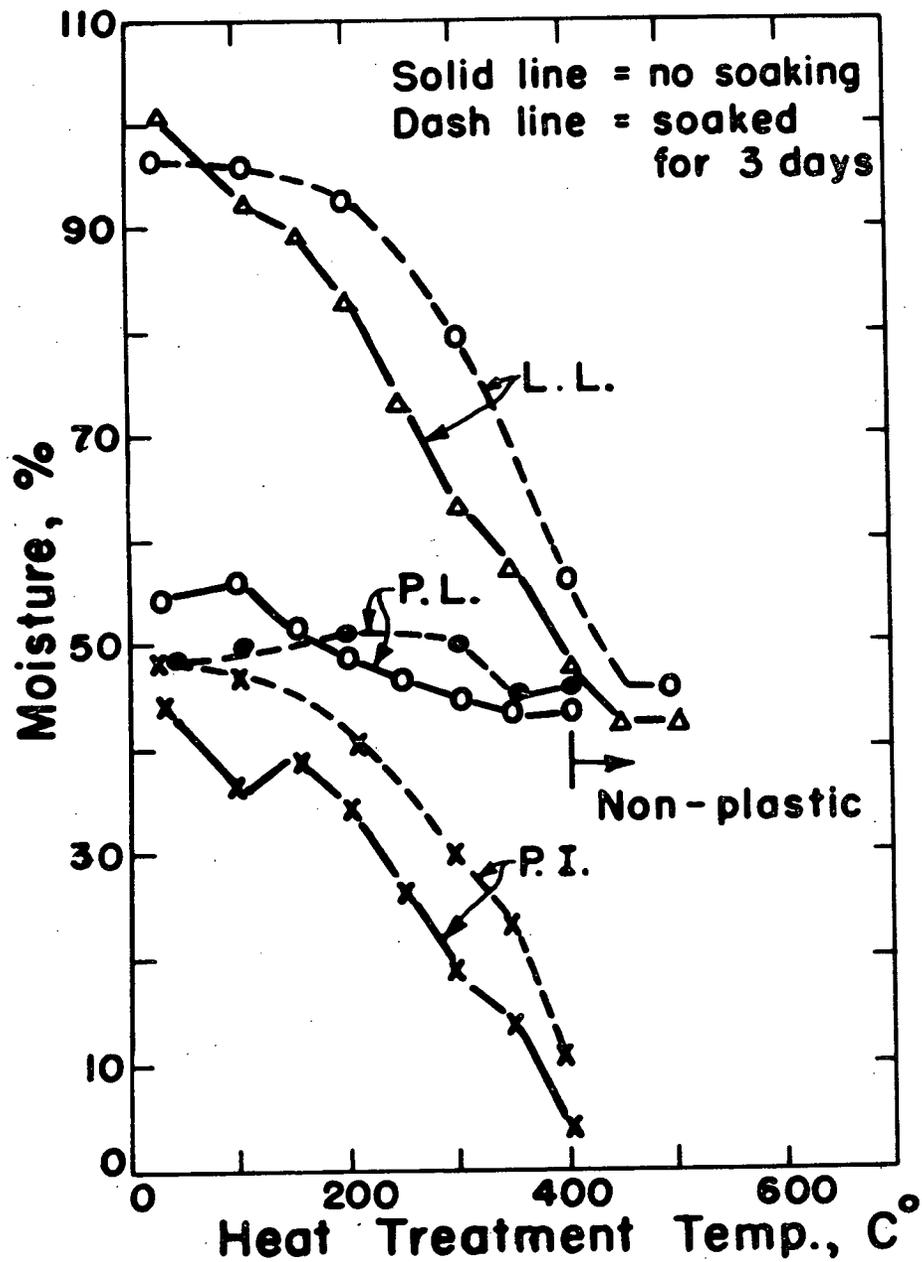
Fig. 5, at left. Plastic limits and liquid limits of heat-treated Ca-montmorillonite

Fig. 6, above. Retention of water by heat-treated Ca-montmorillonite