

# Characteristics of Lime Retention by Montmorillonitic Clays

CLARA HO and R. L. HANDY, respectively, Research Associate and Associate Professor of Civil Engineering, Iowa State University

Previous work has shown that hydrated lime added to clayey soils reduces their plasticity; above a certain percent lime there is a leveling off and no further reduction. The point at which this leveling off begins may be referred to as the lime retention or lime fixation point. The amount of lime needed to satisfy the lime retention requirement of clays must be exceeded if later pozzolanic cementitious reactions are to proceed. Lime retention occurs in clays already calcium saturated, although sodium clays take more lime. The total calcium retained exceeds the cation exchange capacity as measured by the ammonium acetate method.

Lime retention by clays was studied by measurements of plastic limit, pH, viscosity, exchangeable calcium, and X-ray diffraction. The lime retention point was most pronounced in montmorillonitic clays, and coincides with a gradual increase in pH and a sharp rise in viscosity of suspensions as measured by a Stormer paddle-rotation type of viscosimeter. The rise in viscosity was observed with natural sodium- and calcium-saturated bentonites and with Iowa gumbotil and plastic loess soils. Viscosity depends on pH as well as on calcium ion concentration, and reaches a maximum at around pH 11.8. Hypotheses of lime retention are presented.

•TWO TYPES of reactions occur between lime and clayey soils: (a) an almost immediate reduction in plasticity on addition of lime to soil, and (b) pozzolanic cementation reactions, resulting in a long-term strength gain of compacted soil (1). This paper is primarily concerned with the first type.

The plasticity reduction effect of lime was long attributed to cation exchange phenomena (2, 3, 4). In 1952 Goldberg and Klein recognized that lime also reduces plasticity of clay that is already calcium saturated (5). That lime is used in excess of the cation exchange capacity, as measured at pH 7, suggested a "combination or fixation" of excess sodium and calcium ions in insoluble and perhaps in non-crystalline form.

In a discussion to this paper, Johnson (6) suggested that saturation of the clay micelle by OH groups may alter the cation exchange capacity and thus change the system. Hilt and Davidson (7) noted that the plastic limit maxima and minimum quantities of lime required for pozzolanic reactions coincide, and termed this coincidence the "lime fixation point." They demonstrated that lime used for reduction in plasticity is not available for pozzolanic reactions. The lime fixation points of the montmorillonitic soils investigated were found to be

$$L_M = \frac{\% \text{ of } < 2\text{-}\mu \text{ clay}}{35} + 1.25. \quad (1)$$

Whether the lime was fixed in the sense of ammonium or potassium fixation by clay was not indicated. Later work by Pinto et al. (8) showed that the floc sedimentation rate of a gumbotil (sample 528-8) suspension reached a maximum near the lime fixation point and leveled off, indicating that increments of lime below this percentage go to increase the size of the flocs (Fig. 1).

### PROCEDURES

Lime retention (or fixation) in natural sodium and calcium bentonites was studied by means of physical tests, such as plastic limit and suspension viscosity, and by means of physico-chemical tests, such as pH, X-ray diffraction, exchangeable cation determinations, and differential thermal analysis (DTA). Exchangeable cations were measured both at neutral and at alkaline pH's to ascertain the relationship between the pH and exchange capacity. Selected tests were then made on two montmorillonitic clay soils to show if trends were consistent. Methods and samples used in this study are as follows.

**Plastic Limit.**—Plastic limits were determined according to ASTM method D424-59 (9). Most were measured independently by three operators, and the results were averaged.

**pH.**—The pH's of the sample suspensions prepared in 50 percent concentration for soil samples, 30 percent for Ca-bentonite, and 3 percent for Na-bentonite were measured by a Beckman glass electrode pH meter.

**Viscosity.**—Viscosities of the clay suspensions were measured by Stormer paddle-type viscosimeter at 25 C (Fig. 2). The paddle is actuated by a 25-g weight; results are expressed in minutes required for 100 revolutions of the rotor. Details of the method are presented in Appendix A.

**X-Ray Diffraction.**—Aliquots of most clay-lime suspensions were allowed to air-dry on glass slides for X-raying. Autoclaved samples were packed moist into 1- by 2-in. bakelite holders and X-rayed. A General Electric XRD-5 diffraction unit with copper K $\alpha$  radiation was used. The incident beam angle of 4°, detector slit of 0.2°, beam slit of 1°, scan rate of 2° per min, and time constant of 3 sec were used.

**Differential Thermal Analysis.**—Samples equilibrated in a CaCl<sub>2</sub> desiccator were ground to pass a No. 200 mesh sieve before packing into the DTA apparatus. In this apparatus, an automatic controller provides for a heating rate of 10 C per min. A vertical furnace arrangement is used. The sample block of 18-8 stainless steel,  $\frac{3}{4}$  in. high by  $1\frac{3}{4}$  in. diameter is supported by a hollow ceramic pedestal. Two vertical  $\frac{3}{8}$ -in. in diameter by  $\frac{1}{2}$ -in. deep sample holes are symmetrically located in each block with centers 1 in. apart. No. 22 Pt-Pt 10 percent Rh differential thermocouples are used; the furnace temperature couple is a separate chromel-alumel junction inserted in a

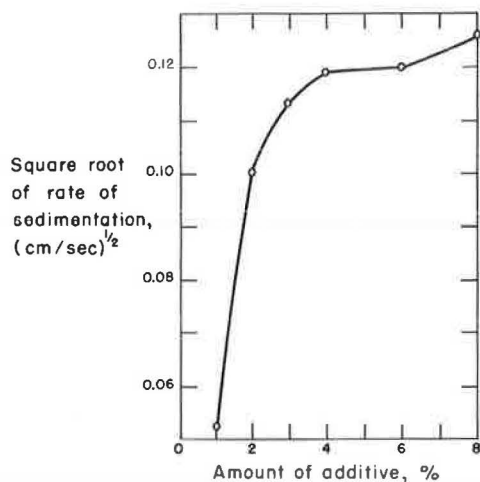


Figure 1. Square root of rate of sedimentation of gumbotil flocculated by additive of lime (12).

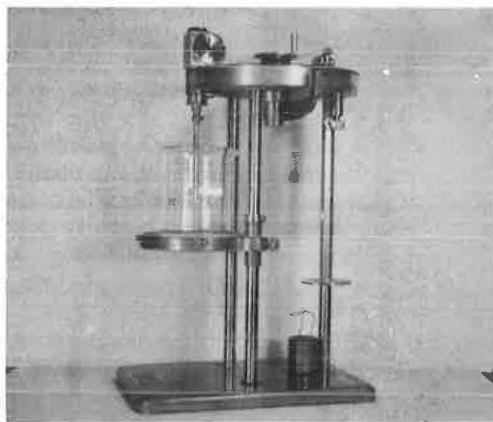


Figure 2. Stormer viscosimeter.

$\frac{3}{8}$ -in. diameter by  $\frac{1}{2}$ -in. deep hole drilled up into the bottom of the block. The inert sample is powdered alumina.

**Autoclaving.**—Mixtures containing 100 g of Ca-bentonite, various amounts of reagent grade  $\text{Ca}(\text{OH})_2$ , and 110 percent distilled water were autoclaved in air-tight polypropylene bottles at 126 C and 22 psi pressure for 8 days to accelerate pozzolanic reaction. Part of each autoclaved sample was dried in a  $\text{CaCl}_2$  desiccator and was ground to pass a No. 200 mesh sieve for DTA analysis.

**Exchangeable  $\text{Ca}^{++}$  and/or  $\text{Ca}^{++} + \text{Mg}^{++}$ .**—Exchangeable  $\text{Ca}^{++}$  and/or  $\text{Ca}^{++} + \text{Mg}^{++}$  displaced by normal KCl was titrated with standard EDTA in presence of pH 10.5  $\text{NH}_4\text{OH} - \text{NH}_4\text{Cl}$  buffer, using Eriochromeschwartz T as an indicator (Appendix B). The determination of exchangeable  $\text{Ca}^{++}$  in presence of free  $\text{Ca}(\text{OH})_2$  and  $\text{CaCO}_3$  is difficult because no salt solution could be found to displace the exchangeable  $\text{Ca}^{++}$  without dissolving  $\text{Ca}(\text{OH})_2$  and  $\text{CaCO}_3$ . Water was added and free  $\text{Ca}(\text{OH})_2$  was removed by mechanical shaking. The quantity of excess water needed was calculated from the solubility of  $\text{Ca}(\text{OH})_2$  at 25 C (0.165 g per 100 ml). The hydrolysis of the exchangeable  $\text{Ca}^{++}$  and the solution of  $\text{CaCO}_3$  are not likely to be appreciable. Displacement of  $\text{Ca}^{++}$  can be performed by leaching with 1 N KCl in about 15 min.

**Cation Exchange Capacity.**—Cation exchange capacities were determined by an ammonium acetate method using a microdistillation apparatus designed by Bremner (Appendix C).

**Samples.**—The Panther Creek bentonite and volclay are naturally Ca- and Na-saturated montmorillonites, respectively. Both were ground to pass a No. 200 mesh sieve.

To check if results were consistent in montmorillonitic soils, two Iowa soils, gumbotil 528-8 and plastic loess 528-4 from subhorizons were tested. The soils were passed through a No. 40 sieve and are essentially free of organic matter. Clay in these soils is predominantly Ca-saturated. Brief physico-chemical properties of the clays and soils are given in Table 1.

TABLE 1  
PROPERTIES OF SAMPLES

Property	Gumbotil (528-8)	Plastic Loess (528-4)	Panther Creek Bentonite	Volclay
Source	Keokuk Co., Iowa	Keokuk Co., Iowa	American Colloid Co.	American Colloid Co.
Series	Paleo	Mahaska	--	--
Horizon	B	C	--	--
Textural composition (%):				
Sand (2-0.074 mm)	16.0	0.2	--	--
Silt (74-5 $\mu$ )	13.5	60.8	--	--
Clay (5 $\mu$ )	70.5	39.0	90.0	90.0
Predom. clay mineral	Mont.	Mont.	Mont.	Mont.
Physical properties (%)				
Liquid limit	75.6	52.1	--	--
Plastic limit	25.6	20.0	70.2	--
Plastic index	50.0	32.1	--	--
Chemical properties:				
pH	6.6	5.9	8.4	9.8
CEC (meq/100 g)	34.3	23.3	82.5	88.3
Predominant cation	$\text{Ca}^{++}$	$\text{Ca}^{++}$	$\text{Ca}^{++}$	$\text{Na}^+$

## RESULTS

Viscosity vs Percent Lime

Na-Bentonite.—The viscosity of Na-bentonite slurries was markedly changed by small additions of lime (Fig. 3). A sharp increase in viscosity occurred at about 2.5 percent  $\text{Ca(OH)}_2$ ; the viscosity reached a maximum at about 6.1 percent lime, then decreased and leveled off. There was a corresponding rapid increase in pH up to 2.5 percent  $\text{Ca(OH)}_2$ , followed by a gradual increase. The pH was 11.85 when the sharp change in viscosity occurred.

The amount of  $\text{Ca(OH)}_2$  causing the sudden change in viscosity coincides with the lime fixation point predicted by Eq. 1 if allowance is made for additional  $\text{Ca}^{++}$  to replace exchangeable sodium (7). Exchangeable  $\text{Na}^+$  of the Na-bentonite is 63 meq per 100 g, the  $<2\mu$  clay is roughly 90 percent, and the milliequivalent weight of  $\text{Ca(OH)}_2 = 0.037$  g. Then  $63 \times 0.037 = 2.33$  g, or 2.33 percent  $\text{Ca(OH)}_2$  would be required to make a Ca-clay. Additional  $\text{Ca(OH)}_2$  used for the development of maximum plastic limit would be  $L_M = \frac{90}{35} + 1.25 = 2.57 + 1.25 = 3.82$ .

Unfortunately the lime retention point for the Na-bentonite could not be verified by the plastic limit method owing to the high swelling property of this clay, which made testing difficult.

The suspension tended to form distinct, large flocs when the concentration of  $\text{Ca(OH)}_2$  was around 6 percent and higher. This was most noticeable in flow patterns of the suspensions on wall of flasks, and is an indication of the lime retention point (Fig. 4).

Ca-Bentonite.—Viscosity and pH data for Ca-bentonite with addition of  $\text{Ca(OH)}_2$  showed a sharp increase in viscosity at 1.5 percent  $\text{Ca(OH)}_2$  (Fig. 5). Viscosity reached a maximum at about 2.2 percent lime; additional  $\text{Ca(OH)}_2$  up to 5.2 percent (140 meq per 100 g) decreased viscosity. Plastic limit data also showed the coincidence between

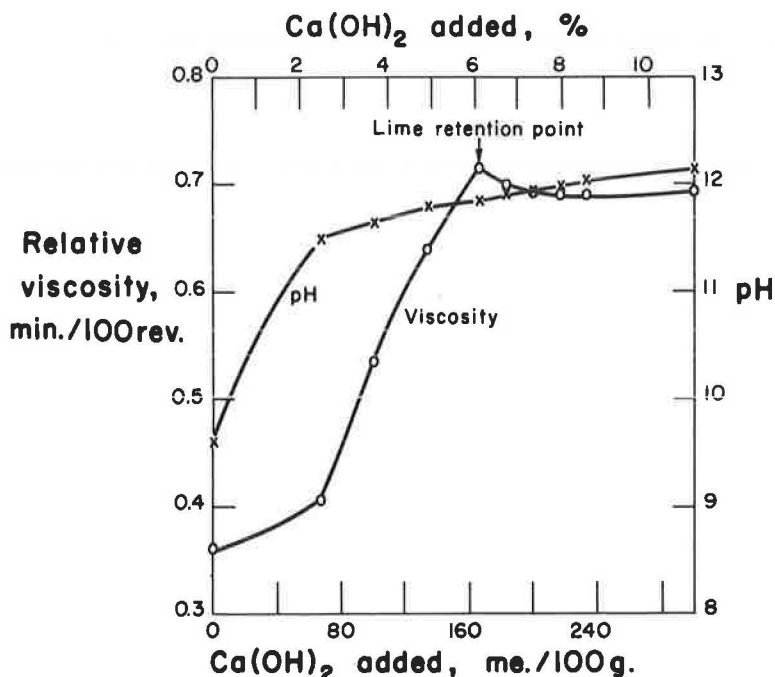


Figure 3. Viscosity and pH changes of 2.7 percent Na-bentonite suspensions with addition of  $\text{Ca(OH)}_2$ .

percent lime for maximum viscosity with that for maximum plastic limit. The pH at this point was about 11.85. The  $\text{Ca}(\text{OH})_2$  content at the lime retention point for the Ca-bentonite is much less than that for the Na-bentonite. The flow pattern shown in Figure 4 was also seen with the Ca-bentonite.

**Viscosity of Ca-Bentonite + Lime vs Time.** — The percent lime for maximum viscosity was found to change with time (Table 2). A clay thixotropy phenomenon should be most in evidence in a dispersed suspension, and this is difficult to relate to the shift in lime retention point, unless lime platelets are actually participating in the set.

Another possibility is that the character of the suspensions is changing due to pozzolanic reaction. If only suspensions containing lime in excess of the retention point react pozzolanically, removal of lime from the high-lime content systems would shift the viscosity vs lime curve to the right.

For the preceding reasons, all viscosity and plastic limit tests were conducted within two hours after mixing clay or soil with lime.

TABLE 2  
RELATION OF PERCENT LIME  
TO TIME

Setting Time (days)	Lime Retention Point (% lime)
0	2.2
1	3.0
2	3.7

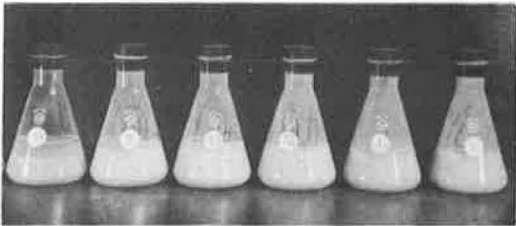


Figure 4. Flow patterns of lime-Na-bentonite suspensions.

**Viscosity vs pH**

The pH's of 30 percent Ca-bentonite suspensions were adjusted to various values by adding N NaOH, with the volumes of added liquid kept constant. A sharp increase in viscosity took place at pH 11.0 (lower curve, Fig. 6). Viscosity reached a maximum at pH 11.6, where a further increase in pH reduced viscosity.

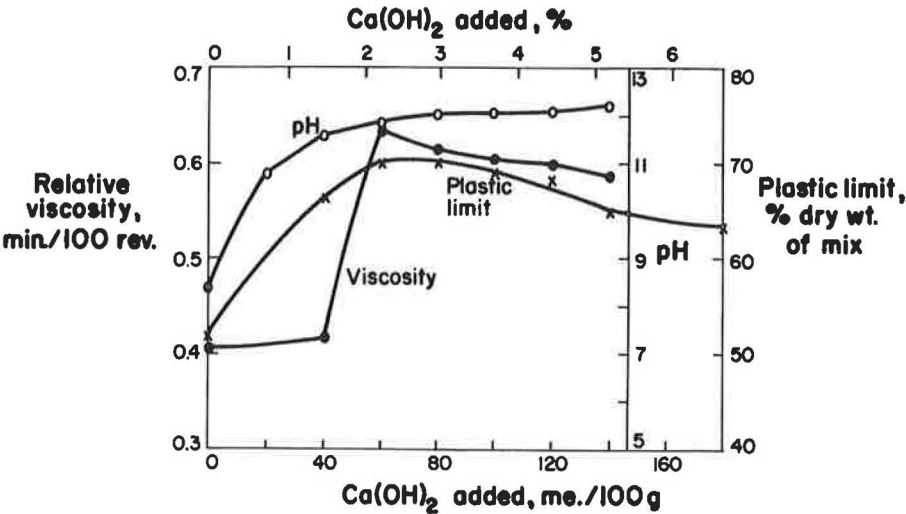


Figure 5. Changes in plastic limit and viscosity (30 percent suspension) of Ca-bentonite with addition of  $\text{Ca}(\text{OH})_2$ .

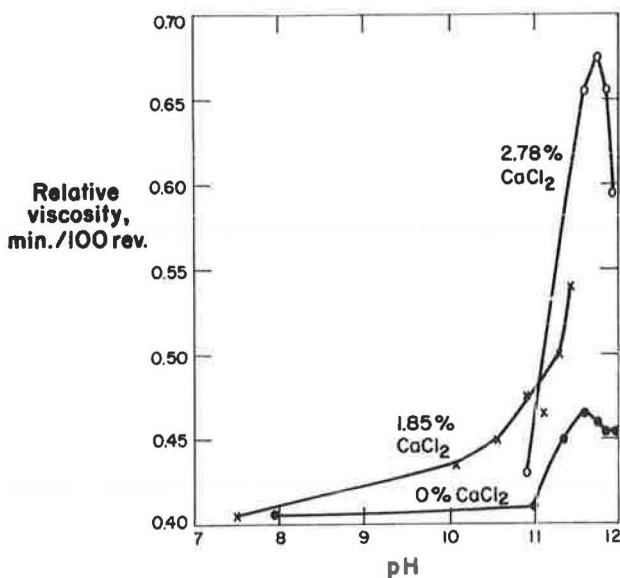


Figure 6. Effect of various pH values and constant  $\text{CaCl}_2$  concentration on viscosity changes of 30 percent Ca-bentonite suspensions (pH adjusted by additions of NaOH).

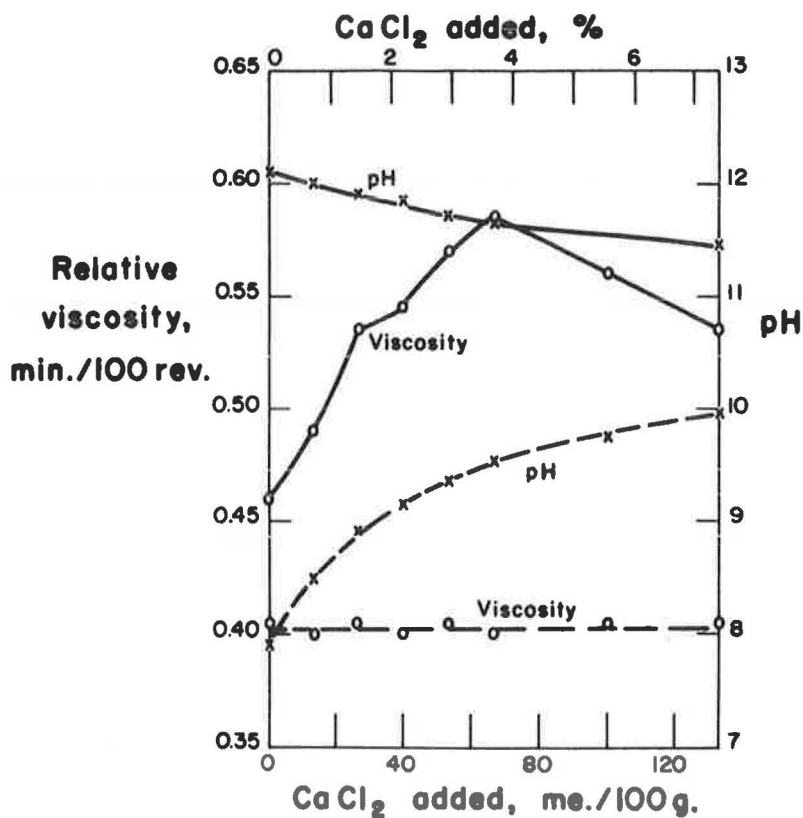


Figure 7. Effect of pH and  $\text{CaCl}_2$  concentration on viscosity of 30 percent Ca-bentonite suspensions.

Figure 6 also shows viscosity results obtained with addition of  $\text{CaCl}_2$ , the pH's being adjusted by addition of  $\text{N NaOH}$ . The viscosity of each suspension was increased considerably, particularly at pH's above 11.00. With 2.78 percent  $\text{CaCl}_2$ , which corresponds to the lime retention value of 50 meq per 100 g, viscosity increased sharply and reached a maximum at pH 11.75.

To test for an optimum  $\text{Ca}^{++}$  ion content at high pH, the pH of 30 percent Ca-bentonite suspensions with various additions of  $\text{CaCl}_2$  was maintained at 11.5 to 12.1 by adding  $\text{N NaOH}$  (top two curves, Fig. 7). The viscosity increased with  $\text{CaCl}_2$  concentration to 3.6 percent (64 meq per 100 g) and then decreased with additional  $\text{CaCl}_2$ . The  $\text{CaCl}_2$  concentration at which the maximal viscosity occurred is roughly in agreement with the lime retention point obtained previously—60 meq per 100 g.

The lower curves in Figure 7 show the results of tests that repeated with various pH's below 10. No viscosity change is shown, which indicates that high pH is a requirement for  $\text{Ca}^{++}$  ions to be effective at increasing viscosity.

### Exchangeable $\text{Ca}^{++}$

Measurements of exchangeable  $\text{Ca}^{++}$  in the lime-bentonite slurries show that exchangeable  $\text{Ca}^{++}$  increased with addition of  $\text{Ca}(\text{OH})_2$ , indicating pH dependence of the cation exchange capacity. There is no break in the exchangeable  $\text{Ca}^{++}$  curve at the lime retention point (Fig. 8).

The amounts of exchangeable  $\text{Ca}^{++}$  extracted were considerably below the amounts of lime added. Excess lime had been leached by water; that part was carbonated during the leaching process is indicated by X-ray diffraction.

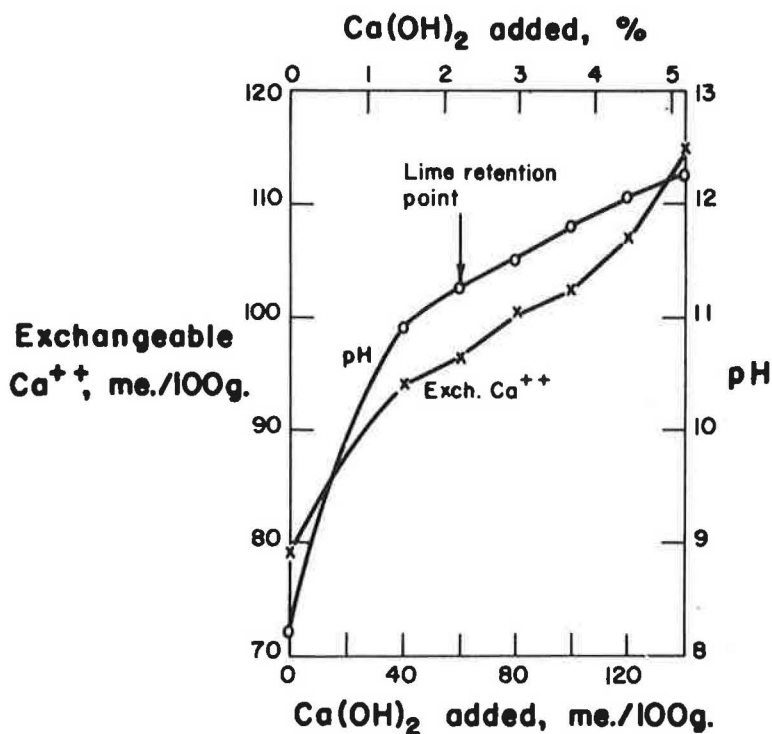


Figure 8. Relationships between  $\text{Ca}(\text{OH})_2$  added, pH, and exchangeable  $\text{Ca}^{++}$  in Ca-bentonite.

Influence of Added  $\text{Na}^+$  at High pH. —Effectiveness of  $\text{Na}^+$  for increasing the suspension viscosity was checked by addition of  $\text{NaCl}$  or  $\text{Na}_2\text{SO}_4$  to 3 percent  $\text{Na}$ -bentonite suspensions of pH 11.85. Viscosity did not increase significantly. The same was true with  $\text{Ca}$ -bentonite (Fig. 9).

Influence of  $\text{Mg}^{++}$ . — $\text{MgO}$  is a constituent of dolomitic monohydrate lime. Addition of  $\text{MgO}$  to 30 percent  $\text{Ca}$ -bentonite suspensions increased their viscosities only slightly, even when the latter were measured the second day after sample preparation (Fig. 10). This could be a result of the low solubility of  $\text{MgO}$ , which gave low pH's (from 8.4 to 10.40) as well as a low  $\text{Mg}^{++}$  ion concentration. However, raising pH's to the range of 11 to 11.6 by addition of  $\text{NaOH}$  did not increase viscosities of the systems to any significant extent, indicating that the availability of  $\text{Mg}^{++}$  was probably further reduced by precipitation of  $\text{Mg}(\text{OH})_2$  at high pH's.

To summarize,  $\text{Ca}^{++}$  ions increased suspension viscosity but only at high pH, the optimum  $\text{Ca}^{++}$  concentration and pH approximately coinciding with those obtained by addition of  $\text{Ca}(\text{OH})_2$  alone.  $\text{Na}^+$  ions were relatively ineffective.  $\text{Mg}^{++}$  ions were ineffective, perhaps because of low solubility at high pH.

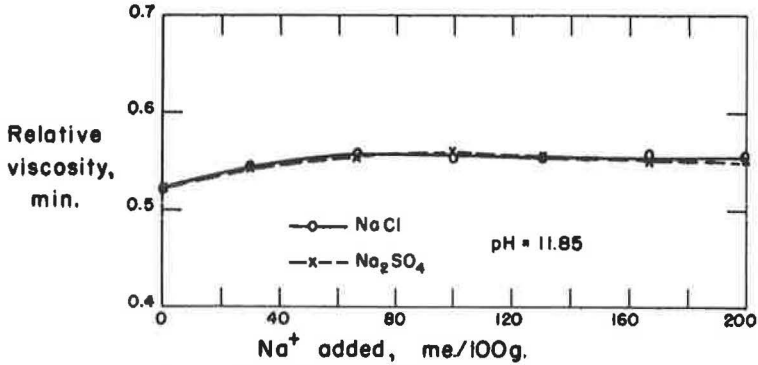


Figure 9. Effect of  $\text{NaCl}$  and  $\text{Na}_2\text{SO}_4$  on viscosity changes of 3 percent  $\text{Na}$ -bentonite suspensions at pH 11.85.

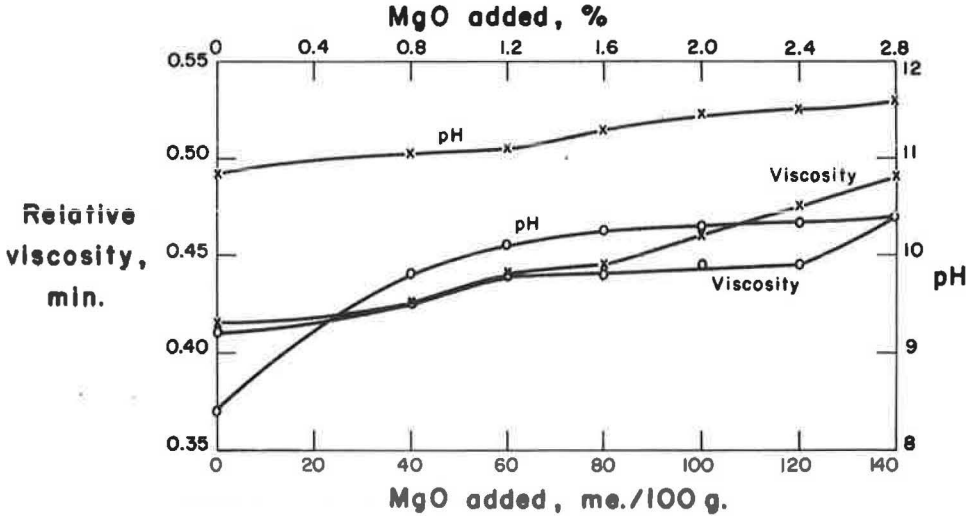


Figure 10. Effect of  $\text{MgO}$  on viscosity changes of 30 percent  $\text{Ca}$ -bentonite suspensions at various pH values.



### Effect of Anions on Viscosity

As previously shown in Figure 9, increments of NaCl or Na<sub>2</sub>SO<sub>4</sub> added to Na-bentonite and Ca-bentonite suspensions together with a constant amount of NaOH to bring the pH of the systems to 11.85 had no significant effect on viscosity. A great increase in viscosity was observed with small additive of Na<sub>3</sub>PO<sub>4</sub> to Ca-bentonite suspensions, even at pH as low as 9.8 (Fig. 11). This abrupt increase in viscosity is clearly different from that observed in the clay-lime system, and probably resulted from the reaction between Ca<sup>++</sup> and phosphate ions to form a Ca-phosphate gel, because addition of Na<sub>3</sub>PO<sub>4</sub> to Na-bentonite suspensions did not increase their viscosities significantly.

### Pozzolanic Reaction

The availability of lime for pozzolanic reaction was evaluated by means of X-ray and differential thermal analysis of the clay-lime slurries after autoclaving. X-ray diffraction showed no new peaks indicative of reaction products, but intensity of the clay mineral (001) peak diminishes with increasing lime content. This could be influenced by other variables, such as preferred orientation or crystal perfection.

Perhaps more reliable are the differential thermal analyses (Fig. 12). Curve A' is for a dry clay-excess lime mix not autoclaved, and shows the characteristic Ca(OH)<sub>2</sub> and montmorillonite dehydration reactions.

Where lime was added in amounts less than the lime retention point, the Ca(OH)<sub>2</sub> peak no longer shows, even with no autoclaving (curve E', Fig. 12), indicating decomposition and utilization of the Ca(OH)<sub>2</sub> in the lime retention reaction. The Ca(OH)<sub>2</sub> peak also is absent in all autoclaved samples. Interesting features of the curves are first that the endothermic peaks due to dehydration of lattice OH groups (650 to 850 C) decreased with increasing Ca(OH)<sub>2</sub> added above the lime retention point. That is, the first 60 meq of lime had no effect on this peak, whereas the next 20 meq and the additional increments reduce it markedly. This further supports the hypothesis that pozzolanic reaction can proceed only when the quantity of lime added exceeds a threshold quantity; i.e., the lime retention point. The exothermic peak (850 C to 1,000 C) increases with increasing Ca(OH)<sub>2</sub> added above the lime retention point, indicating greater availability of ions for recrystallization. Furthermore, the peak gradually shifts to a lower temperature and thus becomes more clearly defined.

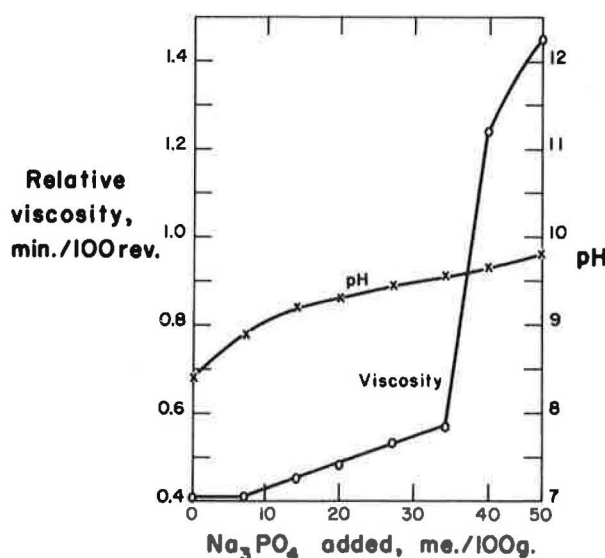


Figure 11. Effect of Na<sub>3</sub>PO<sub>4</sub> on viscosity and pH of Ca-bentonite suspensions (22.4 percent).

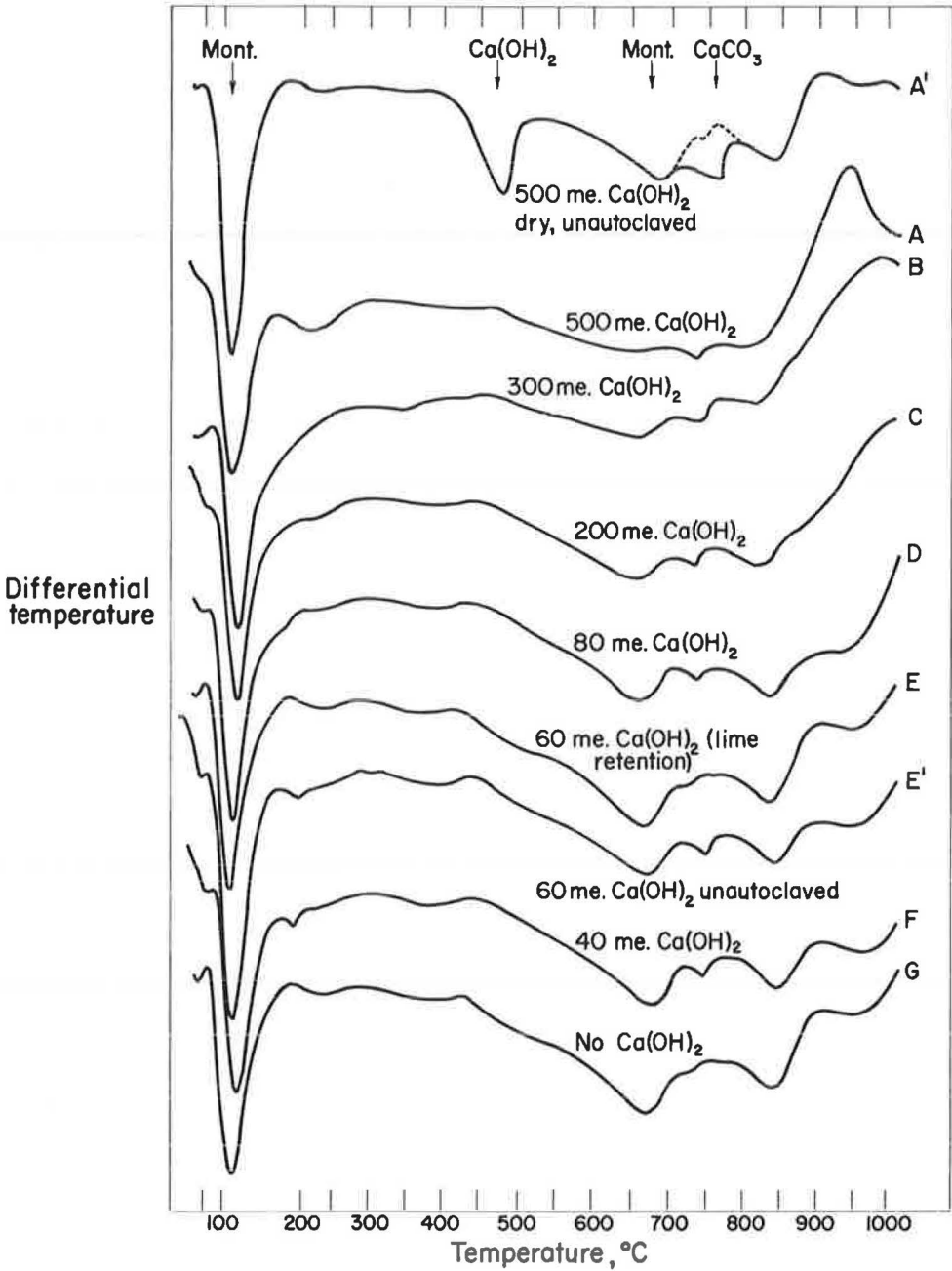


Figure 12. Differential thermal curves for Ca-bentonite treated with various amounts of lime (milliequivalents per 100 g) and autoclaved (126 C and 22 psi pressure for 8 days).

### Soils

Selected tests were utilized with two Ca-montmorillonitic Iowa soils to see if relationships were consistent. Plastic limit and viscosity results from 50 percent soil suspensions indicate that the lime retention point is consistent with the percent clay and Eq. 1 (Figs. 13 and 14).

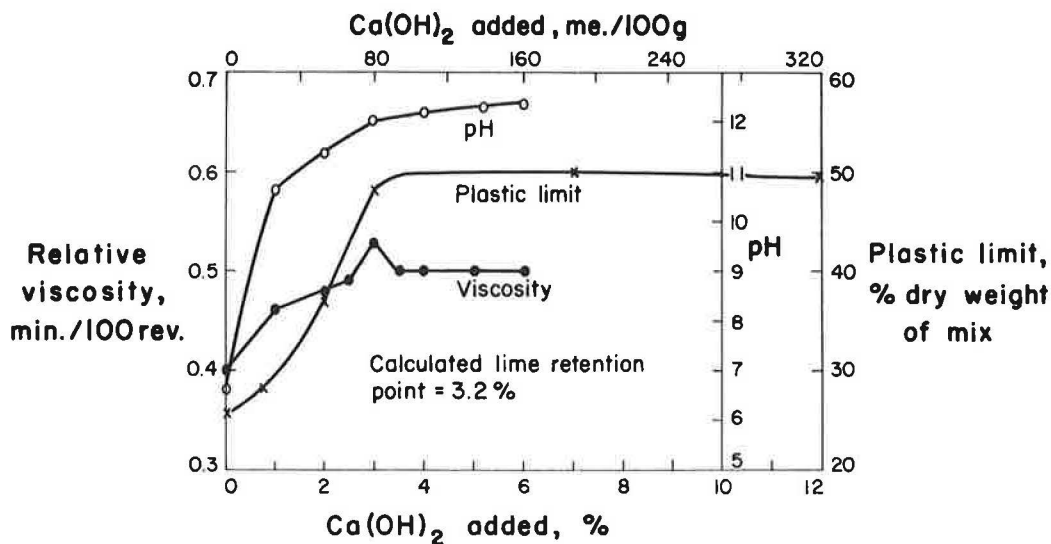


Figure 13. Changes in plastic limit and viscosity (50 percent suspension) of Iowa gum-botil 528-8 with addition of Ca(OH)<sub>2</sub>.

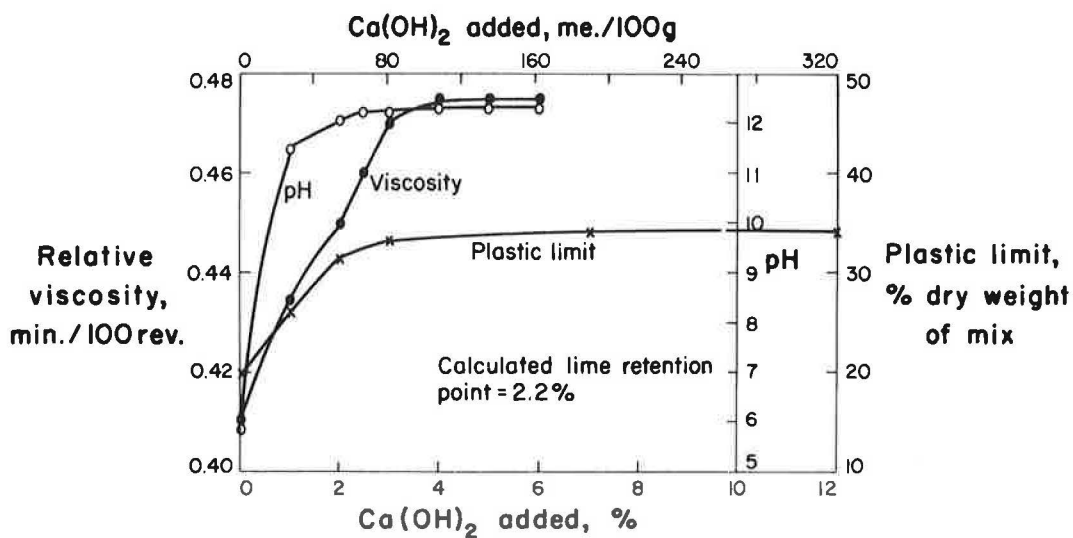


Figure 14. Changes in plastic limit and viscosity (50 percent suspension) of Iowa plastic loess 528-4 with addition of Ca(OH)<sub>2</sub>.

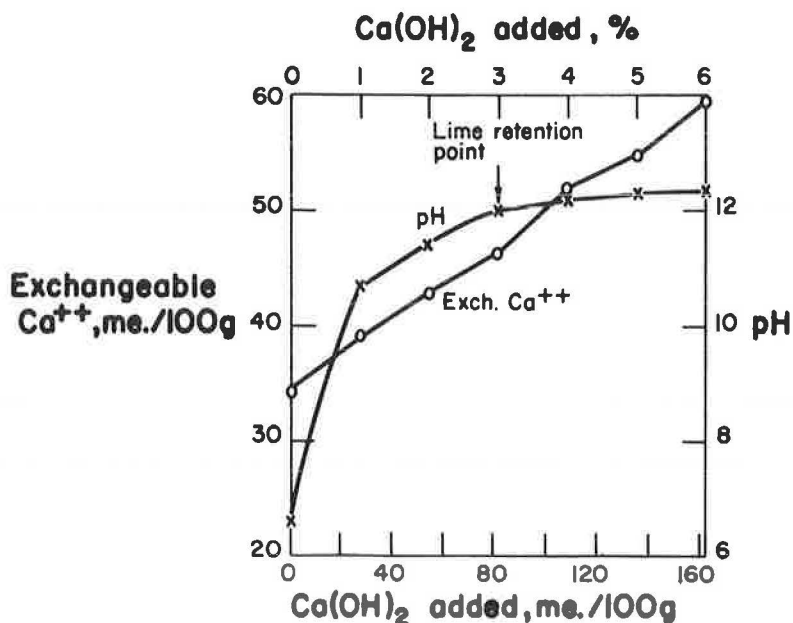


Figure 15. Relationships between  $\text{Ca}(\text{OH})_2$  added, pH, and exchangeable  $\text{Ca}^{++}$  in Iowa gumbotil 528-8.

The viscosity curve of the gumbotil was similar to that of the pure clay systems, forming a maximum at the lime retention point. However, the changes in viscosity in the loess sample were gradual. Although no maximum at the lime retention point could be obtained, the inflection point coincides with that of the plastic limit curve. Furthermore, the viscosity changes with  $\text{Ca}(\text{OH})_2$  in loess were small compared with those obtained with pure clays and gumbotil. These differences probably were caused by the lower percentage of clay fraction (33 percent) in the loess.

Exchangeable  $\text{Ca}^{++}$  data for lime-treated gumbotil indicate that exchangeable  $\text{Ca}^{++}$  increases with  $\text{Ca}(\text{OH})_2$  added and with corresponding increase in pH (Fig. 15). This is in good agreement with data obtained with Ca-bentonite.

#### ANALYSIS

The cation exchange capacity of clays is ordinarily measured at pH 7.0. At higher pH's, more cations are adsorbed, perhaps because of increasing dissociation of weakly acidic  $\text{SiOH-}$  groups exposed on clay crystal edges (10, 11, 12). Below pH 5 the cation exchange capacity is constant (10, 11), usually attributed to isomorphous substitutions in the clay mineral structure.

The pH dependence of the lime retention reaction suggests a close kinship with cation exchange phenomena. In this respect it differs from cation fixation reactions or a "cation crowding" action, and the term "lime retention" is to be preferred. The increased adsorption of  $\text{Ca}^{++}$  to clay surfaces at high pH may be the cause of better bonding between particles, evidenced by bigger flocs, higher suspension viscosity, and higher plastic limit.

The lime-montmorillonite reactions are divided into three levels (Fig. 16). In the first, the total cation exchange is ordinarily measured at pH 7. In the second, the additional lime retention is dependent on an alkaline pH. In the third, after  $\text{Ca}^{++}$ -holding capacities are fulfilled, pozzolanic reactions with additional lime can proceed.

#### CONCLUSIONS

Previous work has shown that the reduction in plasticity, especially the increase in

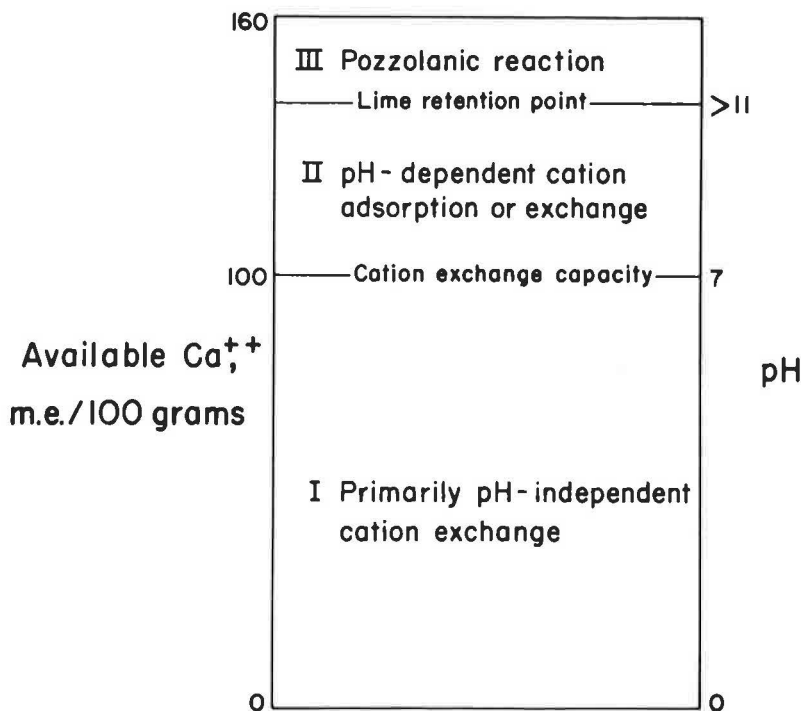


Figure 16. Levels of  $\text{Ca}(\text{OH})_2$  treatment of a montmorillonitic clay.

plastic limit, of a montmorillonitic soil reaches a maximum at a certain percentage of lime, called the lime retention point. Other characteristics of this phenomenon are as follows:

1. The viscosity of slurries and the floc size also reach maxima at the lime retention point.
2. The difference between the lime retention percentages for sodium saturated and calcium saturated montmorillonites equals the cation exchange capacity; i.e., lime first converts the Na-clay to Ca-clay before additional lime is adsorbed to reach the lime retention point.
3. The amount of lime retention increases with setting time, suggesting removal of excess lime from the system by pozzolanic reaction.
4. Lime retention requires an alkaline pH, little or no retention occurs below pH 11.0, and retention is a maximum at about 11.75.  $\text{Ca}(\text{OH})_2$  provides a near optimum ratio of  $\text{Ca}^{++}$  and  $\text{OH}^-$  ions,  $\text{Mg}^{++}$  and  $\text{Na}^+$  ions are relatively ineffective.
5. Lime added below the lime retention point does not reduce autoclaved clay mineral X-ray and DTA peaks; lime in excess of this percentage does. Thus, lime in amounts less than the lime retention point does not engage in pozzolanic reaction. This agrees with earlier compressive strength results.
6. Lime used in the lime retention reaction no longer gives an indication of  $\text{Ca}(\text{OH})_2$  on DTA curves, suggesting use of  $\text{Ca}(\text{OH})_2$  as ions. Argument is made for considering lime retention as a pH-dependent cation adsorption reaction.

#### 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 at their project HR-48. Volclay and Panther Creek clay, respectively, were made available through courtesy of the American Colloid Co., Skokie, Ill.

#### REFERENCES

1. 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).
2. Hogentogler, C. A., "Engineering Properties of Soils." McGraw-Hill (1937).
3. Gallaway, B. M., and Buckman, S. J., "Lime Stabilization of Clay Soil." Texas Eng. Exp. Sta. Bull. 124 (1951).
4. Herrin, M., and Mitchell, H., "Lime Soil Mixtures." HRB Bull. 304, 99-138 (1962).
5. Goldberg, I., and Klein, A., "Some Effects of Treating Expansive Clays with Calcium Hydroxide." Symposium on Exchange Phenomena in Soils, ASTM Special Publication 142 (Discussion) (1952).
6. Johnson, A. L., "Symposium on Exchange Phenomena in Soils." ASTM Special Publication 142 (Discussion) (1952).
7. Hilt, G. H., and Davidson, D. T., "Lime Fixation in Clayey Soils." HRB Bull. 262, 20-32 (1960).
8. de Sousa Pinto, C., Davidson, D. T., and Laguros, J. G., "Effect of Lime on Cement Stabilization of Montmorillonitic Soils." HRB Bull. 353, 64-83 (1962).
9. "Standard Method of Test for Plastic Limit and Plastic Index of Soils." ASTM Designation D424-59 (1961).
10. Schofield, R. K., "The Electric Charges on Clay Particles." Soil and Fertilizers, 2:1-5 (1939).
11. Schofield, R. K., "Effect of pH on Electric Charges Carried by Clay Particles." Jour. of Soil Sci., 1:1-8 (1949).
12. Lin (Ho), Clara, "Sorption Capacities, Ion Saturation and Neutralization Mechanisms of Clays and Soils." Ph. D. thesis, Dept. of Soils, N. C. State College (1959).

### *Appendix A*

#### RELATIVE VISCOSITY WITH THE STORMER PADDLE-TYPE VISCOSIMETER

1. Satisfactory sample sizes for preparation of slurries were found to be as follows:

Na-bentonite	2-3 g
Ca-bentonite	30 g
Soils (33-50 percent Ca-montmorillonite)	50 g

2. Samples plus various measured amounts of reagent grade  $\text{Ca(OH)}_2$  and 100 ml of de-ionized water were placed in 250-ml Erlenmyer flasks, stoppered, and shaken thoroughly by hand or, in the case of Na-bentonite, with an electric stirrer. After 1-hr equilibration with occasional shaking, a suspension is shaken and poured into a 250-ml beaker for viscosity measurement.

3. The relative viscosity was determined with a Stormer viscosimeter using 25-g weight, by counting the exact time required for 100 revolutions for the rotar. The pH reading for each corresponding sample was taken immediately after the viscosity measurement, using a Beckman pH meter.

### *Appendix B*

#### EXCHANGEABLE $\text{Ca}^{++}$ AND $\text{Mg}^{++}$

A sample containing from 1 to 5 meq of exchangeable  $\text{Ca}^{++}$  or  $\text{Ca}^{++} + \text{Mg}^{++}$  is weighed into a Buchner funnel (2 in. in o. d.) fitted with a moist Whatman No. 44 filter paper,

and leached with 80 ml of N KCl (in 10-ml increments). The leachate was made up to 100 ml with de-ionized water, and an aliquot was withdrawn for titration with standard EDTA.

In the  $\text{Ca(OH)}_2$ -treated samples, free  $\text{Ca(OH)}_2$  was first removed by mechanical shaking for 2 hr with excess water which was calculated from the solubility of  $\text{Ca(OH)}_2$  at room temperature and the known quantities of  $\text{Ca(OH)}_2$  added. After samples were filtered and washed with water, the determination of exchangeable  $\text{Ca}^{++}$  can be proceeded as that previously described. However, the time of leaching should be limited to around 15 to 20 min if possible, because prolonged leaching might lead to gradual dissolution of  $\text{CaCO}_3$ .

## *Appendix C*

### MICRODISTILLATION METHOD FOR MEASUREMENT OF CATION EXCHANGE CAPACITY

Cation exchange capacities were determined by ammonium acetate method using Bremner's microdistillation apparatus:

1. A sample containing about 0.2-meq CEC was accurately weighed into a small Gooch crucible fitted with a moist Whatman No. 44 filter paper disc. The sample was leached slowly with 20-ml  $\text{NH}_4\text{AC}$  solution for 20 to 30 min. Excess  $\text{NH}_4\text{AC}$  was then removed by washing three or four times with 75 percent methyl alcohol.
2. The  $\text{NH}_4$ -saturated sample was transferred to a 100-ml distillation flask and steam-distilled for 4 min with about 0.3 g of heavy  $\text{MgO}$  (ignited at 800 C overnight) at a distillation rate of 7.5 ml per min. The distillate was collected in a 50-ml Erlenmeyer flask containing 5-ml boric acid-indicator solution.
3. Solutions in the Erlenmeyer are titrated with standardized 0.01N  $\text{H}_2\text{SO}_4$ .

The boric acid-indicator solution is very sensitive with regard to the change in end point and must be carefully prepared as follows: Dissolve 20 g of reagent grade boric acid in de-ionized water in a 1-l volumetric flask. Dissolve 0.0066 g of methyl red and 0.0132 g of bromocresal green in 225 ml of 95 percent alcohol. Combine the boric acid and the indicator solutions and make approximately 998 ml with de-ionized water. Adjust this mixture with 0.1N  $\text{NaOH}$  (drop by drop) to such an extent that 1 ml of de-ionized water will change 1 ml of the boric acid indicator solution from purplish red to grayish green. Excess addition of  $\text{NaOH}$  must be avoided. Glass- or teflon-stoppered containers should be used because rubber or Tygon tubing will change the color of the solution.

For standardizing the 0.01N  $\text{H}_2\text{SO}_4$ , THAM (i.e., Tris (hydroxy methyl) amino methene) is recommended as the primary standard, using the mixed indicator described.