Isolation and Investigation of a Lime-Montmorillonite Crystalline Reaction Product

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During previous research by the writers it was noted that mixes of lime and a soil rich in montmorillonitic clay mixed with water above the liquid limit would within several days apparently be dried below the liquid limit with no loss in weight. To determine what was occurring, a portion of this sample was subjected to X-ray diffractometer analysis. Strong indications of a new reaction product were observed but the product could not be found under the microscope.

The object of this paper is to investigate one phase of the mechanisms producing cementation by attempting to isolate and determine the properties of a crystalline reaction product associated with the action of lime with clay.

From the results obtained in this research, other studies have developed in exploring additional crystalline products and are now being pursued at the Iowa Engineering Experiment Station Soil Research Laboratory. When this research is completed and the information is evaluated it is expected that the relationships involved in the formation of new products and the breakdown of the original clay lattice can be determined.

The research undertaken was (a) to investigate various lime-soil-water systems varying each of the three parameters one at a time to determine the best phase relationships for growing euhedral crystals of sufficient size to be observed under the microscope, (b) to isolate these crystals, and (c) to determine their physical and chemical properties.

The systems investigations were accomplished by preparing a large number of mixtures and allowing them to cure for periods from two days to eight months before examination. Isolating the crystals was done under the microscope, and the determination of their properties was undertaken primarily by microscopic and X-ray methods.

MATERIALS AND EQUIPMENT

Soils

Five soils were used in this investigation. The choice of these soils was based on the type, purity, and amount of the principal clay mineral present and the availability of the soil. Each of these soils is identified by a letter designating the principal clay mineral and a number indicating the percentage content of the soil less than 2 microns in diameter. For example, the designation, M-75, indicates a soil containing montmorillonite as the principal clay mineral with 75 percent of this soil less than 2 microns in effective diameter.

The locations from which these soil samples were taken and other pertinent information appear in Table 1. Table 2 gives the physical and chemical properties of these soils.

Clays

Two different clays were used, one a bentonite and the other a kaolinite. These particular clays were selected because they contained only small amounts of impurities. Information concerning them is given in Tables 1 and 2.
Lime

Reagent grade calcitic hydrated lime, Ca(OH)$_2$, was used to minimize compositional variables. Individual 1-lb bottles of lime were kept sealed until immediately before use to prevent carbonation of the lime by the carbon dioxide in the air.

Fly Ash

Fly ash is "the finely divided residue that results from the combustion of ground or powdered coal and is transported from the boiler by flue gasses." The fly ash used in

<table>
<thead>
<tr>
<th>Sample</th>
<th>Location</th>
<th>Classification</th>
<th>Soil Series and Horizon</th>
<th>Sampling Depth (in.)</th>
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<tbody>
<tr>
<td>M-67</td>
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<td>Post Kansan paleosol</td>
<td>Mahaska, fossil B horizon</td>
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<td>Coastal plane deposit, largely deltaic</td>
<td>Lake Charles, probably B horizon</td>
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<td>Monroe County, Michigan</td>
<td>Probably Wisconsin-age glacial till</td>
<td>Unknown series, probably C horizon</td>
<td>Unknown</td>
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<td>K-30</td>
<td>Durham County, North Carolina</td>
<td>Residual soil over medium-grained biotite granite</td>
<td>Durham, B horizon</td>
<td>24 in. below bottom of A horizon 120-216</td>
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<td>Bento-</td>
<td>Otay, California</td>
<td>Pliocene age transported altered ash</td>
<td>San Diego formation</td>
<td></td>
</tr>
<tr>
<td>nite</td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>Kaolin-</td>
<td>Bath, South Carolina</td>
<td>Cretaceous age</td>
<td>Upper Hamburg formation</td>
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</table>

this study was collected by a Cottrell precipitator at the St. Clair Power Plant of the Detroit Edison Co. in Detroit, Michigan.

Optical Equipment

Microscope. — A Bausch and Lomb binocular microscope was used for general investigations of samples. With this instrument a maximum magnification of 90 times is obtained.

A Leitz research model petrographic microscope was used in examining the crystals to determine their index of refraction, interference figure, and optic sign.

X-Ray Equipment

Diffractometer. — The General Electric XRD-5 diffractometer was used for general investigations of samples for the presence of crystalline reaction products.

Debye-Scherrer Camera. — The Debye-Scherrer camera was used to determine lattice constants. The camera is 57.5 mm in diameter and 70 mm in length and is manufactured by Siemens and Halske Aktiengesellschaft, Karlsruhe, Germany. The film measuring device is made by the same company and permits an accuracy of linear measurement of ± 0.01 mm.

Weissenberg Camera. — The Weissenberg apparatus used in this study was manufac-
tured by Otto von der Heyde Co. in Newton Highland, Mass. It was used first to obtain rotation pictures of a single crystal. Following this, Weissenberg photographs were taken to index the reflections and to aid in determining the space group to which the crystal belongs.

**MIXTURE PREPARATIONS AND INVESTIGATIONS**

**Preliminary Work**

The first indication of the presence of reaction products was found on subjecting

<table>
<thead>
<tr>
<th>TABLE 2</th>
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<tr>
<td><strong>PROPERTIES OF SOILS AND CLAY</strong></td>
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<tr>
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<td>Sand (2-0.074mm)</td>
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<tr>
<td>Silt (74-5μ)</td>
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<td>Clay (&lt; 5 μ)</td>
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<td>Clay (&lt; 2 μ)</td>
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<tr>
<td>Physical properties</td>
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<tr>
<td>Liquid limit, %</td>
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<tr>
<td>Plastic limit, %</td>
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<tr>
<td>Chemical properties</td>
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<tr>
<td>pH</td>
</tr>
<tr>
<td>C.E.C. (soil passing No. 10 sieve, me/100gm)</td>
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<td>C.E.C. (soil passing No. 40 sieve, mc/100gm)</td>
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<tr>
<td>Carbonates, %</td>
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<td>BPR(AASHO)</td>
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<td>6(20)</td>
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</table>

aTextural gradation tests were performed only on the soil fraction passing the No. 10 sieve. All soils used contained less than 5 percent gravel.
bSymbols are M-montmorillonite, I-illite, C-chlorite, and K-kaolinite. Determinations were made by X-ray diffraction analysis.
cU.S.D.A. textural classification was used.

mixtures of soil M-67, 12 percent lime, and water (above the liquid limit), which had been prepared for the determination of liquid limits, to X-ray diffractometer analysis. The results of this analysis showed new X-ray "peaks" occurring at 8.11 and 7.60 Angstroms. However, in material from 2- by 2-in. specimens compacted at optimum moisture content no such peaks were observable.

Petrographic microscope examinations of the liquid limit mixtures were attempted to isolate the reaction products formed, but no new substances were observed. It then
became the object of this phase of the research to attempt to grow euhedral crystals of these reaction products of at least microscopic size and determine their properties. To accomplish this, various phase relationships were investigated empirically to attempt to produce recognizable crystals.

**Trial Mixtures—Lime-Water-Soil Systems**

**Water as the Variable.**—That the clay fraction of soil M-67 was the actively participating part of the soil in the reaction with lime appeared to be a reasonable assumption. Therefore soil M-67 was shaken through a 325-mesh sieve to obtain the finest fraction of the soil possible through purely mechanical separation. To obtain the most representative sample possible the sieve pan was emptied often and the material remaining on the 325 sieve was continually repulverized. This process was repeated until only a negligible amount of soil passed through the sieve during a 30-min period. Washing the material through the sieve was not attempted in order to avoid any process which might change the nature of the clay before being mixed with lime.

This material was then mixed with 20 percent lime by weight of oven dry soil, and distilled water was added in amounts of 110, 100, 90, 80, 70, 60, 50, 40, 30, and 20 percent by dry weight of soil plus lime. The materials were mixed in soft plastic containers. After thorough mixing the containers were covered with snap-type lids and placed in a controlled temperature-humidity room (70°F and 95 percent relative humidity).

After 30 days the containers were removed and a sample of the mixture from each was subjected to X-ray diffractometer analysis, the results of which appear in Figure 1. Because the mixtures were smoothed into the sample holders by longitudinal strokes with a glass slide, preferred orientation of the particles was attained. From the diffractometer traces it is evident that the reaction products were present in greater quantities at high moisture contents. At moisture contents below 40 percent the product peaks almost disappear, which explains why specimens compacted at optimum moisture give no indication of these reaction products when subjected to X-ray analysis.

Two peaks are evident in Figure 1. The one at 8.11 Å is the second order basal reflection from montmorillonite sharpened considerably by the action of absorbed calcium and reaches maximum height at higher moisture contents. The 7.59 Å peak is that of a crystalline reaction product and is discussed in more detail later.

**Lime as the Variable.**—Using the relation that mixtures should be of high moisture content, the effect of varying the amounts of lime was investigated at a constant moisture content of 105 percent. Lime was mixed with soil M-67 in quantities of 5, 10, 15, 20, 25, 30, and 50 percent by weight of dry soil. X-ray diffractometer traces were run on these mixtures after 30 days moist curing. It was found that the height of the new peaks grew successively larger as the percentage of lime was increased to 20 percent, and above this the height remained relatively constant, whereas the height of the residual calcium hydroxide peak increased. Thus it appeared that for a 30-day period the optimum lime content was about 20 percent for this soil.

Under the microscope, the same extremely small euhedral crystals were observed scattered through the matrix in those samples containing 10 percent lime or more.

**Soil as the Variable.**—Other soils were also investigated as to their reaction with lime. These soils included M-51, IC-44, IC-41 and K-30. Of these only the montmor-
illonite soil M-51 showed any significant height of new peaks. Soil K-30 gave a slight indication and the others none at all. However, these mixtures were allowed to cure for only 30 days. As will be seen later, it would be advantageous to let them cure for six months and then examine them by X-ray diffraction.

![Diagram](image)

**Figure 1.** Diffractometer charts, mixtures of soil M-67, lime, and variable water after curing for 30 days.

**Trial Mixtures—Lime-Water-Bentonite Investigation**

Because the main component in soil M-67 is montmorillonite clay, and because it is the clay fraction which is reacting with the lime, it appeared logical that better re-
suits might be obtained by mixing a bentonite with lime. For this purpose, a bentonite from Otay, California, was selected because of the low amount of impurities it contains. Because the amount of montmorillonite was increased, the amount of lime added was also increased to 40 percent by dry weight of bentonite. Water was added in the amount of 110 percent by dry weight of bentonite plus lime. Several samples were made and one was tested after 30 days moist curing. The results of the X-ray analysis on this sample were disappointing in that only a small peak appeared at the expected interplanar spacing and no crystals could be located with the microscope. The other samples were allowed to remain in the humidity room for seven months before being tested.

When, after seven months, they were examined under the microscope, crystals which were large in comparison with those obtained previously were found in comparative abundance. The larger ones were about 500 μ across the flats by 20 μ thick. From these the size graded down to submicroscopic. A microscopic photograph of this crystal appears in Figure 2, A.

Because crystal formation was so much more rapid in soil M-67 than in the bentonite, the soil montmorillonite must be either less well crystallized or else the soil must contain ions which act as accelerators for the reaction.

Trial Mixtures—Lime-Water-Fly Ash Investigation

Because fly ash is well known for its pozzolanic properties and because it has been used with lime in soil stabilization, a mixture of fly ash plus 30 percent lime plus 100 percent water was placed in the humidity room. After seven months curing it was removed and investigated under the microscope. Large euhedral crystals had been formed throughout the mixture with similar geometry to those from the bentonite. A microscopic photograph of these crystals is reproduced in Figure 2, B.

The 7.59 Å basal spacing was observed, but a Debye-Scherrer photograph was not made for several months. After several months, X-ray analysis showed that the substance had become amorphous, whereas those crystals produced from bentonite retained their crystallinity.

RESULTS

Optical Properties

Crystal Selection.—Under the binocular microscope a search was made for several
of the largest perfect single crystals in the bentonite sample. These crystals were carefully removed from the matrix and placed on a glass slide. Here they were cleaned of all adhering fragments by means of a single hair. They were then transferred to a second slide and a cover glass was placed over them for examination under the petrographic microscope. Doubly polarized light was used to determine which of the crystals selected were, in fact, perfect and free from inclusions, twinning, and intergrowths.

Index of Refraction. — Those crystals determined to be acceptable were transferred to individual slides for determination of the refractive index by the method of central illumination. The crystals were mounted in various immersion media of known refractive index and examined under the microscope. By bracketing the media used, one was found which coincided almost exactly with the refractive index of the crystal; that is, no reflection or refraction occurred at the boundary between the crystal and the immersion media. By this means the index of refraction of the ordinary ray was determined to be between 1.545 and 1.550. Because of the extreme thinness of the crystals, the index of refraction perpendicular to this direction was not determined exactly; however, it was considerably less.

Interference Figure. — A crystal was mounted on a slide so that the basal pinacoid was perpendicular to the axis of the scope and was viewed under convergent doubly polarized light. On inserting the Bertrand lens an axial cross appeared. Therefore, the crystal is uniaxial and must be either in the hexagonal or tetragonal system. No birefringence was observed with the crystal in this position. However, as soon as the pinacoidal face was inclined, marked birefringent colors appeared.

Optic Sign. —A gypsum plate was inserted in the slot above the objective lens. A lens-shaped blue color appeared in the quadrants perpendicular to the direction of the slow ray in the plate thus determining the optic sign to be negative.

Physical Properties

Geometry. — In plane polarized light the crystals were transparent and colorless, platy, and hexagonally shaped with beveling observed on the edges. A measurement of the hexagonal interior angles showed them to be exactly 60 deg.

Specific Gravity. — The heavy liquid method was used to determine the specific gravity of the crystals. In this method the crystal is immersed in a liquid of known density. If the crystal is denser than the liquid it will sink to the bottom; if less dense it will float. At some density of the liquid the crystal will neither sink nor float but will be suspended in the liquid. The density of the liquid and the crystal are then the same.

In this study, mixtures of bromoform (g = 2.890) and carbon tetrachloride (g = 1.595) were varied to bracket the density of the crystal. Near the density of the crystals the mixture was varied in intervals of 0.005 gm/ml. A 5-ml sample was removed by a pipette at each point and weighed on an analytical balance to determine the exact density of the mixture. All of the crystals sank to the bottom at a liquid density of 2.060 and all were floating at 2.080 gm/ml; at intermediate densities crystals were observed in all three positions, floating, suspended, and on the bottom, establishing the specific gravity of the crystals at 2.07 ± 0.01.

X-Ray Investigations

Rotating Crystal Cylindrical Camera. — A single crystal free from inclusions was selected and was mounted on a short fiber of glass wool with Ducot cement thinned with amyl acetate in such a manner that the pinacoid (0001) was perpendicular to the axis of the glass wool fiber. The fiber was attached to a thin glass rod and the assembly was then inserted into the head of a two-circle goniometer which, in turn, was attached to the rotating spindle of the camera. The crystal was first aligned optically and then brought into exact alignment by X-ray methods.

After alignment was completed, a 15-hr exposure was taken. The diffracted rays are recorded on a cylindrical film whose axis is parallel and concentric with the rotation axis. The spots on the film formed by the diffracted rays will produce a two-dimensional pattern following a characteristic geometry. A print from this film is shown in Figure 3.
The Bragg angle $\theta$ was found by measuring the $x$ and $y$ coordinates of each spot on the film and using the relationship

$$\cos 2\theta = \cos \tau \cos x$$

(1)

in which

$\tau = 2x$;  
$x = \cotan 2y/D$; and  
$D$ = camera diameter,  
in millimeters.

Then the interplanar spacing is

$$d = \frac{n\lambda}{2 \sin \theta}$$

(2)

in which

$\lambda$ is the wavelength of copper $K\alpha$ radiation.

The $d$-spacings and intensities for all spots observed on the film are tabulated in columns 1 and 2 of Table 3. Because of the size of the spots these $d$-spacings are not so accurate as those found by other methods.

Weissenberg Method. — The rotating crystal method has several rather serious limitations. A superposition of several reflections occurs causing difficulty in unequivocally indexing the reflections and determining their intensities. The Weissenberg method solves this difficulty by translating the film in a direction parallel to the rotation axis at a rate proportional to the angular rotation of the crystal. So that only one layer line at a time will be recorded, the diffraction cone of that layer is isolated by surrounding the crystal with a closed hollow metal cylinder containing a circular slit through which the desired layer line cone is permitted to emerge.

The equi-inclination Weissenberg method was used in which

$$\mu = -\nu$$

(3)

in which

$\mu$ = the complement of the angle between the direct beam and the lattice rows,  
and  
$\nu$ = the complement of the semi-opening angle of the diffracted cone.

In this method any central layer line projects on the $n$-level Weissenberg photograph as a straight line of slope 2 because this method brings the crystal rotation axis exactly on the circumference of the reflecting circle. Non-central lattice lines project as ovals, the ovals assuming the same geometric pattern for each level. By combining two of these patterns separated 90 deg from each other, a template may be constructed permitting indexing of the reflections directly.

Indexing of Reflections. — Weissenberg photographs were taken of each layer line from 0 to 26. Prints of the zero level and the twentieth level are reproduced in Figures 4 and 5. Each of the 26 levels were indexed by means of the template discussed earlier and the results are tabulated in column 3 of Table 3.

Inasmuch as the central layer lines occurred at 60-deg intervals, the crystal system was confirmed as being hexagonal. Also by noting the Weissenberg projections of chains of diamond-shaped cells which occur along the position-symmetry lines of the
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<thead>
<tr>
<th>Single x-tal Rotation</th>
<th>Hex hkl</th>
<th>Rhom hkl</th>
<th>Powder Camera&lt;sup&gt;a&lt;/sup&gt;</th>
<th>Back Refl. Weissengberg</th>
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<td>d (Å)</td>
<td>I</td>
<td>d (Å)</td>
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</tr>
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<sup>a</sup>In addition to the powder camera data indicated, lines were also observed at 8.39, 5.52, 4.45, and 3.10 Ångstroms, which were identified as montmorillonite.

<sup>b</sup>Other indices observed on Weissenberg photographs in addition to the one listed, xez, when z ≠ 3n, are xz, xez, Oez, Ox2, O3, and xez2.
Weissenberg photographs, it is obvious that the crystals are in the rhombohedral division of the hexagonal system.

To convert the hexagonal indices given in column 3 of Table 3 to rhombohedral indices, the relationship given in Eqs. 4, 5, and 6 were used.

\[ h_r = \frac{1}{3} (2h + k + l) \]
\[ k_r = \frac{1}{3} (-h + k + 1) \]
\[ l_r = \frac{1}{3} (-h - 2k + 1) \]

The results of this conversion appear in column 4 of Table 3.

**Hexagonal Cell Lattice Constants.**—To determine precise lattice constants, chromium K\(_\alpha\) radiation was used to move some of the lines observed with copper radiation into the back reflection region of the powder camera film. A fine collimator (0.7 mm) was used with a helium atmosphere and Straumanis film loading. Temperature during the exposure was maintained at 29 C.

The \(a_0\) and \(c_0\) constants were computed from the measured d-spacings corrected for film shrinkage and were extrapolated against the function

\[ \frac{\cos^2 \theta}{\sin \theta} + \frac{\cos \theta}{\theta} \]

Table 4 gives the \(a_0\) and \(c_0\) constants for the reflections listed which represent results of the ninth a/c approximation and recalculation. Because there was no slope to the \(\theta\) plot, the average value of the computed constants may be used.

The standard deviation of the values in Table 4 is 0.025 which gives 90 percent confidence limits for \(c_0\) of 46.654 ± 0.018.

A further check on the \(a_0\) lattice constant was made by the back reflection Weissen-
berg method data for which appears in column 7 of Table 3. Extrapolation of this data against the \( \theta \) function, Eq. 7, gives an \( a_0 = 5.756 \text{ Å} \). Because the line breadth on the

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\[ a/c = 0.12335 \quad \text{Av. 46.654} \]

TABLE 4

HEXAGONAL LATTIC CONSTANTS, Cr K\( \alpha \) RADIATION

powder camera film is finer than that of the spots on the Weissenberg film, more accurate determinations are possible using the powder camera.

A rough check on the \( c_0 \) spacing is possible by using the single crystal rotation photograph. The layer line spacing, \( \xi_n \), of the reciprocal lattice is given by

\[ \xi_n = \frac{y_n}{\sqrt{r_f^2 + y_n^2}} \]  

in which

\( r_f = \) film radius, and

\( y_n = \) distance from film center to any given layer line.

To find the identity period along the rotation axis (c) of the crystal, Eq. 9 is used.

\[ c_0 = \frac{n\lambda}{\xi_n} \]  

The average of the \( \xi_n \)'s for the first 16 layer lines was used and a value for \( c_0 \) of 46.72 Å was computed. Because film shrinkage could not be computed for this film the \( c_0 \) spacing compares favorably with that given in Table 4.

Hexagonal Cell Volume. —The volume of the hexagonal unit cell is given by

\[ V = \frac{1}{2} \sqrt{3} a_0^2 c \]  

Because \( a_0 = 5.7550 \text{ Å} \) and \( c_0 = 46.654 \text{ Å} \), then the volume is \( 1338.17 \text{ Å}^3 \) or \( 133.817 \times 10^{-23} \text{ cm}^3 \).

Rhombohedral Cell Lattice Constants.—Designating the hexagonal lattice constants as \( a_H \) and \( c_H \), the corresponding rhombohedral constants are

\[ a_R = \frac{1}{2} \sqrt{3a_H^2 + C_H^2} \]

\[ \sin \frac{\alpha}{2} = \frac{3a_H}{2 \sqrt{3a_H^2 + C_H^2}} \]

and \( a_R = 15.902 \text{ Å} \) and \( \alpha = 20.850^\circ \).

Space Group Determination.—It has already been shown that the crystal belongs to the rhombohedral division of the hexagonal system. Other information is also available from the Weissenberg photographs to help in the space group determination.
By comparing the zero level photograph of Figure 4 (and all other 3n levels) with Figure 236 in Buerger (4), it is apparent that these levels have the characteristic appearance of plane point group C\(_{3v}\). On the original films even more so than on the prints, the intensities of spots at the same height about a central line can be seen to be equal. The films of all other levels show the same relationship of the intensities; however, on levels other than 3n, the plane point group is C\(_{3v}\) because the period is 120 deg. Table 28, p. 474, of Buerger (4) identifies this combination as belonging to centrosymmetrical crystal class D\(_{3d}\).

With this information it is now possible to determine the possible space groups to which the crystal may belong by observing any systematic absences of reflections. No systematic absences were observed in the general hkl reflections for the rhombohedral cell. In the hi reflections, the only l indices occurring were for those in which l = 2n indicating a (110) glide plane of component c/2 (c-glide). In the h00, 0k0 and 00l, h, k, and l, respectively, were equal to 2n indicating [100], [010], and [001] screw axes of components \(\frac{a_1}{2}\), \(\frac{a_2}{2}\), and \(\frac{a_3}{2}\).

Unfortunately, X-ray photographs cannot distinguish between the presence or absence of a center of symmetry. Thus, although it is known that a threefold axis is present, it is not possible to determine whether it is a rotation or an inversion axis.

Because it is known that the crystal has a threefold axis, is rhombohedral, has a c-glide, and belongs to the centrosymmetrical class D\(_{3d}\), the space group then must be either D\(_{3d}\) \(\text{(R}3\text{c)}\) or C\(_{3v}\) \(\text{(R}3\text{c)}\).

**Chemical Properties**

**Solubility.**—The crystal is soluble in most dilute acids including 0.05 normal hydrochloric acid, sulfuric acid, and acetic acid.

**Chemical Analysis.**—The total amount of crystals separated during the course of this investigation was about 8 mg. Although the crystals were produced in abundance, the difficulty of separating them from the matrix accounts for the small amount of pure crystals isolated. Even with these relatively pure crystals, it was exceedingly difficult to remove completely all the montmorillonite which clung to them with great tenacity. Therefore a good quantitative analysis was not obtained. Qualitatively it was determined that calcium, aluminum, silicon, and a very small amount of sodium were present; iron was absent.

**X-Ray Analysis.**—Comparison of the observed d-spacings and intensities with those in the X-ray powder data file (2) showed a striking resemblance between the diffraction data of this crystal and the data for two calcium aluminate hydrates: 4CaO·Al\(_2\)O\(_3\)·xH\(_2\)O and 3CaO·Al\(_2\)O\(_3\)·8·12H\(_2\)O. However, small variances in d-spacings and intensities do not permit positive identification with either of these two compounds. Wells (13) reported d-spacings for 4CaO·Al\(_2\)O\(_3\)·13H\(_2\)O which compared almost exactly, except for the basal reflection, with those given in Table 3 for this crystal. However, intensity and indexing data differ considerably.

Others (5) have interpreted the appearance of reflections at 7.8, 3.82, and 2.87 Å to indicate the presence of C\(_4\)A·13H\(_2\)O.

The index of refraction of the ordinary ray of these crystals is the same as that observed by Wells (13) for compounds approaching the formula C\(_4\)A·13H\(_2\)O. This compound was also uniaxial negative.

However, the presence of silicon strongly observed in the qualitative analysis of the crystals leaves a measure of doubt as to the exact formula. Certainly, from the observed d-spacings, the structure of the crystal must be almost isostructural with the tetracalcium aluminate hydrates discussed previously. Deviations in intensities may be due to incorporation of silica in the crystal structure or due to CO\(_2\) in solid solution in the crystal.

On the basis of unit cell volume and density the C\(_4\)A·13H\(_2\)O hypothesized formula would indicate a unit cell composed of 3 molecules because

\[
N = \frac{\rho \text{ Vatom}}{M}
\] (13)
in which

\[ N = \text{number of molecules/unit cell}; \]
\[ \rho = \text{density } (2.07 \text{ gm/cm}^3); \]
\[ V = \text{unit cell volume } (133.82 \times 10^{-23} \text{ cm}^3); \]
\[ A = \text{Avogadro's number } (6.025 \times 10^{23} \text{ molecules/mol}); \]
\[ M = \text{formula weight } (560.49 \text{ gm/mole}). \]

Then \( N = 2.97 \times 10^6 \) molecules per unit cell.

Future Investigations. — The prime objective of future research will be to produce a larger amount of these crystals and completely separate them from all contaminants to obtain an exact quantitative analysis and definitely establish their chemical composition.

CONCLUSIONS

1. In mixtures of lime, soil M-67, and water which are moist cured for 30 days, a crystalline reaction product develops. This product is produced in optimum quantities at lime contents of 20 percent by dry weight of soil and at high moisture contents. Only the clay-size portion of the soil enters into the reaction.

2. The same crystalline reaction product develops in mixes of lime, water and bentonite, but only after a considerably longer curing time is it produced in considerable quantity.

3. The crystals produced are transparent, colorless, platy, and hexagonally shaped. Their density is \( 2.07 \pm 0.01 \text{ gm/cm}^3 \) at 70 °F. Observations under the petrographic microscope prove them to be uniaxial negative with \( \omega = 1.548 \pm 0.002 \).

4. X-ray investigations of the crystal structure prove that it is the rhombohedral division of the hexagonal system in space groups \( \text{D}_3d^5 \) (\( R\bar{3}c \)) or \( \text{C}_{\text{s}}^6 \) (\( R\bar{3}c \)). Intensities from powder camera films and indexing by Weissenberg methods establish the four strongest lines at 7.59 Å, 00.6; 2.87 Å, 110; 2.30 Å, 20.8; and 3.85 Å, 00.12. Lattice constants are \( a = 5.7550 \text{ Å} \) and \( C = 46.654 \text{ Å} \) for the hexagonal cell and \( a = 15.902 \text{ Å} \) and \( a = 20.850^\circ \) for the rhombohedral cell.

5. The chemical composition of the crystal could not be precisely determined; however, the d-spacings indicate a structure similar to that for \( 4\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 13\text{H}_2\text{O} \) and it is possible that this is the composition of this crystal. If so, previously recorded data for indexing and unit cell dimensions are in error and should be revised.

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REFERENCES