

# Mechanisms of Soil-Lime Stabilization

## *An Interpretive Review*

SIDNEY DIAMOND and EARL B. KINTER

Materials Division, Office of Research and Development,  
U. S. Bureau of Public Roads

Literature on the mechanisms of the physicochemical and chemical reactions responsible for soil-lime stabilization is critically reviewed. The importance of cation exchange, flocculation, and carbonation in the stabilization processes is discounted. The rapid "ameliorating" effects of lime on the properties of plastic soils are documented from the literature, and the distinction between these short-time effects and the long-time cementitious reactions responsible for the development of strength is noted.

The cation crowding hypothesis is rejected as an explanation of the ameliorating effects. New results summarized show that the cation crowding is more accurately described as physical adsorption of calcium hydroxide on the clay surfaces. The ameliorating effects may be due to very rapid cementation of the primary clay particles at points of contact within the flocs formed on the addition of lime. This rapid cementation is attributed to immediate formation of tetracalcium aluminate hydrate by reaction of  $\text{Al}(\text{OH})_x$  groups at the edges of the clay particles with adsorbed calcium hydroxide on the faces of adjacent planar surfaces. This may be supplemented by somewhat slower formation of tobermorite gel at the same reaction sites.

The nature and properties of the reaction products responsible for slow development of strength in soil-lime systems are discussed. In general, the products formed are usually tobermorite gel and a calcium aluminate hydrate phase distinguished by a 7.6 Å basal spacing that is stable to moderate drying; other compounds formed under special circumstances include tricalcium aluminate hexahydrate and calcium silicate hydrate (I). Phases involving both silica and alumina in distinguishable lattice positions are not usually formed.

The scant information in the literature on the chemical mechanisms involved in the lime-clay mineral transformations is reviewed. Available literature would tend to suggest a "through-solution" mechanism dependent on the rate of dissolution of the clay (or of silica and alumina from the clay), since it is implied that the reaction depends on attainment of a high pH and since addition of sodium hydroxide accelerates strength development. On the other hand, evidence that the reaction proceeds from an initial state of physical adsorption of lime on the surface of the clay would suggest a surface chemical reaction not dependent on prior dissolution of material from the clay.

• **SOIL STABILIZATION** by the addition of quicklime or hydrated lime is an ancient art, successfully adapted in modern times by perceptive engineers of the Texas Highway Department and now widely practiced. It is not, however, the purpose of this report to discuss either the history or the engineering aspects of soil-lime stabilization as currently practiced, but to attempt to bring together and critically evaluate current knowledge of the mechanism or mechanisms responsible for the stabilization process. Once these are well understood, it should be possible to develop practical stabilization procedures on a more rational basis, so as to take full advantage of this useful and cheap chemical agent.

The responses of soil to treatment with lime are complex and often dramatic. A number of explanations have been proposed to account for these unusual responses, including:

1. Cation exchange, i.e., replacement of the exchangeable sodium, magnesium, or other cations previously held by the soil clay by calcium cations derived from the lime;
2. Flocculation of the clay, and consequent increase in effective grain size;
3. Carbonation, i.e., reaction of the lime with carbon dioxide from the atmosphere to form calcium carbonate, which has been said to exert cementing action; and
4. So-called **pozzolanic** reactions with soil constituents to generate new minerals of a cementitious nature.

Of these phenomena, the first three may occur but are inadequate explanations, as we shall attempt to show. The latter explanation is at least partially correct, and in this paper a more specific picture of the nature of these reactions is presented.

The factor of cation exchange has been mentioned by many authors, yet familiarity with the cation exchange properties of soils should have eliminated this as a serious explanation for the stabilizing effects of lime on soil. As soil scientists know, many natural soils are largely calcium saturated. For example, recent work shows that the montmorillonitic soils of the southwestern United States (Grumosols in soil science classification systems), are normally two-thirds to three-quarters calcium saturated (1). Despite this predominance of calcium in the exchange complex, these soils exhibit all the classic deficiencies associated with montmorillonite soils when used as sub-grades and, thus, require stabilization. Although it may be suggested that complete, rather than predominant, calcium saturation is required for stabilization, it has been demonstrated that even when lime is added in very large excess to dilute clay suspensions, under conditions where cation movement is facilitated, complete exchange for sodium does not take place (2). Exchange in comparatively dry compacted soils is undoubtedly less complete.

The concept that flocculation plays a major part in soil-lime stabilization is often voiced, but careful examination of previously known facts shows that this also is an inadequate explanation. Some soils, including most of the red and yellow soils of the southeastern part of the United States, are flocculated in nature, as can be seen by shaking the soil in water and examining the resulting flocs. Despite this natural flocculation these soils are not stable, and they do respond to lime treatment. Furthermore, it is well known that many chemical agents, including various salts, alcohols, acids, and ketones, induce immediate flocculation when mixed with clays, yet are valueless for stabilization. The fact that flocculation of clay occurs as a consequence of the addition of lime is a well-known phenomenon, but the achievement of flocculation is clearly not the mechanism by which lime stabilizes soils.

The hypothesis that soil-lime stabilization depends on the carbonation of the lime to form calcium carbonate can be dismissed by reference to any of a great number of studies in which reaction with atmospheric carbon dioxide was precluded by sealing the samples and in which the characteristic modification of properties and development of strength associated with lime stabilization were observed. As demonstrated by Eades, Nichols, and Grim (3), carbonation does take place in the field, but the strength gain said to accrue by virtue of cementation of soil grains by calcium carbonate has yet to be conclusively demonstrated. It appears that the additional benefit by long-term reaction of uncarbonated lime with the soil itself would far outweigh any such contribution, and carbonation is probably a deleterious rather than a helpful phenomenon in soil stabilization.

Having rejected these inadequate hypotheses, we may now turn our attention to the more nearly adequate, but still incomplete, explanations of the mechanisms of lime-soil interaction that constitute the subject of this paper. Experience indicates that there are at least two distinct stages of reaction involved: (a) the immediate or rapid processes responsible for the "amelioration" of the water-sensitive properties of untreated clay soil, and (b) the slower, long-term reactions resulting in formation of the final cementitious products that are indicated by the gradual development of strength in compacted soil-lime mixtures. These will be discussed separately.

## RAPID AMELIORATION EFFECTS

### Atterberg Limits

It has been shown by many workers (4, 5, 6) that addition of lime to plastic soils results in reduction of the plasticity index (P. I.). Usually an immediate increase in the plastic limit (P. L.) is observed on the addition of lime. The amount of this increase varies directly with the amount of lime added, up to some limiting lime content; further increments of lime usually bring little or no additional increase. The point of inflection of the plot of lime added vs P. L. has been dignified by the appellation "lime fixation point" (7). The implications involved in this term will be discussed later.

The effect on the liquid limit (L. L.) is less easy to summarize, since the published data conflict. Some authors report decreases in L. L. on addition of lime (4, 5), but others report that this parameter may increase substantially (8, 9). Still other workers (6, 10, 11) report that both increases and decreases occur, depending on the individual soil being tested.

These discrepancies require some explanation. It should be pointed out that the L. L. of a clay is far more sensitive to the kind of cation present than is the P. L. Calcium-saturated clays have substantially lower L. L. than the same clays saturated with sodium or certain other cations (12). Since some (although not complete) cation exchange occurs on addition of lime, the effect of the lime may vary, depending on the extent to which preexisting cations other than calcium are exchanged. Studies on clays of unknown original cation status are consequently difficult to interpret.

Clare and Cruchley (8) give data showing a drastic increase in L. L. with added lime for a particular clay which was almost completely calcium saturated in its natural state. They also state that these data are typical for the other clays tested as well; the other clays varied in original calcium saturation from 35 percent upward. We, as well as many others, have observed that mixtures of lime and calcium-saturated clay, stored so as to prevent evaporation or carbonation, assume an increasingly dry appearance; in extreme cases, a free-flowing slurry mixture may stiffen so that it will no longer pour or take the shape of the container. This behavior would, of course, be reflected in an increase in L. L. It seems that, in general, the L. L. will increase on the addition of lime in the absence of a strong specific tendency in the opposite direction resulting from cation exchange effects.

When the L. L. increases on the addition of lime, the increase is not usually as great as the accompanying increase in P. L. Thus, the separate effects on L. L. and P. L. usually combine to yield a rather sharp decrease in P. I. Extra increments of lime beyond some fairly small percentage do not usually result in significant further decreases; in fact, sometimes the trend is reversed and incremental increases in P. I. are found. It should be kept in mind that the P. I. is a composite parameter that may not accurately reflect real changes in the system; for example, equal increases in L. L. and P. L. following a given treatment would be reflected as "no change" in the P. I.

Aging of the system generally results in further changes. Sometimes this effect is small. Lund and Ramsey (6), for example, found that very little change occurred in the Atterberg limit values of soil-lime mixtures after the first hour. However, often substantial time-dependent changes ensue. For example, Wolfe and Allen (13) report substantial increases in P. I. for a number of lime-soil mixtures when cured for 2 days, as compared with samples tested immediately after the addition of lime. For more extended curing periods (7 to 28 days) the effect was reversed, and significant decreases in P. I. in most cases to a nonplastic condition, were recorded.



### Grain-Size Distribution

Changes in the effective grain size distribution (mechanical analysis) are observed almost immediately following the addition of lime to a clay soil. Data secured by conventional sieve and hydrometer analysis show that a major decrease in the content of clay-size particles occurs within the first hour; subsequent results after periods ranging up to 240 days show only small additional changes (6). The new "grains" produced as a result of the lime treatment are mostly sand sized and, although relatively weakly bonded, are for the most part capable of withstanding a 5-min dispersion period in a mechanical mixer (6, 13).

### Moisture-Density Relations

It has been reported by many workers that the density to which a soil can be compacted at a given moisture content is usually reduced significantly on addition of lime, and delay in compaction results in further reduction. The moisture content needed to achieve maximum density for a given compactive effort usually increases, sometimes rather significantly. However, according to results summarized by Herrin and Mitchell (14), lime in excess of a relatively limited amount, on the order of 5 percent by weight of soil, generally produces little additional increase in the optimum moisture requirement.

### Volume Change Effects

Lund and Ramsey (6) report a drastic reduction in the volume change. This effect was observed within the first hour after the addition of lime; with the soil tested, about 3 percent lime sufficed to give the maximum effect. A corresponding immediate increase was noted on the shrinkage limit itself. Similar results were reported by Wolfe and Allen (13).

Mitchell and Hooper (15) reported that lime (in this case, dolomitic lime) markedly reduced the swelling of specimens tested under a modest surcharge pressure. The effect was observed after an aging period of 24 hr. A reduction in expansion pressure on addition of lime was observed by Wolfe and Allen for some soils, but not for others (13).

### Soil Suction

Clare and Cruchley (8) report significant increases in the amount of moisture held against a given suction following the addition of lime.

### Permeability

Although few data are available, the permeability of compacted soil-lime mixtures has been reported to be much less than that of compacted soil alone (13).

These various short-term effects can be regarded as different aspects of the amelioration effect of lime on the properties of clay soils. We will attempt to define exactly what chemical or physico-chemical action is reflected in these sometimes drastic changes.

Considerable evidence seems to point to the conclusion that these rapid responses are not the result of the pozzolanic reactions to which permanent strength gains are attributed. It has been well documented that the development of strength of specimens, particularly after soaking, is a fair index of the amount of cementitious compound formed (16). The experience of many workers, as summarized by Herrin and Mitchell (14), and the results documented by Anday (17) indicate that strength development in soil-lime systems is a comparatively slow process characteristically requiring periods of several weeks to many months at normal temperatures.

As pointed out by Mitchell and Hooper (15), if significant amounts of lime were consumed by permanent cementing reactions at early ages, delay between mixing and compaction should adversely affect the strength of the final product. They found no such effect for delays up to a day, provided all samples were compacted to the same density.



Similarly, if significant permanent cementing were to occur at early ages, subsequent remolding of the specimen should bring about a strong reduction in the ultimate strength developed. Unpublished data by Shepard (18) indicate that remolding after as long as a week of curing following initial compaction has no deleterious effect on the ultimate strength of soil-lime mixtures. In contrast, Shepard found that soil-cement mixtures, in which cementation occurs rapidly on hydration of the cement, did suffer severe reductions in ultimate strength on remolding after a week of curing.

Thus, extensive development of pozzolanic reaction products seems to be ruled out as a mechanism responsible for the rapid amelioration of the properties of plastic soils by lime. What then is the nature of the mechanism responsible for these effects?

Extensive investigations undertaken by workers at Iowa State University (7, 19-23) have led to the previously mentioned concept of the lime fixation point. This was defined as that percentage of lime beyond which additional increments of lime produced no appreciable increase in P. L. It was hypothesized that excess calcium cations, derived from the lime, in some fashion "crowd onto" the clay particles and cause them to become "electrically attracted," the process resulting in flocculation with weak bonds between the flocs. Additional lime, which produces calcium cations in excess of those which could crowd onto the clay, produces no further change in the P. L. Calcium held by the clay in amounts up to the lime fixation point was considered to be immune to further reaction with the clay to form cementitious compounds. The sedimentation velocity of flocs formed by adding lime to a clay suspension reached a maximum near the lime fixation point, indicating that floc size was at a maximum at this point (21).

Ho and Handy (22) cited evidence that calcium was retained by bentonite from lime-bentonite slurries after a very limited washing treatment. The amount of calcium retained increased with increasing percentage of lime in the slurry, and for modest percentages of lime was far more than the normal cation exchange capacity (C. E. C.) of the clay. These writers hypothesized that the calcium in excess of the normal C. E. C. was held at new exchange sites generated at the edges of clay particles by increasing dissociation of acidic  $-\text{Si}(\text{OH})_x$  groups with increasing pH; hence, the term pH-dependent exchange. However, it was noted (without explanation) that the amount of calcium retained continued to increase steadily with increments of lime far beyond the lime fixation point and no break in the curve was evident.

Ho and Handy also studied several additional features of the lime-bentonite system. Small additions of lime (up to about 2.2 percent) were found to increase the relative viscosity of calcium bentonite slurries; however, aging of the samples continually increased the lime content at which maximum relative viscosity was attained. These authors also made differential thermal analyses (DTA) of dried lime-bentonite slurries, and disclosed that samples to which only a small amount of lime had been added failed to generate the normal endothermic response characteristic of the lime.

In another paper, Ho and Handy (23) reported the results of measurements of the zeta potential (a quantity related to the net negative or positive charge carried by the clay particles in dilute suspension) of lime-treated bentonite aged either for several days ("fresh") or for a year ("aged"). Calcium-saturated bentonite had a zeta potential of about -20 millivolts. Small additions of lime caused a slight increase in this value and larger additions generated a modest decrease for both fresh and aged samples. Sodium-saturated bentonite had a zeta potential of about -40 millivolts; additions of lime to this clay up to about 6 percent caused strong proportional reductions to -26 millivolts for the fresh samples and -22 millivolts for the aged samples, and higher additions of lime caused no further change. Ho and Handy presented a detailed analysis of their results which we consider highly speculative. It is sufficient to note at this point that the large effect found for the sodium bentonite was apparently due to the ordinary process of cation exchange of calcium for sodium, and in accord with the earlier results of Prikryl and Esterka (2) this process was not quite complete.

We were far from satisfied that the interpretations of the early ameliorative effects of lime on clay suggested by the Iowa State University workers could be correct in detail. The apparently unlimited crowding of positively charged cations onto the limited external surface of the montmorillonite would appear to be an unlikely phenomenon; if

it were to occur, one would expect that a large decrease and eventual reversal of the negative charge of the clay would take place, due to the limited number of  $-\text{Si}(\text{OH})_x$  groups on the edges of the clay particles that could dissociate to generate negative charges to balance the cation uptake.

We carried out a series of investigations in an attempt to shed more light on these matters. Details of these investigations will be submitted for publication elsewhere, but some of their results can be summarized here.

Measurements were carried out on Wyoming bentonite which had been saturated with calcium cations by standard laboratory procedures and checked for completeness of saturation. Small quantities of the calcium-saturated clay were shaken with a large amount of saturated calcium hydroxide solution for various periods at room temperature, and then separated by centrifugation. The supernatant solutions were recovered and promptly analyzed for calcium content (using versenate titration) and hydroxyl content (by titration against standard acid). The following results were obtained:

1. A very rapid reduction of the concentration of both calcium and hydroxyl ions in the solution was observed.

2. The proportion of the ions remaining in solution was stoichiometric, indicating that equivalent proportions of hydroxyl and calcium ions (two hydroxyl for each calcium) had been taken up by the clay.

3. About 3 percent of lime (by weight of the clay) was found to be adsorbed within the first 5 min, the minimum time in which the manipulations could be performed. This amount corresponds roughly to the lime fixation point of the Iowa State workers.

4. Further sorption continued at a declining rate as long as the experiments were continued (3 wk). At that time the total amount of lime removed from the solution amounted to about 20 percent of the weight of the clay.

5. Washing the centrifugally separated clay with an amount of distilled water equal to the volume of the saturated lime solution originally used resulted in essentially complete removal of the adsorbed lime, if carried out shortly after the onset of the experiment. However, the ratio of hydroxyl to calcium ions removed was slightly less than stoichiometric.

6. After a sample had been in contact with the lime solution for several days and had adsorbed much additional lime, a single wash as outlined removed only part of the lime; subsequent additional washings removed smaller and smaller amounts. The ratio of hydroxyl to calcium ions removed in successive washings declined from values fairly close to stoichiometric (about 1.7) to about 1.

7. In DTA of dried clay which had sorbed about 4 percent of lime from solution (in about an hour of contact), no lime was detected. A mechanical mixture of dry clay with the same amount of dry lime gives a readily detectable endothermic response at  $500^\circ$ , characteristic of crystalline lime.

8. No X-ray diffraction peaks for crystalline calcium hydroxide were observed for the clay recovered from lime solution as mentioned previously; the corresponding dry mixture produced easily detectable peaks under the same diffraction conditions.

9. Measurements of surface charge of the calcium bentonite were carried out on untreated clay and on clay recovered after immersion in saturated lime solution for an hour. The method used was that which Pike and Hubbard used for a similar determination of the surface charge of hydrating cement particles (24). No significant change in negative charge was found.

10. In other experiments, lime was added to suspensions of calcium-saturated bentonite of restricted water content. At lime contents of 4 percent or less by weight of clay, the electrical conductivity of the suspension was found to decrease to very low values in less than 24 hr. This was regarded as an indication that the lime was being rapidly adsorbed, with the consequent decrease in concentration of the lime electrolyte in the pore solution. Removal of some of the pore solution by high-speed centrifugation and subsequent chemical analysis confirmed this interpretation.

These data indicated that the response to lime in clay-water systems of restricted water content was similar to that occurring in dilute suspensions.

No evidence of heat production or removal was found to accompany the addition of lime to calcium bentonite suspensions of restricted water content, in tests carried out over several hours with a moderately sensitive calorimeter. This is a further indication that the lime sorption process is one of physical adsorption rather than chemical reaction.

These results are interpreted to yield a picture of the initial reactions somewhat different from that previously developed elsewhere.

1. Calcium hydroxide is physically adsorbed from solution at a very rapid rate by calcium-saturated clay, and presumably also by clay saturated with other cations. This adsorption is largely reversible at very early stages, but is soon followed by reaction to produce calcium silicate hydrates. The conclusion that lime is physically adsorbed on clay surfaces was also reached by Prikryl and Esterka (2).

2. The adsorption removes calcium ions and hydroxyl ions from solution concurrently, and does not reflect a crowding of cations only onto new exchange sites generated at high pH levels, as previously postulated.

3. Since both ions are sorbed in equivalent amounts (within the limits of the accuracy of the analysis), no significant change occurs in the net negative charge of the clay particles. This does not preclude small changes in the zeta potential after some period of chemical reaction.

4. The amount of calcium and hydroxyl ions sorbed immediately (about 3 percent by weight of clay) would correspond roughly to sorption of a little more than a monomolecular layer of calcium hydroxide on the external surfaces of the clay. This sorption corresponds roughly to the lime fixation point and suggested that the latter represents approximately a monolayer of lime on the external surfaces of the particular clay concerned.

5. The very large amount of slow sorption beyond this value is thought to reflect several additional processes, but principally the slow reaction of adsorbed lime with the clay surfaces to produce calcium silicate and calcium aluminate hydrates. We think that, at least in wet systems, these products spall from the clay surface, thus liberating fresh clay surface for further adsorption and reaction. Physical adsorption of lime onto the newly formed reaction products is also likely. Finally, a slow, restricted entry of lime into the interlayer spaces of the clay may take place.

The observation that adsorption of lime occurs in clay-lime systems does not in itself provide any particular indication of how the clay properties are so drastically changed within a short time after the addition of lime. The mechanics of this process requires further elucidation.

Strong flocculation is commonly observed when lime is added to clay. In general, according to current colloid-chemical concepts (25), clays flocculate on addition of electrolytes because of the modifying effect of the electrolyte on the extension of the electrical double layer from the surfaces of the clay particles. The electrolyte represses the double layer, thus reducing the electrostatic repulsive forces between clay particles. This results in a net attraction, especially between negatively charged faces and positively charged edges of adjacent particles, and a "card-house" or "double-T" structure develops. The flocculated clay is still sensitive to water and, generally speaking, removal of the electrolyte from the pore solution results in a process whereby the double layer again spreads out, the repulsive forces between particles increase, the flocs weaken and are reduced in size, and eventually the system deflocculates.

In our experiments it was noted that removal of lime from the pore solution results in only low concentrations of electrolyte being present after a few hours; yet the initially formed flocs persist and become, if anything, more pronounced and stable with time. Obviously, the properties of the clay are altered more profoundly by lime than by nonreactive electrolytes such as salts.

One of the authors has demonstrated (26) that lime reacts almost instantaneously with hydrous alumina of high surface area to generate a well-crystallized compound, tetracalcium aluminate hydrate,  $C_4AH_{13}$  (in the shorthand notation commonly used for these compounds,  $C = CaO$ ,  $A = Al_2O_3$ ,  $H = H_2O$ ,  $S = SiO_2$ , etc.). This compound is also probably formed on the hydration of  $C_3A$  in portland cement (27). We postulate



that in lime-clay systems a similar immediate reaction takes place between the alumina-bearing edges of the clay particles and the lime adsorbed on the clay surfaces. In particular, we postulate that this reaction occurs at the points of contact between the edges of one particle and the faces of adjacent particles in the card-house structure of the flocs. Calcium silicate hydrate (tobermorite gel) probably forms at these points of contact also, but more slowly, perhaps over a period of some hours. Formation of very small quantities of these cementing products at the points of contact is thought to be sufficient to stabilize the flocs and knit the particles together so that plasticity, shrinkage and swelling, and other normal clay-water interactions are distinctly inhibited. Thus, the clay becomes ameliorated but not really stabilized, since the flocs have not been bound together well enough for the mass to retain any significant strength after soaking. However, the individual particles are cemented together well enough within the flocs to resist dispersion, and the flocs may act as single grains in mechanical analysis (6).

To develop a material capable of holding together and resisting applied loads after soaking, compaction is required to obtain a minimum void volume, and time must be allowed to permit the slow continuing chemical reaction to develop additional cementing products sufficient to fill the voids at least partially.

As shown by Jambor (16), the strength developed in lime-pozzolan systems depends to some extent on the kind of cementing agent formed, but also in great degree on the proportion of void space occupied by the cementing agent—the "gel/space ratio" familiar in portland cement technology.

The formation of calcium aluminate and calcium silicate hydrates at particle contacts very early in the reaction process does not lend itself to easy demonstration, due to the very small amounts of these products involved and the nature of the system. The concept is offered as a working hypothesis consistent with the known properties of the system. Further work is under way to provide additional information in an effort to prove or disprove this hypothesis.

## PRODUCTS OF LONG-TERM REACTION BETWEEN LIME AND CLAY

The reactions occurring over a long period of time and, in the last analysis, responsible for the stabilization of the soil are of at least as much concern as the ameliorating responses just described. Most soils consist largely of uncombined silica and of silicates of various kinds; aluminosilicates usually predominate in the clay fraction. Consequently, it is not surprising that reaction with lime produces compounds falling largely into two classes: hydrated calcium silicates and hydrated calcium aluminates.

Except when formed under hydrothermal conditions, the calcium silicate hydrates are invariably poorly crystallized and difficult to detect. Three such phases are known in the literature: (a) tobermorite gel, also called C-S-H (gel); (b) C-S-H (I); and (c) C-S-H (II). The gel is a high-calcium phase normally generated in, and responsible for, the strength of portland cement concrete. C-S-H (I) has a distinctly lower calcium content, a somewhat different morphology, and is distinguishable by a very strong exothermic peak at about 850 C on DTA. Although C-S-H (I) may be synthesized in a fairly well-crystallized form in the laboratory, the gel phase is invariably more poorly crystallized and has a maximum of only three peaks on X-ray diffraction. C-S-H (II) is a high-calcium phase whose exact properties are open to some doubt. All of these compounds are presumed to have a layer structure similar but not necessarily identical to that of the well-crystallized mineral tobermorite. The latter may be synthesized readily by hydrothermal means, but its occurrence in soil-lime reaction products produced under normal atmospheric conditions is extremely unlikely.

There are several types of calcium aluminate hydrates. The one commonly formed at normal temperatures is a member of the tetracalcium aluminate hydrate group. This group comprises a number of crystalline modifications and partially dehydrated states, as well as phases of the same basic structure but incorporating carbonate groups in place of some of the hydroxyls. The form generally produced by clay-lime reactions is most similar to a phase with the composition  $C_4AH_{12} \cdot CO_2$  and has a

basal spacing of 7.6 Å which remains unchanged on drying. In contrast, pure  $C_4AH_{13}$  has a basal spacing of 7.9 Å when moist, and the spacing diminishes stepwise to about 7.4 Å or less on drying. It is possible that the soil-lime product may incorporate some silicon in isomorphous substitution for aluminum.

Reactions of lime with clay minerals at slightly elevated temperatures generally give rise to a quite different calcium aluminate hydrate,  $C_3AH_6$ . This is a cubic phase with a crystal structure different from that of the tetracalcium aluminate hydrates; it forms preferentially at temperatures above about 30 C and once formed is stable at room temperature. A good recent monograph covering the status of knowledge of both calcium silicate and calcium aluminate hydrates is that edited by Taylor (28).

Goldberg and Klein (29) carried out the first published X-ray study of lime-clay reaction products, but succeeded in detecting only calcium carbonate, which was probably produced during air drying of the sample prior to X-raying. Eades and Grim (30) reacted lime with pure clay minerals at 60 C and found that new minerals formed. Kaolinite so treated yielded peaks for a poorly crystallized calcium silicate hydrate of unspecified type, and a peak at 5.1 Å (and others) which we interpret as being due to  $C_3AH_6$ . Eades and Grim could not detect any new crystalline product of lime-montmorillonite reaction, although it was obvious that reaction had occurred. Illite reacted somewhat, but no positive statement was made as to the nature of the reaction product or products.

Hilt and Davidson (31) examined the product of a long-time reaction of lime and montmorillonite at room temperature, and finally identified it as a  $C_4AH_{13}$  type material. Its properties were consistent with the previously mentioned product having a 7.6 Å spacing. The published X-ray diffractometer traces indicated weak peaks attributable to poorly crystallized calcium silicate hydrates as well. Glenn and Handy (32) studied the products of reaction between several clay minerals and various forms of lime at room temperature, but their results were not completely interpreted. They found in general that poorly crystallized calcium silicate hydrates and the 7.6 Å calcium aluminate hydrate were found in the kaolinite systems; in addition, an unknown 12.6 Å compound was formed when dolomitic lime was used. Montmorillonite yielded both the 7.6 Å calcium aluminate hydrate and materials whose diffraction peaks were ascribed to a more nearly pure  $C_4AH_{13}$  phase.

Glenn and Handy observed no reaction of lime with quartz, and little reaction with muscovite or vermiculite. In contrast, in studies of the products formed in field soil stabilization projects, Eades, Nichols, and Grim (3) found that considerable reaction had occurred in quartz- and mica-bearing soils. When examined under the petrographic microscope, the quartz and mica particles were found to have developed fuzzy outlines, and visible cementing gel was present not only as a coating on the grains but also in cracks within the grains. Examination by X-ray methods disclosed the presence of calcium silicate hydrates as well as of calcium carbonate. The authors did not refer to the possibility that calcium aluminate hydrates might also have formed.

Diamond, White, and Dolch (33) reported that kaolinite and montmorillonite reacted with lime to produce different products under different reaction conditions. At 60 C, both clays produced calcium silicate hydrate classified as C-S-H (I) and the kaolinite produced the cubic  $C_3AH_6$ ; no crystalline calcium aluminate compound was formed from montmorillonite. At lower temperatures the products from both clays were considered to be tobermorite gel and the 7.6 Å calcium aluminate hydrate. Small peaks at about 9 Å were found in the montmorillonite products under both conditions; but they disappeared on washing, and no explanation for their presence could be offered. These authors found that both the tobermorite gel and the 7.6 Å calcium aluminate hydrate product were formed by reaction of lime with mica, illite, and even pyrophyllite. Reaction with quartz generated tobermorite gel, even at 60 C.

Glenn and Handy (34) recently reported further results on long-term studies of reaction products of lime and montmorillonite at room temperature. In general, the formation of tobermorite gel, C-S-H (I),  $C_4AH_{13}$ , and possibly C-S-H (II) were reported. Interestingly enough, both fresh mixtures of clay and lime and mixtures which had been allowed to react at room temperature for several years yielded only well-crystallized tobermorite on hydrothermal treatment. The aluminum present in the



product was thought to be incorporated as an isomorphous replacement for silicon within the tobermorite lattice.

It is noteworthy that in all the studies discussed so far, no quaternary compounds (that is, compounds in the lime-silica-alumina-water system) were reported. Apparently, where separate calcium aluminate phases were not developed, the aluminum present was incorporated isomorphously in the calcium silicate phase. In contrast to these results, Benton (35) reported that reactions of lime with calcined kaolinite yielded the quaternary compound gehlenite hydrate,  $C_2AS_x$ , also called Stratling's compound. This compound was formed in addition to the more usual products, a poorly crystallized calcium silicate hydrate and the 7.6 Å calcium aluminate hydrate.

In a Japanese study (36) the same gehlenite hydrate and the 7.6 Å calcium aluminate hydrate were reported to result from reactions at normal temperatures between lime and Kanto loam soils, which consist mostly of the amorphous clay mineral allophane. At higher temperatures the same soils produced  $C_3AH_6$  and a hydrogarnet quaternary phase instead of these compounds. When gypsum was also included in the treatment of these soils with lime, excellent stabilization results were obtained. In this case, ettringite or so-called cement bacillus, a sulfate-bearing phase formed in hydrating cements, was the major cementing agent formed.

### MECHANISM OF DEVELOPMENT OF CEMENTATION PRODUCTS

The early physico-chemical reactions of lime that produce the amelioration effects on soil clays and the nature of the cementing compounds that produce the final cemented product have been discussed, but little has been said about the mechanics of the chemical and structural transformations that generate the final compounds. Very little is known about the details of the reaction processes involved, and most information is speculative in nature. This lack of knowledge is one of the major gaps in our understanding of the soil-lime system.

Eades and Grim (30) have suggested that with kaolinite, "the reaction seems to take place by lime eating into the kaolinite particles around the edges with a new phase forming around a core of kaolinite." Electron micrographs by Diamond, White and Dolch (33) tend to confirm this idea, in part, since the edges of residual kaolinite particles were ragged and irregular, as if they had been attacked chemically. The probability that partial exfoliation had taken place was also raised by the latter authors, who called attention to the fact that since two distinct crystalline hydration products were produced, a simple topotactic solid-state mechanism was not a reasonable explanation.

Recently Sloan (37) reported an electron-microscope study of the effects of treating kaolinite with sodium hydroxide and with lime in dilute suspensions. He confirmed that under such conditions the primary attack on the kaolinite particles took place at the particle edges. With lime he observed what appeared to be nucleation of a reaction product at or near the edges of the kaolinite particles; however, this product did not appear to be one previously reported to occur in lime-clay reactions, and the exact significance of this observation is uncertain.

With illite and montmorillonite, Eades and Grim concluded: "Following the saturation of the interlayer positions with calcium ions the whole clay mineral structure deteriorates without the formation of substantial new crystalline phases." In contrast, Diamond, White and Dolch reported that new crystalline phases (tobermorite gel and the 7.6 Å calcium aluminate hydrate) were formed from these two minerals and, even in advanced stages of the reaction when most of the clay had been decomposed, the clay still remaining retained its crystallinity almost intact. For example, a 2M illite retained all the X-ray peaks characteristic of this polymorph, and montmorillonite retained its characteristic (060) spacing.

Eades, Nichols, and Grim (3) suggested that a pH high enough to dissolve silica is an essential feature of the process of formation of calcium silicate hydrates by lime-clay reactions; this idea was seconded by Diamond, White and Dolch (33) who envisioned solution from the edges of the clay crystals as a possible mode of reaction. The addition of sodium hydroxide to a lime-soil mixture has been found by several workers



to accelerate strength development (13, 38). Moh (39) bases his explanation of these benefits in both soil-lime and soil-cement systems partly on the hypothesis of an increased rate of solubilization of potentially reactive silica.

These arguments imply that the reaction path proceeds through solution, with silica liberated from the clay reacting with dissolved lime. In contrast our results seem to suggest that reaction proceeds between adsorbed lime and the surface layers of the clay with which it is in contact. Such a mechanism has been proposed to account for the rapid generation of tobermorite gel by lime sorbed on silica gel surfaces at moderately elevated temperatures (40).

It may be that, as seems to be the case in portland cement hydration, both "adsorbed-state" and "through-solution" reactions take place and both contribute to the development of the final product. However, any ultimate resolution of these rather difficult problems must await further intensive experimental work.

### SUMMARY

Among physico-chemical mechanisms commonly suggested as explanations of the stabilizing effects observed in soil-lime stabilization, cation exchange replacement of existing cations by calcium, flocculation, and carbonation have been prominent. Since many soils in need of stabilization are naturally calcium saturated, flocculated, or both, the first two mechanisms can no longer be seriously considered. Since soil-lime systems sealed from contact with carbon dioxide develop the normal indications of stabilized soils, carbonation must also be rejected.

The effects of lime on soils are such that two stages of reaction can be detected: (a) an early stage in which the properties of the plastic soil are greatly ameliorated but little permanent strength is developed, and (b) a subsequent stage marked by the slow development of strength and the accumulation of soil-lime reaction products. Among the effects observed in the first stage are large increases in the P. L., generally leading to a reduction in the P. I.; a sharp reduction in the apparent content of clay size particles as they are bound into flocs stable against the dispersion incident to mechanical analysis; increase in the moisture and the compactive effort required to achieve a given density; and reduction in such parameters as swell pressure, volume change on drying, and permeability. These changes are commonly produced in periods ranging from minutes to a few hours after the addition of lime.

Recent work by various workers has suggested the existence of a lime fixation point, that is, an amount of lime that must be added to a given soil to maximize these effects. This lime was considered to be unavailable for further reaction. The mechanism of the effect was discussed in terms of an apparent crowding of excess calcium cations onto the clay following the addition of lime. This in turn was tentatively attributed to pH-dependent exchange sites originating at the edges of the clay particles.

The results of our recent experimental work contradict these hypotheses. It is shown that the cation crowding effect is, in reality, one of physical adsorption of calcium hydroxide onto the clay surfaces. We postulate that the ameliorative effects are due to almost immediate but limited chemical reaction at the points of contact between the edges and faces of primary clay particles within the flocs formed by the normal electrolyte effect of added lime. This reaction is visualized as the formation of small amounts of tetracalcium aluminate hydrate by reaction of the exposed  $\text{Al}(\text{OH})_x$  groups at the edges of the clay surfaces with lime sorbed on the faces of adjacent surfaces. This immediate reaction is supplemented by somewhat slower reaction of the silica with lime to generate tobermorite gel.

The nature of the compounds held responsible for the slow development of strength in soil-lime systems has been discussed in some detail. The exact products formed vary somewhat with the kind of clay and the reaction conditions, especially temperature. There are commonly at least two phases produced, a calcium silicate hydrate and a calcium aluminate hydrate. The former is usually tobermorite gel; the latter is a well-crystallized hexagonal compound, which is probably an impure (substituted) tetracalcium aluminate hydrate and is characterized by a 7.6 Å basal spacing independent of drying conditions. At temperatures only slightly above normal room temperature

a different calcium aluminate hydrate phase, the cubic tricalcium aluminate hexahydrate, is produced.

It was found that quartz, mica, and other phases considered less reactive than clays may also react under appropriate conditions and give rise to similar cementitious products. Quaternary phases in which silicon and aluminum atoms occur in distinguishable lattice positions are not commonly formed, except when lime reacts with previously calcined clay or with the amorphous clay mineral allophane.

The present lack of detailed knowledge of the mechanisms of the chemical reactions that produce these final cementitious products is discussed. Evidence exists that the reactions are favored by conditions of high pH which would make silica more soluble; addition of sodium hydroxide to lime-clay systems produces significant strength gains at early ages. This implies a mechanism involving reaction of dissolved silica and alumina with calcium ions. On the other hand, evidence that the reaction is preceded by sorption of the calcium hydroxide from solution strongly implies a direct surface reaction with the clay. It may be that both mechanisms are operative.

#### ACKNOWLEDGMENTS

The authors acknowledge with thanks the contributions made by W. C. Ormsby, National Bureau of Standards, and Donald G. Fohs, U. S. Bureau of Public Roads, in discussions of the literature of soil-lime stabilization.

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## *Discussion*

R. L. HANDY, T. DEMIREL, CLARA HO, R. M. NADY, C. G. RUFF, ET AL.,  
Iowa State University, Ames.—We sincerely congratulate the authors for this timely review and skillful appraisal of the mechanisms of soil-lime stabilization. In this discussion we would like to call attention to two statements in the paper.

The point of inflection of the plot of lime added vs P. L. has been dignified by the appellation "lime fixation point."

This is quite correct. However, for reasons of purification we later substituted "lime retention point" for "lime fixation point" (22). The term "fixation" was a rather unfortunate appellation because analogy with  $K^+$  or  $NH_4^+$  fixation implies an irreversible cation adsorption phenomenon. As pointed out by the authors, this is not so; the  $CA(OH)_2$  is readily removable at early ages even though the increase in plastic limit (P. L.) appears to be immediate.

Ho and Handy presented a detailed analysis of their results which we consider highly speculative.

We agree completely. In addition we would paraphrase this with only the names changed, perhaps with "Diamond and Kinter" for "Handy and Ho." Not that we regard speculation as sinful; on the contrary, speculation is high art, vital for exciting resonant vibrations in others and for decreasing free energy of the authors. With this in mind, let us discuss in detail the speculations of Diamond and Kinter, and also include a few from Iowa State University.

The authors' speculation of physical adsorption of lime is not in disagreement with other hypotheses, since all evidence points to physical rather than chemisorption. However, this adsorption should be explained. If it is an ionic adsorption, it should be consistent with double layer theory, since one cannot adsorb 60 meq or more of negative OH ions on 100 g of clay surface without some kind of incentive. Also, the love for  $OH^-$  appears rather special, since other anions (sulfate, chloride, etc.) are rejected, even when in company with calcium. We, therefore, have suggested an ionic adsorption whereby  $OH^-$  and  $Ca^{++}$  ions repress the double layer (ion "crowding"), a widely accepted trend when an electrolyte is added to a clay suspension.

Then, since the lime adsorption reaction is uniquely dependent on pH of the suspension, it would appear that  $OH^-$  ions react at broken bonds or react with  $H^+$  ions of the clay, increasing the negative charge so it can adsorb more calcium in stoichiometric proportion. Actually, the occurrence of a pH-dependent charge was not invented by us especially for this purpose; it is recognized and well established in the literature, colloid chemists preferring to call it "an electrical double layer created by adsorption of potential-determining ions" (25). The amount of charge available is believed to depend on the pH, broken bonds, and the dissociable hydrogen ions available. We may even speculate that with a long enough time and a high enough pH, montmorillonite could even

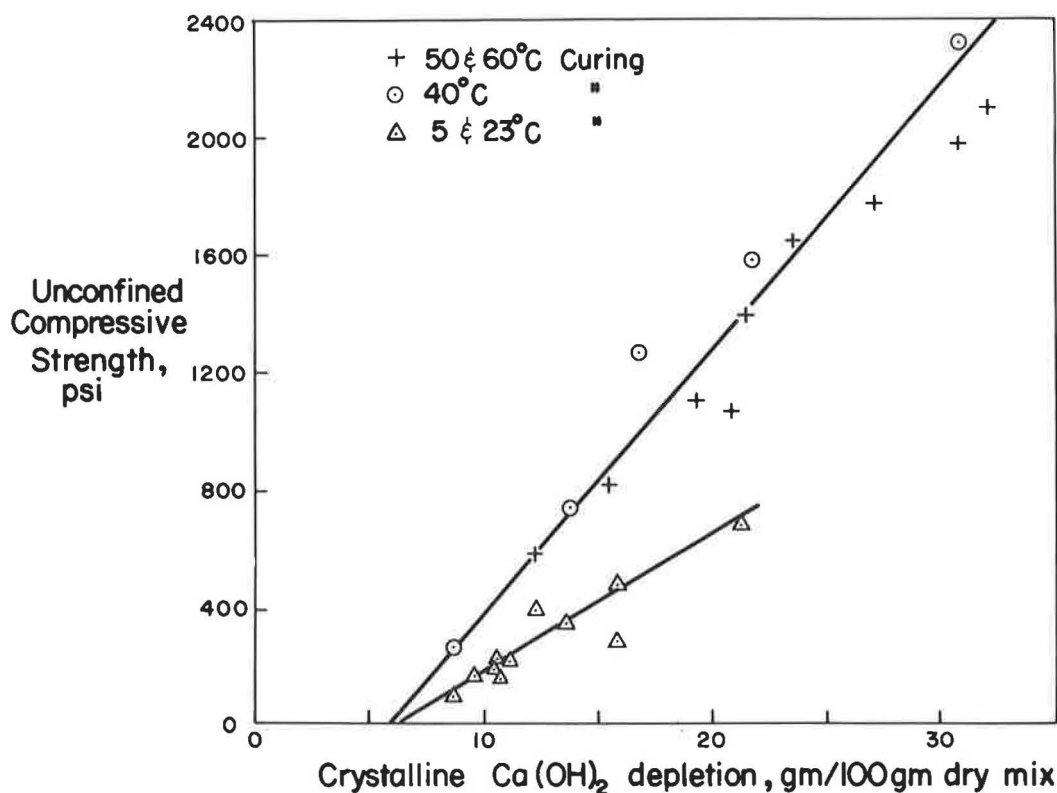


Figure 1. Relation of unconfined strength to  $\text{Ca(OH)}_2$  reacted in lime-Ca-bentonite-water cylinders cured at various times and temperatures.

dehydrolyze from the octahedral layer to contribute as much or more charge than the permanent charge derived from isomorphous substitution. Unfortunately, this is pure speculation, and soil chemists usually work in the pH range from 3 to 8. Recent work on 60 Wisconsin soil samples averaging 13.3 percent clay gave  $\text{C.E.C.} = 30 + 4.4 X$ , where X is the pH; the correlation coefficient was 0.979 (3). That is, increasing the pH 5 points (corresponding to an increase in OH ion concentration of  $10^5$  times) increased the cation exchange capacity 22 meq/100 g. Although applying this relationship to a lime-bentonite mixture involves extrapolation to higher clay content and higher pH range, the prediction is at least in the correct order of magnitude.

Apparently Diamond and Kinter favor molecular rather than ionic adsorption. They also suggest that adsorption results in pozzolanic reaction where the lime coats the clay crystal edges, and cementation of these edges to faces to give a stable floc "card-house" structure, a very attractive and valuable speculation, certain to excite some resonant vibrations. However, we feel that their adsorption mechanism needs additional clarification. From the surface area calculation the authors apparently assume adsorption of a monolayer  $\text{OH}^-$  and  $\text{Ca}^{++}$  ion patchwork in the ionic ratio 2 to 1. Perhaps they will entertain some questions: Why aren't other salts adsorbed (except at high pH)? Why did repeated leaching eventually remove more  $\text{Ca}^{++}$  than  $2(\text{OH})^-$ ? (This is predicted by double layer theory in which OH's react with clay.) What is the shape of the  $\text{Ca(OH)}_2$  molecule, and how does the molecular adsorption pattern fit the clay mineral structure, both on the silica tetrahedral sites and over the holes? Also, if a  $\text{Ca(OH)}_2$  is adsorbed as a monolayer, we would hope that X-ray diffraction will eventually indicate some between the layers, since the same forces of adsorption presumably exist there as on the outside.

The final point we wish to make is the "lime retention" point. Regardless of the details of the adsorption mechanism, the lime retention or adsorption point is a valuable

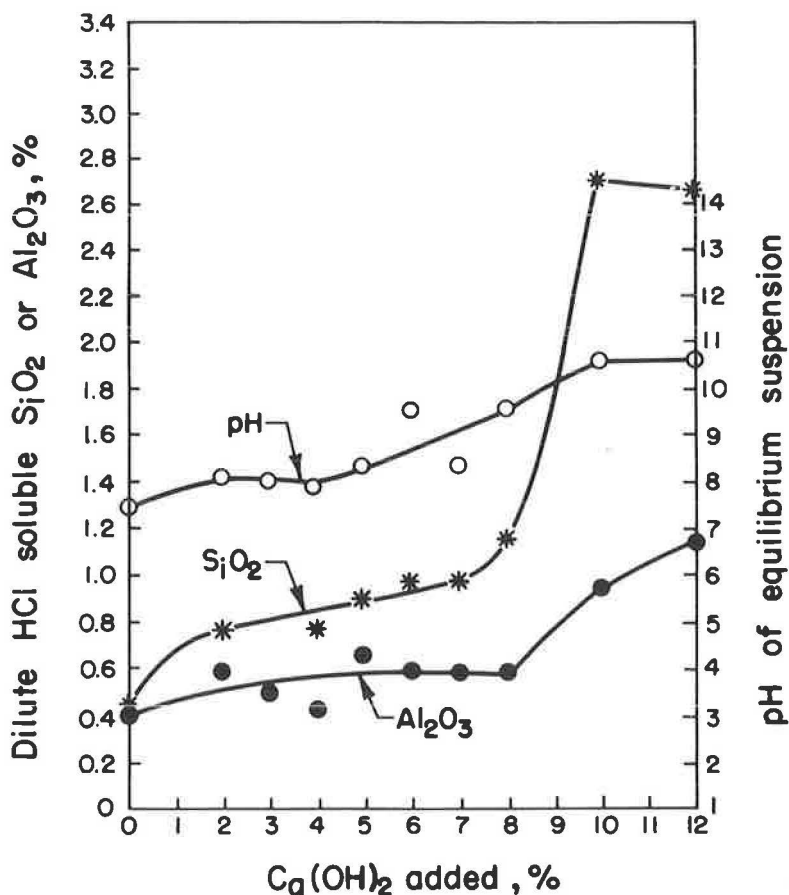


Figure 2. Relations of dilute HCl-soluble  $\text{SiO}_2$ ,  $\text{Al}_2\text{O}_3$  and equilibrium pH of  $\text{Ca}(\text{OH})_2$ -Na-bentonite suspensions cured at room temperature for more than 2 yr.

concept, particularly useful for engineering purposes. To be sure, the lime retention point slowly changes on curing, probably as a result of localized pozzolanic reactions as suggested by Diamond and Kinter. Of more practical importance is that pozzolanic reactions sufficient for cementation do not occur unless lime is added in excess of the lime retention point, readily estimated for the P. L. test. This is further illustrated by new data presented in Figures 1 and 2.

Figure 1 shows the compressive strength of  $\frac{1}{2}$ -in. diameter by 1-in. lime- $\text{Ca}^{++}$ -bentonite-water cylinders vs loss of crystalline lime from the system as measured by X-ray diffraction. Curing was at various times and temperatures. The initial mixes contained 41.6 percent lime, corresponding to a C/S ratio of 1.0 with all lime and clay reacted. Extrapolation of the strength curves to zero strength suggests that about 6 to 7 percent lime was unavailable for much cementation reaction, the strength being about the same as for the pure clay. This lime percentage is somewhat higher than the lime retention point from plasticity tests.

Figure 2 shows silica and alumina soluble by dilute acid treatment of Na-bentonite-lime suspensions which had been sealed and cured at room temperature for over 2 yr. The soluble silica and alumina are assumed to be mainly from pozzolanic reaction products, although as can be seen, about 0.4 percent of each was leached from untreated clay. The amount of reacted silica is approximately doubled by addition of 2 to 7 percent lime, perhaps in part due to glassy or silicious impurities in the bentonite. The



amount of reacted alumina is increased only slightly by addition of 2 to 8 percent lime. However, in the neighborhood of 8 to 9 percent lime, both silica and alumina take a sharp jump, indicative of pozzolanic reaction. It is interesting that in this region pH has stabilized at 10.5, which other evidence suggests is the threshold for pozzolanic reaction (42).

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SIDNEY DIAMOND and EARL B. KINTER, **Closure**—We thank Drs. Handy, Demirel, Ho, Nady, Ruff, et al. of the Iowa State University staff for their "resonant vibrations." Differences in interpretation of data always occur in fields of active scientific investigation, and we are not surprised that our interpretations are not universally accepted.

With regard to specific points raised by the discussors, we would offer the following statements:

1. We concur that the "love (of clay surfaces) for  $\text{OH}^-$  ions appears rather special," not only because other anions are rejected, but also because this love is far less torrid when the  $\text{OH}^-$  ions are accompanied by cations other than calcium. For example, we have immersed calcium-saturated Wyoming bentonite in solutions of sodium hydroxide of the same concentration as saturated lime solutions (0.04 N). Such sodium hydroxide solutions have a pH distinctly higher than those of saturated limewater, approximately 13.6 as compared to 12.4. In a typical experiment in which  $\frac{1}{2}$  g clay was shaken in 100 ml of solution, we found that 48 meq of sodium ions per 100 g of clay were removed from solution by the clay, and 23 meq of calcium ions per 100 g of clay were returned to the solution. Thus, after correcting for cation exchange, an excess of about 25 meq sodium ions per 100 g of clay was adsorbed by the clay, along with approximately the equivalent amount of hydroxyl ions. Thus, in this higher pH system, the clay picked up only about a quarter as many hydroxyls as it does under comparable conditions in saturated lime solutions of lower pH. Obviously, adsorption of  $\text{OH}^-$  ions is not uniquely dependent on the pH of the system, but increases markedly in the specific joint presence of calcium and hydroxyl ions. This is not consistent with the argument advanced by the discussors that the process is one of formation of an augmented double layer created by adsorption of potential-determining (hydroxyl) ions, coupled with indifferent adsorption of accompanying cations.

Prikryl and Esterka (2) performed the reverse experiment, that is, immersion of sodium-saturated bentonite (and other clays) in calcium hydroxide solutions. They found that the ratio of equivalents of Ca adsorbed from solution to equivalents of Na released to solution (which would be 1 if only ordinary cation exchange were taking place) increased uniformly with increasing initial concentration of calcium hydroxide. Again, these results are not explainable on the hypothesis suggested by the discussors, but were taken by Prikryl and Esterka (and by the present writers) to be indicative of physical adsorption of calcium hydroxide.

2. The Wisconsin soil data cited by the discussors (41) yield a statistical prediction of a 22 meq/100 g pH-dependent gain in cation exchange capacity, from pH 7 to pH 12. This is not really of the same magnitude as the amount of lime removed from solution by montmorillonite. Our data show adsorption of the order of 100 meq/100 g clay ( $3\frac{1}{2}$  percent lime by weight of clay) in 10 min, and more than 120 meq/100 g of clay ( $4\frac{1}{2}$  percent lime) in less than an hour. However, the apparent adsorption of sodium hydroxide, cited under point 1 of this closure, is of the same magnitude, and it may well be that adsorption of sodium hydroxide by bentonite is explainable on

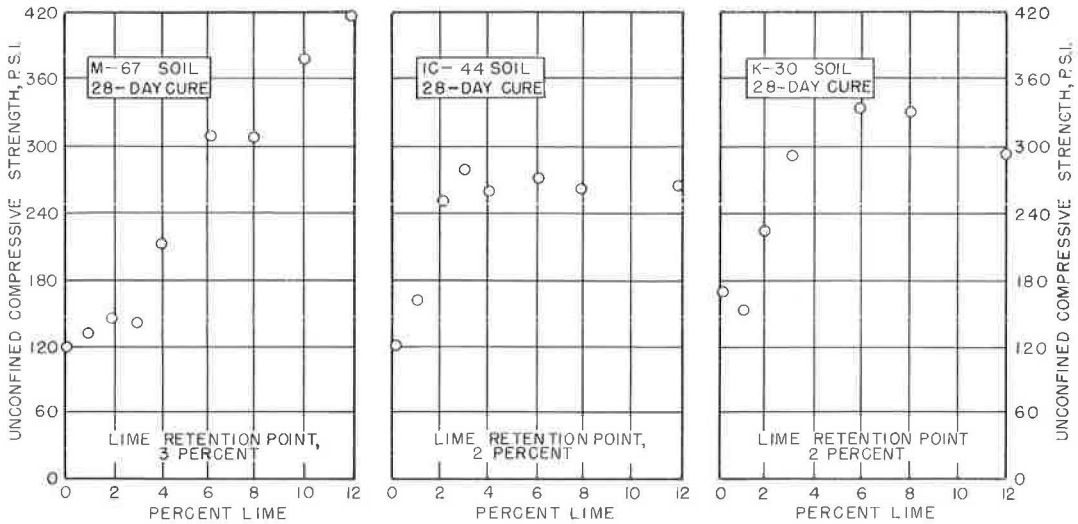


Figure 3. Unconfined compressive strength as function of lime content for a montmorillonite, an illite-chlorite, and a kaolinite soil (7, Figs. 3, 4, 5).

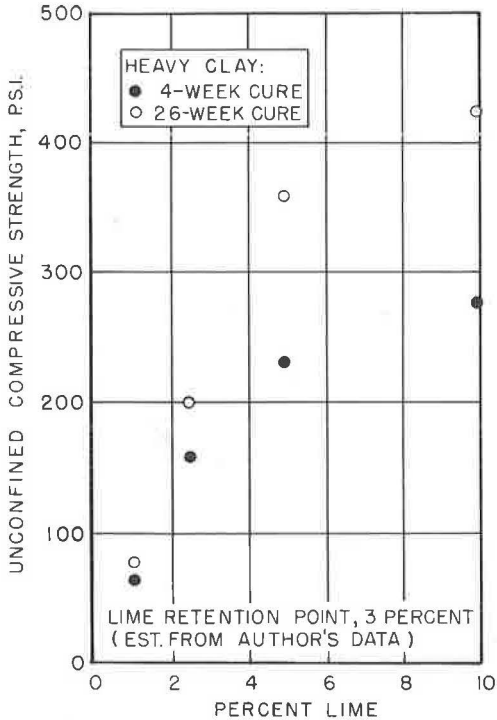


Figure 4. Unconfined compressive strength as function of lime content for heavy clay (London clay) (46, Fig. 1).

the basis of pH-dependent exchange. We do not imply that this is so, only that the possibility exists.

3. In response to the question of why other salts (we take this to mean "other electrolytes") are not adsorbed, we are forced to plead ignorance. Unfortunately, we are not alone, since very little published research has been done on adsorption from solution, and most of this concerns adsorption of organic compounds. A useful discussion of the available literature was given by Brunauer and Copeland (43).

4. With regard to the question of the balance of  $2\text{OH}^-$  and  $\text{Ca}^{++}$  ions released into solution on repeated washing of lime-treated clay, we consider that two factors are responsible. First, during the time of processing, extending over periods of one to several hours, some reaction between the adsorbed lime and the clay has undoubtedly occurred to produce small amounts of tobermorite gel and probably  $\text{C}_4\text{AH}_{13}$ -type compounds. These substances release hydroxyl and calcium ions in ratios less than the 2:1 ratio characteristic of lime. The second cause of the discrepancy is the increasing degree of carbonation one must expect on repeated handling of lime-bearing materials in the atmosphere.

5. The shape of the calcium hydroxide molecule (or ion-triplet) is not, of course,

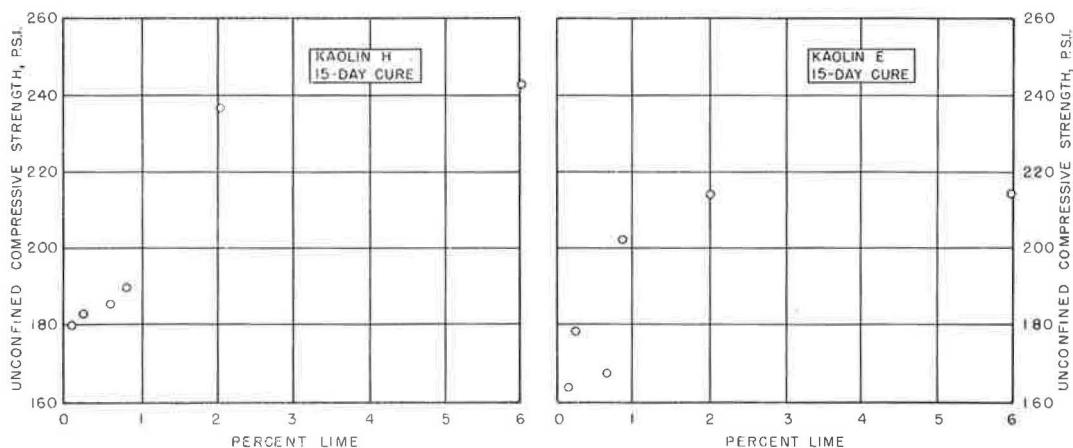


Figure 5. Unconfined compressive strength as function of lime content for two kaolins; lime retention point not available (47, Fig. 7).

amenable to direct determination. Some clue may be obtained from the crystal structure of portlandite, which is hexagonal with  $a = 3.59 \text{ \AA}$  and  $c = 4.91 \text{ \AA}$ . The structure is built up of layers of octahedra, each of which has a calcium ion at its center and a hydroxyl group at each of its six apices; each hydroxyl group is shared by three octahedra (28).

If this arrangement were to be preserved in calcium hydroxide adsorbed on a clay surface, one would expect the thickness of each layer to be about  $4.9 \text{ \AA}$  and the coverage area per molecule to be that of a  $60^\circ$  rhombus with  $3.59 \text{ \AA}$  sides, that is,  $11.2 \text{ \AA}^2$ . In a study of the chemisorption of lime on silica gel, Greenberg (44) used an area of  $25 \text{ \AA}^2$  per  $\text{Ca}(\text{OH})_2$  molecule and found that this gave reasonable results. The present writers have adsorption isotherm data which indicate a coverage area of about  $25 \text{ \AA}^2$  on montmorillonite and a somewhat higher value on kaolinite. Thus, the indications are that adsorbed calcium hydroxide molecules are not as closely packed on the clay surface as they are in crystalline portlandite.

The potential fit of the portlandite structure, that is,  $\text{CaO}_6$  polyhedra, to the hexagonal arrangement of silica tetrahedra that constitutes an idealized representation of most clay mineral surfaces was diagrammed by Taylor and Howison (45), and was shown to be poor, the calcium polyhedra being too large for the hexagonal silica network.

6. Finally, we must address ourselves to the question of the lime retention point. The hypothesis postulates that no significant reaction occurs, and hence, no strength gains accrue, for treatment with lime in amounts less than the lime retention point.

The discussors kindly inclosed two new figures to reinforce this argument. Unfortunately, the present writers have considerable difficulty in appreciating the significance of these figures.

Figure 1 relates strength development to depletion of crystalline lime in systems, all of which contained 41 percent lime by weight of clay. Only very low densities are obtainable in systems with such unusually high lime contents. We suggest that because of these low densities, strength gains obtainable in such systems bear little relationship to those that can be obtained in well-compacted systems of lime contents near the lime retention point, that is, 2 to 4 percent. The lines plotted on this figure intersect the zero strength axis at more than 6 percent lime. Surely the discussors do not mean to imply that a calcium bentonite treated with 6 percent lime and properly compacted and cured will not develop any significant strength.

The relevance of the discussors' Figure 2 to the question at issue is unfortunately not apparent to the present writers.

Data are available from the literature, however, which bear directly on the question of strength gains, and hence reactivity, in soils treated with amounts of lime below the lime retention point. If the concepts of the discussors are correct, a plot of strength vs lime content for properly compacted and cured specimens should show no strength gain below the lime retention point, a distinct inflection at this point, and strength increases from then on as some function of increased lime content. In contradistinction, we suggest that with many soils, small increments of lime less than the lime retention point do in fact add to the strength of such samples as a result of chemical reaction. On this basis, a plot of strength vs lime content should show increases in strength with very small increments of lime starting at or near zero.

Figures 3, 4, and 5 are offered from data in the literature (7, 46, 47). Only the data points are submitted; no trend lines are drawn. Readers of this discussion are invited to draw their own conclusions.

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