

EARLY REACTION DETERMINATION IN TWO HYDROXIDE-KAOLINITE SYSTEMS BY ELECTRON MICROSCOPY AND DIFFRACTION

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ABSTRACT

RESULTS of the study of the kaolinite-sodium hydroxide interaction showed extensive dissolution of the kaolinite structure at particle edges, with some production of "silicate relics" as a secondary effect. The method of specimen preparation for electron microscopy precluded electron-diffraction study of soluble reaction products. The study of the kaolinite-calcium hydroxide interaction revealed a similar attack on particle edges and formation of "silicate relics" and, in addition, formation of an insoluble reaction product that was tentatively identified by electron diffraction as prehnite, $\text{Ca}_2\text{Al}_2\text{Si}_3\text{O}_{10}(\text{OH})_2$. Both studies showed an ephemeral phase that, by selected area electron diffraction, appeared to be a layer lattice silicate in (001) orientation. In the calcium hydroxide-treated kaolinite, formation of the reaction product was followed from nucleation along particle edges, after 24 hr, to growth of particles about 0.5 to 1 μ in size after 15 days. The combination of electron microscopy of surface replicas to detect changes in morphology with selected area electron diffraction of parallel pseudoreplicas for identification shows promise as a tool for study of the early stages in mineral-chemical interaction.

INTRODUCTION

LIME stabilization of highway subgrade soils has been in use in the United States for about 20 years. During the past ten years the use of lime to reduce plasticity and increase the strength of subgrade clayey soils has grown tremendously. Considerable research has been conducted since about 1958 to determine the mechanisms responsible for this improvement in physical properties of lime-treated clayey soils. One such study, by Eades and Grim (1960) was conducted to determine the reactions between hydrated lime and pure clay minerals. The principal tools used in the investigation were X-ray diffraction and differential thermal analysis. Major reactions were found to be: cation exchange, occurring immediately; formation of cementitious pozzolana; and carbonation of the hydrated lime. The latter two appearing only after a considerable time after mixing.

Both of the tools used by Eades and Grim are limited in their ability to detect the formation of new phases soon after nucleation because they require enough new-phase material to have been formed to register above the normal

background noise. Hence, the time of initiation of new-phase formation cannot be determined accurately and, in any case, the nucleation sites cannot be discriminated by these methods. Changes in the morphology of clay particles are difficult to ascertain by X-ray diffraction and impossible by differential thermal analysis. Observation of the decrease in intensity and broadening of the (0 \bar{k} 0) peaks on an X-ray diffraction trace give the inference that the clay particles are being attacked along particle edges. Such attack, however, must be rather extensive and well-developed for these effects on (0 \bar{k} 0) peaks to be apparent. Neither of these instrumental methods is capable of discriminating changes at the individual particle level. Because of these limitations both are inadequate tools for the study of the very early stages of reaction in fine-particle-chemical-reactant systems.

To the writer's knowledge, the only instrument at present available that is capable of discrimination of individual particles in the submicron size range is the electron microscope. This instrument can also be used as an electron diffraction camera.

The study reported in this paper was initiated during the summer of 1963 and completed early in 1964 and was designed to determine whether or not the course of early reactions in simple kaolinite-hydroxide-water systems could be followed by means of electron microscopy and electron diffraction.

INVESTIGATION

The electron microscope may be used in either of two ways to study the morphology of specimens: (1) by direct transmission microscopy of the actual specimens; or (2) by microscopy of replicas of the surface of the specimens. Interpretation of the images produced by transmission electron microscopy is difficult and is complicated by the fact that both top and bottom surfaces of particles, as well as interior faults, are simultaneously imaged and also (in crystalline materials) by the fact that diffraction effects occur that may be misinterpreted as surface detail. The specimen is, however, available for electron diffraction. By contrast, microscopy of surface replicas is not troubled by such ambiguities and gives a remarkably good picture of the surface detail of the surface replicated. Replicas, however, cannot be used for electron diffraction because none of the original specimen is present in the replica. Resolution in replicas is also somewhat poorer than in transmission specimens, ranging from 15 to 40 Å as compared to about 10 Å in crystals. Resolution is adequate for magnifications up to about 50,000 diameters.

Because of the need to determine changes in crystallinity, as well as changes in morphology, it was decided to carry on the study by both of the foregoing methods. Replicas were used to determine changes in morphology, including the appearance of new phases, and transmission specimens were used for selected area electron diffraction of particles having a distinctive morphology as revealed by the replica studies.

A very fine-grained Georgia kaolinite, distributed by the Georgia Kaolin

Company under the trade name Hydrite UF, was selected for the study because of its high crystallinity, fine particle size, and freedom from impurities. All of the chemicals used in treatment and specimen preparation were American Chemical Society reagent grade.

All reactions were carried out in aqueous suspension using double-distilled, de-ionized water. To ensure uniform conditions throughout the study, temperature was controlled in a constant temperature cabinet to $25^{\circ} \pm 1^{\circ}\text{C}$. Reactions were allowed to progress in the suspension in linear polyethylene bottles to prevent solution of silica from any source other than the kaolinite. Carbonation of the hydroxides used in the treatment was prevented by keeping the bottles tightly stoppered and completely full at all times. Stock suspensions, from which aliquot portions were withdrawn at the desired times after mixing, consisted of 5 g of oven-dried kaolinite (dried at 50°C) in 65 ml. of 0.1 N hydroxide solution. Suspensions were thoroughly dispersed initially in the polyethylene bottles by ultrasonic means and thereafter just before withdrawal of each aliquot. Carbonation was prevented by first determining the pH of the suspension just before withdrawal of the aliquot and then filling the bottle after withdrawal with distilled water and hydroxide adjusted to the same pH.

Withdrawn aliquots were diluted to a concentration of 400 mg per l. ultrasonically dispersed, and specimens prepared from the diluted suspension. Two drops of each diluted dispersion were placed on freshly cleaved muscovite substrates and dried rapidly in a vacuum desiccator under moderate vacuum. Vacuum-dried specimens were placed in a high-vacuum, thin-film evaporator and shadowed with platinum by the Williams and Wyckoff (1946) method or by the platinum-carbon pellet technique reported by Bradley (1958). After platinum shadowing, a replicating layer of carbon was evaporated onto the specimens by the Bradley (1954) method. All specimens were prepared in duplicate: one specimen for replica study and one specimen for selected area electron diffraction study.

Replicated specimens were stripped from the mica substrates by floating them onto the surface of dust-free, double-distilled water. Specimens for the replica studies were picked up and transferred to the surface of concentrated hydrofluoric acid for removal of all attached and embedded particles, washed by floating them on the surface of several changes of dust-free, double-distilled water, and finally picked up on standard 200-mesh copper specimen grids. Specimens for the electron diffraction studies were picked up on microscope specimen grids immediately after stripping from the mica substrate and were not otherwise treated. Water-soluble particles were lost from the pseudoreplicas by this process; however, their loss could be detected during scanning in the microscope by the fact that their removal had left a surface replica. It should be noted that better dispersion of particles for selected area electron diffraction was achieved by the foregoing method of specimen preparation than the writer could obtain by spraying the dilute dispersion directly onto carbon film covered microscope grids. Parallel replicas and

pseudoreplicas were made at 24-hr intervals through the first 7 days of treatment and again at 14 or 15 days.

Electron microscopy and electron diffraction were accomplished using an Hitachi HS-6 electron microscope (at the University of California), a Philips Em-100B (at the University of Arizona, Zoology Department), and finally an Hitachi HS-7 (in the writer's laboratory at the University of Arizona). Electron micrographs were made at magnifications ranging from 6000 to 10,000 diameters. Micrographs were enlarged photographically from 2.5–4 diameters for study. Measurements of the single-crystal electron diffraction patterns were made directly on the photographic plates with the aid of a 7-power magnifying, measuring microscope. The shadowing platinum was used as an internal standard for calibration of the electron camera constant. In most cases the platinum diffraction rings were sharp enough to make accurate measurements on the photographic plates, although they were not usually intense enough to show clearly on photographic enlargements. Use of an internal standard for calibration has been reported by Brindley and DeKimpe (1961) and by Oberlin and Mering (1962). Having determined the camera constant, d spacings for the diffraction spots were computed. Measured d spacings were used with the ASTM X-ray Card File and Index (1962) for identification of new phases.

It should be noted that the electron diffraction patterns obtained by selected area diffraction of single particles were single-crystal patterns for a single orientation only. In order to obtain as many different d spacings as possible for better identification, it was usually necessary to search the pseudoreplicas for particles in different orientations. During the latter stages of the investigation a bi-axial tilting specimen stage was available that allowed the individual particle being studied to be tilted into different orientations thus saving considerable time. However, tilt was limited to $\pm 10^\circ$ about two axes, which was not always sufficient to move the specimen into a different orientation favorable for good resolution of diffraction spots.

Because each orientation yielded only a few d spacings and the number of orientations was limited, it was not possible for any given kind of particle to obtain as many d spacings as a randomly oriented polycrystalline aggregate would yield. In addition, it was impossible to compare electron diffraction intensities with X-ray data for several reasons, the most important being that diffraction in the X-ray case arises from X-ray–electron interaction and in the electron case arises from electron–nucleus interaction. Hence, intensity in electron diffraction depends primarily on the mass of the nucleus of the atoms or ions being diffracted and to a much less extent on other factors, such as the structure factor. Also, intensity is a function of crystal thickness (absorption effects) and diffraction of particles of different thickness, although of the same species, yielded different intensities, so that a composite relative intensity scale could not be set up. The foregoing factors, of course, complicated identification using X-ray data; however, in simple controlled systems,

such as the ones studied, the possible reaction products are limited in number, so that a reasonable match with X-ray data can be obtained without relative intensity data.

Noncrystalline or very poorly crystalline particles were detected by the fact that no diffraction effects were observed when the individual particles were subjected to selected area electron diffraction.

RESULTS

The principal results of the research are shown graphically in Plates 1 through 3. Plate 1 shows the morphological changes that occurred during treatment of the kaolinite with sodium hydroxide. Micrograph (a) shows the morphology of the untreated kaolinite. In general, the flakes are sharp-edged with a well-defined hexagonal aspect. A few particles show some irregularity in flake edges, which is probably the result of the mechanical breakdown of the bulk mineral during processing. A thorough scanning of pseudoreplicas of the untreated kaolinite failed to reveal any non-kaolinite or any non-crystalline particles. Micrograph (b) shows the kaolinite particles after 14 days of treatment with 0.1 N sodium hydroxide. Dissolution of the kaolinite particles around particle edges is evident in most of the particles pictured. Beveling and rounding of flake edges was first noted in the 24-hr specimens and grew progressively more pronounced and extensive as the study progressed. Micrograph (c) shows a large particle of a filmy new phase, which began to appear in the replicas and pseudoreplicas after 4 days of treatment. This phase was present in the 7-day specimens but had disappeared from the system by the time the 14-day specimens were prepared. The contourlike markings on the filmy phase reverse contrast when viewed by dark-field illumination, showing that they are not surface features but are a diffraction effect (bend extinction contours). The single-crystal diffraction pattern in (d) was produced by selected area electron diffraction of a portion of the filmy phase in micrograph (c). The diffraction spots are larger and more intense than normal and many show short streaks extending from them; all this indicates that the filmy phase is extremely thin, perhaps only a few unit cells in thickness. The bend extinction contours and the low density of the transmission image also indicate that the crystal is very thin. The spot pattern shown is typical of most layer lattice silicates in (001) orientation. This phase appeared only in this orientation and tilting of the specimens did not produce measurable diffraction patterns in other orientations; therefore, identification of this phase could not be accomplished. The components in the reacting system suggest that this phase might be authigenic kaolinite reconstituted from dissolved silica and gibbsite in the system.

None of the replicas or pseudoreplicas showed other reaction products, either soluble or insoluble, as a result of the sodium hydroxide treatment.

Some of the replicas of the sodium hydroxide-treated kaolinite showed a

few particles that appeared to have suffered some dissolution on basal planes. This effect was noted only in those replicas made after 7 days of treatment.

Plate 2 shows some of the morphological changes in the calcium hydroxide-treated kaolinite system, the final reaction product formed and its corresponding electron diffraction pattern. In Plate 2, micrograph (a) shows the treated kaolinite after 48 hr of treatment. The appearance of a reaction product in this micrograph is the first evidence of formation of a non-soluble reaction product in this system. Reaction-product particles about 400 Å in diameter can be seen throughout the micrograph. At many points the reaction-product particles appear to be lined up along the edges of kaolinite flakes. Dissolution of the kaolinite and beveling along kaolinite flake edges can be seen on many of the flakes in the micrograph. Micrograph (b) shows the appearance of the kaolinite flakes after 15 days of calcium hydroxide treatment. None of the reaction product appears associated with the kaolinite flakes. Extensive edge dissolution and beveling of most of the kaolinite particles is evident. From 48 hr of treatment to the final 15-day specimens, the reaction product showed continued growth. After about 72 hr of treatment, the reaction-product particles began to detach from the kaolinite flakes and to aggregate in foliate clusters. Micrograph (c) shows a typical clump of reaction-product crystals. Many of these reaction-product crystals show a crude hexagonality of outline. At this length of time after mixing, the reaction-product particles have grown to about 0.5 to 1.0 μ in maximum dimension. The single-crystal electron diffraction pattern in (d) is for a single reaction-product particle in a high order orientation. Selected area electron diffraction of this particle and others in other orientations yielded a total of 9 *d* spacings from diffraction spots that were well resolved. On the basis of these *d* spacings a tentative identification of the reaction product as prehnite, Ca₂Al₂Si₃O₁₀(OH)₂, was made by comparing the measured *d* spacings with those listed for prehnite in the ASTM X-ray Card File and Index (1962). Table 1 shows the comparison.

As in the sodium hydroxide-treated kaolinite system, a large thin filmy phase appeared after 5 days of calcium hydroxide treatment, which persisted through 7 days of treatment, but was absent in the 15-day-treated specimens. The selected area diffraction pattern for this phase was also typical of a layer lattice silicate.

Plate 3 illustrates a phenomenon that was observed in both hydroxide treatments. Micrograph (a) shows a typical untreated kaolinite flake at A, framed by the selected area diffraction aperture in the microscope preparatory to electron diffraction. The corresponding electron diffraction pattern for this flake is shown in (b). The kaolinite particle is in (001) orientation. Micrograph (c) shows a particle at A having the typical hexagonal shape of a kaolinite particle and having approximately the same electron optical density. Attempts to produce an electron diffraction pattern for this particle produced the diffraction pattern, or lack of one, shown in (d). This was construed as positive evidence that the particle had no long range order and therefore was

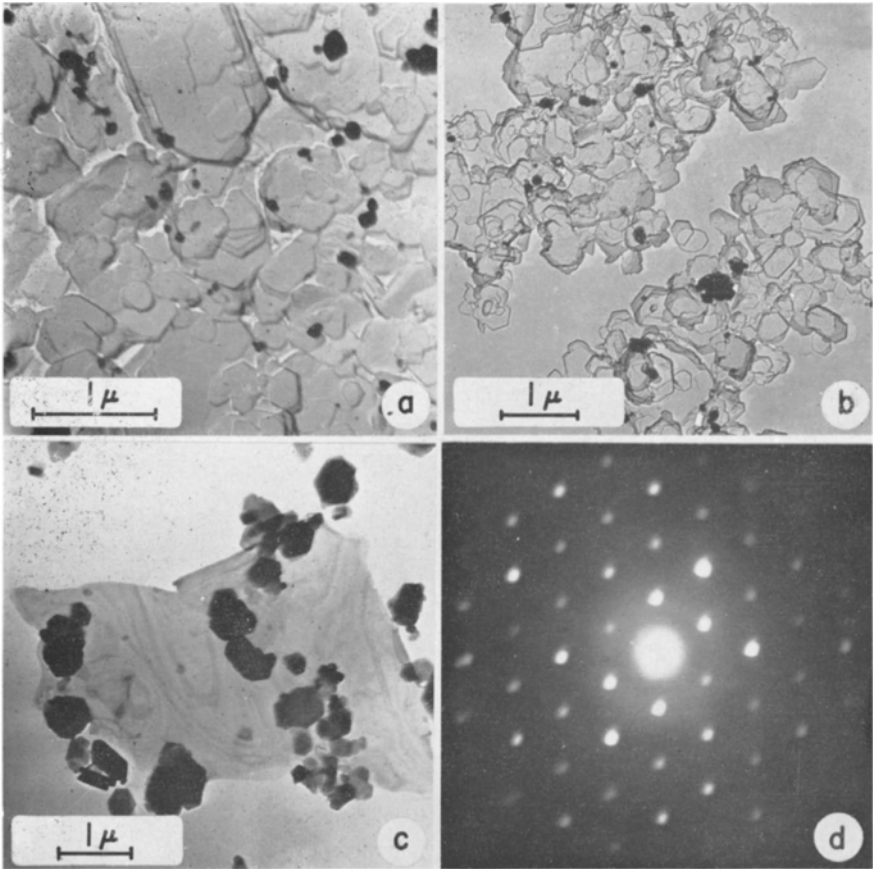


PLATE 1. Sodium hydroxide treated kaolinite. (a) Untreated kaolinite (b) Kaolinite after 14 days of treatment showing extensive dissolution along flake edges. (c) After 7 days of treatment, showing large new filmy phase exhibiting bend extinction contours. (d) Electron diffraction pattern of filmy phase shown in (c).

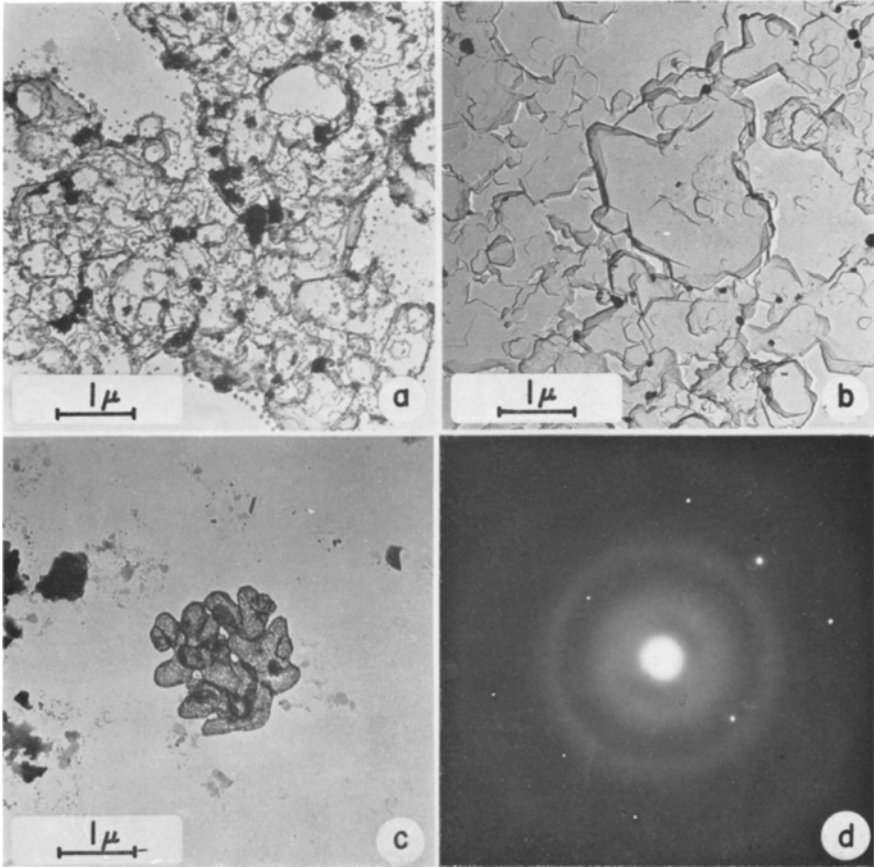


PLATE 2. Calcium hydroxide treated kaolinite. (a) Kaolinite after 48 hours of treatment showing very tiny reaction product particles. (b) Kaolinite after 15 days treatment showing extensive dissolution along flake edges; (c) cluster of reaction product particles after 15 days of treatment (d) Electron diffraction pattern of single reaction product particle in a high-order orientation.

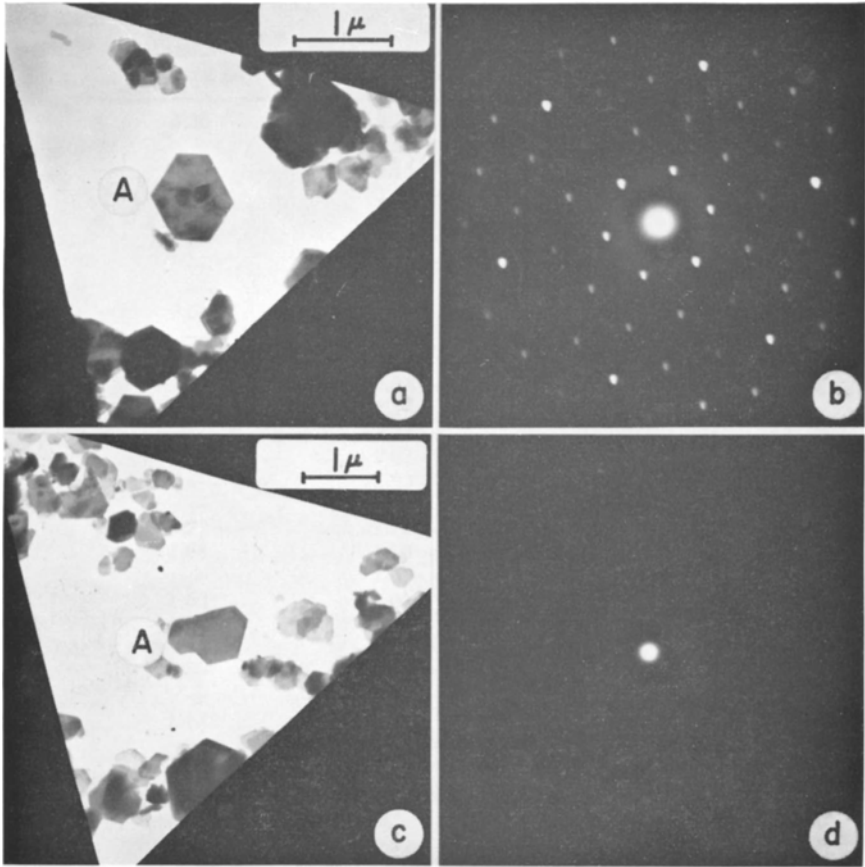


PLATE 3. Production of "silicate relics" (a) Untreated kaolinite flake at A. (b) Electron diffraction pattern of flake shown in (a) (c) Kaolinite flake at A after 7 days of sodium hydroxide treatment (d) Electron diffraction of flake shown in (c) showing the direct beam spot and the absence of resolved diffraction spots.

TABLE 1.—TENTATIVE IDENTIFICATION OF NEW-PHASE REACTION PRODUCT

<i>ASTM Card 7-333: Prehnite</i> $\text{Ca}_2\text{Al}_2\text{Si}_3\text{O}_{10}(\text{OH})_2$ Ortho-rhombic P2cm		
Measured <i>d</i> spacing (Å)	<i>d</i> spacing (Å)*	Indices
5.26	5.28	011
—	4.60	100,004
4.15	4.15	102,013
3.52	3.53	110
3.46	3.48	111
—	3.28	112,104
—	3.08	†
—	2.81	114
2.60	2.62	022
—	2.55	106,115
—	2.37	†
—	2.31	†
—	2.18	123
—	2.13	117,211
—	2.07	108,204
—	1.93	118,214
—	1.84	0010,215
1.77 †	1.77	119,220
1.68	1.69	130
—	1.66	217
1.63	1.64	133
—	1.54	†
—	1.51	302
—	1.46	312
—	1.45	1210,2010
1.435	1.41	228
—	(10 more lines to $d = 1.06 \text{ \AA}$ not given)	

* *d* spacings rounded off to nearest 0.01 Å.

† numerous possible indices.

noncrystalline or at best very poorly crystallized. Inasmuch as no such non-diffracting particles were found in the untreated kaolinite, it would appear that the loss of crystallinity was a result of the hydroxide treatment. Langston and Jenne (1964) report a similar production of “amorphous” material from kaolins treated with 1 N sodium hydroxide solution at boiling temperatures. Ross and Kerr (1934) refer to such particles as “silicate relics”. At the conclusion of the study, between 5 and 10 per cent of all kaolinite particles had been converted to “silicate relics”.

CONCLUSIONS

Under both hydroxide treatments, dissolution of the kaolinite along particle edges was progressive from the first 24 hr of treatment to the conclusion

of the studies after 15 days of treatment. Dissolution was predominantly along flake edges where broken valence bonds existed. In the sodium hydroxide treatment there was some indication of a slight attack of the kaolinite on basal (001) planes.

Under both treatments a very thin filmy phase appeared after 4 or 5 days of treatment and grew to large lateral extent before disappearing from the systems sometime between 7 and 14 or 15 days after treatment began. Electron diffraction patterns obtained for the filmy phase suggest that it may be a layer lattice silicate, possibly authigenic kaolinite.

Under both treatments between 5 and 10 per cent of all kaolinite particles seem to have been leached of most of their lattice cations, or at least to have the majority of lattice bonds broken to the point where no readable diffraction patterns could be obtained. This action was progressive throughout the treatments and suggests that perhaps, given enough time and a continuing high pH aqueous environment at normal ambient temperature and pressure, the majority of the unreacted kaolinite particles might be reduced to "sili-cate relics".

Under the calcium hydroxide treatment, very tiny reaction-product particles appeared after 48 hr of treatment. These very small (400 Å) particles appeared to have nucleated on kaolinite basal (001) planes immediately adjacent to kaolinite particle edges. Such sites would be energetically favorable for nucleation of the reaction product. Early in the growth process the reaction-product particles left the association with kaolinite flakes to form foliate aggregates and intergrowths with their fellows. Such segregation is possible in an aqueous suspension but would probably not show such mobility in a solid or semisolid mixture of the clay and hydrated lime. Electron diffraction data indicate that the reaction product may be prehnite, $\text{Ca}_2\text{Al}_2\text{Si}_3\text{O}_{10}(\text{OH})_2$. Eades and Grim (1960) do not report this product from their X-ray studies of longer-term reactions; therefore, it would appear probable that the reaction product found in this study is also an ephemeral phase.

Other than the ephemeral filmy phase, no reaction products of any kind were found as a result of the sodium hydroxide treatment.

The results of the studies demonstrate that electron microscopy and electron diffraction can be used effectively in following the course of early reactions in clay-inorganic chemical-water systems.

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