Reactions and Strength Development in Portland Cement-Clay Mixtures

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The purpose of this study is to extend the knowledge and understanding of the reactions and rates of reactions in mixtures of cement and relatively pure clays. The investigative approach utilized was to examine the materials and reacted mixtures physically by optical microscopy and X-ray diffraction, and chemically by measuring the change in pH with time of dilute suspensions of mixtures, analyzing the leachates of distilled water and 1.5 N HCl obtained from mixtures cured for 1, 3, 7, 14, 56 and 112 days for Ca, Al, and Si, and by making chemical analyses of the untreated clay materials.

Measurements of strength development with a Type II portland cement were also made and compared with similar measurements made on cement-clay mixtures containing a Type I portland cement.

The following conclusions are presented: (a) the cement in the cement-Anna kaolinite mixtures experienced the most rapid hydration, with the cement-Fithian illite mixtures hydrating one-half to three-fourths, and the cement-Aberdeen montmorillonite mixtures hydrating one-tenth to one-fifth as rapidly as the cement-Anna kaolinite mixtures; (b) the strength gain appears to result from early flocculation of the clay particles (thus making their joint cementation easier), hydration of the cement and possible chemical combination of SiO_2, Al_2O_3 and $Ca(OH)_2$ to create additional cementitious particles, and crystallization of $Ca(OH)_2$ which cements discrete particles as well as floccules to each other; (c) the clays suffered deterioration from the alkaline environment of the hydrating cement in the order Aberdeen montmorillonite, Anna kaolinite, and Fithian illite; (d) the hydration of cement grains may be restricted by encapsulation of the cement by very fine-grained clay and recently crystallized gels of calcium silicate hydrate and, perhaps, calcium aluminate hydrate; and (e) up to a curing period of 7 days, the Type I portland cement-clay mixtures developed somewhat greater strengths than the Type II mixtures because of the larger content of tricalcium aluminate and similar content of $CaSO_4$ in the Type I portland cement.

•IN THE first progress report (Sherwood and Noble, 11) on this project, initial studies of the reactions and reaction products in portland cement-clay mixtures were presented. It was noted that:

1. There was a significant gain in strength in cement-treated clay samples relative to untreated clays.

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TABLE 1

CHEMICAL AND PHYSICAL ANALYSES OF CEMENTS UTILIZED*

Category	Type I	Type II
Oxide Analysis:		
SiO_2	21.20	22.62
Al_2O_3	5.90	3.32
Fe_2O_3	2.34	3.36
CaO	64.44	63.63
MgO	2.83	2.58
SO_3	2.18	2.21
Ign. loss	0.68	0.85
Na_2O	0.12	0.09
K_2O	0.73	0.60
Na_2O equiv.	0.60	0.48
Free CaO	1.00	0.67
Compounds (Calculated):		
C_3S	52.0	53.5
C_2S	21.6	24.5
C_3A	11.68	3.12
C_4AF	7.11	10.21
$CaSO_4$	3.71	3.76
Fineness:		
% passing No. 325 mesh	91.8	93.9
Blaine (cm^2/gm)	3396	3396

*Cements and analyses courtesy of Standard Lime and Cement Division of Martin-Marietta.

TABLE 2

PHYSICAL PROPERTIES

Properties	Anna Kaolinite	Fithian Illite	Aberdeen Montmorillonite
Size Ranges:			
>16 μ	20.6	23.5	20.0
16-8μ	6.0	14.2	7.2
8-4μ	12.0	11.1	10.4
4-2μ	10.6	6.6	3.5
2-1μ	13.6	9.5	14.9
< 1μ	37.2	35.1	44.0
Cation exchange capacity (me/100gm)	18	28	64.7
Maximum density (pcf)	116.8	103.9	70.1
Optimum moisture content (%)	13.82	20.84	46.48

2. The several clay species develop different strengths; the more hydrophi clays (montmorillonites, and attapulgit developed the least strength gain; the l hydrophilic clays (kaolinite, illite, gru developed the greatest strength gains.

3. The portland cement appeared to fully hydrated after curing for 43 days 79 C.

4. No crystalline lime was detected X-ray diffraction.

5. Based on the presence of the 3.0 3.09 Å peak, a calcium silicate hydrate seems to have formed.

All the specimens prepared for the str tests were cured for 7 days in a moistu room at 21 C, and the specimens prepa for chemical and X-ray diffraction ana were mixed at a water to solids ratio o 1 with the exception of attapulgite and Wyoming montmorillonite which were mixed at water to solids ratios of 3 and respectively, and cured for periods of and 100 days at 100 percent relative hu midity and 79 C.

The work performed in a later phase (Noble, 10) was designed to further the understanding of the nature of the reac tions and to establish rates of reaction cement-clay mixtures. Strength data f cement-clay mixtures using a Type II cement, because of its low tricalcium aluminate content, were obtained and c pared with the strength data from the f phase for which a Type I cement was u The chemical and physical analyses of these two types of cement are given in Table 1.

EXPERIMENTAL PROCEDURES

Eight clays were employed in the initial phase of the project (Sherwood and Noble. These 8 clays were also used in the strength studies with a Type II portland cement, the investigation of the change in pH with time of dilute suspensions of cement-clay mixtures, and in the total chemical analysis. However, to permit a more exhaustive study of individual specimen in the principal body of studies for this phase of the investigation, we decided to use only 3 clays, Anna kaolinite, Fithian illite, and Aberde montmorillonite. The physical properties of these clays are given in Table 2. The mixtures were prepared with 40 percent Type I portland cement and were cured at 100 percent relative humidity and 25 C for periods of 1, 3, 7, 14, 56, and 112 days. water to solids ratio of 1 was used for all the mixtures prepared for the second phas of this investigation. Twelve specimens per clay were prepared, 2 for each curing period, 1 for chemical and X-ray diffraction analyses and 1 for petrographic micros studies.

Physical Studies

Petrographic Investigation—Inasmuch as the petrographic microscope and X-ray diffraction techniques provide data that supplement each other, it was decided to lim

the number of specimens studied with the petrographic microscope. Therefore, powders of the untreated clays, and the clays mixed with 40 percent portland cement and cured for 1 and 43 days, were studied utilizing index oils. The material cured 43 days had been stored as a powder in a relatively airtight vial for approximately 1 yr. Thin sections were cut from 112-day and 2-yr 40 percent mixtures cured at 100 percent relative humidity and 25 C. Two ½-in. thick disks were cut from cylinders of these mixtures which had been dried at 80 C. The disks were then impregnated under vacuum with "Permount," a synthetic resin cut with 40 percent of toluene. After saturation, which usually required 24 hr, the samples were put into an oven (80 C) for 24 to 48 hr to harden. The disks were then ground on a plate glass and mounted with an epoxy, Resiweld Adhesive 7004. After hardening, one of the samples was ground down to approximately 30 μ and the other to approximately 15 μ. Cover glasses were added using index oil so that removal and use of another oil could easily be accommodated.

X-Ray Analysis—Powder specimens were mixed in Nujol and spread in a shallow well holder. They were X-rayed through an arc from 2° two theta to 40° two theta. The X-ray diffractometer used was a G. E., model XRD-5 with Cu K α radiation and a Ni filter.

Chemical and Physicochemical Studies

pH of Dilute Suspensions of Mixtures—Dilute suspensions of cement-clay mixtures (0.3 gm clay + 0.2 gm portland cement in 70 ml of H_2O) were prepared and tightly capped. The variations with time of their pH's were measured. Nitrogen was played over the surface of the suspension to prevent carbonation when the pH measurements were made. The variation in pH of the several clays with variations in mix concentrations was also investigated for supplemental information.

Analyses of Leachates Made With Distilled Water and HCl—During the organization of this investigation, consideration was given to the importance and source of soluble Ca in the mixtures. Inasmuch as the hydration products of alumina, silica and iron are extremely insoluble in the liquid phase of hydrating cement (Copeland and Kantro, 3), it appears that the $Ca(OH)_2$ produced by the hydrating cement is the most soluble of the calcium compounds present. However, it was realized that $Ca(OH)_2$ is not especially soluble. Therefore, the quantity of distilled leach water used was more than needed to dissolve all the $Ca(OH)_2$ that could be produced by complete hydration of the cement present.

Two-gram aliquots of the various cement-clay mixtures were repeatedly leached with 200 ml of distilled water. The leachings were carried out in a nitrogen atmosphere to prevent carbonation. At least three leachings were run with distilled water prior to an acid leach, using 200 ml of 1.5 N HCl. The leachings were accomplished by placing cement-clay mixtures and distilled water in a stainless steel cup and rapidly agitating them with a Hamilton Beach mixer, model No. 33. An agitator blade of the standard type used to disaggregate soils was used. The pH was taken before and after removal of the suspended material, which was removed by centrifugation. Analyses of the leachate were made for Ca, Al, and Si, and are reported and discussed as oxides. The quantitative analyses for these selected cations were made using testing procedures currently used in the Council's geochemistry laboratory for analysis of soils and cement. Calcium was determined by titration with EDTA as described by Davis (4). Al and Si were determined by absorption spectrophotometric techniques also as detailed by Davis.

Total Chemical Analysis—A chemical analysis, which first required fusion of the specimen, was made of each of the untreated clays to provide supplementary information.

RESULTS AND DISCUSSION

Physical Studies

Observations With the Petrographic Microscope—These observations were divided into two parts: (1) work with powdered samples and index oils, and (2) work with thin sections and index oils.

Powders—Untreated Anna kaolinite occurs predominantly in well-developed flocs averaging about 30 μ in diameter. Quartz of comparable size is clear and relatively

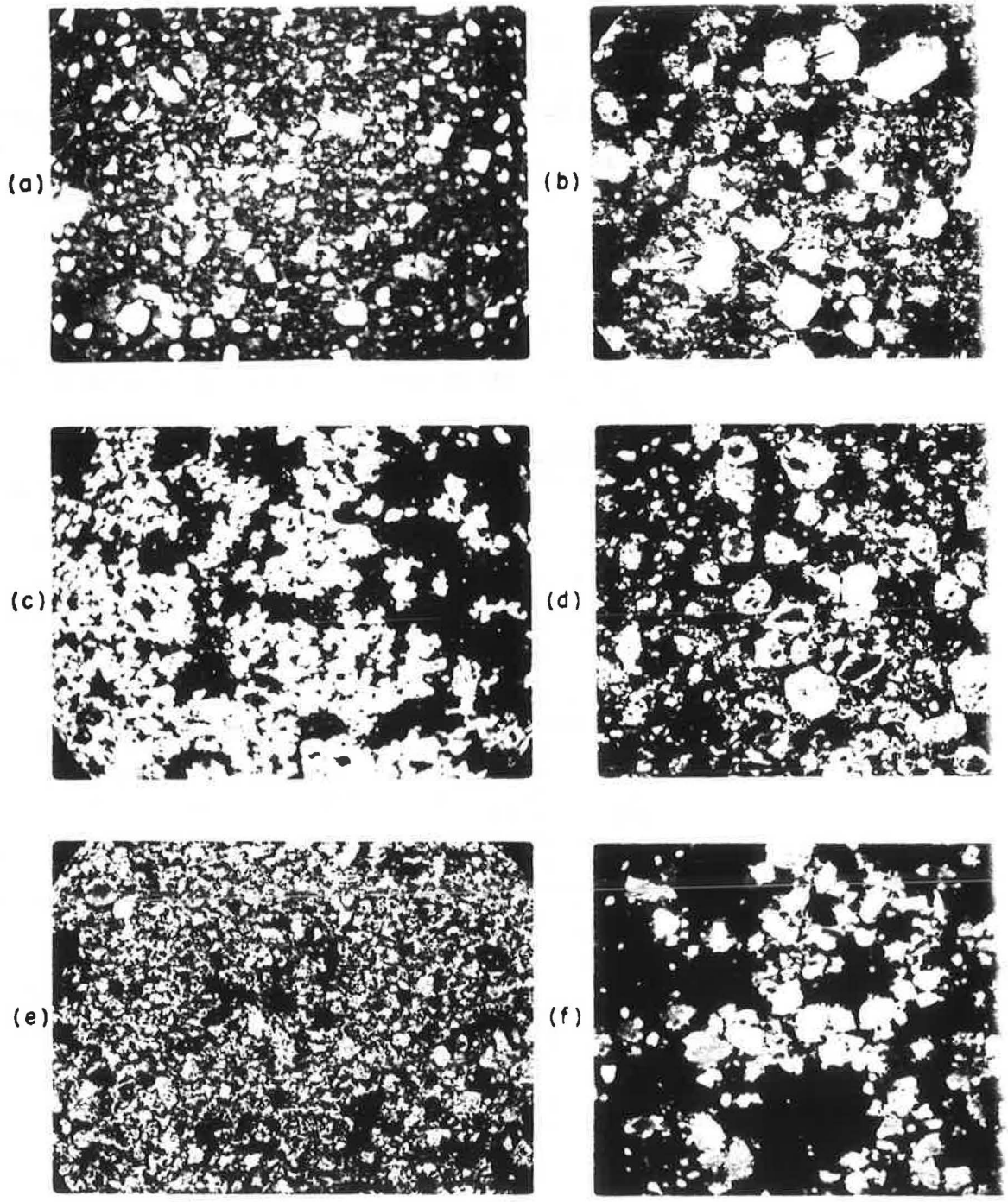

Figure 1. Photomicrographs of powders; enlargement X70: (a) untreated Anna kaolinite, (b) Anna kaolinite plus 40 percent cement, (c) untreated Fithian illite, (d) Fithian illite plus 40 percent cement, (e) untreated Aberdeen montmorillonite, and (f) Aberdeen montmorillonite plus 40 percent cement.

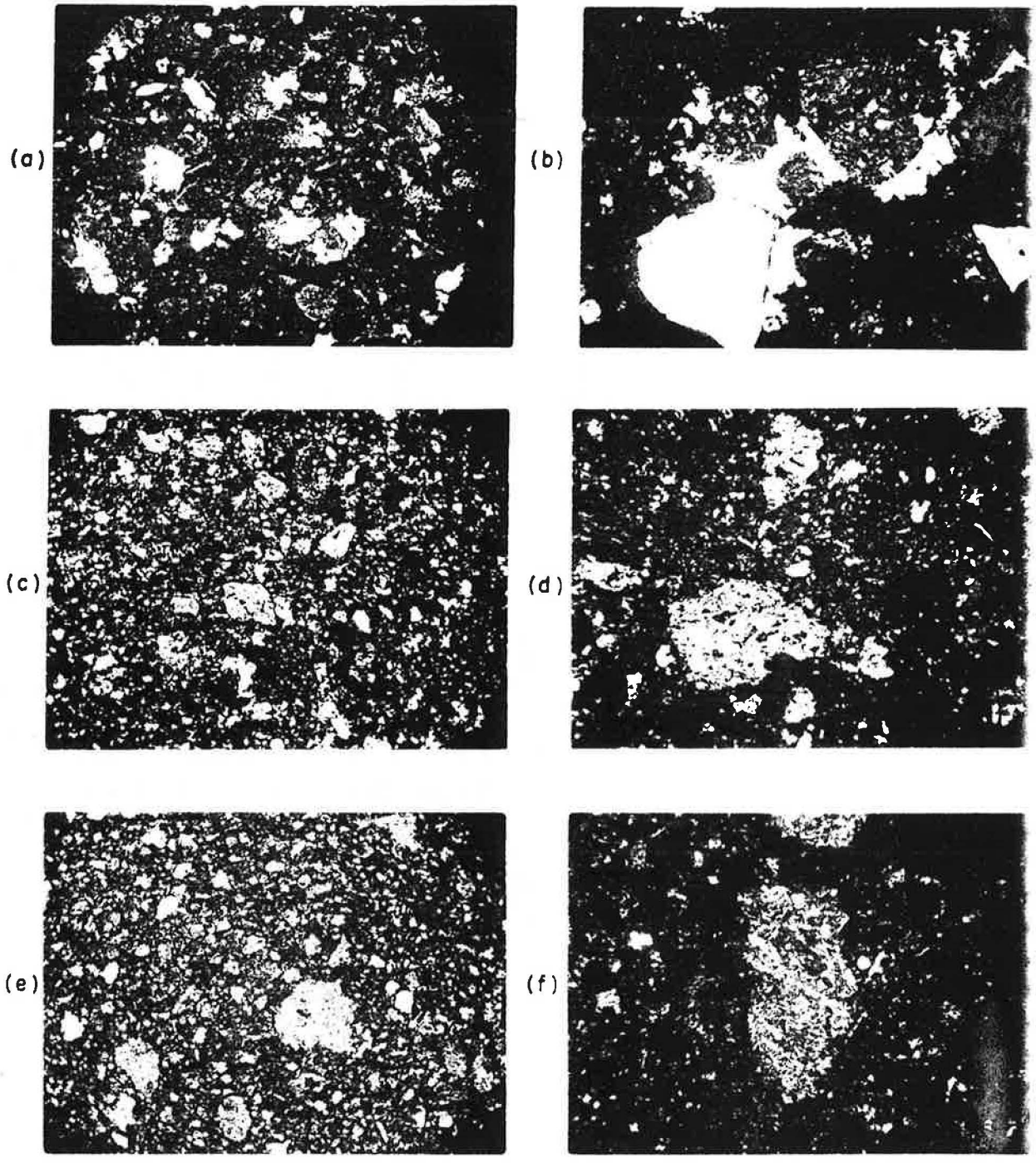

Figure 2. Photomicrographs of thin sections of cured clay-cement mixtures: (a) Anna kaolinite X70, (b) Anna kaolinite X270, (c) Fithian illite X70, (d) Fithian illite X270, (e) Aberdeen montmorillonite X70, and (f) Aberdeen montmorillonite X270.

free of clay coating (see Fig. 1a). Accelerated curing results in larger (100 μ) flocs and partially clay coated quartz (see arrows, Fig. 1b). Particles of lime, $Ca(OH)_2$, occur in the mixture cured one day at 25 C.

The slightly coarser grained Fithian illite contains mica shards. Flocculation is ragged in the untreated clay (see Fig. 1c), but is much better developed in the mixture subjected to accelerated curing (see Fig. 1d), with flocs up to 170 μ common.

The untreated Aberdeen montmorillonite contained minor amounts of calcite, was very fine grained and only weakly flocculated (see Fig. 1e). After one day with 40 per cent cement the clay was strongly flocculated (see Fig. 1f).

Thin Sections—The Anna kaolinite mixtures were characterized by profuse, well-developed clay flocs. Profuse irregular patches of well-crystallized lime, $Ca(OH)_2$, occur throughout the slide. This lime was deposited on clay flocs and quartz grains and has even cemented two discrete grains together (see Fig. 2a and b). The size of the flocs, 60-80 μ, is approximately the same as noted for the powders.

Flocculation in the Fithian illite mixtures was not as pronounced as it was in the kaolinite and montmorillonite mixtures. Mica shards are still present (see Fig. 2c and d). Irregular but fairly extensive patches of lime occur, but they are neither as profuse nor as well developed around the preexisting grains as in the kaolinite mixture

In the Aberdeen montmorillonite mixtures, flocculation is well developed with most flocs approximately 40 μ in diameter and with a few ranging up to 250 μ (see Fig. 2e and f). Lime is absent, but some high birefringent grains, probably calcite, are scattered throughout the mixture.

Observations showed that:

1. Flocs or aggregations of the clay are much better developed and larger in the cement mixtures than in the untreated clays.
2. Where quartz is present, the cement-clay mixtures appear to coat the quartz grains to a much greater extent than the untreated clays.
3. Unhydrated cement could not be identified in 40 percent cement-clay mixtures cured for 43 days at 79 C.
4. Lime was common in the thin sections of cement-Anna kaolinite mixtures as a coating, or as cement on or between the clay flocs and quartz grains.
5. Lime was common in the cement-Fithian illite mixtures as very irregular patch
6. Lime was not observed in the cement-Aberdeen montmorillonite mixtures.

X-Ray Analyses of Mixtures—By using the naturally occurring quartz in the clays as an internal standard, it was possible to make semi-quantitative estimates of the relative changes in quantity of several of the hydration products of cement occurring in the mixtures. Inasmuch as $Ca(OH)_2$ is a product of the hydration of two of the principal anhydrous compounds of portland cement and is used in the formation of several compounds, it is interesting to note the variation with curing time in quantity of crystalline $Ca(OH)_2$ and calcium monosulfoaluminate in the several cement-clay mixtures. Observation of the variations in quantity of crystalline $Ca(OH)_2$ may permit speculation as to the extent of hydration of the cement and the extent of interaction between the $Ca(OH)_2$ and the clays. In considering the early hydration reactions of a typical portland cement, Greene (8) states that very early after the addition of water to form a paste, "The C_3S is hydrating, and as evidence of this, crystalline calcium hydroxide begins to form. This compound can sometimes be detected by DTA after 2 or 3 hours. It continues to increase in amount with time, and is a rough indicator of the development of the calcium silicate hydrate phase." Greene's data also show a very steady, significant increase in crystalline $Ca(OH)_2$ up to 7 days, which is the longest curing period for which data were presented. If, as suggested, the extent of crystallization of $Ca(OH)_2$ is commensurate with the extent of hydration in a portland cement paste, then the X-ray reflections should approach an apparent maximum intensity by a curing time of 7 to 10 days, when according to Copeland, et al (2), 72-80 percent of the C_3S, 78-87 percent of the C_3A, and 36-46 percent of the C_2S should be hydrated.

A comparison of the diffractogram traces (see Figs. 3-5) shows that in the Anna kaolinite mixtures there was an increase in crystalline $Ca(OH)_2$ up to a curing time of 14 days and that from 14 to 112 days there was little or no apparent change. The 8.2 Å

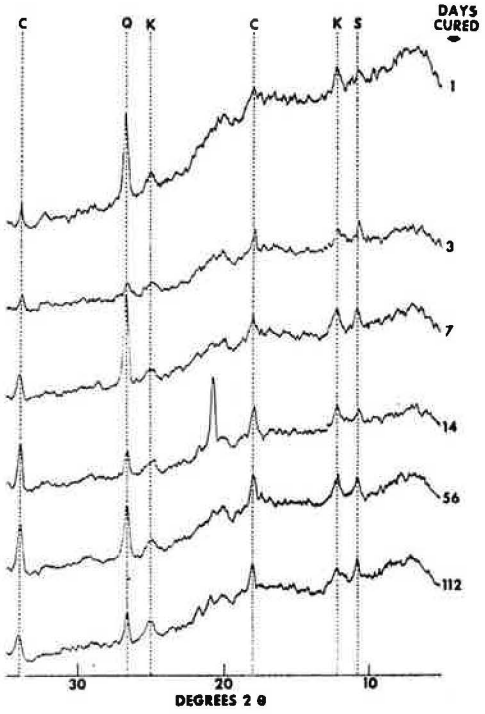

Figure 3. X-ray diffractogram patterns of cement-Anna kaolinite mixtures for the various curing periods.

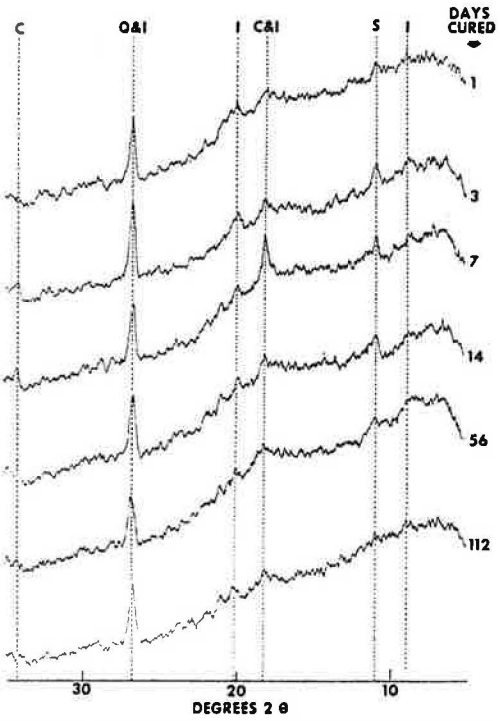

Figure 4. X-ray diffractogram patterns of cement-Fithian illite mixtures for the various curing periods.

reflection of calcium monosulfoaluminate is quite distinct after one day of curing, and by the third day attains a maximum intensity which is maintained through 112 days. In the Fithian illite mixtures, there was a pronounced increase in crystalline $Ca(OH)_2$ up to the 7-day curing period; followed by an apparent decrease at 14 days which continued to 56 days, when it reached the level it maintained through the 112-day curing period. The quantity of calcium monosulfoaluminate increased through 3 days, maintained that concentration to 14 days, and diminished through 56 and 112 days. After 1 day of curing, there were no $Ca(OH)_2$ or calcium monosulfoaluminate reflections for the Aberdeen montmorillonite mixtures; 3-day material showed distinct reflections for both compounds; at 7 days the $Ca(OH)_2$ reflection was very weak and the calcium monosulfoaluminate reflection was absent. There was no reflection for either compound from 14 days through 112 days. The diffractogram traces shown in Figure 6 are of cement-clay mixtures similar to those discussed above, except that they were cured for 2 yr. The prominence of the crystalline $Ca(OH)_2$ in the kaolinite mixture seems to discount the possibility of any extensive clay-$Ca(OH)_2$ interaction. The paucity of crystalline $Ca(OH)_2$ in the illite mixture, and its absence in the montmorillonite mixture, suggests that either clay-$Ca(OH)_2$ interaction is extensive in these mixtures or little $Ca(OH)_2$ is produced initially because of a lack of cement hydration. It will be shown later, during a discussion of the leachates, that those processes which use $Ca(OH)_2$ rapidly could not use enough $Ca(OH)_2$ to account for the differences in $Ca(OH)_2$ leached from the kaolinite mixtures, as compared to that leached from the illite and the montmorillonite mixtures; and that restricted hydration of the cement appears to be a plausible explanation of the paucity of crystalline $Ca(OH)_2$.

On the basis of the X-ray diffraction data, the relationship of the rate of hydration of the portland cement with the subsequent production of crystalline $Ca(OH)_2$ to the rate of usage of crystalline $Ca(OH)_2$, as represented in Figure 7, can be observed. It is obvious that the accumulation of crystalline $Ca(OH)_2$ in the kaolinite mixtures most

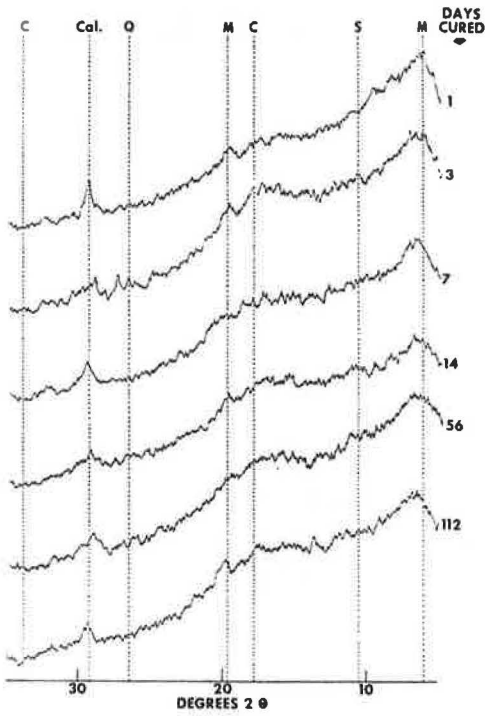

Figure 5. X-ray diffractogram patterns of cement-Aberdeen montmorillonite mixtures for the various curing periods.

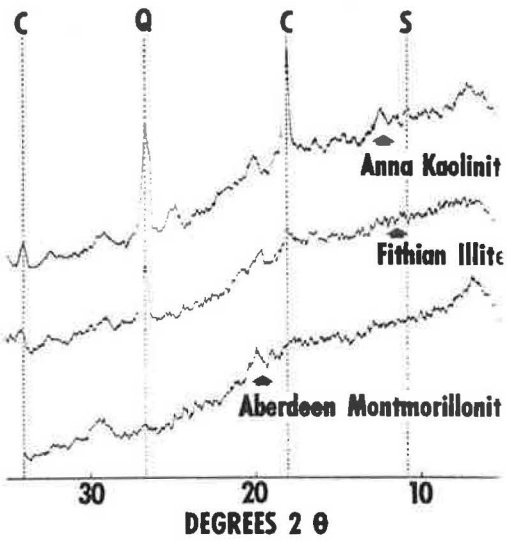

Figure 6. X-ray diffractogram patterns of cement-clay mixtures cured for two years.

closely approximates Greene's description of the buildup of crystalline Ca(OH in a cement paste. It also appears that the buildup of crystalline $Ca(OH)_2$ is slower in the illite mixtures and very slow in the montmorillonite mixtures. As mentioned previously, this can be caused by usage or lack of production. Usa is certainly a factor when the crystalline $Ca(OH)_2$ decreases. However, the importance of this usage depends on the degree of hydration of the cement.

Chemical and Physicochemical Studies

It might be beneficial to the following discourse to list some of the processes, whic are thought to occur in more isolated systems and which probably occur in the more complex system of cement-clay mixtures, in as near to the chronological order of their inceptions as is possible.

1. Hydration of cement compounds with production of $Ca(OH)_2$.
2. Adsorption of Ca onto the cation exchange sites.
3. Adsorption of $Ca(OH)_2$ on clay surfaces (relatively easily leached by distilled water, Diamond and Kinter, 7).
4. Occurring concurrently.

   (a) Encapsulation of $Ca(OH)_2$ crystallites by gels of calcium silicate hydrates an possibly calcium aluminate hydrates and clay particles.
   (b) Possible encapsulation of cement grains by clay and gels.
   (c) Chemical combination of $Ca(OH)_2$ and suggested SiO_2 and Al_2O_3.

pH of Dilute Suspensions of Mixtures–Figures 8 and 9 show that 7 of the 8 pH plots from the dilute suspensions of mixtures belong to the same family of curves, with Wyoming montmorillonite being the exception. Despite the wide variation in the pH's of the untreated clays (see Table 3), the mixtures start at a high pH of 11.52 to 11.65 because of the rapid production of $Ca(OH)_2$ by the hydrating cement. The pH of 0.2-gr

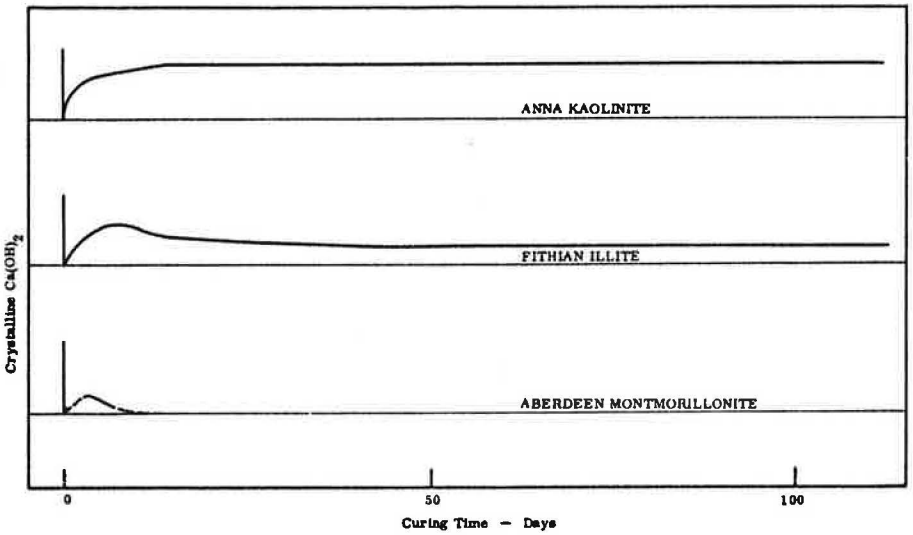

Figure 7. Schematic representation of the rate of accumulation of crystalline $Ca(OH)_2$ in the cement-clay mixtures.

Type I portland cement in 70 ml of distilled water with nitrogen played over the surface of the water was 12.00 at the start of hydration and 11.83 after 15 min of hydration. Thus the effect of the clay minerals in the mixtures is readily apparent. This instantaneous decrease in pH probably corresponds to the very rapid adsorption of $Ca(OH)_2$

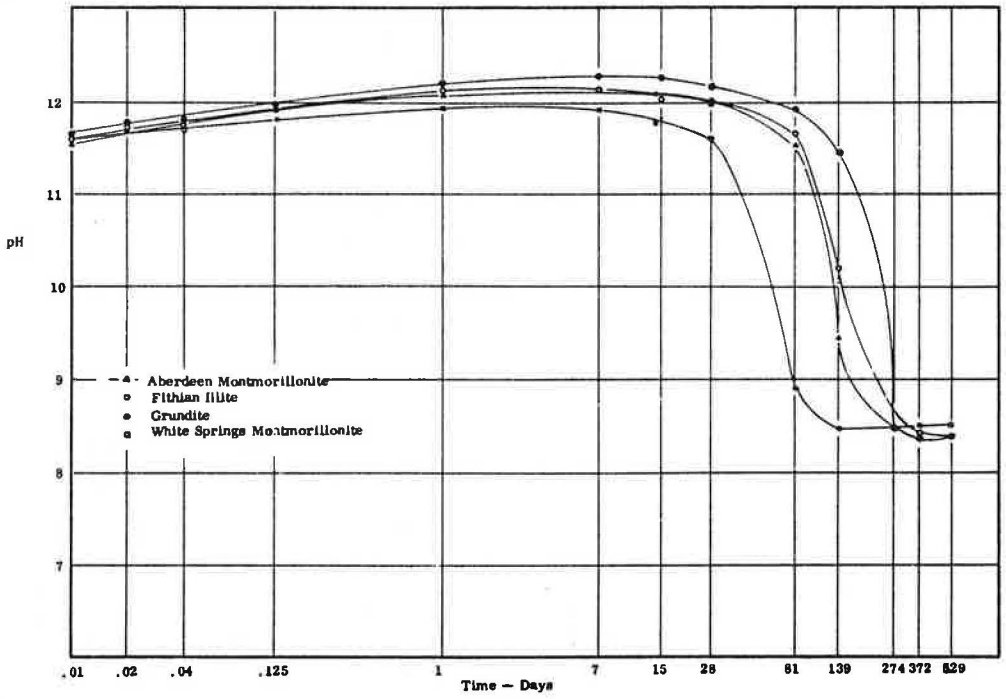

Figure 8. pH vs time.

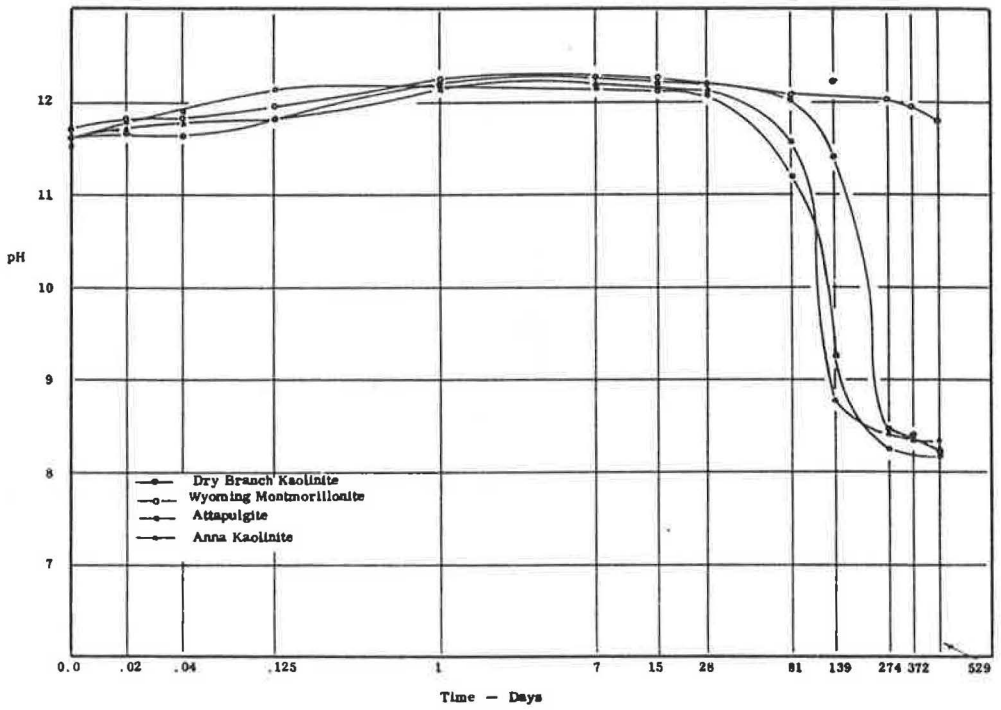

Figure 9. pH vs time.

as reported by Diamond and Kinter (7). The pH curves rise slowly from the start, and with the exception of the curve for the Wyoming montmorillonite, reach a peak at approximately 7 days with pH's which range from 12.10 to 12.25. Then the curves start to drop gradually, until at 28 days they start a rapid decline. From 28 t 274 days the curves within the family have their greatest variation. The steepest par of the curves occur between the following times:

Clay in Cement-Clay Mixture	Time Period in Days
White Springs montmorillonite	28- 81
Anna kaolinite	81-140
Aberdeen montmorillonite	81-274
Fithian illite	81-274
Attapulgite	81-274
Grundite	140-274
Dry Branch kaolinite	140-274

The steepest parts of the curves probably represent the times at which the $Ca(OH)_2$ produced by hydration of the cement was depleted. Inasmuch as X-rays showed that all these mixtures had become carbonated, it is possible that the depletion of the dissolved $Ca(OH)_2$ was due to carbonation.

Perhaps the most startling aspect of the pH curves is their similarity through 7 da of reacting. If the one variant, White Springs montmorillonite, is ignored, this similarity or tight bunching of the curves continues to 28 days at which time the pH's rang from 12.0 to 12.2. It seems unlikely that if a $Ca(OH)_2$ consuming process were extremely active that the pH's could be maintained at the 12.0 and above level through 28 days. It should be kept in mind that these specimens were dilute suspensions rathe than pastes, and that the reactions may be quite different from those occurring in the pastes.

TABLE 3

pH OF CLAYS

Clay	pH
Aberdeen montmorillonite	9.1
White Springs montmorillonite	4.92
Wyoming montmorillonite	9.4
Fithian illite	4.18
Grundite	7.05
Anna kaolinite	6.48
Dry Branch kaolinite	4.88
Attapulgite	9.6

Notes: 1. Distilled water—pH 5.7.
2. 0.4-gm clay to 70-ml distilled water used.

All the mixtures, with the exception of the Wyoming montmorillonite, have pH's between 8.22 and 8.50 during the period of 274 to 529 days. The Wyoming montmorillonite reached a peak pH of 12.22 at a time of 1 day, maintained that pH until the 15-day reading, and then started a slow decline to a pH of 11.78 at 529 days.

X-ray analyses of the mixtures, after drying at 80 C, show reflections at 7.70 Å and 8.07-8.30 Å in all but the White Springs montmorillonite. These reflections may be interpreted as indicating the presence of a tricalcium aluminate hydrate, similar to that type produced by the long-term interaction of $Ca(OH)_2$ and $Al(OH)_3$.

Analyses of Leachates Made With Distilled Water and HCl—Data for the chemical analyses of the distilled water and acid leachates of the cement-clay mixtures are presented in Tables A-1 to A-9 in the Appendix.

Throughout the following discourse, reference is made to the percentage of CaO leached in terms of how much could be leached if complete hydration of the cement occurred. The calculations for these percentages were based on $Ca(OH)_2$ being 25 percent of fully hydrated cement (Brunauer and Copeland, 1). Reference is also made to the theoretical maximum amount of Al_2O_3 capable of being leached from the mixtures with HCl, provided the clays are not altered by exposure to the hydrating cement environment. This quantity of Al_2O_3 should be no more than the sum of the quantity of Al_2O_3 in the cement plus the quantity of Al_2O_3 leached with HCl from the untreated clay.

$Ca(OH)_2$—An attempt will be made to use the quantity of CaO leached from the mixtures as an indication of the relative rates of production of $Ca(OH)_2$ and thus also as an indication of the relative rates of cement hydration.

A brief discussion of the sources of Ca^{++} and its degree of availability should prove beneficial to the interpretation of the CaO data. Calcium may be leached from:

1. Crystalline $Ca(OH)_2$ and $Ca(OH)_2$ dissolved in interstitial water.
2. $Ca(OH)_2$ adsorbed on the external surfaces of the clays and other alumino-silicates.
3. Ca^{++} adsorbed on the internal and external cation exchange sites of the clays.
4. The hydrated cement compounds.
5. Pozzolanic compounds, from pozzolanic reaction of the $Ca(OH)_2$ with the clays.
6. The anhydrous cement compounds.

Calcium is easily leached by distilled water from the first two sources only. Although the other sources will undoubtedly contribute Ca^{++} to the leachate, the quantity contributed would be expected to be minor. The Ca^{++} held in the cation exchange sites and that consumed in the pozzolanic reactions was taken from the $Ca(OH)_2$ produced by the hydrating cement. Any interpretation of hydration rate based on the Ca^{++} removed by the distilled water leachate will yield an erroneously slow hydration rate if some allowance is not made for the Ca^{++} so consumed.

There was a rough but decided correspondence between the quantity of CaO leached from the cement-clay mixtures and the pH's of the leachates, which, coupled with the magnitude of the pH's, suggests that the CaO was principally derived from $Ca(OH)_2$.

The change in quantity of CaO leached from the mixtures (Fig. 10) reflects the change in production and consumption of $Ca(OH)_2$. As the quantity increases, production exceeds consumption, and the converse is true. It is interesting to note that from 3 to 112-days curing the relationship of production and consumption of $Ca(OH)_2$ in the Anna kaolinite and Fithian illite mixtures is approximately the same, as illustrated by the parallelism in the curves. In the Aberdeen montmorillonite-cement mixtures, the relationship of production and consumption of $Ca(OH)_2$ is different from that of the other mixtures, with the quantity of CaO leached reaching a maximum level at 3 days and diminishing from 14 through 112 days.

Figure 10 also shows the difference in quantity of CaO leached from the several cement-clay mixtures for the various periods of curing. The Anna kaolinite mixtures

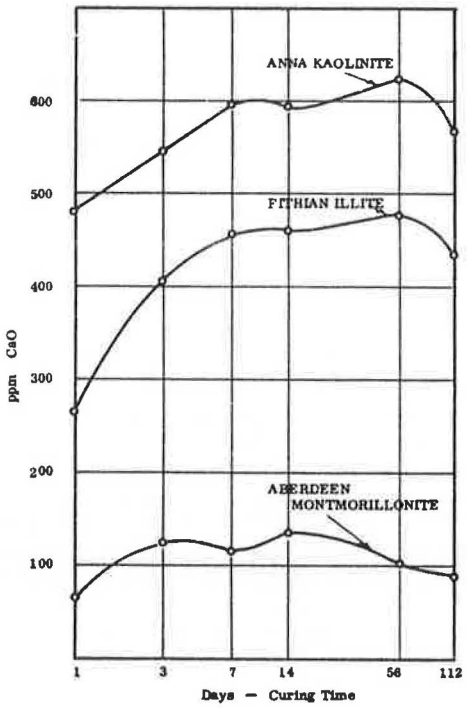

Figure 10. CaO (ppm) derived from first distilled-water leachate.

yielded 130 to 215 ppm more CaO than did the Fithian illite mixtures, and 415 to 520 ppm more than the Aberdeen montmorillonite mixtures. These differences in easily leachable CaO may be interpreted as indicating the extent of cement hydration in the several mixtures, provided no processes are active which tend to combine the calcium in compounds only slightly soluble in distilled water. Cation exchange on internal and external exchange sites and pozzolanic reaction are the principal processes known to occur in cement-clay mixtures which will tie up calcium in a relatively insoluble form.

The difference in cation exchange capacity between Anna kaolinite and Fithian illite, and between Anna kaolinite and Aberdeen montmorillonite, can account for 16-26 and 30-38 percent, respectively, of the differences in quantity of CaO leached from their mixtures. If pozzolanic action is considered to have consumed the remainder of the difference in easily leached CaO, it seems that the Fithian illite and Aberdeen montmorillonite mixtures would have developed greater strengths. Should cation exchange and pozzolanic action not account for the differences, it seems the only other plausible explanation is restricted hydration of the cement.

Diamond (5) has shown that silica, in solution, will rapidly react at the surface of $Ca(OH)_2$ crystals to create an impermeable envelope of reaction product which effectively shields the remaining $Ca(OH)_2$ from further reaction with the silica. Considering the alkaline nature of the micro-environment about a particle of hydrating cement, it seems possible that the more hydrophilic and/or finer grained the clays, the more they would tend to form relatively impermeable envelopes about the cement particles, thus slowing or virtually stopping hydration.

A second look at the data, based on the percentages of the total potential $Ca(OH)_2$ that they are, shows that the mixtures yielded the following:

Mixtures	Percent of Total Potential $Ca(OH)_2$
Anna kaolinite	56-72 on first leach
Fithian illite	31-55 on first leach
Fithian illite	60-90 through third leach
Aberdeen montmorillonite	8-16 on first leach
Aberdeen montmorillonite	20-34 through third leach

Significant quantities of calcium could not be tied up in slightly soluble compounds and still have the percentages of total potential $Ca(OH)_2$ leached as were leached from the kaolinite and illite mixtures. The data and the preceding discussion and hypothesis indicate that hydration was very rapid in the kaolinite mixtures; slower in the illite mixtures, possibly because of envelopment of the cement grains; and slowest in the montmorillonite mixtures. The additional CaO yielded through the third leaches is probably due to hydration of cement during the leaching process. The amount of this additional CaO might be interpreted as an indication of the tightness of the relatively impermeable envelope enclosing the grains of unhydrated cement.

TABLE 4

WET CHEMICAL ANALYSES OF CLAYS

Oxides	Aberdeen Mont.	Attapulgite	Anna Kaolinite	Dry Branch Kaolinite	Fithian Illite	Grundite	Wyoming Mont.	White Springs Mont.
SiO_2	56.66	55.80	57.60	43.32	56.85	57.60	57.15	55.05
CaO	2.66	1.42	0.24	0.00	0.30	0.30	0.50	0.90
MgO	4.44	12.21	1.26	1.05	3.30	2.56	4.45	3.75
Al_2O_3	14.00	10.75	22.50	37.75	9.75	17.00	16.50	14.00
Fe_2O_3	4.70	4.25	0.98	0.00	6.00	5.75	4.10	9.50
TiO_2	0.57	0.48	1.43	1.30	2.22	0.76	0.11	0.63
SO_3	0.12	0.21	0.46	0.36	0.89	0.31	0.48	0.28
K_2O	0.77	1.25	0.25	0.05	4.90	0.45	4.58	1.35
Na_2O	0.85	1.10	0.58	0.78	3.55	3.43	4.28	0.80
Loss on ignition	11.51	13.11	9.81	14.42	11.08	8.02	7.02	10.08
Total	96.28	100.58	95.11	99.03	98.84	96.20	99.17	96.34

Al_2O_3—Previously, the theoretical maximum quantity of Al_2O_3 capable of being leached from the mixtures with HCl was established as being no more than the sum of the quantity of Al_2O_3 in the cement plus the quantity of Al_2O_3 leached with HCl from the untreated clay. Inspection of Tables A-4 to A-6 in the Appendix shows that the total Al_2O_3 leached from the Aberdeen montmorillonite mixtures for all the curing periods exceeded the theoretical maximum leachable Al_2O_3 by 100 to 195 ppm. The total Al_2O_3 leached from the Anna kaolinite mixtures exceeded the theoretical maximum for all the curing periods except the 112-day period. The Fithian illite mixtures did not yield Al_2O_3 in excess of the theoretical maximum, except for the 56-day curing period, for which the data are questionable.

The only possible source of the excess Al_2O_3 was the clays. The only plausible reason for the clays to yield more Al_2O_3 in the presence of hydrating cement is that the alkaline environment established by the hydrating cement causes some degree of deterioration of the clay structure, thus making the Al_2O_3 more susceptible to leaching. The quantities of excess Al_2O_3 leached seem to indicate that the clays suffered deterioration, from greatest to least, as follows: Aberdeen montmorillonite, Anna kaolinite, and Fithian illite.

SiO_2—Inasmuch as the leachate was acid, it is unlikely that much SiO_2 was removed from the clay structures. The data for CaO show that more than 93 percent of the potential CaO was removed from the mixtures. Therefore, the cement constituents must have been thoroughly broken down. It is possible that the SiO_2 data reflect the extent to which the SiO_2 that was dissolved from the cement compounds had polymerized and been removed from solution between the time of dissolution and analysis for SiO_2.

Total Chemical Analysis—The results of the total chemical analysis of the clays are presented in Table 4.

STRENGTH STUDIES WITH TYPE II PORTLAND CEMENT

Harvard-size specimens were molded and processed in much the same method as they were for the first phase of the study, with the exception that only 10 and 20 percent Type II portland cement by weight of the dry clay was added to the mixtures.

Figure 11 shows that there is not much difference between the strength development in cement-clay mixtures with a Type I and a Type II portland cement. The strength curves for the Type II cement-stabilized mixtures approximately parallel the curves for the Type I cement-stabilized mixtures, and have from 10 to 180 psi lower strengths.

The strengths reported are for 7 days of curing. After 7 days of curing at 21 C, it is expected that the dicalcium silicate and the tricalcium silicate will be approximately 36 and 72 percent hydrated, respectively (Copeland, et al, 2). A comparison of the compound compositions of the Type I and Type II cements (see Table 1) shows that the Type II cement contained only slightly more dicalcium silicate and tricalcium silicate, approximately the same quantity of $CaSO_4$, but only 3.12 percent of tricalcium aluminate, whereas the Type I cement contained 11.68 percent tricalcium aluminate. It is unlikely that the difference in strength development between the two cements is due to their content of dicalcium silicate and tricalcium silicate, because they are similar in their

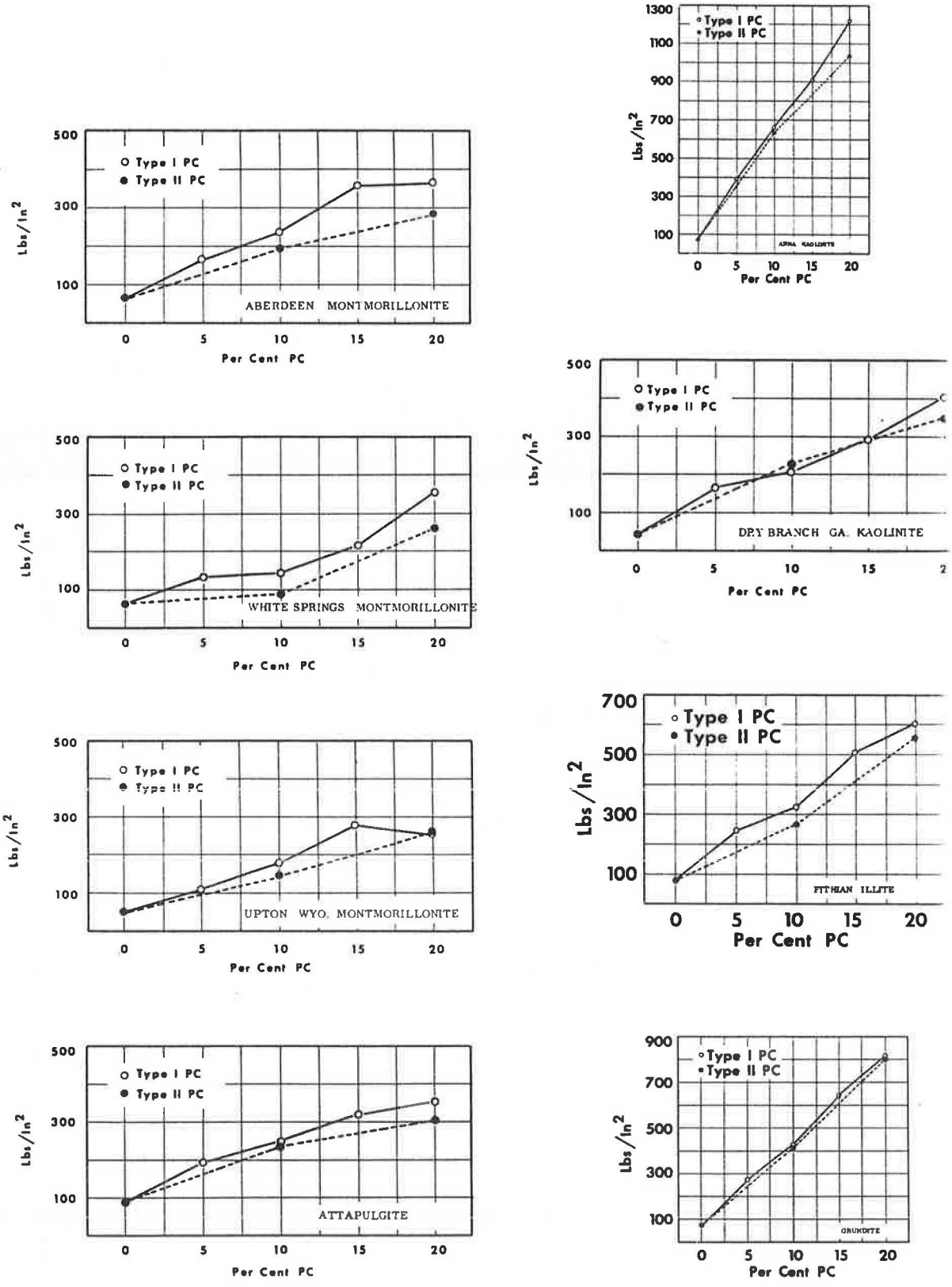

Figure 11. Strength development of clay-cement mixtures.

content of these two compounds. However, inasmuch as tricalcium aluminate is the principal compound contributing to the early strength of cement, the larger quantity of tricalcium aluminate and the higher ratio of tricalcium aluminate to $CaSO_4$ in the Type I cement could account for the higher strength development.

CONCLUSIONS

1. Based on the amount of $Ca(OH)_2$ produced, the cement in the cement-Anna kaolinite mixtures experienced the most rapid hydration. The hydration of the cement in the cement-Fithian illite mixtures started at a rate of approximately one-half and increased after 3 days to a rate of three-fourths that of the cement in the cement-kaolinite mixtures. The cement in the cement-Aberdeen montmorillonite mixtures was by far the slowest to hydrate. Its rate of hydration started at approximately one-tenth and increased to one-fifth the rate for the cement in the cement-kaolinite mixtures.
2. The strength gain noted in Harvard mold specimens cured for 7 days appears to result from the following conditions:
   a. Early flocculation of the clay particles, which brings them into a state of proximity to each other and thus makes their joint cementation easier.
   b. Hydration of the cement, which creates many minute cementitious particles with a very large surface area, as well as chemical combination of SiO_2, Al_2O_3 and $Ca(OH)_2$ to create additional cementitious particles.
   c. Crystallization of $Ca(OH)_2$, which cements discrete particles as well as floccules to each other. The microscope study showed that the cement-Anna kaolinite mixtures had the most extensive development of well-crystallized $Ca(OH)_2$; the cement-Fithian illite mixtures had moderately well developed but irregular patches of $Ca(OH)_2$; and that the cement-Aberdeen montmorillonite mixture, which developed the least strength, had no visible $Ca(OH)_2$.
3. The alkaline environment of the hydrating cement caused deterioration of the clays. The clays suffered deterioration, from greatest to least, as follows: Aberdeen montmorillonite, Anna kaolinite and Fithian illite.
4. A mechanism for restricting the hydration of cement grains is encapsulation of the cement grains by the very fine-grained clay and recently crystallized gels of calcium silicate hydrate and, perhaps, calcium aluminate hydrate. This concept of encapsulation is a modification of the concept for encapsulation of $Ca(OH)_2$ crystals by an amorphous calcium silicate hydrate gel presented by Diamond (5).
5. Up to a curing period of 7 days, the Type I portland cement-clay mixtures developed somewhat greater strengths than the Type II portland cement-clay mixtures, probably because of the larger content of tricalcium aluminate and similar content of $CaSO_4$ in the Type I portland cement.
6. From the observations presented in this report, it appears that very early in the life of cement-Aberdeen montmorillonite mixtures the cement grains become encapsuled and hydration is slowed to a negligible rate. Diamond (5) has demonstrated that if a large surface area silicate is present in a dilute suspension of $Ca(OH)_2$, at a ratio of say 5/1 silicate to $Ca(OH)_2$, the adsorption of $Ca(OH)_2$ onto the silicate surface is so fast that there is no opportunity for encapsulation of the crystalline lime and it is soon depleted. Of course, the preceding reaction might not occur if the silicate and $Ca(OH)_2$, in the same proportions, were in paste form. The preceding information suggests that a comparison of a cement-montmorillonite system with a lime-montmorillonite system would be an area for fruitful investigation.

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The freely given advice and stimulating discussion of Dr. W. Cullen Sherwood on all aspects of this study are gratefully acknowledged.

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Appendix

TABLE A-1

LEACHINGS OF CaO AND pH OF LEACHATE
Cement-Anna Kaolinite Mixtures

Curing Period, Days	Leach								Acid Leach, ppm	Total Leached, ppm
	1 st		2 nd		3 rd		4 th			
	pH	ppm	pH	ppm	pH	ppm	pH	ppm		
Untreated clay	6.72	0.0	6.62	2.2	6.70	3.4			9.0	14.6
1	12.00	480.5	11.30	122.1	11.27	87.4			1601.6	2291.6
3	12.15	545.4	11.59	149.0	11.35	90.7			1550.1	2335.2
7	12.18	595.8	11.56	153.4	11.31	96.3			1357.4	2202.9
14	12.20	593.6	11.60	150.1	11.32	93.0			1458.2	2294.9
56	12.17	621.6	11.62	190.4	11.38	109.8	11.24	87.4	1344.0	2353.2
112	12.20	567.0	11.70	194.9	11.42	108.6			1395.5	2266.0

TABLE A-2

LEACHINGS OF CaO AND pH OF LEACHATE
Cement-Fithian Illite Mixtures

Curing Period, Days	Leach														Acid Leach, ppm	Total Leached, ppm
	1 st		2 nd		3 rd		4 th		5 th		6 th		7 th		8 th			
	pH	ppm	pH	ppm	pH	ppm	pH	ppm	pH	ppm	pH	ppm	pH	ppm	pH	ppm		
Untreated clay	4.76	19.0	5.23	1.7	5.60	0.0											11.2	31.9
1	11.80	265.4	11.46	132.2	11.30	98.6											1895.0	2391.2
3	12.00	406.6	11.50	152.3	11.36	109.8											1648.6	2317.3
7	12.06	457.0	11.48	155.7	11.25	101.9											1673.2	2387.8
14	12.00	460.3	11.50	170.2	11.30	117.6											1561.3	2309.4
56	12.12	474.9	11.61	175.8	11.44	121.0	11.30	88.4	11.20	67.2	11.00	50.4	10.90	41.4	10.71	35.8	1209.6	2264.5
112	12.03	432.3	11.65	178.1	11.51	137.8	11.39	94.1	11.18	69.4	11.01	50.4	10.88	43.7	10.78	39.2	1377.6	2422.6

TABLE A-3

LEACHINGS OF CaO AND pH OF LEACHATE
Cement-Aberdeen Montmorillonite Mixtures

Curing Period, Days	Leach										Acid Leach, ppm	Total Leached, ppm
	1st		2nd		3rd		4th		5th			
	pH	ppm	pH	ppm	pH	ppm	pH	ppm	pH	ppm		
Untreated clay	8.65	15.7	8.61	12.9	8.35	10.1					147.8	186.5
1	11.13	63.8	11.00	50.4	10.90	53.8					2380.0	2548.0
3	11.50	125.4	11.30	95.2	11.17	71.7					2334.1	2626.4
7	11.46	115.4	11.21	81.8	11.06	63.8					2275.8	2536.8
14	11.58	137.8	11.30	86.2	11.05	66.1					2266.8	2556.9
56	11.43	101.9	11.24	71.7	11.11	59.4	10.96	48.2	10.82	40.3	2139.2	2460.7
112	11.40	89.6	11.22	67.2	11.06	53.5	11.04	53.2	10.92	44.0	2268.5	2576.0

TABLE A-4

LEACHINGS OF Al_2O_3
Cement-Anna Kaolinite Mixtures

Curing Period, Days	Leach, ppm				Acid Leach, ppm	Total Leached, ppm	*a	Total in Mixture, ppm
	1st	2nd	3rd	4th				
Untreated clay	0.0	0.0	0.0		134.0	134.0		1251.0
1	13.9	8.0	8.0		496.8	526.7	352.3	1469.0
3	2.4	8.8	9.0		360.0	380.2	352.3	1469
7	1.6	10.4	10.4		420.0	442.4	352.3	1469
14	0.0	2.4	10.4		432.0	444.8	352.3	1469
56	0.0	0.0	0.0	0.0	356.0	356.0	352.3	1469
112	0.0	0.0	0.0		336.0	336.0	352.3	1469

*a = ppm leached from pure clay plus ppm possible from fully dissolved portland cement.

TABLE A-5

LEACHINGS OF Al_2O_3
Cement-Fithian Illite Mixtures

Curing Period, Days	Leach, ppm								Acid Leach, ppm	Total Leached, ppm	*a	Total in Mixture, ppm
	1st	2nd	3rd	4th	5th	6th	7th	8th				
Untreated clay	0.0	0.0	0.0						166.4	166.4		
1	5.0	4.8	3.2						348	361	384	760
3	3.2	5.6	1.6						316	326.4	384	760
7	0.0	6.4	4.8						340.4	351.6	384	760
14	2.4	40.0	5.6						320	368	384	760
56	9.5	7.5	10.2	11.2	9.3	5.6	4.8	2.4	473.6	534.1	384	760
112	0.0	3.2	0.0	0.0	0.0	0.0	0.0	0.0	376.0	379.2	384	760

*a = ppm leached from pure clay plus ppm possible from fully dissolved portland cement.

TABLE A-6

LEACHINGS OF Al_2O_3
Cement-Aberdeen Montmorillonite Mixtures

Curing Period, Days	Leach, ppm					Acid Leach, ppm	Total Leached, ppm	*a	Total in Mixture, ppm
	1st	2nd	3rd	4th	5th				
Untreated clay	0.0	0.0	0.0			172.0	172.0		778.4
1	0.0	0.0	0.0			552.0	552.0	390.3	997.0
3	3.2	3.2	1.6			484.0	492.0	390.3	997.0
7	12.0	6.4	9.6			496.0	524.0	390.3	997.0
14	15.2	16.8	13.1			524.8	569.9	390.3	997.0
56	0.0	3.2	0.0	0.0	0.0	528.0	531.2	390.3	997.0
112	0.0	0.0	0.0	0.0	0.0	585.6	585.6	390.3	997.0

*a = ppm leached from pure clay plus ppm possible from fully dissolved portland cement.

TABLE A-7

LEACHINGS OF SiO_2
Cement-Anna Kaolinite Mixtures

Curing Period, Days	Leach, ppm			Acid Leach, ppm	Total Leached, ppm	Total in Mixture, ppm
	1 st	2 nd	3 rd			
Untreated clay	0.0	0.0	0.0	0.0	0.0	3202.0
1	0.0	4.8	3.2	188.3	196.3	3986.0
3	0.0	3.2	2.4	202.0	207.6	3986.0
7	0.0	3.2	0.0	169.6	172.8	3986.0
14	0.0	3.2	0.0	128.0	131.2	3986.0
56	0.0	4.8	20.0	103.2	128.0	3986.0
112	0.0	2.4	3.2	54.4	60.0	3966.0

TABLE A-8

LEACHINGS OF SiO_2
Cement-Fithian Illite Mixtures

Curing Period, Days	Leach, ppm								Acid Leach, ppm	Total Leached, ppm	Total in Mixture, ppm
	1 st	2 nd	3 rd	4 th	5th	6 th	7 th	8 th			
Untreated clay	0.0	0.0	0.0						12.8	12.8	3160.8
1	0.0	9.6	8.0						152.0	169.6	3945.0
3	0.0	3.2	6.4						145.6	155.2	3945.0
7	0.0	0.0	0.0						153.6	153.6	3945.0
14	0.0	0.0	0.0						160.0	160.0	3945.0
56	0.0	0.0	6.4	4.8	12.8	8.0	11.2	12.8	*N.A.		3945.0
112	3.2	8.0	14.4	8.0	11.2	14.4	20.0	18.4	78.4	176.0	3945.0

*Note: No analysis.

TABLE A-9

LEACHINGS OF SiO_2
Cement-Aberdeen Montmorillonite Mixtures

Curing Period, Days	Leach, ppm					Acid Leach, ppm	Total Leached, ppm	Total in Mixture, ppm
	1 st	2 nd	3 rd	4 th	5 th			
Untreated clay	0.0	0.0	0.0			12.8	12.8	3150.0
1	11.2	12.8	9.6			201.6	235.2	3935.0
3	0.0	6.4	11.2			195.2	212.8	3935.0
7	6.4	10.4	11.2			200.0	228.0	3935.0
14	0.0	0.0	4.8			196.8	201.6	3935.0
56	0.0	4.8	4.8	1.6	4.8	*N.A.		3935.0
112	6.4	4.8	3.2	0.0	0.0	153.6	168.0	3935.0

*Note: No analysis.