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Clay minerals organic ions and differential thermal analysis.

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CLAY MINERALS, ORGANIC IONS AND DIFFERENTIAL THERMAL ANALYSIS

Robert A. Litke

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AND
DIFFERENTIAL THERMAL ANALYSIS

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FOREWORD

For many years the identification of clay minerals has been a challenging and important problem in the sciences of soil mechanics, geology, and ceramics. Although much work has been done in this field, much still remains to be accomplished.

For stimulating the interest for further exploration through the medium of differential thermal analysis, for providing guidance and encouragement when needed, the author is grateful to Professor Edward J. Kilcawley.

The author is indebted to Assistant Professor John E. Munzer for a thorough indoctrination in the operation of apparatus and many helpful suggestions given during the course of experimentation.

Acknowledgment for timely advice and constructive criticisms is appreciatively made to Associate Professor Stanley V. Best, and Assistant Professor William J. Kelleher.

ABSTRACT

The specific problem investigated in this study is the effect of an inert atmosphere on the differential thermal analysis of clay minerals with adsorbed organic ions. In conjunction with this study, the effectiveness of hydrogen peroxide pretreatment for removal of adsorbed organic matter was investigated.

A group of natural clay samples were pretreated alternately with two organic liquids, piperidine and methylene blue. These pretreated specimens were subjected to differential thermal analysis and found to have exothermic reactions of varying magnitude due to oxidation of organic matter. The exothermic reactions experienced in each case appeared to be in proportion to the cation exchange capacity of the sample concerned. The exothermic reactions recorded with pretreated samples of montmorillonite and illite, run in air, were of such a magnitude as to preclude the use of the thermal curves for identification purposes. On the other hand, pretreated kaolinite samples experienced exothermic reactions of such minor proportions that the sample could be readily identified from the thermal curves.

The use of an inert atmosphere of helium for the conduct of differential thermal analysis was found to be an effective means of suppressing exothermic reactions due to oxidation of adsorbed organic matter. It was noted that endothermic reactions under these conditions were of smaller

magnitude than those obtained in the natural sample. This phenomena was attributed to displacement of water by organic ions.

Hydrogen peroxide pretreatment was found to be generally ineffective in removing adsorbed organic ions. While it appeared that organic ions on exposed lattice discontinuities were removed, ions in the relatively inaccessible interlayer positions of montmorillonite were little affected by this pretreatment.

PART I

INTRODUCTION

A. Historical Review

Scientist and engineer alike have been attempting for centuries to solve problems in foundation engineering and soil mechanics. A truly scientific solution to these problems can be arrived at only on the basis of a reasonably accurate conception of the mechanical properties of the materials involved.

A number of significant soil properties have been conceived, together with suitable standards of measurement. Grain size analyses, Atterburg Limits, friction angle, and cohesion determinations are examples of these significant properties.

Numerous experimental analyses have indicated that the mechanical properties of a soil are dependent, in large measure, on the nature and amount of the finer fraction of the soil. For this reason, investigators have been particularly active in determining not only the amount but the nature of the finer fractions, among which are the clay minerals.

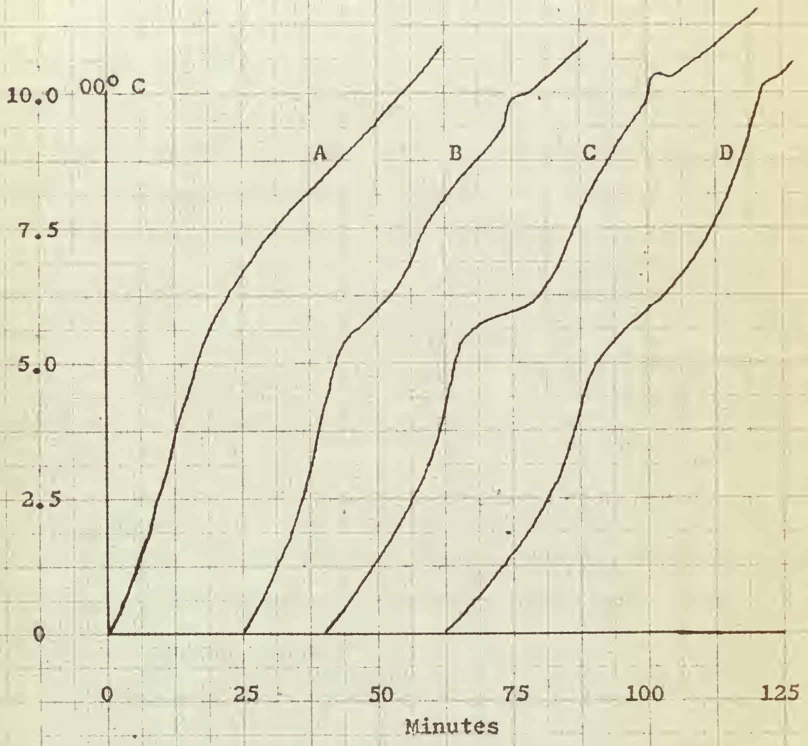
The scientist and engineer, in their endeavor to discover the nature of the clay minerals, have followed a number of different approaches. Each of these paths of investigation produces a share of information and when taken collectively, yields a more complete concept of the nature

of the clay mineral. Differential thermal analysis is one of these approaches. Some of the other approaches are X-ray diffraction, electron microscope, petrographic microscope and infra-red absorption. The most useful and complete analyses are those utilizing several methods of study for the same sample.

The concept of identification by noting the thermal reactions which take place upon heating was first introduced by M. LeChatelier (12)[*], in 1887. LeChatelier, a remarkable french scientist adept in many fields, used his methods in the study of minerals.

Other scientists were slow to make use of LeChatelier's methods, probably because the possibilities of his concept were not yet evident. This pioneer work in thermal analysis was accomplished by placing the material in a small platinum crucible with a single thermocouple junction in the center of the material. The whole mass was placed in a furnace and heated at a rapid (2° C/min) and relatively uniform rate. The thermocouple was connected to a galvanometer which was read periodically. Thermal reactions in the material caused variations in the galvanometer record, as compared to that obtained when the furnace contained no sample. Typical results obtained are exemplified in Figure I.

[*] Throughout this thesis, numbers in parentheses refer to similarly numbered items in PART VII, LITERATURE CITED, used in support of statments accompanying the numbers.



Thermal reactions in clay superimposed on furnace heating rate, as recorded by Wohlin. Curve A is furnace heating curve. Curves B to D show furnace heating rate with thermal reactions for clays superimposed.

FIGURE I

LeChatelier and Salodin published a paper in 1904 describing a modified apparatus with which they were unable to produce reproducible results. Introduction, in 1899, of the differential thermocouple by Roberts-Austin (20), was to provide a valuable tool for measuring temperature differences. Fenner (4) made the first application of this difference thermocouple in 1913, when he used it in the study of the stability relations of silicate minerals. Subsequently, in 1929, the method was used by Kracek and others in the study of inorganic chemical compounds.

The applicability of the methods of differential thermal analysis to clay mineral studies was conclusively established through research conducted in 1933 by Orcel (18), and Orcel and Caillere (19), in 1935. Since that time the method has been used by many investigators in every part of the world.

Norton (17), in 1939, using concepts credited to Orcel, presented the first applications of differential thermal analysis to quantitative determinations of clay content. Norton's method involved the comparison of the area under endothermic and exothermic peaks between a sample under investigation and a sample of pure mineral.

During the 1940's, the use of differential thermal analysis was widespread in the critical examination of clay minerals. Many papers worthy of note were published, such as those by Grim and Rowland in 1942, and those by Speil,

Berkelhamer, Pask and Davies in 1945. Papers by Kerr and Kulp in 1947, 1948 and 1949, added to the accumulation of knowledge and introduced the multiple method of differential thermal analysis. Differential thermal analysis is not limited to the scope of clay minerals, but can be used to study any substance which will undergo exothermic and endothermic changes upon heating.

A most noteworthy work on the identification of clay minerals was that contained in Research Project 49, American Petroleum Institute (10). In this Project 49, was a report covering differential thermal analysis which included a reasonably complete outline of the method, the basic theory and the details of the most recent experimental techniques. The report set forth the differential thermal curves for the reference clay mineral specimens. This, in a sense, set up a set of standards which would prove invaluable for the work of future investigators.

Costello (3) initiated the study of clay minerals by differential thermal analysis at Rensselaer Polytechnic Institute in 1948. The differential thermal curves of the three principal clay minerals and suggestions for procedure to be followed in future investigations was the result of this pioneer work. The nature of the equipment available at this time prevented obtaining conclusive test data. Results obtained illustrated the need for heating program controller and continuous recording equipment.

In 1949, a Speedomax autographic recorder and a Brown potentiometer were added to the differential thermal analysis equipment. The autographic recorder provided a means for a relatively continuous record of sample temperature and difference in temperature between sample and inert substance. The potentiometer provided a means of continuously recording the temperature of inert substance and, more important, a means of controlling the heating rate of the furnace.

In 1950, Hoskins and Hudson (9) conducted an investigation of the effect of various factors, both experimental and in technique, on results obtained. These factors included heating rates and variable grain size.

Merritt and White (15), in 1951, did further work on the effect of different experimental techniques and test conditions on results. Included in these studies were the effect of sample pretreatment, sample weights and ratios, and ionic saturation. Conclusions included notes on quantitative studies.

Harper and Kitterman (6), in 1953, also investigated the effects of experimental methods on differential thermal results.

In 1954, Miller (16) studied the effect of vacuum on differential thermal analysis research, particularly with respect to clays containing organic material.

In 1955, Heid (7) completed a thorough investigation of the effects of vacuum and inert gas on clays

containing discrete particles of organic material. This research was the most recent work done on differential thermal analysis at Rensselaer Polytechnic Institute.

In the past few years much research has been done in the United States and abroad on clay minerals by differential thermal analysis. One of the most recently published works is that of Silfverberg (21), of the Royal Swedish Geotechnical Institute, who investigated the effect of organic matter on differential thermal analysis of clays.

B. Statement of the Problem

The presence of organic matter in clay minerals complicates the ready identification of the clay by the method of differential thermal analysis. Each family of clay, in its pure form, possesses a certain molecular structure, water adsorbing, and water combining characteristic which causes it to yield a distinctive thermogram when heated. This distinctive thermogram provides the basis for identification.

Organic matter, when present in the clay, is the cause of exothermic reactions which tend to obscure the distinctive portions of a clay mineral thermogram. Therefore, organic matter, if present in sufficient quantity, can render a clay thermogram worthless for purposes of qualitative or quantitative analysis of a clay sample.

This organic matter can be present in a clay in either or both of two forms. It can be present as discrete

particles of decaying vegetable or animal matter. It can also be present in the form of organic ion complexes adsorbed on the lattice structure of the clay mineral.

In any event, the worth of a differential thermal analysis for identification purposes is dependent upon the removal of this organic matter or the suppression of its effects if allowed to remain. For this reason, several experimental techniques to accomplish this objective have been conceived through the years. Among these techniques are chemical pretreatment for removal through oxidation, and the use of vacuum or inert atmosphere for suppression.

Many investigators feel that chemical pretreatment, principally with hydrogen peroxide and acetyl bromide, may alter the structure of the clay mineral. For this reason, they tend to lean toward the use of vacuum and inert atmosphere for suppression of organic effects.

The effect of inert atmospheres on the differential thermal analysis of clay minerals containing discrete organic particles has been investigated in the past. To the author's knowledge, no such investigation has been done specifically on clays containing organic complexes adsorbed on the lattice structure of the clay. It is the object of this investigation to do so.

PART II

THEORY

A. General

Differential thermal analysis provides a means for the identification and study of clay minerals. It is not the sole means of identification. It shares honors with such methods as X-ray diffraction, chemical analysis, electron microscope, equilibrium dehydration, and infrared absorption.

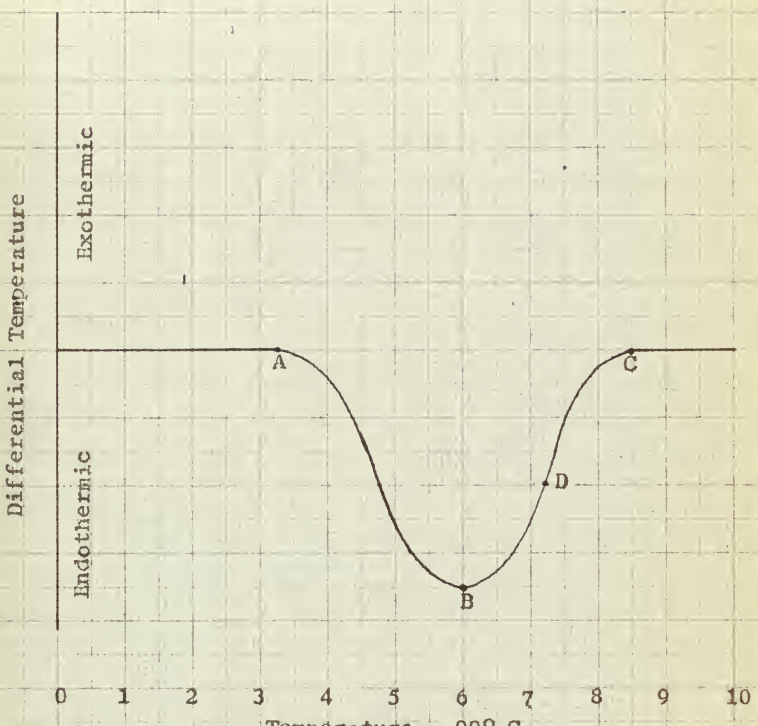
Differential thermal analysis is the study of a substance made by examining the thermal reactions which take place during controlled heating at elevated temperatures. As such a process, differential thermal analysis is not limited to the study of clay minerals alone, but is applicable to any substances which experience the required reactions while being heated. These reactions should be of such a nature that they begin abruptly and are completed in a short period. The term "differential" is logically derived from thermal analysis which utilizes the temperature difference between a sample and an inert material, as both are being heated at a constant, controlled rate.

The thermal reactions are either endothermic or exothermic in nature. Endothermic reactions are attributed to dehydration and to loss of crystal structure. Exothermic reactions result from the formation of new phases at elevated temperatures and from the oxidation of organic

matter. As a result of the phase-changing exothermic reactions differential thermal analysis provides a means of studying high temperature reactions as well as hydration phenomena.

A hypothetical differential thermal curve exhibiting a single endothermic reaction is shown in Figure II. Below point a the heat inflow to the sample and inert material is equal, as are their respective temperatures. Hence, no difference in temperature is recorded. This portion of the curve forms part of the baseline. Starting at point a the sample begins to undergo an endothermic reaction which, for its progression, absorbs heat from the surrounding material. The sample temperature then lags that of the inert counterpart and a differential temperature is recorded. This differential temperature increases until the heat supplied to the reaction equals the differential heat conductivity into the specimen. The amplitude of point b is a measure of the intensity of reaction. After point b the rate of heat inflow increases more rapidly than the heat absorption and the differential temperature decreases. At some point d, exact position unknown, the reaction ceases and at point c the sample and inert matter are once again at the same temperature.

It would be highly unusual for two dissimilar minerals to produce thermal curves registering various reaction peaks at the same temperatures. On this characteristic



THEORETICAL DIFFERENTIAL THERMAL CURVE

FIGURE II

is based the qualitative analysis of the specimen minerals. Generally speaking, the amplitudes of reactions are dependent upon the amount of the active minerals present in the sample. Quantitative analyses, when obtainable, are based on this characteristic.

Results obtained from differential thermal analyses are a function of many variables. Consideration of many of these variables is important in individual curves and consideration of all is important in obtaining reproducible and comparable thermal curves. A number of factors producing variations are discussed in the following paragraphs.

Different Equipment - Differences in equipment present an inherent source of variation to thermal curves. Generally, tests run with different equipment are not exactly reproducible for purposes of quantitative analysis, although they might compare favorably for qualitative purposes.

Thermal Diffusivity - Temperatures at the beads of the differential thermocouples depend in a large measure upon the coefficients of thermal diffusivity of the sample and the inert material. The cooling rate of a point in a hot body, under specified surface conditions, is known as the thermal diffusivity. It is equivalent to $\frac{K}{dc_p}$, where K is the coefficient of thermal conductivity, d the density, and c_p the specific heat. The sample diffusivity may be different from that of the inert material, and may even change during heating due to formation of a new phase or

sample shrinkage. The effect of this difference on the thermal curve would be an offset baseline while changes occurring during a test would result in a sloping baseline.

Heating Rate - The heating rate will normally affect thermal curves produced by differential thermal analysis. The usual effect of a slower heating rate is a broader peak obtained at a lower temperature. Faster heating rates have the opposite effect. Some investigators report the area under a peak is not affected by the heating rate. In previous work conducted in differential thermal analysis at Rensselaer Polytechnic Institute, a heating rate of 1023° C/hr has proven satisfactory. In any event, the heating rate, whatever it may be, should be uniform, lest changes in rate be reflected in the differential thermal curve.

Grain Size - The general effect of decreasing grain size, as reported by many investigators, is the reduction in magnitude of thermal reaction and reduction of peak temperature. In some materials this can be explained by a corresponding reduction in crystallinity.

Organic Matter - The presence of organic matter in a sample heated in an oxidizing atmosphere, such as air, causes exothermic reactions in proportion to the amount of organic matter present. These reactions result from the heat formed when substances are oxidized. These exothermic reactions can cause considerable difficulty in clay mineral identification. The exact nature of the difficulties,

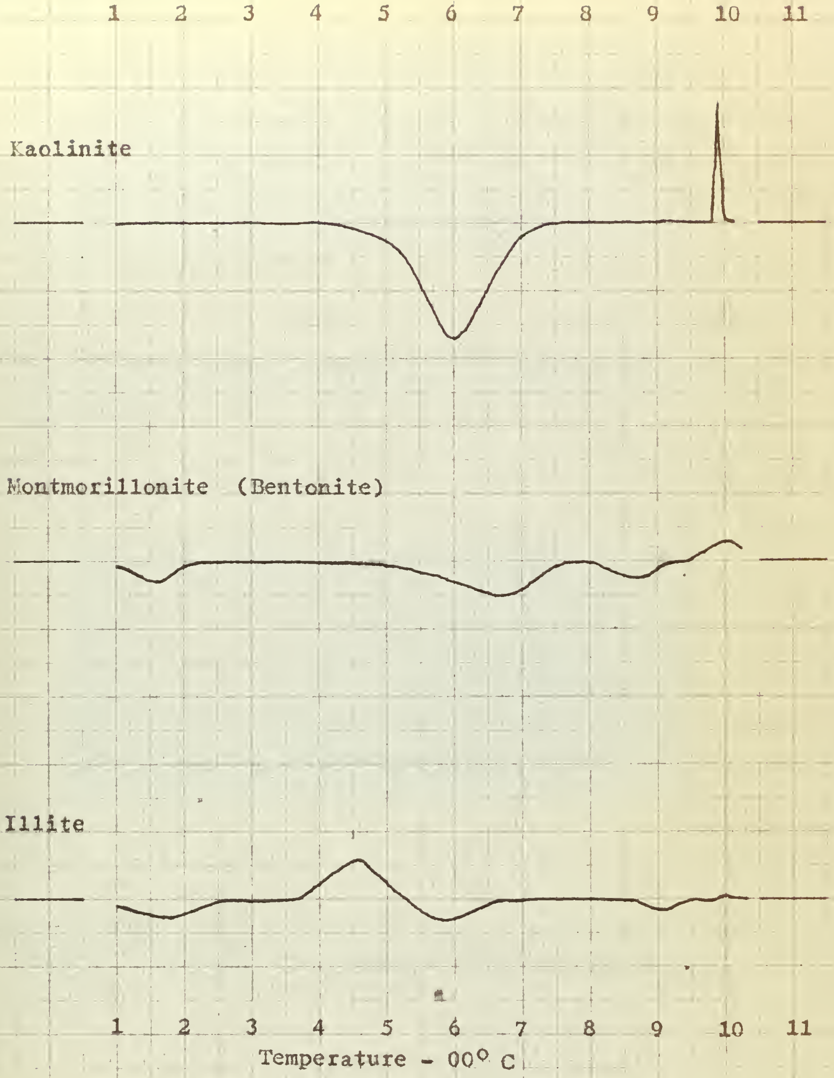
together with compensating techniques, will be discussed in greater detail in another section.

B. Analysis of Thermal Curves for Kaolinite, Montmorillonite and Illite

This investigation was confined to differential thermal analyses of the principal members of the three clay mineral families. These are the Kaolinites, the Illites, and the Montmorillonites. The nature of characteristic thermal reactions obtained will be explained in succeeding paragraphs. Typical differential thermal curves for the minerals are shown in Figure III.

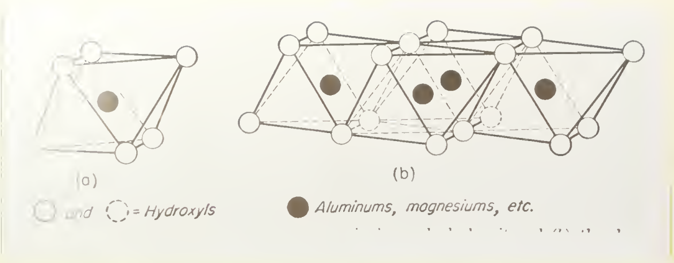
General - The clay minerals are built up of units of alumina and silica. The alumina or gibbsite unit, shown in Figure IV(a), consists of two sheets of rather closely packed oxygen atoms or hydroxyl groups which are held together by aluminum atoms, or hydroxyl groups, three in each sheet. The silica unit, shown in Figure IV(b), consists of a sheet of oxygen held together by silicon atoms. The silicon atoms are surrounded by four oxygen atoms, three in a sheet and one above. The oxygen atom above provides a means for linking the silicon tetrahedron to the gibbsite sheet.

Kaolin - The kaolin group is composed of minerals having a crystal lattice made up of one silicon tetrahedron linked to a gibbsite sheet. This is referred to as a 1:1

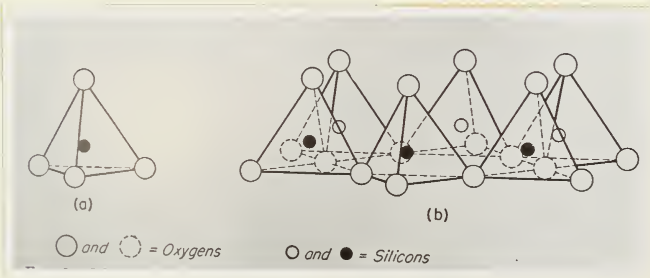


TYPICAL THERMAL CURVES

FIGURE III



(a) Diagrammatic sketch showing (left) single octahedral unit and (right) the sheet structure of the octahedral units, after Grim.



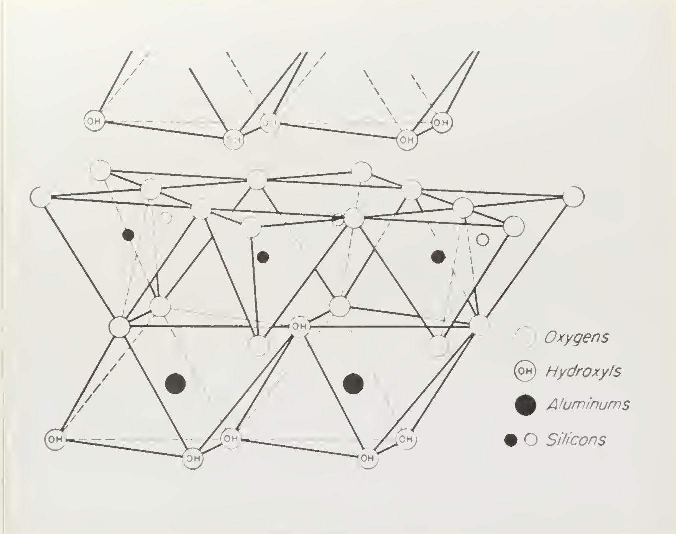
(b) Diagrammatic sketch showing (left) single silica tetrahedron and (right) sheet structure of silica tetrahedrons arranged in a hexagonal network, after Grim.

FIGURE IV

lattice structure and is shown in Figure V. Some of the minerals included in this group are kaolinite, halloysite, metahalloysite, nacrite and dickite.

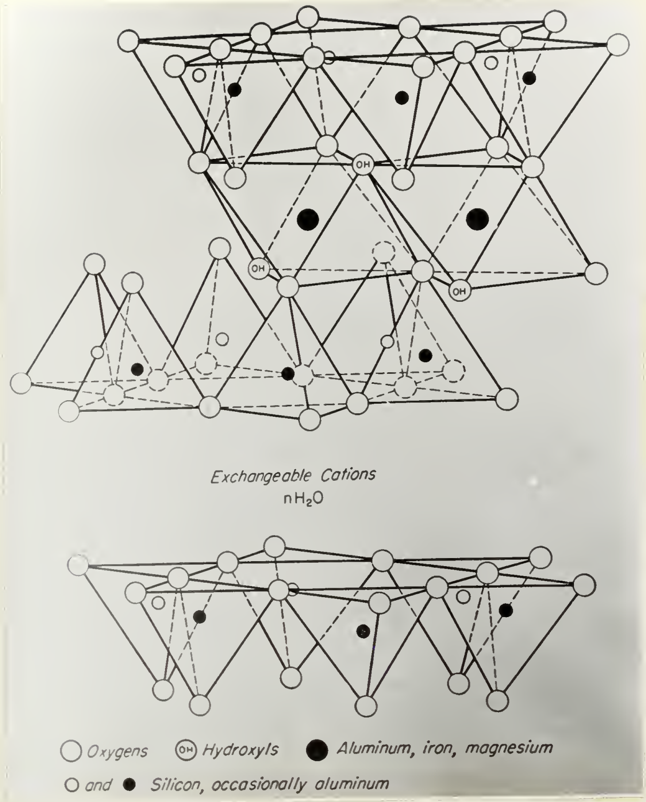
The thermal curve for kaolinite is almost flat up to 400° C. This indicates a lack of interlayer water and is explained by the strong attractive forces of the oxygen atoms of one sheet for the hydroxyls of the adjacent unit. Poorly crystalline kaolinites, with greater c axis spacing may show small endothermic reactions in the low temperature region. Thermal curves show an endothermic reaction of large magnitude beginning at about 400° C, with a peak around 600° C, and ending at about 700° C. The shape of this endothermic reaction assists in the identification of the minerals within the kaolin group. The presence of this reaction is due to the loss of OH lattice water and formation of amorphous alumina. An exothermic reaction is shown between 900° and 1000° C. The cause of this reaction is the formation of a new crystalline phase, the exact nature of which is disputed by different investigators; some report the formation of gamma-Al_2O_3, while others report the formation of mullite.

Montmorillonite - The montmorillonite group is composed of minerals having a crystal lattice of two silicon tetrahedrons linked to opposite sides of a gibbsite unit. This is referred to as a 2:1 lattice structure and is shown in Figure VI. Some of the minerals in this group are montmorillonite, bentonite, pyrophyllite, beidellite, nontronite, and hydrous mica.



Diagrammatic sketch of the structure of the kaolinite layer, after Gruner.

FIGURE V

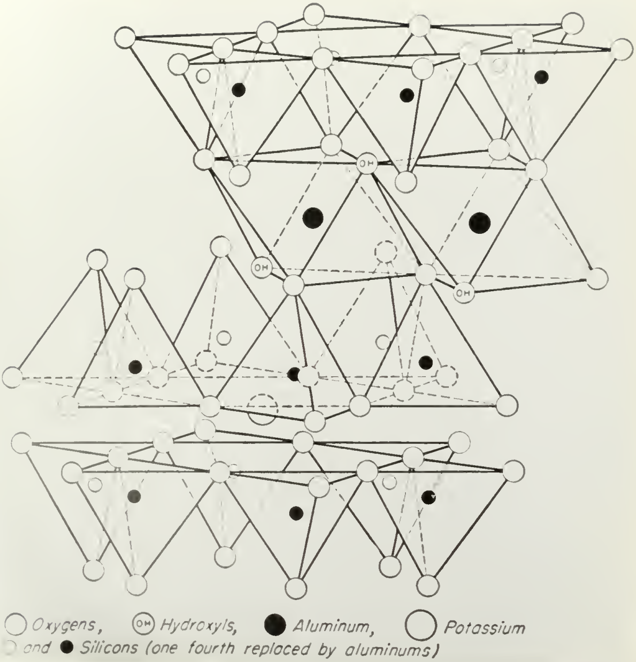


Diagrammatic sketch of the structure of montmorillonite according to Hofmann, Endell, and Wilm, Marshall, and Hendricks.

FIGURE VI

The differential thermal curves for montmorillonite (bentonite) show endothermic reactions which indicate a considerable water loss in the 100° to 200° C range. This water is interlayer water occurring between the sheets of the mineral lattice. The magnitude of this reaction depends on the amount of interlayer water which, in turn, is dependent on the nature of adsorbed ions, sample pretreatment, amount of drying, and relative humidity. Interlayer water is permitted by the loose attraction, or bond, between sheets of like atoms in adjoining lattices. A second endothermic reaction begins at about 450° to 500° C and ends at about 750° C with a peak at about 680° C. This thermal reaction probably results from the loss of OH lattice water. A third endothermic peak is evident in the 850° to 900° C range. Some investigators attribute this reaction to further loss of OH lattice water bonded with magnesium, while others report lattice destruction. An exothermic reaction occurring at about 1000° C is attributed to the formation of spinel.

Illite - The illites have a 2:1 crystal lattice arrangement which is similar in constitution to the montmorillonite family. They are differentiated from the montmorillonites by the presence of an adsorbed interlayer potassium ion. This potassium ion accounts for a relatively strong bonding action between adjacent sheets. Lack of large quantities of interlayer water, and fixed c axis spacing, is explained by this strong bonding. Lattice arrangement is shown in Figure VII. The endothermic reactions on the



Diagrammatic sketch of the structure of illite, after Grim.

FIGURE VII

thermal curve of the illite shown are similar to those of the montmorillonite family. The first endothermic peak indicates the loss of adsorbed interlayer water. The second endothermic peak manifests the loss of OH lattice water. The third endothermic peak represents the final destruction of the lattice and loss of the remainder of the OH lattice water. A small phase-forming exothermic peak is evident at about 1000° C indicating formation of spinel. The presence of organic matter explains the exothermic reaction manifested in the peak at 460° C.

C. Ion Adsorption on Clay Minerals

Organic matter may be adsorbed on the crystalline structure of the clay minerals through the mechanism of ion exchange or through adsorption of polar molecules. Smith (22), in 1934, reacted organic bases and their salts with montmorillonites, and presented evidence that the reaction was one of ion exchange and ion adsorption. Bradley (1)(2) and MacEwan (13)(14), about 1945, showed conclusively that non-ionic organic molecules of polar character could be adsorbed by the clay minerals.

While this latter physical phenomena is of some importance in clay mineral-organic reactions, only the mechanism of ionic adsorption will be discussed here, since, in this investigation, organic ions were used. There are three causes of cation exchange capacity in the clay minerals. They are cited by Grim (5).

Broken bonds around the edges of the silica-alumina are the source of unsatisfied charges. These charges can be satisfied by available ions. The broken bonds are predominately on non-cleavage faces of the layered clay minerals. In the kaolinitic and illitic minerals, such broken bonds account for the major portion of the exchange capacity. Broken bonds account for a proportionally smaller share (about 20%) of the exchange capacity of montmorillonites.

Substitutions within the lattice structure of trivalent aluminum for quadrivalent silicon in the tetrahedral sheet and of ions of lower valence, particularly magnesium, for trivalent aluminum for trivalent aluminum in the octahedral sheet result in unbalanced charges in the structural units of some clay minerals. While in some cases such substitutions are balanced by other lattice changes, they are frequently balanced by adsorbed cations. Substitutions within the lattice account for about 80% of the exchange capacity of montmorillonites.

The hydrogen of exposed hydroxyls may be replaced by a cation which would be exchangeable. Some hydroxyl groups would be exposed around the broken edges of all clay minerals, and cation exchange due to broken bonds would, at least in part, be replacement of hydrogens of exposed hydroxyls. This cause of exchange capacity would be important for kaolinite because of the presence of the sheet of hydroxyls on one side of the basal cleavage plane.

In clay minerals where cation exchange capacity results from broken bonds, the exchangeable cations are held around the edges of the crystalline structure. In clay minerals where cation exchange capacity is due to lattice substitutions, the cations are mostly held on the basal plane surfaces. Hence, in kaolinite, the cations are held on the edges whereas in montmorillonite the cations are held mostly on the basal plane surfaces with the remainder on the edges.

Hendricks (8) has indicated that organic ions are held not only by the forces previously described, but, in addition, by Van der Waals forces. Generally, the larger organic ions are more strongly adsorbed because of the greater Van der Waals forces. Hence, larger organic ions have proven difficult or impossible to replace with smaller ions.

The water adsorbing properties of the montmorillonites are gradually reduced as the basal plane surfaces of the mineral are coated with the organic ions. Generally, the larger the organic ion the greater the reduction in water adsorbing capacity.

PART III

APPARATUS AND MATERIALS

A. General

The equipment currently available at Rensselaer Polytechnic Institute for differential thermal analyses meets the standards required for a well controlled heating and recording program. The equipment, as used by the author, is substantially the same as that used by previous investigators since 1950. A general view of the equipment is shown in Figure VIII.

B. Furnaces

Three furnaces are presently available. These furnaces are horizontal, heavy duty, combustion type, Hoskins Model FH-305, and are rated at 1750 watts. They are 12 inches long, have an inside diameter of 2 1/32 inches, and are insulated with asbestos. Power is supplied through double pole, single throw switches from a transformer, with a 120 volt primary and a secondary output of 118 amps at 17 volts.

Furnace No. 1 is outfitted with a 12 inch cemented alumina combustion tube and was used for runs made under atmospheric pressure only.

Furnaces No. 2 and No. 3 were utilized with removable 24 inch fused silica combustion tubes, sand finished. These tubes are closed at one end and have the interior of the open end ground for stopper insertion. These combustion

General View of Equipment Used
in Differential Thermal Analysis

FIGURE VIII

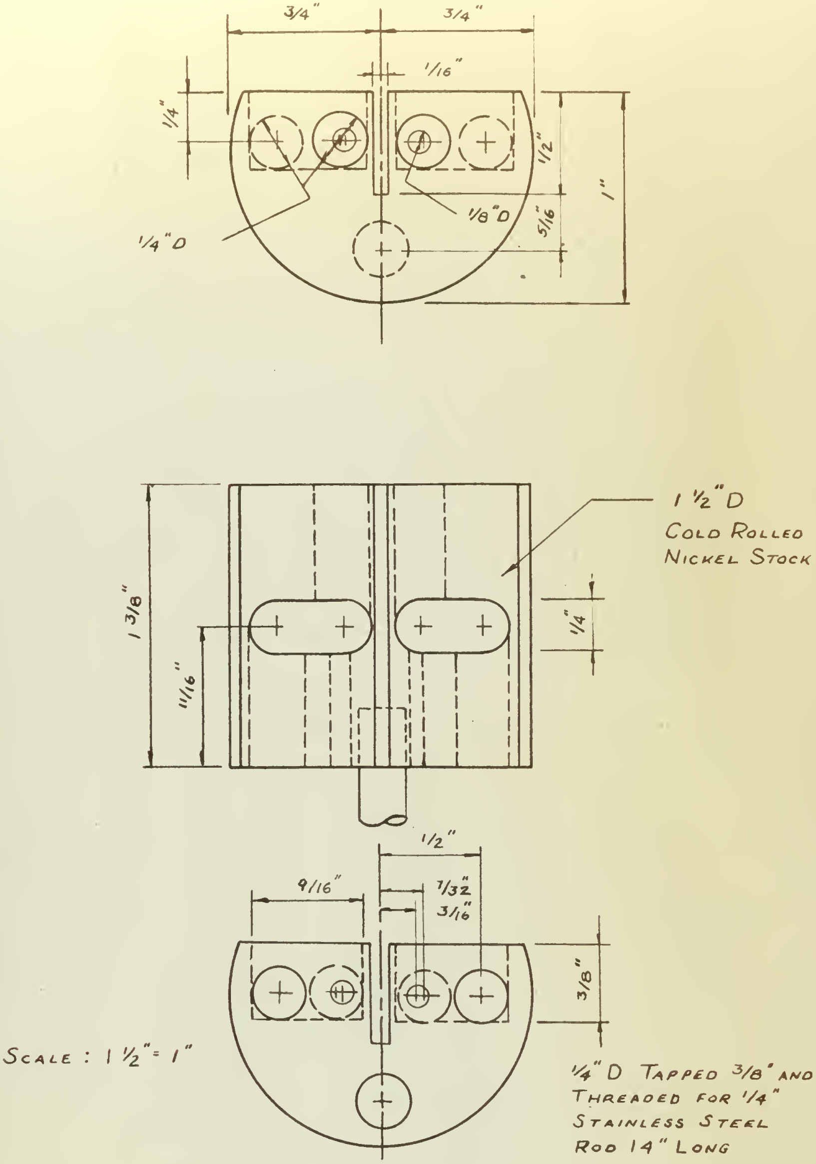
tubes are manufactured under the trade name "Vitreosil", by Thermal American Fuzed Quartz Company, Lynbrook, Long Island, New York.

C. Heating Control Equipment

The heating rate in the furnaces is controlled by a Brown Recording Potentiometer Pyrometer, Model No. 113661-X54#1-H. In this pyrometer, a constant speed motor is connected to an appropriate set of gears which determines a uniform heating rate. The desired temperature at any time, for a uniform rate, is shown by a pointer on the face of the instrument. The temperature in the thermal standard in the specimen holder is shown by another pointer which also makes a continuous record of this temperature. The relative position of these two pointers actuates a motor driven variable transformer, Variac Model V20, which in turn controls the input voltage, between 0 and 135 volts, to the primary of the power transformer for the purpose of maintaining a uniform heating rate. In addition, a compensating rheostat is provided in the control circuit to balance the system, as required, for this uniform, non-fluctuating heating rate.

D. Sample Holders

The sample holders used in this investigation were designed by Assistant Professor J. E. Munzer, of the Civil Engineering Department of Rensselaer Polytechnic Institute. A drawing of this holder is shown in Figure IX.



1 1/2" D
Cold Rolled
Nickel Stock

Scale : 1 1/2" = 1"

1/4" D Tapped 3/8" and
Threaded for 1/4"
Stainless Steel
Rod 14" Long

SAMPLE HOLDER

FIGURE IX

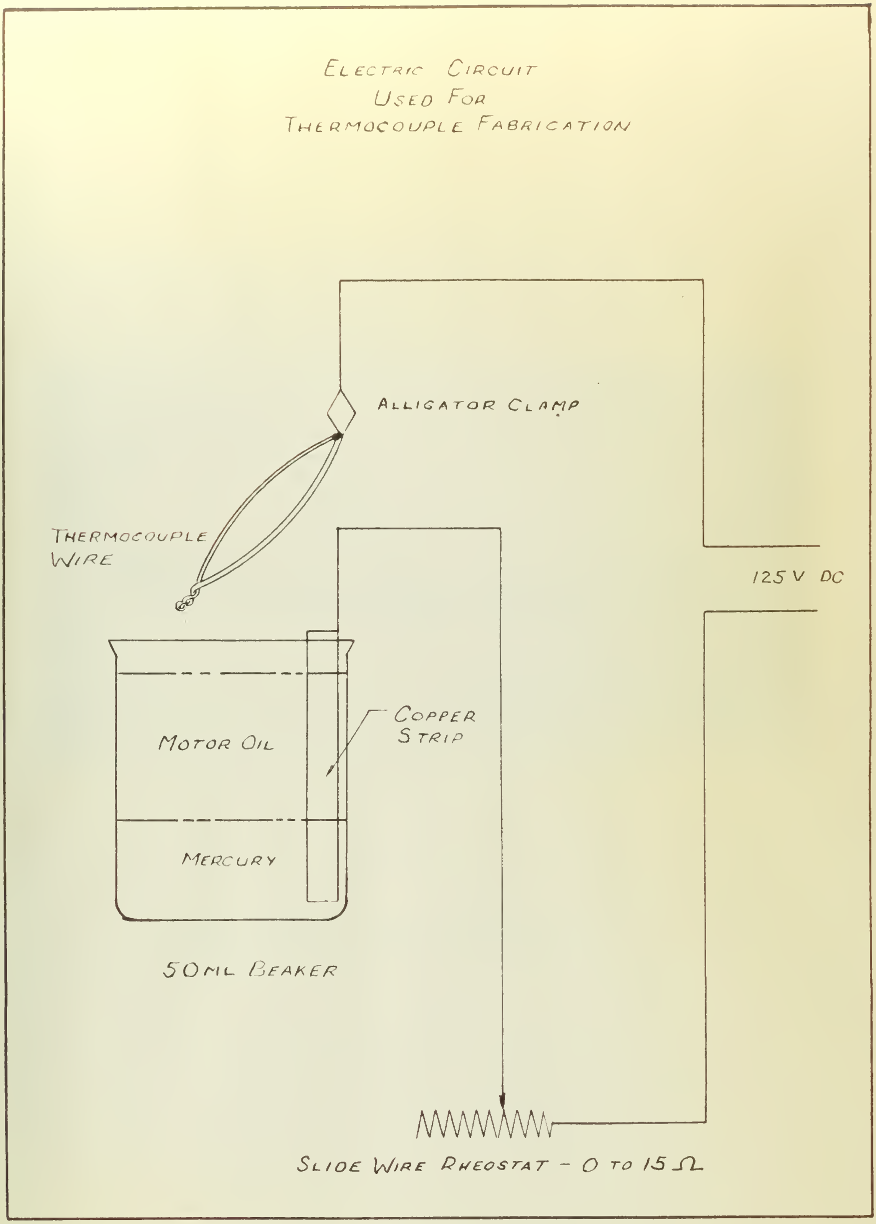
The block is machined from cold rolled nickel stock. Wells are provided for the sample and the thermal standard as shown. The slot between the wells was so placed to prevent heat transfer during thermal reactions. Holes are provided for the insertion of two thermocouples into each well. The sample holder is drilled for a $\frac{1}{4}$ inch stainless steel rod which is used to facilitate handling.

E. Thermocouples

All thermocouples were made from 18 gauge chromel and alumel wire stock. Thermocouple beads were fused by a direct current arc and quenched in an oil bath. A schematic of the circuit used for making thermocouples is shown in Figure X. Thermocouple beads formed in this manner are small and highly satisfactory.

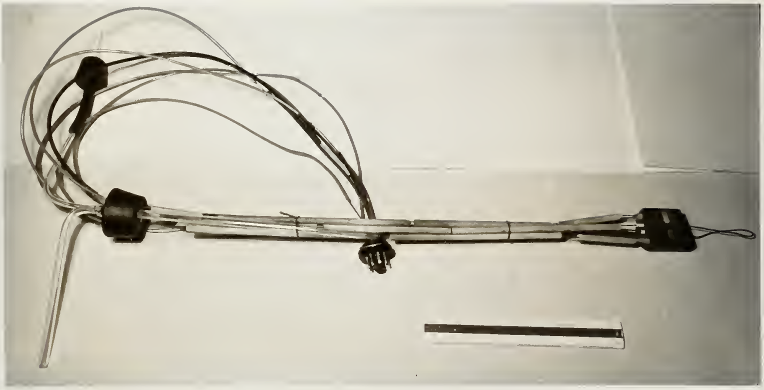
Differential thermocouples were fabricated with chromel lead-in wires, joined by a short section of alumel between the two thermocouple beads. Thermocouples were placed in the sample holder as shown in Figure XI.

Subsequent to thermocouple preparation the thermocouples were calibrated against a standard in a Hevi-Duty Multiple Unit Electric Muffle Furnace, Type 66P. A Brown Portable Potentiometer, Model 126W3 was used for these calibrations. Differential thermocouples were calibrated with the sample holder placed in the Hoskins furnace, and with an equal charge of gamma aluminum oxide in each of the sample holder wells.



Electric Circuit Used For Thermocouple Fabrication

FIGURE X



Sample Holder with Thermocouples

FIGURE XI

Thermocouples were tested for electrical continuity with the ammeter-battery tester constructed by Harper and Kitterman (6).

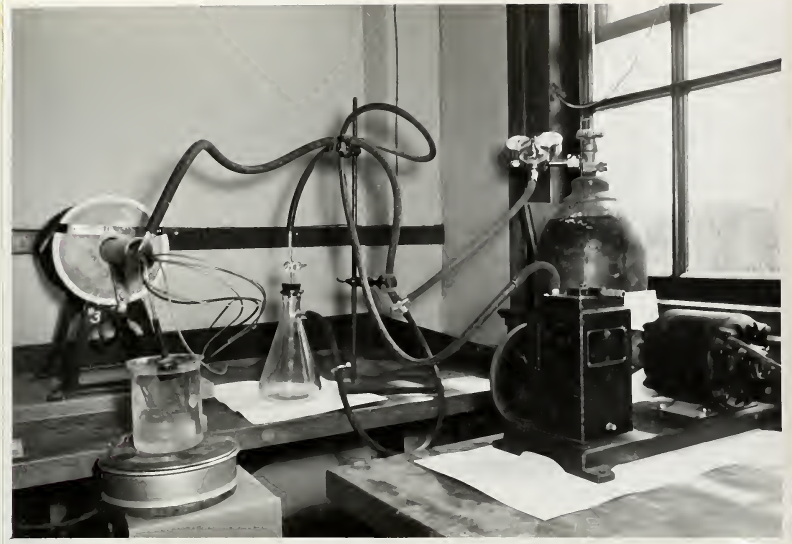
F. Recording Equipment

The temperature in the thermal standard material is recorded by a Brown Recording Potentiometer Pyrometer, as discussed previously in connection with heating rate control. This potentiometer pyrometer is calibrated for use with chromel - alumel thermocouples and has a scale range from 0 to 1400 degrees centigrade.

The temperature in the clay sample and the differential temperature between the sample and standard were recorded by a Speedomax Type G Recorder, Model 560000 Series. Sample temperature and differential thermocouple millivoltage are recorded every six seconds resulting in a relatively continuous thermal record. The temperature range of this instrument is 0 to 1200 degrees centigrade. Millivolt equivalents, which are in the range of ± 1.5 millivolts, must be scaled from the differential temperature record because the scale is not on the recording paper.

G. Inert Atmosphere Equipment

A general view of the equipment used to provide an inert atmosphere in the vitreosil tube during experimentation is shown in Figure XII. It consists of a cylinder of helium with pressure regulator, vacuum reservoir, a vacuum pump, tubing, and a rubber stopper for the vitreosil tube.



Apparatus Used to Provide Inert Atmosphere

FIGURE XII

The helium used for the inert atmosphere was manufactured by the Air Reduction Company. It is welding grade, double charcoal refined, and has an impurity analysis as follows:

CO_2	0.0006%	N_2	0.002%
A	0.0005%	CH_2	0.000002%
H_2	0.00003%	O_2	0.00000 (trace)

Pressure control was attained with a two stage Victor SR200 regulator.

Prior to placing helium in the furnace tube, air was removed by a Cenco Pressovac - 4 Pump. A two liter glass container provided a "vacuum reservoir", the nature of which will be discussed under PROCEDURE.

A rubber stopper was used in the open end of the vitreosil tube, which was ground smooth for stopper seating, both to prevent the entry of air and the unnecessary escape of helium. The stopper was fitted with two $\frac{1}{4}$ inch access holes, one for entry of helium through a glass tube, and one for a controlled bleeding line of glass tubing. The bleeding line terminated in a water-filled beaker. In this manner, the continuous flow of gas through the system was insured. A positive pressure in the vitreosil tube provided protection against air infiltration. Openings around the glass tubing were sealed with Behr Manning "Bearcat" adhesive. In addition, the six thermocouple leads passed through the stopper and terminated in a standard eight prong amphenol plug.

H. Clay Mineral Samples

Clay minerals used in this investigation were obtained from Ward's Natural Science Establishment, Rochester, New York. They are listed below.

H4	Kaolinite	Macon, Georgia
H24	Bentonite	Otay, California
H26	Bentonite	Clay Spur, Wyoming
H28	Bentonite	Little Rock, Arkansas
D496	Bentonite	Osage, Wyoming
H36	Illite	Morris, Illinois

A sample of Albany Clay obtained from the site of the proposed addition to the State Education Building in Albany, New York, was also used. The sample was obtained from a depth of about 25 feet.

I. Sample Preparation Apparatus

Samples were ground with mortar and pestle, and sieved through standard sieves. During pretreatment with organic materials, the sample was vacuum drained on a 9 cm Buchner Funnel.

J. Sample Pretreatment Materials

Piperidine (practical) manufactured by Eastman Kodak Company, was one of the two organic materials used for adsorption on clay mineral samples. The Merck Index (Sixth Edition) gives the following data (in part):

Piperidine - Hexahydropyridine. $C_5H_{11}N$ mol. wgt. 85.15. C 70.52% H 13.02% N 16.45%. Liquid. Characteristic odor.

Soapy feel. b_{760} - 106° C. Infra-red absorption spectrum. Strong base. Miscible with water.

Methylene Blue (USP) manufactured by the J. T. Baker Chemical Company was the other organic material used for adsorption. The Merck Index gives the following data (in part):

Methylene Blue - Methylthionine Chloride. $C_{16}H_{18}ClN_3S.3H_2O$ mol. wgt. 373.90. One gram dissolves in about 25 ml of water.

Hydrogen Peroxide - (Reagent) (30%) manufactured by Fischer Company, was used, with dilution to 15% strength, for attempted removal of organic matter.

PART IV

METHOD OF PROCEDURE

A. General

In the conduct of experimental work the author was guided generally by a set of theoretical requirements for the conduct of a differential thermal analysis set down by Lambe (11). These requirements are quoted as follows:

> "1. The mass, specific heat and conductivity of the sample must be equal to those of the inert.
>
> These properties depend on the particle size and shape, void ratio (degree of packing), moisture content, and specific gravity of both the sample and the inert. Void ratio and moisture content can be controlled, but little can be done about the other variables. Changes in mass, specific heat and conductivity which occur in either the inert or the sample because of temperature changes, or in the sample because of reactions such as decomposition, can be controlled only slightly.
>
> 2. The beads on the differential thermocouples must be located at the centers of the sample and the inert.
>
> Since there are thermal gradients in both the sample and the inert, it is necessary that the

bead.......be at the same corresponding location, the center being the most convenient, in order that the temperature drops from the heat transfer be the same.

3. The inert material must be truly inert (thus have no thermal reactions in the range of the investigations).

4. The sample and the inert must reside in an infinite thermal reservoir. (This requirement is attained by the use of a container of sufficiently large mass that its temperature is unchanged by reactions taking place within the test sample.)"

B. Sample Preparation

Samples of pure clay minerals, for the natural condition tests, were prepared by crushing with mortar and pestle to pass a 100 mesh sieve. Samples were then placed in an oven and held at 100° C for 18 hours. After this heating period, the clay was placed in a calcium chloride charged desiccator until required for use. Prior to placing the sample in the sample holder, the sample was re-sieved and weighed on an analytical balance to .001 gram. As the sample was placed in the sample holder the holder was tapped gently on a working surface to insure that no voids would result in the sample well. The material was then lightly compacted with a nail, the head of which just fit into the sample well.

The thermal standard, alumina, was ground in a manner similar to that of the sample. The alumina was placed in the muffle furnace and heated to 350° C. It was then put into the drying oven and left for 48 hours. The alumina was removed at that time and placed in the desiccator until required. Since other investigators have reported the observation that alumina has a ready tendency to pick up water from the atmosphere the entire drying cycle was repeated several times during the eleven weeks' course of investigation. When required for use, the alumina was weighed and placed in the sample holder in a manner similar to that of the clay sample. Equal weights of alumina and sample were used, with due regard for the necessity to cover, handsomely, the thermocouple beads.

Piperidine saturated samples were prepared from clay minerals received from Ward's Natural Science Establishment. The clay was ground to pass a 100 mesh sieve and treated with a 1:50 HCL solution for 30 minutes. The sample was then placed in a Buchner Funnel, vacuum drained, and washed with distilled water. Schleichler and Schuell #507 filter paper, suitable for very fine materials, was used on the funnel. Faster papers allowed the finer clay particles to pass through. A piperidine solution consisting of 25 cc of piperidine (practical) and 25 cc of distilled water was placed on the clay material in the funnel and allowed to remain there for 20 minutes. The sample was then vacuum

drained and washed with distilled water. After washing, the sample was removed from the funnel, and placed in the drying oven at 100° C and allowed to remain overnight. The dried sample was reground to pass a 100 mesh sieve and placed on the Buchner Funnel in the dry state. A piperidine solution of the same normality as before was then placed on the clay sample. The solution was allowed to remain on the clay for detention periods of 24 hours for the bentonites, and 30 minutes for the illite and the kaolinite. The illite and kaolinite seem to adsorb their maximum capacity of ions in considerably less time than the bentonites. This is in consonance with their respective cation exchange capacities. After the detention period, the piperidine solution was vacuum drained and the clay was thoroughly washed, while on the funnel, with distilled water. Samples were then placed in the drying oven at 100° C for 18 hours. The remainder of the procedure is as described for the natural samples.

Methylene blue saturated samples were prepared from clay minerals obtained from Ward's Natural Science Establishment. This pretreatment was similar to that used for piperidine. The methylene blue solution used for adsorption was made up of 1 gram methylene blue (practical) per cc of distilled water. 50 cc of this methylene blue solution were used on the Buchner Funnel for each of the two adsorption steps.

Hydrogen peroxide pretreatment for attempted removal of organic matter was performed on piperidine and methylene blue saturated samples. Samples were ground to pass a 100 mesh sieve, mixed in a small beaker with 15% hydrogen peroxide (reagent) and boiled for 45 minutes over a bunsen burner and evaporated to dryness in the drying oven at 100° C. The remainder of the sample preparation was identical to that used for natural samples.

C. Differential Thermal Analyses in Atmosphere

Prior to charging, the sample holder thermocouples were tested for electrical continuity, then the clay specimen and thermal standard were placed in the sample holder as described in Sample Preparation. The sample holder was inserted into the furnace, which was at room temperature, in such a manner that sample wells were maintained in an upright position to prevent spilling of the sample or uncovering of thermocouple beads. The thermocouple circuit to the recording equipment was completed by inserting the amphenol plug into its receptacle.

The recording equipment was then energized. The batteries in the Speedomax Recorder and Brown Potentiometer were balanced against their respective standard cells. The Brown Potentiometer was de-energized temporarily when the temperature controller indicated 75° C. The thermal standard temperature indicator on the potentiometer was then set at 60° C. When the Speedomax Recorder attained a steady state

condition, as indicated by straight lines for sample and differential temperatures, the furnace heating coils were energized. As the sample temperature passed 75° C, the Brown Potentiometer was energized. This procedure, together with occasional adjustment of a compensating rheostat in the Variac circuit, was necessary to obtain a smooth heating rate. A heating rate of 1023° C/hr was reported to be satisfactory and was maintained throughout this investigation. This rate is determined by the currently installed gear ratio in the potentiometer and was not changed. The temperature range covered in these investigations was to 1050° C. Mention should be made of the fact that free access of atmospheric air was allowed. This was accomplished by leaving the rubber stopper, on furnaces 2 and 3, or the transite plate on furnace 1, slightly ajar. The reason for this will be discussed under RESULTS.

D. Differential Thermal Analysis in Helium

With the exception of procedure described below, the methods used were identical to those chronicled for analyses in atmosphere.

After the sample holder was inserted into the combustion tube, the stopper seated tightly and the hose connections made, a vacuum pump was used to evacuate the "vacuum reservoir". Then a hose clamp between the reservoir and the combustion tube was opened slowly to allow a gentle flow of air from the combustion tube. This step was found

necessary to prevent disturbing the samples in the wells of the sample holder. A rapid evacuation of air was observed to lift a portion of the sample from the wells. This was to be avoided if possible to prevent uncovering thermocouple beads and disrupting the baseline.

When evacuation was as complete as practicable, helium was allowed to flow into the system. Flow of helium through the system was maintained by observation of bubbles from the bleeder line, whose outlet was placed in a beaker of water. It was reasoned that leakage, if any, in the tube would be from, and not into, the combustion tube because of the slight pressure differential maintained.

E. Test Data

In addition to the machine-made records, a number of data, as summarized below, was recorded.

1. Number of runs
2. Dates of runs
3. Identification of sample
4. Sample pretreatment
5. Sieving data
6. Weight of sample
7. Furnace used
8. Thermocouple calibration data source
9. Cold junction temperature
10. Sample color after firing was afixed to data book with cellophane tape.

PART V

DISCUSSION OF RESULTS

A. General

The testing schedule accomplished can be outlined as follows:

1. Analyses performed on natural clay samples, under atmospheric conditions.
2. Analyses performed on natural clay samples with organic ions adsorbed, under atmospheric conditions.
3. Analyses performed on natural clay samples with organic ions adsorbed, under conditions of an inert atmosphere.
4. Analyses performed on natural clay samples with organic ions adsorbed and then treated with hydrogen peroxide, under atmospheric conditions.
5. Analyses of a clay sample obtained from the site of the proposed addition to the State Education Building in Albany, New York, under both atmospheric and inert atmospheric conditions.

It is reasoned that a more lucid presentation can be effected by consideration of the samples in accordance with their crystalline structures. Hence, the results, analyses, and discussion thereof, will be discussed in succession under each of the clay mineral family groupings.

B. Kaolinite

The thermal curves resulting from the differential thermal analysis of kaolinite are shown in Figures XIII and XIV. The kaolinite sample was one from Macon, Georgia, and is identified as H4 by the American Petroleum Institute, Project 49.

The thermal curve for the natural sample compares favorably with that obtained by Kerr, Kulp and Hamilton (10) for the same material. The absence of a low temperature endothermic reaction indicates that a negligible amount of water was present on the edges of the clay mineral crystals, which, in turn, suggests good crystallinity in this specimen. The pronounced endothermic peak occurred as anticipated at 600° C, and indicated the destruction of the lattice structure with loss of OH lattice water and the formation of amorphous alumina. The exothermic peak at about 990° C results from the formation of a new phase, probably gamma alumina. The sharpness of this reaction suggests good crystallinity.

The thermal curves for the sample pretreated with piperidine in one case, and methylene blue in the other, show medium size exothermic reactions beginning at about 200° C and ending at about 450 to 500° C in each case. This exothermic reaction is the result of the oxidation of organic ions placed on the sample during pretreatment. The size of these thermal reactions are small in comparison with those obtained from illite and bentonite which will be discussed subsequently. The reason for the relatively small reaction

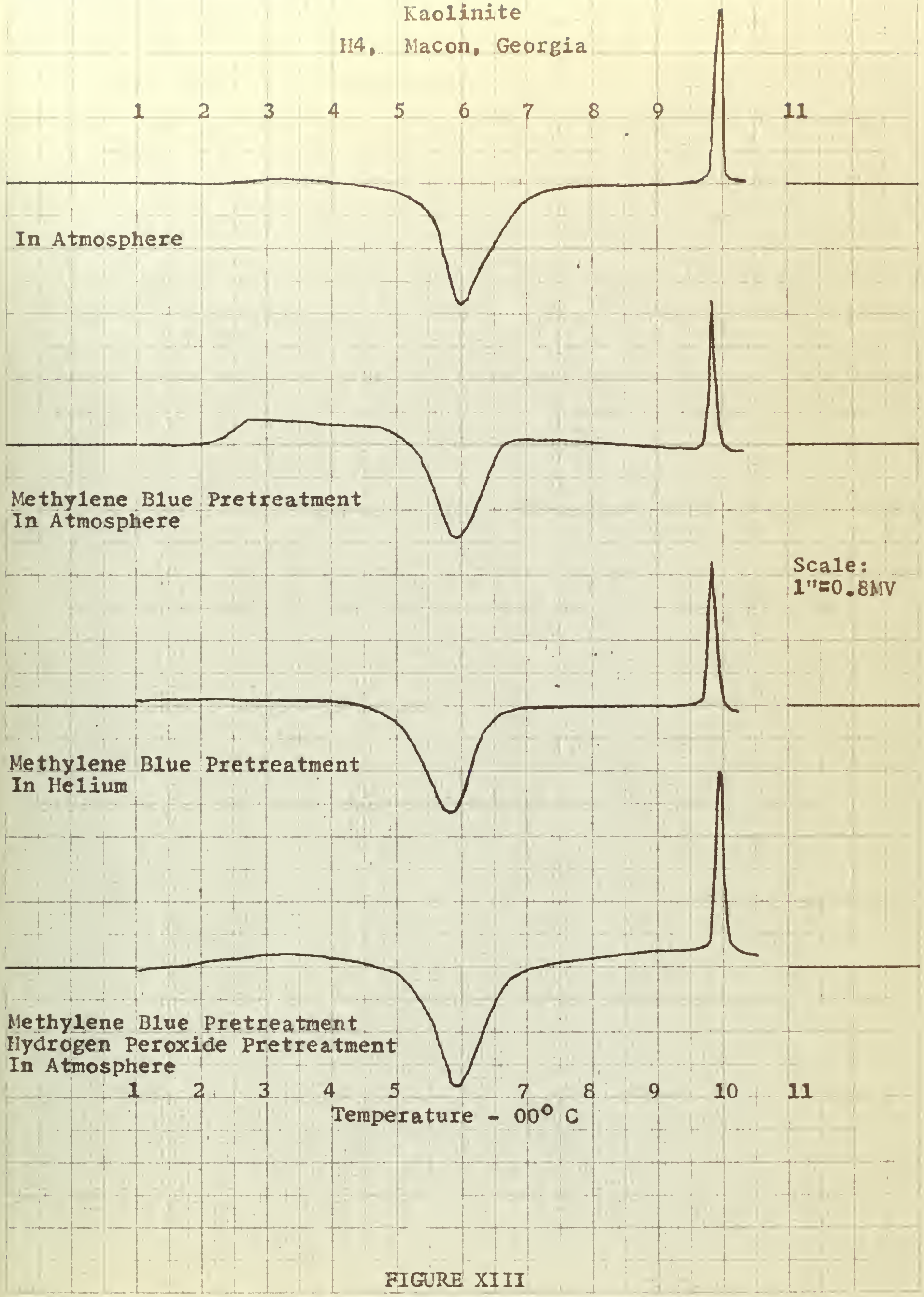

Kaolinite
H4, Macon, Georgia
1 2 3 4 5 6 7 8 9 11
In Atmosphere
Methylene Blue Pretreatment
In Atmosphere
Scale:
1"=0.8MV
Methylene Blue Pretreatment
In Helium
Methylene Blue Pretreatment
Hydrogen Peroxide Pretreatment
In Atmosphere
1 2 3 4 5 7 8 9 10 11
Temperature - 00° C

FIGURE XIII

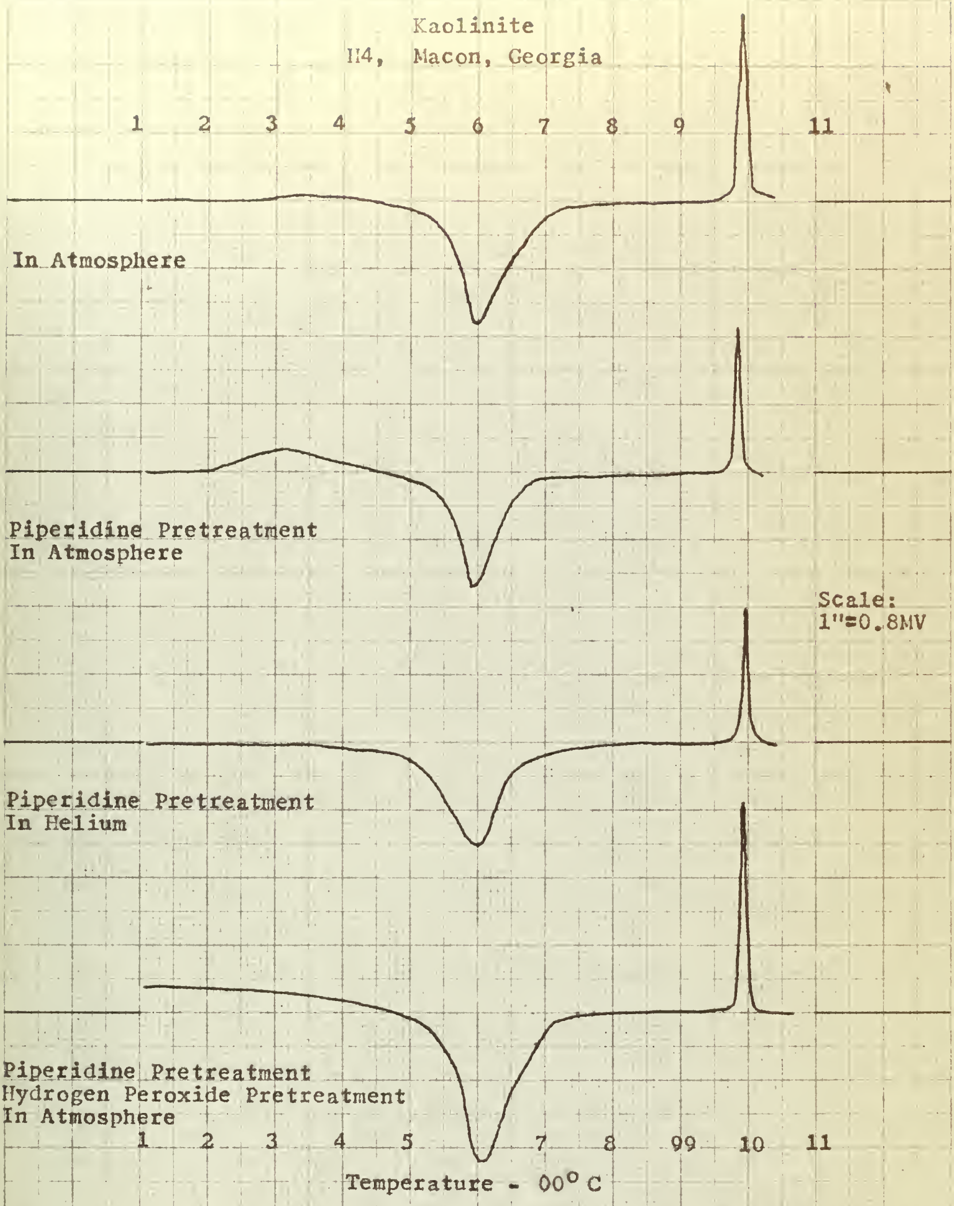

Kaolinite
H4, Macon, Georgia
1
2
3
4
5
6
7
8
9
11
In Atmosphere
Piperidine Pretreatment
In Atmosphere
Scale:
1"=0.8MV
Piperidine Pretreatment
In Helium
Piperidine Pretreatment
Hydrogen Peroxide Pretreatment
In Atmosphere
1
2
3
4
5
7
8
99
10
11
Temperature - 00° C

FIGURE XIV

can be explained by consideration of the small cation exchange capacity of kaolinite, which ranges from 3 to 15 me/100g. The broken bonds on the edges of particles provide the only position for any quantity of organic ions to become adsorbed. Hence, a low adsorption is understandable. Because of the limited exothermic reaction obtained in this case, the mineral appears to be readily identifiable, even with adsorbed organic matter.

The thermal curves for the pretreated samples heated in an inert atmosphere of helium show substantially the same thermal characteristics as those for the natural sample. This demonstrates the effectiveness of an inert atmosphere in suppressing the exothermic reactions due to adsorbed organic ions. The presence of unburned carbonaceous matter in the sample well after firing was noted. A slight reduction of the major endothermic peak was noted. This may be attributed to replacement of some of the OH lattice water by organic ions on the lattice discontinuities due to broken bonds at the edges of particles.

The thermal curves for samples further pretreated by boiling in 15% hydrogen peroxide are substantially the same as those for the natural sample. This indicates that hydrogen peroxide effectively removed the organic ions held on the broken bonds of particle edges. The removal was graphically presented in the case of the sample pretreated with methylene blue. During the boiling process, the sample color changed

gradually from a brilliant royal blue to its natural grey-white as the ions were removed.

C. Montmorillonites

The thermal curves resulting from the differential thermal analysis of montmorillonites are shown on Figures XV through XIX inclusive. The samples used in this investigation were H24 Bentonite, Otay, California; H26 Bentonite, Clay Spur, Wyoming; H28 Bentonite, Little Rock, Arkansas; and D496 Bentonite, Osage, Wyoming.

The thermal curves for natural samples of H24, H26, and H28 compare favorably with those obtained by Kerr, Kulp and Hamilton (10) for the same materials. The low temperature endothermic peaks are of smaller magnitude, however. This can be explained by consideration of the fact that adsorbed low temperature interlayer water is dependent upon the conditions of temperature and humidity at which the sample was held prior to thermal analysis, as well as the water adsorbing capacity of the clay mineral. The thermal curve for D496 is reasonable and reproducible. All thermal curves of natural samples had three endothermic peaks representing the loss of interlayer water, the loss of OH lattice water and further loss of OH lattice water or lattice rearrangement respectively. High temperature exothermic reactions are manifested at about 1000° C, or a bit lower in the case of sample H28. This reaction is usually associated with the formation of spinel.

Montmorillonite
H24 Bentonite, Otay, California

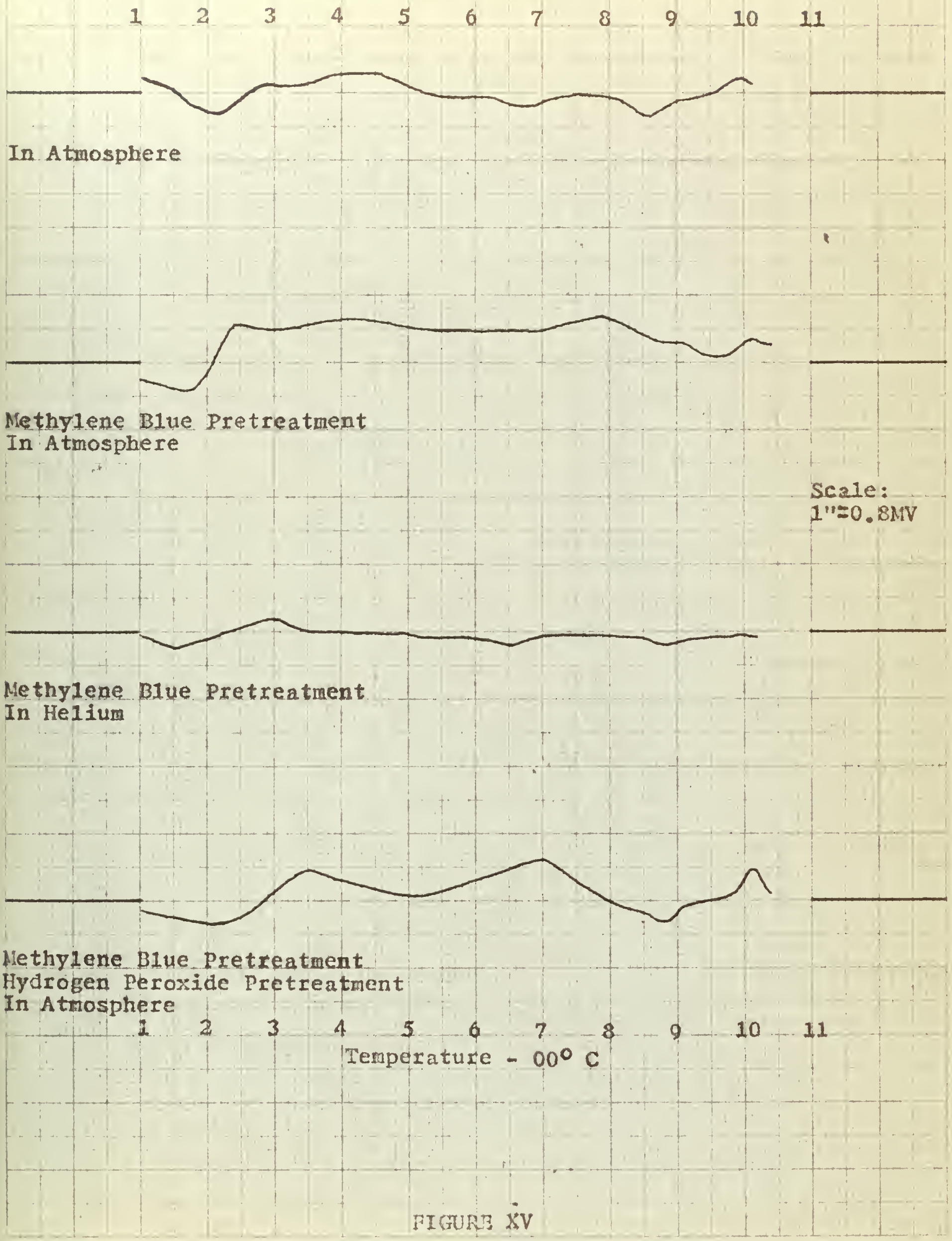
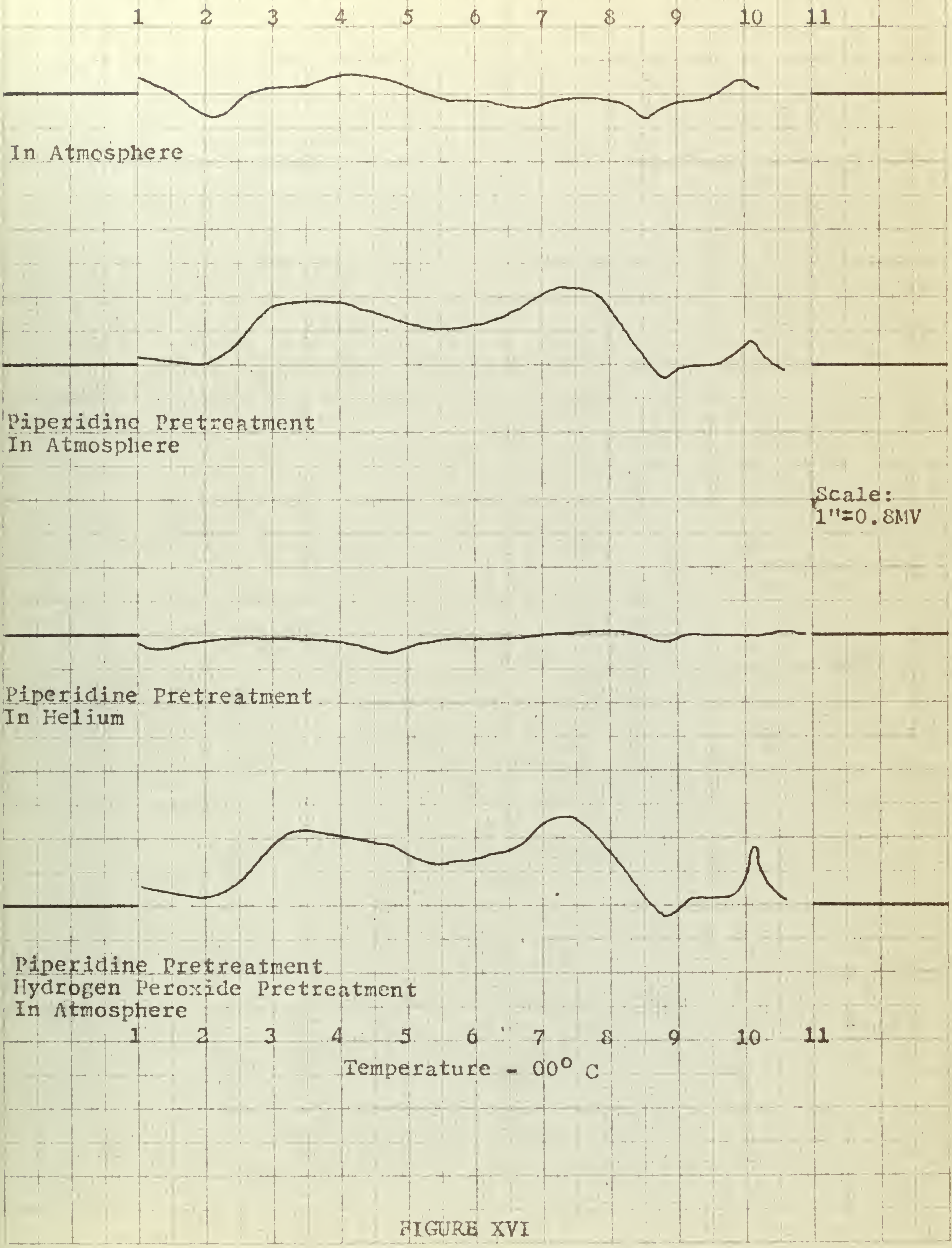


FIGURE XV



Montmorillonite
M24 Bentonite, Otay, California

FIGURE XVI

Montmorillonite
H26 Bentonite, Clay Spur, Wyoming

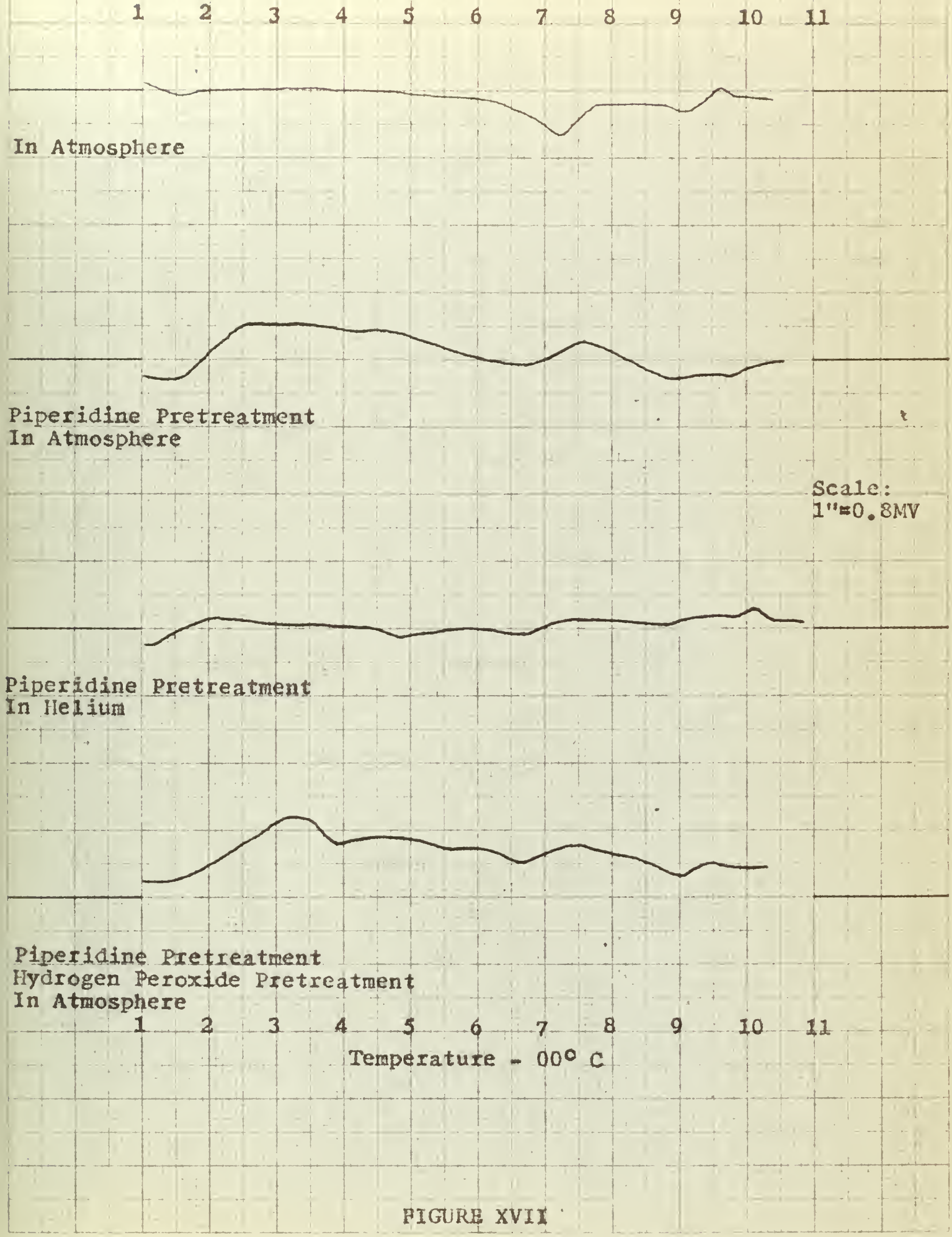


FIGURE XVII

Montmorillonite
H28 Bentonite, Little Rock, Arkansas

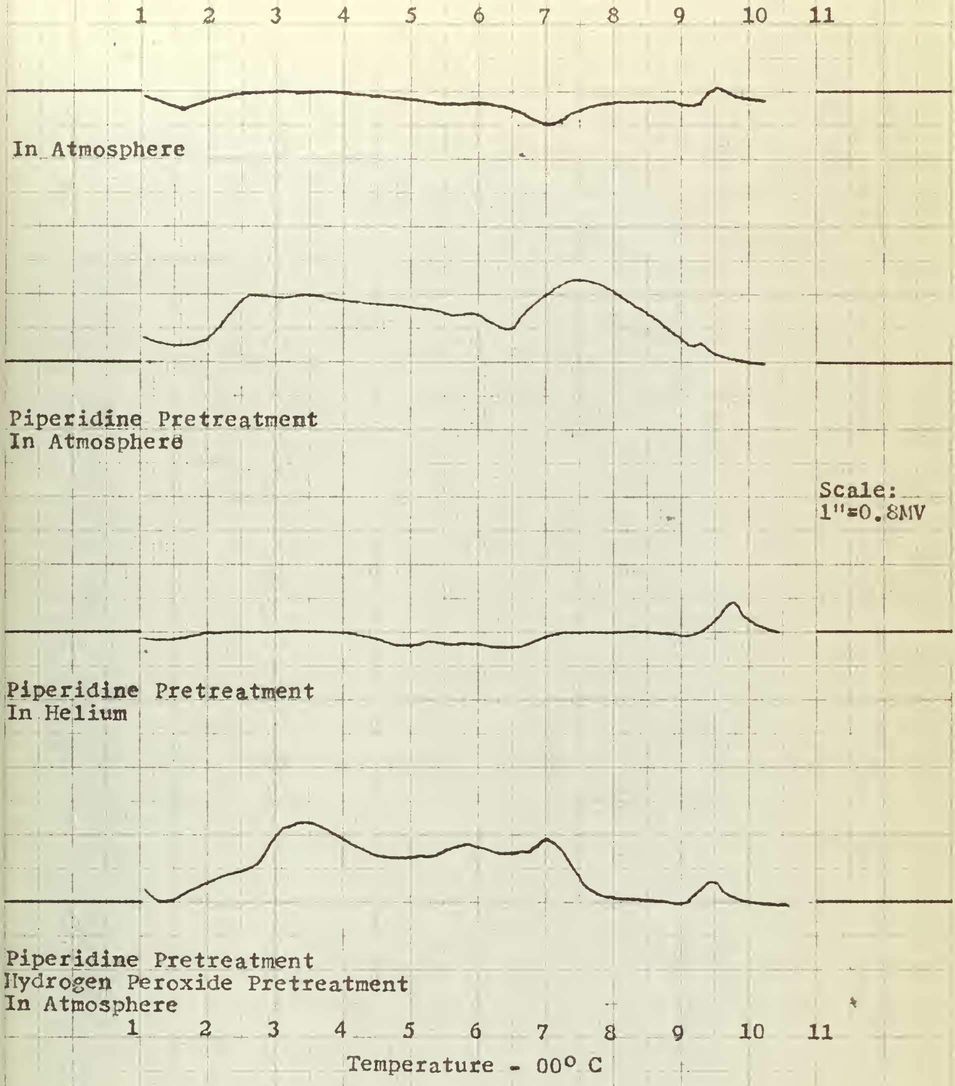


FIGURE XVIII

Montmorillonite
D496 Bentonite, Osage, Wyoming

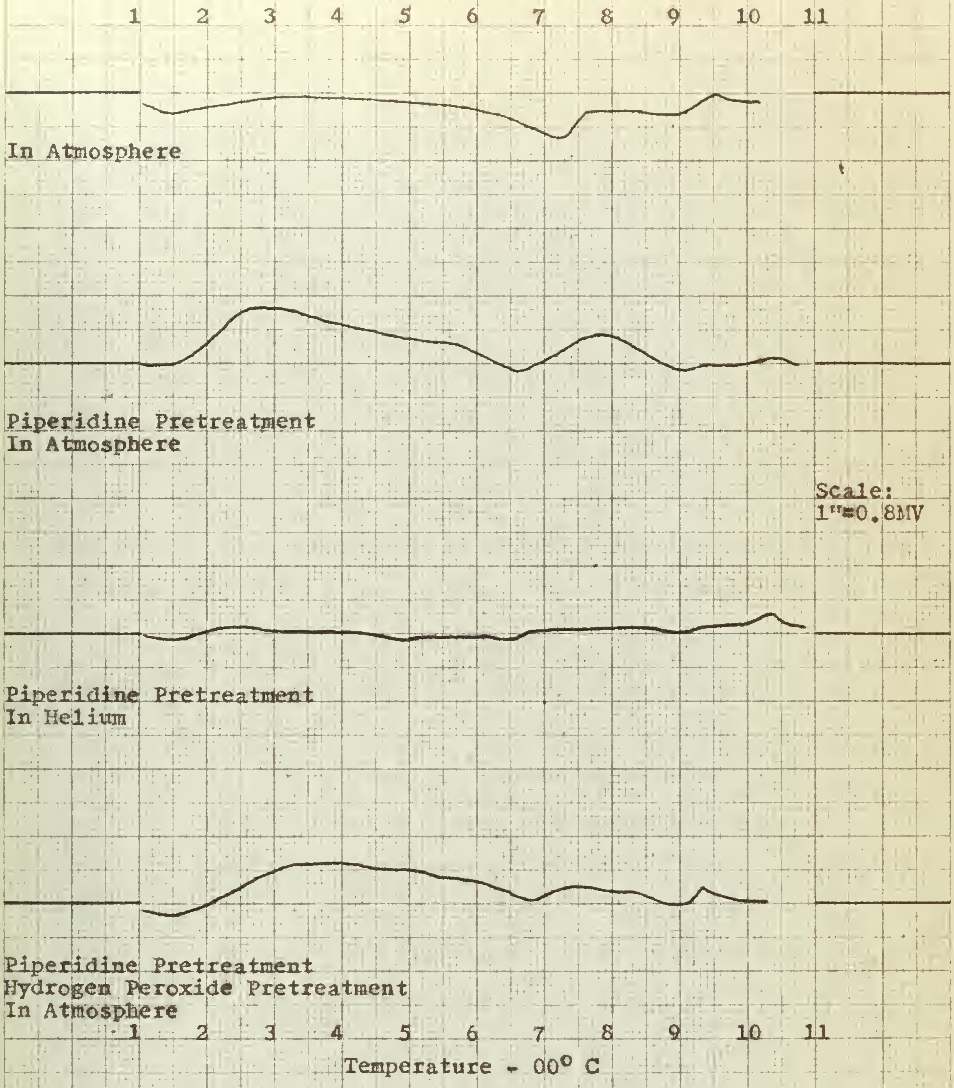


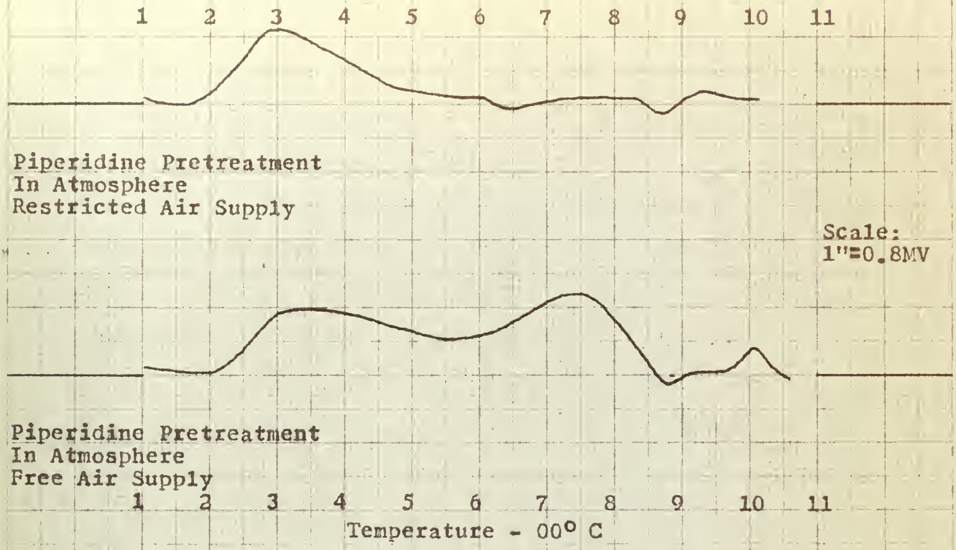
FIGURE XIX

The thermal curves for the samples pretreated with piperidine and methylene blue respectively, show large exothermic reactions in the temperature range from about 200° C to about 800° C. These exothermic reactions result from the oxidation of organic matter. They are large compared to those experienced in kaolinite and illite samples, which is understandable when the relative cation exchange capacities are considered. Hendricks (8) cites a cation exchange capacity for one montmorillonite of 90 me/100g when piperidine is the adsorbed ion. This exchange capacity is large compared to those of illite (under 40 me/100g) and kaolinite (3 to 15 me/100g). The exothermic reactions noted are quite effective in covering up the endothermic reactions necessary for identification of the specimen.

A phenomena worthy of mention was noted quite by accident when the pretreated samples were heated in a normal atmosphere. This phenomena has to do with the availability of air to the sample undergoing thermal analysis. While check runs were being made to obtain reproducible curves, it was noted that in some cases exothermic reactions continued to about 850° C, while in other cases, with the same sample, exothermic reactions were substantially complete at 500° C. Thermal curves for these two conditions are shown in Figure XX. In one case, the high temperature phase-forming exothermic peak was absent. In addition, the final colors after firing were different, one color being the expected light tan, while the other was black. The only apparent significant difference

Montmorillonite
H24 Bentonite, Otay, California

DIFFERENTIAL THERMAL CURVES



INFRA-RED ABSORPTION SPECTRUM

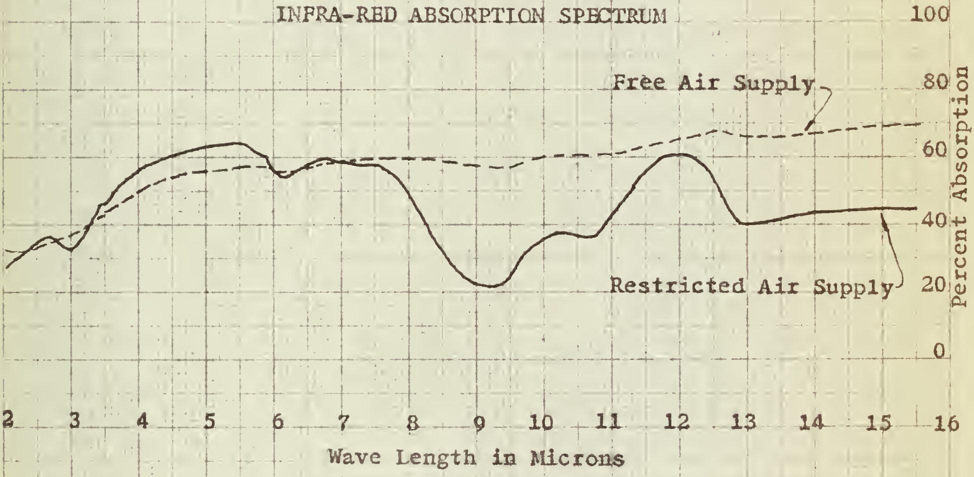


FIGURE XX

in conditions between the two cases was the fact that in furnace No. 1 a relatively free air supply was available in the combustion tube, while in furnaces 2 and 3 the air supply in the combustion tube was restricted because of the stopper in the mouth of the tube. It was reasoned that the black color, present in the analyses made in a restricted air supply, was due to unburned carbonaceous matter which had been released during lattice destruction.

Confirmation of this hypothesis was attempted by running an infra-red absorption spectra on the sample, for each of the conditions, after firing. The infra-red absorption spectra was performed by D. M. Welton, in conjunction with a thesis investigation of infra-red absorption spectra of clay minerals. This thesis is available in the Rensselaer Polytechnic Institute Library. Results of this infra-red spectra are shown in Figure XX. The curve for the specimen run in restricted air is substantially the same as that for the mineral before firing. Irregularities at 3.5 and 7.0 microns wave length indicate the presence of carbon in the sample. From the nature of this curve, it appears that the crystalline structure of the sample has not been destroyed. On the other hand, the absorption spectra for the sample run with free air supply indicates the lattice structure has been completely changed. Hence, the conclusion that in cases of clay minerals with any quantity of organic matter adsorbed, a free air supply is necessary for complete oxidation of organic matter, appears justified.

The thermal curves for the pretreated samples heated in an inert atmosphere demonstrate the efficacy of the inert gas in suppressing the exothermic reactions found when the sample is heated in air. It is noted that the endothermic peaks of the thermal curves in helium are of considerably less magnitude than those experienced in the natural sample. This is reasonable when it is considered that the adsorption of organic ions would tend to reduce the amount of adsorbed interlayer water by satisfying unbalanced charges within the lattice structure and perhaps replacing some of the H ions in the hydroxyls of the gibbsite sheets. The second endothermic peak seems to occur at a slightly lower temperature than is evident in the natural sample. The positions of the third endothermic peaks are not greatly affected. The high temperature phase-forming exothermic peaks are delayed somewhat in all the bentonite samples. An additional endothermic peak was noted at 500° C in samples pretreated with piperidine, although not evident in samples pretreated with methylene blue. It is reasoned that the strength of the piperidine solution, a relatively strong base, may have been sufficient to disturb the lattice structure of the mineral, thereby permitting the release of a portion of the OH lattice water at a lower temperature.

The thermal curves for samples subjected to further pretreatment by boiling in 15% hydrogen peroxide differ greatly from the curves of the natural sample. In all cases, the exothermic reactions are of somewhat less magnitude than

those obtained from analysis of samples pretreated with organic matter and run in air. It appears, therefore, that some of the organic ions, perhaps those adsorbed on the edges and lattice discontinuities, were removed while the bulk of organic matter remained adsorbed on the sample. This observation confirms an opinion expressed by Hendricks (8) that organic ions, especially large ones, are often difficult or impossible to replace. Methylene blue is a source of relatively large organic ions. When sample H24, pretreated with methylene blue was further treated with hydrogen peroxide, it was noted that the blue-black color did not change during boiling, as did the illite and kaolinite samples. Hence, based on observation of color it appeared that methylene blue ions were not removed from the sample by hydrogen peroxide. This, of course, reinforced the data from the thermal curves.

D. Illite

The thermal curves resulting from the differential thermal analysis of illite are shown in Figures XXI and XXII. The illite sample was one from Morris, Illinois, and is identified as H36 by the American Petroleum Institute, Project 49.

The thermal curve for the natural sample compares favorably with that obtained by Kerr, Kulp and Hamilton (10) for the same material. The low temperature endothermic reaction is small in magnitude, however. This is understandable when it is considered that the amount of absorbed low

Illite
H36, Morris, Illinois

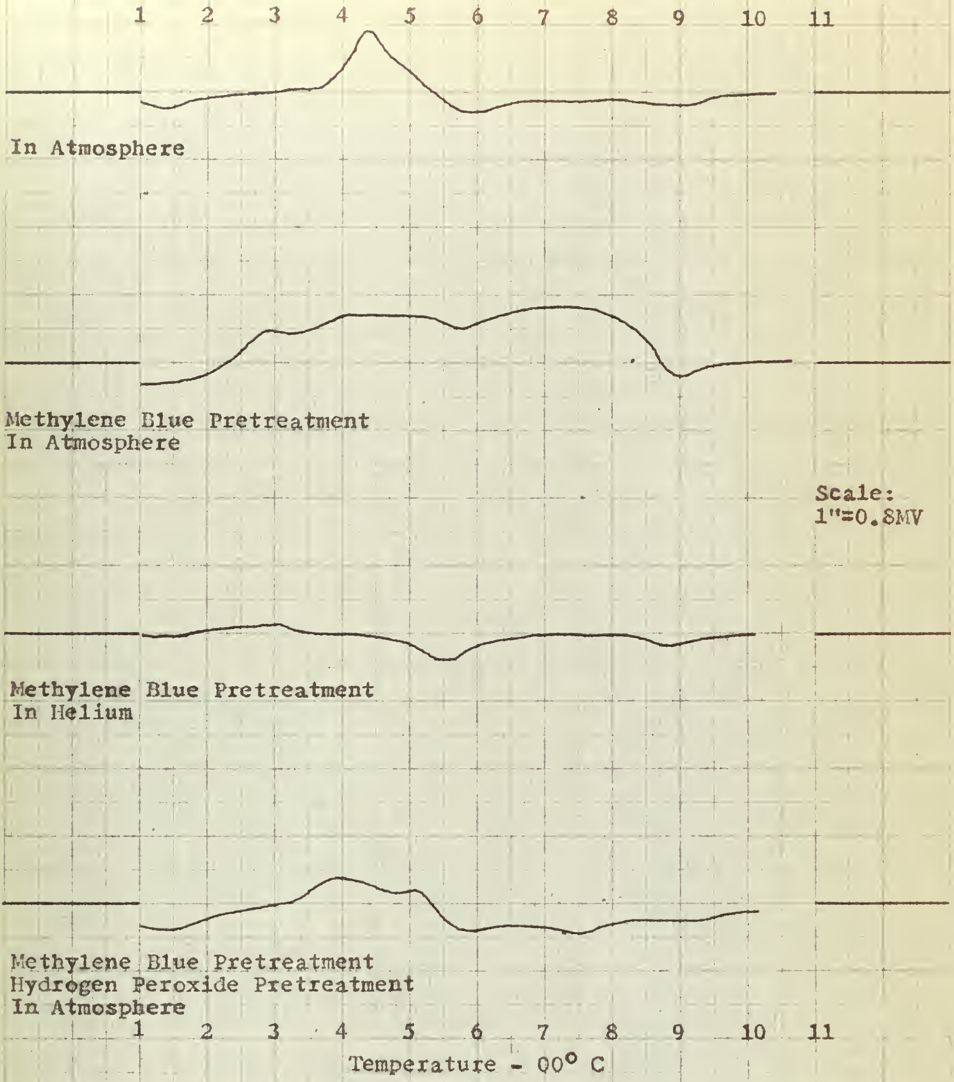
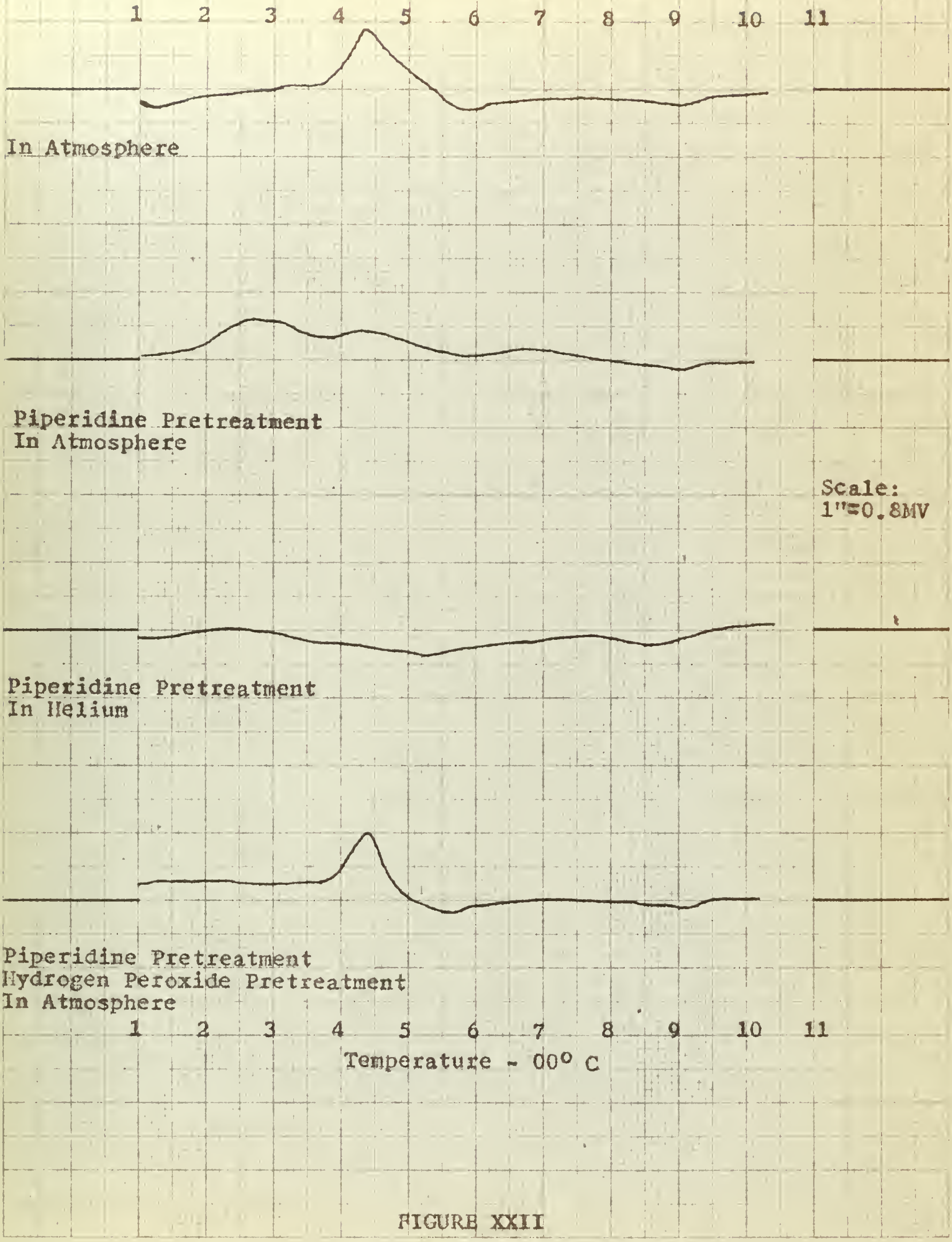


FIGURE XXI



Illite
H36, Morris, Illinois

FIGURE XXII

temperature interlayer water is a function of the temperature and humidity at which the sample was held prior to the thermal analysis, as well as the water adsorbing capacity of the clay mineral. A well defined exothermic reaction, with a peak at about 440° C, was evident on this thermal curve. This reaction may be the result of oxidation of organic matter, or impurities, since it was suppressed when the thermal analysis was made in an inert atmosphere. An endothermic reaction with a peak at about 600° C was observed, and corresponded to a partial loss of crystalline structure and OH lattice water. Another endothermic reaction with a peak at about 900° C signified complete destruction of the lattice and loss of OH lattice water.

The thermal curves for the sample pretreated with piperidine and methylene blue respectively, show exothermic reactions of considerable magnitude in the temperature range of 200° - 800° C. These exothermic reactions, which result from the oxidation of organic matter, effectively mask the reactions necessary for identification of this sample. These exothermic reactions are large compared to those experienced with kaolinite and can be explained on the basis of a larger cation exchange capacity than kaolinite. Three exothermic peaks are evident on the overall exothermic reaction. One depression in the exothermic reaction closely approximates the second endothermic peak of the thermal curve for the natural sample.

The thermal curves for the pretreated samples heated in an inert atmosphere show almost complete suppression of exothermic reactions. Not only was the exothermic reaction due to organic pretreatment suppressed, but, in addition, the exothermic reaction occurring at 440° C in the natural sample was eliminated. It is noted that high temperature endothermic peaks occurred at slightly lower temperatures than corresponding peaks in the natural samples. The true peak of the second endothermic reaction in the natural sample may have been masked as a result of the exothermic reaction in that sample.

The thermal curves for samples subjected to further pretreatment by boiling in 15% hydrogen peroxide indicate reasonably complete removal of organic matter adsorbed as a result of pretreatment with organic ions. It is interesting to note, however, that the organic matter or impurities present in the natural sample were not removed by hydrogen peroxide. The failure of this treatment to remove the organic matter or impurities may be the result of the inaccessibility of these ions in interlayer positions. When the sample pretreated with methylene blue was further treated by boiling with 15% hydrogen peroxide, the color of the sample changed gradually from a deep blue to the greenish color of the natural sample, indicating graphically the removal of adsorbed methylene blue ions.

E. Albany Clay

Differential thermal curves for the sample of Albany clay are shown in Figure XXIII. Two endothermic reaction peaks and one small exothermic reaction peak are evident. Thermal curves for samples run in a helium atmosphere show the same thermal reaction peaks at somewhat reduced temperatures.

The thermal curve obtained for this sample indicates that a large part of the thermally active portion of the sample is a chloritic mica type of clay mineral. The first endothermic peak occurring at about 620° C signifies the loss of OH lattice water and lattice destruction in the brucite layer. The OH lattice water is lost over a range of temperatures in the mica layer, culminating in an endothermic peak at about 815° C with mica lattice destruction and final loss of OH lattice water. The small exothermic peak at about 895° C probably signifies the development of olivine. The dehydration characteristic of chloritic clay minerals was chronicled by Grim (5). Grim also cites the frequent presence of considerable amounts of chloritic mica in glacial sediments, which this sample is believed to be.

This sample was obtained from the site of the proposed addition to the State Education Building in Albany, New York, at a depth of about 25 feet. J. H. Petersen utilized this sample in his thesis analysis of consolidation and permeability characteristics of clays, which is available in the Rensselaer Polytechnic Institute Library. The Bureau

Albany Clay
Albany, New York

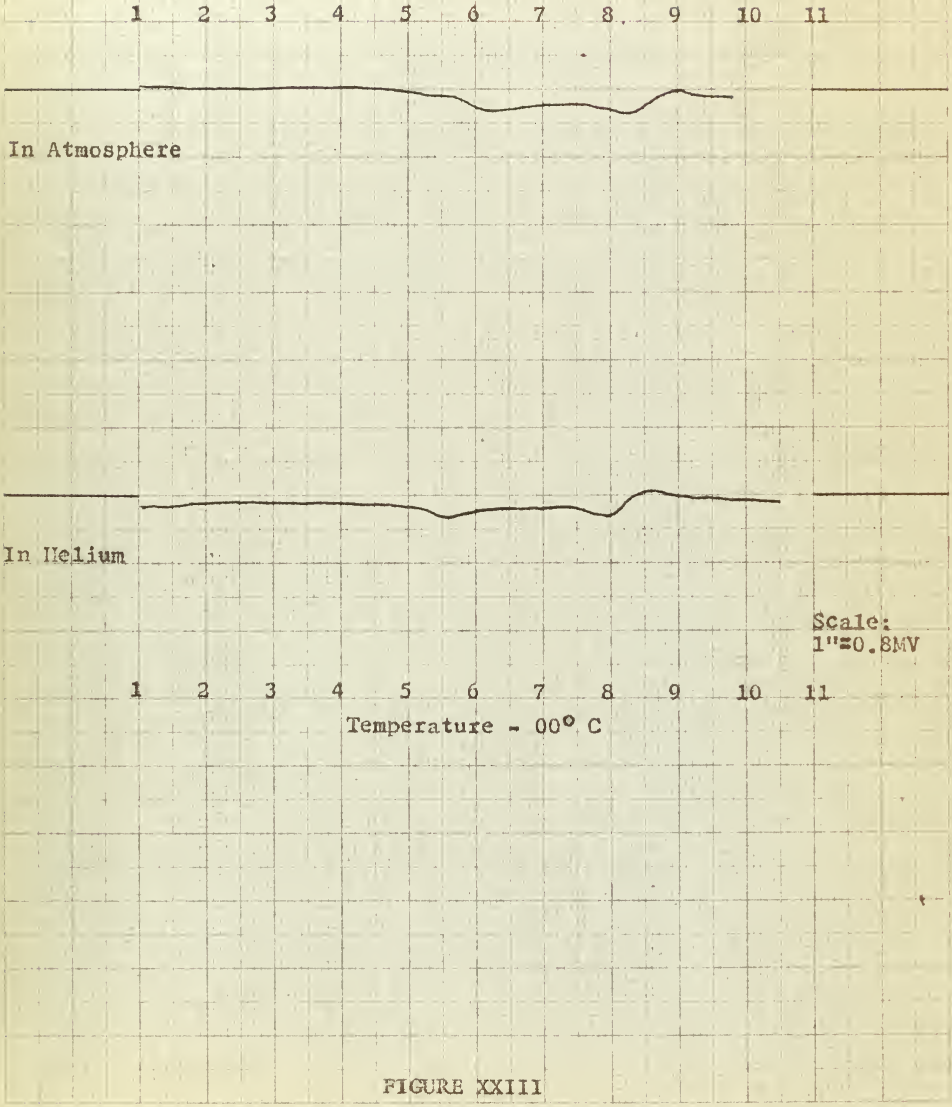


FIGURE XXIII

of Soil Mechanics, New York State Department of Public Works, located in Latham, New York, reports only about 20% clay mineral sizes in this sample, which accounts for the low thermal reactions experienced. It is also reasonable to assume that a portion of the clay sizes are in reality rock flour instead of clay minerals.

The author realizes the danger involved in attempting to make an identification of material of this type on the basis of only one method of analysis. If feasible, several methods should be used, prior to making a firm decision.

PART VI

CONCLUSIONS AND RECOMMENDATIONS

Based on the results of differential thermal analyses conducted, it is felt that the following conclusions can appropriately be made:

1. That the quantity of organic matter which can be adsorbed as ions on a clay mineral lattice is in proportion to the cation exchange capacity of the clay. For this reason, the thermal curves for clay minerals with low cation exchange capacities, such as kaolinites and some illites, may be satisfactory for identification purposes even if the analysis is made in air. This reasoning, of course, cannot be extended to clay minerals in which discrete particles of organic matter are present or in which polar organic molecules are adsorbed.
2. That organic ion complexes adsorbed on the lattice structure of clay minerals with large base exchange capacities, such as montmorillonite, and some illites, can cause exothermic reactions of sufficient magnitude, when the differential thermal analysis is run in air, to obscure the endothermic reactions required for identification purposes.
3. That exothermic reactions due to organic matter are retarded by the lack of a free air supply. This would suggest the possibility of using some

type of air-tight cover on the sample holder if inert gasses were not available. A note of caution should be interjected at this point, however, since it was noted that the high temperature phase-forming exothermic peak was not evident in the temperature range of the analysis. The infra-red absorption spectra for this sample indicated that at least a portion of the lattice structure of montmorillonite had not been destroyed by firing at 1020° C.

4. That the use of an inert atmosphere is a feasible and convenient method for the suppression of exothermic reactions resulting from the oxidation of adsorbed organic matter.

5. That pretreatment of a natural clay sample with hydrogen peroxide to remove adsorbed organic ions is not a dependable process. While it appears that organic ions adsorbed on exposed lattice discontinuities, such condition predominating in kaolinites and illites, can be removed, results show that ions adsorbed between the basal cleavage planes cannot be removed with any degree of efficiency.

6. That when natural clay samples, such as the Albany clay, are subjected to thermal analysis, larger, more easily interpreted reactions might be obtained if the clay size fraction were separated, by mechanical means, from the rest of the sample.

Recommendations for future studies in differential thermal analysis are:

1. Investigation of the use of hydrogen peroxide and acetyl bromide treatment for the removal of organic matter from natural clay samples. Silfverberg (21) has done some work on this method.
2. Investigation of heat pretreatment of natural clay samples for removal of organic matter. This pretreatment ostensibly would be at a temperature below that of lattice destruction. Silfverberg (21) has also done some investigation on this.
3. Investigation of the possibilities of differential thermal analysis as a means of measuring the cation exchange capacities of clay minerals. This measurement might be based on the area under exothermic peaks for an organically pretreated sample as compared to the area for similarly pretreated sample of known cation exchange capacity.

PART VII

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