PRELIMINARY STUDY OF THE EFFECTS OF WATER VAPOR PRESSURE ON THERMOGRAMS OF KAOLINITIC SOILS

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ABSTRACT

Kaolinites found in soils generally give poorer thermograms than commercial kaolins. When run under dynamic steam atmospheres up to 90 psi, the endothermic peaks are sharpened and moved upward; the exotherm is made less intense and moved downward. Because of the effects observed, the method promises to be of interest in theoretical studies of hydrates and hydroxides.

INTRODUCTION

As indicated by the title of the paper, this study is only preliminary and is intended to illustrate the effects of water vapor pressure on the thermograms of kaolinitic soils. No great amount of interpretation is given at this time because the data on the pure components are incomplete and unpublished. The pressure of water vapor has profound effects on the reactions, as shown by the thermograms, but only conjectures are made as to the fundamental interpretation. It is hoped that this preliminary study will serve as a stimulus to others to study the reactions in detail.

FUNDAMENTAL CONSIDERATIONS

The thermogram is a recorded expression of reactions taking place within the test material, hence thermograms of a material at several pressures of a gas give records of the effects of the gas on the inherent reactions.

The reactions responsible for loops in thermograms are of two basic types: (1) those not involving a gas, e.g., the alpha-to-beta quartz inversion, and (2) those involving a gas, e.g., the decomposition of calcite or of kaolinite. In the first of these types, the pressure of the gas has no appreciable effect. (The effect is very real, of course, but is only a fraction of a degree per atmosphere, hence is not likely to be detected by thermal methods.) The decomposition-type reactions are the more common ones in D.T.A. work; hence the pressure (concentration) of the active or de-composition-product gas is of great importance. The effect of presence of a nonparticipating gas on such reactions is merely to slow down the rate of reaction because the gaseous particles reduce the number of contacts per second of the participating components by literally getting in the way.

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The pressure of the participating gas affects the reaction equilibrium temperature according to the Clausius-Clapeyron and van't Hoff equations. The applicability of these equations to the thermal decomposition of the clay minerals has been reviewed in detail by Stone (1951). Summarily, the plot of the logarithm of the pressure of the participating gas vs. the reciprocal of the equilibrium temperature in degrees absolute is a straight line (called the van't Hoff line), and the slope of the line (except when the slope equals infinity) is a function of the heat of the reaction. When the slope of this line is infinity, the reaction is nonreversible, but when the slope is other than infinity or zero, the reaction is reversible.

Three features of an endothermic loop on a thermogram have significant meaning.[1] These are: (1) the slope of the down side, (2) the slope, or steepness, on the return-to-zero side, and (3) the spread (in degrees) which is a result of (1) and (2). The usual interpretation given when the spread for a major reaction is narrow is simply that the reaction proceeds rapidly; and, if the spread is broad, that the reaction proceeds slowly. Kerr (1949), in his A.P.I. Reports on clay minerals, frequently suggests that a gradual slope on the down side is due to a wide distribution in crystal size; however, this explanation is rather superficial.

A more fundamental explanation is given by the Boltzmann distribution law which is:

$$\frac{n_2}{n_1} = Ae^{-\frac{\Delta E}{RT}}$$

where n_2 is the number of particles (or bonds) having energy E_2, and n_1 is the number of particles (or bonds) of energy E_1. A is a constant, R is the gas constant, and T is the absolute temperature. The statistical value of the energy of a bond is an average value of all the like bonds, or of a single bond over an extended period of time. Of a thousand such bonds, at any instant, some are smaller than this value and others are larger; some may be near the breaking point and others are very far from it. At the next instant, the distribution of individuals will be different, but the average will remain the same. Since temperature increases the vibration and modifies other factors affecting bonds, there will be a temperature which first penetrates the distribution curve where the momentarily weakest bond reaches its activation energy, and the reaction will proceed. However, this does not change the shape of the distribution curve, so that in the next instant another bond is ready for reaction. As the total number of bonds, n_1, is thus decreased, the number of activated bonds, n_2, per second is decreased; hence, the reaction slows down and eventually seems to stop. An increase in temperature moves the point further into the energy distribution curve so that there are more activated bonds per second and the reaction proceeds faster. Hence, the shape of the distribution curve affects the rate of reaction vs. temperature behavior, and, consequently,

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[1] A doublet or impure endotherm is not considered here.

the shape or contour of the thermogram; a broad distribution curve will give a broad loop and a narrow distribution curve will give a narrow loop. Also a symmetrical distribution curve will give a nearly symmetrical loop and an asymmetrical distribution curve will give an asymmetrical loop. In general, a poorly crystalline material will give an asymmetrical loop whereas a perfectly crystalline sample of the same material will give a more symmetrical loop.

TEST SAMPLES

Three kaolinite-containing soils from North Carolina were chosen for this report because they show three degrees of crystallinity of the kaolinite and varied types of associated minerals. By using these three mixed-mineral soils it is possible to illustrate in a relative way the effects of water vapor pressure on several soil minerals. Pure monomineralic materials, of course, would be necessary to show with exactness the effects of water vapor pressure on each mineral.

The three soils chosen are: (1) a gouge clay from the pyrophyllite deposit near Stem, Granville County, N. C.; (2) the colloid from the Davidson soil, Lynwood, N. C.; and (3) the colloid from the Mayodan soil, Stokes County, N. C. The gouge clay represents a soil containing rather well crystallized kaolinite, and small amounts of illite, a montmorillonitic mineral, and quartz; the Davidson soil contains mainly halloysitic material with a small amount of a 14A mineral and no quartz; and the Mayodan soil contains very poorly crystalline kaolinite, plus appreciable amounts of illite and quartz. All three soils are high in ferric iron minerals; the gouge clay contains both lepidocrocite and goethite, the Davidson contains lepidocrocite and hematite, and evidence indicates the Mayodan contains lepidocrocite only. The estimation of the ferric iron minerals is based upon the raw color plus the shape of the thermogram in the region of 300° to 350°C.

The Davidson sample was furnished through the courtesy of J. F. Lutz (1934) and the other two samples were collected by the author.

PROCEDURE AND APPARATUS

None of the samples were treated with chemicals. All were centrifuged in distilled water.

All x-ray patterns[1] were obtained with the Norelco wide-angle spectrometer. Specimens were prepared by sedimenting on glass slides and drying at 60°C. Filtered copper radiation was employed.

The differential thermal analysis procedure and apparatus used in this study represent an advanced state of development and hence are described in some detail. Stone (1951) was the first to describe the technique of employing variable pressures of dynamic gases having controlled compo-

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[1] The x-ray patterns were made by Dr. E. J. Weiss of the Department of Ceramic Engineering.

sition wherein partial pressures of the active or participation gases up to one atmosphere were employed. The apparatus was redesigned and the pressure range extended to six atmospheres or 90 psi.

The first report on the redesigned unit was given by Stone (1954) on the decomposition behavior of magnesite where pressures of CO_2 were varied from a fraction of a millimeter of mercury to 90 psi. The same basic machine was used in the present study, the only revision being the addition of a steam generator. A photograph of the unit (except for the recorders) is given in Plate 1. The black dome-shaped container on the left is the pressure chamber and in it are housed the furnace and sample-holder components. The panel on the right contains the preheater and furnace heating-rate controllers. The white cylindrical shapes in the back are the steam generator and superheater.

In the dynamic gas system of D.T.A., two cavities are employed in the sample holder as in the usual method: one is the standard alumina and the other is the test material. The sample holder is connected by special tubing to the source of the specified dynamic gas so that the gas can be bled through the standard and test powders at the desired rate. In practice it is found that the maximum rate is such that the gas within the powders is changed completely at least twice per second. It is thereby possible continuously to sweep out a gas being evolved during a reaction and replace it with a gas of known composition.
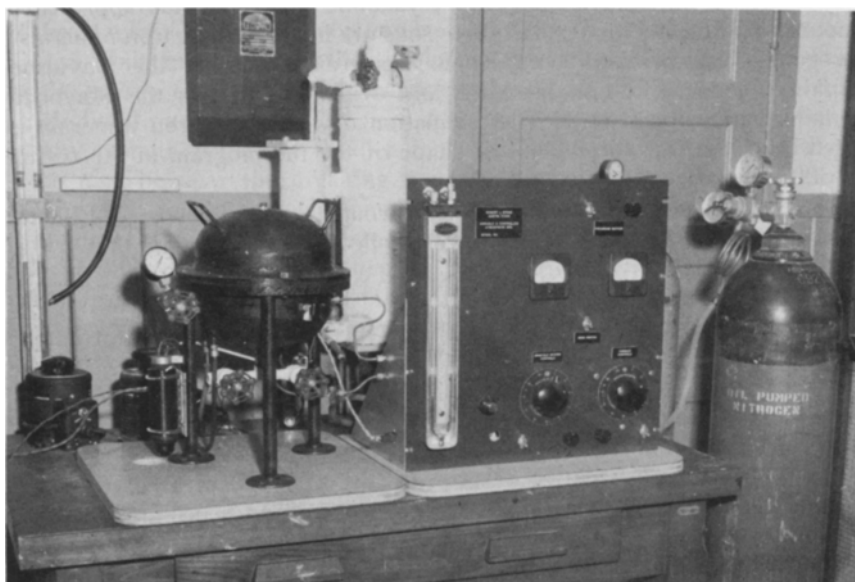

PLATE 1. — Photograph of the variable pressure and controlled atmosphere DTA apparatus employing the dynamic gas system.

The dynamic gas system makes possible the control of steam (water vapor) atmospheres by using two gases. The pressure (for example, 3 atmospheres) of the system is created by using nitrogen in the pressure chamber. Water vapor as the dynamic gas then is forced through the powders in the cavities at a pressure just slightly greater than 3 atmospheres. About twenty cubic centimeters per minute of water vapor is used. This quantity is so small that condensation does not occur within the pressure chamber; therefore, the pressure chamber does not need to be kept above room temperature.

Three pressures were used: (a) vacuum at an absolute pressure of approximately 1.0 psi.; (b) one atmosphere; and (c) three atmospheres. In the vacuum runs, oil-pumped nitrogen was used as the dynamic gas, thus reducing the water vapor concentration to a very low figure of the order of 0.001 mm of Hg equivalent. At one atmosphere and three atmospheres, the runs were started with dynamic nitrogen and then changed to dynamic water vapor at 220°C.

RESULTS

The thermograms, along with the respective x-ray patterns, are shown in Figures 1, 2, and 3. Each figure includes three thermograms, one for each pressure employed.

There are five features of the thermograms of each figure to be discussed with respect to the effect of an increasing pressure of water vapor: (a) the temperatures of the endotherms (the starting peak, and return-to-zero temperatures) are moved upward, (b) the return-to-zero side of the endotherms steepens as the pressure is increased from vacuum to one atmosphere of water vapor, (c) the intensity of the endotherms decreases, (d) the temperature of the exotherms decreases, and (e) the intensity of the exotherms decreases.

The 600° endothermic reactions of the clay minerals involve loss of water as hydroxyls; for this reason one would expect an increase of water vapor pressure to raise the decomposition temperature as indicated by the beginning of the endotherm. With monomineralic materials the beginning temperature of the endotherm is very important and diagnostic for this reason, but in mineral mixtures where two or more endotherms overlap almost completely, it is impractical to use the beginning temperature as a diagnostic feature for mineral identification. In such cases the shape of the endotherm, particularly that of the shoulders, becomes important. It is very improbable that there exist two minerals in nature whose endotherms occur at the same temperature and are affected to the same degree per unit pressure; therefore, for a mixture of two minerals whose endotherms coincide indistinguishably at one atmosphere, the effect of making the run under vacuum or at three atmospheres is to separate the reactions producing a predominant endotherm with a shoulder.

For all of the kaolinitic materials in this study the runs made under vacuum have endotherms that are broad and peak at 515° to 525°C. Under one atmosphere water vapor pressure, they peak at 595° to 600°C.

The return-to-zero side of the endotherm of the kaolinitic gouge clay becomes steeper as the pressure is increased, whereas the return side of
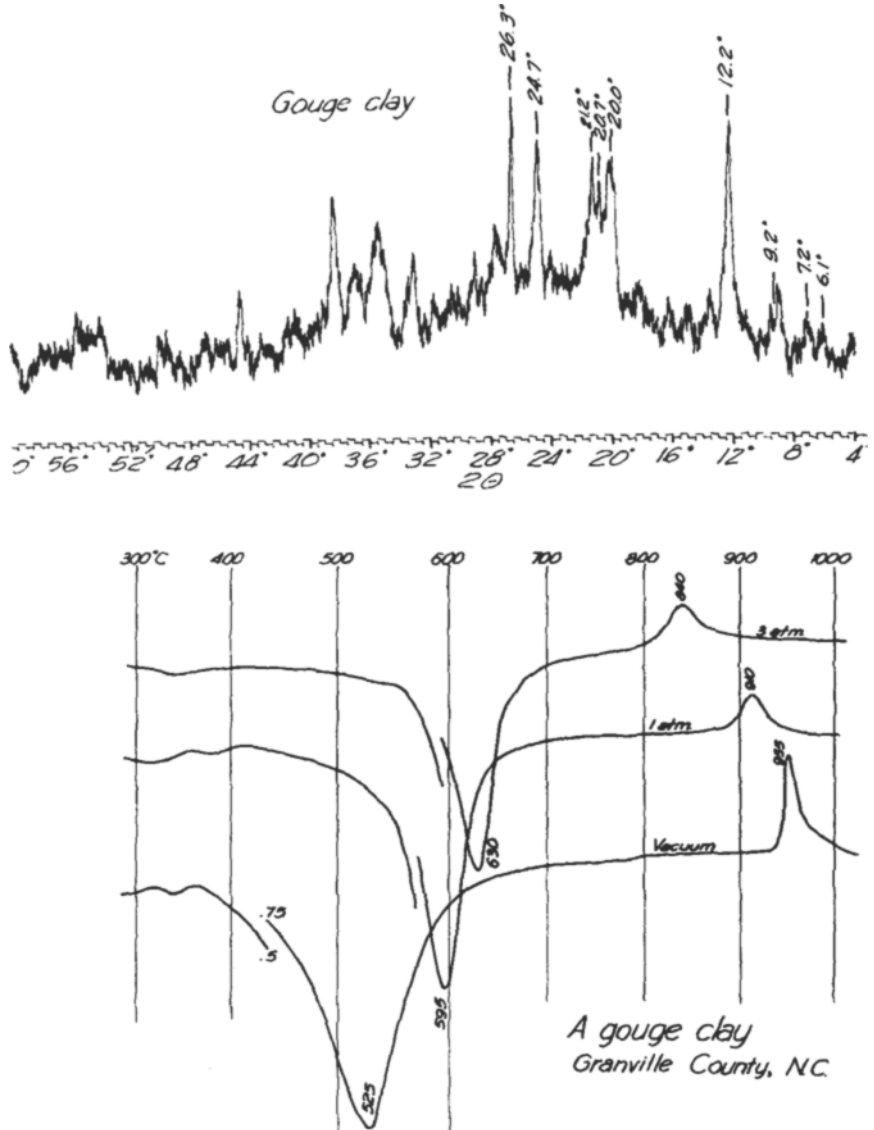

FIGURE 1. — X-ray pattern and thermograms of the gouge clay.

the Mayodan endotherm does not become steeper. This is because of the illite in the Mayodan soil which keeps the endotherms in the shape of a "V". The endotherm of the Davidson soil is steep even under vacuum; this is characteristic of halloysite.

Both the temperature and the intensity of the exotherm on all three clays were decreased. For example, the exotherm of the gouge clay peaked
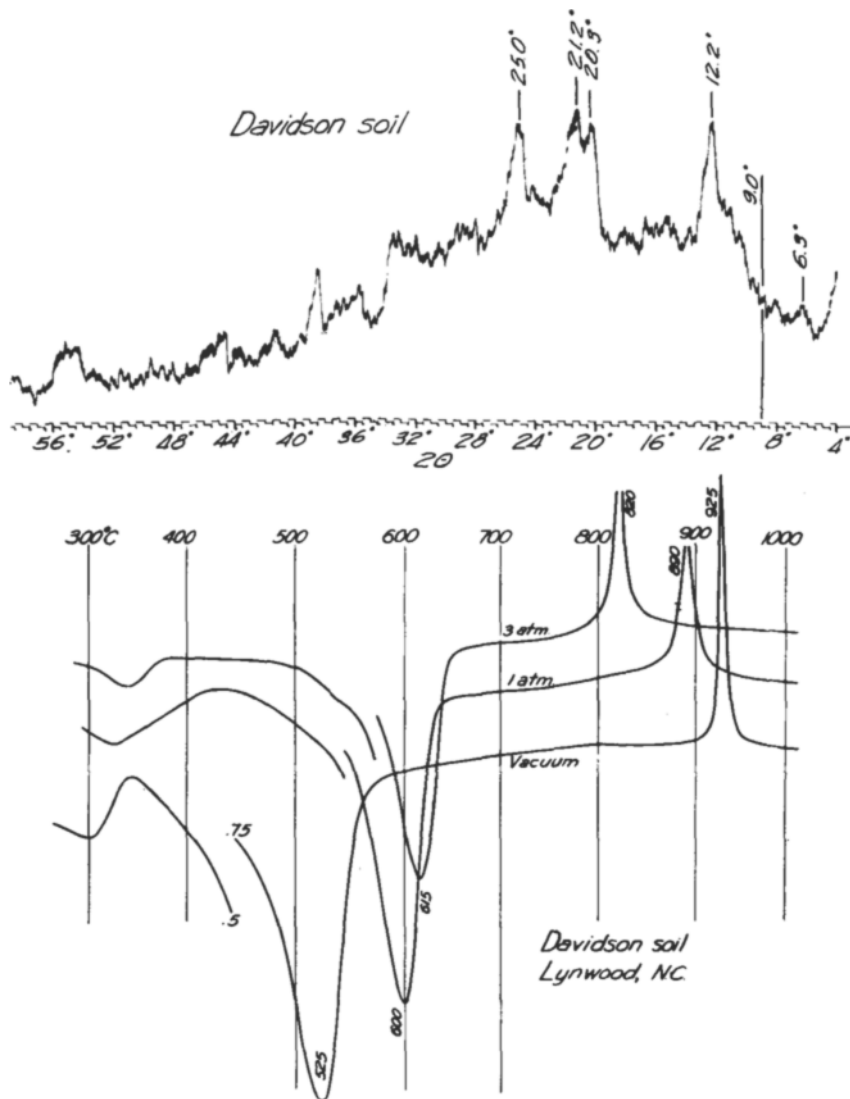

FIGURE 2. — X-ray pattern and thermograms of the Davidson soil colloid.

at 955°C in vacuum and at 840°C in three atmospheres water vapor; for the Davidson soil the corresponding temperature drop was from 925°C to 820°C.
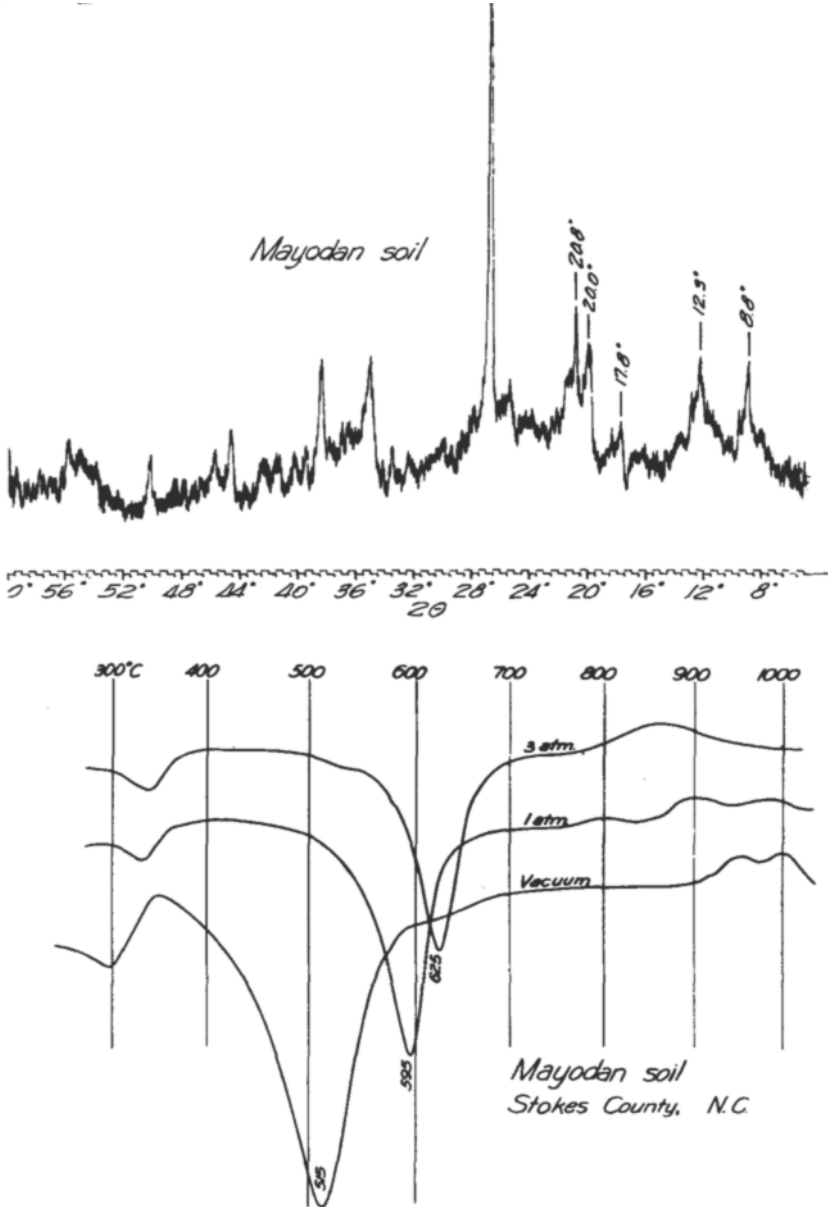

Figure 3. — X-ray pattern and thermograms of the Mayodan soil colloid.

The exotherm peak temperatures in all cases are low compared with high-grade kaolinitic materials such as those used for standards. The exotherm is profoundly affected by associated minerals, particularly iron-bearing and alkali-bearing minerals, which decrease both the intensity and temperature. The lowering effect caused by the water vapor is probably of the same type.

For comparison of the thermograms of Figures 1, 2, and 3 with a standard material, the following values are given for a Huber, Georgia, kaolinite under one atmosphere water vapor pressure: beginning of the endotherm, 470°C; peak of the endotherm, 620°C; beginning of the exotherm, 930°C; and peak of the exotherm, 965°C. All of these points are well defined for the monomineralic material.

CONCLUSIONS

The following conclusions are based on the results reported herein:

1. The principal endotherm of a kaolinitic-type clay soil peaks at approximately 525°C when run in a vacuum, and its peak temperature is raised to approximately 625°C when run under three atmospheres pressure of dynamic water vapor.

2. The principal exotherm of a kaolinitic-type clay soil peaks at approximately 950°C when run in a vacuum, and its peak temperature is lowered to approximately 830°C when run under three atmospheres pressure of dynamic water vapor.

3. The return-to-zero temperature of the principal endotherm of kaolinitic-type soils is not raised by increasing water vapor pressure to the same degree as is the beginning temperature.

4. The intensity of the exotherm of kaolinitic-type soils is decreased markedly by increasing the water vapor pressure.

ACKNOWLEDGMENT

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