Early Reactions in the Kaolinite-Hydrated Lime-Water System

Réactions primaires dans les mélanges de kaolinite et de chaux hydratée

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SUMMARY

The sequence of early reactions between kaolinite and hydrated lime in an aqueous suspension was studied by electron microscopy and electron diffraction. Changes in particle morphology and the first appearance of new phases were observed by electron microscopy of replicas of vacuum-dried specimens. Changes in particle crystallinity and identification of new phases were determined by selected area electron diffraction of individual particles in pseudo-replicas. Techniques for simultaneous preparation of specimens were developed. Reactions during the first fourteen days were found to be: (1) dissolution of kaolinite around particle edges, (2) formation and growth of a calcium aluminum silicate hydrate reaction product, (3) production of some non-crystalline "silicate relics," and (4) growth and subsequent disappearance of authigenic kaolinite.

SOMMAIRE

La suite des premières réactions entre kaolin et chaux éteinte dans une suspension aqueuse a été étudiée par microscopie et diffraction électronique. Les changements dans la morphologie des particules et le début des phases nouvelles ont été observés par microscopie électronique dans les répliques des spécimens séchés dans le vide. Les changements dans la cristallinité des particules et l'identification des phases nouvelles ont été déterminés par microdiffraction électronique des particules isolées dans les pseudo-répliques. Des techniques ont été développées pour la préparation simultanée des spécimens. Les réactions pendant les premiers quatorze jours étaient les suivantes: (1) dissolution du kaolin autour des bords des particules, (2) formation et croissance d'un silicate hydraté de calcium et aluminium comme produit de réaction, (3) production de quelques "reliques silicates" non-cristallines, et (4) croissance et disparition subséquente de kaolin authigénique.

LIME STABILIZATION OF HIGHWAY SUBGRADE SOILS has been in use in the United States for about twenty years, having been initiated on an experimental basis by the Texas State Highway Department in 1945. During the past ten years the use of lime, particularly hydrated lime, to reduce plasticity and increase the strength of clay soils has grown tremendously. Since about 1958 considerable research has been conducted to determine the mechanisms underlying this improvement in clay soil properties through studies of the reactions between lime and clay minerals. One such study, by Eades and Grim (1960), was conducted principally by means of X-ray diffraction and differential thermal analysis and found that the principal reactions were: cation exchange, formation of cementitious pozzolans, and carbonation of the hydrated lime. The pozzolans were identified by X-ray diffraction as predominantly calcium silicate hydrates with some calcium silica aluminates also being formed. This study was concerned mostly with the long-term reactions occurring in the system.

X-ray diffraction and differential thermal analysis have limitations on the sensitivity of detection of new phases, both requiring sufficient new product to be formed to register above the background. In any case, the point of initiation of a reaction cannot be determined by these methods. Changes in clay morphology as a result of chemical treatment are difficult to ascertain by X-ray diffraction and impossible by differential thermal analysis. From the decrease in intensity and broadening of (OkO) peaks on a diffraction trace, as an example, it may be inferred that clay particles are being attacked along particle edges. However, such attack must be extensive and well-developed for the effects on (OkO) peaks to be apparent. Because X-ray diffraction requires reinforcement of reflections from many particles for peaks to become visible above the background on a diffractometer trace, changes in individual particles cannot be discriminated. Differential thermal analysis is similarly unable to discriminate at the individual clay-size particle level.

The above-noted limitations on the sensitivity and discrimination of X-ray diffraction and differential thermal analysis make them rather poor tools to use in answering such questions as: when reactions begin, where nucleation occurs, what changes in particle morphology occur, and whether or not disappearing phases are present in the system. Electron microscopy and selected area electron diffraction, used in conjunction with one another, have the potential capability of answering these questions. By means of electron microscopy of surface replicas, detail of the order of 25 to 40 Å can be discriminated, hence changes in particle morphology and the appearance of new phases can be easily detected very early in the reaction process. Selected area electron diffraction can be performed readily on individual particles to determine changes in crystallinity and to furnish data for identification of new phases.

To determine the effectiveness of electron microscopy and diffraction as a means of closely following the course of reactions, the author undertook to study the reactions of hydrated lime and a pure kaolinite during the early stages of reaction. This paper reports the results of the investigation.

INVESTIGATION

An ultra-fine-grained Georgia kaolinite, processed and distributed by the Georgia Kaolin Co. under the trade name Hydrite UF, was selected for this study because of its high purity, well-defined crystallinity, and fine particle size (under two microns). The hydrated lime used in the study was an American Chemical Society standard, chemically-pure grade. All reactions were carried out in aqueous suspension using double-distilled water. Other chemicals used in electron microscope specimen preparation were American Chemical Society reagent grade.

To insure uniform conditions throughout the study the temperature was controlled in a constant-temperature cabinet at 25 C ± 1 C. To insure that any solution of silica would come only from the kaolinite lattice, reactions were carried out in polyethylene bottles. Prevention of carbonation of the dissolved hydrated lime was accomplished by keeping the polyethylene bottles tightly capped and completely full of suspension at all times. All utensils used in specimen preparation were cleaned ultrasonically in double-distilled water immediately prior to use to prevent contamination of specimens.

Stock suspensions, from which aliquot portions were withdrawn at the desired times after mixing, were prepared in duplicate using a concentration of 5 grams of air-dried kaolinite to 65 ml of saturated $Ca(OH)_2$ solution (approx. 0.1N). Suspensions were thoroughly dispersed ultrasonically in the polyethylene bottles until the temperature had risen to 25 C (approx. five minutes), after which they were placed in the constant temperature cabinet. Thereafter the suspensions were dispersed ultrasonically for two minutes (after shaking for one minute) prior to withdrawal of each aliquot. A similar suspension of five grams of air-dried kaolinite to 65 ml of double-distilled water was prepared for use in electron microscopy and diffraction specimen preparation of the untreated kaolinite.

Electron microscopy and diffraction specimens were prepared in duplicate from the stock suspensions by withdrawing small aliquots and diluting them to a concentration of 400 mg per liter. Two drops of each diluted aliquot were placed on freshly cleaved muscovite mica substrates and dried rapidly in a vacuum desiccator. Vacuum-dried specimens were shadowed lightly with platinum in a high-vacuum, thin-film evaporator by the Williams and Wyckoff (1946) method or by the platinum-carbon pellet technique reported by Bradley (1958). After shadowing, a heavy replicating layer of carbon was evaporated onto the specimens normal to their surface by the method of Bradley (1954).

Replicated specimens were stripped from the mica substrates onto the surface of dust-free, double-distilled water. Replicas for electron microscopy were cleaned of attached particles by floating them on 48 per cent hydrofluoric acid, then washed on the surface of double-distilled water, and finally picked up on standard 200-mesh copper specimen screens. Pseudo-replicas for selected area electron diffraction were picked up on specimen screens immediately after stripping and were not otherwise treated. Parallel microscopy and diffraction specimens were made at 24-hour intervals through seven days of age and again at 14 days of age.

The preliminary investigation, completed at the University of California, made use of an Hitachi HS-6 electron microscope of 50 kv accelerating potential. The final investigation, completed at the University of Arizona, was done with a Philips EM-100B electron microscope having an electron accelerating potential ranging from 40 kv to 100 kv in 20 kv steps.

At each age after mixing, the platinum-carbon replicas were scanned at 5,800 diameters magnification and either 50 kv or 60 kv accelerating voltage to provide good image contrast. Micrographs of typical areas were made on glass plates. Parallel pseudo-replicas were scanned at 5,800 diameters magnification and individual particles were subjected to selected area diffraction at sufficiently high accelerating potential to produce good electron transmission. Both typical and atypical kaolinite particles, selected at random on each pseudo-replica, were also routinely subjected to selected area diffraction to determine changes in particle crystallinity. Electron diffraction patterns were recorded on photographic glass plates.

Electron micrographs were enlarged photographically to 15,000 diameters magnification and scrutinized carefully for changes in particle morphology and for the appearance of new phases. Single-crystal and polycrystal electron diffraction patterns were measured directly on the photographic plate by means of an 8-power measuring microscope. Measurements were used to compute crystal interplanar d-spacings for each diffraction spot by the relation: $d = \lambda L/r$, where d = interplanar spacing in Å, λ = electron beam wavelength in Å, L = electron camera length in centimeters, and r = radial distance in centimeters of the diffraction spot from the direct beam spot. The quantity (λL), in the above equation, is called the electron camera constant (Thomas, 1962) and for this investigation was determined from measurement of the (220) ring for the shadowing platinum used in the specimen preparation and the known (220) d-spacing for the metal. This ring is particularly evident in Fig. 1e. The platinum (220) ring appeared on all electron diffraction patterns. Interplanar d-spacings were computed by dividing the camera constant by the measured radial spot distances. The platinum used in specimen shadowing was an internal standard to fix the electron camera constant and thus permit accurate calculation of d-spacings for the diffraction patterns. Use of an internal standard for this purpose has been reported by Brindley and DeKimpe (1961) and by Oberlin and Mering (1962).

It should be noted that the electron diffraction patterns obtained were generally single-crystal patterns and therefore were for only one orientation of the diffracting crystal; hence many diffraction spots for planes not in the diffracting position were missing from each pattern. Because of this it was necessary to tilt the individual microcrystal into other orientations by means of a biaxial tilting specimen stage in order to pick up enough diffraction spots on which to base crystal identification. In some cases it was necessary to search the pseudo-replicas for crystals in different orientations to secure adequate data because of the limitation on the tilting capability of the specimen stage.

The d-spacings, obtained by the foregoing procedure for each crystal, were used with the *ASTM X-ray Card File and Index* (1962) to arrive at identification. In one or two cases insufficient d-spacings were secured, because of orientation capability limitations, to arrive at a completely positive identification. Non-crystalline particles were identified as non-crystalline by the fact that no diffraction patterns were obtained from them by selected area diffraction.

During the fourteen-day period covered by this study, the pH of the stock kaolinite-hydrated lime suspension was checked daily by means of a Beckman pH meter. The pH varied from a maximum of 12.7 immediately after mixing to a minimum of 12.2 after 14 days indicating that some reaction was taking place.

RESULTS

Fig. 1(a–d) shows the morphological changes which occurred in the kaolinite during the first fourteen days of hydrated lime treatment. Fig 1a is a micrograph of the untreated kaolinite in which the majority of the kaolinite flakes show sharp edges and corners. A few particles show some rounding and bevelling which is believed to be the result of the mechanical breakdown of the bulk mineral to the final less than two micron particle size. Pseudo-replicas

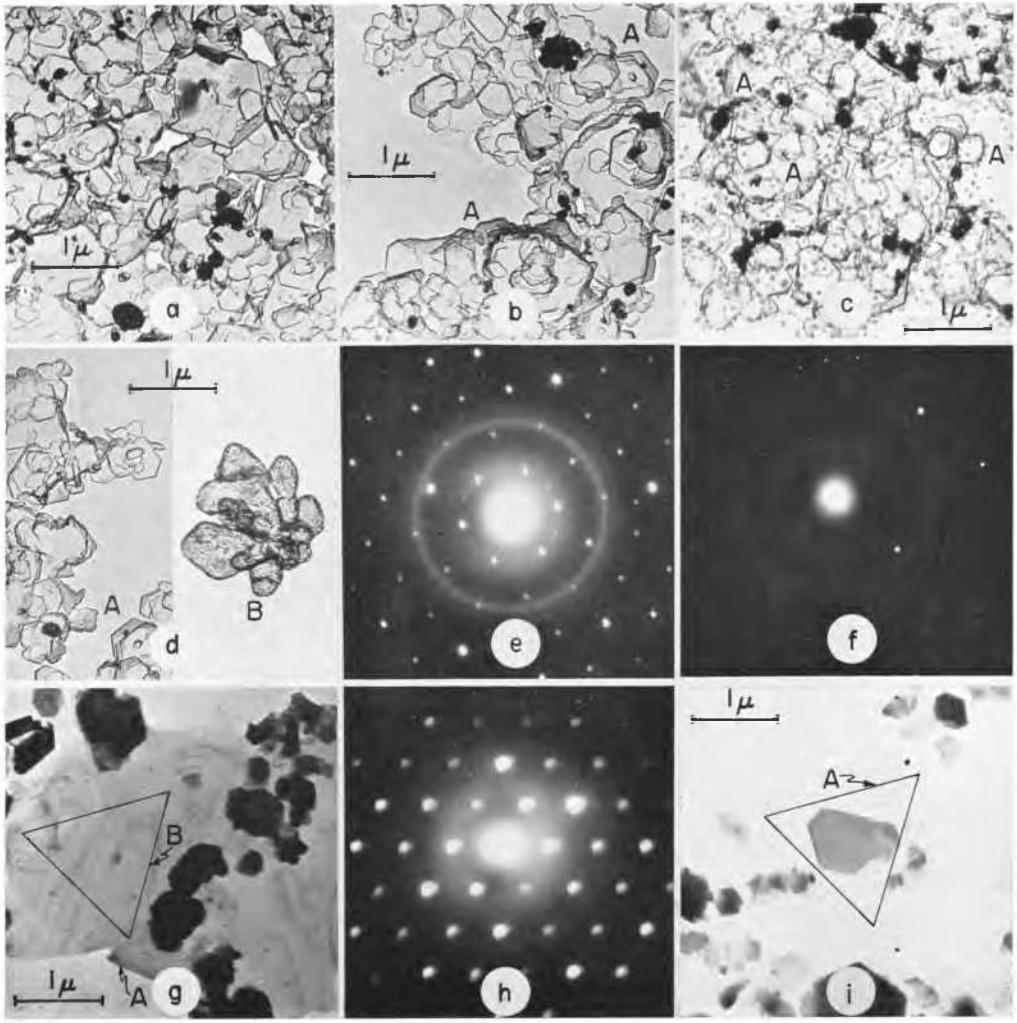

FIG. 1. a, Platinum-shadowed carbon replica of untreated kaolinite; b, platinum-shadowed carbon replica of kaolinite treated 1 day with $Ca(OH)_2$ showing edge dissolution of particles at A; c, platinum-shadowed carbon replica of kaolinite treated 2 days with $Ca(OH)_2$ showing first appearance of reaction product and clustering along particle edges at A; d, platinum-shadowed carbon replica of kaolinite treated 14 days with $Ca(OH)_2$ showing extensive edge dissolution of kaolinite particles at A and cluster of segregated reaction product crystals at B; e, single-crystal electron diffraction pattern of kaolinite in (001) orientation; f, single-crystal electron diffraction pattern of reaction product in (9.27.4)(?) orientation; g, transmission micrograph of authigenic kaolinite at A and area selected for diffraction at B (pseudo-replica); h, single-crystal electron diffraction pattern of area shown in Fig. 1g; i, transmission micrograph of kaolinite particle altered to "silicate relic" and area selected for diffraction at A (pseudo-replica). All micrographs are at a magnification of 15,000 ×.

of the untreated kaolinite were scanned and almost every particle subjected to electron diffraction without finding a single impurity or non-crystalline particle.

Fig. 1b shows the treated kaolinite after one day of treatment with hydrated lime. Pronounced etching and bevelling of many particles is evident along particle edges as at A. Dissolution of the kaolinite has been the result of the high pH of the suspension at which both the lattice silica and alumina are relatively soluble. No trace of a new phase can be seen.

Fig. 1c shows the treated kaolinite two days after treatment began. In this micrograph myriads of tiny new

particles can be seen, many clustered around the edges of kaolinite flakes, as at A. At this stage of development the new particles range in size from 200 to 400 Å. Appearance of these new particles in the two-day treated material and not in the one-day treated kaolinite indicates that nucleation must have occurred during the second day. Clustering of the particles around kaolinite flake edges suggests that nucleation took place there because of the favourable energy level resulting from the broken bonds in the kaolinite lattice.

The new phase continued to grow in size and, after about five days of treatment, became detached from the nucleation sites and aggregated in clusters in the suspension. Particles in these clusters continued to grow until, after fourteen days, most were equal in size to or larger than the kaolinite flakes. This can be seen in Fig. 1d which is a composite micrograph of two closely adjacent areas on the same replica. Kaolinite particles at A show a more severe dissolution around the edges and there is a suggestion that dissolution of some flakes may have followed definite crystallographic planes. The cluster of new-phase particles at B shows the typical foliate arrangement and the crude pseudo-hexagonality of the individual particles. The shape of the new-phase particles suggests that growth may have occurred on the basal (001) planes of the kaolinite flakes, immediately adjacent to particle edges, epitaxially with the pseudo-hexagonal packing of ions in the kaolinite basal planes.

Fig. 1e is a single-crystal electron diffraction pattern of untreated kaolinite in (001) orientation. This is the orientation of almost all of the flakes in the micrographs. Fig. 1f is a single-crystal electron diffraction pattern of a rather large new-phase particle lying in the pseudo-replica in apparently the same orientation as the kaolinite flakes. However, indexing of the spots after identification and application of the zone law indicate that the particle is actually in a high order (hkl) orientation. This would seem to reinforce the hypothesis that growth has been epitaxial with the basal structure of the kaolinite because the new phase is of a different crystal class (orthorhombic) from the kaolinite (triclinic). Electron diffraction patterns of the new phase in other orientations were obtained to give a total of nine *d*-spacings from which an identification could be made using the *ASTM X-ray Card File and Index* (1962). A close match with the *d*-spacings for a calcium aluminum silicate hydrate was found as shown in Table I. Eades and Grim (1960) do

TABLE I. IDENTIFICATION OF NEW-PHASE REACTION PRODUCT

Measured d-spacing in Å	ASTM Card 7-333 *d*-spacing in Å	Indices (hkl)
5.26	5.28	011
4.15	4.15	013
3.52	3.53	110
3.46	3.48	111
2.60	2.63	310,022
1.77+	1.77	119
1.68	1.69	130
1.63	1.64	133
1.435	1.41	228

not report the formation of such a phase which suggests the possibility that this phase is either ephemeral (disappearing) beyond the fourteen-day level of treatment or that growth does not progress to the point where enough is formed to be discerned by X-ray diffraction.

Fig. 1g is a transmission micrograph of a portion of a pseudo-replica after four days' treatment. Large filmy particles, such as the one at A, began to appear in the specimens at this time and persisted through the seventh day of treatment. No trace of these particles could be found in the fourteen day specimens. Dark-field imaging of these particles showed a reversal of contrast in the contourlike markings indicating that these particles were crystalline and that the markings were a diffraction phenomenon (bend extinction contours). Selected area diffraction of the area enclosed by the triangle at B gave the diffraction pattern of Fig. 1h which is closely similar to that of kaolinite in (001) orientation. The increase in spot size and intensity and some discernible streaking of the spots are similar to line-broadening in X-ray diffraction and indicate that the particle is very thin, possibly only a few unit layers thick, in the *c*-axis direction. While diffraction patterns for other orientations could not be secured, it appears possible that this phase may be authigenic kaolinite reconstituted from the dissolution products.

Within a few days after treatment began, non-diffracting particles such as the one at A in Fig. 1i appeared. Electron diffraction of these particles was attempted without producing diffraction effects of any kind. The conclusion is evident that these particles are non-crystalline although retaining the characteristic morphology of kaolinite. Inasmuch as no such particles were found in the untreated kaolinite it must be concluded that they resulted from the hydrated lime treatment. Langston and Jenne (1960) reported a similar production of "amorphous" material in their study of kaolins subjected to sodium hydroxide treatment. Ross and Kerr (1934) refer to such particles as "silicate relics". After fourteen days of hydrated lime treatment between 5 per cent and 10 per cent of all particles were found to be "silicate relics".

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REFERENCES

American Society for Testing and Materials (1962). *ASTM X-ray card file and Index*. Philadelphia, Pennsylvania, American Society for Testing and Materials.

Bradley, D. E. (1954). Evaporated carbon films for use in electron microscopy. *Jour. Applied Physics*, Vol. 5, pp. 65 & 96.

——— (1958). Simultaneous evaporation of platinum and carbon for possible use in high-resolution shadow-casting for the electron microscope. *Nature*, Vol. 181, p. 875.

Brindley, G. W., and C. DeKimpe (1961). Identification of clay minerals by single crystal electron diffraction. *American Mineralogist*, Vol. 40, p. 1005.

Eades, J. L., and R. E. Grim (1960). *Reaction of hydrated lime with pure clay minerals in soil stabilization*. Highway Research Board, Bulletin 262. Washington, National Academy of Sciences–National Research Council.

Langston, R. B. and E. A. Jenne (1960). NaOH dissolution of some oxide impurities from kaolins. *Proc. Twelfth National*

Conference on Clays and Clay Minerals, pp. 633–47. London, Pergamon.

OBERLIN, A., and J. MERING (1962). Observations en microscopie et microdiffraction électroniques sur la montmorillonite Na. *Journal de Microscopie*, Vol. 1, p. 107.

ROSS, C., and P. F. KERR (1934). *Halloysite and allophane.* U.S. Geological Survey Professional Paper 185-G. Washington, Government Printing Office, Superintendent of Documents.

THOMAS, G. (1962). *Transmission electron microscopy of metals.* New York, Wiley.

WILLIAMS, R. C., and R. W. G. WYCKOFF (1946). Applications of metallic shadow-casting to microscopy. *Jour. Applied Physics*, Vol. 17, p. 23.