

Reactions Accompanying Stabilization Of Clay with Cement

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This paper reports the results of an investigation aimed at delineating the nature of the reactions accompanying the stabilization of clay with portland cement. Consideration of the nature of cement hydration, the physico-chemical characteristics of clays and lime-clay interaction leads to the hypothesis that during the hydration of a clay-cement mixture, hydrolysis and hydration of cement could be regarded as primary reactions which form usual cement hydration products, increase the pH, and liberate lime. The high pH and $\text{Ca}(\text{OH})_2$ concentration could initiate attack of the clay particles and also cause breakdown of amorphous silica and alumina which then could combine with calcium to form secondary cementitious material. A clay-cement skeleton and a clay matrix are likely.

Mechanical, X-ray diffraction, and chemical tests on kaolinite and montmorillonite stabilized with portland cement and with pure tricalcium silicate (C_3S), the major strength-producing compound in portland cement, gave results in agreement with this hypothesis. Compacted clay-cement mixtures were cured at 100 percent relative humidity and at 60 C (to accelerate hardening) and studied at different times after molding. X-ray analyses showed that calcium hydroxide was formed in hydrating clay-cement, but was rapidly used up in reaction with the clay. Minor alteration of the kaolinite-cement X-ray pattern and marked alteration of the montmorillonite-cement X-ray pattern were indicated after curing periods of 12 weeks, suggesting clay mineral structure breakdown and/or interaction with cement at particle surfaces. The pH of hydrating neat portland cement or neat C_3S did not change with time but decreased during the curing of clay-cement, suggesting the presence of $(\text{OH})^-$ consuming processes. The results of conductivity measurements indicate that soluble salts formed by cement hydration are converted to less soluble compounds in the presence of clays. Water soluble calcium and free calcium hydroxide analyses showed that all clay-cement specimens contained only a fraction of the $\text{Ca}(\text{OH})_2$ that would be present if normal hydration of the cement took place without cement-clay interaction. The "missing" $\text{Ca}(\text{OH})_2$ may have participated in a pozzolanic-type reaction with the clay mineral. Clay-cement cannot, therefore, be regarded as a simple mixture of hydrated cement particles bonding together unaltered clay particles, but must be considered as a system in which both the clay and hydrating cement combine through secondary reactions.

•SOIL-CEMENT stabilization has been used on an ever-increasing scale in recent years because of the significant improvement in soil properties that may be achieved as a result of cement treatment. The improvement in engineering properties of cement-treated soils is believed to be due mainly to the hardening of portland cement, but the processes taking place during the hydration of cement in the presence of clays are not fully understood.

If the hardening of soil-cement were due solely to the hydration of cement, the soil could be regarded as a chemically inert component. The cement particles would bind adjacent soil grains together during hardening and form a more or less continuous skeleton of a hard, strong material enclosing a matrix of unaltered soil. This skeleton could also be expected to "plug" some of the voids of the soil, reducing permeability and swelling, and increasing the resistance of soil-cement to the deleterious effects of changes in ambient moisture conditions.

If, in addition to hardening, reactions take place between hydrating cement and clay components, additional cementitious material could be generated leading to the strengthening of the bonds between the soil grains themselves and between soil and cement particles. At the same time, the clay participating in such reactions could suffer alteration to the extent that it would become less plastic and less expansive when exposed to water.

Improved techniques of soil-cement stabilization may be expected to follow the development of a better understanding of cement-clay interaction. Several investigators have recently postulated that the cementitious material formed during the hardening of soil-cement differs in composition from hardened cement paste. Lambe, Michaels and Moh (16) suggest that strong bases formed during the hydration of cement dissolve silica and alumina from clay, and that calcium ions liberated during the hydrolysis of cement react with dissolved silica and alumina forming cementitious material. Interaction between soil and cement has also been suggested by others (2, 3, 10, 18).

This paper reports the results of an investigation aimed at further delineating the nature of the reactions accompanying the stabilization of clay with portland cement. In the formulation of a hypothesis for cement-clay interaction, a general understanding of the nature of cement hydration, the physico-chemical characteristics of clays, and lime-clay interaction is useful. These factors are summarized briefly.

HARDENING OF NEAT PORTLAND CEMENT PASTE

The dry portland cement particle is a heterogeneous material containing small crystals of C_3S , C_2S , C_3A , and a solid solution commonly described as C_4AF (21). (According to nomenclature used in cement chemistry $C = CaO$, $S = SiO_2$, $A = Al_2O_3$, $F = Fe_2O_3$, $H = H_2O$.) A simplified summary of reactions during the hydration of cement is given by Lea and Desch (17). During cement hydration the components react with water. Hydrated silicates, hydrated aluminates and calcium hydroxide (from C_3S and C_2S) are the main reaction products. Taylor (22) points out that the silicate and aluminate phases are intimately mixed and that probably none of them is fully crystalline. Part of the $Ca(OH)_2$ may also be intimately mixed with the other hydrated phases and be only partly crystalline.

The composition of the cement hydration products is not uniquely defined by chemical formulas, but may vary considerably. For instance, the Ca:Si ratio of calcium silicate hydrate, CSH, which is formed from C_3S , and which is the main strength-producing compound, can vary between 0.8 and 1.33 (22). CSH type of compounds are similar to the natural mineral tobermorite. Taylor (22) reports the results of a study in which CSH was treated with water and lime solutions. A gain in the lime content of CSH in the presence of lime-rich solutions and a loss in the lime content of CSH in the presence of solutions of low lime concentration were observed. Thus in soil-cement the pore water could extract lime from the hydrating cement in the event that the lime content of the pore water was maintained at low level as a result of reaction with the clay.

Changes in the composition of hydrated calcium silicates are not necessarily accompanied by a change in their X-ray patterns. Taylor (22) found that irrespective of the Ca:Si ratio of CSH the X-ray pattern resembles that of tobermorite, but that only the strongest reflections can be observed.

SOIL PROPERTIES RELEVANT TO CLAY-CEMENT INTERACTION

One prerequisite for the formation of additional cementing materials in cement-clay interaction is the solubilization of silica and alumina from clay components. The solubility of clay minerals is not as well defined as that of pure chemical compounds. The amount of impurities present, the degree of crystallinity of the minerals and particle size distribution are some of the factors influencing solubility. In general, acids are effective in removing alumina and other metallic oxides from clay minerals, while alkalies dissolve mainly silica (9), although alumina may be attacked in a high pH environment as well.

Correns (4) reported the dissolution of small amounts of Al_2O_3 and SiO_2 from montmorillonite and kaolinite with distilled water. Hashimoto and Jackson (11) observed the dissolution of about 3 percent SiO_2 from oven dry kaolinite and approximately 8 percent SiO_2 from montmorillonite by boiling in 0.5 N NaOH. The solubility of the clay minerals would be expected to increase with decreasing particle size and decreasing degree of crystallinity because of a greater specific surface and less resistant crystal structure.

Minerals having a three-layer structure (e.g., montmorillonite) are usually more soluble than minerals having a 2-layer structure (e.g., kaolinite) because of the greater specific surface of the 3-layer minerals and because these minerals are less resistant to penetration of interlayer cations.

High cation exchange capacity could lead to the binding of cations that would otherwise participate in the formation of cementing material. Soil components other than clay minerals, particularly finely divided amorphous silica and alumina, are less resistant to chemical attack and represent a potential source for cementitious matter. Such components may play a very significant role in clay-cement stabilization.

LIME-CLAY MINERAL INTERACTION

Inasmuch as lime is generated during the hydration of portland cement, the interaction of lime and clay minerals would be expected to have an important influence on the overall clay-cement interaction process. The colloid chemistry of lime stabilization of soils has been reviewed by Anderson (2), and a comprehensive bibliography of lime stabilization was presented by Herrin and Mitchell (13). Reactions taking place between clay minerals and lime may be divided into two distinct types: those which are completed rapidly (ion exchange and flocculation) and reactions which proceed slowly (carbonation, pozzolanic reactions, and the formation of new materials).

Addition of lime to clays causes flocculation because of the increased electrolyte content of the pore water and also as a result of ion exchange by the clay to the calcium form. Although flocculation and ion exchange may be complete in a few days, the slower reactions producing cementitious material may proceed for years. Cementitious material in lime-clay mixtures may be formed by carbonation and by chemical reactions between clay components and lime. Carbonation normally is confined to surfaces exposed to air and involves the conversion of lime to calcium carbonate by carbon dioxide absorbed from the air. The calcium carbonate cements soil particles together and enhances their stability.

Pozzolanic chemical reactions between lime and soil materials have been utilized for centuries. Little was known about the composition of the reaction products before 1960 because of the probable amorphous nature of the initial products and the fact that crystalline products, often poorly defined, usually do not appear until after long curing periods, and then only in cases where a high percentage of lime was added. Pozzolanic materials are defined as silicious or silicious and aluminous materials, which themselves possess little or no cementitious value but will, in finely divided form and in the presence of moisture, chemically react with calcium hydroxide at ordinary temperatures to form compounds possessing cementitious properties (ASTM Designation C219-55). Clay minerals and some other soil components possess pozzolanic properties (2). The addition of lime to soil causes an instantaneous rise in the pH of the molding water (15) due to solution and dissociation of the $\text{Ca}(\text{OH})_2$. The high pH

increases the reactivity of surface silica and alumina. The calcium ions combine with the reactive hydrous silica and alumina and form gradually hardening cementitious material.

Goldberg and Klein (8) treated Wyoming bentonite with up to 8 percent calcium hydroxide. They reported the disappearance of $\text{Ca}(\text{OH})_2$ lines from the X-ray spectrum, observed no other changes in the X-ray pattern of the clay, and suggested the conversion of calcium hydroxide to CaCO_3 and some other compound.

Eades and Grim (6) investigated the reaction of hydrated lime with pure clay minerals and noted the formation of new crystalline phases, probably calcium silicate hydrates, produced by lime-kaolinite interaction.

This reaction appeared to take place by the lime eating into the kaolinite particles around the edges with a new phase forming around the core of kaolinite. In contrast, the reactions of lime with three layer minerals (illite, montmorillonite) begin by a replacement of existing cations between the silicate sheets with Ca^{++} . Following the saturation of the interlayer positions with Ca^{++} the whole clay mineral structure deteriorates without the formation of substantial new crystalline phases.

The X-ray diffraction pattern of well crystallized kaolinite showed some weakening of the prism reflections. The effect was accompanied by the weakening of the basal reflections and was more pronounced on less resistant, poorly crystallized material. Halloysite behaved in the same manner as kaolinite.

The formation of new minerals by lime stabilization under field conditions was proven by Eades, Nichols and Grim (7), who identified calcium silicate hydrates by X-ray methods on soils which were stabilized with lime in 1956-57 and sampled in 1960. Hilt and Davidson (14) isolated a crystalline calcium aluminate hydrate reaction product from a mixture of bentonite, 40 percent lime and 110 percent water after 7 months' curing.

Some of the more significant points emerging from the preceding review may be summarized by the following statements:

1. Hydrating cement is a partly crystalline, multiphase, alkaline system containing calcium hydroxide, calcium silicate hydrates and hydrated aluminates. The system is capable of releasing lime and may vary in composition without significant changes in its X-ray diffraction pattern.
2. Silica and alumina may be dissolved from clay minerals, and from amorphous material also present in most clays, by alkalis or calcium hydroxide.
3. Flocculation and ion exchange take place rapidly when lime is mixed with moist clay minerals. Lime in excess of the exchange requirement of the clay may react with clay minerals. This pozzolan-type reaction proceeds slowly. The initial reaction products are amorphous and may later change to a crystalline form. The X-ray diffraction patterns indicate a destruction of montmorillonite mineral structure by lime, but only moderate attack on kaolinite.

A HYPOTHESIS FOR CLAY-CEMENT INTERACTION

Primary and secondary processes may be distinguished during the hardening of a clay-cement mixture. Hydrolysis and hydration of cement could be regarded as primary reactions. These processes would initially form usual cement hydration products and increase the pH of the pore water. The fresh calcium hydroxide formed during this period would be more reactive than ordinary lime.

Clay may participate in the secondary processes. The calcium ions produced by cement hydration first convert the clay to the calcium form and tend to intensify the flocculation initiated by the increase in total electrolyte content accompanying the addition of cement. The calcium hydroxide initiates attack of the clay particles and amorphous constituents. Dissolved silica and alumina combine with calcium ions and precipitate additional cementitious material.

Calcium hydroxide used up in the secondary processes could be replenished to some extent by the release of lime from the hydrating cement. Thus, products of the primary reaction provide a reactant necessary for the continuation of the secondary processes.

Since the secondary cementitious matter would be mainly formed on or near the surface of clay particles, the flocculated clay particles would be "glued" together at points of contact by the secondary cementitious material. Even stronger bonds may be expected to develop between the hydrating cement paste and clay particles coating cement grains. The structural similarity between some cement hydration products and clay minerals even suggests possible epitaxy; i.e., a direct propagation of a similar structure from clay crystal to cement particles.

The overall effect of the postulated cement-clay interaction would be the formation of primary and secondary cementitious matter. The primary products harden into a high strength "aggregate" and differ from normally hydrated cement in that their calcium content is lower. The secondary processes enhance the strength and stability of soil-cement by producing additional cementitious matter which increases interparticle bond strength.

EXPERIMENTAL STUDIES

The experimental work was carried out on compacted clay-cement specimens. Monomineral clays were used in preference to natural clays of more complex composition. Kaolinite and montmorillonite were selected to represent the least and most reactive type of clay minerals. Compacted clay-cement cylinders were cured at 100 percent relative humidity and 60 C for 1 day, and 1, 4 and 12 weeks. After each curing period the specimens and appropriate blank control materials were tested.

To test the hypothesis, experimental procedures were selected as follows:

<u>Purpose of Test</u>	<u>Test Used</u>
1. To index the formation and hardening of primary and secondary cementitious material	Unconfined compression test on soaked specimens
2. To follow the variation of water content and to assess dimensional stability during curing and soaking	Water content, linear shrinkage, and swelling
3. To identify crystalline products from primary and secondary reactions and to observe changes in the crystal structure of clay minerals	X-ray diffraction
4. To observe changes in the alkalinity of specimens after various curing periods	pH
5. To determine changes in the available (free) $\text{Ca}(\text{OH})_2$ content of specimens with curing time	Free calcium hydroxide content
6. To determine changes in concentration of all water soluble electrolytes in specimens with curing time	Conductivity of water extract
7. To determine changes in the relative concentration of certain water soluble cations with curing time	Ca, Na and K content of water extract

Materials

Materials used in the investigation were as follows:

1. Georgia kaolin, representing a coarse-grained well crystallized kaolinite. This material has a cation exchange capacity of 5 meq/500g with calcium accounting for about 70 percent of the total exchange complex. The pH was 5.5, determined in a 1:5 clay-water suspension.

2. Wyoming bentonite, a commercially available Na montmorillonite with a cation exchange capacity of 85 meq/100g. Exchangeable cations included 70-meq Na^+ , 8-meq Ca^{++} and 1-meq K^+ per 100-g montmorillonite. The pH of the montmorillonite was 8.6, determined in a 1:5 clay-water suspension.

3. Portland cement, a Type I low alkali cement from the Permanente Cement Co. of California. Chemical analysis of the cement is given in the Appendix.

4. Tricalcium silicate, C_3S . Type I portland cement contains about 50 percent tricalcium silicate, C_3S , which is the main contributor to the strength of hardened cement. It was hoped that by using pure C_3S as cementing material the effects of any clay mineral-cement interaction would be more readily detectable. The tricalcium silicate was a synthetic material of high purity, made at the University of California, Berkeley. Characteristics of this preparation have been described by Polivka, Klein and Best (19).

Methods

Preparation of Specimens.—Eight series of specimens were prepared, four with kaolinite (K) and four with montmorillonite (M). Each clay was stabilized with portland cement (P) or with tricalcium silicate (C_3S). For each clay-cement combination, 15 percent and 30 percent (by weight of dry clay) of cementing material was employed. The symbols used to identify each test series indicate the clay mineral (K or M), the cementing material (P or C_3S) and the percent cement (15 or 30) in the specimens. Thus, MP refers to specimens made from montmorillonite with 15 percent portland cement.

Clay and cement were blended together in the dry state to obtain a uniform mix. Distilled water was added from a burette and mixed by hand with the dry materials for 7 minutes. The samples were prepared by kneading compaction using a Harvard miniature compactor type apparatus. The hand-mixed material was compacted in 5 layers at a molding water content exceeding the optimum value by about 2 percent in order to insure adequate water for cement hydration. The resulting cylindrical samples were 0.75 in. in diameter and 1.5 in. high.

Figure 1 shows compaction curves of the clay-cement mixtures for the applied compactive effort. The compactive effort for the montmorillonite series was higher than that used for the kaolinite series in order to obtain about the same water/cement ratio and a similar dry density in each series.

Specimens were cured at 100 percent relative humidity in screw-top glass jars at 60 C for 1 day and 1, 4 and 12 weeks. The curing temperature of 60 C was selected to accelerate hydration reactions. Each batch consisted of at least four specimens of the same composition. Compositional data on specimens of all test series are given in Tables 1 and 2.

Linear Swelling and Moisture Content.—The length of each test cylinder was measured after compaction, after curing and after soaking. The moisture content of the material used during compaction and the fractured test cylinders was determined by oven drying at 110 C. Because some hydration of cement takes place during oven drying, some of the water originally present in the sample will become tied up in cement hydration; therefore, moisture content values are relative rather than absolute.

Unconfined Compression Tests.—At the end of each curing period the test cylinders were submerged in distilled water and soaked for 24 hours. The wet specimens were tested in unconfined compression, after the removal of surface moisture, at a strain rate of 1.6 percent per minute in a Universal testing machine.

X-Ray Tests.—Cured samples were ground in a mortar and packed into a bakelite holder. Care was taken to avoid particle orientation. The tests were carried out with a North American Phillips Geiger counter X-ray spectrometer, type No. 12021. Copper $\text{K}\alpha$ radiation was used with a nickel filter. The scanning speed was 2 deg 2 θ per min.

pH and Conductivity Tests.—Cured specimens not soaked in water were ground up in a mortar. Ten grams of the ground specimen were mixed with 50-cc distilled water with an electric stirrer for 10 minutes. The suspension was filtered immediately and

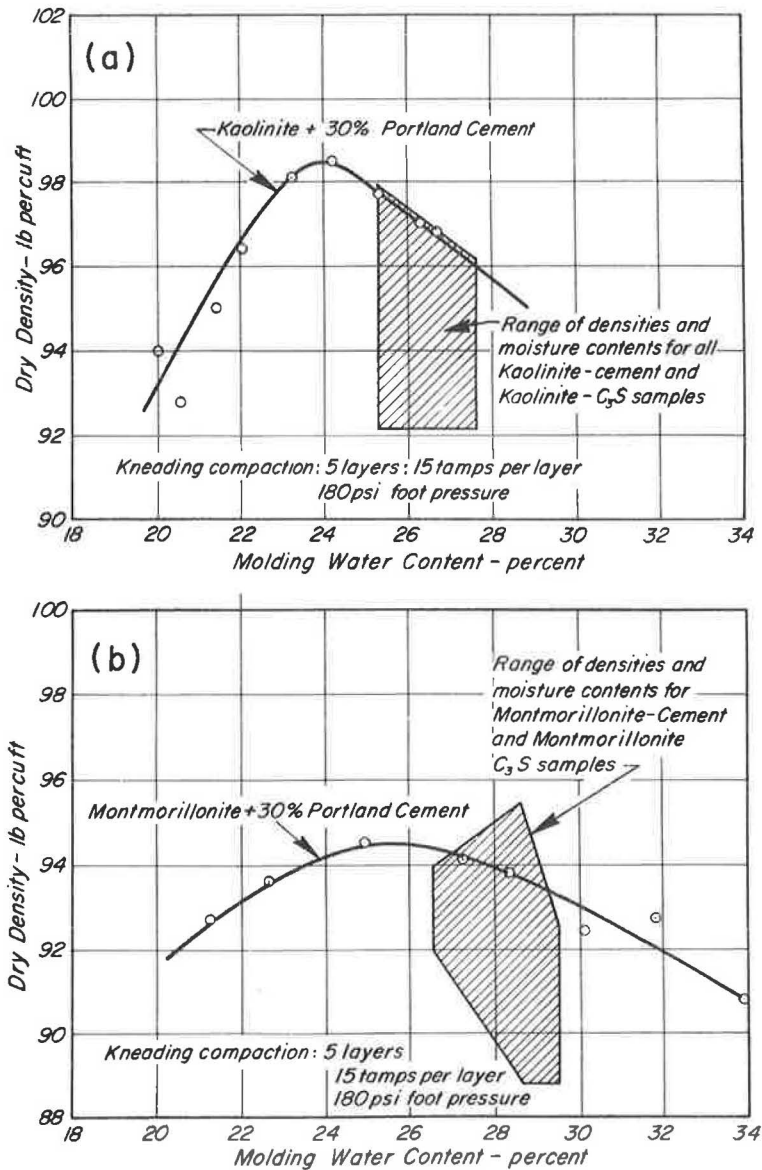


Figure 1. Compaction of mixtures: (a) kaolinite-cement; (b) montmorillonite-cement.

the filtrate collected in a polyethylene bottle. The pH of the filtrate was determined with a Beckman model H2 pH meter. The conductivity of the filtered extract was tested with a "Solu Bridge" type RD conductivity bridge.

The moisture content of the pulverized specimens was determined on a separate sample. Conductivity results are based on the oven dry weight of the ground material.

Calcium, Sodium and Potassium Content of Water Extract.—The filtrate from the previously described extraction was used for the determination of water soluble Ca^{++} , Na^+ , and K^+ content of the specimens. The tests were carried out with a Perkin-Elmer model 52 flame photometer. Results are presented on the same basis as conductivity data.

In an attempt to avoid the carbonation of the fresh lime and the hydrated calcium compounds in the specimens, the exposure of chemical test samples to open air was

TABLE 1
COMPOSITION AND MECHANICAL PROPERTY DATA^a
KAOLINITE-CEMENT SPECIMENS

Sample	Cement or C ₃ S Content (%)	Molding Water Content (%)	Dry Density (pcf)	Age at Test (days) ^b	Axial Swell During Soaking (%)	Water Absorption During Soaking (%)	Compressive Strength (psi)
K	0	26.4	92.2	0	—	—	134 ^c
KP 15	PC 15	26.0	92.2	2	0.35	5.5	432
		26.5	92.4	8	0.09	4.4	704
		25.4	95.7	29	0.09	4.0	862
		26.3	92.2	85	0.19	2.4	1,305
KC ₃ S 15	C ₃ S 15	27.6	92.1	2	1.72	4.9	633
		26.8	92.5	8	0.17	3.9	832
		27.3	92.4	29	0.08	3.1	1,630
		27.0	92.2	85	0.07	1.3	1,830
KP 30	PC 30	25.6	97.6	2	0.10	3.3	1,030
		26.5	96.6	8	0.22	2.5	1,130
		26.4	97.0	29	0.21	4.8	1,830
		27.0	98.5	85	0.15	1.7	2,180
KC ₃ S 30	C ₃ S 30	25.3	97.6	2	1.48	3.1	1,130
		25.9	96.5	8	0.44	2.8	1,450
		25.6	97.4	29	0.04	2.7	2,550
		26.0	98.5	85	0.09	2.2	2,600

^aValues represent the average of the values for a minimum of three samples.

^bSamples cured at 60 C and 100 percent relative humidity and soaked without confinement for final 24 hours.

^cUntreated samples disintegrated upon immersion; strength value is for unsoaked specimen.

TABLE 2
COMPOSITION AND MECHANICAL PROPERTY DATA^a
MONTMORILLONITE-CEMENT SPECIMENS

Sample	Cement or C ₃ S Content (%)	Molding Water Content (%)	Dry Density (pcf)	Age at Test (days) ^b	Axial Swell During Soaking (%)	Water Absorption During Soaking (%)	Compressive Strength (psi)
M	0	29.0	92.3	—	—	—	100 ^c
MP 15	PC 15	28.6	95.5	2	1.01	5.0	237
		28.7	91.8	8	0.17	3.5	472
		28.4	95.1	29	0.00	1.5	475
		28.9	90.4	85	0.08	1.6	527
MC ₃ S 15	C ₃ S 15	27.9	90.3	2	1.06	7.1	427
		29.5	90.0	8	0.11	5.9	628
		28.7	88.9	29	0.65	1.0	631
		28.8	88.7	85	0.13	1.4	612
MP 30	PC 30	27.0	98.4	2	0.36	4.9	462
		27.7	94.1	8	1.47	5.3	581
		27.7	94.0	29	0.28	5.0	1,020
		27.5	93.5	85	0.00	1.0	1,470
MC ₃ S 30	C ₃ S 30	26.6	92.8	2	0.88	5.4	800
		28.0	93.1	8	0.61	4.6	950
		27.0	92.0	29	0.08	6.4	1,150
		27.0	91.4	85	0.13	1.0	1,570

^aValues represent the average of the values for a minimum of three samples.

^bSamples cured at 60 C and 100 percent relative humidity and soaked without confinement for final 24 hours.

^cUntreated samples disintegrated upon immersion; strength value is for unsoaked specimen.

TABLE 3
CHEMICAL TEST RESULTS, KAOLINITE-CEMENT SPECIMENS

Sample ^a	Age at Test (days)	pH ^b	Soluble Salts by Conductivity (meq/100g)	Free Ca(OH) ₂ (meq/100g)	Water Soluble Ca ⁺⁺ (meq/100g)	Water Soluble Na ⁺ (meq/100g)	Water Soluble K ⁺ (meq/100g)
K	0	5.50	0.80	0	—	—	—
P	1	12.60	60.5	260	56	0.91	0.85
	7	12.65	87.5	400	74	0.87	0.79
	28	12.63	79.0	420	72	0.83	0.76
	84	12.65	81.0	440	70	0.71	0.69
C ₃ S	1	12.65	36.1	280	35	0	0
	7	12.63	94.2	430	88	0	0
	28	12.64	91.0	460	79	0	0
	84	12.65	89.7	500	80	0	0
KP 15	1	11.80	5.8	2.8	4.0	0.4	0.3
	7	11.75	5.1	3.0	3.3	0.4	0.3
	28	11.65	4.9	2.8	2.9	0.3	0.3
	84	11.55	3.7	2.0	2.9	0.2	0.3
KC ₃ S 15	1	12.30	13.8	5.2	3.8	0.4	0
	7	12.10	6.4	5.2	3.0	0.3	0
	28	11.95	6.0	4.4	2.9	0.3	0
	84	11.60	3.8	2.2	2.8	0.2	0
KP 30	1	12.15	12.6	12.2	8.0	0.4	0.6
	7	12.00	8.1	11.2	5.0	0.5	0.6
	28	11.90	7.7	10.8	4.6	0.5	0.5
	84	11.58	5.8	4.2	4.1	0.5	0.4
KC ₃ S 30	1	12.50	20.7	15.2	12.1	0.5	0
	7	12.20	8.5	11.5	5.1	0.4	0
	28	12.00	7.1	9.8	4.8	0.3	0
	84	11.60	5.2	3.2	4.7	0.2	0

^aP = portland cement, C₃S = tricalcium silicate, 15 = 15 percent cement or C₃S by weight of dry clay, 30 = 30 percent cement or C₃S by weight of dry clay.

^bDetermined in suspension of one part solid in five parts water.

prevented insofar as possible. These efforts are believed to have served their purpose but prevented the use of techniques (repeated grinding and sieving, multiple extraction and filtration, etc.) required for complete extraction. Thus data on conductivity and water soluble salts do not represent absolute values but serve as comparative figures for the interpretation of the processes during clay-cement interaction.

Free Calcium Hydroxide Content.—The method used for determination of free calcium hydroxide content is based on extraction with a nonaqueous solvent from dried specimens to prevent the formation of additional Ca(OH)₂ from unhydrated cement during extraction. Cement paste and clay-cement specimens were ground and dried to constant weight in vacuum over P₂O₅. The free Ca(OH)₂ content was determined by using several extraction times in accordance with the modified Franke method (20).

RESULTS

The results of the mechanical tests are given in Tables 1 and 2; the chemical test results in Tables 3 and 4.

Unconfined Compression Tests

Figure 2 shows compression test results for kaolinite-cement specimens, and Figure 3 for montmorillonite-cement specimens. Each point represents the average of at least 3 test results obtained on clay-cement samples soaked for 24 hours before testing. Because blank specimens containing no stabilizer disintegrated rapidly on

TABLE 4
CHEMICAL TEST RESULTS, MONTMORILLONITE-CEMENT SPECIMENS

Sample ^a	Age at Test (days)	pH ^b	Soluble Salts by Conductivity (meq/100g)	Free Ca(OH) ₂ (meq/100g)	Water Soluble Ca ⁺⁺ (meq/100g)	Water Soluble Na ⁺ (meq/100g)	Water Soluble K ⁺ (meq/100g)
M	0	8.50	8.70	0	—	—	—
P	—	—	—	— ^c	—	—	—
C ₃ S	—	—	—	— ^c	—	—	—
MP 15	1	11.80	23.3	1.0	0.6	16.2	0.2
	7	11.70	22.2	4.6	5.3	16.4	0.2
	28	11.40	20.5	3.2	4.3	16.3	0.2
	84	10.90	17.2	2.8	2.0	15.0	0.1
MC ₃ S 15	1	12.15	32.7	1.0	0.9	17.0	0
	7	12.10	23.6	5.8	5.0	17.7	0
	28	11.55	18.0	5.0	4.3	13.3	0
	84	11.10	13.0	3.0	1.4	10.8	0
MP 30	1	12.25	27.3	1.6	2.7	16.8	0.2
	7	12.10	24.2	7.2	4.6	16.5	0.2
	28	11.95	21.0	6.2	4.3	16.2	0.2
	84	11.48	16.6	5.2	1.8	13.2	0.2
MC ₃ S 30	1	12.30	38.5	3.8	4.1	17.9	0
	7	12.25	29.7	10.0	5.2	17.6	0
	28	12.00	23.0	8.0	4.7	17.3	0
	84	11.65	14.2	5.4	1.6	13.0	0

^a P = portland cement, C₃S = tricalcium silicate, 15 = 15 percent cement or C₃S by weight of dry clay, 30 = 30 percent cement or C₃S by weight of dry clay.

^b Determined in suspension of one part solid in five parts water.

^c See Table 3.

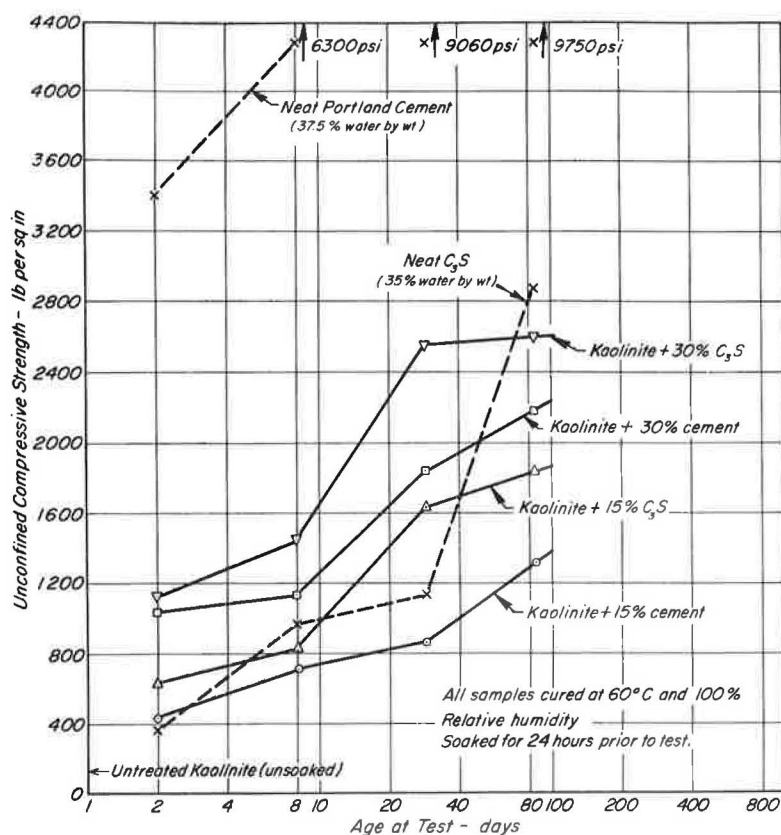


Figure 2. Strength of kaolinite-cement as a function of curing time.

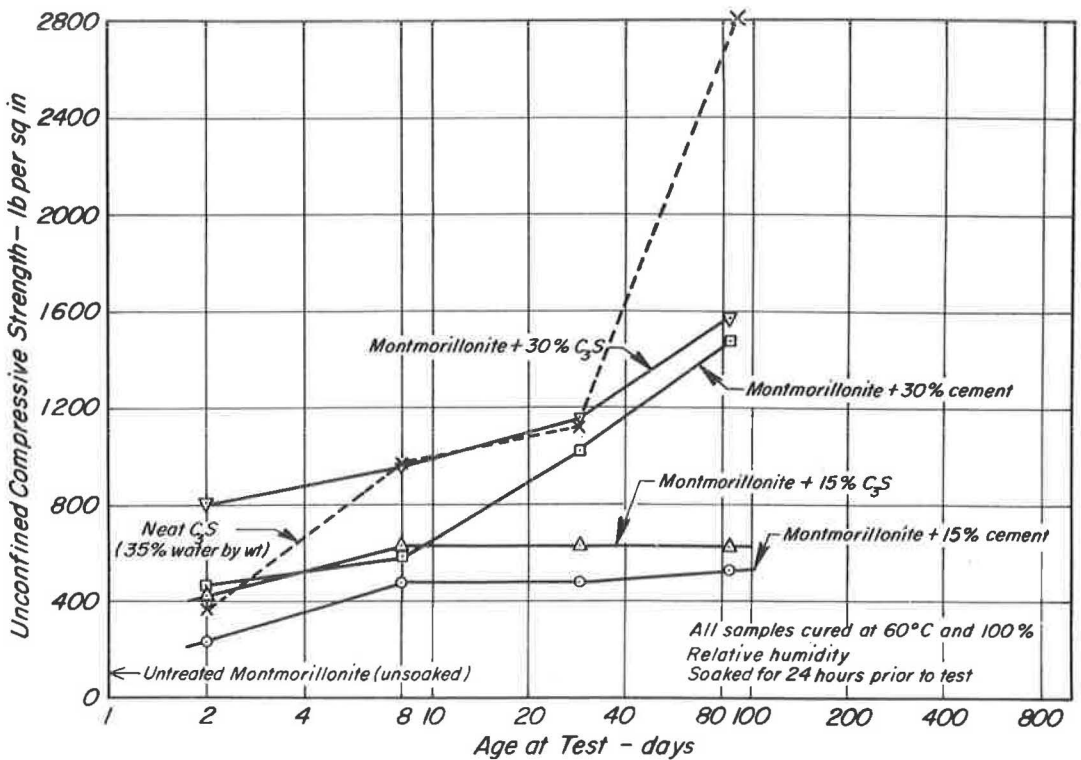


Figure 3. Strength of montmorillonite-cement as a function of curing time.

exposure to water, their strength was determined without previous soaking. Clay-cement specimens failed at axial strains ranging from 0.3 percent to 1.3 percent. Cement treatment led to a several-fold strength increase in all cases, indicating effective stabilization at the treatment levels used.

All KP and KC₃S specimens had a higher 1-day strength than the corresponding MP and MC₃S specimens. The rate of strength increase from 1 to 7 days was about the same for all series, but kaolinite samples gained strength more rapidly from 1 to 4 weeks than montmorillonite specimens. The strength of MP 15 and MC₃S 15 test cylinders remained practically unchanged for curing times exceeding 7 days.

Samples of the C₃S series were always stronger than the corresponding specimens in the portland cement series. Since alite, a C₃S type clinker component, is the major contributor to the strength of portland cement, stabilization with pure C₃S would be expected to increase the compressive strength above that obtained with ordinary cement.

Specimens made of neat C₃S paste were found to have only a fraction of the early strength of neat portland cement paste specimens of the same age (Fig. 2). The high purity of the C₃S preparation used in this work could possibly be responsible for this as a result of the formation of a low strength intermediate hydration product in a neat paste. All clay-C₃S specimens developed higher strengths after 24 hours than neat C₃S specimens cured for 1 day. This anomalous behavior could be explained by assuming an interaction between C₃S and clay which modifies the C₃S hydration process in such a manner that high strength hydration products are formed rapidly in the presence of clays. Finally, compression tests on specimens of kaolinite plus 30 percent cement and montmorillonite plus 30 percent cement cured at room temperature gave strengths approximately equal to the strengths of mixtures containing 15 percent cement but cured at 60°C, thus illustrating the acceleration in rate of strength gain effected by elevated temperatures during curing.

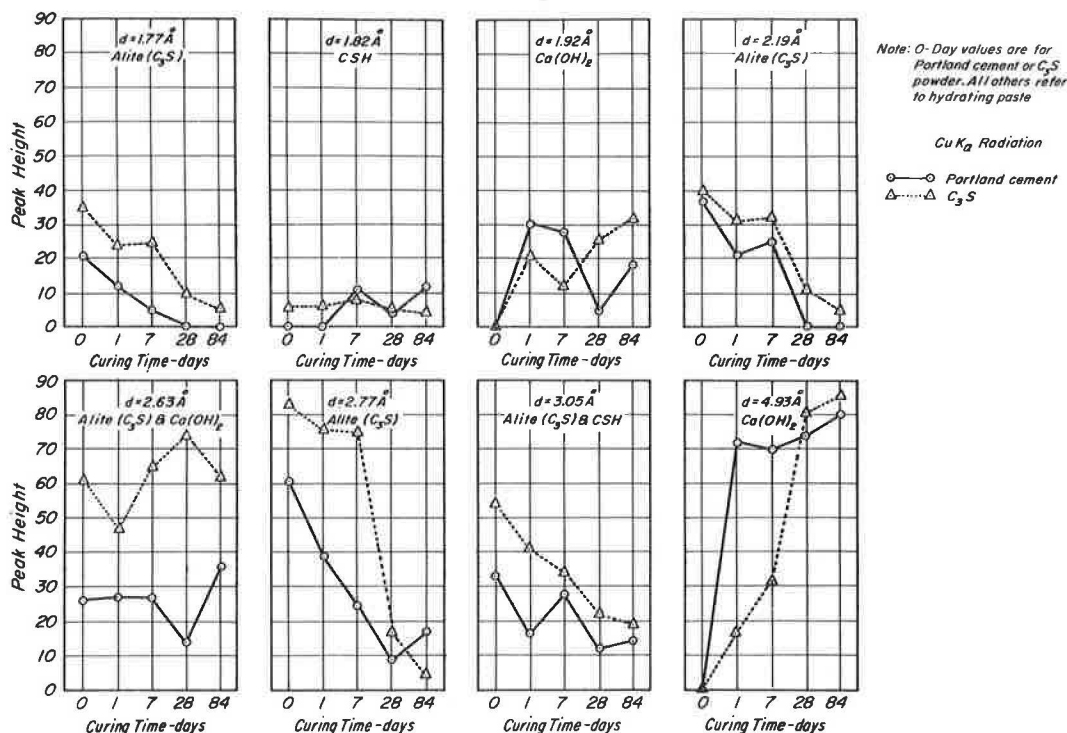


Figure 4. X-ray diffraction peaks for hydrating portland cement and hydrating tricalcium silicate.

X-Ray Diffraction Tests

Portland Cement.—Strong reflections at 1.77, 2.19, 2.60, 2.77 and 3.02 Å, characteristic of the principal clinker component alite prevail in the X-ray spectrum of unhydrated cement. As the hydration of the cement progresses the intensity of the alite lines decreases strongly (Fig. 4).

The spectra of hydrating cement samples are dominated by calcium hydroxide lines at 1.92, 2.63 and 4.93 Å (1). The intensity of the 2.63- and 4.93-Å lines increases with the curing age, indicating the accumulation of crystalline calcium hydroxide during hydration. Changes in the intensity of the 3.05-Å CSH line, which increases in intensity with time, are obscured by the initially present 3.02-Å alite line, which decreases in intensity with time, but strengthening of this reflection after 12 weeks is evidence for the presence of CSH.

C₃S.—The intensity of C₃S reflections at 1.77, 2.19, 2.77 and 3.05 Å decreases markedly with curing time (Fig. 4). Sharp peaks at 1.92, 2.63 and 4.93 Å increase with curing age and confirm the continuous formation of calcium hydroxide during hydration.

Only weak CSH lines can be observed at 1.82 Å and the intensity of the 3.05-Å reflection consistently decreases. This suggests the absence of a significant amount of crystalline CSH hydration products in the C₃S preparation used in this experimental work and may be responsible for the slow strength development in neat C₃S paste during hydration.

Kaolinite-Cement.—Figure 5 shows results of X-ray diffraction tests on kaolinite-cement and kaolinite-C₃S mixtures. (These tests were run at high amplification to accentuate detail; as a result, the first order basal reflections for the clay minerals were off scale and are not reported in Fig. 5.) Reflections at 1.82 Å and 3.05 Å appeared in kaolinite-cement specimens after 1-day curing, indicating formation of CSH. The strengthening of CSH reflections with time suggests normal cement hydration. No

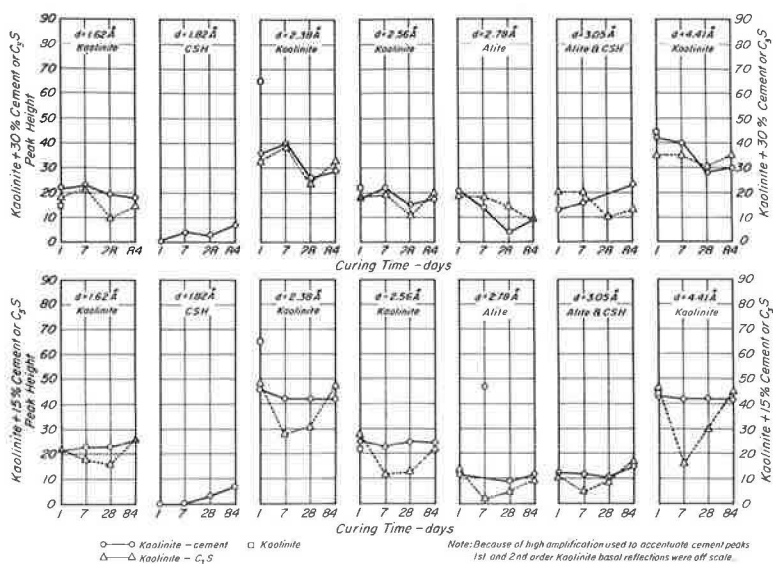


Figure 5. X-ray diffraction peaks for hydrating kaolinite-cement and kaolinite- C_3S mixtures.

$Ca(OH)_2$ lines were observed on cement or C_3S -treated samples of kaolinite except for KC_3S 30 specimens cured for 1 day. However, 4.87-Å and 2.62-Å $Ca(OH)_2$ lines appear on the X-ray trace of kaolinite powder blended with 30 percent (by weight) of 3-month-old ground, hydrated portland cement (Fig. 6). This indicates that the absence of $Ca(OH)_2$ lines on kaolinite cement X-ray traces for samples cured for more than 1 day is not due to masking effects by kaolinite. Since compression tests indicate large increases in the strength of stabilized specimens, the cement or C_3S can be assumed to hydrate normally and form $Ca(OH)_2$ during hydration. Because this $Ca(OH)_2$ is not present in a crystalline form in clay-cement, it must either be in an amorphous form or used up by a secondary process.

In both KP 15 and KP 30 specimens, the intensity of kaolinite lines generally decreased slightly with curing time. The weakening of kaolinite lines was more pronounced on KP 30 samples than on KP 15 specimens cured for the same periods. The increased weakening of kaolinite lines at higher cement content suggests the possibility of an attack on the kaolinite structure and/or a coating of clay particles and aggregates by reaction products.

The kaolinite lines in KC_3S 15 specimens (Fig. 5) show an initial weakening with subsequent recovery beginning after 1 week. The overall change in intensity during 3 months is about the same as in the KP 15 series. No 1.82-Å CSH line appeared, but in contrast to the C_3S paste trace, the 3.05-Å reflection became stronger from 1 week onwards.

Changes in reflection intensities of kaolinite and CSH lines in the KC_3S 30 series followed the same general trend as in the KC_3S 15 series. The increase of the 3.05-Å line after 1 month's curing of KC_3S 15 and KC_3S 30 is in contrast with the consistent weakening of this line on C_3S paste traces. It indicates that the hydration of C_3S is modified in the presence of kaolinite. As previously noted, KC_3S specimens are stronger at a given age than KP specimens, whereas neat cement is found to be many times stronger than neat C_3S paste of the age. Both of these observations support the hypothesis that kaolinite modifies the hydration of the C_3S material used.

Two $Ca(OH)_2$ lines, 2.63 Å and 4.93 Å, were noted on a KC_3S 30 specimen cured for 1 day but could not be observed after longer curing periods. This suggests the existence of a lime producing process and a simultaneous operation of a $Ca(OH)_2$ consuming mechanism. The rate of $Ca(OH)_2$ formation appears to exceed the rate of $Ca(OH)_2$ consumption only at high C_3S concentration and only during the first day or

days of hydration. Only under these conditions would it be expected that $\text{Ca}(\text{OH})_2$ reflections would appear on the X-ray pattern.

The gross effects of hydrating cement on kaolinite are shown by a comparison of X-ray diffraction traces of KP 30 cured for one day and for twelve weeks. Figure 7 shows a slight decrease in height of the 3.57-Å and 7.15-Å basal reflections after 12 weeks and a general broadening of some of the low-intensity peaks.

Montmorillonite-Cement.—Figure 8 shows the results of the X-ray diffraction tests on montmorillonite-cement and montmorillonite- C_3S mixtures. $\text{Ca}(\text{OH})_2$ lines were missing from the diffraction patterns of all MP and MC_3S specimens. $\text{Ca}(\text{OH})_2$ peaks were observed, however, on a mixture of montmorillonite and 30 percent (by weight) of ground hydrated cement (Fig. 9). Thus, the "dilution" of hydrated cement powder with montmorillonite could not have masked the appearance of $\text{Ca}(\text{OH})_2$ lines.

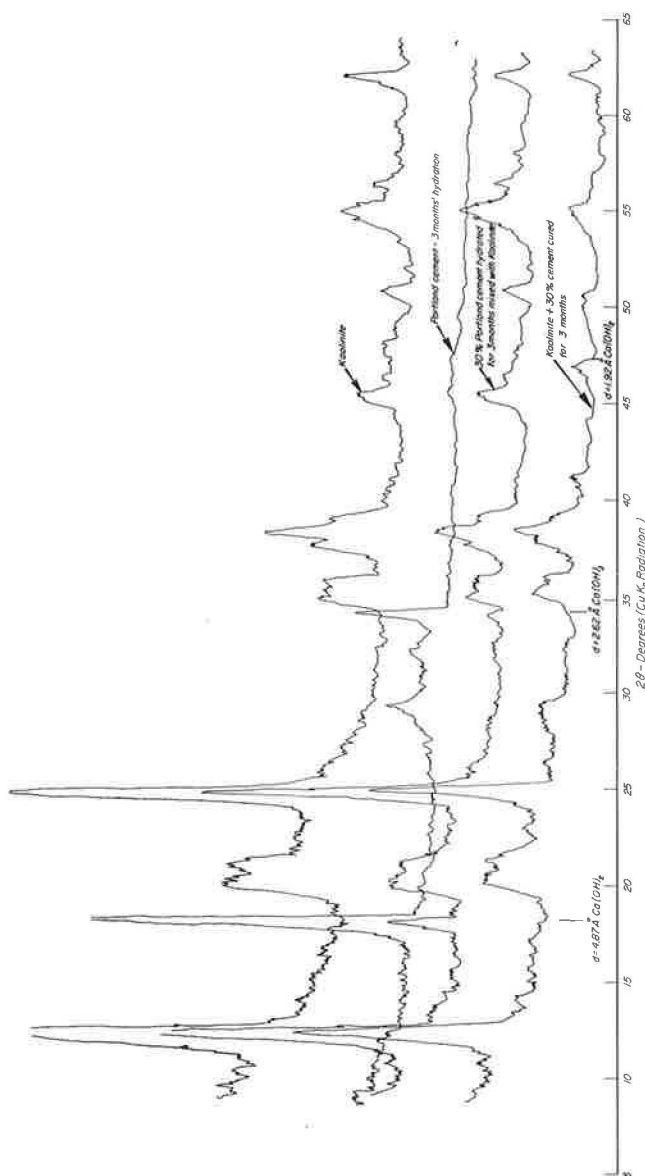


Figure 6. X-ray diffraction patterns for kaolinite, hydrated cement, and hardened kaolinite-cement.

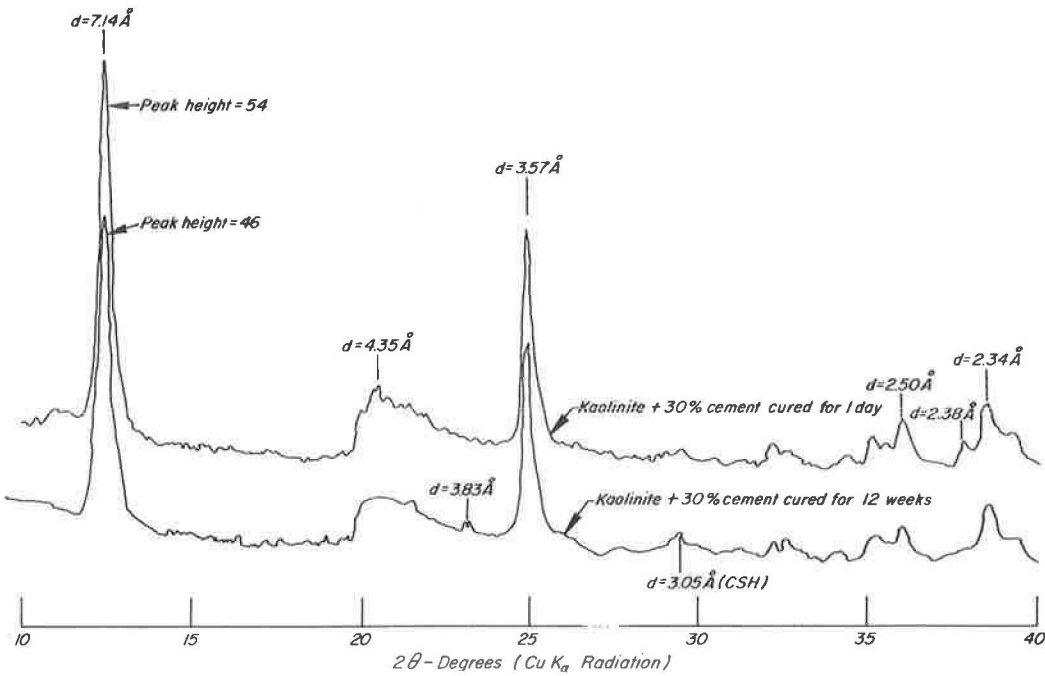


Figure 7. X-ray diffraction patterns for kaolinite + 30% cement samples cured for 1 day and 12 weeks.

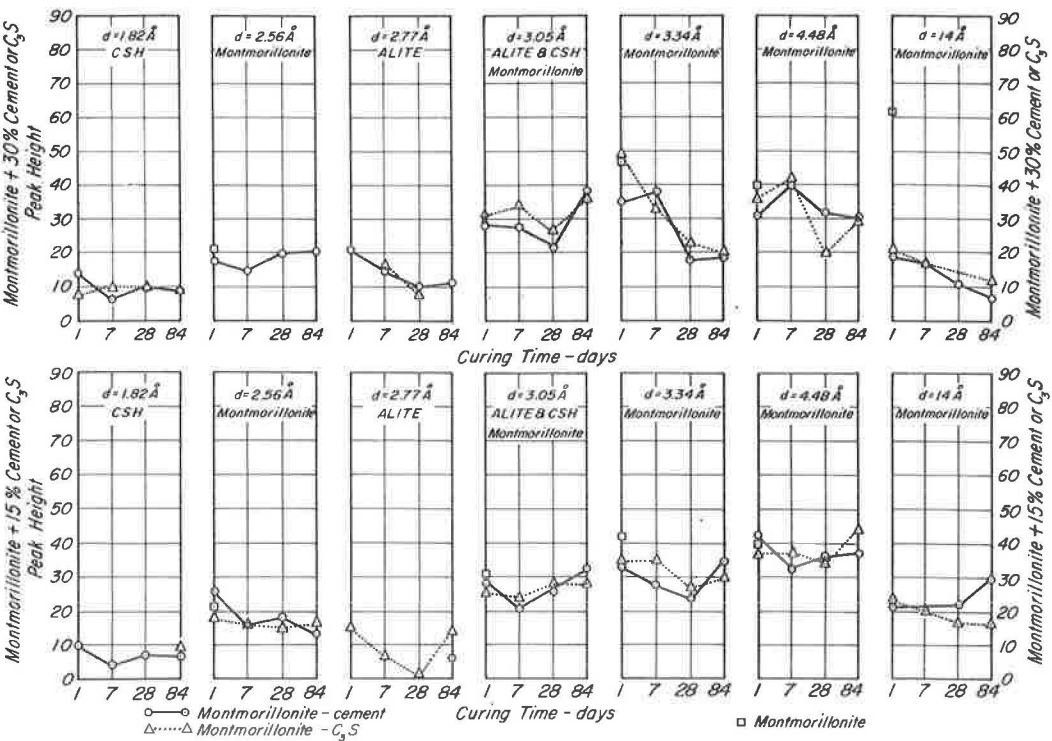


Figure 8. X-ray diffraction peaks for hydrating montmorillonite-cement and montmorillonite- C_3S mixtures.

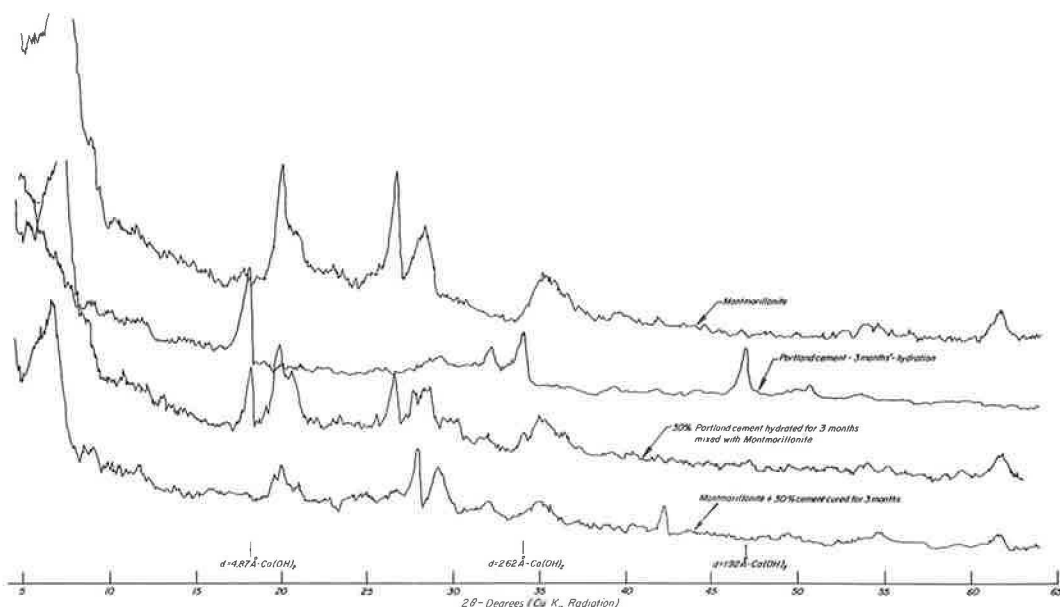


Figure 9. X-ray diffraction patterns for montmorillonite, hydrated cement, hydrated cement mixed with montmorillonite, and hardened montmorillonite-cement.

Montmorillonite lines interfere with the observation of CSH peaks at 1.82 Å and 3.05 Å for samples of the MP 15 series. Minor montmorillonite diffraction peaks at 2.56, 3.09, 3.34 and 4.48 Å weakened initially and became somewhat higher after 1 month. The 14-Å peak increased in height and sharpness during the last 8 weeks of curing for this series. An intensification of montmorillonite basal reflections caused as a result of the addition of small amounts of lime was found by Eades and Grim (6). The intensity of the 14-Å montmorillonite peak consistently decreased with increasing curing time for samples of the MC₃S 15 series, in which more lime would be generated than in the MP 15 series. Other montmorillonite lines showed a weakening tendency also. CSH reflections could not be clearly identified.

Degradation of the clay mineral structure was strongly indicated in MC₃S 30 specimens by the pronounced decrease of the 14-Å peak height, the reduction of the 3.34-Å line intensity by more than one-half and the decline of the 4.48-Å peak. CSH formation was indicated by the strengthening of the 1.82-Å and 3.05-Å lines with curing time.

Montmorillonite reflections weakened and the peaks became broader with increased curing time in mixtures of montmorillonite with 30 percent cement. Gross effects of hydrating cement on such mixtures are demonstrated by low amplification X-ray traces (Fig. 10). The considerable decrease of the 14-Å line intensity after 12 weeks suggests major structural breakdown of the montmorillonite.

During the preparation of extracts for chemical tests the separation of slowly settling, flocculent material from a rapidly settling, granular, dark sediment was observed in suspensions after 10 minutes of mechanical stirring. X-ray examinations of these two phases from specimens cured for 4 and 12 weeks showed that the 14-Å peak was higher and sharper on flocculent material than on the dark sediment. In the case of the specimens cured for 4 weeks, for example, the 14-Å peak height for the dark material was only 75 percent of the height of the corresponding peak for the light material. Upon further grinding, the dark sediment gave a 14-Å peak of intermediate intensity between that of the separated sediment and of the flocculated material.

The difference in 14-Å peak intensities between the flocculent and the rapidly settling fractions suggests the nonuniform degradation of montmorillonite. Clay particles

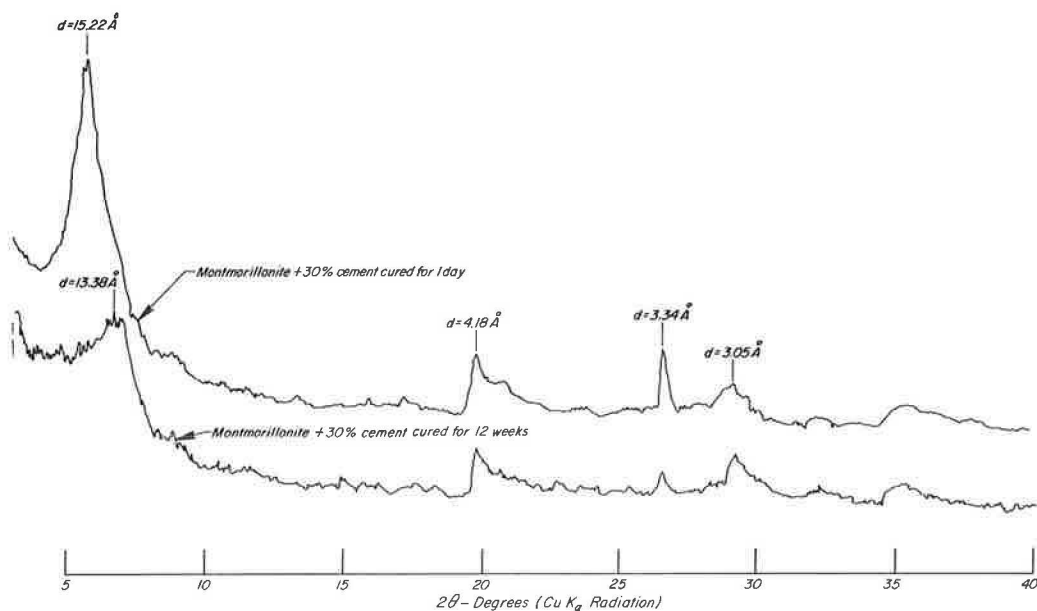


Figure 10. X-ray diffraction patterns for montmorillonite + 30% cement samples cured for 1 day and for 12 weeks.

in the immediate vicinity of cement grains are probably strongly attacked by the fresh lime from the hydrating cement and undergo greater structural degradation than clay particles located farther away from hydrating cement particles. It is also possible that clay particles close to cement grains become coated with reaction products leading to a decrease in peak intensities.

Recognizing that cement particles are very large (silt size) relative to the clay crystals, cement-stabilized montmorillonite could be regarded as composed of a clay-cement skeleton and a clay matrix. Units of the skeleton may be visualized as containing a core of hydrated cement gel to which layers of altered clay particles are attached. Such units may form larger size aggregates, trapping less altered clay in the intercellular space.

If the alteration of the clay mineral structure caused by $\text{Ca}(\text{OH})_2$ is associated with the formation of cementitious material, severely altered particles would be strongly glued to each other and to cement grains. They could not be washed off during stirring with water from the large, heavy cement rich grains of the skeleton, and, after sedimentation, they would be part of the quickly settling sediment.

The least affected clay particles would be expected to be only weakly attached to each other and would readily go into suspension as flocculent matter. Thus, the less altered clay should be found in the suspended flocculent fraction; the more decomposed clay cemented to the heavier portland cement grains should be part of the sediment.

Further evidence for changes in montmorillonite character is given by the results of X-ray patterns of heat-treated and of glycolated specimens. Samples of MP 30 cured for 12 weeks were heated to 600 F, cooled in a dessicator and X-rayed. While untreated Ca montmorillonite exhibited a collapse of the basal spacing to 10.1 Å, the MP 30 samples showed only a partial collapse. The term "partial collapse" is used to describe a broad sawtooth-like peak with apexes at 10.4 Å and 12.06 Å, implying a nonhomogeneous material which had been altered to such a degree that basal spacings had become fixed at distances greater than 10 Å. Expansion as a result of ethylene glycol treatment could not be detected, indicating that the basal spacing had become fixed.

The most important results and conclusions that may be drawn from the X-ray phase of this investigation may be summarized as follows:

1. Portland cement hydrated normally in clay-cement and formed calcium hydroxide during hydration.
2. The hydration of the C_3S preparation was modified in the presence of clay.
3. Calcium hydroxide was identified in one set of clay- C_3S specimens after 1-day curing.
4. No calcium hydroxide lines were found in stabilized specimens after 1 week's curing time.
5. Small decreases in the intensity of kaolinite reflections and pronounced decreases in the intensities of montmorillonite reflections were observed after 12 weeks' curing of clay-cement mixtures.
6. Clay-cement appears to have a skeleton-matrix type structure.
7. New lines of low intensity were observed in some patterns for specimens containing 30 percent cement or C_3S at long curing times. This suggests the formation of new crystalline reaction products. Because of the low intensity of these peaks and the irregular patterns of their occurrence, the new compounds could not be identified specifically.

pH Determinations

Changes in pH accompanying the hardening of the clay-cement specimens are shown in Figures 11 and 12. The high pH values of all samples containing hydrating cement may be attributed to the dissociation of $(OH)^-$ ions from $Ca(OH)_2$ formed during cement hydration.

The pH did not change with time in neat portland cement, neat C_3S and blank clay specimens but decreased during curing in clay-cement specimens. This suggests the

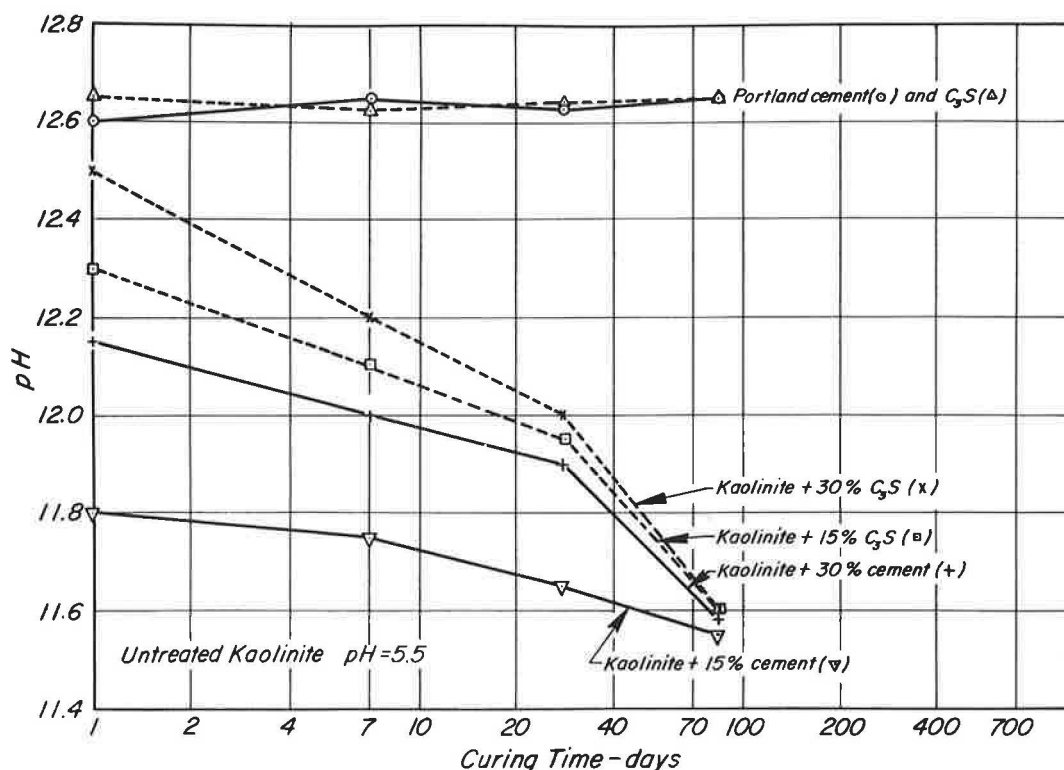


Figure 11. pH changes accompanying the hydration of kaolinite-cement and kaolinite- C_3S mixtures.

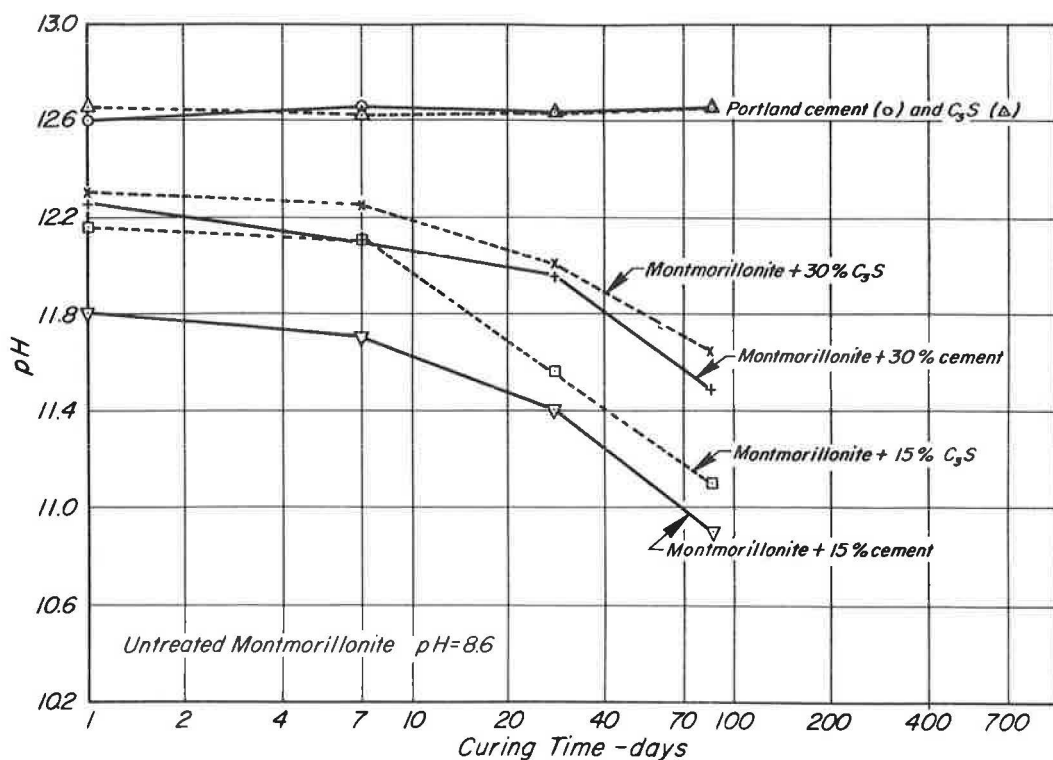


Figure 12. pH changes accompanying the hydration of montmorillonite-cement and montmorillonite-C₃S mixtures.

presence of an $(\text{OH})^-$ -consuming process in hardening clay-cement. The existence of such a process is most evident in KC₃S 30 specimens (Fig. 11). Samples of this composition had the highest pH among all clay-cement specimens after 1-day curing and contained crystalline $\text{Ca}(\text{OH})_2$ as previously noted. After longer curing periods the pH was always lower and no crystalline $\text{Ca}(\text{OH})_2$ was detected in the X-ray patterns for the samples.

The pH values of montmorillonite-cement samples were lower than those of the corresponding kaolinite samples for curing times greater than 1 day. This is probably due to the greater solubility of montmorillonite in an alkaline environment than kaolinite and therefore higher $(\text{OH})^-$ consumption of montmorillonites. Other factors could also contribute to this result. Montmorillonite has greater buffering capacity than kaolinite and therefore could be responsible for the greater pH drop. Montmorillonite would be expected to contain a greater amount of non-crystalline silica and alumina than kaolinite. If this material were involved in rapid reaction with $(\text{OH})^-$ then the pH of the montmorillonite-cement should drop at a faster rate than the pH of the kaolinite-cement. The greatest decrease in pH with curing time was observed in the MP 15 and MC₃S 15 mixtures (Fig. 12). This large decrease in pH may have impeded the normal hydration of the cement and prevented strength increase after 1 week (Fig. 3).

It is also conceivable that a reduction in pH could be caused by adsorption of $(\text{OH})^-$. If only adsorption and no chemical reaction took place, however, the mineral structure of the clay would remain unchanged. The pH in such a case would be the lowest after 1-day curing since adsorption reactions could be expected to be essentially complete after this time. $\text{Ca}(\text{OH})_2$ generated by the hydrating cement after the first day could also be adsorbed and cause no change in the pH or would increase the pH after the adsorption capacity is satisfied.

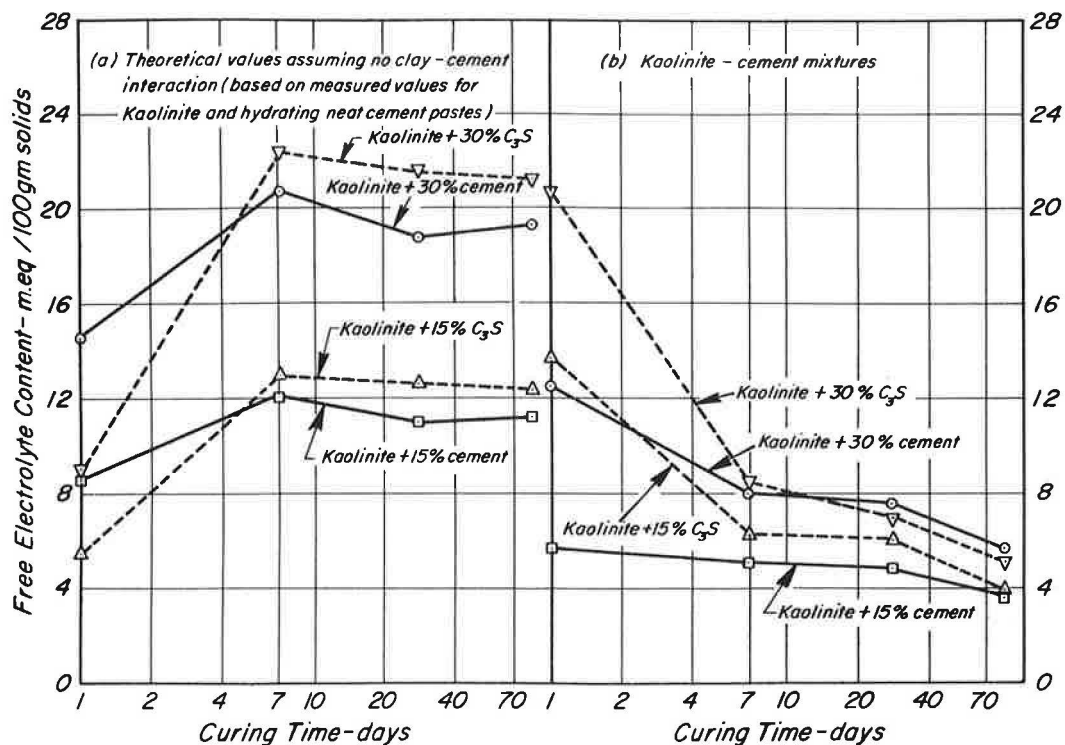


Figure 13. Free electrolyte content of hydrating kaolinite-cement and kaolinite- C_3S mixtures as indicated by conductivity of extract solutions.

The decrease of the pH of clay-cement with time, therefore, cannot be explained by adsorption. The data support the existence of a chemical reaction between $(OH)^-$ ions and the clay minerals or amorphous materials which leads to partial solubilization and the formation of secondary cementitious compounds.

Conductivity

Conductivity values of solutions prepared from specimens after each curing period are shown in Figures 13 and 14. Also shown are theoretical values that would be anticipated if there were no interaction by the clay and the hydrating cement. These values were obtained by taking the appropriate proportions of the conductivity values for neat cement and pure clay. The conductivity is indicative of the concentration of electrolytes readily extractable with water from the samples. The formation of water soluble salts, including $Ca(OH)_2$ during hydration would increase the electrolyte concentration. Conversely, the transformation of water soluble salts to compounds of lower solubility and/or the entrapping of soluble salts by the cementation of grains would decrease the electrolyte concentration of the water extract.

The conductivity of hydrating cement and C_3S extracts increases initially and decreases only slightly after 1 week, as do also the theoretical values for clay-cement mixtures (Figs. 13 and 14).

All clay-cement extracts indicate a significantly lower electrolyte content and a decrease of the electrolyte content with curing time. The observed decrease in conductivity suggests that in clay-cement the soluble salts formed by cement hydration are converted to less soluble compounds, perhaps precipitating with the mass and bonding particles together.

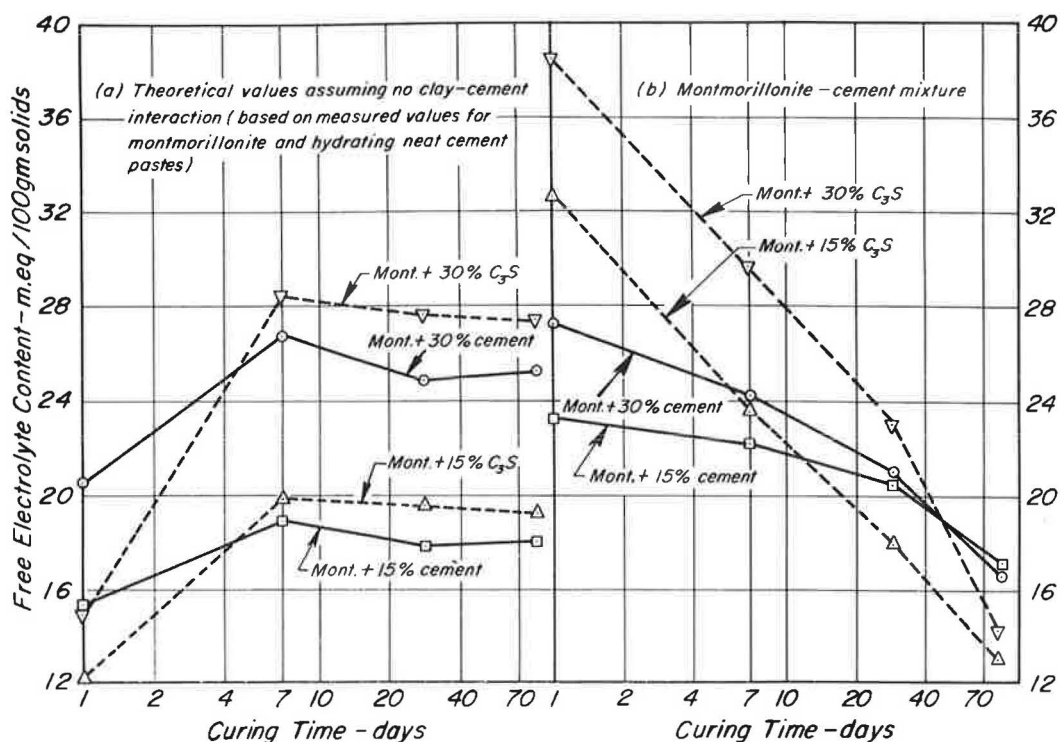


Figure 14. Free electrolyte content of hydrating montmorillonite-cement and montmorillonite C_3S mixtures as indicated by conductivity of extract solutions.

Calcium, Sodium and Potassium Content of Water Extracts

The extractable calcium content of all kaolinite-cement samples as a function of curing time is shown in Figure 15. Sodium and potassium contents are given in Table 3. If no interaction between the clay and hydrating cement took place, it would be anticipated that the extractable calcium content would be as given by the upper curves where values have been computed on the basis of a proportion of the values for neat cement. The observed values are significantly lower than those computed on this basis, suggesting that water soluble calcium ions liberated during cement hydration are to a considerable extent converted during the first day to a form not readily extractable with water.

The calcium content of water extracts of cement and C_3S sharply increased from 1 to 7 days, but declined in kaolinite-cement extracts, indicating further formation of insoluble compounds.

Montmorillonite-cement extracts were found to behave similarly except for a much higher sodium and lower calcium content than corresponding kaolinite samples at early ages (Fig. 16 and Table 4). The replacement of exchangeable sodium by calcium offers an explanation for this difference.

Free Calcium Hydroxide

Results of the free calcium hydroxide determinations using the nonaqueous extraction method are shown in Figures 17 and 18. The values of calcium content obtained for neat cement and C_3S were considerably higher than those determined with the flame photometer on water extracts. The longer extraction time and the higher temperature during extraction could be responsible for these higher values.

All clay-cement specimens contained only a fraction of the free calcium hydroxide that would be present if normal hydration of their cement content took place without

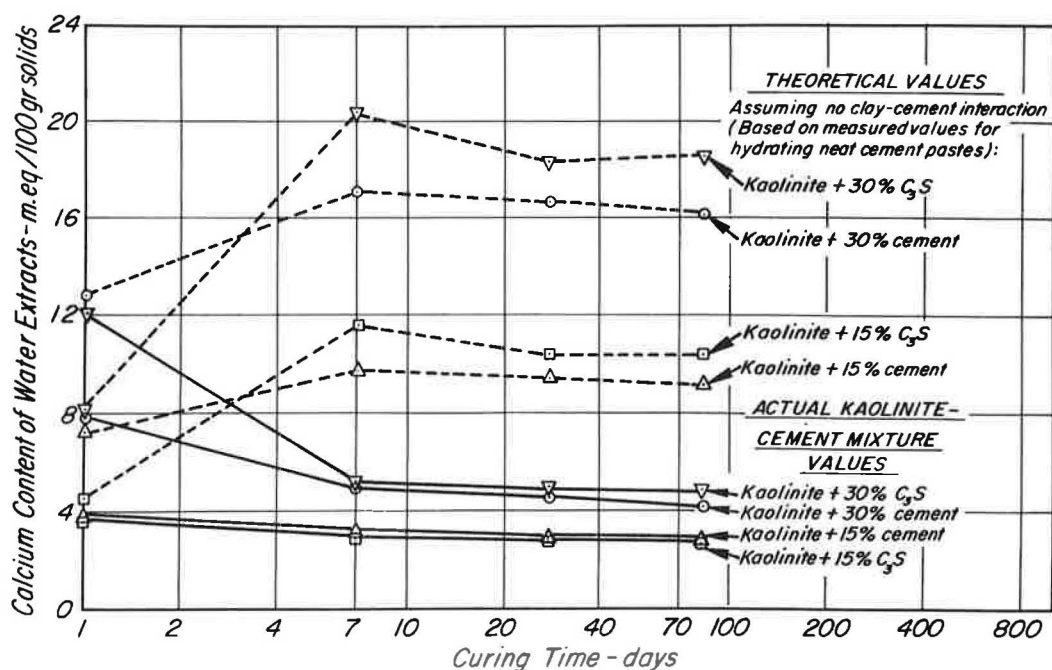


Figure 15. Calcium content of water extracts from kaolinite-cement and kaolinite- C_3S mixtures.

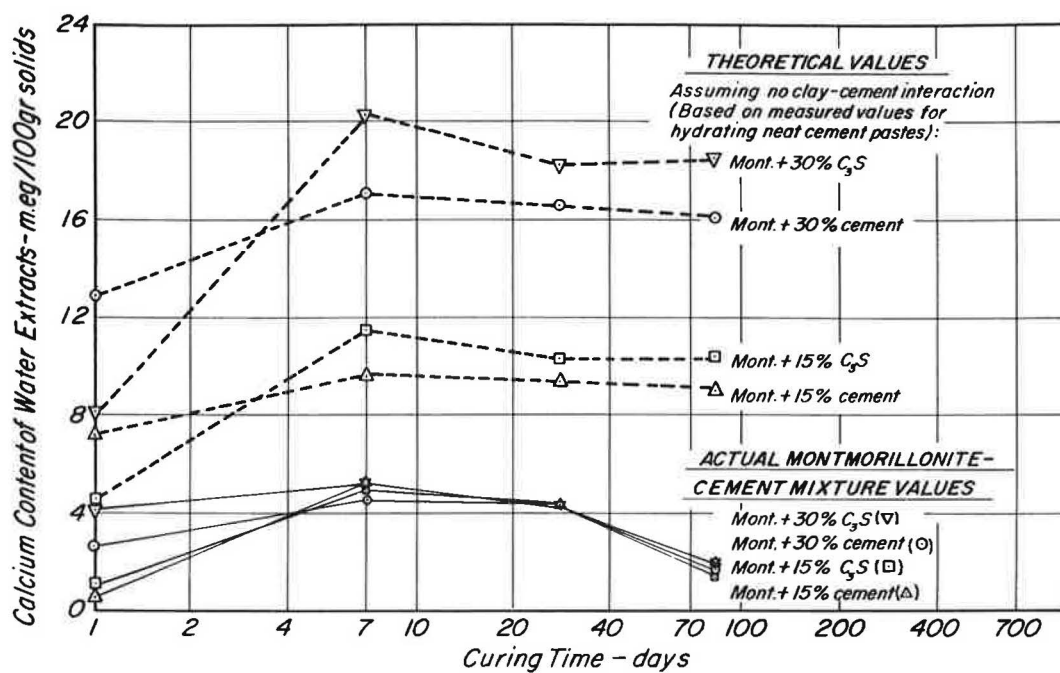


Figure 16. Calcium content of water extracts from hydrating montmorillonite-cement and montmorillonite- C_3S mixtures.

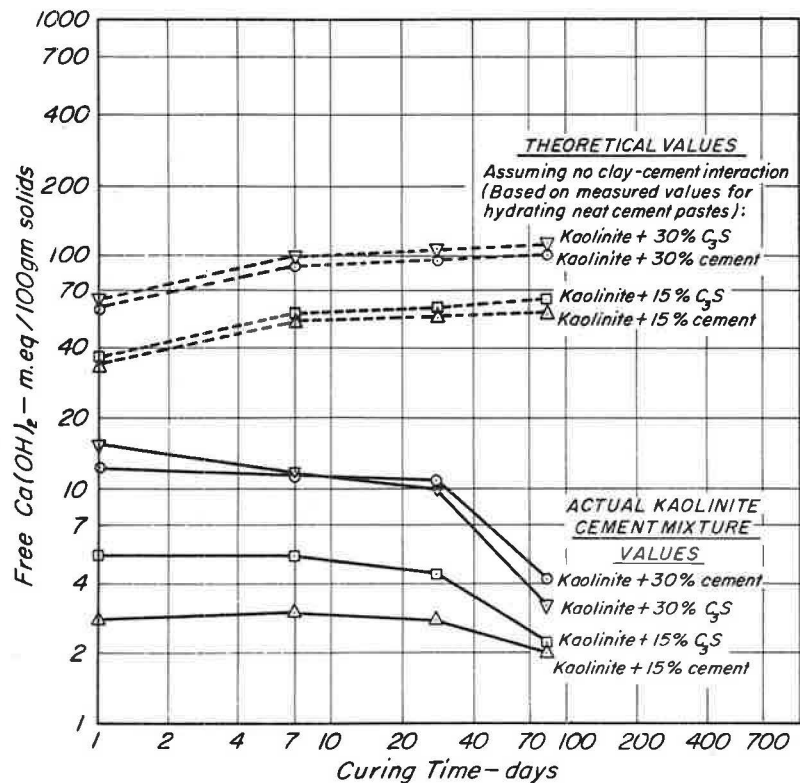


Figure 17. Free calcium hydroxide content of hydrating kaolinite-cement and kaolinite- C_3S mixtures.

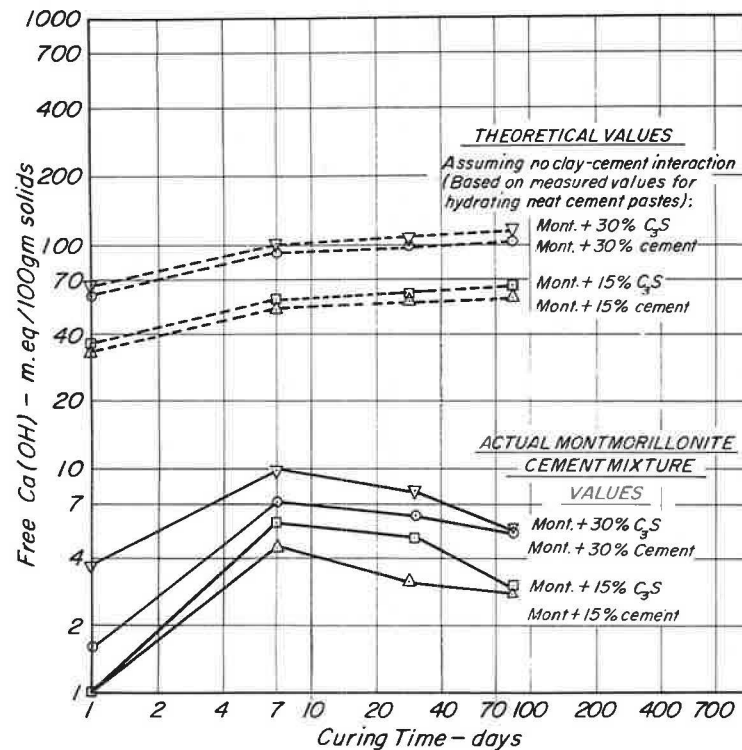


Figure 18. Free calcium hydroxide content of hydrating montmorillonite-cement and montmorillonite- C_3S mixtures.

interaction between cement and clay (Figs. 17 and 18). The calcium hydroxide formed by such hydration but missing from clay-cement could be assumed to have participated in a pozzolanic type reaction with the clay. Lime clay-mineral interactions producing cementitious material have been suggested, as previously noted. Inasmuch as freshly formed calcium hydroxide is more reactive than ordinary lime, the formation of cementitious material by a pozzolanic type reaction appears to be likely.

SUMMARY AND CONCLUSIONS

It has been postulated that the hardening of a clay-cement mixture involves alteration of clay mineral structures and amorphous constituents resulting in the formation of secondary cementitious material in addition to the usual hydrolysis and hydration of the cement, which may be regarded as primary stabilizing reactions. The results of mechanical, X-ray diffraction, and chemical tests all tend to support this hypothesis. The most significant results and conclusions that may be drawn from the experimental work are as follows:

1. Very effective stabilization of both kaolinite and montmorillonite was obtained using both normal portland cement and a pure tricalcium silicate compound, as reflected by the compressive strength of specimens soaked for 24 hours after curing for specified periods.
2. Specimens made from neat C_3S paste had only a fraction of the strength of specimens of neat portland cement; however, clay- C_3S specimens were always stronger than clay-portland cement samples, suggesting a modification of the C_3S hydration process in the presence of clay minerals. Hydrated C_3S is the main contributor to the strength of hardened portland cement.
3. X-ray diffraction studies of hydrating clay-cement mixtures showed that:
 - a. Portland cement formed calcium hydroxide in hydrating clay-cement.
 - b. The hydration of C_3S was modified in the presence of clay.
 - c. After 1-week curing no crystalline calcium hydroxide was detectable in clay-cement specimens.
 - d. Small decreases in the intensity of kaolinite reflections and large decreases in the intensity of montmorillonite reflections were observed after 12 weeks' curing of clay-cement.
 - e. New lines of low intensity were observed in some clay-cement patterns after long curing times, suggesting the formation of new crystalline reaction products.
4. The pH of hydrating neat portland cement, hydrating neat C_3S , and blank clay specimens remained constant with time but decreased markedly during the curing of clay-cement mixtures indicating the existence of an $(OH)^-$ consuming process.
5. Conductivity values of clay-cement extracts indicate a significantly lower electrolyte content than would be expected if the cement hydrated without interaction with the clay, suggesting that in clay-cement the soluble salts formed by cement hydration are converted to less soluble compounds which may serve to bond particles together.
6. The actual extractable calcium contents of all clay-cement mixtures were significantly lower than values computed on the assumption of no clay-cement interaction.
7. All clay-cement specimens contained only a fraction of the free calcium hydroxide that would be present if normal hydration of the cement took place without interaction between cement and clay. This missing calcium hydroxide could have participated in pozzolanic reactions with the clay minerals.
8. Clay-cement cannot be regarded as a simple mixture of hydrated cement particles bonding together unaltered clay particles, but must be considered as a system in which both the clay and the hydrating cement combine through secondary reactions.

These results and conclusions, in conjunction with additional observations during the preparation of extracts for chemical tests, support the following clay-cement structure. Because cement particles are very large relative to clay particles, a clay-cement skeleton and a clay matrix are likely. Units of the skeleton contain a core of hydrated cement gel to which layers of altered clay particles are attached.

Alteration of the clay adjacent to the cement grains will be caused by the dissolution of silica and alumina from both clay particles and amorphous constituents in the high pH environment formed as a result of the generation of highly reactive Ca(OH)_2 by the hydrating cement. The dissolved material can combine with calcium ions and form additional cementitious material which bonds adjacent clay particles together. The material in the vicinity of cement grains could form aggregates which trap less altered clay in the intercellular space. In addition, in the case of montmorillonite the altered clay particles lose their expansive characteristics.

Although it is recognized that the stabilization of natural soils may involve the interaction of cement with all the soil components, only the interaction between cement and monomineral clay minerals was studied in this investigation in order to limit the number of variables. Once the behavior of such relatively pure systems is understood, investigation of more complex systems may be undertaken. It is hoped that improved understanding of soil-cement interaction will lead ultimately to improved techniques of soil stabilization.

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Appendix

PROPERTIES OF CEMENT

Chemical (% by wt.)

SiO ₂	24.54
Fe ₂ O ₃	2.89
Al ₂ O ₃	2.97
CaO	66.38
MgO	0.36
SO ₃	1.93
Ignition loss	0.73
Insoluble residue	0.08
C ₃ S	54.00
C ₂ S	29.70
C ₃ A	3.00
C ₄ AF	8.80
CaSO ₄	3.30
Na ₂ O	0.14
K ₂ O	0.27

Physical

Surface area	3150 cm ² /gm
Initial set	2 hr 50 min
Final set	5 hr 0 min
Autoclave expansion	-.016%
Compressive strength	
1 day	943 psi
3 days	1,892 psi
7 days	2,220 psi