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COMMISSIONER OF HIGHWAYS

ADDRESS REPLY TO
DEPARTMENT OF HIGHWAYS
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MEMO TO: D. V. Terrell
Director of Research

The attached report, "The Effect of Thermal Treatment on the Engineering Properties of Clays," by George R. Laughlin, is a direct outgrowth of earlier studies by the Research Division on clay mineralogy and soil stabilization. Mr. Laughlin has worked with three basic soils and has subjected these materials to the temperature ranges available in the differential thermal apparatus.

The engineering properties were modified by the heat treatments. It is significant that the plastic properties were reduced, the grain sizes were increased, the maximum densities were lowered, and the shearing strengths were increased.

This study and report is somewhat basic and may not presently have direct practical application. It is quite possible that with the availability of nuclear energy that heat stabilization may be feasible.

Respectfully submitted,

W. B. Drake
Associate Director of Research

WBD:d1
Enc.

cc: Research Committee Members
Bureau of Public Roads (3)

Commonwealth of Kentucky
Department of Highways

THE EFFECT OF THERMAL TREATMENT ON
THE ENGINEERING PROPERTIES OF CLAYS

by

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June, 1959

INTRODUCTION

Of the cohesive soils the property of plasticity is usually of the most concern to the engineer. The clay minerals rather than the clay size material present in a soil determine the degree and magnitude of plastic properties. In turn, the plasticity of the clay minerals varies according to their mineralogy and particle size. Of the various types of clay minerals present in a soil, only kaolinite, illite and montmorillonite occur in sufficient abundance to be of general engineering significance.

Much prior work (1)(2)(3) has been performed to alter these plastic properties of clay soils. This has been accomplished in some instances by the use of solidifiers and cationic modifiers. Although these methods have proved effective in many instances, they have shown definite difficulties and limitations. All of these efforts have been directed toward one principal objective: soil stabilization -- that is, rendering clay particles into larger aggregates or otherwise rendering them non-plastic. One such method which may be feasible in the near future is thermal treatment. Perhaps ultimately a technique may be devised for transforming soil into a continuous vitreous roadway base or pavement. Although such a method is still visionary, there are considerable possibilities at the present for more limited techniques of thermal treatment of soils.

Since the noncohesive components of a soil have rather definite physical properties in relation to moisture contents and have high heats of transformation, it seems logical to approach the method

of thermal treatment as a means of stabilization by treating materials having physical properties which vary greatly in relation to moisture content but which have low heats of transformation.

The purpose of this study was to further explore the effects of thermal treatment on the physical properties and mineralogy of the clay minerals: kaolinite, illite and montmorillonite.

MATERIALS

The clay minerals used in the tests were selected from the locations listed in "Reference Clay Localities - United States"(4). The reference locality for the kaolinite is near Macon, Georgia. This clay occurs in the Middendorf formation of Upper Cretaceous age. The sample was supplied by the Georgia Coating Clay Company of Macon, Georgia. The reference locality for illite is near Fithian, Illinois. This clay is of middle McLeansboro age. The sample was obtained by the author. The reference locality for montmorillonite is near Belle Fourche, South Dakota. This clay occurs at the top of the Graneros shale of Upper Cretaceous age. The sample was obtained from the American Colloid Company.

EQUIPMENT

Triaxial Cell

This cell consisted of an aluminum base plate and an aluminum top plate separated by a lucite cylinder (see Fig. 1). Lateral air pressure was supplied to the cell through a valve in the base plate.

The top plate contained a pressure gauge to register the lateral air pressure in pounds per square inch. The vertical pressure was applied by means of a stainless steel loading piston inserted through a brass bushing in the top plate. The applied vertical pressure was registered by means of a proving ring mounted on top of the loading piston. The dial was calibrated to 1/10,000 inch. The deflection of the specimen was registered by means of an Ames dial mounted on the underneath side of the proving ring. This dial was calibrated to 1/1000 inch.

X-Ray Apparatus

The x-ray apparatus (see Fig. 2) consisted of a Hayes x-ray unit supplied with two powder cameras. The effective radius of each camera was 6.995 centimeters. The x-ray tube contained a copper target and beryllium windows.

Differential Thermal Apparatus

The differential thermal apparatus (see Fig. 3) consisted of a Speedomax recorder which registered the temperature differential between the inert material and the specimen being tested. This temperature difference was registered in millivolts. A Micromax recorder was used to chart the furnace temperature (temperature of inert material) from 0°C to 1000°C. These units were connected to a Hoskins furnace, style FA 120 wound with a chromel heating element to give a linear heating rate. The rate of heating was controlled by a synchronous motor and a variable transformer. The specimen container consisted of a nickel block, 1-3/4 inches in diameter.

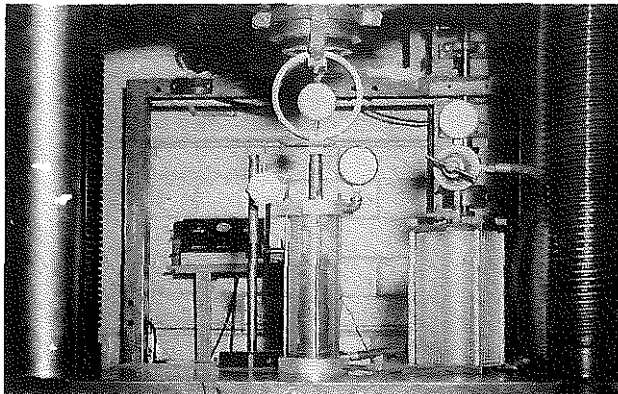


Fig. 1. -Specimen Being Tested in Triaxial Cell

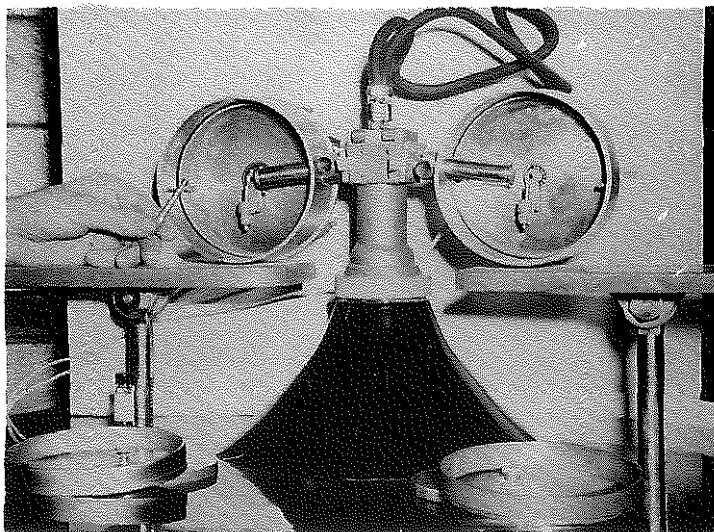
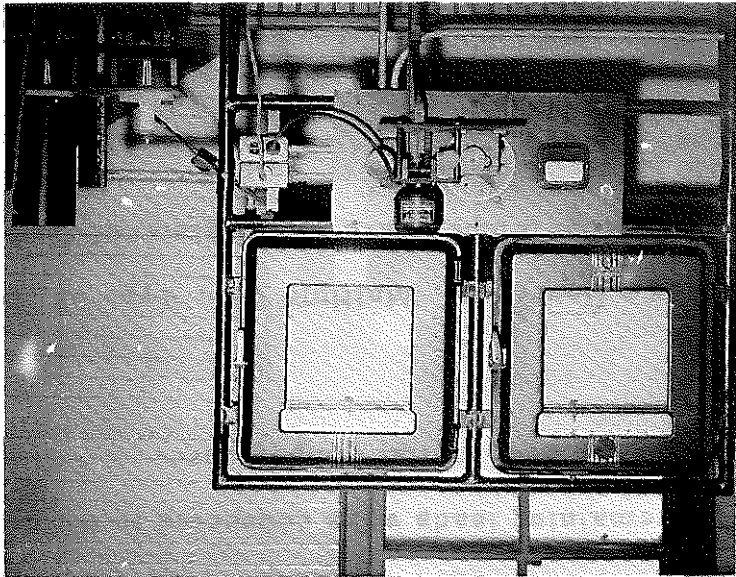


Fig. 2. -Hayes X-ray Unit with Camera Covers Removed

Fig. 3.-Differential Thermal Analysis Apparatus



After preparatory treatment, the specimens were ground to a fine powder to give all possible orientations and mounted in the cameras in wedge holders. The film was inserted in the cameras and exposed for 2-1/2 hours.

After development, the diffraction lines on the films were measured by use of a centimeter scale equipped with a vernier. These measurements were converted to ångstroms using the formula:

$$d = \frac{0.77}{(\sin 4.119 \times L)}$$

The derivation of this formula is as follows:

$$n\lambda = 2 d \sin \theta$$

$$2d = \frac{n\lambda}{\sin \theta}$$

$$2\theta = \frac{180 L}{\pi r}$$

$$\theta = \frac{180 L}{2 r \pi}$$

$$\theta = 4.119 \times L$$

$$d = \frac{n\lambda}{2 \times \sin(4.119 \times L)}$$

$$d = \frac{0.77}{\sin(4.119 \times L)}$$

where:

$$n = 1$$

$$\lambda = 1.54\text{Å}$$

d = inter planar spacing

2θ = reflection angle

θ = Bragg angle

L = measured length of arc in centimeters

r = effective radius of camera

The three strongest "d" values of each film were then compared with "d" values listed in Alphabetical and Numerical Indexes of X-Ray Diffraction Patterns, ASTM, 1955, and other reported values (6)(7) for mineral identification.

Differential Thermal Analysis Technique

Each specimen was prepared for differential thermal analysis by grinding the material to the size passed by the U.S. Standard Sieve No. 325, after which it was oven dried for 18 hours at a temperature of 205°F.

The material was placed in the specimen holder by tamping small amounts at a time with a metal rod, with special care taken to keep the thermocouple centered. With the inert material in two of the holes and the unknown material in the other hole, the furnace was heated at a rate of 10°C per minute up to 1000°C.

From the differential thermal graphs and the furnace temperature graphs, thermograms were prepared for each clay sample. These were compared with generally accepted standard thermograms such as those listed in "Differential Thermal Analysis" (8) for identification of the minerals.

Specific Gravity Determination

The specific gravity determinations were performed according to ASTM Designation D 854-45T.

Mechanical Analysis Determination

The quantitative determination of the distribution of grain sizes were determined according to ASTM Designation D 422-39.

Liquid Limit Determination

The liquid limit of each material was determined according to ASTM Designation D 423-39.

Plastic Limit and Plasticity Index

The plastic limit and plasticity index of each material were determined according to ASTM Designation D 424-39.

Shrinkage Limit Determination

The shrinkage limit of each material was determined according to ASTM Designation D 427-39.

Moisture-Density Relationship

The moisture-density relationship for each material was determined according to ASTM Designation D 698-42T.

Shear Strength Determination

Shear strength determinations were made by the triaxial method using specimens prepared at optimum moisture and maximum unit dry weight. The tests were a "Q" type.

The material was molded into cylindrical specimens two inches in diameter and four inches high. These specimens were encased in thin rubber membranes, placed in the triaxial cell and tested at a deformation rate of 0.05 inch per minute. The lateral pressure varied from zero to 20 pounds per square inch.

Mohr diagrams were constructed from the stress-strain data and the values of internal friction and cohesion were determined.

Thermal Treatment of Material

Each clay material was subjected to thermal treatment by placing 200 grams at a time in a porcelain dish and centering in the furnace with a thermocouple placed above the material and another thermocouple placed in the center of the material. This double arrangement of thermocouples was used to insure proper temperature control of the material. The temperatures to which the materials were heated were selected from the thermograms of each clay mineral and were chosen so as to represent two or more stages of isothermal reactions.

PROCEDURE

Specimens of each clay sample were subjected to x-ray analysis using the powder method for mineral identification. Differential thermal analysis was performed on each clay as another means of mineral identification and to establish the necessary temperatures for thermal treatment.

The following determinations were made on the untreated clays: absolute specific gravity, mechanical analysis, liquid limit, plastic limit, plasticity index, shrinkage limit, moisture-density relationship, and shear strength.

Each clay sample was then subjected to thermal treatment (see Fig. 4). The kaolinite was thermally treated to 800°C. This temperature occurred approximately between the 600°C endothermic reaction and the 980°C exothermic reaction. The illite was thermally treated to 750°C. This temperature occurred after the 580°C

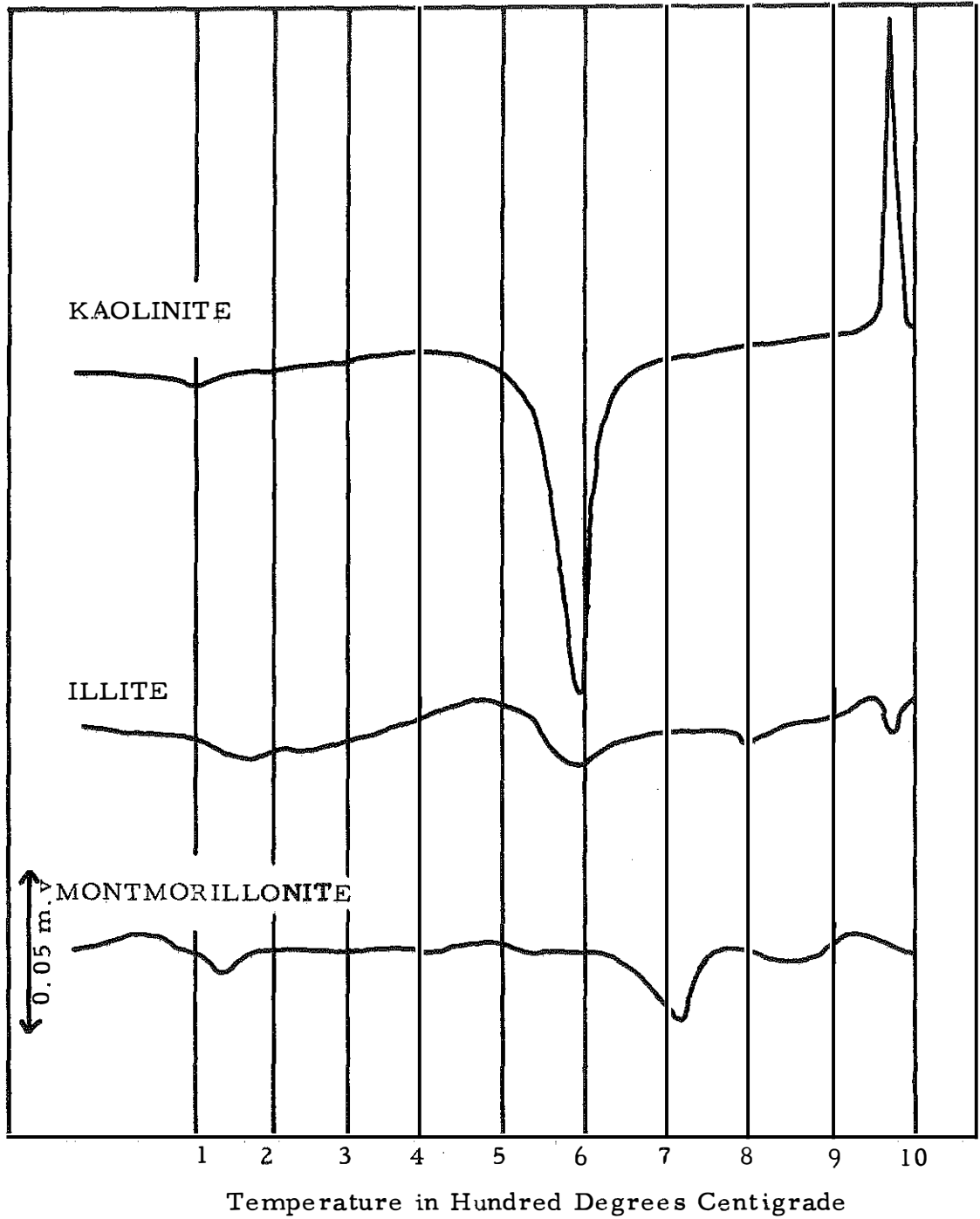


Fig. 4 - Differential Thermograms

endothermic reaction of illite and before the 980°C exothermic reaction of illite. The exothermic reaction at 475°C was probably due to decarbonation of siderite. The small endothermic reaction at 795°C may have been due to a small amount of montmorillonite. The montmorillonite was thermally treated to 600°C. This temperature represented the point at which the "c" lattice became collapsed but was just under the temperature where total decomposition of the mineral began.

After the clays were thermally treated to the above mentioned temperatures, physical determinations were made.

The clay samples were then subjected to a higher thermal treatment. The kaolinite was thermally treated to 1000°C. This temperature occurred just after completion of the 980°C exothermic reaction. The illite was subjected to thermal treatment of 1000°C. This temperature occurred after the 950°C exothermic reaction and after the 975°C endothermic reaction. The montmorillonite was thermally treated to 850°C. This temperature occurred after the 710°C endothermic reaction and before the completion of the 875°C endothermic reaction.

After the second thermal treatment the previously mentioned physical determinations were made on each material.

A portion of the montmorillonite thermally treated to 600°C was soaked in water for a period of six months after which the liquid limit, plastic limit, plasticity index and shrinkage limit were determined.

RESULTS AND DISCUSSION - KAOLINITE

X-Ray Analysis

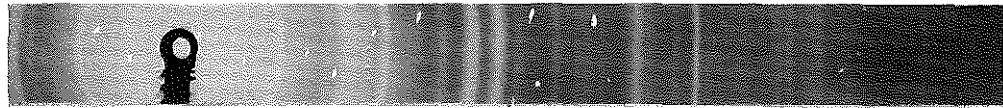
The x-ray pattern of the unheated kaolinite displayed strong diffraction lines occurring at 7.15 \AA , 3.57 \AA and 2.33 \AA . These "d" values corresponded to the three principal "d" values for kaolinite listed in Alphabetical and Numerical Indexes of X-ray Diffraction Patterns, ASTM 1955, and were in general agreement with other published values (6)(9).

The x-ray pattern of the kaolinite after being subjected to thermal treatment of 800°C displayed diffraction lines corresponding to 2.45 \AA , 1.99 \AA and 1.39 \AA , which indicated that the clay decomposed into $\gamma\text{-Al}_2\text{O}_3$ and SiO_2 . Upon thermal treatment to 1000°C the x-ray pattern displayed diffraction lines occurring at 5.4 \AA , 3.39 \AA and 2.54 \AA , which indicated at least partial transformation into mullite. These results were also in general agreement with results reported by other investigators (10)(11).

Of the three common types of clay minerals, kaolinite was most amenable to analysis by x-ray diffraction because of its crystal purity and near perfect lattice structure. Diffraction patterns for this mineral, as shown in Fig. 5, usually exhibit very discrete lines, even from deep reflecting planes.

Specific Gravity Analysis

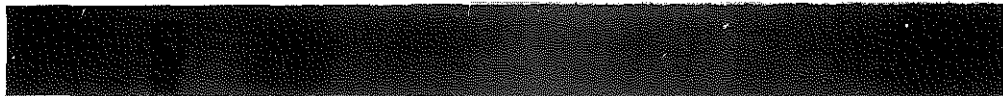
The specific gravity of the untreated kaolinite as computed by ASTM Designation: D 854-45T was 2.616 as compared to water at 4°C . The theoretical density calculated from the diffraction data



Not Thermally Treated



Thermally Treated to 800°C



Thermally Treated to 1000°C

Fig. 5. -X-ray Patterns of Kaolinite

was 2.612. In solving for the theoretical density, the dimensions of the a, b and c axes of the triclinic cell are :

$$a = \frac{d(010)}{\cos p}; \text{ Angle } \alpha = 91^\circ 48'$$

$$\cos p = \frac{1}{\sin \alpha} \sqrt{1 - \cos^2 \beta - \cos^2 \gamma - \cos^2 \alpha + 2 \cos \beta \cos \gamma \cos \alpha}$$

$$= \frac{1}{0.99951} \sqrt{1 - 0.96815^2 - 0.03141^2}$$

$$= 1.0004 \times 0.2482$$

$$= 0.24822$$

$$a = \frac{1.276 \text{ \AA}}{0.24822}$$

$$= 5.14 \text{ \AA}$$

$$b = \frac{d(100)}{\cos p'}; \text{ Angle } \beta = 104^\circ 30'$$

$$\cos p' = \frac{1}{\sin \beta} \sqrt{1 - \cos^2 \gamma - \cos^2 \alpha - \cos^2 \beta + 2 \cos \gamma \cos \alpha \cos \beta}$$

$$= \frac{1}{0.96815} \sqrt{1 - 0.03141^2 - 0.25038^2}$$

$$= 1.0328 \times 0.968$$

$$= 0.99975$$

$$b = \frac{8.928 \text{ \AA}}{0.9975}$$

$$= 8.93 \text{ \AA}$$

Second order reflection (200) = 4.464 \AA, thus (100) = 8.928 \AA

$$c = \frac{d(001)}{\cos p''}; \text{ Angle } \gamma = 90^\circ 00'$$

$$\cos p'' = \frac{1}{\sin \gamma} \sqrt{1 - \cos^2 \alpha - \cos^2 \beta - \cos^2 \gamma + 2 \cos \alpha \cos \beta \cos \gamma}$$

$$= \frac{1}{1} \sqrt{1 - 0.02^2 - 0.25^2}$$

$$= 1 \times 0.964$$

$$= 0.964$$

$$c = \frac{7.149 \text{ \AA}}{0.964}$$

$$= 7.42 \text{ \AA}$$

The values of $d(100)$, $d(010)$ and $d(001)$ were calculated from the x-ray pattern of kaolinite. The cell angles γ , β and α were taken from Winchell and Winchell (5) since these could not be determined by the powder method of x-ray analysis.

The volume of the triclinic cell is:

$$\begin{aligned} V &= a \cdot b \cdot c \sqrt{1 - \cos^2 \alpha - \cos^2 \beta - \cos^2 \gamma + 2 \cos \alpha \cos \beta \cos \gamma} \\ &= 5.14 \text{ \AA} \times 8.93 \text{ \AA} \times 7.42 \text{ \AA} \sqrt{0.9272} \\ &= 328.319 \times 10^{-24} \text{ cubic centimeters} \end{aligned}$$

Using the formula of $\text{Al}_2 \text{Si}_2 \text{O}_5 (\text{OH})_4$ (12), the molecular weight is 516.814. The number of molecules in one gram-molecule is 6.02×10^{23} , hence $\frac{516.814}{6.02 \times 10^{23}} = 857.448 \times 10^{-23}$ grams per molecule. Accordingly, the theoretical density is: $\frac{857.448 \times 10^{-23}}{328.319 \times 10^{-24}} = 2.612$ grams per cubic centimeter.

After thermal treatment to 800°C , the specific gravity of kaolinite was found to be 2.68 as compared to water at 4°C . This increase is in accordance with the transformation of the mineral into SiO_2 and $\gamma\text{-Al}_2\text{O}_3$. This transformation has been reported previously by Grim (6) and Lambe (7).

The specific gravity of the material heated to 1000°C was also 2.68 as compared to water at 4°C . Although the diffraction patterns indicated mullite, it was not present in a sufficient quantity to significantly alter the specific gravity.

Mechanical Analysis

The untreated kaolinite contained 71 percent in the clay-size range (-5u) and 29 percent in the silt-size range (+5u). The thermally treated materials had approximately 42 percent in the clay-size range and approximately 55 percent in the silt-size range. Since the kaolinite

decomposed to form Al_2O_3 and SiO_2 and then mullite, the newly formed particles must have aggregated and, or fused to give an increase in particle size.

Limits Analysis

The liquid limit of the untreated kaolinite and that of the materials formed from the thermal treatment of the kaolinite differed only slightly (see Table I). Since the kaolinite did not absorb inter-lattice water, and weakly absorbed water on its surface, the liquid limits seem to reflect the quantity of material in the clay and silt sizes. Over 95 percent of each of the three materials was in the clay-size and silt-size range.

Of the three material only the untreated kaolinite exhibited a plasticity index (L.L. - 45.40 percent, P.L. - 25.03 percent and P.I. - 20.37 percent). Since the plasticity index is largely a function of the amount of water-adsorbing clay mineral present, it seems logical for the transformed products not to have a plasticity index.

The shrinkage limit of the kaolinite thermally treated to 800°C was significantly higher than the shrinkage limit of the untreated kaolinite, and the shrinkage limit of the kaolinite thermally treated to 1000°C was even greater than for the 800°C material. Since the gradation was changed considerably by heating, which could greatly alter the packing characteristics of the particles, the change in the shrinkage limits must have been due to a change in size and/or shape of the particles.

Moisture-Density Relationship

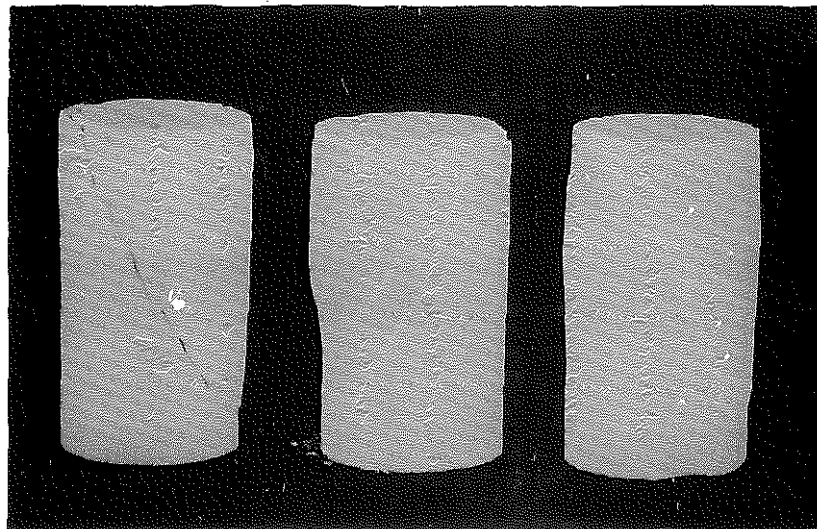
The untreated kaolinite displayed a dry unit weight of 94.30 pounds per cubic foot and an optimum moisture content of 26 percent

(39.30 percent by volume). The calculated volume occupied by the solid material was 57.90 percent. Since the combined volumes of solids and water equaled 97.20 percent of the total (approaching zero air voids), the optimum moisture content simply reflects the volume of voids within the closely packed particles. The optimum moisture content practically coincides with the plastic limit (25 percent) and is in close agreement with the shrinkage limit.

Of the materials thermally treated, the dry unit weight was about 22 pounds per cubic foot less than for the untreated kaolinite, despite the fact that their specific gravities were higher. Here, the volume occupied by solids was 43.10 percent, and all of the limits approached a common value of about 45 percent (52 percent by volume) -- indicating again an alteration in the packing characteristics of the particles and the complete absence of plastic properties.

Shear Strength Analysis

The untreated kaolinite as tested by the triaxial method at optimum moisture content (see Fig. 6) gave an angle of internal friction of $19^{\circ}30'$ and a cohesion value of 22.30 pounds per square inch. With increasing moisture content these values would normally diminish. Of the material thermally treated, the internal friction angles varied between $40^{\circ}00'$ to $45^{\circ}30'$ and the cohesion values varied between 2.4 to 6 pounds per square inch. Varying the moisture content of a granular material only slightly affects the internal friction angle. With zero moisture content the cohesion value should be nil; but as moisture is added the apparent cohesion would increase due to internal meniscus tension and then would tend to decrease as the internal pores become flooded and all meniscus destroyed.



Untreated Thermally Treated Thermally Treated
 to 800°C. to 1000°C

Fig. 6. -Specimens of Kaolinite after Triaxial Testing

RESULTS AND DISCUSSION - ILLITE

X-Ray Analysis

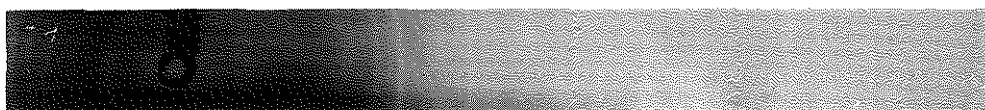
The illite which had not been subjected to thermal treatment displayed three strong diffraction lines at 10 \AA , 4.46 \AA and 2.56 \AA (see Fig. 7). These "d" values corresponded to the three "d" values for illite listed in Alphabetical and Numerical Indexes of X-ray Diffraction Patterns, ASTM 1955, and were in general agreement with other published values (6)(9).

The x-ray pattern of the material thermally treated to 750°C displayed the normal illite pattern, except that the $d(001)$ value was increased from 10 \AA to 10.15 \AA . This increase has been previously observed by Grim and Bradley (13), and is characteristic of illite clays.

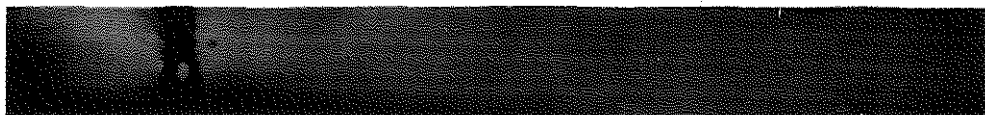
The x-ray pattern of the material thermally treated to 1000°C gave diffraction lines considerably different from those of the normal illite pattern. These lines are believed to be due to the formation of a spinel (13); however, most of the material was transformed into a glass.

Specific Gravity Analysis

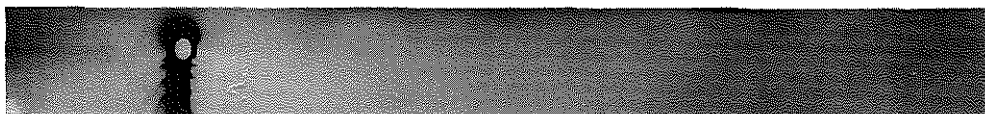
The specific gravity of the untreated illite as computed by ASTM Designation: D-854-45T was 2.83 as compared to water at 4°C . The theoretical density calculated from the diffraction data was 2.839. In solving for the theoretical density, the dimensions of the a, b and c axes of the monoclinic unit cell are:



Not Thermally Treated



Thermally Treated to 750°C



Thermally Treated to 1000°C

Fig. 7. -X-ray Patterns of Illite

$$\begin{aligned}
 a &= \frac{d(100)}{\sin \beta^*} ; \quad \text{Angle } \alpha = 90^\circ 00'; \quad \beta^* = 180^\circ - \beta \\
 &= \frac{5.176 \text{ \AA}}{0.954} ; \quad (400) = 1.294 \text{ \AA}, \text{ thus } (100) = 5.176 \text{ \AA} \\
 &= 5.20 \text{ \AA} \\
 b &= d(010) ; \quad \text{Angle } \beta = 95^\circ 30' \\
 &= 9.00 \text{ \AA}; \quad (060) = 1.50 \text{ \AA}, \text{ thus } (010) = 9.00 \text{ \AA} \\
 c &= \frac{d(001)}{\sin B^*} ; \quad \text{Angle } \gamma = 90^\circ 00' \\
 &= \frac{9.954 \text{ \AA}}{0.9954} \\
 &= 10 \text{ \AA}
 \end{aligned}$$

The values of d(100), d(010) and d(001) were calculated from the x-ray pattern of illite. Since the angles of the unit cell can not be determined by the powder method of x-ray analysis, the angle "B" was taken as 95° 30' (14).

The volume of the monoclinic cell is:

$$\begin{aligned}
 V &= a \cdot b \cdot c \cdot \sin \beta \\
 &= 5.2 \text{ \AA} \times 9.0 \text{ \AA} \times 10 \text{ \AA} \times 0.9954 \\
 &= 465.847 \times 10^{-24} \text{ cubic centimeters.}
 \end{aligned}$$

The formula for illite is taken as the idealized formula for muscovite. It is $(\text{OH})_4\text{K}_2(\text{Si}_6 \cdot \text{Al}_2) \text{Al}_4 \text{O}_{20}$ (14). The molecular weight is 796.404. The number of molecules in one gram-molecule is 6.02×10^{23} , hence $\frac{796.404}{6.02 \times 10^{23}} = 132.293 \times 10^{-23}$ grams per molecule. The theoretical density then is:

$$\frac{132.293 \times 10^{-23}}{465.847 \times 10^{-24}} = 2.839.$$

The specific gravity of the illite thermally treated to 750°C was 2.80 as computed by ASTM Designation: D 854-45T. This drop of 0.03 in specific gravity from the non-thermally treated illite was compatible with the increase in the cell height of 1.5 percent in the "c" direction.

The specific gravity of the material thermally treated to 1000°C was 2.59 as computed by ASTM Designation: D 854-45T. This reduction in gravity was due to the formation of glass and the destruction of the clay configuration.

Mechanical Analysis

Of the untreated illite, 98 percent was in the clay-size range. When thermally treated to 750°C the clay-size particles decreased to 48.50 percent. Although there was no transformation of the clay mineral at this temperature, there was an obvious aggregation of the particles. When thermally treated to 1000°C, the clay sizes decreased to 10.40 percent, but here the material was transformed into a spinel and a glass. The increase in particle size is attributed to fusion and aggregation of the material. Duration of heating at or near fusion would logically be one of the factors controlling the size and shape of the particles produced.

Limits Analysis

The liquid limit of the untreated illite was 83.00 percent. After thermal treatment, the liquid limit decreased to 53.40 percent for the material heated to 750°C and to 37.00 percent for the material heated to 1000°C. At the same time, the plastic limit increased, and, of course, all indications of plasticity disappeared at the high temperature of treatment.

Moisture-Density Relationship

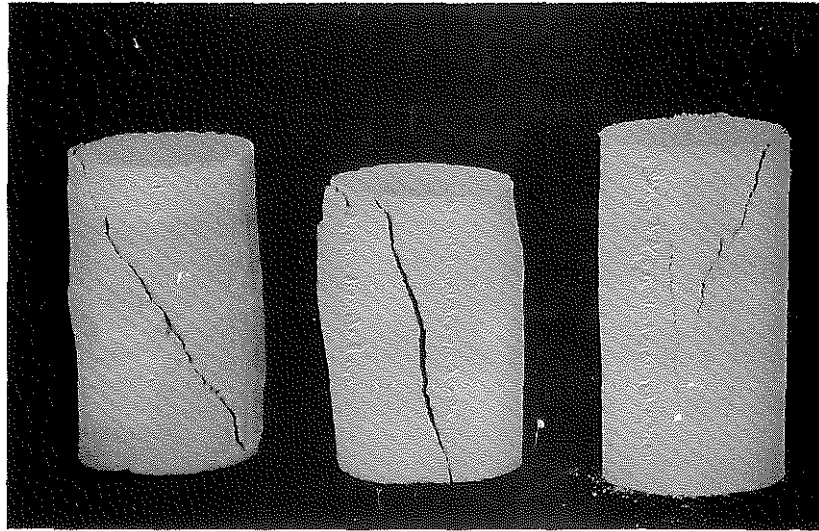
The dry unit weight of the unheated illite was 82.30 pounds per cubic foot and the optimum moisture content was 31 percent. The calculated volume of this solid material was 46.60 percent and the volume of water giving maximum density was 40.80 percent. Thus, the sum of these volumes equals only 87.40 percent of the whole; whereas, for kaolinite the sum of these volumes was 97 percent.

The dry unit weight of the material thermally treated to 750°C was 80.24 pounds per cubic foot with an optimum moisture content of 35.40 percent. The volume of the solids was 45.95 percent.

Of the material thermally treated to 1000°C, the dry unit weight was 80.40 pounds per cubic foot and the optimum moisture content was 31.00 percent. The volume of solids increased to 49.70 percent.

Shear Strength Analysis

The untreated illite as tested by the triaxial method (see Fig. 8) gave an angle of internal friction of $40^{\circ} 30'$ and a cohesion value of 14.90 pounds per square inch. When thermally treated to 750°C, the angle of internal friction dropped to $23^{\circ} 30'$ and the cohesion value dropped to 14 pounds per square inch. When thermally treated to 1000°C, the angle of internal friction was $37^{\circ} 00'$ and the cohesion value dropped to 2.53 pounds per square inch. This low value of cohesion is attributed to meniscus water tension only, since the material is granular.



Untreated Thermally Treated Thermally Treated
 to 750°C to 1000°C

Fig. 8. -Specimens of Illite after Triaxial Testing

RESULTS AND DISCUSSION - MONTMORILLONITE

X-Ray Analysis

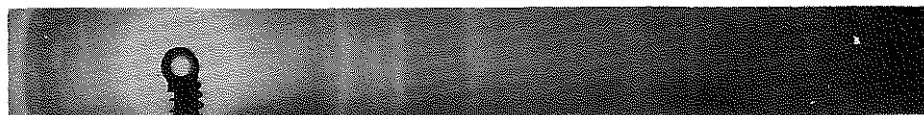
The montmorillonite which was not subjected to thermal treatment displayed three strong diffraction lines at 15 \AA , 4.45 \AA and 1.49 \AA (see Fig. 9). These "d" values corresponded to the three principal "d" values for montmorillonite listed in Alphabetical and Numerical Indexes of X-Ray Diffraction Patterns, ASTM 1955, and were in general agreement with other published values (6)(9).

The x-ray pattern of montmorillonite thermally treated to 600°C was almost identical to the normal pattern obtained when the c axis has been collapsed except that the d(001) value was 9.7 \AA . Since the d(001) value of montmorillonite is 9.6 \AA , when no polar molecules are between the unit layers (15), the d(001) value of 9.7 \AA for this particular mineral thermally treated to 600°C represents an increase of one percent in cell height.

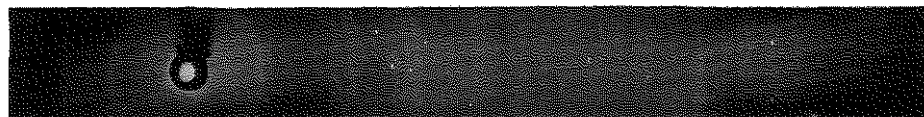
The x-ray pattern of the material thermally treated to 850°C indicated that the clay mineral was transformed into glass and spinel. The pattern also indicated the presence of some quartz which obviously could not have been formed under the prevailing conditions imposed. Therefore, the quartz must have been present in the original material, but its presence was obscured in the diffraction pattern by the more prominent lines of the montmorillonite.

Specific Gravity Analysis

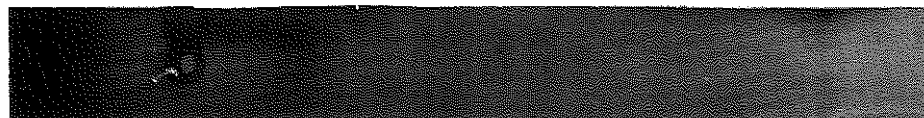
The specific gravity of the untreated montmorillonite as computed by ASTM Designation: D 854-45T was 2.78 as compared to water at 4°C . The theoretical density calculated from diffraction



Not Thermally Treated



Thermally Treated to 600°C



Thermally Treated to 850°C

Fig. 9. -X-ray Patterns of Montmorillonite

data was 2.799. In solving for the theoretical density, the dimensions of the a, b and c axes of the monoclinic cell are:

$$\begin{aligned}
 a &= \frac{d(100)}{\sin \beta^*}; \quad \text{Angle } \alpha = 90^\circ 00'; \quad \beta^* = 180^\circ - \beta \\
 &= \frac{5.126 \text{ \AA}}{0.9954}; \quad (200) = 2.563 \text{ \AA}, \text{ thus } (100) = 5.126 \text{ \AA} \\
 &= 5.15 \text{ \AA} \\
 b &= d(010); \quad \text{Angle } \beta = 95^\circ 30' \\
 &= 8.95 \text{ \AA}; \quad (060) = 1.492 \text{ \AA}, \text{ thus } (010) = 8.95 \text{ \AA} \\
 &= \frac{d(001)}{\sin \beta^*}; \quad \text{Angle } \gamma = 90^\circ 00' \\
 &= \frac{9.556 \text{ \AA}}{0.9954} \\
 &= 9.6 \text{ \AA}
 \end{aligned}$$

The values of d(100) and d(010) were taken from the x-ray pattern of montmorillonite. The d(001) value was taken as the minimum value, 9.6 Å. Again, since the cell angles can not be determined by the powder method of x-ray analysis, the angle β is taken as 95° 30', the value for muscovite (16).

The volume of the monoclinic cell is:

$$\begin{aligned}
 V &= a \cdot b \cdot c \cdot \sin \beta \\
 &= 5.15 \text{ \AA} \times 8.95 \text{ \AA} \times 9.6 \text{ \AA} \times 0.9954 \\
 &= 440.45 \times 10^{-24} \text{ cubic centimeters}
 \end{aligned}$$

The formula of the Belle Fourche montmorillonite calculated from the chemical analysis is $(Al_{1.63} Fe_{.17} Mg_{.25})(Al_{.07} Si_{3.93}) O_{10} (OH)_2 (Na_{.24} \frac{Ca}{2} \cdot 04)(17)$. The average molecular weight of the unit cell is 742.076. The number of molecules in one gram-molecule is 6.02×10^{23} , hence $\frac{742.076}{6.02 \times 10^{23}} = 123.2684 \times 10^{-23}$ grams per cm^3 . The theoretical density is then: $\frac{123.2684 \times 10^{-23}}{440.45 \times 10^{-24}} = 2.7986$.

Mechanical Analysis

Of the untreated montmorillonite, 91 percent was within the clay-size range. When thermally treated to 600°C the amount of material in the clay sizes dropped to 33 percent. Since there was no transformation of the material, the increase in grain size must have been due to a more obscure form of aggregation of the particles. When thermally treated to 850°C, the clay-size content dropped to 6 percent and the silt-size content increased to 76 percent. This increase in grain size is attributed, of course, to fusion of the particles.

Limits Analysis

The liquid limit of the untreated montmorillonite was 664.00 percent. When thermally treated to 600°C the liquid limit dropped to 75.10 percent. When thermally treated to 850°C the liquid limit dropped to 35.46 percent. The high liquid limit of the untreated montmorillonite is attributed to the surface area, surface activity and absorption of interlayer-water. The montmorillonite thermally treated to 600°C, being unable to absorb interlayer-water, the liquid limit is similar to that of the untreated illite. Thus, the liquid limit of the 850°C thermally treated montmorillonite is more directly related.

After soaking the 600°C thermally treated montmorillonite in water for a period of six months, the liquid limit increased to 140.80 percent; and it must be concluded that the collapsed lattice made a partial recovery.

The material thermally treated to 850°C, being granular and non-absorptive, did not exhibit plasticity. The attendant increase in shrinkage limits as the material was thermally treated is attributed to the change in particle shape and change in gradation of the material.

Moisture-Density Relationship

The volume of compacted solids, at optimum moisture and maximum density, in the untreated montmorillonite was 42.10 percent. The volume of solids in the material thermally treated to 600°C was 45.87 percent. The volume of solids in the material thermally treated to 850°C was 53.85 percent.

Shear Strength Analysis

The untreated montmorillonite as tested by the triaxial method gave an angle of 21° 30' for the internal friction and a cohesion value of 7.13 pounds per square inch. (see Fig. 10). When thermally treated to 600°C, the angle of internal friction increased to 40° 00' and the cohesion value increased to 8.5 pounds per square inch. This great increase in internal friction is attributed to the collapse of the c-axis and the removal of all interlayered water. This observation infers that interlayered water in this type of clay functions more or less as a glide-plane having considerably greater mobility than the absorbed water layers between crystal surfaces. When thermally treated to 850°C, the angle of internal friction increased to 46° 00' and the cohesion value dropped to 3.5 pounds per square inch. This low cohesion value is again attributed entirely to meniscus water tension.



Untreated Thermally Treated Thermally Treated
to 600°C. to 850°C

Fig. 10 - Specimens of Montmorillonite after Triaxial Testing.

CONCLUSIONS

When heated to destruction of the clay mineral configuration, the kaolinite decomposed into γ - Al_2O_3 and amorphous silica. It is believed that the alumina octahedral sheet formed γ - Al_2O_3 and the tetrahedral sheet formed amorphous silica. Upon further heating the products recombined to form mullite, leaving some amorphous silica in excess.

Illite, when decomposed by heating, formed spinel and glass. Supposedly the octahedral sheet formed spinel; the tetrahedral sheets, in combination with various impurities and alkalis present, formed glass.

The montmorillonite containing exchangeable cations and impurities also formed spinel and glass, when heated sufficiently to decompose the clay mineral structure.

It may be concluded that the products of thermal treatment depend upon the rate of heating, the temperature to which the treatment is carried, the clay mineral structure, the amount and type of exchangeable cations present and impurities present.

It may be concluded that the pycnometer method of determining the specific gravities of clays is highly satisfactory since the results approximated the theoretical densities.

It is believed that the liquid limit of a clay mineral is due to one or more of the following: surface area, surface activity, and the absorption of interlayer-water. The kaolinite, not being able to absorb interlayer-water and having very low surface activity, had a

liquid limit very similar to the liquid limits of its thermally treated products. The liquid limit of the montmorillonite when thermally treated to 600°C to collapse the lattice, is similar to the liquid limit of the untreated illite; yet, when the lattice is fully expanded, the liquid limit was extremely high.

The plasticity index is related to the amount and type of clay mineral present. When thermally treated to decompose the mineral structure, the products did not exhibit plasticity.

An interesting observation from these tests was the low internal friction value of the untreated montmorillonite. The properties of the untreated illite and the montmorillonite thermally treated to 600°C were very similar (see Tables 2 and 3), and it is concluded from this comparison that the low internal friction value of the untreated montmorillonite is due to the formation of glide-planes within the lattice by the absorption of interlayer-water.

APPENDIX

Table 1 - Physical Properties of Kaolinite

	Untreated	Thermally Treated to 800 °C	Thermally Treated to 1000 °C
Specific Gravity	2.616	2.68	2.68
Mechanical analysis			
coarse sand size	00.00%	00.00%	00.00%
fine sand size	00.00%	03.00%	03.60%
silt size	29.00%	56.00%	54.40%
clay size (-5u)	71.00%	41.00%	42.00%
Liquid Limit	45.40%	45.50%	40.10%
Plastic Limit	25.03%	45.50%	45.66%
Plasticity Index	20.37	00.00	00.00
Shrinkage Limit	23.77%	45.02%	60.27%
volume of solids	59.20%	45.00%	39.00%
volume of water	37.95%	54.80%	61.00%
Moisture-Density Relationship			
unit dry weight	94.30 lbs/ft ³	72.00 lbs/ft ³	72.40 lbs/ft ³
optimum moisture	26.00%	41.10%	41.80%
volume of solids	57.80%	43.10%	43.25%
volume of voids	39.30%	47.30%	48.50%
Shear Strength			
angle of internal friction	19° 30'	45° 30'	40° 00'
cohesion	22.30 lbs/in ²	2.4 lbs/in ²	6 lbs/in ²

Table 2 - Physical Properties of Illite

	Untreated	Thermally Treated to 750 °C	Thermally Treated to 1000 °C
Specific Gravity	2.83	2.80	2.59
Mechanical Analysis			
coarse sand size	00.00%	00.00%	11.50%
fine sand size	00.40%	24.40%	43.50%
silt size	01.60%	24.10%	34.60%
clay size (-5u)	98.00%	48.50%	10.40%
Liquid Limit	83.00%	53.40%	37.00%
Plastic Limit	36.70%	43.13%	00.00%
Plasticity Index	46.30	10.27	00.00
Shrinkage Limit	21.59%	39.08%	47.00%
volume of solids	59.00%	46.75%	46.02%
volume of water	36.40%	50.04%	50.08%
Moisture-Density Relationship			
unit dry weight	82.30 lbs/ft ³	80.24 lbs/ft ³	80.40 lbs/ft ³
optimum moisture	31.00%	35.40%	31.00%
volume of solids	46.60%	45.95%	49.70%
volume of water	40.80%	45.50%	39.95%
Shear Strength			
angle of internal friction	40° 30'	23° 30'	37° 00'
cohesion	14.90 lbs/in ²	14.00 lbs/in ²	2.53 lbs/in ²

Table 3 - Physical Properties of Montmorillonite

	Untreated	Thermally Treated to 600 °C	Thermally Treated to 600 °C, & Water Soaked, for 6 Months	Thermally Treated to 850 °C
Specific Gravity	2.78	2.76		2.50
Mechanical Analysis				
coarse sand size	00.00%	00.00%		00.00%
fine sand size	02.10%	18.00%		18.00%
silt size	06.00%	49.00%		76.00%
clay size (-5u)	91.00%	33.00%		06.00%
Liquid Limit	664.00%	75.10%	140.80%	35.46%
Plastic Limit	45.00%	42.32%	50.88%	00.00%
Plasticity Index	619.00	32.78	89.92	00.00
Shrinkage Limit	11.50%	36.50%	24.25%	31.59%
volume of solids	75.40%			53.90%
volume of water	23.80%			42.40%
Moisture-Density Relationship				
unit dry weight	73.00 lbs/ft ³	79.40 lbs/ft ³		84.00 lbs/ft ³
optimum moisture	38.00%	35.00%		26.60%
volume of solids	42.10%	46.05%		53.85%
volume of water	44.45%	44.55%		35.80%
Shear strength				
angle of internal friction	21° 30'	41° 00'		46° 00'
cohesion	7.13 lbs/in ²	8.5 lbs/in ²		3.53 lbs/in ²

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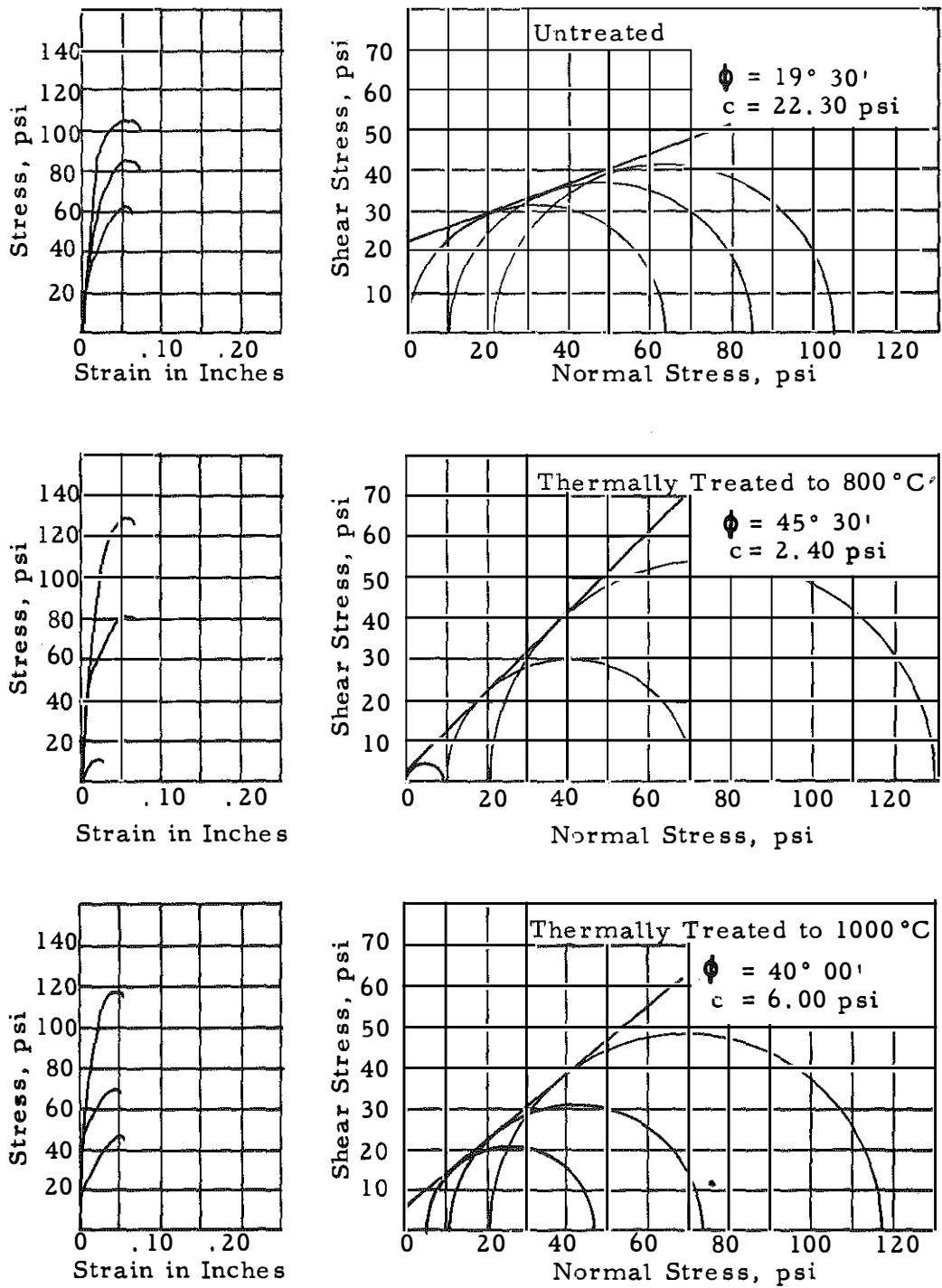


Fig. 11 - Stress-Strain Curves and Mohr's Diagrams for Kaolinite.

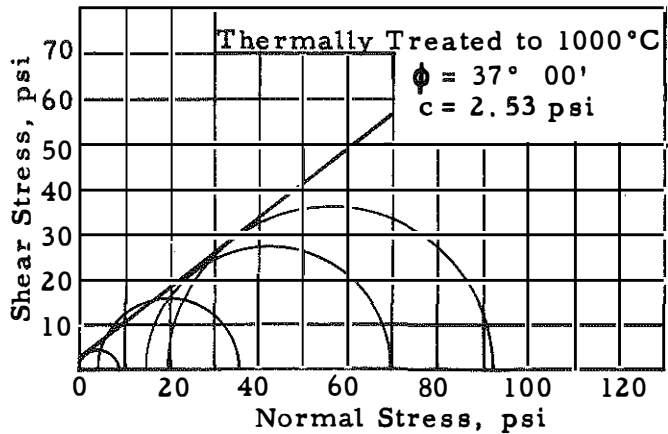
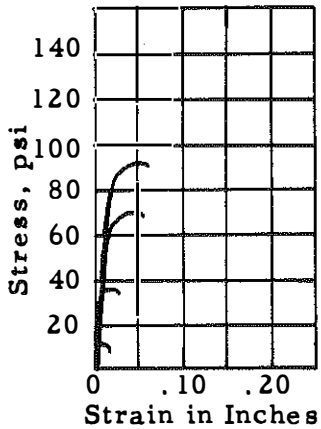
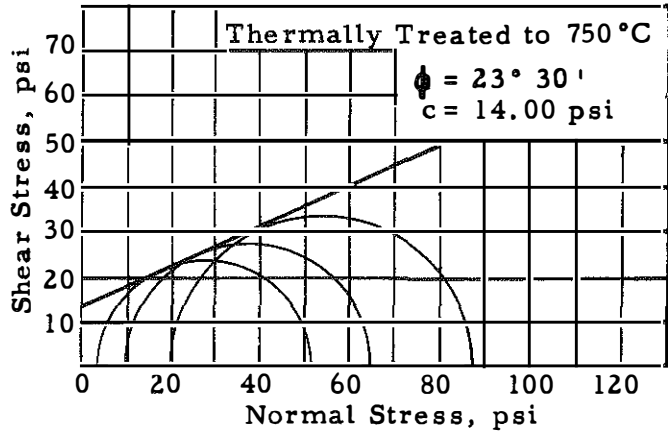
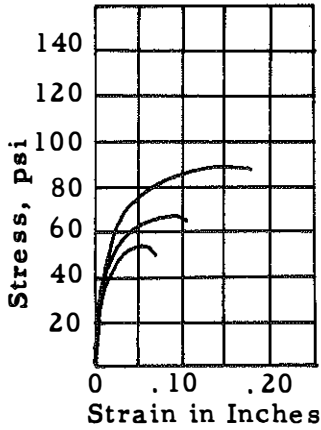
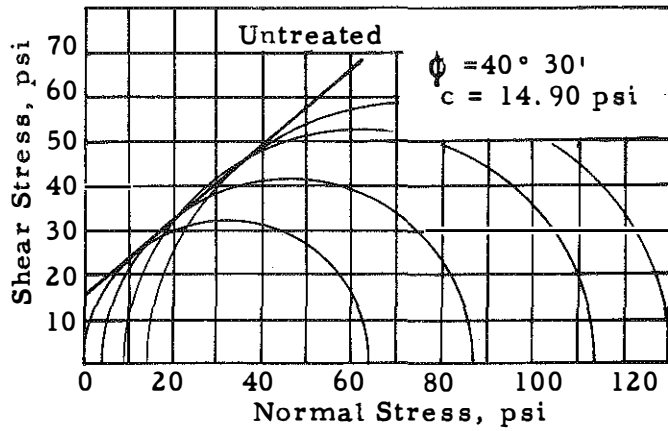
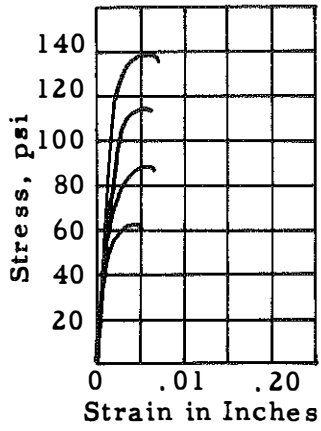


Fig. 12 - Stress-Strain Curves and Mohr's Diagrams for Illite.