

Effect of Exchangeable Calcium on Montmorillonite Low-Temperature Endotherm and Basal Spacing

J. G. LAGUROS and RICHARD L. HANDY, Respectively, Graduate Assistant and Associate Professor of Civil Engineering, Iowa Engineering Experimental Station, Iowa State University; and LEWIS L. REIGN, Major, Corps of Engineers, U.S. Army

Tests on mixtures of "reference" bentonite that had been equilibrated in vacuo four days with a 50 percent relative humidity gave quantitative relationships between (a) weight loss and area under the DTA low temperature endotherm, (b) exchangeable calcium and first and second areas under the DTA low temperature endotherm, and (c) exchangeable calcium and the X-ray d_{001} spacing. Increase in calcium saturation increases both the first and second low temperature endotherm areas. This increase suggests that at 50 percent humidity, occurrence of calcium-bound water also encourages absorption of free water.

Application of the X-ray and DTA methods to study lime fixation in sodium bentonite- $\text{Ca}(\text{OH})_2$ dried slurries shows that most Ca^{++} ions remain adsorbed at outer positions at first, and relatively few penetrate the interlayer. Similar studies of calcium bentonite show that with 1 percent lime practically all adsorbed calcium stays outside the clay. When either 2 or 4 percent lime is added, additional Ca^{++} ions attach outside, and also crowd into the montmorillonite interlayer. Outer adsorption therefore appears to be the major factor in reduction of PL, and is measureable from DTA.

The X-ray method was also applied to measure Ca^{++} saturation in two natural soils. Results show acceptable agreement with chemical data.

•SYSTEMATIC X-ray diffraction and differential thermal studies have shown that montmorillonite is the most abundant clay mineral in Iowa soils, with calcium the most common cation. The purpose of the investigation undertaken was to determine feasibility of using either differential thermal analysis (DTA) or X-ray diffraction or both to measure exchangeable calcium in natural montmorillonitic soils, or to measure the amount of lime fixation in stabilized montmorillonitic soils (6).

PROCEDURE

Samples

Two reference bentonites, a sodium (No. 1) and a calcium clay (No. 5) (Table 1), were proportioned to give three intermediate mixtures (Nos. 2, 3, and 4) with amounts of exchangeable calcium and sodium ions shown in Table 2. X-ray tests later indicated intimate interlayering of clays in the mixtures.

Hydration of montmorillonites to equilibrium varies with relative humidity. To eliminate this variable all samples were equilibrated at standard conditions by keeping the samples in vacuo for at least four days over a saturated salt solution of $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$,

TABLE 1
 PROPERTIES OF REFERENCE BENTONITES

Exchangeable Cation	Laboratory Sample (meg/100g)	
	No. 1 ^a	No. 5 ^b
Na	85.5	0.4
K	5.0	2.8
Ca	22.0	64.7
Mg	1.0	1.0
Total	113.5	68.9
Corrected for sulfates	89.2	60.1

^aVolclay Wyoming bentonite supplied by American Colloid Co.

^bPanther Creek clay supplied by American Colloid Co.

which gives a relative humidity near 50 percent at 70 ± 3 F (7). This humidity has the advantage of being near average room conditions and giving prominent and different sized DTA peaks for sodium and calcium montmorillonites (5).

Apparatus for DTA

The heating apparatus was a vertical furnace suspended from the ceiling and counter-balanced for ease in lifting. An automatic heating rate controller is set for a rate of 10 C per min. The sample block is $\frac{3}{4}$ in. high by $1\frac{3}{4}$ in. in diameter, machined from 18-8 chrome-nickel stainless steel. Two vertical $\frac{3}{8}$ -in. diameter by $\frac{1}{2}$ -in. deep sample holes are symmetrically located in the sample block with their centers one inch apart. No. 22 Pt-Pt 10 percent Rh thermocouples are used. The furnace temperature couple is a separate chromel-alumel junction inserted in a $\frac{3}{8}$ -in. diameter by $\frac{1}{2}$ -in. deep hole drilled in the bottom of the block. The block is supported by a ceramic pedestal.

DTA Curves and Interpretation

The size and shape of a DTA peak are affected by many factors such as heating rate, thermal conductivity, and specific heat. Peak areas rather than peak heights were measured to minimize effects of variable heating rate and thermocouple misalignment (4).

The low-temperature endotherm for montmorillonite is attributed to loss of adsorbed water. In Ca^{++} montmorillonite, part of the water is more tightly bonded to give a small second peak at about 200 C (3). For purposes of measurement, the two overlapping areas have been resolved and separated as shown by the dotted lines in Figure 1. The areas are bounded by an arbitrary straight line; the dotted lines are drawn in

TABLE 2
 PROPERTIES OF SYNTHESIZED MIXTURES

Exchangeable Cation ^a	Laboratory Sample (meg/100g)				
	No. 1	No. 2	No. 3	No. 4	No. 5
Na	75.4	61.0	47.3	23.5	0.6
K	4.4	4.4	4.3	4.1	4.0
Ca	19.4	33.6	47.3	71.3	94.0
Mg	0.8	1.0	1.0	1.1	1.4

^aCorrected to 100 percent.

such a way as to produce two equal areas, Q and S. Area 1 is the sum of areas P and Q, and area 2 the sum of areas Q and R. Thus, the summation of the two areas gives the total area $P + Q + Q + R = P + Q + R + S$. This method of establishing two distinct areas introduces difficulty and attendant error in measurement, especially when one of the areas is very small, as it appears when the exchangeable calcium is less than 20 percent.

Weight Loss

Due to variability of the low temperature endotherm (LTE) related to interlayer cations, for comparison purposes moisture contents were determined by drying samples to constant weight at 100, 150, and 300 C. Samples were cooled in a desiccator before weighing.

X-Ray Analysis

When the interlayer water is driven off, the basal d-spacing of montmorillonite changes. X-ray diffractometer patterns were obtained at room temperature and also after the samples had been heated to 150 and 300 C and cooled. Copper Ka radiation was used. Mean diffraction angles and corresponding d_{001} spacings were determined from the centroid of the diffraction peak, located with base-line bisectors of an inscribed triangle (Fig. 2). Peak breadth, B_0 , expressed in degrees 2θ , is an inverse measure of crystallite size or crystallinity, and was measured at a height of half the intensity maximum (Fig. 2). All X-ray curves were run three times, and average measurements are reported.

RESULTS

Differential Thermal Analysis

Area-Weight Loss. —DTA peak area is ideally proportional to ΔH , or the amount of heat involved in the reaction. This in turn depends on the amount of each reactant, which in the case being investigated involves the loss of two kinds of adsorbed water, that held by the clay and that held by Ca^{++} cations.

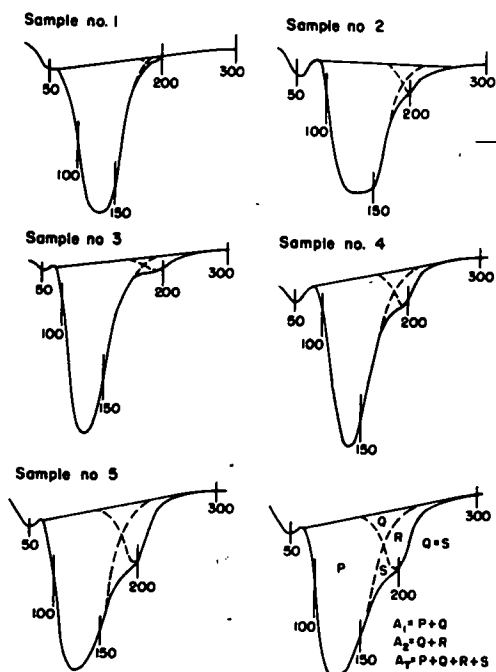


Figure 1. DTA curves of synthesized mixtures.

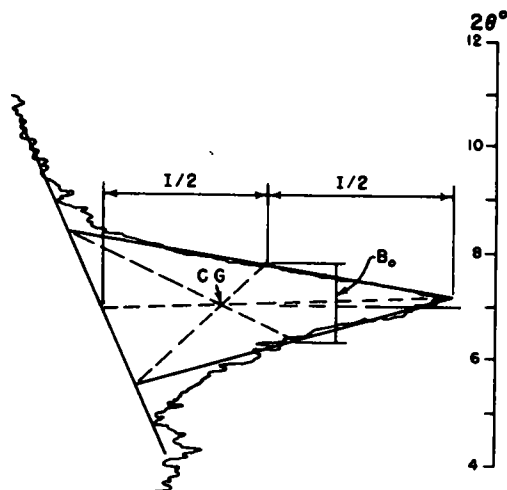


Figure 2. Determination of mean 2θ angle from X-ray diffraction pattern.

TABLE 3
DTA AND WEIGHT LOSS DATA

Sample No.	% Ca ⁺⁺ Saturat.	Area Under Endotherm (cm ²)			Weight Loss (%)		
		Area 1	Area 2	Total	100 C	150C	300C
1	19.4	7.47	0.064	7.54	8.83	9.12	10.25
2	33.6	7.80	0.645	8.45	9.61	10.23	11.44
3	47.3	8.08	0.709	8.79	10.25	10.63	12.26
4	71.3	8.64	0.852	9.49	11.03	11.71	13.25
5	94.0	9.21	1.95	11.16	11.99	12.56	14.93

The relation of weight loss at various temperatures to endotherm peak areas (Table 3) is shown in Figure 3. Variable peak areas do not reflect variable clay contents but are the result of different interlayer cations. Some nonlinearity in the curves is therefore expected.

The drying temperatures of 100 and 150 C were selected to see if either of these weight losses might correlate with area A₁, and 300 C was chosen to correlate with total area under the endotherm. As can be seen from the top of Figure 3, total area A_T is best predicted by the weight loss at 300 C, designated ΔW₃₀₀. A line fit through the origin with 90 percent confidence limits on the slope gives

$$A_T = \Delta W_{300} \times (0.73 \pm 0.01). \quad (1)$$

Nonlinearity in the upper portions of the other curves may be ascribed to area A₂ water, held by Ca⁺⁺ cations and not driven off at 100 or 150 C.

Nonlinearity is apparent in the lower portions of all three lower curves of Figure 3, and extrapolated curves do not pass through the origin. Extrapolations of linear portions of the curves show that the 100 and 150 C curves would come closest to the origin, the errors being in the direction of too much Area 1 for zero weight loss. The most likely explanation for this and for the curvatures appears to be changing thermodynamic conditions during the test, probably related to shrinkage of the sample away from walls of the block. High Na⁺ samples shrink the most, reducing the rate of heat transfer and

increasing the area under the endotherm. In natural soils this effect should be less, and one would expect less curvature in the lower portions of the curves. From the linear portion of the 100 C curve the prediction equation for Area 1 is

$$A_1 = 0.64 \Delta W_{100} + 1.6 \quad (2)$$

in which ΔW₁₀₀ is the percent weight loss at 100 C.

Area-Ca⁺⁺ Saturation.—Increased calcium saturation not only increases the endotherm Area 2, (A₂), indicative of Ca⁺⁺-held water, but also increases the Area 1, indicative of free water (Table 3). A plot and equations of Area 1, (A₁), and total area, A_T, vs calcium saturation are shown in Figure 4. By difference, Area 2 will be

$$A_2 = 0.016 Ca \quad (3)$$

in which Ca is the percent calcium saturation.

The increase in Area 1 with increased

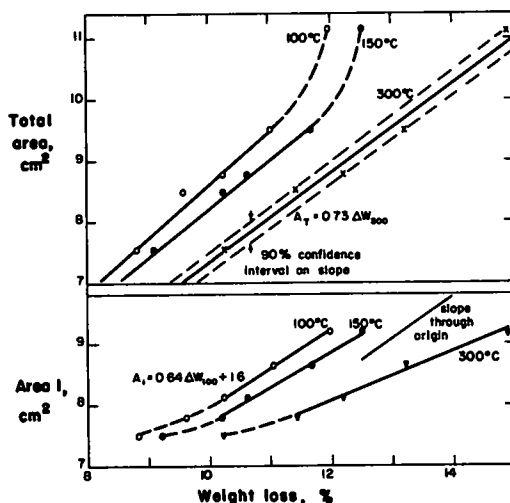


Figure 3. Relations of endotherm peak areas to weight loss at several temperatures.

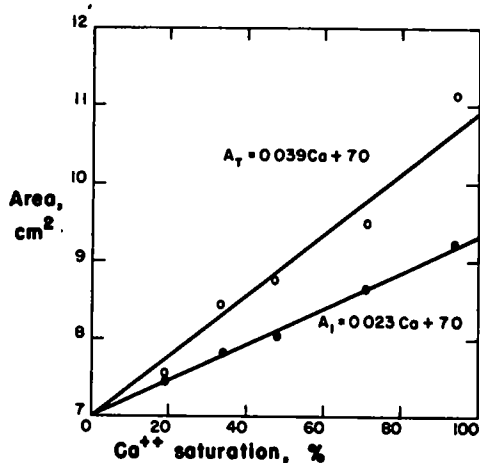


Figure 4. Effect of Ca^{++} content on areas under the LTE curve.

calcium saturation suggests that calcium, in addition to holding some water ionically, also either allows more free water in the clay or somehow increases the energy of binding. A plot of weight loss vs calcium saturation (Fig. 5) shows that the former suggestion is correct, indicating that at 50 percent relative humidity the calcium-bound water encourages absorption of free water.

Area Ratios.—Because DTA absolute peak areas vary not only with exchangeable cation but also with the amount of clay, a ratio of area A_1 and A_2 should give a more satisfactory measure of exchangeable calcium. Unfortunately due to variability of the data, this procedure did not give an accurate measure.

X-Ray Diffraction

Basal d-Spacings.—The basal d-spacing of montmorillonite reflects the amount of interlayer water. Previous investigators have reported the tendency for a sodium montmorillonite to retain one layer of water between the mineral sheets when dried under room conditions, and the tendency for calcium montmorillonite to retain two layers. This is essentially true for samples 1 and 5 equilibrated at 50 percent relative humidity, the basal d-spacings being 12.6 Å and 14.9 Å, respectively (Table 4). Of particular interest is that the intermediate samples show intermediate spacings according to

$$d = 0.031 \text{ Ca} + 12.0 \quad (4)$$

in which Ca is the percent calcium saturation (Fig. 6). Diffraction line broadening

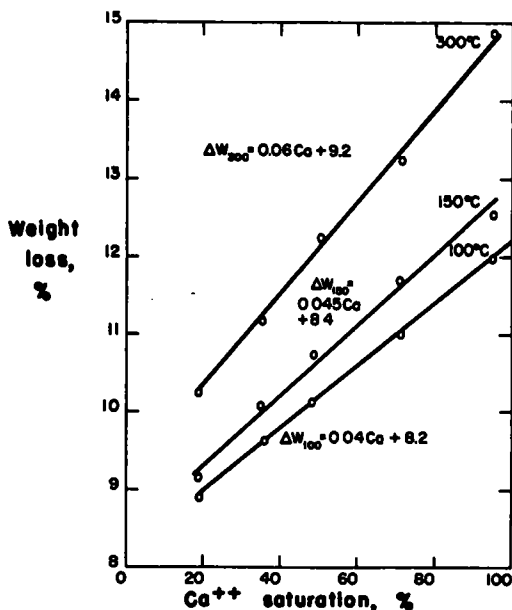


Figure 5. Water content-calcium relationship.

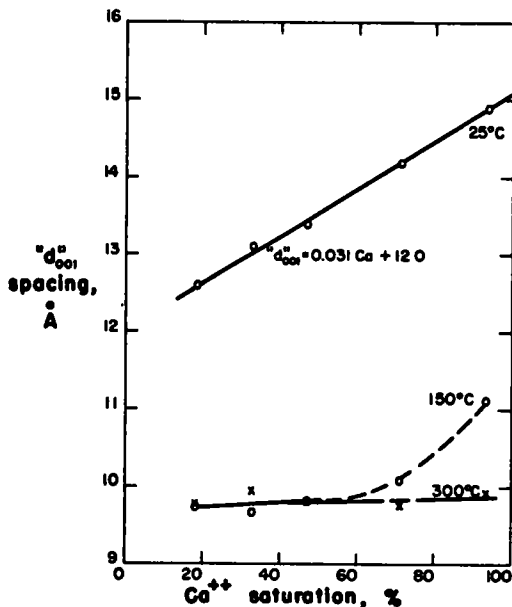


Figure 6. Effect of Ca^{++} cations on d_{001} spacing of samples at various temperatures.

is more pronounced in the intermediate samples (Table 4), suggesting appreciable interlayer disorder when both cations are present.

To check the effectiveness of the equilibration procedure, a portion of sample No. 5 was normally wetted, and another portion was dried at 60 C; after equilibration the basal d-spacings of these samples became 14.72 and 14.86 Å, respectively, which compare well with the previously obtained value of 14.89 Å. Diffraction line broadening also remained essentially unchanged.

Drying at 150 C causes reduction of the interlayer spacing to less than 10 Å for all samples except the high calcium samples (Nos. 4 and 5), verifying DTA and weight loss results, which indicated incomplete dehydration at this temperature. Considerable broadening of the diffraction line for No. 5 suggests an irregular distribution of the remaining interlayer water, which averages less than one molecule thick.

TABLE 4
d₀₀₁ SPACINGS OF SAMPLES TREATED AT VARIOUS TEMPERATURES

Sample No.	Ca ⁺⁺ (%)	Na ⁺ (%)	d ₀₀₁ (Å)				Line Breadth (deg)			
			25C	150C	300C	500C	25C	150C	300C	500C
1	19.4	75.4	12.62	9.80	9.74	-	1.47	0.70	0.50	-
2	33.6	61.0	13.12	9.71	9.97	-	1.70	0.80	0.61	-
3	47.3	47.3	13.38	9.82	9.84	-	1.67	0.95	0.70	-
4	71.3	23.5	14.17	10.10	9.78	-	1.46	1.43	0.70	-
5	94.0	0.6	14.89	11.15	9.95	9.71	1.22	2.30	0.93	0.72

TABLE 5
LIME FIXATION BY Na⁺ AND Ca⁺⁺ BENTONITES

Sample No.	Added % Ca(OH) ₂	Area Under LTE (cm ²)		d ₀₀₁ (Å)		Percent Ca ⁺⁺ Saturation	
		A ₁	A ₂	25 C	150C	From Eq. 4 ^a	From Eq. 3 ^b
1	0	7.47	0.064	12.62	9.80	20.0	4
	3.34	12.50	1.25	12.75	9.93	24.2	78
5	0	9.21	1.95	14.89	11.15	93.4	122
	1	11.27	2.52	14.89	10.91	93.5	157
	2	13.84	2.52	15.31	10.71	106.9	157
	4	14.37	3.75	15.15	10.73	102.7	234

^ad₀₀₁ at 25C.

^bA₂.

TABLE 6
MEASUREMENT OF Ca⁺⁺ SATURATION IN TWO NATURAL SOILS

Sample	Exch. Cations (meq/100 g)			100 Ca-Mg ¹	d ₀₀₁ 25 C (Å)	Ca ⁺⁺ Sat. from X-ray (Eq. 4)
	Na	K	Ca-Mg ¹	Na + Ca - Mg ¹		
55-1	1.4	2.0	7.8	84.8	14.77	89.6
43 ¹ / ₂ - 1	1.3	1.3	21.8	94.4	14.97	95.6

¹Ca-Mg = combination Ca⁺⁺ and Mg⁺⁺.

Drying at 300 C reduces all spacings to less than 10 \AA , with no consistent trend in spacings related to sodium or calcium interlayer cations. However, diffraction intensities regularly decrease and line broadening increases from the high sodium to the high calcium clay (Table 4). To check if this was due to relict interlayer water, sample No. 5 was heated to 500 C for 5 hours, which further decreased its basal d-spacing and sharpened and increased the intensity of the diffraction peak.

CONCLUSIONS

1. Total area under the low-temperature endotherm of sodium-calcium bentonites may be predicted from weight loss at 300 C (Eq. 1).
2. Area under the second portion of the low-temperature endotherm relates linearly to the amount of exchangeable calcium (Eq. 3).
3. Weight losses of pre-humidified samples after heating to several temperatures relate linearly to the amount of exchangeable calcium (equations in Fig. 5).
4. Basal d-spacing of the sodium-calcium bentonites equilibrated at 50 percent relative humidity relates to amount of exchangeable calcium (Eq. 4).
5. Basal spacing diffraction line broadening of sodium-calcium bentonites varies according to treatment and the amount of exchangeable calcium.

APPLICATIONS

The relationships most pertinent to measurement of exchangeable calcium and lime fixation in montmorillonitic soils would appear to be conclusions 2, 3, and 4. All involve pre-treatment of samples at room temperature and at 50 percent relative humidity.

Of these three methods the one most applicable to measurement of exchangeable calcium in natural soils containing an unknown amount of montmorillonite is X-ray diffraction (conclusion 4). Both other measurements are influenced by the amount of clay; the X-ray d-spacing is not. The three methods look equally applicable for determination of the amount of lime fixation in montmorillonitic soils treated with variable amounts of lime or portland cement. Weight loss is perhaps the least definitive. While X-ray diffraction measures calcium-held water in the interlayer position, DTA may show total Ca^{++} -held water.

Lime Fixation

Samples 1 and 5 of the bentonites were treated with several amounts of reagent grade $\text{Ca}(\text{OH})_2$, wetted to form a slurry, stored for 8 hours, dried at 30 C, ground, and equilibrated for 7 days at room temperature and 50 percent relative humidity. The calcium bentonite, No. 5, plus 1, 2, and 4 percent $\text{Ca}(\text{OH})_2$ was chosen to represent lime stabilization of a montmorillonitic soil already calcium saturated; and a sodium bentonite, No. 1, was treated with 3.34 percent $\text{Ca}(\text{OH})_2$ to correspond to its cation exchange capacity. Mixes and pertinent data and results are given in Table 5.

X-ray data on the sodium bentonite + 3.34 percent $\text{Ca}(\text{OH})_2$ show very little influence of additional calcium in expanding the clay interlayer, yet DTA area 2 data indicate considerably more exchangeable calcium. From these, one would conclude that added Ca^{++} from lime is held mostly to the outside of the mineral. DTA area 1 and weight loss data were confounded by remnant calcium hydroxide.

Effect of lime on calcium montmorillonite is of considerable interest because properties of such clays show a drastic change, yet there is no logical ion exchange reaction. This has led to the hypothesis of calcium crowding on the clay (2).

X-ray data suggest relatively little interlayer effect of 1 percent lime but there is an increased DTA area 2, suggesting that calcium ions present are held to the outside of the clay, as before. Addition of 2 percent lime noticeably affects interlayer spacing, leading to a calculated Ca^{++} oversaturation in the clay interlayer with additional Ca^{++} remaining on the outside. With 4 percent lime, there is no further increase in interlayer oversaturation, but there is a marked increase in adsorbed calcium ions, indicated by a further increase in DTA area 2. The hypothesis of ion crowding in lime-treated soils thus appears to be confirmed.

Natural Soils

Two soils (a calcareous loess and a leached loess) were examined by X-ray diffraction of 50 percent humidity equilibrated samples. Results (Table 6) show fairly close agreement with ion exchange data, particularly if the relatively high exchangeable K^+ is assigned to 10-A mineral (illite). The close agreement precludes the possibility of much interlayering.

ACKNOWLEDGMENTS

The material for this paper was obtained as part of the research being done under Project 340-S of the Iowa Engineering Experiment Station, Iowa State University of Science and Technology. Project 340-S is under contract with the Iowa Highway Research Board of the Iowa State Highway Commission as their Project HR-48.

REFERENCES

1. Alexander, L. T., and Haring, M. M., "Vapor Pressure-Water Content Relations for Certain Typical Soil Colloids." *Jour. Phys. Chem.*, 40:195-205 (1936).
2. Davidson, D. T., and Handy, R. L., "Lime and Lime-Pozzolan Stabilization." in Woods, K. B. (Ed.) "Highway Engineering Handbook." Pp. 21-100, McGraw-Hill (1960).
3. Grim, R. E., "Clay Mineralogy." McGraw-Hill (1953).
4. Handy, R. L., and Demirel, T., "Notes on Determination of Carbonates in Soils by Chemical Means, DTA, and X-Ray." *Proc., Iowa Academy of Science*, 66: 222-236 (1959).
5. Hendricks, S. B., Nelson, R. A., and Alexander, L. T., "Hydration Mechanism of the Clay Montmorillonite Saturated with Various Cations." *Jour. Am. Chem. Soc.*, Part I, 62:1457-1464 (1940).
6. Hilt, G. H., and Davidson, D. T., "Lime Fixation in Clayey Soils." *HRB Bull.* 262, 20-32 (1960).
7. Mackenzie, R. C., "The Differential Thermal Investigation of Clays." *Mineralogical Society (Clay Minerals Group)*, Central Press, London (1957).
8. McConnell, D., "Crystal Chemistry of Montmorillonite." *Amer. Miner.* 35:166-172 (1950).
9. Mering, J., "On the Hydration of Montmorillonite." *Trans. Faraday Soc.*, 42B:205-219 (1946).
10. Page, J. B., "Differential Thermal Analysis of Montmorillonite." *Soil Science*, 56:273-283 (1943).