THERMAL, DEHYDRATION, AND X-RAY STUDIES ON MONTMORILLONITE

J. W. EARLEY, I. H. MILNE, and W. J. McVEAGH,
Gulf Research & Development Company, Pittsburgh, Pennsylvania.

ABSTRACT

The thermal reactions, water loss and changes in crystal structure have been investigated between 500° C. and 950° C. for five montmorillonite samples with varying chemical composition.

The water loss during the first high temperature endotherm accounts for the water proposed by the Hofmann-Endell-Wilm structure. This reaction involves changes in the spacings of the x-ray diffraction lines which probably reflect symmetry differences. There is some additional water loss between the first and second high temperature endotherms with a gradual change in the spacings of the x-ray diffraction lines but no loss in the intensity of the pattern. Crystal water is essentially completely removed by the end of the second high temperature endotherm. Water loss during this endotherm may well contribute to the thermal reaction but cannot account for it. During the endotherm the intensity of the x-ray powder pattern decreases rapidly indicating breakdown of the crystal structure and the formation of a disordered state which results in an increase in entropy. Thermodynamically the effect of increased entropy can be expressed by the general equation of the third law, $dS = dq(rev.)/T$, where S is entropy; T, temperature; and dq (*rev.*) heat absorbed. Thus dq increases with S and manifests itself as an endothermal reaction in the second high temperature endotherm. The exothermic reaction which follows is attributed to the formation of spinel or enstatite and partial return to an ordered state.

INTRODUCTION

The relationship between the thermal reactions of montmorillonite during differential thermal analysis and the physical and chemical changes which take place simultaneously in the sample has occupied the attention of many investigators. Some of these reactions are well understood but certain phenomena connected with the high temperature reactions remain controversial. Several theories have been proposed to account for the high temperature reactions in montmorillonite but in the opinion of the authors none have been adequately proven.

It is generally accepted that the endothermic reactions which occur between 100 and 250° C. are due to the loss of interlayer and adsorbed water and that their configuration is influenced greatly by the exchangeable cation. Nutting (1) and Page (2) have shown that the endotherm at 650–750° C. is associated with a further loss of water which accounts for most of the water remaining after loss of the low temperature types and must, therefore, be derived from the hydroxyl groups in the octahedral layer, assuming the crystal structure proposed by Hofmann-Endell-Wilm (3). Evidence has been presented by Page (2) that a small amount of water is lost beyond the 650–725° C. endotherm in some mont-

morillonites. It has been suggested that this water loss is indicated by the second high temperature endotherm (4) at 800–890° C. Various theories have been proposed to account for the presence of additional water: McConnell (4) has proposed to account for this water as discrete $(OH)_4$ groups in the tetrahedral layers; Edelman and Favejee (5) have suggested the substitution of hydroxyl groups for oxygen in the tetrahedral layer; Page (2) has suggested a relationship between this water and the high magnesium content of some montmorillonites.

The present studies have been undertaken in order to obtain a more precise explanation of the high temperature thermal reactions of montmorillonite in terms of accompanying changes in crystal structure and water losses. Experimental work has been carried out on five montmorillonite samples from Clay Spur, Wyoming; Belle Fourche, South Dakota; Little Rock, Arkansas; Plymouth, Utah; and Otay, California. These samples, which have been described by Earley, et al. (6) were sodium saturated and separated into particle size fractions by centrifugation. Fractions with particle size less than 300 mμ in equivalent spherical diameter, as calculated by Hauser's (7) modification of Stoke's law were used in each case.

APPARATUS

Differential thermal analysis studies were carried out using the equipment described by McConnell and Earley (8). The samples were dried at 65° C., ground to about 200-mesh and packed in the sample holder with a tamping action (8).
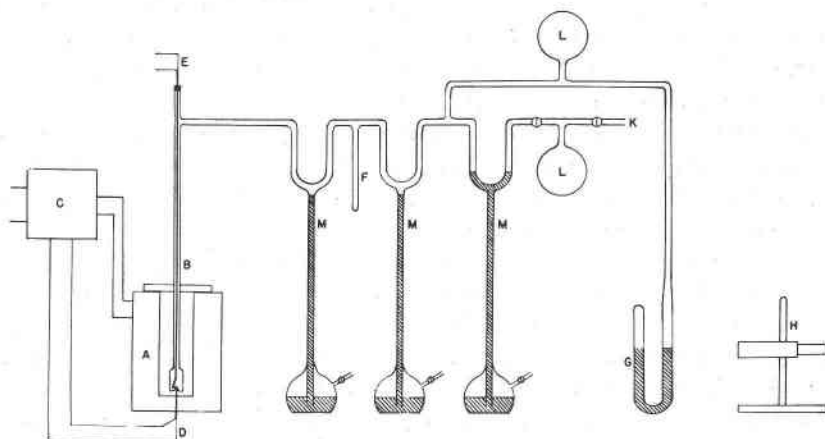

FIG. 1. Dehydration apparatus. A—Furnace, B—Reactor tube, C—Controller, D—Control thermocouple, E—Inside thermocouple, F—Freeze-out Trap, G—Mercury manometer, H—Cathetometer, K—Connection to vacuum pump, L—Reservoirs, M—Mercury traps.

X-ray powder diffraction photographs of the montmorillonite samples were obtained with Debye Scherrer type cameras of radius $180/\pi$ mm.

Dehydration studies were carried out by measuring the vapor pressure of water developed during heating of the sample in an evacuated system which is illustrated in Fig. 1. The clay sample is placed in a silica glass reactor tube which is connected to the pressure apparatus through a ground glass joint. The pressure apparatus is equipped with a freeze-out trap which permits a reduction of the water vapor pressure to about 0.1 mm. when the trap is surrounded by a mixture of ethyl alcohol and dry ice. Mercury traps are used to isolate the freeze-out trap and to separate a calibrated reservoir from the rest of the system. The traps permit separation of various parts of the system without movement of stopcocks and act as sensitive indicators of leaks which may develop. The system is sealed to a mercury manometer with which the pressure in the system is measured to ± 0.02 mm. by means of a cathetometer. The calibrated reservoir is used to determine the total volume of the pressure system. The temperature of the sample in the reactor is measured by a thermocouple which extends from the bottom of the surrounding furnace into a recess in the base of the reactor tube. A second thermocouple inserted inside the reactor tube and touching the sample was found necessary in certain experiments to record sample temperatures more accurately.

Two procedures were used in the dehydration experiments. In the first the sample was heated by a surrounding furnace in suitable increments with the temperature being held at each point by a controller until no further increase in pressure was noted over a twenty-four hour period. During these runs the water vapor pressure over the sample was kept as near to zero as possible by means of a freeze-out; during measurement of the pressure in the system the sample was closed off from the rest of the apparatus by a mercury trap. The attainment of equilibrium at any one temperature and zero pressure required up to five days. In the second method of dehydration study the sample was heated at approximately 10° C. per minute using a model S micromax recorder (0°–1400° C. uniform scale for Pt-Pt 10 per cent Rh), a controller and timer. The sample temperatures were obtained from the inside thermocouple and readings of temperature and cumulative pressures were recorded at one or two minute intervals.

EXPERIMENTAL RESULTS

The five purified montmorillonite samples were analyzed by differential thermal analysis using a recording sensitivity of ± 2.5 microvolts per chart division and a heating rate of 10° C. per minute. The thermal curves shown in Fig. 2 are described by Earley, et al. (6). The materials from
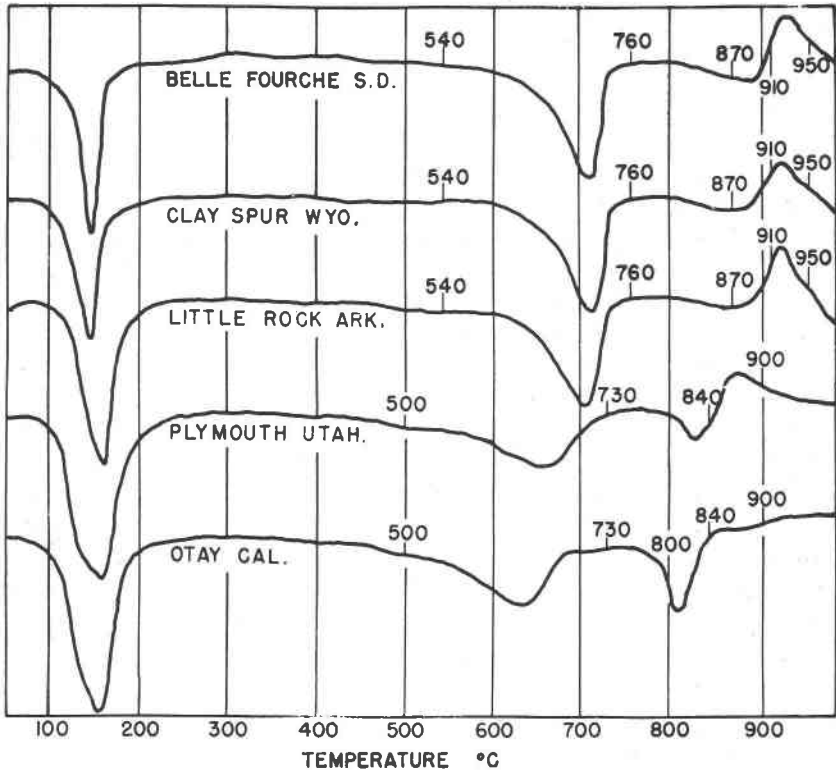
FIG. 2. Differential thermal curves of sodium saturated montmorillonites; Pt/Pt 10% Rh thermocouples.

Belle Fourche, Clay Spur, and Little Rock give very similar results, showing a marked endotherm at 710–715° C., a small broad endotherm at 880–885° C., followed by a pronounced exotherm at 925–930° C. The Plymouth and Otay samples show much lower temperatures for all of their thermal reactions. Both of these materials give well defined second high temperature endotherms at 820–830° C. The Plymouth material gives an exotherm at 870° C. while the Otay sample shows an exothermic drift above 850° C.

To study the changes which take place in montmorillonite during thermal reactions, samples were heated in the *DTA* equipment to the temperatures indicated in Fig. 2 and quenched in an air stream. In this way it was possible to heat a sample to a precise reaction point, stop the reaction, and study the phase or phases by *x*-ray diffraction. The material used for *x*-ray study was carefully taken from the area nearest the thermocouple in order to eliminate the effect of thermal gradients within
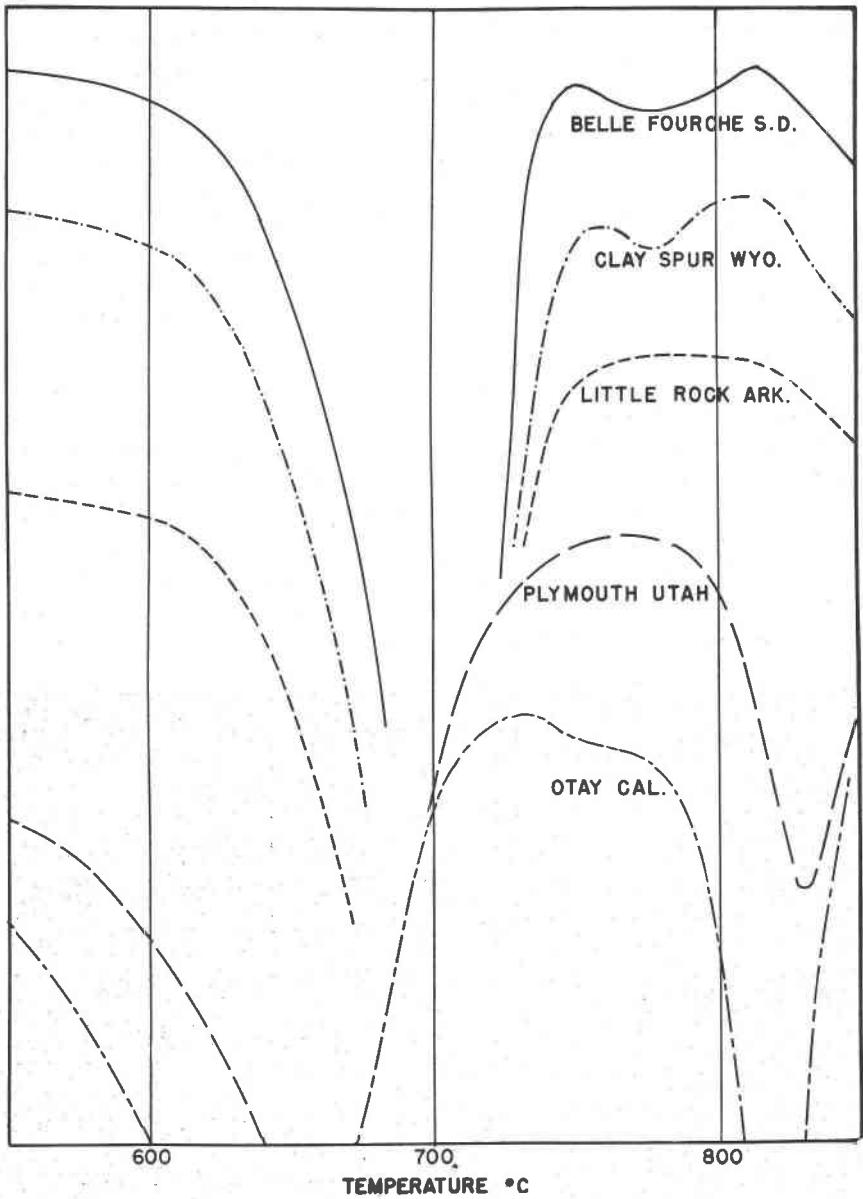
FIG. 3. Portions of differential thermal curves of sodium saturated montmorillonites obtained at maximum sensitivity.

the sample and thus the state of reaction should correspond closely with the recorded thermal state. In addition to these thermal analyses, each of the montmorillonites was thermally analyzed at the maximum sensitivity of the recorder (± 0.25 microvolts per chart division). Portions of these *DTA* curves in the vicinity of the first high temperature endotherm (600–800° C.) are shown in Fig. 3. With this sensitivity this endothermic reaction is off scale in each case, but a minor endotherm is given by the Belle Fourche, Clay Spur, and Otay samples immediately after the first high temperature endotherm; this minor endotherm is not shown by the Little Rock and Plymouth samples. The significance of this reaction will be considered later in this paper in terms of *x*-ray diffraction and dehydration results.

X-ray powder diffraction studies have been carried out on samples heated to the temperatures indicated in Fig. 2. A detailed study of the diffraction photographs has permitted a correlation of structural changes with thermal reactions. The *x*-ray powder diffraction photographs of the Little Rock samples have been reproduced in Fig. 4 and the diffraction data from these photographs are given in Table 1.

From Table 1 it will be seen that at 540° C., before the first high temperature endotherm, the clay appears to be unchanged from its condition at room temperature. It has absorbed some of the organic liquid used as
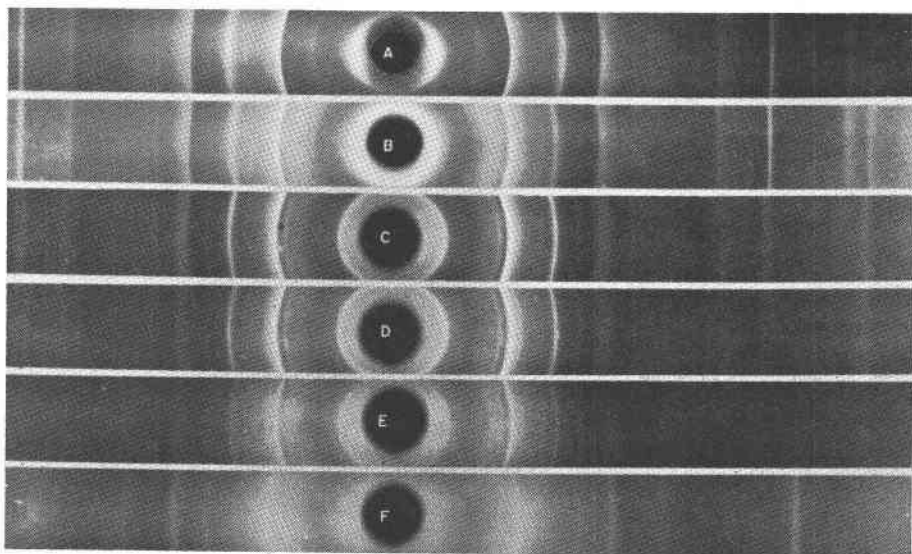

Fig. 4. *X*-ray powder photographs of sodium saturated montmorillonite, Little Rock, Arkansas, after heating in *DTA* equipment. FeKα radiation; camera radius, $180/\pi$ mm. A—Unheated, B—540° C., C—760° C., D—870° C., E—910° C., F—950° C.

TABLE 1. X-RAY DIFFRACTION DATA (FeKα RADIATION) SODIUM SATURATED MONT-
MORILLONITE—LITTLE ROCK, ARKANSAS (<300mμ FRACTION) HEATED
IN DIFFERENTIAL THERMAL ANALYSIS EQUIPMENT

540° C.		760° C.		870° C.		910° C.		950° C.		Interpretation
I	dÅ	I	dÅ	I	dÅ	I	dÅ	I	dÅ	
10b	12.9									(001) Expanded
		6	9.83	7	9.75	7	9.74			(001) Anhyd. mont.
1b	6.55									(002) Expanded
		2	4.86	2	4.79	2	4.79			(002) Anhyd.
7	4.51	10	4.48	10	4.45	10	4.44			(110) (020)
1	4.32									(003) Expanded
								1	4.29	Spinel
1	4.12	1	4.14	1	4.10	2	4.09	10	4.11	Cristobalite
		1	3.73							?
		1	3.56	½b	3.53	1	3.53			Kβ (003) Anhyd.
2	3.25									(004) Expanded
		5	3.23	4	3.23	5	3.23			(003) Anhyd.
		2	2.86	1	2.87	2	2.85			?
				1	2.83					?
								2	2.81	Spinel
2b	2.58	2b	2.59	1	2.57					(130) (200)
								1	2.53	?
		1	2.482	1	2.474					?
						1b	2.459	5b	2.437	Spinel
½	2.245	2	2.242	2	2.232	1	2.222			(220) (040)
								1	2.011	Spinel
				1	1.999	½	1.990			?
		½	1.938	½	1.936					?
½	1.876									(007) Expanded
		½	1.750							?
		1	1.732	1	1.744	1	1.746			?
2	1.700									(240) (310) (150)
		1b	1.681	1	1.685	1	1.677			?
								1b	1.542	Spinel
		1	1.522	1	1.527	½	1.523			?
4	1.503									(330) (060)
		1	1.495	1	1.495					?
						2b	1.414	4b	1.421	Spinel
1b	1.293	1	1.321	1	1.332	2	1.326			(260) (400)
1	1.251	1	1.249	1b	1.262	½	1.258			(350) (170) (420)

a mounting medium in preparation of the specimen to give an expanded
"c" dimension of 12.9 Å. A further test which was carried out showed
that this material also will absorb interlayer water to give a 12.6 Å
basal spacing. At 760° C., past the first high temperature endotherm, the
clay will no longer expand with water or organic liquids and gives a basal

spacing of 9.8 Å. Some structural change has taken place as would be expected with the loss of the hydroxyl groups, such that the (110) (020) diffraction line at 4.50 Å is now reduced to 4.47 Å and other lines of the normal clay pattern are split into doublets and reduced in intensity. Without trying to analyze the precise nature of the structural changes it may be said that the new structure has different "a" and "b" dimensions and probably a different symmetry. This modification of the montmorillonite structure has been referred to by Bradley and Grim (9) as the anhydride phase of montmorillonite. In this paper the anhydride phase will be referred to as anhydrous montmorillonite.

At 870° C. near the minimum of the second endotherm a further change is apparent in the same direction as observed at 760° C. The (110) (020) spacing is further reduced to 4.45 Å and lines already resolved into doublets are spread farther apart. At 910° C. between the second endotherm and the exotherm, anhydrous montmorillonite diffraction lines are still evident but much reduced in intensity and two spinel diffraction lines have appeared. It seems apparent that the decrease in the intensity of the anhydrous montmorillonite diffraction pattern at this point, which reflects a breakdown of the structure, must be related to the second high temperature endotherm. The formation of an amorphous or disordered state from a crystalline one must be accompanied by an increase in the entropy of the sample. According to the third law of thermodynamics, $dS = dq$ (*rev.*)$/T$, where S is entropy; T, temperature, and dq (*rev.*) is reversible heat absorbed, an increase in entropy is accompanied by an absorption of heat. Thus the breakdown of the anhydrous montmorillonite structure can account for the second high temperature endotherm, without the necessity of any accompanying water loss.

In the case of the Little Rock sample the second endotherm is followed immediately by an exotherm which coincides with the appearance of spinel in the sample. It must be concluded that spinel formation accounts for this exotherm. Spinel formation begins before complete destruction of the anhydrous montmorillonite and the exotherm may have modified the shape of the preceding endotherm.

It will be observed that a diffraction line of cristobalite is present in all of the Little Rock samples as recorded in Table 1. The cristobalite is an impurity which could not be removed in the purification process. The quantity of this material as determined by the intensity of the diffraction line did not appear to change at any of the temperatures.

The samples from Belle Fourche and Clay Spur gave results very similar to those recorded for the Little Rock sample. In the case of the Plymouth material the thermal reactions occur at lower temperatures but the general relationship between structure and thermal properties

remains constant. The material remains unchanged up to the first high temperature endotherm and then passes into the anhydrous modification. At this point the (110) (020) spacing becomes smaller as in the previous samples, but the development of doublets from other normal montmorillonite lines has not been observed. The second high temperature endotherm coincides with the disappearance of the anhydrous montmorillonite diffraction pattern and spinel is very evident at temperatures beyond the exotherm.

The Otay montmorillonite also shows similar x-ray diffraction changes related to the thermal reactions up to the exothermic drift at 850° C. At

TABLE 2. SUMMARY OF THERMAL REACTION PRODUCTS OF MONTMORILLONITES

Temperature	Relationship With Thermal Reactions	Phases Present				
		Belle Fourche	Clay Spur	Little Rock	Plymouth	Otay
500° C.	Before 1st H.T. endo.				Normal mont.	Normal mont.
540° C.	Before 1st H.T. endo.	Normal mont.	Normal mont.	Normal mont.		
730° C.	Past 1st H.T. endo.				Anhyd. mont.	Anhyd. mont.
760° C.	Past 1st H.T. endo.	Anhyd. mont.	Anhyd. mont.	Anhyd. mont.		
800° C.	Within 2nd H.T. endo. before minimum					Anhyd. mont.
840° C.	Half way out of 2nd H.T. endo.				Minor anhyd. mont. +amorph.	
840° C.	Just beyond 2nd H.T. endo.					Minor enstatite +amorph.
870° C.	Near minimum of 2nd H.T. endo.	Anhyd. mont.	Anhyd. mont.	Anhyd. mont.		
900° C.	Beyond H.T. endo.				Spinel +amorph.	
900° C.	Within exo. drift					Increased enstatite +amorph.
910° C.	Half-way out of 2nd H.T. endo.	Weak anhyd. mont. +amorph.				
910° C.	Almost out of 2nd H.T. endo.		Weak anhyd. mont. +amorph. +weak spinel	Weak anhyd. mont. +amorph. +weak spinel		
950° C.	Beyond H.T. exo.	Spinel +amorph.	Spinel +amorph.	Spinel +amorph.		
1000° C.	Within exo. drift					Enstatite +cristobalite +amorph.

this point the anhydrous montmorillonite structure has disappeared and a new pattern appears which increases in intensity and number of lines at 900° C. and again at 1000° C. This phase has been tentatively identified as enstatite. At 1000° C. a very small amount of cristobalite has developed. The phases present in each of the samples at various temperatures between 500° C. and 1000° C. are given in Table 2.

Dehydration studies were carried out on each of the samples with the same rate of heating as used in differential thermal analysis. However, the dehydration experiments were carried out at pressures not over 20 mm. while in thermal analysis the experiments were carried out at atmospheric pressure. This difference in pressure is likely to result in reducing the temperature at which water is recovered during dehydration. The differences should not be great because the partial pressure of water vapor over the sample during thermal analysis will not be great at elevated temperatures although it may be appreciable in the sample during water loss reactions since there is a definite interval of time between the release of the hydroxyls and the removal of water from the sample. Thus, the temperature of the endotherm peak does not coincide precisely with the greatest rate of pressure increase in the dehydration experiments. It is assumed that the steepest part of the dehydration curves, Figs. 5 and 6, corresponds to the peak of the endothermal reaction. If this assumption is correct there is about a 40° C. difference between the reaction temperature as given by thermal and dehydration analysis. Figures 5 and 6 show the dehydration curves for each of the five samples heated at 10° C. per minute. From these curves it is apparent that there is a small but real increment of water released after the main water loss in the Otay, Belle Fourche, and Clay Spur samples, but not in the Plymouth or Little Rock samples. It is proposed that this small increment of water is the cause of the small endothermal reaction after the first high temperature endotherm in the same samples.

To examine the effect of rate of heating and partial pressure of water vapor on water loss a sample of the Plymouth montmorillonite was heated to predetermined temperatures until all of the water was removed at each temperature. This curve, Fig. 6, in general, has the same shape as that of the 10° C. per minute run except that the octahedral water appears to come out of the structure as low as possibly 150° C. and is virtually all removed at 600° C., a much lower temperature than in the other experiments. In this curve it is interesting to note that if one takes the water removed above 150° C., the inflection point of the curve, this water accounts for 4.96% of the sample weight at 150° C. This value is in fair agreement with the water content (4.77%) computed from the chemical analysis of the material assuming the Hofmann-Endell-Wilm
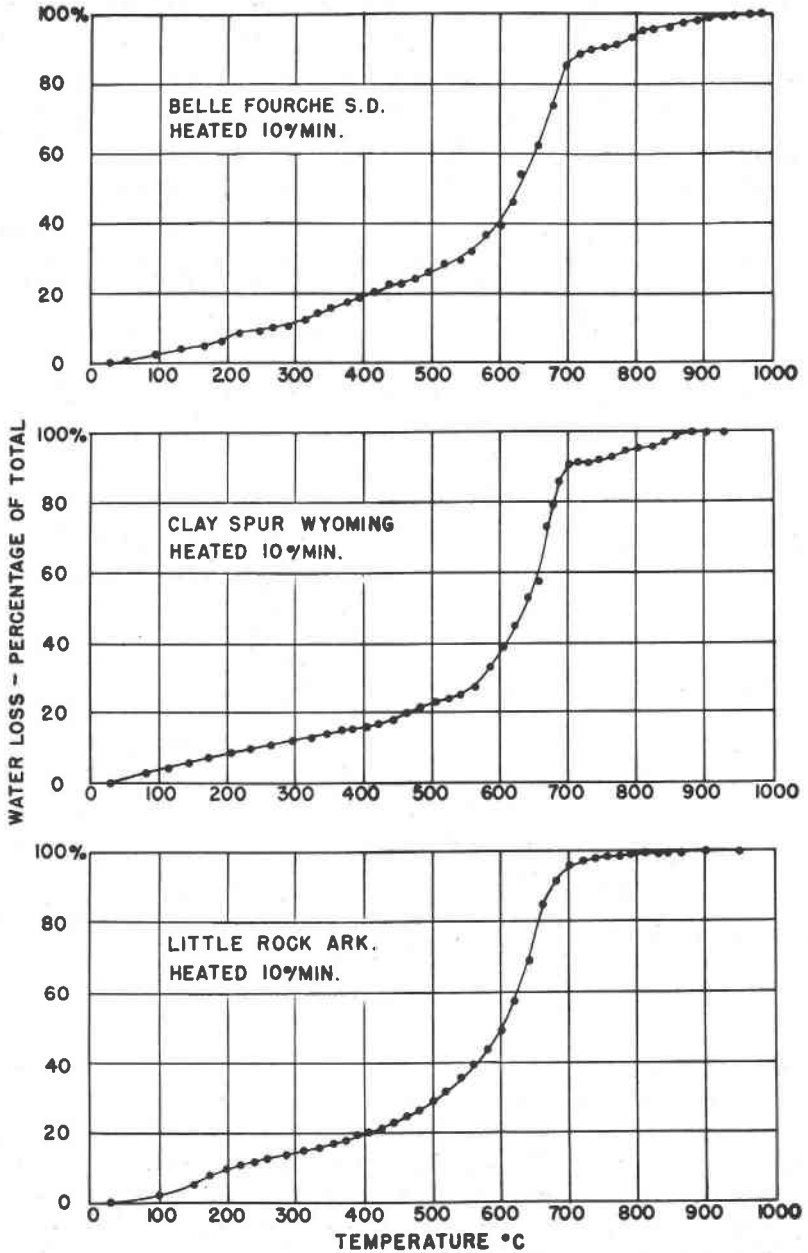
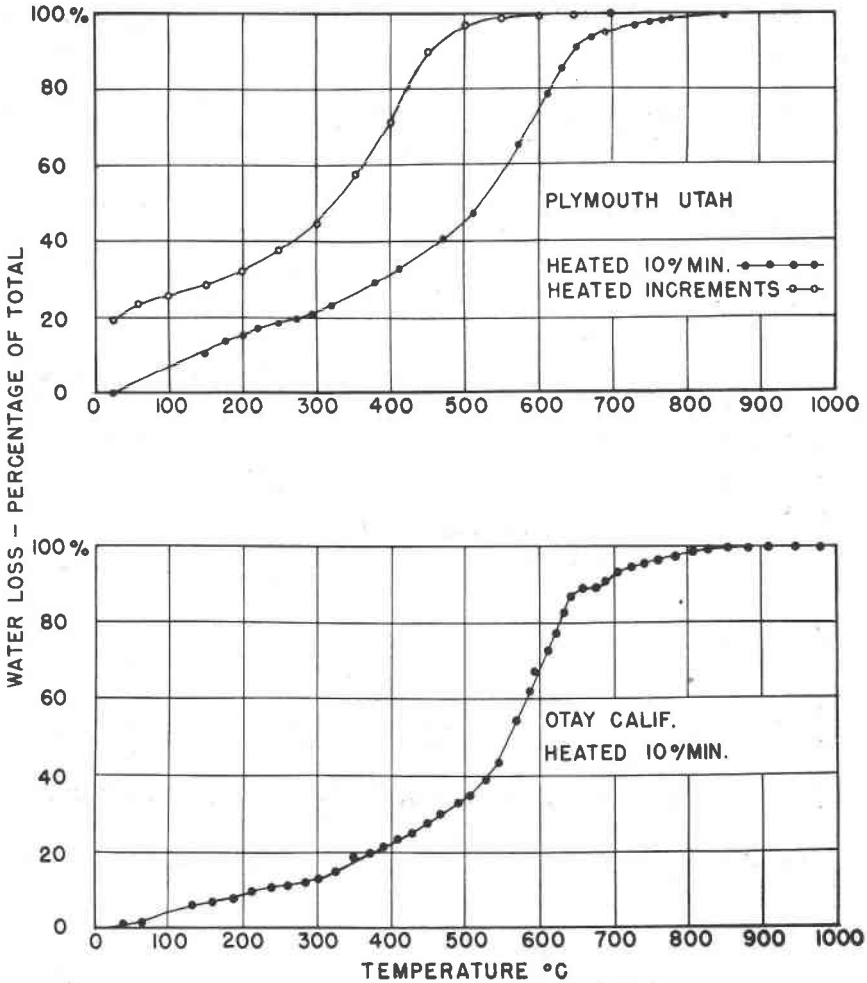FIG. 5. Dehydration curves of sodium saturated montmorillonites.

Fig. 6. Dehydration curves of sodium saturated montmorillonites.

structure. None of the dehydration curves show a significant water loss in the region of the second high temperature endotherm. It is true that there is some water coming off in this region but the amount is exceedingly small and removal takes place at a nearly uniformly decreasing rate. Further, the temperature at which the water is completely removed corresponds with the end of the second high temperature endotherm and the breakdown of the montmorillonite structure as evidenced by x-ray examination. Thus, the second high temperature endotherm can scarcely be due to the removal of water from the crystal structure.

DISCUSSION

A comparison of the *DTA* curves and the *x*-ray diffraction patterns obtained at different temperatures confirms the findings of Bradley and Grim (9) that an anhydrous phase which is structurally different is present after the first high temperature endotherm. This phase is inert to layer absorption of liquids. No evidence of an expansion of (001) was observed in this phase as compared with (001) of montmorillonite dried at temperatures below the first high temperature endotherm. This behavior is common to the five clay samples examined although some minor details differ.

There is no doubt that in these samples the second high temperature endotherm is associated with the breakdown of the anhydrous clay structure. During this reaction the *x*-ray films show a loss of intensity of clay lines and in the following exotherm, spinel or enstatite lines appear. Where enstatite is formed (Otay), a distinct exotherm is not apparent and this can only be associated with the formation rate and energy of this mineral. As pointed out by Bradley and Grim (9) investigation has shown that the crystallization processes accompanying enstatite formation do not give distinct thermal effects.

The formation of enstatite from Otay montmorillonite has been unique in this investigation. Enstatite has been mentioned by Bradley and Grim (9) as forming during the firing of high magnesium montmorillonites. It is interesting to note that the first product of recrystallization here involves both the tetrahedral and octahedral layers. At 1000° C. this clay shows the development of minor cristobalite. In the other clays, spinel is formed, presumably from the octahedral layer constituents. The Otay clay has both a high magnesium content and a very low substitution of aluminum for silica (6) either of which may influence the formation of recrystallized products.

The water given off by the Clay Spur, Belle Fourche, and Otay montmorillonites after the prominent water loss corresponding to the first high temperature endotherm remains largely unexplained. It has not been possible to correlate the presence or absence of this small increment of water with any properties of this group of montmorillonites as described by Earley, et al (6). The suggestion of Page (2) that this water is directly related to the magnesium content of the montmorillonite has not been substantiated. This is illustrated by the fact that the Belle Fourche and Otay materials have low and high magnesium contents respectively and do contain the additional water while the Plymouth sample with an intermediate magnesium content does not contain this water. The dehydration curves (Figs. 5 and 6) indicate that the additional water is lost before the second high temperature endotherm and the breakdown of the

anhydrous clay structure. The lack of relationship between this water loss and the second high temperature endotherm is further illustrated by the Plymouth sample which has a very distinct second high temperature endotherm but does not lose any additional water.

Possible explanations for this small increment of water beyond the normal hydroxyl groups of the octahedral layer are provided for by the $(OH)_4$ tetrahedral groups of McConnell (4) or the (OH) groups in the tetrahedral layer suggested by Edelman and Favejee (5). However, the apparent lack of correlation between this increment of water and other properties of montmorillonite suggests that this water is more likely due to small amounts of an unidentified impurity which has been concentrated in the purified samples or created in the purification process. The lack of identification may be due to a colloidal nature of the impurity or to its close association with the montmorillonite in a mixed layer structure.

ACKNOWLEDGMENTS

REFERENCES

1. NUTTING, P. G., Some standard dehydration curves of minerals: *U.S.G.S., Professional Paper* 197-E (1943).
2. PAGE, J. B., Differential thermal analysis of montmorillonite: *Soil Sci.,* 56, 273–283 (1943).
3. HOFMANN, U., ENDELL, K., AND WILM, D., The crystal structure and the swelling of montmorillonite: *Zeits. Krist.,* 86-A, 340–348 (1933).
4. MCCONNELL, DUNCAN, The crystal chemistry of montmorillonite: *Am. Mineral.,* 35, 166–172 (1950).
5. EDELMAN, C. H., AND FAVEJEE, J. C. L., On the crystal structure of montmorillonite and halloysite: *Zeits. Krist.,* 102-A, 417–431 (1940).
6. EARLEY, J. W., OSTHAUS, B. B., AND MILNE, I. H., Purification and properties of montmorillonite: *Am. Mineral.,* 38, 707–724 (1953).
7. HAUSER, E. A., AND REED, C. E., Studies in thixotropy. I. Development of a new method for measuring particle size distribution in colloidal systems: *Jour. Phys. Chem.,* 40, 1169–1182 (1951).
8. MCCONNELL, DUNCAN, AND EARLEY, J. W., Apparatus for differential thermal analysis: *Jour. Am. Cer. Soc.,* 34, 183–187 (1951).
9. BRADLEY, W. F., AND GRIM, R. E., High temperature thermal effects of clay and related materials: *Am. Mineral.,* 36, 182–201 (1951).