

# Reactions and Strength Development in Portland Cement-Soil Mixtures

RODGER W. PLASTER and DAVID F. NOBLE, Virginia Highway Research Council

The ultimate goal of this study was to gain insight into the reactions occurring in portland cement-soil mixtures. Soils of the Frederick, Iredell, and Lloyd series commonly found in Virginia were investigated. The effect of their chemical, mineralogical, and engineering properties and soil weathering stage on such processes as the deterioration of the soil constituents, the production and consumption of calcium hydroxide, and strength development of the mixtures is discussed. Investigative techniques used included X-ray diffraction and microscopic analyses, and chemical analyses of water (for Ca) and HCl (for Si, Al, and Fe) leachates of the mixtures. The Frederick soil constituents did not appreciably react with the cement, although some of the clays in the soil were slightly deteriorated after cement treatment. The clays and probably other constituents in the B- and C-horizons of the Iredell and Lloyd soils suffered deterioration after cement treatment, as indicated by the release of large amounts of silica and alumina and by the diminution of mineral X-ray peaks. When the major clay mineral in the soils was considered, the soils suffered deterioration after cement treatment from greatest to least in the following order: montmorillonitic soils, kaolinitic soils, illitic soils. The instability of the C-horizon Iredell soil constituents in a cement system appeared related to mineralogy. The minerals were not greatly weathered and were susceptible to the harsh conditions of an alkaline environment. The greatest quantities of calcium hydroxide were consumed with kaolinite as the dominant clay mineral. It appears that reaction of calcium hydroxide with the soil constituents was directly proportional, and the development of strength was inversely proportional, to the magnitude of the clay-size fraction.

♦THIS RESEARCH is an outgrowth of a previous study conducted by David F. Noble in 1967 on the reactions occurring in mixtures of portland cement and relatively pure clays. It was decided to extend the work of Noble to the consideration of clays in their natural environment of soils. As an ultimate goal it was hoped to gain insight into the reactions occurring in portland cement-soil mixtures by studying the reaction products of the mixtures; the rates of reaction of the mixtures; the deterioration or lack of deterioration of clay minerals in the mixtures; and the development of strength in the mixtures.

## MATERIALS INVESTIGATED

### Cement

Chemical and physical analyses of the type I cement used in this study are given in Table 1.

TABLE 1  
CHEMICAL AND PHYSICAL ANALYSES OF  
CEMENT UTILIZED

Item	Amount	Item	Amount
<u>Oxide Analysis, percent</u>		<u>Compounds, percent</u>	
SiO <sub>2</sub>	21.20	C <sub>2</sub> S	52.0
Al <sub>2</sub> O <sub>3</sub>	5.90	C <sub>3</sub> S	21.8
Fe <sub>2</sub> O <sub>3</sub>	2.34	C <sub>4</sub> A	11.68
CaO	64.44	C <sub>4</sub> AF	7.11
MgO	2.83	CaSO <sub>4</sub>	3.71
SO <sub>3</sub>	2.18	<u>Fineness</u>	
Ign. loss	0.68	<u>Percent passing</u>	
Na <sub>2</sub> O	0.12	No. 325 mesh	91.8
K <sub>2</sub> O	0.73	Blaine, cm <sup>3</sup> /gm	3,396
Na <sub>2</sub> O equiv.	0.60		
Free CaO	1.00		

Note: Cement and analyses courtesy of Standard Lime and Cement Division of Martin Marietta.

TABLE 2  
SOIL SAMPLE DESIGNATIONS

Soil Series	Sample	Depth Sampled (ft)	Soil Horizon
Frederick	F-1	0 to 1.9	A
	F-2	1.9 to 3.8	B
	F-4	5.6 to 7.5	C
	F-8	13.1 to 15.0	C
	F-12	20.6 to 22.5	C
Iredell	I-1	0.7 to 1.3	A <sub>2</sub>
	I-2	1.3 to 2.0	B
	I-5	3.3 to 4.0	C
Lloyd	L-1	0.5 to 2.2	B <sub>1</sub>
	L-3	4.3 to 6.4	B <sub>2</sub>
	L-5	8.5 to 10.6	C
	L-9	16.9 to 19.0	C

## Soils

The 3 types of soil chosen for this study were (a) a limestone-derived silty clay of the Frederick soil series that is characterized by its yellowish-red to brownish-red color and fine-grain size (10); (b) a basic intrusive residuum of the Iredell soil series that is characterized by the shallow profile, dark color, poor internal drainage, and extremely plastic clay-pan horizon of the soil (14); and (c) a resilient micaceous soil of the Lloyd series that is characterized by its thick, heavy-textured subsoil, good drainage, high mica content, and deeply weathered profile (4). These types were chosen because they are residual, and thereby allow some correlation between parent material and derived soil.

The soils were sampled from fresh road cuts or sampling pits. Twelve specimens, each representative of a specific varied horizon of the soils, were selected for detailed study, although the entire profile of the soils was originally sampled. The properties of these selected samples are given in Tables 2 through 6. The properties were determined using standard soils, mineralogical, and chemical laboratory techniques.

TABLE 3  
MINERALOGY OF THE SOILS

Sample	Sand Fraction <sup>a</sup>	Clay Fraction <sup>b</sup>
F-1	Fine-grained quartz, limonite, ferruginous quartz aggregates	Quartz, illite, mixed layer clay, kaolinite, montmorillonite, goethite
F-2	Like F-1	Mixed layer clay, quartz, illite, kaolinite
F-4	Like F-1 except for a few chert fragments	Illite, quartz, mixed layer clay, kaolinite
F-8	Like F-4	Quartz, illite, kaolinite, mixed layer clay
F-12	Like F-4 except for a slight increase in ferruginous material	Quartz, illite, kaolinite, mixed layer clay, montmorillonite, goethite
I-1	Quartz, limonite, chlorite, talc, hornblende, feldspar, biotite, ferruginous quartz aggregates	Vermiculite, quartz, illite, chlorite, kaolinite
I-2	Biotite, chlorite, quartz, limonite, hornblende, feldspar, epidote	Illite, vermiculite, quartz, chlorite, kaolinite
I-5	Chlorite, biotite, hornblende, feldspar, quartz, many gabbroic fragments	Montmorillonite, illite, vermiculite, quartz, chlorite, kaolinite
L-1	Mica, quartz, feldspar, limonite	Kaolinite, illite, mixed layer clay, quartz
L-3	Mica, limonite, quartz, feldspar	Like L-1
L-5	Mica, limonite, quartz	Kaolinite, illite, quartz, mixed layer clay, montmorillonite
L-9	Quartz, mica, feldspar, several gneiss fragments	Kaolinite, illite, mixed layer clay, quartz, montmorillonite

<sup>a</sup>Minerals listed in order of decreasing abundance.

<sup>b</sup>Minerals listed in order of decreasing X-ray intensity

TABLE 4  
CHEMICAL ANALYSES OF THE SOILS, PERCENT

Sample	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	CaO	MgO	Na <sub>2</sub> O	K <sub>2</sub> O	Ign. Loss	Total
F-1	74.50	12.07	5.27	0.14	2.10	1.74	1.95	4.28	102.05
F-2	68.00	15.43	6.88	0.26	1.85	0.16	1.95	5.70	100.04
F-4	69.33	14.38	6.38	0.00	2.06	1.01	2.01	5.48	100.65
F-8	67.50	14.47	5.98	0.10	2.31	1.55	2.43	5.63	99.97
F-12	72.00	12.98	5.80	0.06	1.76	1.88	2.56	4.98	102.02
I-1	54.40	10.40	23.89	1.43	0.00	2.60	0.67	6.65	99.94
I-2	49.92	21.32	14.93	1.86	1.34	2.06	0.68	9.31	101.45
I-5	45.89	17.07	10.87	7.90	10.09	1.61	1.55	3.64	98.42
L-1	39.36	30.55	16.33	0.28	0.00	0.34	1.53	11.75	100.14
L-3	43.67	25.22	18.44	0.00	0.79	0.58	2.41	10.03	101.14
L-5	42.03	23.43	18.46	0.14	1.28	1.16	3.48	8.65	98.63
L-9	60.43	19.05	6.36	0.22	0.00	2.13	5.30	6.41	98.12

TABLE 5  
GRAIN SIZE ANALYSES OF THE SOILS

Sample	Percentage by Size Ranges in Microns									
	> 2,000	2,000-420	420-62	62-31	31-16	16-8	8-4	4-2	2-1	< 1
F-1	0.23	0.49	3.31	11.58	12.33	12.62	9.54	7.64	5.82	36.44
F-2	0.95	1.47	4.67	6.27	7.49	10.62	8.89	8.05	6.35	45.24
F-4	0.87	1.02	4.26	8.68	10.43	8.93	7.42	7.36	5.19	45.84
F-8	0.68	1.06	4.60	10.35	9.11	10.51	10.15	13.28	7.97	32.31
F-12	0.62	1.96	3.22	9.90	7.96	10.25	10.15	10.15	6.78	39.01
I-1	23.58	24.81	8.94	4.15	3.07	7.29	5.61	4.89	3.92	13.74
I-2	3.71	7.01	0.78	3.60	2.26	4.97	3.29	3.37	4.51	61.50
I-5	13.70	29.71	32.61	7.26	2.52	2.72	1.50	1.19	0.80	7.99
L-1	0.42	0.89	19.03	4.53	4.71	5.30	4.06	2.47	3.02	55.57
L-3	0.77	0.91	43.50	5.66	8.15	6.90	5.12	2.89	1.86	24.44
L-5	0.36	1.80	53.03	10.03	10.86	6.89	4.21	2.39	1.77	8.66
L-9	1.43	7.35	45.71	17.35	8.54	7.27	3.52	1.97	1.21	5.65

TABLE 6  
ENGINEERING PROPERTIES OF THE SOILS

Sample	Liquid Limit (percent)	Plastic Limit (percent)	Plasticity Index (percent)	Optimum Moisture Content (percent)	Maximum Dry Density (lb/cu ft)	Engineering Classification
F-1	38	23	15	21.0	102.4	—
F-2	47	30	17	24.8	97.3	A-7-5 (12)
F-4	46	28	18	26.3	96.1	—
F-8	43	27	16	24.4	98.4	A-7-5 (11)
F-12	42	26	16	23.7	99.1	—
I-1	32	22	10	15.5	121.8	—
I-2	84	32	52	29.5	91.0	A-7-5 (20)
I-5	35	24	11	14.1	124.2	A-6 (8)
L-1	51	—	0	26.6	95.2	A-5 (10)
L-3	—	—	0	27.5	92.4	—
L-5	—	—	0	26.3	92.9	—
L-9	—	—	0	21.6	96.8	A-4 (0)

## EXPERIMENTAL PROCEDURES

### Leachates Made With $H_2O$ and $HCl$

A more complete description of the procedures than that which follows is presented by Plaster (13).

As a means of investigating the chemistry of soil-cement reactions, the minus No. 230 sieve fraction of the soils was dry mixed with 40 percent portland cement by weight. These mixtures were then combined with distilled water at a solids-to-liquid ratio of 1 to 1 (by weight) and stored in plastic vials at room temperature for curing periods of 2, 21, and 56 days.

In order to determine what chemical interplay had occurred between the soil and cement, it was decided that a series of leaches made with distilled water and acid solutions might provide some insight into the reactions. After the distilled water leach, the pH was taken and the suspended material then removed by centrifugation. The distilled water leachate was set aside for calcium oxide analysis. Another sample of the soil-cement was leached with 200 ml of 1.0 N  $HCl$ . The acid leachate was set aside for analyses of silica, alumina, and iron oxide.

Calcium oxide was determined by titration with EDTA as described by Davis (6). Silica, alumina, and iron oxide were determined by absorption spectrophotometry (6).

### X-Ray Studies

Randomly oriented powder specimens were X-rayed through an arc from 2 deg 2 theta to at least 45 deg 2 theta.

### Microscopic Investigations

Because a study of the fabric and physical bond of soil-cement was considered of value, thin sections were made of representative specimens prepared as previously described. The curing periods were varied because of the convenient time for making the thin sections. The curing periods of the thin-section specimens were as follows:

<u>Sample</u>	<u>Curing Period (days)</u>
F-2	125
F-8	150
I-1	97
I-2	97
I-5	97
L-1	95
L-9	95

Thin discs were cut from the centers of the vials and impregnated under vacuum with Permout, a synthetic resin mixed with 40 percent toluene. After the discs were ground down to approximately 30 microns, the thin sections were studied under the petrographic microscope.

### Strength Studies

In an effort to relate unconfined compressive strength gain to soil-cement reactions, 6 Harvard-size specimens of each soil sample and 6 more containing 10 percent portland cement were molded at optimum moisture content and maximum density. After curing for 7 days in a moisture room at 23 C, the specimens were tested in a Soiltest Versatester, Model 30M, stress-strain apparatus.

## RESULTS AND DISCUSSION

### Leachings of Calcium Oxide Made With Distilled Water

Water leaches, as stated earlier, were conducted at 2- and 56-day curing periods in order to determine the amount of easily soluble calcium in the various soil-cement

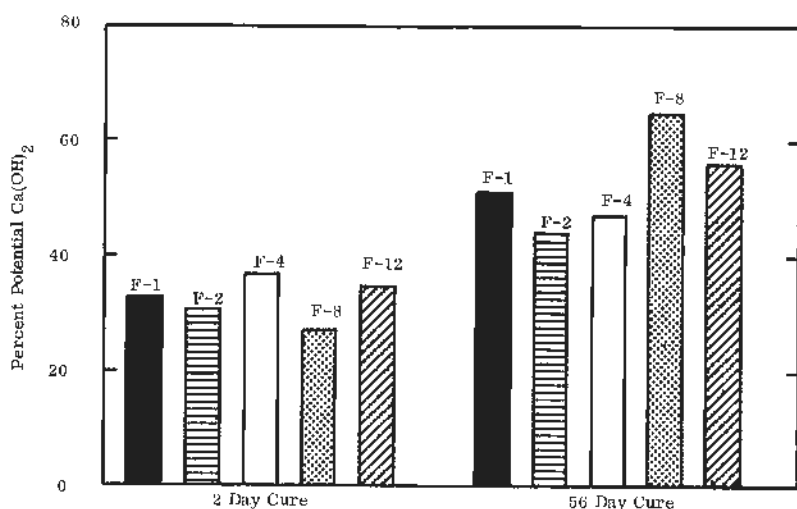


Figure 1. Percentage of potential  $\text{Ca(OH)}_2$  leached from the Frederick soil-cement specimens.

mixtures. The mixtures, as shown by X-ray analysis, were either noncarbonated or only very slightly carbonated.

Calcium in hydrating cement is easily leached from only one source—calcium hydroxide, either crystalline or noncrystalline (11). It was therefore hoped that the quantity of calcium leached might serve as a measure of the amount of calcium hydroxide in the soil-cement specimens. This measure, in turn, when compared with other data, might serve as a guide to the extent of hydration of the samples and might offer some insight into any reactions occurring between the soil and portland cement.

Throughout the following discussion calcium data, given as a measure of calcium hydroxide production, are often referred to as a percentage of potential calcium hydroxide. This percentage of potential calcium hydroxide is based on calcium hydroxide being 25 percent of fully hydrated cement (3). The reader is reminded, however, that at neither the 2- nor 56-day curing periods would the cement be fully hydrated (5). Therefore, percentages of potential calcium hydroxide will always be less than 100 percent.

**Frederick Soil-Cement Specimens**—Although there were A-, B-, and C-horizons present in the Frederick soil sampled, physical and chemical properties did not vary greatly down the soil profile. Therefore, it was not surprising that, as is shown in Figure 1, the amount of potential calcium hydroxide leached from the 5 different samples was remarkably similar for the same curing periods.

The amounts of calcium leached by water after each curing period seem to indicate that cement hydration and the formation of calcium hydroxide were proceeding at a normal rate (15). The increase in amount of calcium leached from the 2-day curing period to the 56-day curing period indicates that calcium hydroxide was being produced at a rate greater than its consumption. Thus it is implied that no significant reaction has occurred between the soil constituents and the cement and that the soil materials have not restricted the hydration of the cement.

The data given in Table 7 attempt to show the correlation of the difference in percentage of potential calcium hydroxide leached by water from the 2-day and 56-day cured specimens to the mineralogy and magnitude of the clay-size fraction. As the data given in Table 3 show, the gross mineralogical composition of the Frederick clay-size fraction was relatively constant, although traces of montmorillonite and goethite were in F-1 and F-12. However, the relative quantities of the minerals varied slightly. With quartz and illite the dominant clay-size minerals in F-8, the greatest increase in leached calcium

hydroxide occurred. The principal variation in F-1 and F-12 as compared with F-8 was the presence of montmorillonite, and the difference in leached calcium hydroxide decreased. Without montmorillonite but with the relative abundance of quartz decreased and the total clay-size fraction increased, as in F-2 and F-4, the calcium hydroxide leached further decreased. It is apparent that even extremely fine-grained quartz neither impeded the formation nor contributed to the consumption of calcium hydroxide. However, with a significant increase in the relatively inactive illite as well as the mixed-layer clay, or with the appearance of montmorillonite, either the production of calcium hydroxide is hindered or some calcium hydroxide is consumed.

The pH data on the Frederick soil-cement specimens do not seem to indicate anything in particular other than that there was little disparity in pH among the samples. The highest pH value was 11.61 (F-2, 56-day cure) and the lowest pH value was 11.12 (F-8, 2-day cure). These data again point up the uniformity of the Frederick samples in their reaction with cement.

There was a direct relationship between the pH of the Frederick soil-cement specimens and the amount of calcium leached. Thus, it appears that the amount of calcium hydroxide present in the specimens determines the alkalinity of the soil-cement system.

**Iredell Soil-Cement Specimens**—The Iredell soil, unlike the Frederick, displays a great deal of variation in properties with profile depth. As a result, samples from different horizons of the soil reacted somewhat differently to cement treatment.

The leached A-horizon of the Iredell soil (sample I-1), as shown in Figure 2, yielded approximately 10 percent more calcium than the B- and C-horizons of the soil, and there was a slight increase from the 2-day to the 56-day cure in calcium leached. The specimens containing soil from the B- and C-horizons not only yielded less of the potential calcium hydroxide at both curing periods but also showed decreases from the 2-day to the 56-day cure in the amount of calcium leached. The factors influencing this

TABLE 7  
LEACHED  $\text{Ca}(\text{OH})_2$  AND CLAY SIZE DATA

Sample <sup>a</sup>	Clay Size Mineralogy <sup>b</sup>	Percent Clay of Material Passing No. 230 Sieve	Difference in Leached $\text{Ca}(\text{OH})_2$ 56-days minus 2-days, percent
F-8	Q, I, K, ML	45.0	+38
F-1	Q, I, ML, K, M, G	44.2	+18
F-12	Q, I, K, ML, M, G	49.5	+21
F-2	ML, Q, I, K	55.5	+13
F-4	I, Q, ML, K	55.4	+10
I-5	M, I, V, Q, Ch, K	34.8	-6
I-1	V, Q, I, Ch, K	42.4	+5
I-2	I, V, Q, Ch, K	79.5	-1
I-9	K, I, ML, Q, M	17.2	-3
I-5	K, I, Q, ML, M	20.0	-6
I-3	K, I, ML, Q	48.2	-15.5
I-1	K, I, ML, Q	73.7	-31.0

<sup>a</sup>Listed in order of increasing clay percentage.

<sup>b</sup>Q = quartz; I = illite; K = kaolinite; ML = mixed layer; M = montmorillonite; G = goethite; V = vermiculite; and Ch = chlorite

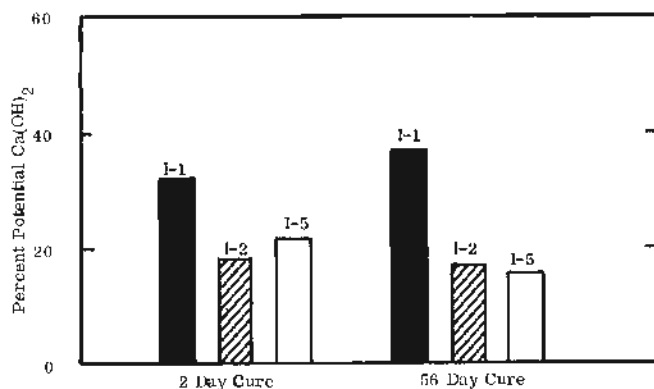


Figure 2. Percentage of potential  $\text{Ca}(\text{OH})_2$  leached from the Iredell soil-cement specimens.

disparity between the leached A-horizon and the B- and C-horizons concerning reactions to cement treatment will be discussed in the section on acid leaches.

The calcium value for the 2-day cure of the Iredell leached A-horizon soil-cement specimen very closely resembles those of the Frederick specimen, although all 3 Iredell specimens yielded much less calcium than the Frederick at 56 days. Apparently, in the leached horizon specimen of the Iredell, calcium hydroxide production was slowed after 2 days of curing, or calcium hydroxide was consumed in some manner other than in normal cement hydration processes. One possibility is that reaction of the cement with soil materials may have occurred, causing deletion of calcium hydroxide.

Calcium data on the specimens containing soil from the B-horizon (I-2) and the C-horizon (I-5) are remarkably similar, as is shown in Figure 2. This similarity is surprising because sample I-2 was a clay-pan soil and sample I-5 was a sandy saprolite. The data on both samples indicate that the presence of soil constituents either restricted the production of calcium hydroxide or caused rapid consumption of calcium hydroxide. Because the C-horizon of the Iredell soil is coarse-grained, it would not be expected that this soil would react to cement treatment in the same manner as the clayey B-horizon. It should be remembered, however, that only material passing the No. 230 sieve was used in the leachate studies. Of the minus No. 230 material, approximately 35 percent of the C-horizon soil was clay sized ( $< 2$  microns). This high percentage of clay, in combination with other factors such as mineralogy, may account for the similar behavior of the B- and C-horizon soil-cement samples.

Data on pH's of the Iredell specimens were lower than those of the Frederick specimens. The values ranged from 10.21 (I-2, 56-day cure) to 11.30 (I-1, 56-day cure). Like the Frederick samples, the pH values roughly paralleled the amounts of calcium leached.

**Lloyd Soil-Cement Specimens**—Calcium data on the specimens containing Lloyd soil were neither consistently similar as in the Frederick specimens nor predictably dissimilar as in the Iredell specimens. As shown in Figure 3 the amount of potential calcium hydroxide leached varied widely in soil-cement specimens containing soil from different depths in the Lloyd profile.

One relationship of the specimens is immediately obvious in Figure 3—less calcium hydroxide was leached from the specimens cured for 56 days than those cured for 2 days. This relationship indicates that calcium hydroxide was originally formed and

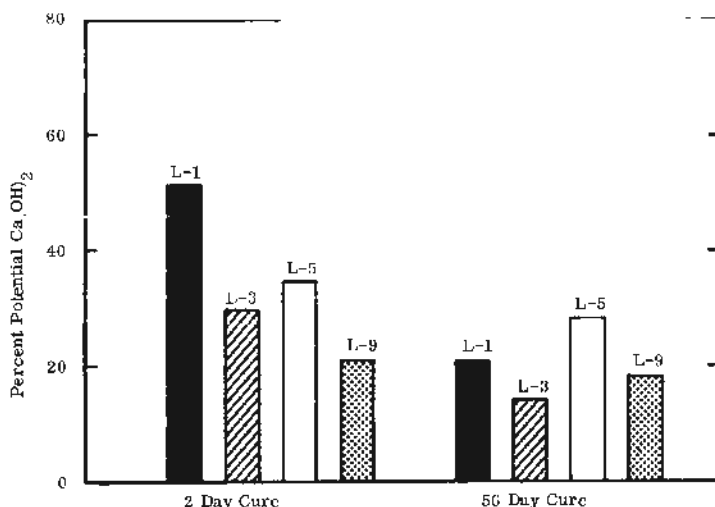


Figure 3. Percentage of potential  $\text{Ca(OH)}_2$  leached from the Lloyd soil-cement specimens.

then was consumed in some manner. This consumption process was more pronounced in some specimens, especially the clay-rich ones, than in others (Table 7). The clay-size mineral suites of the Frederick and Lloyd specimens are so similar that they permit evaluation of the effect of kaolinite on the difference in quantity of leached calcium hydroxide with curing time (Table 7). Very small quantities of kaolinite were present in the Frederick specimens, and the difference in quantity of leached calcium hydroxide increased with curing time, i.e., calcium hydroxide accumulated. Kaolinite is the dominant clay in the Lloyd specimens, and the negative difference in quantity of calcium hydroxide leached became greater as the clay content increased. Thus the rate of calcium hydroxide consumption must have exceeded the rate of production, and did so to a greater extent with kaolinite than with any other clay mineral present.

If the typical B-horizon (L-1) and C-horizon (L-9) samples of the Lloyd soil are considered, 2 vastly different sets of calcium leachate data are available. (The Lloyd A-horizon, or leached horizon, has been eroded.) Approximately 52 percent of the potential calcium hydroxide was leached from soil-cement specimen L-1 after 2 days of curing, but only 21 percent of the potential was leached after 56 days of curing. From specimen L-9, however, only 21 percent of the potential was leached at 2 days and 18 percent at 56 days. This difference in the calcium leachate data indicates a difference in behavior of the B- and C-horizon soils when treated with portland cement. As pointed out earlier, neither sample appeared to hydrate at a normal rate, and therefore each has reacted with the cement in some manner. Large amounts of calcium hydroxide formed early in the B-horizon specimens indicating quick, almost accelerated, hydration of the cement. With further curing the calcium hydroxide appears to have been consumed and the calcium converted to a less leachable form, thus explaining the low 56-day leachate values. In the case of the C-horizon specimens, small amounts of the potential calcium hydroxide were leached after 2 days of curing and even smaller amounts at 56 days. This situation lends itself to either or both of 2 explanations: (a) Soil constituents may have prevented the initial formation of large quantities of calcium hydroxide; or (b) calcium hydroxide may have been produced in quantity but was rapidly consumed and the calcium tied up in less leachable compounds.

The pH values of the Lloyd specimens varied widely, ranging from a low of 9.48 (specimen L-1, 56-day cure) to a high of 11.30 (specimen L-5, 56-day cure). Although a general trend prevailed, the pH did not always decrease or increase correlative to a decrease or increase in calcium leached from the 2-day to the 56-day cure. Soil properties must have affected the pH of the soil-cement systems in some manner; unfortunately, these properties and subsequently their effects could not be determined.

#### Leachings of Silica, Alumina, and Ferric Oxide Made With Hydrochloric Acid

The soil and soil-cement specimens were leached with 1.0 N HCl in order to determine the solubility of silica, alumina, and ferric oxide in the soils before and after cement treatment. It was thought that, if these compounds were more or less acid soluble after cement treatment, some knowledge of the reactions occurring in the specimens might be derived. Whenever possible, information obtained from the water leachate and X-ray studies was correlated with the acid leachate results.

In the following discussion frequent reference is made to the calculated values given in Table 8. These values represent the amount of silica, alumina, or ferric oxide expected to be leached from each of the soil-cement specimens, assuming a normal rate of cement hydration and considering the dilution effect of the water of hydration. The values are the sum of the ppm of silica, alumina, or ferric oxide leached from the amount of soil in a soil-cement specimen plus the ppm of silica, alumina, or ferric oxide that it is theoretically possible to leach from the amount of cement in a soil-cement specimen, provided the cement is 50 percent hydrated. If normal type I portland cement hydration rates are considered, the specimens cured for 2 days would be approximately 50 percent hydrated, those cured for 21 days would be about 75 percent hydrated, and those cured for 56 days would be better than 80 percent hydrated (5). It is considered, therefore, that the assumption of 50 percent hydration of the cement in



TABLE 8  
ACID LEACHINGS OF OXIDES FROM SOIL AND CALCULATED VALUES

Sample	Oxide	Soil Only (ppm)	Calculated Value <sup>a</sup> (ppm)	Sample	Oxide	Soil Only (ppm)	Calculated Value <sup>a</sup> (ppm)
F-1	SiO <sub>2</sub>	5.4	193.4	L-1	Al <sub>2</sub> O <sub>3</sub>	9.9	61.9
F-2	SiO <sub>2</sub>	3.2	191.2	L-3	Al <sub>2</sub> O <sub>3</sub>	7.2	59.2
F-4	SiO <sub>2</sub>	4.8	192.8	L-5	Al <sub>2</sub> O <sub>3</sub>	7.2	59.2
F-8	SiO <sub>2</sub>	3.5	191.5	L-9	Al <sub>2</sub> O <sub>3</sub>	8.8	60.8
F-12	SiO <sub>2</sub>	1.6	189.6	F-1	Fe <sub>2</sub> O <sub>3</sub>	0.8	21.3
I-1	SiO <sub>2</sub>	3.2	191.2	F-2	Fe <sub>2</sub> O <sub>3</sub>	4.8	25.3
I-2	SiO <sub>2</sub>	7.2	195.2	F-4	Fe <sub>2</sub> O <sub>3</sub>	0.8	21.3
I-5	SiO <sub>2</sub>	9.3	197.3	F-8	Fe <sub>2</sub> O <sub>3</sub>	4.8	25.3
L-1	SiO <sub>2</sub>	6.4	194.4	F-12	Fe <sub>2</sub> O <sub>3</sub>	1.0	21.5
L-3	SiO <sub>2</sub>	5.1	193.1	I-1	Fe <sub>2</sub> O <sub>3</sub>	2.4	24.9
L-5	SiO <sub>2</sub>	4.8	192.8	I-2	Fe <sub>2</sub> O <sub>3</sub>	5.1	25.6
L-9	SiO <sub>2</sub>	4.0	192.0	I-5	Fe <sub>2</sub> O <sub>3</sub>	2.9	23.4
F-1	Al <sub>2</sub> O <sub>3</sub>	8.2	60.2	L-1	Fe <sub>2</sub> O <sub>3</sub>	0.0	20.5
F-2	Al <sub>2</sub> O <sub>3</sub>	13.1	65.1	L-3	Fe <sub>2</sub> O <sub>3</sub>	1.3	21.8
F-4	Al <sub>2</sub> O <sub>3</sub>	13.6	65.6	L-5	Fe <sub>2</sub> O <sub>3</sub>	2.7	23.2
F-8	Al <sub>2</sub> O <sub>3</sub>	13.1	65.1	L-9	Fe <sub>2</sub> O <sub>3</sub>	2.1	22.6
F-12	Al <sub>2</sub> O <sub>3</sub>	10.4	62.4				
I-1	Al <sub>2</sub> O <sub>3</sub>	9.1	61.1				
I-2	Al <sub>2</sub> O <sub>3</sub>	13.9	65.9				
I-5	Al <sub>2</sub> O <sub>3</sub>	8.8	60.8				

<sup>a</sup>ppm possible from cement (50 percent hydrated) plus ppm leached from soil sample only.

the specimens is not unwarranted and for the last 2 curing periods is, in fact, a conservative estimate.

The data shown in Figures 4 through 12 are the ppm of silica, alumina, or iron oxide acid leached from the soil-cement specimens in excess of the calculated values.

It will be shown in the following discussions that all the soil-cement specimens leached more than the expected calculated values. This situation may be explained in 2 ways: (a) The cement in the specimen may not be 50 percent hydrated, thus resulting in greater than expected leachates of silica, alumina, and iron oxide because of the absence of predicted water of hydration; or (b) some of the clays in the soil may have slightly deteriorated releasing small quantities of silica, alumina, and iron oxide.

**Frederick Soil-Cement Specimens**—Acid leaches of the Frederick specimens again pointed up the uniformity of soil properties down the profile. Figures 4, 5, and 6 show that even at different curing periods all 5 soil-cement specimens leached almost the same amounts of silica, alumina, and ferric oxide.

Comparison of the leachate data of the Frederick specimens shows that in all instances the specimens leached practically the expected amounts of silica, alumina, and iron oxide. Because the leachate data were neither noticeably lower nor higher than the expected values, it must be concluded that the cement in the specimens hydrated at a normal rate and that there was little or no soil-cement reaction with its attendant deterioration of the clays.

However, 2 relationships of the lines may indicate some slight reaction of the soil with the cement: (a) Most of the curves show increased leachate values after 56 days of curing, thus indicating that limited deterioration of the soil components may have occurred with time; and (b) the specimens containing soil from the leached horizon (sample F-1) always leached less than the specimens made with soil from the zone of clay accumulation (sample F-2), thus implying that the clay zone in the Frederick is more susceptible to cement attack than the other horizons in the soil.

The reason for the very slight reaction of the soil constituents with the cement appears related to mineralogy. The major clay in the Frederick soil is illite. In previous studies concerned with this project (11), it was noted that of the relatively pure clays investigated the one showing least deterioration when mixed with cement was illite. It appears, therefore, that the apparent lack of soil-cement reactions in the Frederick specimens may be

related to the fact that the soil contains large amounts of the more stable clay, illite, instead of less stable minerals.

**Iredell Soil-Cement Specimens**—As was the case with the water leaches, the various horizons of the Iredell also yielded different acid leachate results. Figures 7, 8, and 9 show that when mixed with cement the leached horizon specimens (I-1) released much smaller quantities of silica, alumina, and iron oxide than did the B- and C-horizon specimens (I-2 and I-5).

The specimens made with soil from the Iredell leached zone (I-1), like all of the Frederick specimens, appear to have hydrated at a normal or almost normal rate with little soil-cement chemical interaction occurring. The amounts of silica, alumina, and iron oxide leached were only slightly higher than the expected calculated values. The apparent lack of chemical reactions appears related to weathering and the resultant mineralogy. The severe leaching of the Iredell A-horizon has developed a relatively stable mineralogical suite, with vermiculite, quartz, and illite

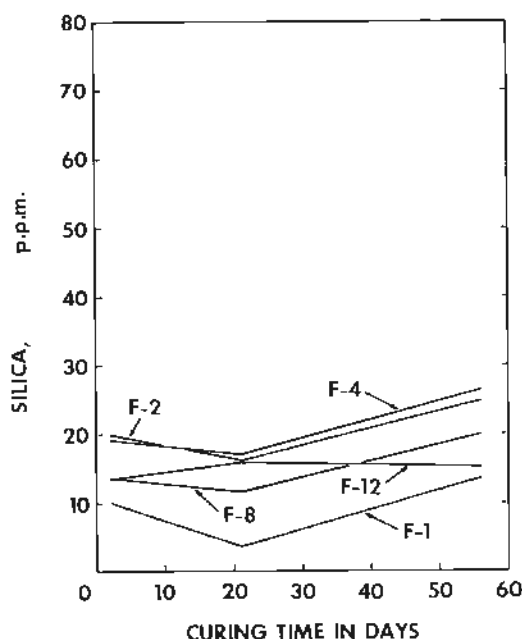


Figure 4. Excess silica acid leached from Frederick soil-cement specimens.

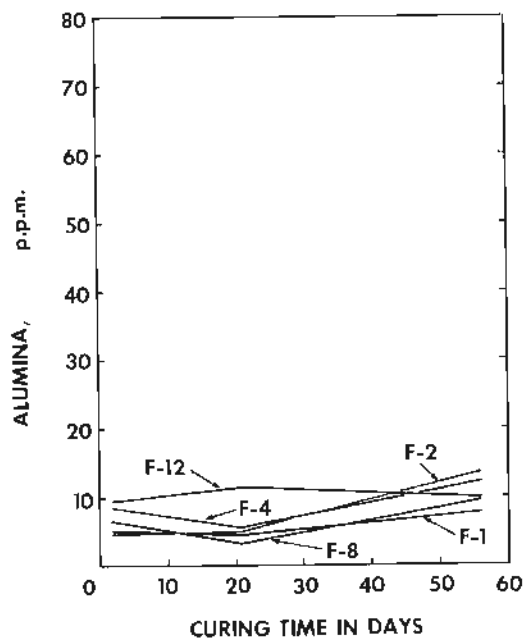


Figure 5. Excess alumina acid leached from Frederick soil-cement specimens.

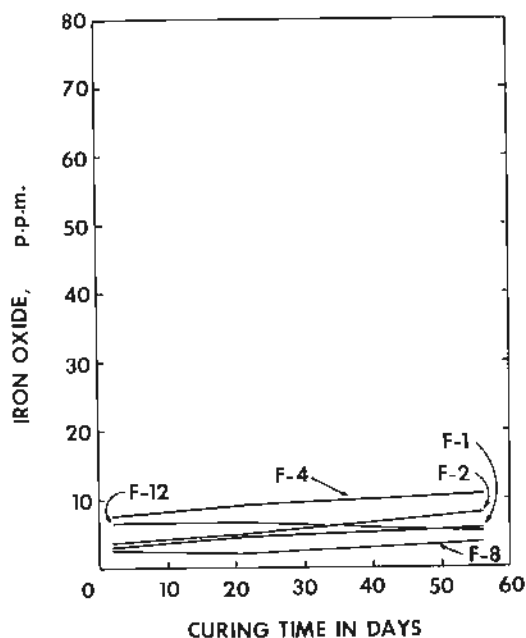


Figure 6. Excess iron oxide acid leached from Frederick soil-cement specimens.

respectively the principal clay-size minerals. If the Iredell A-horizon is in equilibrium with weathering conditions near the land surface, and if the cement environment is analogous to a weathering environment, albeit rigorous, then it follows that further breakdown and reaction of the soil with cement would not be expected.

The B-horizon soil-cement specimens (I-2), as shown in Figures 7, 8, and 9, leached much more silica, alumina, and iron oxide than the leached horizon specimens (I-1). When compared with the expected calculated values, the B-horizon soil-cement specimens leached an average of 89.1 ppm more silica, 28.5 ppm more alumina, and 22.9 ppm more iron oxide. Furthermore, the excess amounts leached increased with the length of the curing period. These excess amounts of silica, alumina, and iron oxide cannot be explained by slowed curing of the cement. In such a case lesser amounts of water of hydration would cause the calculated values to be higher, but not greatly higher. The excess amounts can be explained only by cement

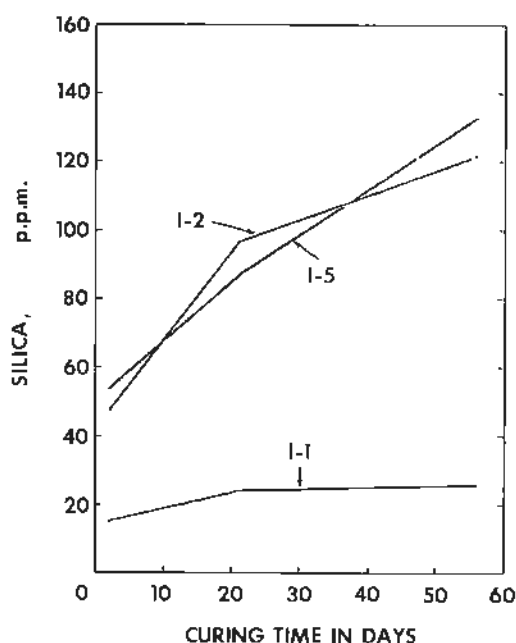


Figure 7. Excess silica acid leached from Iredell soil-cement specimens.

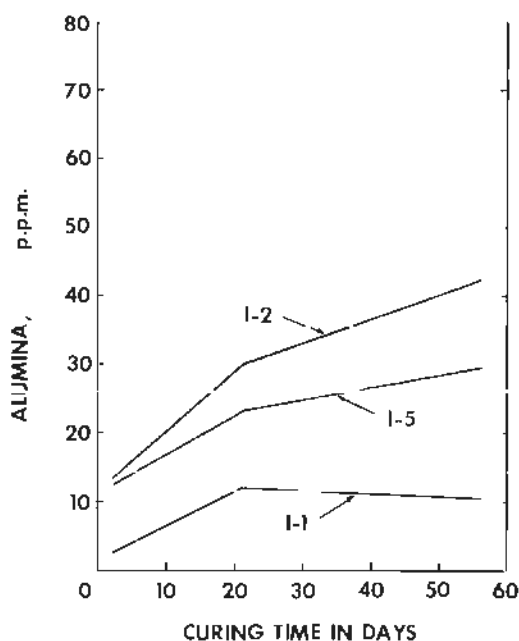


Figure 8. Excess alumina acid leached from Iredell soil-cement specimens.

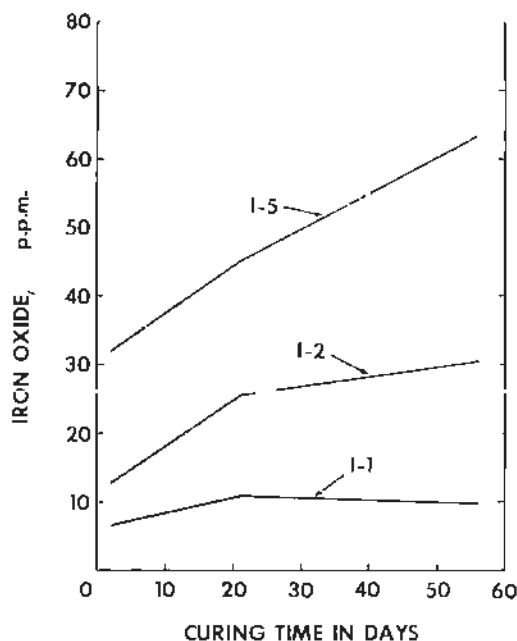


Figure 9. Excess iron oxide acid leached from Iredell soil-cement specimens.

attack and breakdown of the clays in the soil. The reactions possibly could have occurred with amorphous materials, but the end result is the same—cement reaction has caused these soil materials to deteriorate and become more acid leachable.

A relationship between the water leachate (calcium) data and the acid leachate (silica, alumina, and iron oxide) data exists for specimen I-1 and other specimens described later in which deterioration of the soil constituents appears to have occurred. The calcium data were always low, and the silica and alumina data were always high; in some instances the iron oxide data were also high. This relationship suggests that the clays have deteriorated and that contemporaneous combination of the silica, alumina, and iron oxide with calcium hydroxide has resulted in the formation of relatively insoluble hydrated calcium silicates, aluminates, and ferrites.

The C-horizon soil-cement specimens (I-5) of the Iredell, like the B-horizon specimens, yielded acid leachate values much larger than expected. Also, as in the B-horizon specimens, the values increase with the curing time. Again it appears that soil-cement reactions have caused silica, alumina, and iron in the soil to become more acid leachable. It would be interesting to postulate which soil constituents were involved. As was noted earlier, although the C-horizon of the Iredell is a saprolite, the soil fraction used in the leachate studies contained appreciable clay. This clay is largely montmorillonite, which has been shown to deteriorate rapidly in a cement environment (9, 11). This deterioration would result in high silica and alumina (and possibly iron) concentrations when the specimens were leached with acid. Also, in contrast to the leached zone of the Iredell, the C-horizon has not undergone as severe weathering. The lower subsoil is protected from downward seeping waters by an overlying impermeable clay zone. The minerals in the C-horizon are not in equilibrium with surface conditions and would be extremely susceptible to weathering. The harsh alkaline conditions of a cement environment might very easily cause deterioration of these minerals, again resulting in high silica, alumina, and iron leachate values.

A final comment on the C-horizon specimens concerns the very high iron leachate values, which increase with continued curing. Iron is abundant in the Iredell soil and near the land surface has been oxidized into limonitic concretions. This oxidized iron is not readily soluble, especially in an alkaline environment (7), and the low iron leachate values of specimen I-1 would be expected. Lower in the soil profile, however, the iron has not been oxidized and in the stagnant, poorly drained environment of the C-horizon it probably is present in the more soluble ferrous state (8). It appears, therefore, that the ferrous iron originally dissolved in the specimens reacted with the cement and was precipitated as acid soluble compounds. More of the ferrous iron was dissolved, reacted, and precipitated. This continuing process would explain the increasingly high iron leachate values found for the C-horizon specimens. In order to confirm this hypothesis, however, further work needs to be done on the hydration of cement in a ferrous iron-rich solution.

**Lloyd Soil-Cement Specimens**—In the section on water leaches it was noted that the different Lloyd specimens leached varied amounts of calcium. Figures 10, 11, and 12 show that the specimens also had varied acid leachate results. Also, it was stated that the amount of calcium leached from the specimens by water decreased from the 2- to the 56-day cure. With the exception of the silica data for specimen L-5, a reverse trend is noted for the acid leachate results. The amount of silica, alumina, and iron oxide leached increased with the curing time. Figures 10, 11, and 12 show that much more than the expected amounts were leached from all of the specimens. This inverse relationship between the water and acid leachate data seems to indicate, as was mentioned earlier, that calcium hydroxide formed in the specimens and then was consumed in reactions with soil constituents. Thus, the amount of calcium leached would decrease with the usage of calcium hydroxide, and the amount of silica, alumina, and iron oxide leached would increase with the formation of acid soluble reaction products.

If the specimens containing pure B-horizon soil (L-1) and those containing pure C-horizon soil (L-9) are considered, it will be noted that they have similar leachate data. The L-1 and L-9 curves shown in Figures 10, 11, and 12 roughly parallel each other, illustrating this similarity. The large amounts of silica and alumina leached from both

sets of specimens after cement treatment indicate that the soil constituents have deteriorated in the cement environment. The very large amounts of alumina leached seem to indicate breakdown of the abundant kaolinite in the soil. In comparison with the Frederick and Iredell specimens, it appears that kaolinite is much more susceptible to cement attack than illite and practically as susceptible to cement attack as montmorillonite. This same ranking of pure clay minerals was found by Noble (11). The very high silica and alumina leachate data of specimen L-1 are easily explained because the soil used contained over 70 percent clay. The large amounts leached from the L-9 specimens, however, are more difficult to explain because the soil fraction used contained less than 15 percent clay. Deterioration of the clay may have contributed some of the excess silica and alumina, but breakdown of some of the primary minerals in the soil must also have taken place. Probably the easily weathered feldspar in the C-horizon was broken down by the cement.

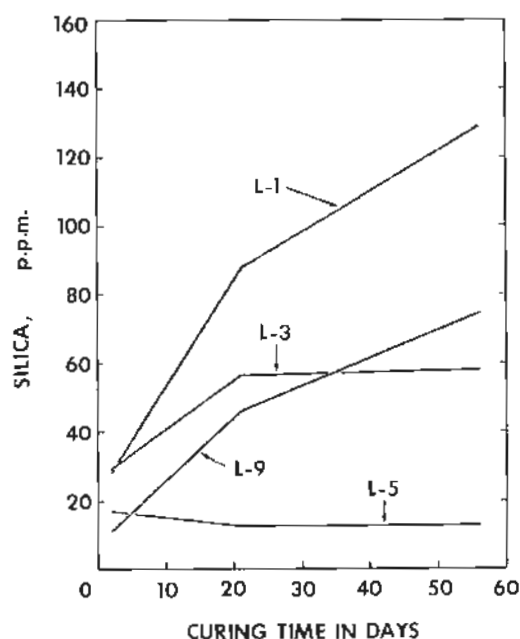


Figure 10. Excess silica acid leached from Lloyd soil-cement specimens.

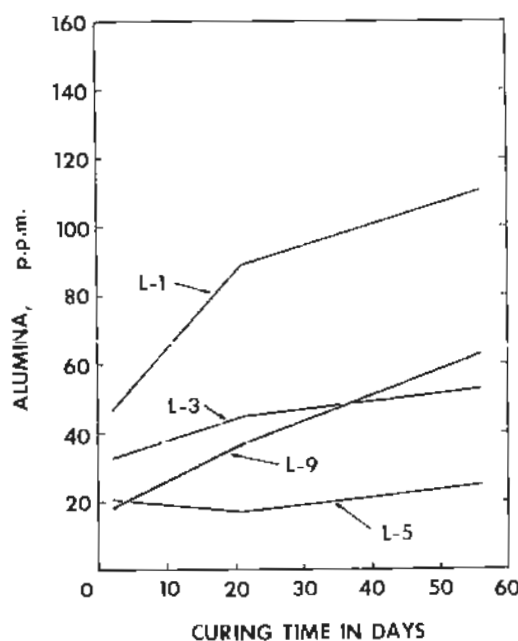


Figure 11. Excess alumina acid leached from Lloyd soil-cement specimens.

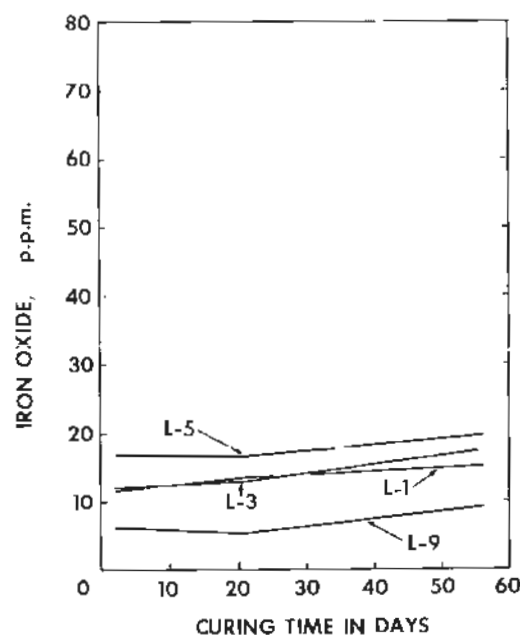


Figure 12. Excess iron oxide acid leached from Lloyd soil-cement specimens.

## X-Ray Investigations

Unfortunately the slides prepared for this part of the study were X-rayed at different times by different technicians using different diffractometer settings and possibly different diffractometer alignments. It was not possible, therefore, to immediately distinguish changes in relative X-ray intensities of the soil-cement constituents. Intensities could be approximated, however, by using quartz occurring in the soils as an internal standard; i. e., it was assumed that, in the presence of reactive clay minerals, the quartz was nonreactive and did not change in X-ray intensity in any of the slides of the same sample. In the following discourse, therefore, any reference to intensity changes is based on the use of such a quartz standard.

Also it should be pointed out that primary attention was focused on any changes in crystallinity of the clays in the soils, because these minerals were thought the ones most likely to react with cement.

**Frederick Soil-Cement Specimens**—In the X-ray studies the uniformity of the Frederick soil was again evident. There was little difference in the X-ray data of soil-cement specimens prepared with soil from different profile depths. Consequently, all of the Frederick specimens are treated collectively in this discussion.

Illite, the major clay mineral of the soil, was present in both the 2- and 56-day cured specimens, although its peak intensities were slightly diminished. Mixed layer clay was evident in all of the specimens, but the basal d-spacings were more disordered than in the untreated soil, indicating at least some lattice disruption. Kaolinite, the third most abundant clay mineral in the soil, was noticeably diminished or absent in all of the specimens. Basal kaolinite peaks were recognizable, but considerably reduced in intensity in specimens F-2, F-8, and F-12 at 2 days, and were absent at 56 days. The same peaks were absent at both 2 and 56 days in specimens F-1 and F-4.

Although the masking effect of fine-grained cement hydration products may have affected the X-ray reflections of the clay minerals, the data appear to indicate something more. The slight peak intensity diminution of illite, the lattice disruption of mixed layer clay, and the disappearance of kaolinite peaks are interpreted as evidence of cement attack of the clays. This evidence may account for the minor amount of soil deterioration that was postulated in the discussion of the leachate studies.

Several cement hydration products were developed in the Frederick as well as the Iredell and Lloyd soil-cement specimens. Identification of these compounds was hampered, however, because of their poor crystallinity and the interference offered by X-ray reflections of soil minerals. As a result, attention was focused on the better crystallized compounds of calcium hydroxide and calcium monosulfoaluminate. Calcium silicate hydrates of the tobermorite variety may have developed in all of the specimens, but the definitive peaks of tobermorite were, in all cases, shadowed by the peaks of other constituents.

Calcium hydroxide was evident in all of the Frederick specimens after 2 days of curing and at 56 days showed even greater development. Because calcium hydroxide is a major product of the hydration of cement, it seems that the presence of the Frederick soil constituents has not greatly inhibited cement hydration. Instead it appears that hydration has proceeded at a steady, if not increasing, rate. Calcium monosulfoaluminate was developed in all of the specimens except F-1 at the 2-day cure. It was present, however, in F-1 at 56 days and the 9 Å X-ray peak was increased in intensity at 56 days in specimens F-8 and F-12.

**Iredell Soil-Cement Specimens**—Soil-cement specimens made with material from different horizons of the Iredell soil had contrasting X-ray data.

The most abundant clay in the leached horizon (specimen I-1) is vermiculite. After 2 days of curing this mineral persisted, but with reduced X-ray intensity. The same situation prevailed at 56 days. The minor clay constituents of the soil, illite and chlorite, were also slightly reduced in intensity at 2 and 56 days. The X-ray peaks of all 3 clays were more disordered after cement treatment than in the untreated samples, indicating some deterioration of the clays. X-ray peaks of calcium hydroxide were easily recognized and of about equal intensity in both the 2- and 56-day cured I-1 specimens. Development of the compound appeared about the same as that in the Frederick

specimens, again demonstrating the similarity of reaction of the Iredell leached zone and the Frederick specimens. If calcium hydroxide production is again used as an index, the soil of the leached horizon showed more enhanced cement hydration than the 2 horizons lower in the Iredell profile.

The high clay content of the Iredell B-horizon showed a great effect on cement hydration. Also the X-ray diffractograms indicated that the clays had been substantially affected by the cement.

Illite, vermiculite, and chlorite were evident in the B-horizon specimens after 2 days of curing, but after 56 days only vermiculite was readily identified. Calcium hydroxide was not detectable at 2 days and appeared with only trace intensities at 56 days. These data might appear to indicate that only small amounts of calcium hydroxide formed. The diffractogram absence of calcium hydroxide, however, may not mean that it was never formed, but it may have been produced and then reacted with silica and alumina in the clay minerals. It is also possible that noncrystalline calcium hydroxide formed, which would not be detected by X-rays. Leachate data, however, will not support this latter hypothesis because only small amounts of calcium were leached from the specimens.

The C-horizon of the Iredell contained very little quartz. As a result, no standard was available for semiquantitative estimation of peak intensities. Nevertheless, it was obvious that montmorillonite, the major clay mineral of the C-horizon, was affected by the cement environment. The original 14.5 Å peak of the mineral appeared after cement treatment as a broad, disordered band of peaks ranging up to 17 Å. The increased d-spacing and resultant lattice expansion may indicate that cement attack was taking place between the mineral layers, or the expansion may simply have been due to the absorption of interlayer water. The low intensity illite peak at 10 Å originally present in the soil samples appeared unaffected after cement treatment, again illustrating the stability of illite in a cement environment.

Calcium hydroxide was developed in the C-horizon soil-cement specimens, but not nearly as well as in the leached zone specimens. It appeared about equally developed in both the 2- and 56-day cures. Calcium monosulfoaluminate was well developed in both the 2- and 56-day cures.

**Lloyd Soil-Cement Specimens**—X-ray data of the Lloyd specimens indicated that deterioration of some of the mineral constituents had occurred. Also, all 4 specimens showed some development of calcium hydroxide, but the compound appeared much less developed than in the Frederick specimens. The following is a discussion of the B-horizon (L-1) and C-horizon (L-9) soil-cement specimens.

In the B-horizon specimens kaolinite was considerably reduced in X-ray intensity, but the peaks were still easily discerned. The other major clay minerals in the B-horizon, mixed layer clay and illite, displayed very disordered X ray peaks in diffractograms of the soil alone, and it was extremely difficult to determine if any changes had taken place after cement treatment. Calcium hydroxide displayed low intensity peaks after 2 days of curing and even lower ones after 56 days. The low peaks at 56 days are understandable because only small amounts of calcium were leached from specimen L-1 at that time. But the low peaks at 2 days were not expected because very large amounts of calcium were leached. It is possible that at 2 days large amounts of calcium hydroxide were present, but the compound had not crystallized and was largely in an amorphous state. It is also possible that the calcium hydroxide was entirely crystalline, but the abundant clays in specimen L-1 were absorbed onto the surface of the crystals. Thus, many of the X-ray reflections of the calcium hydroxide might be masked. Calcium monosulfoaluminate was slightly developed in the L-1 specimens at 2 days, but at 56 days it was absent.

X-ray diffractograms of the C-horizon specimens (L-9) were practically identical at the 2- and 56-day curing periods. Kaolinite peaks were greatly diminished in intensity, indicating deterioration of the clay. Illite was not reduced in intensity. Mixed layer clay was slightly diminished. Feldspar peaks were reduced in intensity, perhaps indicating that this mineral had reacted with the cement, as was postulated in the sections on leachates. Small amounts of calcium hydroxide were detected in the L-9 specimens, and calcium monosulfoaluminate was well developed.

## Microscopic Studies

Petrographic investigations of thin sections showed the gross structure and general composition of the soil-cement specimens. Most of the constituents were extremely fine grained and, as a result, detailed studies of the soil-cement relationships could not be conducted.

In the Frederick sections some of the clay was flocculated, but generally clay, quartz, and cement products were diffusely distributed. Some of the quartz grains were coated with clay. A few patches of calcite were present and calcium hydroxide was developed.

Clay, quartz, biotite, calcium hydroxide, and a small amount of calcite were identified in the leached horizon section (I-1) of the Iredell specimens. The constituents were coarser grained than in the Frederick section, and the clay was highly flocculated. In several instances cementation of 2 mica shards by calcium hydroxide and other cement products had taken place. The cement products were often seen penetrating into the clay flocs.

The soil and cement constituents in the Iredell B-horizon section (I-2) were extremely fine grained. The clay was well flocculated into irregular masses, often including several quartz grains. In general, the cement surrounded the clay flocs, but in a few cases cement was present within the flocs. Calcium hydroxide was not identified.

Calcium hydroxide was not identified in the C-horizon specimens (I-5) of the Iredell. Hornblende, biotite, and chlorite were present. Very little of the clay was flocculated, but it was intimately mixed with the cement matrix. In one instance cement was noted eating into the edges of a biotite flake.

The clay was well flocculated in the B-horizon soil-cement section (L-1) of the Lloyd specimens. Illitic material appeared more abundant than X-ray studies had indicated. In some cases clay had coated quartz grains and surrounded patches of cement. The matrix was a mixture of clay, quartz, and cement. Calcium hydroxide was not identified.

Again calcium hydroxide was not identified in the C-horizon soil-cement section (L-9) of the Lloyd specimens. Very little clay was present in the slide, but quartz, feldspar, and mica were abundant. Many of the smaller soil particles were cemented together in isolated patches, and larger quartz and feldspar grains were often coated with cement.

## Strength Development Studies

The results of the unconfined compressive strength tests are given in Table 9. The following observations were made:

1. Unconfined compressive strengths increased at least fourfold for the specimens after cement treatment, and in several instances increases were greater than twentyfold;

2. In general, the B-horizon specimens had lower strengths than the C-horizon specimens after cement treatment;

3. Specimen I-1, the only highly leached soil investigated, had a high strength after cement treatment;

4. Comparisons with the grain size distributions of the soils appear to indicate that the amount of clay in the soils was more important in determining short-term soil-cement strength gain than was the type of clay; and

5. No easily recognized relationship existed between the leachate and X-ray data of the soil-cement specimens and the development of strength. The strength gain of the specimens did not appear related to chemical reactions of the soil and cement.

TABLE 9  
SEVEN-DAY UNCONFINED COMPRESSIVE STRENGTHS  
OF HARVARD-SIZE SOIL AND SOIL-CEMENT  
SPECIMENS

Sample	Strength (psi)	
	No Cement	10 Percent Cement
F-1	52.9	329.1
F-2	79.2	354.2
F-4	47.8	302.3
F-8	48.4	196.5
F-12	47.4	321.2
I-1	19.6	461.3
I-2	40.0	250.2
I-5	19.8	520.6
L-1	23.6	200.1
L-3	51.5	268.0
L-5	21.2	191.1
L-9	17.0	436.4



## CONCLUSIONS

The following are some of the more important conclusions obtained from this study.

1. The Frederick soil constituents did not react appreciably with the cement, although some of the clays in the soil were slightly deteriorated after cement treatment.
2. As shown in the Frederick specimens, quartz neither impeded the production of nor contributed to the consumption of calcium hydroxide.
3. The clays and probably other constituents in the B- and C-horizons of the Iredell and Lloyd soils suffered deterioration after cement treatment, as indicated by the release of large amounts of silica and alumina and by the diminution of mineral X-ray peaks.
4. When the major clay mineral in the soils was considered, the soils appeared to suffer deterioration after cement treatment from greatest to least in the following order: montmorillonitic soils, kaolinitic soils, illitic soils.
5. The greatest quantities of calcium hydroxide were consumed with kaolinite as the dominant clay size mineral.
6. It appeared that reaction of calcium hydroxide with the soil constituents was proportional to the magnitude of the clay size fraction.
7. It appeared that amorphous calcium hydroxide was present in at least two of the specimens investigated.
8. The instability of the C-horizon Iredell soil constituents in a cement system appeared related to mineralogy. The minerals in the soil were not greatly weathered and were susceptible to the harsh conditions of an alkaline environment.
9. Iron in at least two of the Iredell specimens was highly reactive with or easily dissolved by the cement or both. This situation appeared related to the probable ferrous state of the iron.
10. The amount of clay in the soil-cement specimens appeared more important than the type of clay in determining short-term strength development.

## ACKNOWLEDGMENTS

This research was conducted under the general direction of the late Dr. Tilton E. Shelburne, State Highway Research Engineer, and Mr. Jack H. Dillard, State Highway Research Engineer, and was financed by HPR funds administered by the U.S. Department of Transportation, Federal Highway Administration, Bureau of Public Roads.

## REFERENCES

1. Standard Specifications for Highway Materials and Methods of Sampling and Testing—Part II: Methods of Sampling and Testing. American Association of State Highway Officials, Washington, D.C., 1961, 617 pp.
2. Brown, G. X-ray Identification and Crystal Structures of Clay Minerals. Mineralogical Soc., London, England, 1961, 544 pp.
3. Brunauer, S., and Copeland, L. E. The Chemistry of Concrete. Scientific American, Vol. 210, No. 4, 1964, pp. 80-92.
4. Coleman, C. S., et al. Soil Survey of Culpeper County, Virginia. U.S. Govt. Printing Office, Washington, D.C., 1952, 126 pp.
5. Copeland, L. E., Kantro, D. L., and Verbeck, G. Chemistry of Hydration of Portland Cement. In Chemistry of Cement, National Bureau of Standards, Monograph 43, 1960, pp. 429-465.
6. Davis, C. E. S. A Rapid Method of Analyzing Cements and Rock Products. Commonwealth Scientific and Industrial Research Organization, Melbourne, Australia, Tech. Paper 3, 1961, 30 pp.
7. Hem, J. D. Study and Interpretation of the Chemical Characteristics of Natural Water. U.S. Geol. Survey, Water-Supply Paper 1473, 1959, 269 pp.
8. Hem, J. D., and Cropper, W. H. Survey of Ferrous-Ferric Chemical Equilibria. U.S. Geol. Survey, Water-Supply Paper 1459-A, 1959, 31 pp.
9. Herzog, A., and Mitchell, J. K. Reactions Accompanying Stabilization of Clay With Cement. Highway Research Record 36, 1963, pp. 146-171.

10. Journey, R. C., et al. Soil Survey of Augusta County, Virginia. U.S. Govt. Printing Office, Washington, D.C., 46 pp.
11. Noble, D. F. Reactions in Portland Cement-Clay Mixtures. Virginia Highway Research Council, Charlottesville, Phase Rept. 2, 1966, 37 pp.
12. Noble, D. F. Reactions and Strength Development in Portland Cement-Clay Mixtures. Highway Research Record 198, 1967, pp. 39-56.
13. Plaster, R. W. Reactions in Portland Cement-Clay Mixtures. Virginia Highway Research Council, Charlottesville, Phase Rept. 3, 1969, 148 pp.
14. Porter, H. C., et al. Soil Survey of Fairfax County, Virginia. U.S. Govt. Printing Office, Washington, D.C., 1963, 103 pp.
15. Pressler, E. E., et al. Determination of the Free Calcium Hydroxide Contents of Hydrated Portland Cements and Calcium Silicates. Anal. Chem., Vol. 33, 1961, pp. 877-882.
16. Warshaw, C. M., and Roy, R. Classification and a Scheme for the Identification of Layer Silicates. Geol. Soc. Am. Bull., Vol. 72, 1961, pp. 1455-1492.