Reactions of Soil Minerals With Cement and Chemicals

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The nature of reactions accompanying the stabilization of soil with lime and cement and the mechanisms involved in the alteration of soil-cement (or soil-lime) reaction by chemical additives were studied. One of the main objectives was to compare the similarities and differences for lime and cement reactions with two soil minerals. Mixtures of mono-mineral soils and 10 percent cementing compounds, with or without sodium additives, were examined after compaction and various curing periods by a number of analytical techniques, including flame photometry, colorimetry, X-ray diffraction, and differential thermal analysis.

Both mono-mineral soils, quartz and kaolinite, reacted with the three calcium stabilizers (hydrated lime, tricalcium silicate and Type I portland cement). Addition of sodium additives greatly intensified the reaction between the soil and the stabilizer and increased the abundance of reaction products. Reactivity of kaolinite with any one of the cementing compounds was higher than that of quartz. The principal reaction products produced in quartz mixtures were hydrous calcium silicates of various compositions with $CaO:SiO_2$ ratio varying from 0.2 to 1, and in kaolinite mixes were hydrous calcium silicates, hydrous calcium aluminates and a mixed calcium aluminosilicate. Sodium from the additive associated with soluble compounds early in cure and later with insoluble mixed sodium-calcium silicates (or aluminates).

•SOILS ENGINEERS have for many years considered portland cement and hydrated lime the most successful soil stabilizers. The use of cement and lime has increased steadily in recent years in the construction of airfields, roadways and other engineering works in many parts of the world. However, until the late 1950's very little was known about the mechanisms of the stabilization and the nature of the reaction products. Investigators have proposed various hypotheses for soil-lime (9, 12, 20) and soil-cement stabilization (13, 14, 22).

In 1957, the U. S. Bureau of Reclamation (7) initiated an extensive study on the pozzolan-cement reaction by establishing a library of X-ray diffraction patterns and differential thermal analysis (DTA) curves of hydration products of pure compounds used individually and in combination as normal constituents of commercial cement. Benton (1) reported that in the cement-pozzolan reactions all the compounds identified, except a Stratling's compound, are recognized normal hydration products of cement.

Goldberg and Klein (12) concluded from their limited results of X-ray and DTA studies of mixtures of lime and Wyoming bentonite that the calcium hydroxide in the soil-lime mixture is converted to calcium carbonate, not calcium silicates. More recently, Eades and Grim (9) investigated the reaction of hydrated lime with pure clay

minerals and noted the formation of new crystalline phases, probably tobermorite-like calcium silicate hydrates. Diamond, White and Dolch (8) treated various clay minerals and silicates with 40 to 400 percent (by weight of the mineral) of calcium hydroxide at elevated temperatures. They identified the reaction product as poorly crystallized calcium silicate hydrates of the tobermorite family and various forms of calcium aluminate hydrates. Hilt and Davidson (15) reported the isolation of a crystalline calcium aluminate hydrate reaction product from a mixture of montmorillonite and 40 percent lime. Glenn and Handy (11) found that the products of the reaction in slurry form of several varieties of lime and soil minerals include a 10 Å tobermorite, tetra-calcium aluminate hydrates and several compounds of unknown composition. The formation of new products by lime stabilization under field conditions was confirmed by Eades, Nichols and Grim (10). Herzog and Mitchell (14) reported an investigation of the reaction of two clay minerals with 15 and 30 percent of tricalcium silicate and portland cement at the relatively high temperature, 50 C. They suggested a clay-cement structure with "primary" cementitious materials due to the cement hydration and "secondary" cementitious matter resulting from reactions between the calcium hydroxide (a reaction by-product of the "primary") and clay mineral.

Most of these studies employed either a relatively high concentration of the stabilizer or high temperature curing. In several investigations, the reacted samples were subjected to drying (air or oven) before examination by X-ray or DTA. This paper reports the results of an investigation to elucidate further the nature of the reactions accompanying lime and cement stabilization and also the effect of sodium additives on the reactions. One of the primary objectives of the study was to compare the similarities and differences between lime and cement reactions with soil minerals. The stabilizer concentration selected for the study was 10 percent by dry soil weight. All mineral-stabilizer-additive mixtures were humid cured at room temperature for various periods of time and then subjected to examination with no drying.

<div align="center">NOTATIONS</div>

Materials

Q	Quartz
K	Kaolinite
M	Montmorillonite
L, $Ca(OH)_2$	Lime, calcium hydroxide
T, C_3S	Tricalcium silicate
PC	Portland cement

Chemical Terms

C	CaO
S	SiO_2
A	Al_2O_3
H	H_2O
N	Na_2O
X	Anion of sodium additive

X-Ray Diffraction Patterns

I	Relative intensity
d	Diffuse
v, V	Very
b, B	Broad
s, S	Strong
m, M	Medium
w, W	Weak

EXPERIMENTAL INVESTIGATION

The experimental investigation was carried out on specially prepared soil-cement-additive specimens. In view of the extreme complexity of this type of system, mono-mineral soils were used in preference to natural soils. Various combinations of the mono-mineral soils, cementing compounds and selected additives were examined at various stages during the reaction process by a number of special analytical techniques. The solid phase of each system was examined by X-ray diffraction and DTA techniques. Variations in the chemical composition of the solution phase of the system were also analyzed.

Materials

Soil Components. — Two mono-mineral soils, quartz (Q) and kaolinite (K), representing a silicate and an aluminosilicate, were selected for the study of the mechanisms of soil stabilization with cement, lime and sodium additive.

The quartz sample was obtained by grinding Ottawa sand to 100 percent passing No. 200 sieve. The freshly ground mineral was mixed well and allowed to stand in air under room temperature and humidity for at least 3 months before use to minimize any effect of grinding on the reaction pattern of the mineral with the stabilizers. X-ray and DTA data indicated that the quartz sample was reasonably pure. Tests of the kaolinite (Peerless No. 2 kaolin) showed that this product was free of any montmorillonoids and had very little soluble salts. A third mono-mineral soil, montmorillonite (Volclay 325), was used to augment the data on the evaluation of the nature of reactions between the soil minerals and cements. Table 1 summarizes some of the properties of these mono-mineral soils. The X-ray patterns are tabulated in Table 2 and the DTA curves are shown in Figure 1.

Primary Stabilizers. — Reagent grade calcium hydroxide (L), synthesized tricalcium silicate (T) and commercial Type I portland cement (PC) were selected as primary stabilizers. The concentration of 10 percent by dry soil weight used in all experiments represents the average stabilizer content utilized in practical soil stabilization work. Table 3 summarizes the composition of tricalcium silicate and Table 4 shows the composition of the portland cement used. Shown in Figure 2 are thermograms of the three stabilizers in the unhydrated state. ("Cement" is used to denote any of the three primary stabilizers; portland cement is used to denote the particular compound.)

Secondary Additives. — Three alkali sodium compounds (hydroxide, metasilicate and sulfate) were chosen for this study because results from previous studies (20, 22) indicated that alkali metal compounds beneficial to cement stabilization were those forming insoluble salts with calcium and that these three chemicals were the most effective ones on a range of soils investigated. The secondary additive concentration used in the present investigation was equivalent to one normal sodium ion in the molding water.

Procedure

Preparation of Soil-Stabilizer-Additive Specimens. — Individual specimens were prepared for each series of X-ray and DTA tests. Air-dried mineral and stabilizer were first dry mixed; chemical solution or distilled water was then added and mixed by hand until uniform. Samples were compacted immediately after mixing in a specially made miniature mold (to give a sample size just sufficient for one DTA and one X-ray test) with a tamping rod. A second specimen of each combination was prepared for the chem-

TABLE 1

PROPERTIES OF SOIL MINERALS

Soils	Textural Composition (% by wt.)			Physical Properties						Chemical Properties	
	0.074 mm	0.074-0.002 mm	0.002 mm	L.L. (%)	P.L. (%)	P.I. (%)	Spec. Gr.	Max. Dry Density[a] (pcf)	Opt. Water Cont. (%)	Organic Matter (%)	Total Sol. Salt (m.eq. NaCl/100 gm)
Quartz	0	100	—	N.P.	N.P.	N.P.	2.65	96.7	20.1	0	0.3
Kaolinite	2	41	57	52	29	23	2.66	93.8	25.1	0	0.2
Montmorillonite	3	97	—	—	—	—	—	79.1	38.2	-	31.0

[a]Harvard miniature compaction, 40 lb tamper, 3 layers, 25 blows per layer.

TABLE 2
X-RAY PATTERNS OF TWO SOIL MINERALS AND THREE STABILIZERS

Quartz		Kaolinite		Calcium Hydroxide		Tricalcium Silicate		Portland Cement	
d (Å)	I	d (Å)	I	d (Å)	I	d (Å)	I	d (Å)	I
4.25	S	7.13	VS	4.91	S	6.06	VW	3.98	W
3.34	VS	4.44	–	3.12	M	3.90	VW	3.63	W
2.45	M	4.34	M	2.63	VS	3.02	S	3.32	W
2.28	M	4.15	–	1.93	M	2.76	VS	3.02	S
2.24	W	3.84	W	1.80	M	2.60	VS	2.76	VS
2.13	W	3.56	VS	1.69	M	2.39	VW	2.61	S
1.98	W	3.32	W	1.63	VW	2.34	W	2.31	WB
1.82	S	2.56	M			2.31	–	2.17	S
1.67	W	2.49	–			2.18	S	2.10	WB
		2.38	M			1.94	M	2.04	WB
		2.34	M			1.77	S	1.97	W
		2.29	M					1.92	MB
		1.99	M					1.76	S
		1.94	VW						
		1.89	VW						
		1.84	VW						
		1.79	W						
		1.66	M						

TABLE 3
COMPOSITION OF TRICALCIUM SILICATE[a]

Analysis	% by Weight	Composition	% by Weight
Total CaO₂	72.74	C_3S	95.12
Total SiO₂	26.30	β-C_2S	1.92
Al₂O₃	0.02	$C_2S \cdot 2H_2O$	1.79
MgO	0.10	$Ca(OH)_2$	0.55
SO₃	0.03	$CaCO_3$	0.25
H₂O	0.46	$C_3A \cdot 6H_2O$	0.07
CO₂	0.11	$CaSO_4$	0.05
Na₂O	—	MgO	0.10
K₂O	—	SiO₂	0.15
Total	99.76		100.00

[a]Data obtained from Brunauer, Hayes and Hass (5).

Figure 1.   Thermograms   of   mono-mineral soils.

TABLE 4
COMPOSITION OF CEMENT[a]

Analysis	% by Weight	Pot. Phase Comp.[b]	% by Weight
SiO₂	19.78	C_3S	51.9
Al₂O₃	5.54	C_2S	17.7
Fe₂O₃	3.45	C_3A	8.8
CaO	62.59	C_4AF	10.5
MgO	3.90		
SO₃	2.25		
Na₂O	0.25		
K₂O	0.71		
Loss on ignition	1.30		
Insol. residue	0.08		
Mn₂O₃	0.07		

[a]Spec. surface (Blaine), 3,270 sq cm/g.
[b]Calculated based on equilibrium crystallization (2).

ical analysis. These specimens were compacted statically in a mold 0.625 in. in diameter and 1.600 in. high. The moisture content and dry density of each mineral-stabilizer-additive combination were approximately equal to the optimum moisture content and maximum dry density of the untreated mineral, as determined by the Harvard miniature compaction procedure (1.313-in. diameter 2.816-in. high sample, compacted by a 40-lb tamper in 3 layers with 25 blows per layer). Immediately after molding, specimens were cured at approximately 100 percent RH and room temperature for various periods of time.

X-Ray Diffraction Analysis.—X-ray diffraction patterns were obtained with unfiltered chromium radiation in an evacuated powder camera of 114.6-mm diameter. All cured specimens were crushed at as-cured moisture content (with no drying), and mixed with a droplet of glycerol (used to expand the clay minerals and/or the hydrous calcium silicates to enhance the basal reflections), and worked into a thick
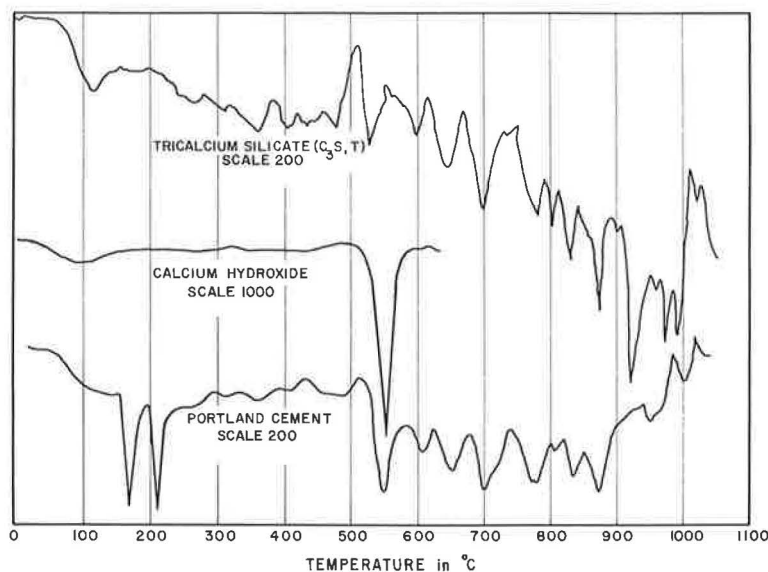
Figure 2. Thermograms of calcium stabilizers.

paste with a spatula. A small amount of collodion was added and the paste was rolled between two ground glass plates to a thin rod approximately 0.5 mm in diameter. The specimen was then mounted in the center of the camera on a rotating shaft. Double-emulsion films were used to record the diffraction patterns. The film extended over half the circumference of the camera. The specimen was exposed for 1.5 hours with continuous rotation to give a random orientation. During the exposure period, the camera was evacuated to reduce air scattering and required exposure time.

X-ray diffraction patterns of the pure materials, e.g., the two minerals and three stabilizers, were checked with a Norelco diffractometer. Excellent agreement was obtained.

Differential Thermal Analysis.—DTA experimental conditions were single-unit nickel steel block with platinum-platinum plus 10 percent rhodium thermocouples, heating rate at 12.5 C/min, sample volume 0.08 cu in. (approximately 1.5 g in weight). A detailed description is given by Lambe (21), except that $^3/_{22}$-in. diameter ceramic tubes were used to protect the thermocouples in the two wells. Calcined aluminum hydroxide (γ-Al_2O_3) was used as reference material. No control of relative humidity of the inert reference material was undertaken.

Specimens were crushed immediately after curing. To avoid the effect of drying on the properties of the test mixture, specimens were crushed as fine as possible (approximately passing a No. 20 sieve) under as-cured moisture condition. The crushed sample and the reference material were firmly packed into the wells. Access to air was limited by a cover.

Amplification of the differential voltage was varied (noted on the DTA traces as "scale") during the test as necessary to provide a maximum degree of sensitivity, since it was desired to study very small changes in the thermal patterns. The same variation in the degree of amplification was used for all DTA tests on the same mineral.

Extraction for Chemical Analysis.—The as-cured specimens were crushed and pulverized to pass a No. 20 sieve after various ages of cure. (The sieve size was chosen somewhat arbitrarily. However, it was difficult to pulverize the wet specimen any further without causing excessive drying of the mixture.) A 10-g portion of the wet pulverized sample was mixed with 50 ml distilled water with continuous stirring for 1 minute, then vacuum filtered immediately. By this extraction procedure, a minimum of time was allowed for the sample to contact a large excess of water. The whole ex-

traction process required less than 2 minutes. The clear filtrate was preserved in capped 50 ml polyethylene containers for analysis of the ionic compositions. A separate sample of the wet pulverized mixture was taken for determination of the moisture content. Results of the chemical analyses are reported on the basis of ovendry weight of the pulverized material.

Chemical Analysis of the Aqueous Extracts. — The clear filtrates were quantitatively analyzed for silica, alumina, sodium and calcium. Silica and alumina contents were determined colorimetrically. Ammonium molybdate was used to develop the blue color for silica determinations (25), and aluminon reagent was used for aluminum determinations (25). Sodium and calcium concentrations were analyzed with a Baird flame photometer. Careful consideration was given to the interference of other ions present in the extract on these determinations. The methods adopted are believed to be completely satisfactory to ± 5 percent, which is adequate for the present study.

RESULTS AND DISCUSSION

The test results obtained indicate that the reaction patterns of one soil mineral with any of the three calcium stabilizers are not greatly different from each other. The major differences are found more in the rate of reaction and the relative amounts of the various reaction products rather than in the formation of entirely different products. Therefore, the following discussion is confined to the results of several selected mixtures. Detailed results and discussion are given elsewhere (26).

Since the primary objective of this research is to attain a better understanding of the fundamentals in the alteration of soil properties with cement and sodium additives, the emphasis of the analysis of the test results is on the examination of the types and trends of the interactions between the various constituents rather than on the formulation of the exact chemical reaction or the final products. Nevertheless, the reaction products are identified whenever possible. Interpretation of these products is largely based on published information concerning similar systems.

X-Ray Diffraction and Differential Thermal Analysis

Quartz-Calcium Hydroxide Series. — In the thermograms of quartz-calcium hydroxide mixes, with or without additive, the dehydration endotherm of calcium hydroxide at approximately 550 C and the quartz inversion peak are the two predominant features, as illustrated by the curves in Figure 3. The decrease in amplitude of the two peaks with curing time (Fig. 4) clearly demonstrates the reaction between the two constituents.

X-ray diffraction patterns (Table 5) show that most calcium hydroxide lines diminish after 1-day curing and the only remaining line at 2.62 Å decreases in relative intensity with time as the amplitude of the endothermic peak of this compound in the DTA curves also decreases. A new phase appears to develop, increasing in quantity with curing as indicated by the diffraction line at 3.03 Å. Although the identity of the new reaction product
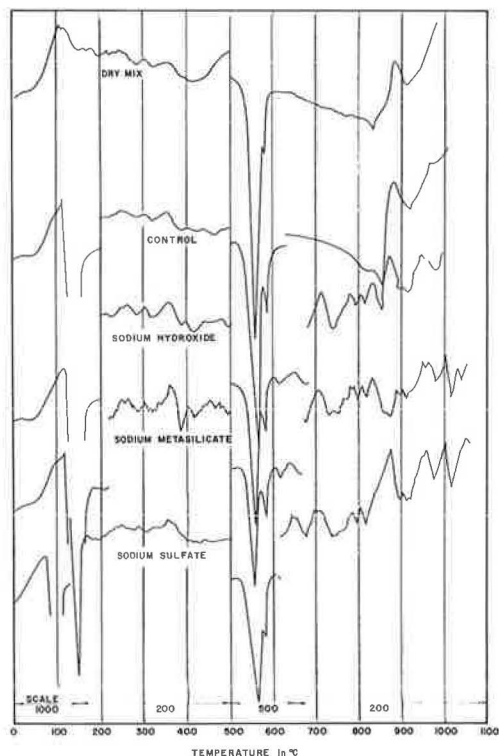

Figure 3. Effect of sodium additives on thermogram of 1-day cured quartz-calcium hydroxide mix.
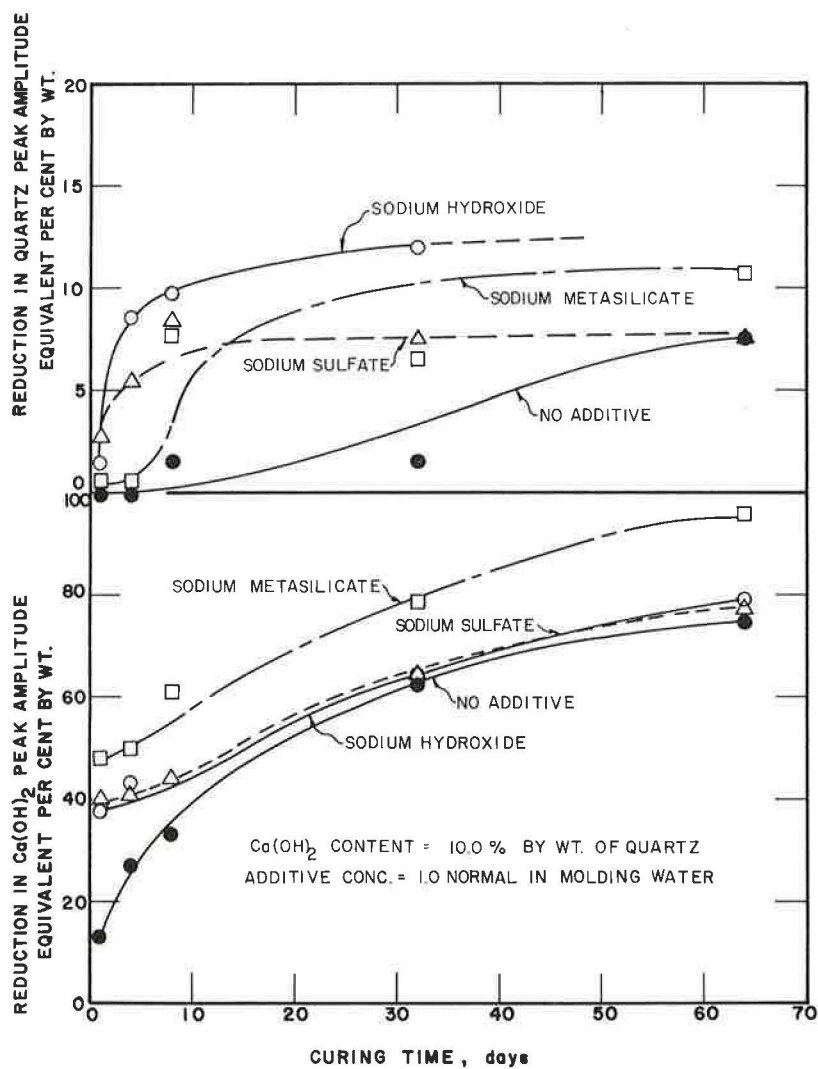
Figure 4.   Effect of curing time on DTA peaks of quartz and lime in quartz-lime mixes.

TABLE 5

X-RAY ANALYSES OF QUARTZ-CALCIUM HYDROXIDE MIXTURES

Spacing (Å)	Dry Mix	No Additive		Sodium Hydroxide		Sodium Metasilicate		Sodium Sulfate		Identi-fication[a]
		1-Day	64-Day	1-Day	64-Day	1-Day	64-Day	1-Day	64-Day	
3.33	10	10	10	10	10	10	10	10	10	Quartz
3.25	—[b]	—	—	—	2	—	—	—	—	CSH
3.03	—	—	2	—	3	1	3	—	3	CSH (I)
2.62	4	2	2	3	1	2	—	2	1	Lime
2.36	—	—	—	—	—	—	1	—	—	CSH

[a]See text for explanation.   [b]Line not present in pattern.

is uncertain, the data indicate that the new phase is a poorly crystalline calcium silicate hydrate of CSH(I) type (29). The 3.03 Å line is attributed to CSH, not to calcite, because the X-ray diffraction data indicate that other CSH lines also develop in these mixes. Furthermore, calcite, even at a very small percentage, exhibits very strong endothermic reaction at temperatures above 900 C (23). Examination of the thermograms and X-ray patterns reveals no correlation between the calcite thermal reaction and the observed 3.03 Å line. Since this is the strongest line of a poorly crystalline CSH, it is used to represent this compound in all discussions.

From the amplitude of the thermal peaks in the DTA curves, an attempt is made to estimate quantitatively the amount of materials reacted after various hydration time as shown in Figure 4. At 64 days, only 2.5 percent calcium hydroxide (percentage based on the weight of soil mineral unless otherwise noted) remains in the mix; that is, 75 percent of the original amount of calcium hydroxide has combined into new products or lost its identity. The amount of quartz that disappeared in this sample corresponds to 7.5 percent. If all the missing quartz and calcium hydroxide reacts with each other, a hydrous calcium silicate with lime-silica ratio of 0.8 is formed. This compound is within the range of Taylor's CSH(I) or Bogue's $C_2S_3H_2$ (2) which produces the strongest X-ray diffraction line at 3.03 Å.

As shown in Figure 4, the most obvious effect of a sodium additive is to intensify the reaction between the soil and the stabilizer. The strong alkali additive, sodium hydroxide, greatly increases the reactivity of the quartz mineral toward the lime, particularly early in the cure. However, the general pattern of the DTA curves remains essentially the same as those of the additive-free samples. One additional effect of the caustic is the development of a small endothermic bulge at about 610 to 620 C which is probably a sodium-bearing phase of hydrous calcium silicate (19). The X-ray diffraction data reveal an earlier formation of CSH; the 3.03 Å line first appeared in the 4-day specimen as compared to the 32-day specimen of the additive-free mix.

With sodium metasilicate as additive, the calcium hydroxide is consumed much more rapidly and completely than it is in either the additive-free or the caustic-treated mix. The major reaction occurring early in the cure (about 1 day) is the precipitation by calcium of the highly reactive silicate from the additive to form insoluble calcium silicate hydrate. Thus, very little of the quartz mineral, which is much less reactive than the additive silicate, would enter into the reaction. Gradually, the alkali component of the sodium additive attacks the quartz silica which, in turn, reacts with the remaining lime or with the hydrous calcium silicate already formed. These reaction processes are clearly demonstrated by the very small changes in the quartz thermal peaks for samples cured less than 4 days and the greater reduction in peak size with longer cure. The major reaction product, hydrous calcium silicate, appears to develop after only 1 day of cure and is more abundant than in the additive-free sample. It is also interesting to note that the sodium-bearing phase of CSH formed at early ages gradually diminished after 32 days of reaction as shown by the endothermic reaction between 610 and 620 C in Figure 5. This indicates that in this mix the sodium-bearing phase of the CSH is a metastable phase which transforms to a calcium silicate hydrate with time. The large exotherm at about 875 C of the 64-day sample seems to support this interpretation.

As shown by the DTA and X-ray data, the reactions in the sodium sulfate-treated quartz-calcium hydroxide mixes are essentially analogous to that in the caustic-treated samples, except that a smaller amount of quartz enters into the reaction. The exothermic reaction at approximately 875 C, which corresponds to a calcium silicate hydrate with lime-silica ratio of 1.09 to 1.25 (17), appears on the thermograms of all specimens.

Quartz-Tricalcium Silicate Series.—Assuming that the tricalcium silicate does not react with the soil component during its hydration, the stoichiometry of the hydration of C_3S can be represented by (6):

$$2\,Ca_3SiO_5 \;+\; 6\,H_2O \;\longrightarrow\; Ca_3Si_2O_7 \cdot 3\,H_2O \;+\; 3\,Ca(OH)_2 \qquad (1)$$

The calcium silicate hydrate produced is the high lime end-member of Taylor's CSH(I). It is obvious from Eq. 1 that calcium hydroxide is the major hydration by-
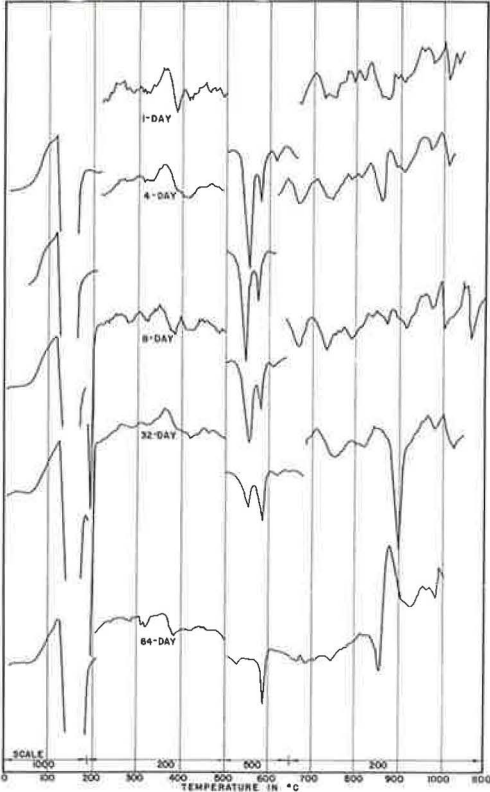
Figure 5. Thermograms of quartz-calcium hydroxide-sodium metasilicate mixes.
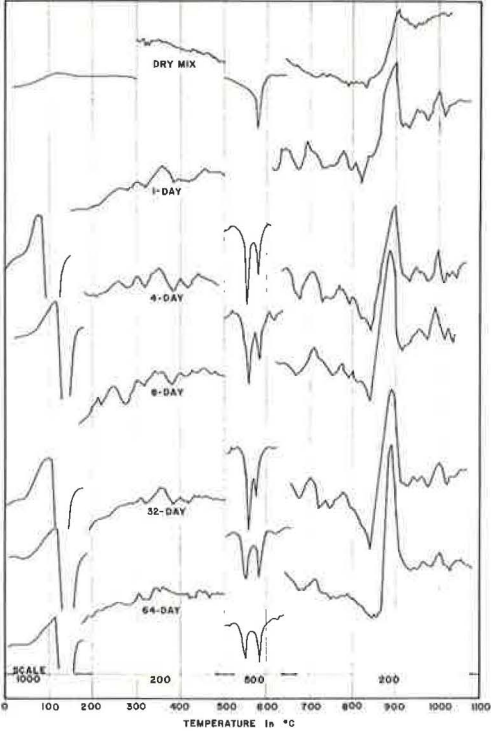

Figure 6. Thermograms of quartz-tricalcium silicate mixes.

TABLE 6
X-RAY ANALYSIS OF QUARTZ-TRICALCIUM SILICATE MIXTURES

Spacing (Å)	Dry Mix	No Additive			Sodium Hydroxide			Sodium Metasilicate			Sodium Sulfate			Identi- fication
		1-Day	32-Day	64-Day	1-Day	8-Day	64-Day	1-Day	8-Day	64-Day	1-Day	8-Day	64-Day	
8.8	—	—	—	—	—	—	4	—	—	—	—	—	—	CS_2H_2
7.6	—	—	1	1	—	2d	2	—	2	2	—	—	—	$C_2S_3H_2$, Q
7.1	—	—	2	1	—	—	2	—	—	2	—	1	—	$C_2S_3H_2$, Q
3.34	10	10	10	10	10	10	10	10	10	10	10	10	10	Quartz
3.25	—	—	—	—	—	2	—	—	—	—	—	—	—	CSH
3.03	—	—	2	2	—	vw	2	1	1	2	—	—	2	CSH (I)
3.01	2	1	—	—	vw	—	—	—	—	—	—	—	—	C_3S
2.84	—	—	—	—	—	—	—	—	—	—	—	—	—	CS_2H_2
2.80	—	—	—	vw	vw	—	—	—	vw	—	—	—	—	CSH (I)
2.62	—	1	vw	vw	2	1	—	—	—	—	1	1	—	Lime
2.60	2	1	—	—	—	—	—	vw	vw	—	—	—	—	C_3S

product of the C_3S. Thus, the amount of calcium hydroxide present in the sample may be utilized as an indication of the rate of C_3S hydration. By assuming complete hydration of the C_3S present in these mixes, a maximum of 4.2 percent of calcium hydroxide will be produced. Both DTA curves (Fig. 6) and X-ray data (Table 6) show the presence of this compound at all curing ages. The calcium hydroxide increases from 3.6 percent
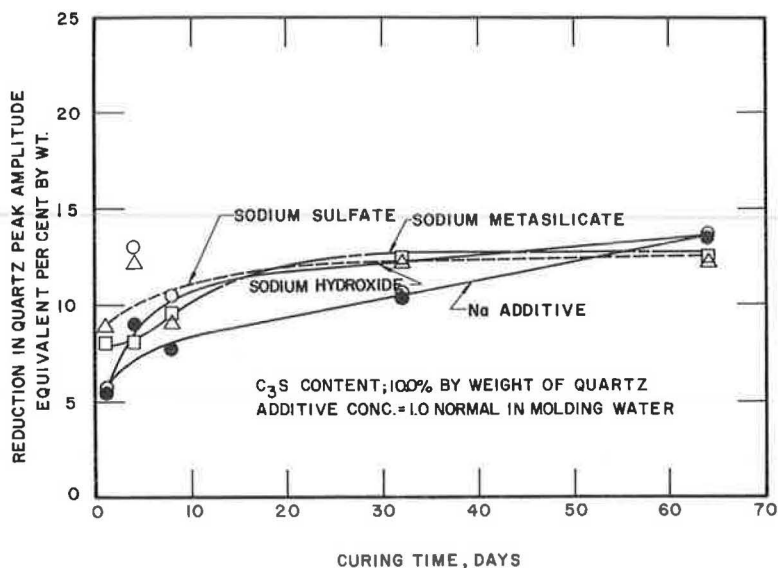
Figure 7. Effect of curing time on DTA peak of quartz in Q-C₃S mixes.
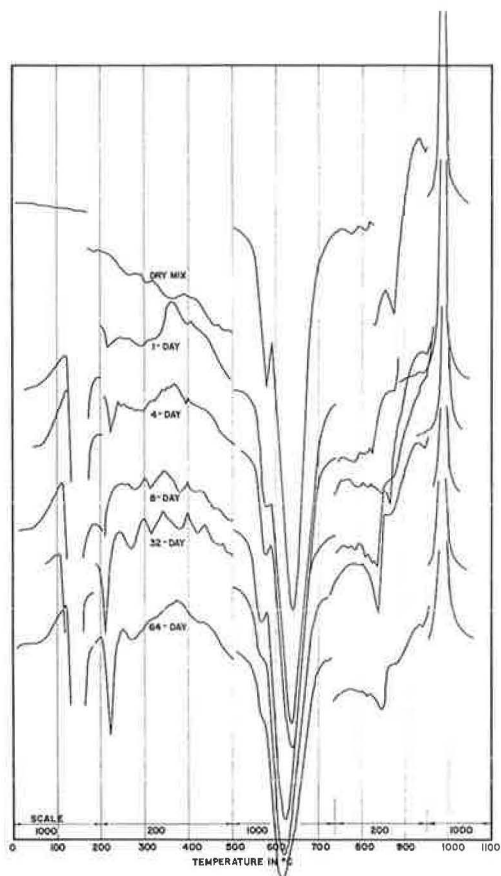

Figure 8. Thermograms of kaolinite-calcium hydroxide mixes.

at 1 day to 4.1 percent at 8 days, which corresponds to almost complete hydration of the C₃S, and gradually decreases with further cure. The presence of the maximum amount of Ca(OH)₂ in the 8-day sample indicates that during that time practically no reactions occurred between the lime released from the C₃S hydration and the quartz mineral. However, approximately 5 percent of the quartz is lost after only 1 day of cure, as determined from the size of the quartz thermo-peak shown in Figure 7. This quartz must then either react with the CSH or be fluxed by the CSH. The new product (or products) formed in this mix, as revealed by the progressively stronger exothermic reaction at 890 to 900 C, is a calcium silicate hydrate with lime-silica ratio of 1.33 to 1.6 (18). This product is very close to the product shown by the stoichiometric equation of the C₃S hydration. If all the missing quartz, as indicated by the thermo-reactions, truly reacts with the calcium stabilizer to form calcium silicate hydrate, then the corresponding lime-silica ratio in the new product would be much lower. The ratio further indicates that not all the missing quartz (at all curing ages) is truly reacted with the lime and/or CSH; part of it is probably adsorbed, enters into the structure of the hydration product, or is masked by the reaction products during the thermal analysis. The CSH formed appears to be a poorly crys-
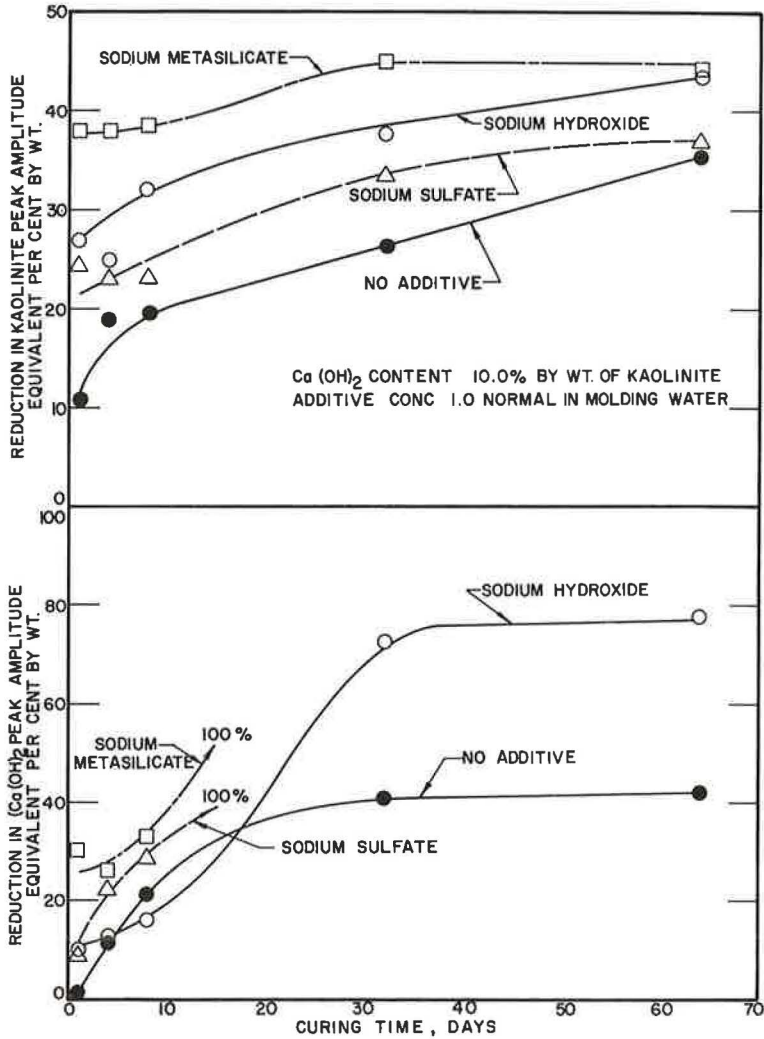
Figure 9. Effect of curing time on DTA peaks of kaolinite and lime.

talline variety at early cure and gradually develops a more orderly structure with time as shown by the X-ray patterns.

The most obvious effect of the addition of sodium hydroxide to the quartz-C_3S mix is the acceleration of the C_3S hydration and hydrolysis, which is virtually completed after only 1 day of curing. The X-ray data show an early appearance (at 4 days as compared to 32 days for the additive-free mix) of the major CSH (I) line at 3.03 Å and also indicate a somewhat more abundant quantity. The appearance of a diffraction line at 8.9 Å in the 64-day sample shows that in addition to the high-lime member of the CSH, there is also some low-lime member of CSH formed. And since part of the quartz mineral would become more reactive due to the addition of the strong alkali, it is reasonable to conclude that most of the missing quartz in these mixes probably truly participates in the reaction. The DTA curves further prove that the CSH formed is of lower lime-silica ratio than that in the alkali-free mixes. The two exotherms at 830 and 870 C belong to the CSH with lime-silica ratios of 0.8 to 1.0 and 1.25, respectively. The gradual increase in the size of the lower temperature exotherm and the decrease in size of the other with time definitely indicate that the high-lime member of CSH is transformed to a lower lime member.

TABLE 7

X-RAY ANALYSES OF KAOLINITE-CALCIUM HYDROXIDE MIXTURES

Spacing (Å)	Dry Mix	No Additive			Sodium Hydroxide			Sodium Metasilicate		Sodium Sulfate		Identification
		1-Day	32-Day	64-Day	1-Day	32-Day	64-Day	1-Day	64-Day	1-Day	64-Day	
14	-	-			-			-	-	-		
13	-	-			-			-		-	2bd	C_2ASH_x
11	-	-	2b	3b	-	3bd	4bd	2	2bd	-		CSH (I)
9.8	-	-			-			2		2		
9.6	-	-			-			-	-	-	-	
8.7	-	-			-			-	-	2	-	CS_2H_2
7.2	10	10	10	10	10	10	10	10	10	10	10	Kaolinite
3.03	-	-	2	2	vw	3	2	1	1	1	2	CSH (I)
2.87			-	-				-	-	-	-	
2.81	1b	1b	2b	2b	vw	1b	1b	2b	2b	2b	2b	C_2ASH_x
2.73												
2.62	2	2	-	-	2	-	-	2	-	2	-	Lime
2.09	-	-	-	-	-	1	1	-	-	-	-	$C_4A_3H_3$

Sodium metasilicate appears to delay the C_3S hydration, whereas sodium sulfate affects the reactions in essentially the same manner as does the hydroxide. The reaction products formed appear to consist of several varieties of hydrous calcium silicate as illustrated by the X-ray data in Table 6.

Kaolinite-Calcium Hydroxide Mixes.—In the kaolinite-calcium hydroxide series, the reactions are considerably more complex. The X-ray diffraction patterns are more difficult to interpret because of the presence of large amounts of water in the specimens which tend to diffuse and broaden the diffraction lines. Experimental results indicate that the reaction products consist of a mixed calcium aluminosilicate (C_2ASH_x) identified as the Stratling's compound, hydrous calcium silicates, and probably a hydrous calcium aluminate of the composition C_4AH_{13}.

The thermograms in Figure 8 show that both the lime endotherm at about 565 C and the kaolinite dehydration endothermic peak decreased considerably in size as reaction proceeded. Interpretation of the changes in the intensity of the thermal peaks quantitatively, as summarized in Figure 9, indicates that at the end of 64 days, 42 percent of the initial lime is consumed and approximately 35 percent of the kaolinite has lost its identity. The fact that the 32-day sample consumes about the same amount of lime as the 64-day specimen, whereas the amount of kaolinite lost increases, tends to indicate that a portion of the lime is probably adsorbed on the surface of the clay at early ages of reaction. The dehydration characteristics of the adsorbed lime are different from the normal lime which exhibits an endothermic reaction at about 565 C. The endotherm at about 210 C is probably caused by both C_4AH_{13} and the Stratling's compound. The amplitude of this endotherm increases in size with hydration time of the mixture.

The X-ray diffraction lines, as summarized in Table 7, tend to be diffused and broad. The 2.62 Å line of lime diminishes after 32 days of cure. The diffraction lines of the Stratling's compound (C_2ASH_x) appear in all patterns and seem to be stronger with curing time. A line at 3.04 Å appearing in the patterns of 32- and 64-day samples indicates the rather late development of the CSH compound. This CSH compound has been shown (1) to be capable of holding a considerable amount of alumina in its lattice structure.

Although the DTA curves indicate that a rather large amount of kaolinite has lost its thermal identity after various periods of curing, the X-ray data do not show such a big change. It must be pointed out that the experimental procedure used in the X-ray diffraction tests does not allow any reliable quantitative analysis of the extent of reaction. Moreover, other investigators have shown that much higher stabilizer concentrations

and longer curing periods are required to affect the intensities of the basal reflections of the clay (9.14).

Addition of the strong alkali additive sodium hydroxide accelerates the decomposition of the clay and also encourages the earlier formation of CSH. X-ray diffraction patterns (Table 7) show the presence of the 3.03 Å line in the 1-day sample; this line also tends to increase in intensity with curing time. Figure 9 also indicates that addition of caustic soda decreases the initial consumption of lime. This is due to the high alkalinity of the additive which depresses the solubility of calcium hydroxide and therefore retards the rate of reaction of the calcium ions and the clay. However, the total consumption of lime after 64 days of cure is much higher in the mixes with additive.

As noted before, sodium metasilicate not only is a strong alkali additive capable of attacking the soil minerals, but also provides additional reactive silica to the system which would greatly accelerate the formation of calcium silicate hydrates. The X-ray diffraction patterns summarized in Table 7 show the development of 11 and 10 Å lines, as well as the familiar 3.03 Å line of the CSH. The lime and kaolinite endotherms are reduced even more as compared to the caustic-treated samples, particularly in the early ages of cure. As estimated from the DTA peaks and as revealed by the X-ray patterns, no lime can be detected after 8 days of reaction.

The salt sodium sulfate produces a similar effect on the kaolinite-lime reaction as do the other two additives but has somewhat less influence on the kaolinite endotherm. In these mixtures, the formation of Stratling's compound is questionable.

Kaolinite-Tricalcium Silicate Series.—In the kaolinite-tricalcium silicate mixes, as in kaolinite-calcium hydroxide samples, hydrous calcium silicates of various compositions are the major reaction products (Table 8). Judging from the relative intensity of the dehydration endothermic reaction of calcium hydroxide and the X-ray data, it appears that the lime liberated during the early hydration of tricalcium silicate combines with the clay mineral more rapidly than in the quartz-C_3S mix.

As in the kaolinite-lime series, the three sodium additives appear to intensify the reaction between the clay mineral and the stabilizer and also to produce a larger quantity of reaction products, mainly calcium silicate hydrates. The X-ray data given in Table 8 indicate that the various hydrous calcium silicates formed in the additive-treated samples are of lower lime-silica ratio than those in the additive-free samples. In the latter, the lime-silica ratios in almost all CSH are close to a molar ratio of 1.

As shown in Figure 10, the amplitudes of the kaolinite dehydration endotherms are considerably smaller than those of the kaolinite-calcium hydroxide samples at all curing ages. This could be due to more intensive reaction between the clay and the C_3S stabilizer or to a greater fluxing effect because of the different reaction products. However, it should be pointed out that the thermal behavior of these mixtures gives consistent trends for various treatment as in the kaolinite-lime series.

TABLE 8

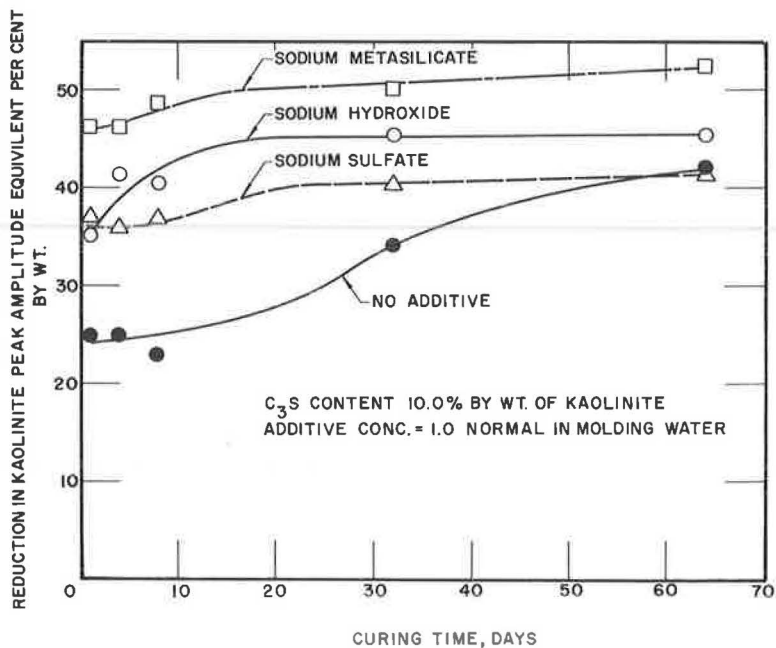X-RAY ANALYSES OF KAOLINITE-TRICALCIUM SILICATE MIXTURES

Spacing (Å)	Dry Mix	No Additive			Sodium Hydroxide			Sodium Metasilicate			Sodium Sulfate			Identification
		1-Day	4-Day	64-Day	1-Day	4-Day	64-Day	1-Day	4-Day	64-Day	1-Day	4-Day	64-Day	
13.8	-	2		2				-	-	-	-	-	-	$CSH_{1.5}$
12.8	-	-		-		1d	1	-	-	-	-	-	CSH, C_2ASH_x
11.8	-	-	1bd	-	2d	2d	-	-	-	-	-	-	-	CSH
11.0	-	2		2			-	1	-	2	2	3	CSH
10.0	-	2		2		3	2	2	2	2	2	2	2	CSH (I)
8.9	-	1		1	3	3	2	1	2	2	-	-	-	CS_2H_2
7.1	10	10	10	10	10	10	10	10	10	10	10	10	10	Kaolinite
4.18	4b	6b	5b	7b	5b	6b	4b	5b	8b	5b	5b	4b	6b	Kaolinite, C_2ASH_x
3.05	-	vw	1	1	-	-	-	-	-	-	-	-	-	C_2SH
3.04	-	-	-	-	-	-	-	-	-	-	-	-	-	C_2SH (C)
3.03	-	-	-	-	1	1	1	vw	1	1	-	-	-	CSH (I)
3.01	1	-	-	-	-	-	-	-	-	-	1	vw	-	C_3S
2.60	1	2	1	-	1	2	-	-	-	-	-	-	-	C_3S

Figure 10. Effect of curing time on DTA peak of kaolinite in K-C_3S mixes.

Extent of Reaction. — The DTA results obtained in this study reveal that the major thermal reaction peaks of the two mono-mineral soils decrease considerably after curing with calcium stabilizer, with or without sodium additive. This apparent change in the thermal behavior of the mixture indicates that certain reactions or interferences must have occurred among the constituents. However, the DTA records only the net heat effect which may result in a seriously distorted thermogram when several reactions proceed simultaneously. Martin (24) has reported anomalous thermal behavior carbonates. Therefore, it is necessary to verify the observation that the disappearance of the mineral constituent, as indicated by the reduction in the intensity of its thermal reaction, is due to true reaction with other constituents in the mixture and not to merely a flux effect. Three series of tests have been made in an attempt to evaluate the extent of reactions of the soil minerals with other constituents.

Quartz-Acid Digestion Tests. — Investigators at the U. S. Bureau of Reclamation (7) have reported that no reaction was evidenced between calcium hydroxide and quartz by either X-ray or DTA. On the other hand, Diamond, White and Dolch (8) reported complete reaction of quartz mineral in clay size with a large excess of calcium hydroxide (400 percent based on the weight of the quartz). Therefore, it is important to confirm the reactions observed in the present investigation between the lime and quartz are true reactions, not just surface absorption phenomena, particularly since in the present investigation the ratio of calcium hydroxide and quartz was much lower than in any of the other studies.

In this study, hydrous calcium silicates are identified as the principal reaction products. These compounds are alkali in nature and thus will dissolve in strong acid solution. A series of experiments were conducted by digesting three samples, approximately 9 g each in 100 ml of 1.0 N hydrochloric acid at 70 C for one hour with intermittent agitation. The three samples tested were a pure quartz, an 8-day cured quartz-lime mixture and a 4-day cured quartz-C_3S-NaOH mix. After the acid digestion, each sample was washed with distilled water five times and then oven-dried and weighed. The weight lost due to this treatment should be an indication of the extent of reaction between the quartz mineral and the stabilizer. The results in Table 9 show that the pure quartz sample has lost only 0.1 percent of its original weight after the acid treat-

TABLE 9

ACID-DIGESTION TESTS OF QUARTZ MIXTURES[a]

Stabilizer (%)	Additive (%)	Weight (g)		Wt Loss (% of total wt.)	Loss of Quartz (%)	Loss of Quartz From DTA[b] (%)	Curing Days
		Before Test	After Test				
None	None	9.94	9.93	0.1	0.1	0	0
10 Ca(OH)$_2$	None	9.04	8.03	11.8	3.0	1.5	8
10 C$_3$S	0.97 NaOH	8.58	7.45	13.2	4.0	8.5	4

[a]Acid-digestion test: sample after curing mixed with 100 ml of 1.0 N HCl, placed in 70 C water bath for 1 hour, then washed with distilled water 5 times, oven dried at 105 C; all percentages, except where noted, based on weight of quartz.
[b]Estimated from the change in quartz endothermic peak amplitude.

ment, which is certainly within the experimental accuracy of this test. The lime-treated and the C$_3$S-NaOH-treated samples have lost 3.0 and 4.0 percent of quartz by weight, respectively. The amount of quartz lost in the C$_3$S-NaOH-treated sample as determined by the acid-digestion test is only about half of the amount estimated from DTA curves. This further substantiates the previous conclusion that in cement-treated samples, part of the quartz lost in the DTA records has not been truly reacted with the calcium stabilizer. All these observations (the DTA, X-ray and acid-digestion test) tend to suggest that the nature of reactions occurring in lime-stabilized and cement-stabilized quartz mixtures may be quite different.

Thermal Reactions of Mixtures of Kaolinite and Hydrated Cementing Compounds.— Since in a kaolinite-calcium stabilizer system, with or without sodium additive, the major constituents are the raw ingredients and their hydration products, they are principally hydrous calcium silicates and hydrous calcium aluminates. Two mixtures of kaolinite and partially hydrated cementing compounds have been prepared for DTA investigation. The cementing compounds (C$_3$S and portland cement) were hydrated in paste form with a water-solid ratio of 0.7 by weight. Figure 11 shows the thermograms of (a) 50 percent kaolinite and 50 percent oven-dried 32-day hydrated tricalcium silicate, and (b) 57 percent kaolinite plus 43 percent 4-day as-cured hydrated cement. Comparison with the thermograms of their constituents (the clay and the partially hydrated cementing compounds) shows no anomalous thermal behaviors. These test results lead to three possible explanations for the large reduction in kaolinite thermal peak observed in the thermograms:

1. The loss of kaolinite after curing as identified by the thermal behavior is due to true decomposition of the clay mineral. However, the missing kaolinite underwent significant changes in its thermal behavior without complete destruction of its crystalline structure. Several other investigators (9, 14) have reported that a much higher stabilizer content and longer curing period are required to cause any significant effect on the basal reflections of this clay mineral.

2. The reaction products responsible for the fluxing effect are different from those added in these two tests.

3. The fluxing effect is different when the reaction products are mixed in separately from what occurred in the mixture.

Reactions between Montmorillonite and Calcium Hydroxide.— The test results indicate that the reactivity (reactivity of the mono-mineral soils is compared on the basis of the amount of the mineral participating in reaction with the stabilizer in a particular system) of the clay mineral kaolinite is much higher than that of quartz. Obviously, therefore, much stronger reaction could be anticipated when montmorillonite is the soil component. Since the basal spacing of montmorillonite crystals will expand by glycerol treatment and collapse by heating, these characteristics are thus utilized to study the changes in the character of the soil component due to stabilization.

Four mixtures were prepared for X-ray and DTA tests: (a) a pure montmorillonite, (b) montmorillonite plus 10 percent calcium hydroxide dry mix, (c) montmorillonite plus 10 percent calcium hydroxide humid cured for 1 and 8 days, and (d) montmorillon-
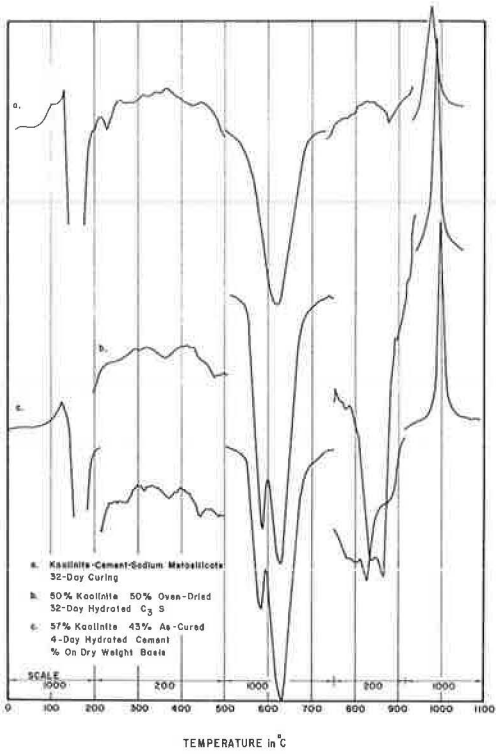
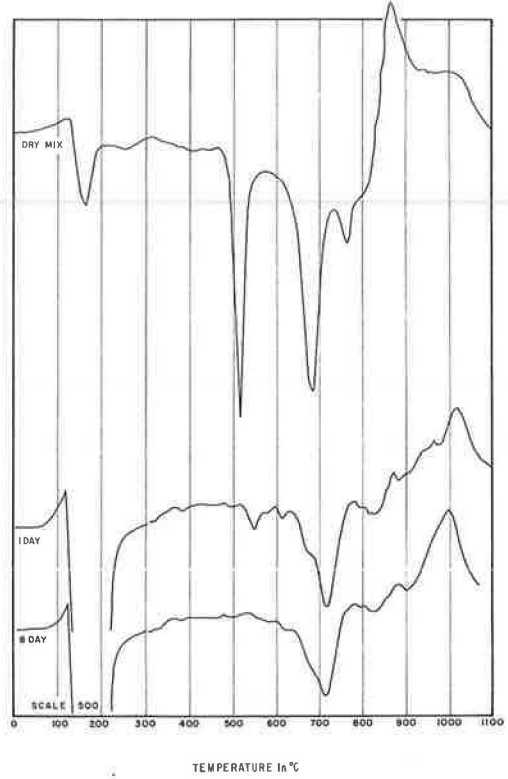Figure 11. Thermograms of kaolinite-hydrated cementing compound mixes.

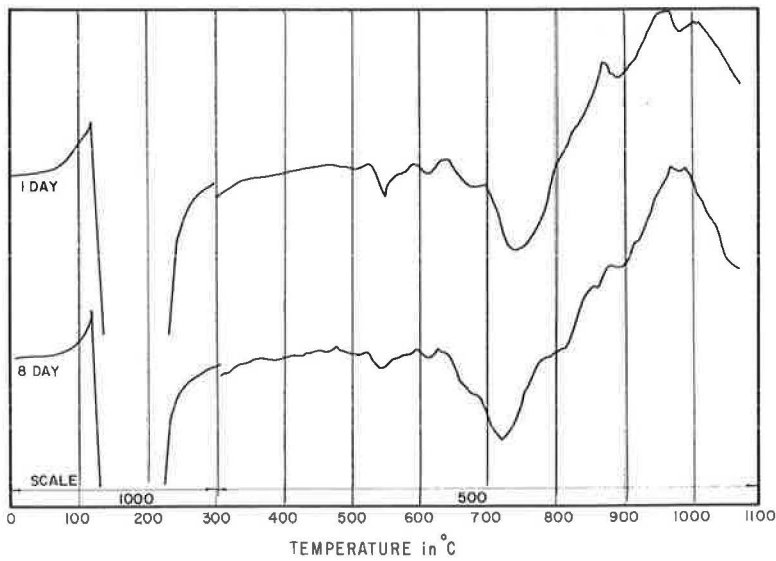Figure 12. Thermograms of montmorillonite-calcium hydroxide mixes.

Figure 13. Thermograms of montmorillonite-calcium hydroxide-sodium hydroxide mixes.

TABLE 10

d_{001} X-RAY SPACING OF MONTMORILLONITE-CALCIUM HYDROXIDE MIXTURES[a]

Treatment Temperature (C)	Montmoril- lonite	Montmorillonite-Lime			Montmorillonite-Lime-Sodium Hydroxide	
		Dry Mix	1-Day	8-Day	1-Day	8-Day
25[b]	18 vvs[b]	18 vvs	18 m	14 vvs	18 vvs	18 vs
			14 vs		14 w	14 vs
400	10 vs	10 vs	10 vs	10 vs	10 vs	10 vs
600	10 vs	10 vs	10 vs	10 vs	10 vs	10 vs
700	10 vs	10 s	10 m	10 vvw	10 m	10 gone
800	10 s	10 s	N.D.	10 gone	N.D.	10 gone
900	VW Pattern	10 vw	N.D.	10 gone	N.D.	10 gone

[a]Numbers refer to d_{001} spacing in angstroms, and letters refer to relative intensity; d values are approximate; N.D. indicates no data.
[b]Glycerol treated.

ite plus 10 percent calcium hydroxide and 1.0 N sodium hydroxide solution cured for 1 and 8 days.

A portion of each mixture was first analyzed by DTA and X-ray as for all other mixes. Another portion of the sample was heated in the DTA furnace to various temperatures at the same heating rate as for DTA, i.e., 12.5 C/min. Oriented aggregate specimens of the heat-treated samples were then prepared for X-ray examination. The specimens were mounted in a horizontal position to enhance the 001 lines.

Figure 12 shows the thermograms of montmorillonite-lime mixes and Figure 13 shows the thermograms of NaOH-treated montmorillonite-lime mixtures. Even the dry mix shows evidence of reaction between the clay and lime. This reaction must occur during the heating process. The 725 C endothermic peak of the montmorillonite is lowered to 680 C, a second endothermic peak appears at 760 C, and the exothermic reaction of the clay is lowered from 930 to 860 C. The shifting of the thermal peak temperatures could, nevertheless, be due to some fluxing effect. However, reaction between the clay and lime after curing is apparent and intensive. The lime endotherm practically disappears after only 1 day of cure. Comparison of the thermogram of the 8-day specimens with and without NaOH indicates some difference between the reaction produced by lime alone and that by lime plus caustic soda. Furthermore, there appear to be more reaction products produced with time and with additive; both the DTA and X-ray data are consistent in this respect.
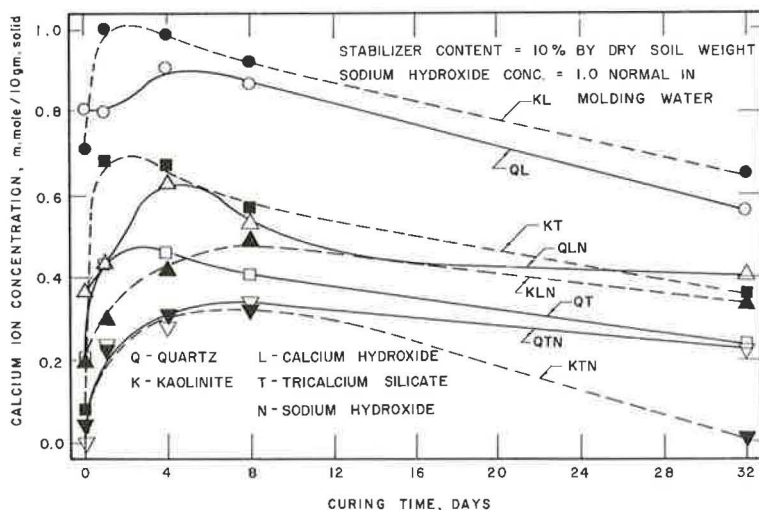

Figure 14. Calcium ion concentration in aqueous extracts of stabilized soil mixtures.

Table 10 summarizes the most obvious and important differences of X-ray data of these mixes. Variations in the basal expansion (glycerol treated at room temperature) give consistent trends for the different treatments and must be real. The reasons for these variations are not clear but they probably reflect the structural differences of various reaction products. Apparently, sodium hydroxide alters the reaction between the clay and lime because 1-day cured specimens in the absence of additive give 14 Å as the strongest line, whereas the caustic-treated 1-day specimen gives 18 Å as the strongest line. Addition of the strong alkali may retard the formation of the reaction product obtained from montmorillonite and lime.

The remaining X-ray data show the effect of the reaction due to stabilization on the decomposition temperature of the montmorillonite mineral. The clay-lime reaction lowers the clay decomposition temperature and addition of sodium hydroxide lowers it still further. Thus, it can be concluded that clay-lime reaction produces real marked changes in subsequent thermal behavior of the mixture and sodium additive further alters the reaction.
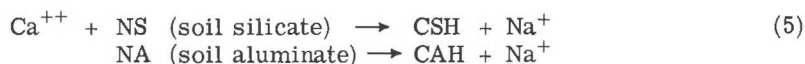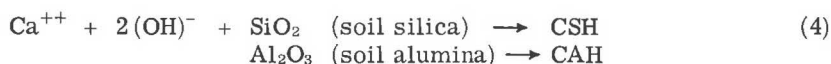
Chemical Analyses of Aqueous Extracts

As illustrated by the calcium ion concentrations in the aqueous extracts of various stabilizer-mineral mixtures in Figure 14, the trends of variation of the ion concentration with curing time are similar for the various soil-stabilizer systems. Furthermore, the effect of any one of the sodium additives on the extractable ion concentration is generally the same, regardless of the soil mineral and the kind of the calcium-bearing raw ingredient. Figure 14 also shows the effect of sodium hydroxide on the calcium ion concentration. The following presentation is a generalized summary of salient results with specific reference to one mixture, the kaolinite-tricalcium silicate series.

Soil Mineral-Cement Mixes.—In a mineral-cement mix, any calcium ions liberated from the cement (in the particular case discussed here, tricalcium silicate), or directly from the lime, during hydration and hydrolysis react rapidly with the silicates and aluminates from the soil mineral to form insoluble products. Therefore, the amount of extractable silica (Si) and alumina (Al) will be low throughout the curing period. Figure 15a shows the results obtained from the analyses of the aqueous extracts of kaolinite-tricalcium silicate mixtures. Since the clay contains some sodium (Na) in its natural state, the Si concentration (and possibly that of Al) is somewhat higher initially due to the higher solubility of the sodium silicates (or aluminates).

The extractable calcium (Ca) is the portion of the lime Ca in excess of that reacting with Si and/or Al. Therefore, it is apparent that the amount of extractable Ca at any given time is controlled by the balance between the rate of release of Ca and the rate of Ca consumption by precipitation to form insoluble silicates and/or aluminates. The former is determined by the rate of cement hydration and the pH of the system, and the latter depends on the nature of the soil in the system. Thus, the Ca concentration in extract, as shown in Figure 15a, is low at the start, increases to a maximum after a short period of cure, and then decreases slowly to nothing with time. This variation of the extractable Ca concentration follows the same trend as the variation of the amount of lime present in the mixture as shown in the DTA curves in Figure 10.

The reaction scheme of the foregoing process can be represented in a simplified fashion by the following equations:

$$C_3S + H_2O \longrightarrow C_3S_2H_X \text{ (hydrated compounds)} + Ca(OH)_2 \qquad (2)$$

$$Ca(OH)_2 \longrightarrow Ca^{++} + 2(OH)^- \qquad (3)$$

$$
\begin{aligned}
Ca^{++} + 2(OH)^- + SiO_2 \text{ (soil silica)} &\longrightarrow CSH \\
Al_2O_3 \text{ (soil alumina)} &\longrightarrow CAH
\end{aligned} \qquad (4)
$$

$$
\begin{aligned}
Ca^{++} + NS \text{ (soil silicate)} &\longrightarrow CSH + Na^+ \\
NA \text{ (soil aluminate)} &\longrightarrow CAH + Na^+
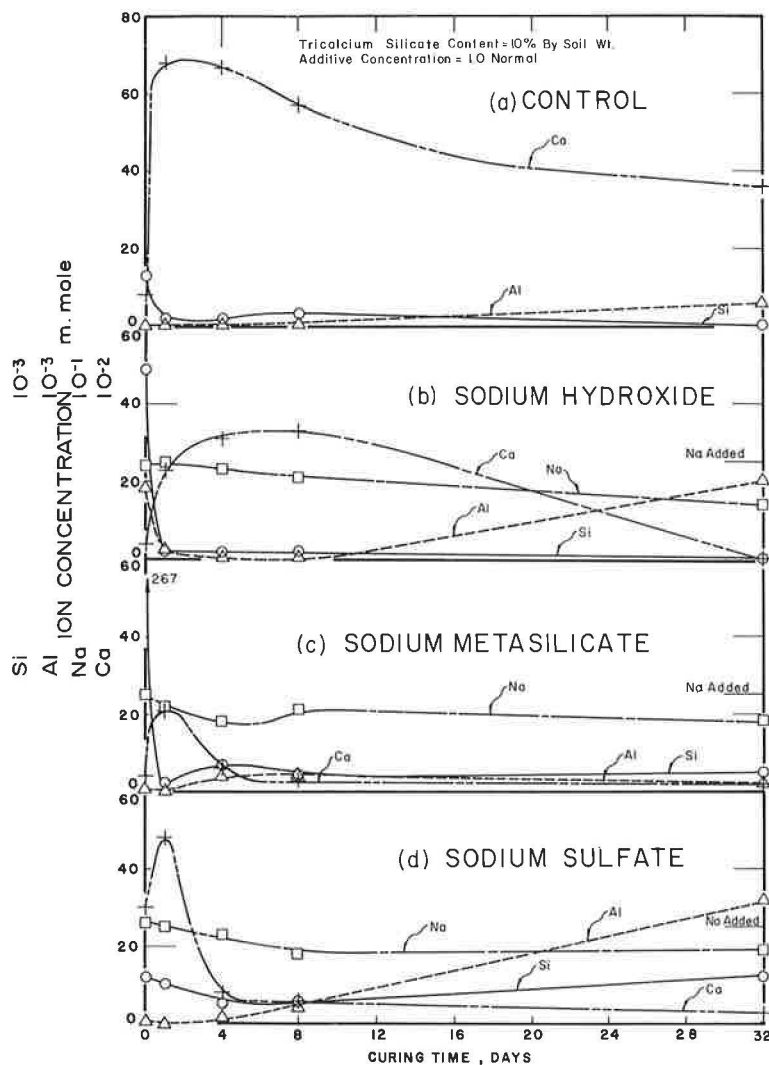\end{aligned} \qquad (5)
$$

Figure 15. Composition of aqueous extracts of kaolinite-tricalcium silicate mixes.

These equations are for illustration only; therefore, they are not necessarily in equilibrium, and the symbols used are not necessarily the correct ones. When lime is the initial Ca-bearing raw ingredient, Reaction 2 is bypassed. As Reactions 2 and 3 proceed, Ca in solution increases; as Reaction 4 proceeds, Ca decreases; and as Reaction 5 progresses, extractable Ca decreases with the increase in extractable Na. The last reaction occurs only when the soil mineral contains considerable amount of Na in its natural state.

Effect of Sodium Hydroxide.—A comparison of Figure 15b with Figure 15a indicates that the addition of sodium hydroxide to a mineral-cement system causes the following reactions:

1. Suppression of Ca concentration in the pore fluid by the common ion effect, and

2. Acceleration and intensification of the solubilization of Si and Al as the hydroxyl (OH) is consumed by the reaction

$$Na^+ + OH^- + SiO_2 \longrightarrow NSH \text{ (soluble)} + H_2O \tag{6}$$
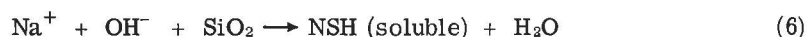
With curing, Reactions 2 and 3 proceed and are followed promptly by

$$Ca^{++} + NSH \longrightarrow CSH + Na^+ \quad\quad (7)$$
$$\text{or} \quad CNSH + Na^+$$
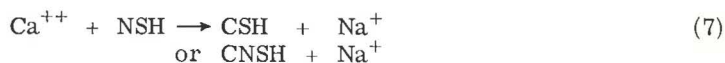
Initially at zero cure, due to the common ion effect, the Ca ion concentration in the pore fluid is much lower than in fluid without caustic. As curing progresses, the suppression of Ca in the pore fluid is reduced due to the consumption of (OH) in Reaction 5; in addition, the cement continues to hydrate to release calcium hydroxide, thereby increasing the Ca concentration. Later in cure, soluble silicate is precipitated as insoluble product with Ca, and also the Ca reacts with the soil silicates; thus, the extractable Ca concentration decreases with time, as shown in Figure 15b.

The Si concentration in the extract of cured specimens is limited by the solubility of calcium silicate. However, it is high initially due to the immediate solubilizing effect of the caustic.

Early in cure, the sodium primarily associates with soluble silicates and aluminates as indicated by the extractable Na content which is equal to that added. With curing, the soluble Na:Ca ratio increases as Ca is decreased by precipitation. This favors the formation of mixed Na-Ca silicates. Thus, the extractable Na is high early but lower later.

Inasmuch as the solubility of calcium aluminate is probably higher than that of calcium silicate, if calcium is consumed as insoluble silicates, any aluminate must end up as soluble salt. Hence, there is rapid increase in the extractable Al content with decrease in extractable Ca and Si.

Effect of Sodium Metasilicate.—With sodium metasilicate as an additive, the preliminary step of solubilization of silica is bypassed. Therefore, whatever Ca is available from cement can precipitate immediately with $SiO_3^=$ present in the pore fluid, as shown by the very low Ca content at zero cure immediately after mixing in Figure 15c. Also, the initial extractable Si concentration is much less than the amount of soluble silicate added. As the soluble silicate (from the additive) in the pore fluid is insolubilized by the Ca, hydroxyl attack of the soil silicates takes place. However, the low solubility of calcium silicate reduces the Ca concentration in the pore fluid, and thus tends to delay the transport of Ca from cement to soil. Nevertheless, the rate of consumption of free Ca should be much faster in the mix with sodium silicate than with sodium hydroxide, as shown by the lower Ca concentration in the former mix (Fig. 15c) compared to the latter (Fig. 15b) at same age of cure.

Effect of Sodium Sulfate.—On addition of sodium sulfate to the soil-C_3S system, the following caustization reaction takes place after the cement hydration process shown by Eq. 2:

$$Na_2SO_4 + Ca(OH)_2 \longrightarrow CaSO_4 + NaOH \quad\quad (8)$$

Since the silica-attack caustic is formed by this reaction, the rate of attack of the soil silicate or aluminate will be less rapid at start than that with sodium hydroxide, and thus less soluble sodium silicate will be formed as illustrated by Eq. 6.

Because of the higher solubility of calcium sulfate and lower alkalinity of the system compared with the caustic-treated mixtures, the initial Ca concentration in the extract is higher and the initial Si concentration is lower. Soon afterwards, hydroxyl attack of soil silicates takes place, greatly aided by the solubilizing action of the sodium ions. Since the Ca concentration in the pore fluid is high initially, the rate of transport of the Ca from cement to soil silicates is markedly accelerated as compared to that in the sodium hydroxide mixes. Therefore, the free Ca in cement rapidly depletes and the extractable Ca content drops rapidly with curing. This is indicated by the Ca concentration after 4 days of cure in Figure 15d.
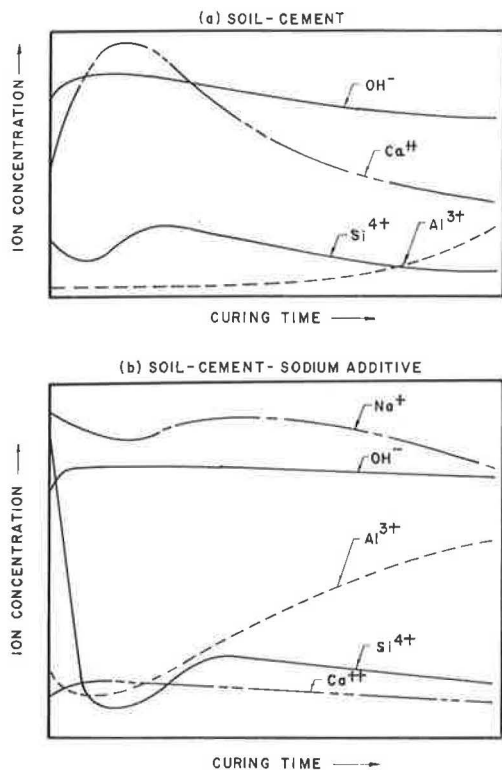
(a) SOIL - CEMENT

ION CONCENTRATION

CURING TIME

OH⁻

Ca⁺⁺

Si⁴⁺   Al³⁺

(b) SOIL-CEMENT-SODIUM ADDITIVE

ION CONCENTRATION

CURING TIME

Na⁺

OH⁻

Al³⁺

Si⁴⁺

Ca⁺⁺

Figure 16.   General variation of composition of aqueous extracts of soil-cement mixes.
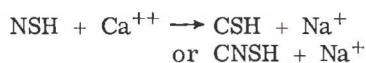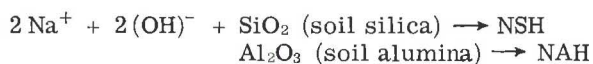
SUMMARY AND CONCLUSION

This paper describes an experimental investigation aimed at delineating the nature of reactions accompanying the stabilization of soils with cementing agents and elucidating the mechanisms by which a group of alkali metal compounds improves the stability of stabilized soils. Mixtures of two mono-mineral soils (quartz and kaolinite), three cementing compounds (calcium hydroxide, tricalcium silicate and portland cement), and selected sodium additives (hydroxide, metasilicate and sulfate) were examined during the course of cure. The solid phases were examined by employing X-ray diffraction and DTA techniques. The pore fluid phases were analyzed for soluble calcium, sodium, silica and alumina contents. The following summarizes some of the salient results and conclusions:

1. Both mono-mineral soils react with the three calcium stabilizers under conditions of approximately 100 percent RH and room temperature. Addition of sodium additives greatly intensifies the reaction between the soil and the stabilizer and increases the abundance of reaction products.

2. The reaction patterns between any one soil mineral with the three calcium stabilizers are generally the same, the effect of various sodium additives on the reactions is also similar, regardless of the kind of initial calcium-bearing ingredient. The major differences are more in the relative amounts of the various reaction products and the rate of their formation than in the formation of entirely different products.

3. The reactivity of the two mono-mineral soils to any one of the cementing compounds is higher in kaolinite than in quartz.

4. With one particular mineral, the reaction is most intensive when the stabilizing agent is tricalcium silicate and least intensive with calcium hydroxide.

5. The principal reaction products produced in quartz mixtures are hydrous calcium silicates (CSH) of various compositions with lime-silica ratio varying from 0.2 to 1. In kaolinite mixes, the principal products are hydrous calcium silicates, hydrous calcium aluminates and a mixed calcium aluminosilicate.

6. The reaction scheme of a soil-stabilizer system and the effect of sodium additive can be represented by the following simplified equations:

Soil-cement

$$Cement + H_2O \longrightarrow CSH + Ca(OH)_2$$

$$Ca(OH)_2 \longrightarrow Ca^{++} + 2(OH)^-$$

$$Ca^{++} + 2(OH)^- + SiO_2 \text{ (soil silica)} \longrightarrow CSH$$
$$Al_2O_3 \text{ (soil alumina)} \longrightarrow CAH$$

Soil-cement plus sodium additive

$$Cement + H_2O \longrightarrow CSH + Ca(OH)_2$$

$$Na_2X + Ca(OH)_2 \longrightarrow CaX + 2Na^+ + 2(OH)$$

$$2\,Na^+ + 2\,(OH)^- + SiO_2\ (\text{soil silica}) \longrightarrow NSH$$
$$Al_2O_3\ (\text{soil alumina}) \longrightarrow NAH$$

$$NSH + Ca^{++} \longrightarrow CSH + Na^+$$
$$\text{or } CNSH + Na^+$$

$$NAH + Ca^{++} \longrightarrow CAH + Na^+$$

7. All sodium additives depress the Ca concentration in the pore fluid but do not decrease the hydroxyl availability, and may actually increase it.

8. The variations of the ionic composition in the solution phase of a soil-cement system with curing age can be simplified as shown in Figure 16a. Figure 16b illustrates the effect of sodium additive on the extract composition.

9. The rate of reaction between the soil mineral and stabilizer depends on the nature of the sodium additive and the initial calcium-bearing ingredient.

10. The sodium in the additive-treated mixture primarily associates with soluble constituents early in cure, and later with insoluble mixed sodium-calcium silicates (or aluminates). The amount of sodium retained in the insoluble compounds after 32 days of cure decreases in the order of initial sodium additive, hydroxide, sulfate and meta-silicate.

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