Lime-Clay Mineral Reaction Products

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Separate slurries of high calcium hydrated lime or dolomitic monohydrate or dihydrate lime were made with pure bentonite, kaolinite, pulverized muscovite, quartz, or vermiculite mineral and various amounts of water. The mixes were sealed in plastic containers to prevent loss of water or entry of carbon dioxide, and cured at 70 F for two years, after which X-ray diffraction and differential thermal analysis showed varying proportions of conversion of minerals and lime into pozzolanic reaction products.

Reaction products were identified on the basis of diffractometer d-spacings. Single crystals of several of the products were isolated and unit cell parameters obtained by use of a diffractometer single crystal orienter. Debye-Scherrer powder diffraction data from crushed single crystals are presented in ASTM format and related to the diffractometer data.

Among the reaction products are the calcium silicate hydrate 10-Å tobermorite, 8.2- and 7.9-Å polymorphs of tetracalcium aluminate hydrates, and several compounds of unknown composition.

●HYDRATED LIME added to clayey soils causes two beneficial modifications: (a) there occurs a rapid depression of the plasticity index, usually attributed to cation exchange and ion adsorption phenomena (1); and (b) lime added in excess of the lime fixation capacity causes a long-term cementation attributed to the chemical reactions between lime and silicious minerals or glasses. The latter reactions are termed pozzolanic reactions.

REVIEW

Pozzolanic Reactions

In investigations of pozzolanic reaction products, Leonard and Davidson (2) report new X-ray diffraction peaks at 17.3, 12.6, and 3.08 Å after reaction of $Ca(OH)_2$ and fly ash in a slurry for one year at room temperature, and report no new peaks for mixes cured at 40, 60, and 80 C. They conclude from lime depletion data that the initial product in either case is non-crystalline, after which there is slow crystallization to calcium silicate hydrate I, similar to the mineral tobermorite.

Minnick (3) reports new diffraction peaks at 3.31, 3.05, 2.97, and 2.77Å for $Ca(OH)_2$-fly ash samples either cured at 140 C or autoclaved, and essentially the same peaks with dolomitic lime, $Ca(OH)_2 + MgO$. He also notes that MgO goes to $Mg(OH)_2$.

From pozzolanic reactions with natural clay minerals, Eades and Grim (4) report new diffraction lines for $Ca(OH)_2$-kaolinite cured at 60 C, the lines being at 5.09, 3.04, 2.8, and 1.8 Å. New lines were weaker for lime-illite or lime-montmorillonite cured at the same temperature. Hilt and Davidson (5) report new diffraction lines at 8.11

and 7.59 Å for Ca(OH)$_2$-montmorillonite reacted for 30 days at room temperature. The 7.59-Å compound was isolated and found to be rhombohedral, with lattice constants in the hexagonal system $a_0 = 5.7550$ Å and $c_0 = 46.654$ Å. The compound was tentatively identified as a hydrated calcium aluminate. Despite its sharpness, the 8.11-Å peak was assigned to montmorillonite. In mixes with variable water content the 8.11-Å peak was stronger in the water mixes. Other peaks appear on diffractometer traces at about 10 and 7.1 Å. Glenn and Handy (6) isolated a 7.94-Å mineral formed from reaction of montmorillonite and dolomitic lime [Ca(OH)$_2$ + MgO] and indexed it in the triclinic system.

Silicate Hydrates

In the field of portland cement chemistry, hydration of tricalcium silicate six days at room temperature in a ball mill resulted in a product identified as the calcium silicate hydrate afwillite, C$_3$S$_2$H$_3$, with a faint suggestion of tobermorite structure with the same formula (7). The strong afwillite lines are at 6.61, 3.18, 2.83 (strongest), and 2.73 Å. Hydration for 21 to 30 months in a paste gave only poorly crystallized 11-Å hydrate tobermorite, with a very broad line at 3.03 Å and weaker lines at 11, 2.83, and 1.82 Å.

Extensive Italian work on portland-pozzolan cements indicates formation of a tobermorite gel, a hexagonal calcium aluminate hydrate, C$_4$AH$_{13}$, and possibility of C$_2$SAH$_x$ (Stratling's compound) (8). The latter was first reported from reaction of Ca(OH)$_2$ and calcined kaolinite.

Aluminate Hydrates

Hydrated calcium aluminates crystallize in a variety of stable and metastable hexagonal and cubic structures. Recent work indicates existence of a family of hexagonal, platey aluminates, sulfoaluminates (9), and carboaluminates (8). Most pertinent to the present work are α and β polymorphs of C$_4$AH$_{13}$, with 8.2 and $\overline{7}$.9 Å maximum, d-spacings, respectively, which may dehydrate to C$_2$AH$_8$ (d$_{max}$ = 10.6 Å) or CAH$_{10}$ (d$_{max}$ = 14.6 Å). (There is now evidence that the 8.2-Å form may be a hemicarbonate.)

A summary of strongest d-spacings for pertinent compounds is given in Table 1.

METHODS

Difficulties inherent in the powder X-ray method have limited positive interpretations in both cement and pozzolan chemistry. Fortunately, slow pozzolanic reaction at room temperature yields crystals as large as 200 μ in diameter, large enough to be picked from the matrix and examined by single crystal X-ray techniques (5, 6). The objective of the present investigation is to gain further single crystal data and relate to powder diagrams and to known compounds. A General Electric XRD-5 single crystal orienter was used. Most of the single crystals examined were also crushed and photographed in a Siemens Debye-Scherrer camera to give accurate powder identification data. Studies of chemical compositions are planned by means of an electron-microprobe.

Slurries of clay minerals with lime and variable amounts of water were prepared, sealed in plastic containers, and allowed to cure at 70 ± 2 F for up to two years. The clay minerals are as follows:

1. Otay, Calif., bentonite, AAPG reference clay mineral 24 (10).
2. Lewiston, Mont., kaolinite, AAPG reference clay mineral $\overline{17}$ (10).
3. Montana vermiculite, Lincoln County, Mont.
4. Muscovite.

Three types of lime were used each with clay mineral:

1. High calcium hydrated lime, Ca(OH)$_2$
2. Dolomitic monohydrated lime, Ca(OH)$_2$ + MgO
3. Dolomitic dihydrated lime, Ca(OH)$_2$ + Mg(OH)$_2$

TABLE 1

MEDIUM AND STRONG POWDER DIFFRACTION LINES FOR SOME HYDRATED CALCIUM SILICATES AND ALUMINATES[1]

Compound	Cryst. System	Ref. No.	d	I	hkl	Compound	Cryst. System	Ref. No.	d	I	hkl
Tobermorite group (CSH I)	Ortho	15	9-14	vs	002	CAH_{10} (Cont.)			2.26	6	
			3.06	vs	220				2.18	6	
			2.81	s	400				2.11	4	
			1.83	s	040				2.06	4	
			1.67	m	620				1.94	5	
			1.54	w	440				1.83	3	
			1.40	m	800				1.79	4	
10-Å tobermorite CSH	Ortho	15	10	vs	002				1.71	3	
			3.05	vs	220				1.64	5	
			2.93	s	206				1.60	6	
			2.80	s	400				1.38	4	
			1.83	s	040	C_3AH_6	Cubic	16	5.13	s	211
Afwillite $C_3S_2H_3$	Monoclinic	15	6.46	s	$20\overline{2}$				4.45	s	220
			5.74	s	200				3.36	s	321
			5.08	mw	110				3.14	s	400
			4.73	s	002				2.814	vs	420
			2.84	vs	$31\overline{4}$				2.47	m	510
			2.74	vs	$51\overline{2}$				2.30	vs	521
			2.35	m	004				2.04	vs	611
			2.145	s	$40\overline{6}, 42\overline{4}, 510$				1.679	s	642
			1.989	m	222				1.595	m	
			1.949	s	$80\overline{6}, 62\overline{3}, 624$				1.572	m	
			1.862	m	$62\overline{5}$				1.372	m	
			1.805	s	024				1.342	m	
			1.776	s	$204, 80\overline{2}$				1.199	m	
			1.704	m	$91\overline{6}$	C_2ASH_x (Stratling's compound)	Hex	18	12.7	vs	001
			1.683	m	330, 133				6.3	s	002
			1.630	m	$33\overline{4}, 10.0\overline{6}$				4.20	bs	111
			1.604	s	$53\overline{2}, 82\overline{6}$				2.89	m	210
			1.589	m	512				2.62	m	212
$\alpha\,C_4AH_{13}$	Hex	16	8.2	vs	001				2.51	m	301
			4.1	m	002				2.37	m	302
			3.9	m	111				1.90	m	313
			2.9	m	210				1.83	m	402
			2.45	m	301				1.67	mw	411
			2.24	m	203	$C_3AH_{11} \cdot CaCO_3$	Hex	19	7.567	100	001, 100
			1.67	m	410				3.784	44	002, 111, 200
$\beta\,C_4AH_{13}$	Hex	17	7.92	vvs	001				2.858	30	112, 210
			3.99	vs	002				2.725	14	202?
			2.87	s	110				2.524	18	003, 300
			2.70	m br	11ℓ				2.488	18	
			2.46	s br	11ℓ, 02ℓ, 20ℓ				2.441	18	103?
			2.24	m	11ℓ				2.419	24	301?
			2.05	m	10ℓ, 01ℓ				2.339	22	
			1.657	ms	300				1.943	10	
C_2AH_8	Hex	16	10.6	vs	001				1.824	12	
			5.3	s	002				1.661	12	402
			3.55	m	201				1.652	16	321
			2.87	s	120				1.642	12	410
			2.48	m	301	Pozz. reac. prod. (C_3AH_{8-12}?)	Hex	5	7.59	10	006
			1.667	m	410				3.85	7	008
			1.443	m	420				3.42	4	10.10
CAH_{10}	Hex	19	14.3	10					2.87	9	110, 113
			7.16	10					2.52	6	10.16, 11.9
			5.39	4					2.33	6	11.12
			4.75	4					2.30	8	208
			4.52	3					2.20	4	02.10
			4.16	3					2.11	5	01.20
			3.72	5					1.93	3	11.18, 02.16
			3.56	7					1.86	3	21.4, 12.5
			3.26	6					1.72	4	20.20
			3.10	5					1.66	5	300
			2.88	6					1.63	4	306
			2.69	5					1.53	4	30.12
			2.55	7					1.475	4	12.20
			2.47	5							
			2.36	6							

[1] $a_0 = 5.7550$ Å; $C_0 = 46.65$ Å.

Limes were synthesized from reagent-grade laboratory chemicals. In soil stabilization the dolomitic monohydrate lime has been shown to be most effective for pozzolanic strength (11).

Powder Diffractometer Method

Reacted slurries were X-rayed under conditions approaching 100 percent r.h. with a CO_2-free atmosphere (Fig. 1).

Initially the reacted slurries were hand-packed into flat bakelite holders. Later it was found that the denser packing obtained from use of a circular brass ring mount and 1,000-psi pressure gave much higher reaction product intensities, and this proce-
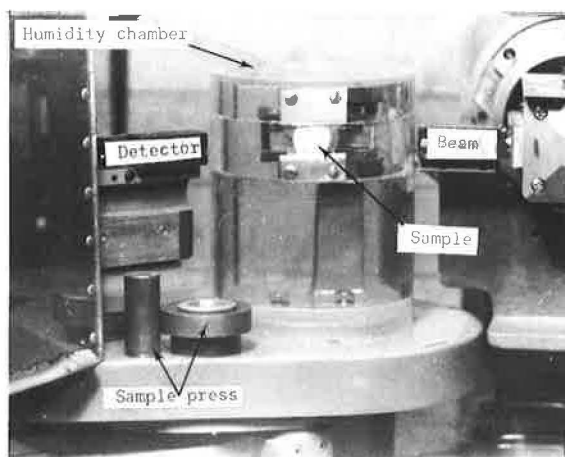
Figure 1. X-raying under 100 percent r. h. in CO_2-free atmosphere. Before entering chamber, air is passed through CaC_{12}, ascarite, and warm water. Window for passage of X-rays is Mylar plastic.

dure was employed for most curves. (Sample holders are nominal $\frac{1}{2}$-in. brass washers, 1.25 in. o.d. and 0.091 in. thick, with the center drilled out to give a $\frac{1}{2}$-sq in. hole area.)

Occurrence and intensity of new peaks relate to amount of water in the mix as well as kind of mineral and kind of lime, suggesting solubility as an important factor. Slurries with the largest new peaks were selected for detailed study.

Selection of Single Crystals

Sections were sliced from cured mixtures, broken up manually, and placed in a flat transparent dish illuminated on a dark background. A binocular microscope having about 90X provided sufficient magnification to permit picking of crystals with a glass fiber. The crystals were placed in a container such that most surficial material could be picked away manually under the microscope.

Pairs of similar crystals were then chosen and cemented to glass fibers using Canada balsam so that the long dimension of the crystal was perpendicular to the fiber. Preliminary rotating single crystal films were made to assure that the crystals were of similar internal structure. A Siemens 70-mm by 50.8-mm diameter camera and chromium Kα radiation were used for these explorations. Final selection was made of the pairs of crystals that gave a strong d-spacing previously shown as a reaction product in diffractometer traces of the slurries. One of the crystals was then demounted, placed on a glass plate and crushed for a powder photograph using the Siemens camera and CrKα radiation. A very fine glass fiber dipped in a thin solution of rubber cement was rolled in the powder and Debye-Scherrer film was made. Films were measured directly to 0.01 mm with a Kirem coincidence scale. Four or five of the strongest lines were measured to determine θ angles and expedite the oriented single crystal studies.

Single Crystal Orienter

The remaining single crystal was mounted, optically oriented on the single crystal orienter, and the unit was mounted on an XRD-5 diffractometer. A search for a reflection was made utilizing CuKα radiation, first setting 2θ for one of the strongest lines observed in the powder film. This search was made with the approximate ab (basal) plane horizontal (X = 0^0), rotating the crystal about the polar or φ axis (the near-vertical glass fiber) in the X-ray beam. If no reflection was found in a 360^0 rotation, 2θ settings for other strong film lines were searched in a similar manner until a reflection was found. The crystal orientation was then adjusted by means of the

goniometer head until the intensity of the diffracted X-ray beam was balanced for this and its 180° φ related reflection (12).

A second reflection was sought and found, preferably with the crystal rotated about the φ-axis between 60° and 90° from the first reflection. Usually the most difficult reflection to find, this is required for plotting the reciprocal lattice of the basal plane. When the second reflection was obtained and balanced under fine conditions in conjunction with the first, the two were plotted on polar coordinate paper and predictions of other reflections were made by extension of the two-dimensional reciprocal lattice plane. Reflections were checked and their intensities recorded. From this, polar planes were identified, and searches were extended to the third dimension by varying the inclination of the polar axis (θ angle) so as to identify the principal crystallographic axes of the crystal.

Indexing Reflections

The reciprocal space plots of all reflections obtained in the basal and polar planes were indexed based on the assignment of crystallographic axes and choice of the unit cell. Unit cell constants and d-spacings were then calculated using Buergers' procedure (13).

Powder Data

After determination of crystal parameters the single crystal was demounted and crushed to obtain further powder diffraction data on the pure compound. A Debye-Scherrer camera was used. The powder method enables quick measurement of d-spacings and intensities which would require much time to find by single crystal methods.

Differential Thermal Analysis

Differential thermal analysis of reacted clay-lime mixtures was run using an apparatus similar to that of Kerr et al. (10). The heating rate was 10 C per min, with an air atmosphere.

RESULTS

X-Ray Diffraction of Cured Mixtures

Kaolinite. —X-ray diffraction shows a reduction in kaolinite peak intensities after reaction with lime (Fig. 2). However, much unreacted $Ca(OH)_2$ remains in the calcitic lime mix after two years. Small amounts of $Ca(OH)_2$ and much $Mg(OH)_2$ remain in the dolomitic lime mixes. New diffraction peaks are given in Table 2, and include evidences of 12.6-Å material from reaction with dolomitic limes, and a 7.6-Å product which appears strongest from reaction with calcitic lime but is also present in the other mixes.

Vermiculite. —The raw, wet vermiculite sample shows, in addition to vermiculite, considerable regular interlayering of the 15.2-Å Ca-vermiculite with 10-Å biotite to give strong 27-, 12.6-, and 8.7-Å spacings (Fig. 2). This interlayer is sometimes called rectorite (14). On treatment with any of the three kinds of lime, vermiculite and rectorite spacings shift to 15.0 and 25 Å, respectively, and higher orders of these, perhaps indicating additional adsorption of Ca^{++} as exchangeable ion, similar to the reaction of lime with montmorillonite (1). Assignment of peaks on the diffractometer charts is aided by this shift of basal spacing multiples.

Although the mineral peaks are reduced in the lime mixes compared with the raw sample, few new peaks were found, and much lime remained unreacted after two years. The mix with calcitic lime showed moderate peaks at 8.1 and 4.59 Å.

Muscovite. —In the muscovite mixes, only that with $Ca(OH)_2$ showed any crystalline reaction product, the peak being at 7.5 Å (Fig. 2). All mixes contained appreciable unreacted lime.
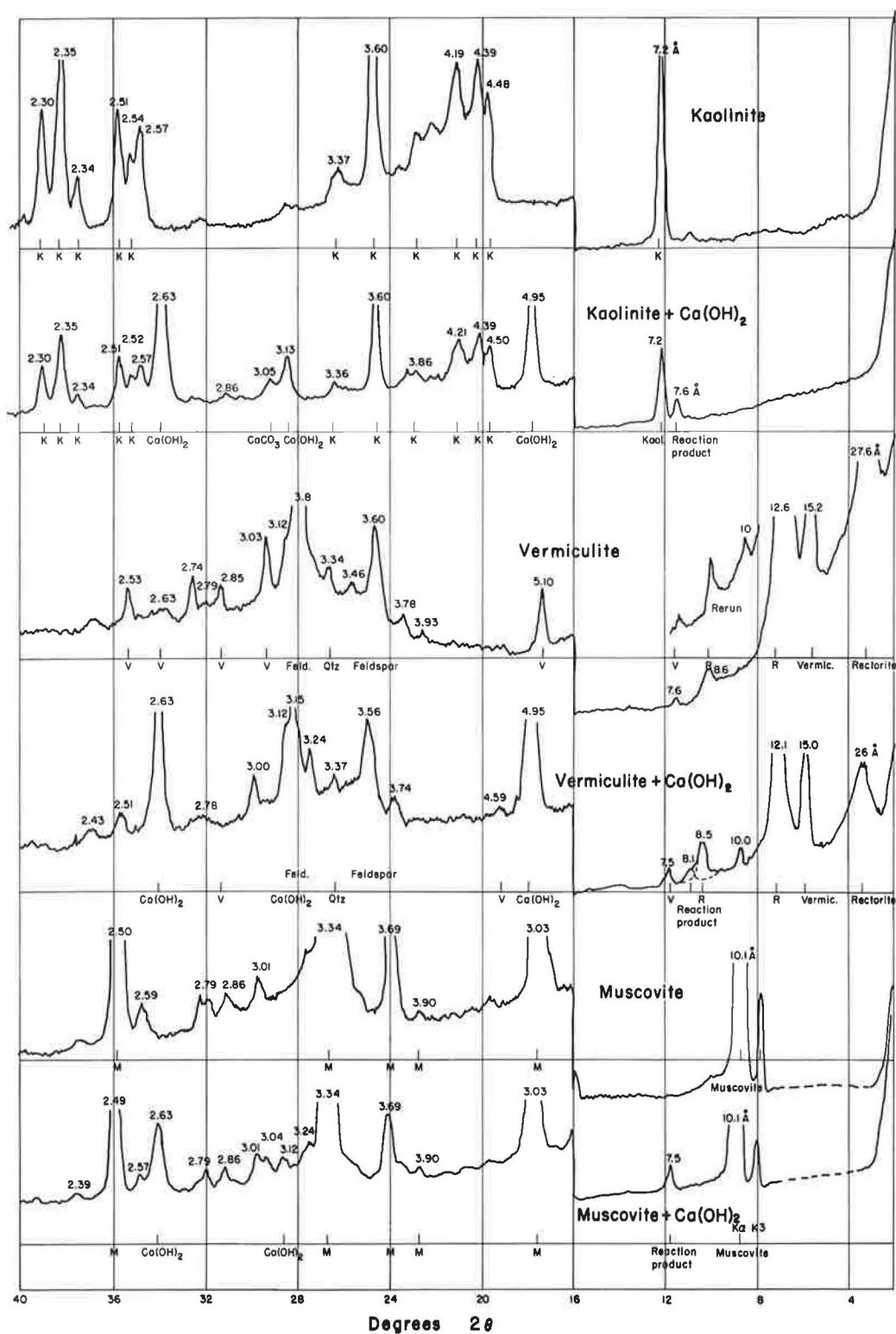
Figure 2. X-ray diffractometer curves for kaolinite, vermiculite-rectorite, and musco-
vite, with and without reaction with lime.

TABLE 2

REACTION PRODUCT d-SPACINGS FROM SELECTED MIXES

Mineral	Lime	New Peaks (Å)
Kaolinite	$Ca(OH)_2$	7.6m, 3.8w, 3.05m, 2.8w
	$Ca(OH)_2 + MgO$	12.6m vb, 7.6vw, 3.05m, 2.10vw
	$Ca(OH)_2 + Mg(OH)_2$	12.6m vb, 7.6vw, 3.80vw, 3.05s, 2.85vw, 2.10w
Vermiculite	$Ca(OH)_2$	8.1m, 4.59w
	$Ca(OH)_2 + MgO$	3.03w?
	$Ca(OH)_2 + Mg(OH)_2$	None
Muscovite	$Ca(OH)_2$	7.5m
	$Ca(OH)_2 + MgO$	None
	$Ca(OH)_2 + Mg(OH)_2$	None

Quartz. —No reactions were observed in the quartz-lime mixtures except hydration of MgO in the monohydrate lime.

Montmorillonite. —The bentonite mixtures showed appreciable crystalline pozzolanic reaction products (Fig. 3; Table 3). In the $Ca(OH)_2$ mix, 14 new peaks were found which could not be assigned to the clay, lime, or carbonates. Seven of these coincide with reflections from 10-Å tobermorite, CSH (15). In the dolomitic monohydrate lime mixes, some of the same and some different peaks appear, with seven of those present being characteristic of the tobermorite group. In the dihydrate lime mixes fewer peaks occur, all being characteristic of tobermorite.

If 10-Å tobermorite is assumed as a reaction product in all three montmorillonite mixes, unexplained peaks remaining in the $Ca(OH)_2$ mix are at 8.1, 7.9, 7.6, 4.05, 3.94, 3.79, 2.89, and 2.54 Å. Four of these coincide with the first four peaks listed for αC_4AH_{13} (Table 1). This leaves 7.9-, 7.6-, 3.79-, and 2.54-Å peaks unexplained. The 7.9-Å line may indicate presence of βC_4AH_{13} (Table 1), and the line at 7.6 Å could be $C_3AH_{11} \cdot CaCO_3$ or the compound reported by Hilt and Davidson (5). The former is reported to further carbonate and decompose on exposure to air, and may have been found in reacted lime-fly ash (5).

In the monohydrate dolomitic lime, peaks not accounted for by tobermorite and βC_4AH_{13} are at 8.8 (vw), 3.30 (s), 4.31 (w), 1.74 (w), and 1.54 (w) Å.

In the dihydrate lime mix, all reaction product peaks may be ascribed to tobermorite.

Differential Thermal Analysis of Cured Mixtures

Differential thermal analysis shows that montmorillonite endotherms at 650 and 850 C have disappeared from bentonite reacted with any of the three types of lime (curves 1 to 4, Fig. 4), suggesting weakening of the octahedral layer. X-ray shows the basal and (060) dimensions to be unchanged, but the peaks are smaller. Small endotherms from 200 to 400 C (curves 2 to 4) may be reaction products.

The DTA curves for the kaolinite mixture (curve 6) show considerable reduction of the kaolinite 600 C endotherm, but unreacted $Ca(OH)_2$ and kaolinite are still present after two years.

DTA of the vermiculite-$Ca(OH)_2$ slurry shows only unreacted mineral and lime (curve 7), whereas the curve for muscovite-$Ca(OH)_2$ indicates depletion of the lime and new peaks at 240 and 470 C. The latter suggests a degraded muscovite structure rather than a pozzolanic reaction product.

Single Crystal Data

7.95-Å Hexagonal Platey Product. —Single crystal data for 7.95-Å crystal picked
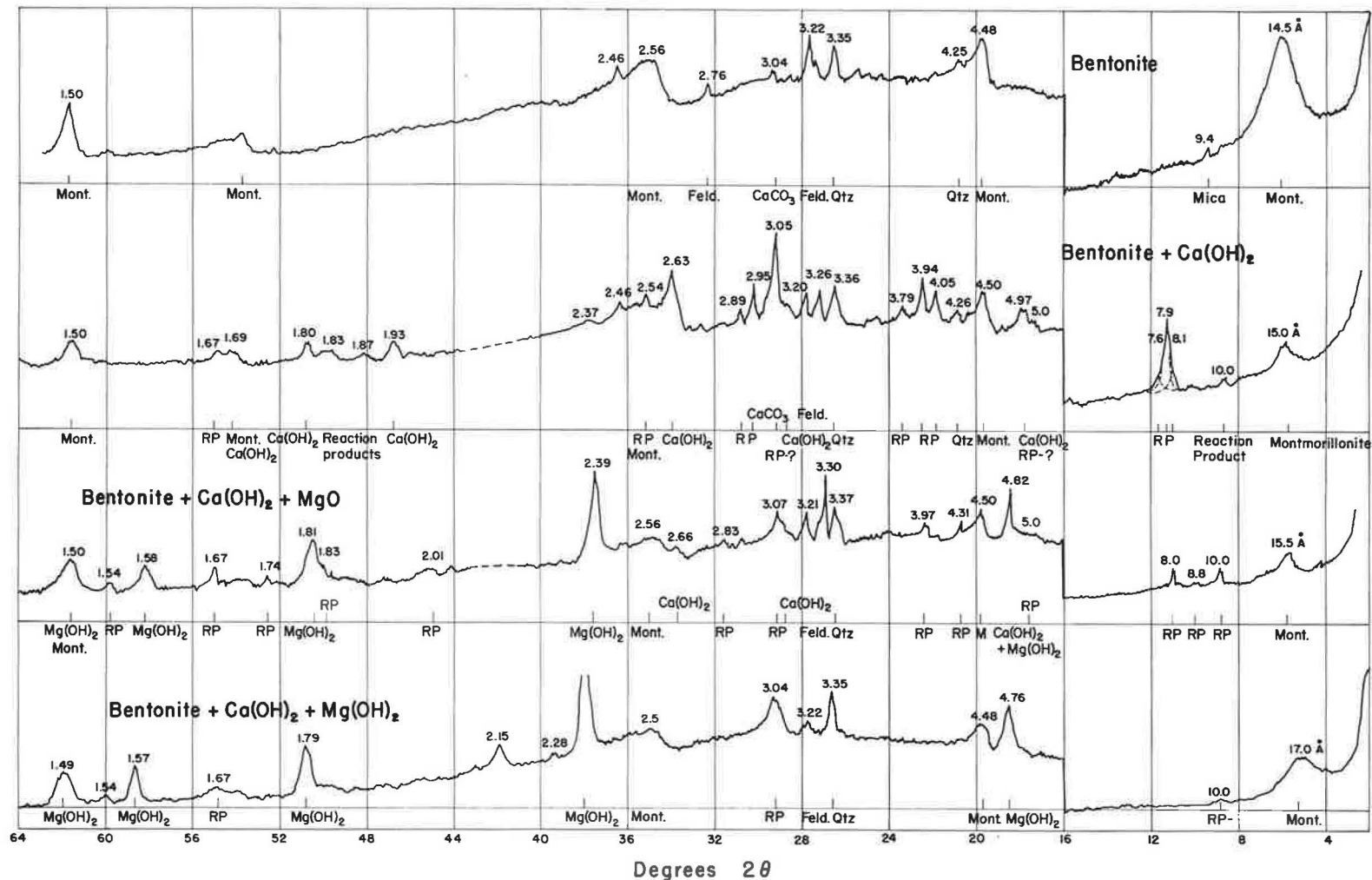
Figure 3. X-ray diffractometer curves for montmorillonite slurries with various kinds of lime.

TABLE 3
REACTION PRODUCT d-SPACINGS FROM
CURED LIME-BENTONITE MIXTURES

Ca(OH)$_2$		Ca(OH)$_2$ + MgO		Ca(OH)$_2$ + Mg(OH)$_2$	
d	I	d	I	d	I
10	w	10	m	10	vw
		8.8	vw		
8.1	m				
7.9	vs	7.95	m		
7.6	m				
5.0	mvb	5.0	m vb		
		4.31	w		
4.05	m				
3.9	s	3.97	w		
3.79	w				
		3.30?	s		
3.05	vs	3.07	vs b	3.04	s b
2.95	s				
2.89	m				
		2.83	w b		
2.54	w				
		2.01	w b		
1.83	mvb	1.83	m vb		
		1.74	w		
1.67	mb	1.67	m	1.67	m b
		1.54	w	1.54	w
				1.43	w

Figure 4. DTA curves for various clay-lime mixes.

from a cured Ca(OH)$_2$-bentonite mix are given in Table 4. The powder data show a close resemblance to $\beta C_4 AH_{13}$ (Table 1), but Miller indexes differ, primarily because of discovery of a (11·2) reflection and its second, third, and fourth, and fifth orders. Representative single crystal data and the powder data from a crushed single crystal are also given in Table 4. The refractive index of the ordinary ray was determined by the immersion method to be 1.548 ± 0.004. The crystal is uniaxial negative.

A previously described 7.94-Å triclinic crystal (unit cell parameters are a$_0$ = 8.49; b$_0$ = 12.62; c$_0$ = 8.31; α = 109.42°; β = 110.29°; γ = 95.33°) from the monohydrate dolomitic lime mix (6) gives only a weak 7.94-Å reflection on a Debye-Scherrer X-ray film of the crushed crystal. The three strongest lines were 3.22, 1.80, and 3.76 Å, which do not correspond with strong lines observed in the mixes. Therefore, the strong 7.95-Å peaks seen in Figure 2 are believed to relate to the hexagonal product.

8.1-Å Product. —An 8.1-Å peak occurs in Ca(OH)$_2$ reacted with either montmorillonite or vermiculite. As previously mentioned, this and other peaks occurring in the montmorillonite mix coincide with those of $\alpha C_4 AH_{13}$. Single crystals have not been isolated.

10-Å Product. —Although powder data tend to confirm existence of 10-Å tobermorite in the cured montmorillonite mixes, 10-Å crystals that were not tobermorite were
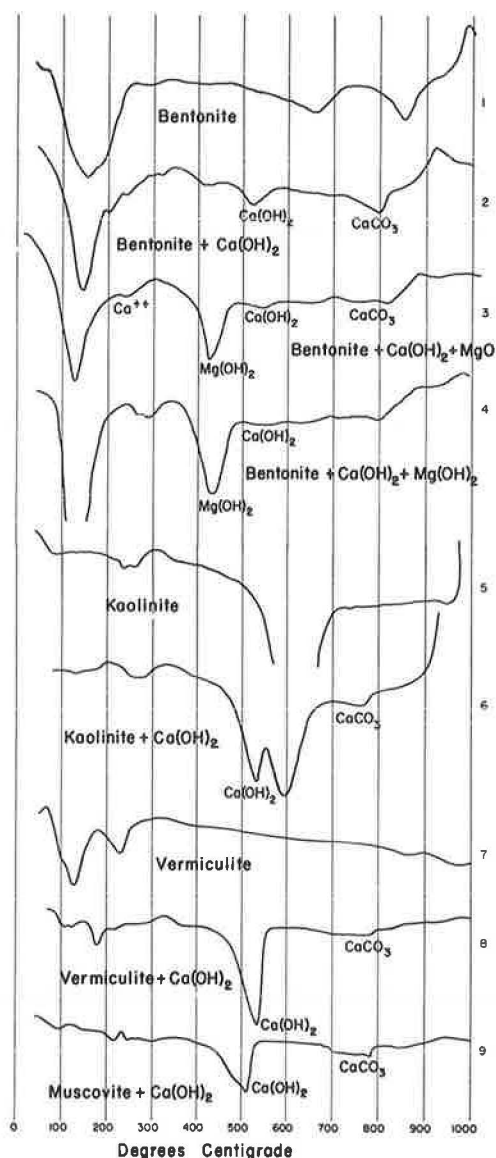
TABLE 4

X-RAY DIFFRACTION DATA FOR A HEXAGONAL 7.95-Å REACTION PRODUCT
ISOLATED FROM CURED MONTMORILLONITE+ $Ca(OH)_2$-WATER MIXTURE

Single Crystal[a]				Powder[b] of Crushed Crystal (d-spacing)	
d-Spacing			Index (hexagonal) (hk.1)		
Observed	Calc.	Intensity		Observed	Intensity
7.95	7.95	10	00.6	7.92	10
4.90	4.89	~1	11.2		
3.91	3.98	7	00.12	3.95	7
				3.73	5
				3.37	1
				2.98	1
2.88	2.88	~1	30.0	2.85	8
2.85	2.84	~1	30.3		
2.72	2.71	~1	30.6	2.67	2
2.60	2.65	~1	00.18		
2.54	2.53	2	30.9	2.51	7
2.45	2.44	3	22.4	2.43	6
2.34	2.33	1	30.12	2.32	5[c]
				2.19	2
2.13	2.14	~1	30.15	2.11	5[c]
1.96	1.99		00.24	1.99	1
1.95	1.95		30.18	1.96	1
				1.90	1
				1.86	1
				1.70	2[c]
1.67	1.67	5	33.0	1.66	7
1.63	1.63	1	33.6	1.63	4
1.56	1.59		00.30		
1.54	1.54	~1	33.12	1.53	1
1.44	1.44	2	60.0	1.47	1
1.43	1.43	2	60.3	1.45	1[c]
1.42	1.42	~1	60.6	1.41	1[c]
				1.38	1[c]
1.36	1.35	1	60.12	1.35	1[c]
				1.31	1[c]
1.27	1.27	~1	60.18	1.28	1[c]
				1.26	1[c]
				1.25	1[c]
1.22	1.22	~1	44.8	1.23	1[c]
				1.21	~1[c]
0.98	0.98	~1	55.10		
0.83	0.83	5	66.0		

[a] Incomplete data; unit cell parameters: a_o = 9.98 Å; c_o = 47.4 Å.
[b] Debye-Scherrer film.
[c] Broad.

picked from the monohydrate dolomitic lime mix. The crystal is in the monoclinic
system, with strongest powder diffraction peaks at 10, 4.5, 3.73, 3.20, 2.54, 2.38,
and 1.51 Å. The diffraction patterns and β-angle are very similar to synthetic 1M mus-
covite (14), except for much weaker basal spacing peaks. Refractive indexes and
analysis for potassium may indicate whether this is a micaceous contaminant or a true
reaction product. Single crystal and powder data are given in Table 5.

TABLE 5

X-RAY DIFFRACTION DATA FOR A MONOCLINIC 10-Å PRODUCT ISOLATED FROM A MONTMORILLONITE-$Ca(OH)_2$-MgO-WATER MIXTURE

Single Crystal[a]			Index (monoclinic) (hk.l)	Powder[b] of Crushed Crystal (d-spacing)	
d-Spacing					
Observed	Calc.	Intensity		Observed	Intensity
10.03	10.03	2	002	10.06	10[c]
5.01	5.02	1	004		
4.53	4.53	2	020		
4.53	4.52	3	$\bar{1}11$	4.50	9
4.47	4.48	6	110		
				4.30	
4.11	4.13	~1	022	4.13	
3.88	3.87		112	3.89	
				3.73	6
3.49	3.48		113	3.52	
				3.45	
				3.38	
3.35	3.36		024		
3.34	3.34	9	006		
				3.29	
				3.20	7
				3.10	
				2.98	
				2.90	
				2.84	
				2.79	
				2.62	
2.60	2.60	6	130		
2.57	2.58	7	200		
				2.54	10
2.50	2.51	1	008		
				2.45	8
				2.38	
2.26	2.26	1	040		
2.25	2.24		220, $\overline{2}20$	2.25	
2.21	2.21	~1	040	2.21	
2.19	2.19	~1	221	2.21	
2.16	2.14	2	204	2.14	
2.05	2.06	~1	044		
				2.00	
1.89	1.89	~1	206		
				1.71	
1.67	1.66	~1	208	1.66	
				1.64	
				1.61	
				1.56	
				1.53	
1.51	1.51	10	060, 330	1.51	8
1.14	1.13	~1	080		

[a] Incomplete data; unit cell parameters: a_o = 5.235 Å; b_o = 9.054 Å; c_o = 20.386 Å; β = 100.20°.
[b] Debye-Scherrer film.
[c] Spotty.

12.6-Å Product. —A very broad 12.6-Å peak occurs only in kaolinite-dolomitic lime mixes. Broadness of the peak indicates that the material is very finely or poorly crystalline, preventing use of the single crystal technique. Identification and composition of this compound remain highly speculative.

7.6-Å Product. —The 7.6-Å product previously isolated from $Ca(OH)_2$-bentonite and given in Table 1 is absent from bentonite mixes with dolomitic lime, but occurs in kaolinite reacted with any of the three limes. A similarity of basal plane dimensions to those of the aluminates has been noted [5], and d-spacings somewhat correspond to C_3AH_{8-12} [20] as well as $C_3AH_{11} \cdot CaCO_3$ (Table 1). The former composition has been discredited and variously assigned to the carbo-aluminate [21] or a solid solution of C_2A and C_4A hydrates [9].

CONCLUSIONS

1. Powder diffraction and single crystal data indicate that room temperature reactions between various minerals, lime, and water yield the crystalline products given in Table 6.

TABLE 6
CRYSTALLINE PRODUCTS

Mineral	Crystalline Product		
	$Ca(OH)_2$	$Ca(OH)_2$ + MgO	$Ca(OH)_2$ + $Mg(OH)_2$
Montmorillonite	10-Å tobermorite αC_4AH_{13}, βC_4AH_{13}, 7.6-Å aluminate? 3.79 Å 2.54 Å	10-Å tobermorite βC_4AH_{13}, 8.8 Å unknown	10-Å tobermorite
Kaolinite	7.6-Å aluminate? 3.05-Å silicate?	12.6 Å unknown 7.6-Å aluminate? 3.05-Å silicate?	12.6 Å unknown 7.6-Å aluminate? 3.05-Å silicate?
Vermiculite	8.1 Å, 4.59 Å unknown	3.03 Å?	None
Muscovite	7.5 Å unknown	None	None
Quartz	None		

2. X-ray and DTA show unreacted lime remaining in the mixes after two years, and unreacted mineral in all but montmorillonite mixes. DTA of the montmorillonite and muscovite mixes indicates weakening of the octahedral layer structure.

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