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Time-temperature-strength-reaction product relationships in lime-bentonite-water mixtures

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TIME-TEMPERATURE-STRENGTH-REACTION PRODUCT RELATIONSHIPS IN LIME-BENTONITE-WATER MIXTURES

by

Clarence Gerald Ruff

A Dissertation Submitted to the
Graduate Faculty in Partial Fulfillment of
The Requirements for the Degree of
DOCTOR OF PHILOSOPHY

Major Subject: Soil Engineering

Approved:

Signature was redacted for privacy.

In Charge of Major Work

Signature was redacted for privacy.

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Signature was redacted for privacy.

Dean of Graduate College

Iowa State University
Of Science and Technology
Ames, Iowa

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TABLE OF CONTENTS

INTRODUCTION

Because of the increased highway construction in the past two decades, the demand for suitable aggregates for base courses has exceeded the supply in many parts of the country. To compensate for this shortage of aggregates there has been an increased use of stabilized soil.

Adding lime or portland cement to the soil are two means of stabilization that have been widely used. Both of these additives have been tested extensively in a practical way to determine their efficiency in the stabilization of various soils. Portland cement pastes have also been thoroughly investigated to determine the mechanisms by which cementation occurs. Less investigation has been made of the soil-lime reaction, but what has been done indicates that the reaction products are similar to those formed during the hydration of portland cement. However, most of the work that has been done in determining the mechanism of the soil-lime reaction has been concerned with the effect of time on the strength of the soil-lime mixture, and the effect of time and/or temperature on the reaction products formed. Little attention has been given to the interrelation of time, temperature, and strength of lime stabilized soil.

The objective of this investigation is to study this interrelation of curing time, curing temperature, strength, and reactions in lime-clay mixtures. It will be noted that previous time-temperature-strength studies were done before lime-clay reaction products were known or identifiable, so it seemed appropriate to try and draw together these two paths of research, using one to explain or show the significance of the other.

REVIEW OF LITERATURE

Soil-Lime Stabilization

Lime is effective in stabilizing heavy clays, a fact well established by many investigators. Herrin and Mitchell (24) have compiled an excellent summary of the published knowledge of soil-lime mixtures to 1960. Up to that time it was recognized that lime improved the strength characteristics of the soil by a mechanism that was not fully understood, but it appeared that the lime reacted with the clay size portion of the soil to form reaction products that cement the soil particles together (24). Since then several investigators have established that the reaction products formed in the soil-lime reaction are similar to those formed during the hydration of portland cement (7,12,14,15,17,30,45,66).

Lime-Bentonite Reaction

The production of hydrates by a lime-clay reaction has been termed a "pozzolanic" reaction. A pozzolan is a siliceous or siliceous aluminous material which has little or no cementitious value, but will react with calcium hydroxide in the presence of moisture to form cementitious compounds (1,41). A pozzolan can be either a natural or artificial material.

The beneficial effect of lime on the workability and strength of clayey soils has long been recognized. However, it is only in the past few decades that the mechanisms by which this improved strength and workability are obtained have gradually become understood.

It now appears that the lime-clay reaction takes place in two steps. Davidson and Handy (11) suggest three basic reactions: first, the calcium ions cause a reduction in the plasticity of the clay; second, the lime may be carbonated by the carbon dioxide of the air resulting in the formation of a weak cement; and third, a cementitious reaction takes place between the lime and clay mineral. According to Hilt and Davidson (26) before any pozzolanic reaction takes place, the lime content of the lime-clay mixture must exceed the amount needed to modify the clay.

Studies made on the products of lime-clay systems have shown that calcium silicate and calcium aluminate hydrates are formed in various forms at temperatures ranging from room temperature up (17,18,25,45,66).

Several investigators have studied the strength characteristics of the calcium silicate hydrates and have characterized all the products as cementitious (33,42,48,55,62). Furthermore, the formation of calcium aluminate and calcium silicate hydrates during the hydration of portland cement is believed to be responsible for the strength and cementing ability of portland cement concrete (6,10,40), although the aluminates play a less significant role (6). The calcium silicate hydrate known as tobermorite gel, a poorly crystalline colloidal substance, has been called the "heart of concrete" (7). Jambor (30) found that the kind and microstructure of calcium silicate hydrate as well as the amount formed has an effect on the strength developed by hardened lime-pozzolana pastes. Studies have also been made comparing the amount of combined silica to the compressive strengths of sand-lime bricks, but no conclusions were reached (5).

Reaction Products

The major reaction products now recognized to be formed during the lime-clay reaction are tobermorite, CSH(I)[1], CSH(II), CSH(gel), calcium aluminate hydrates, and hydrogarnet (17,25,30,66).

The first four of these compounds are members of what is known as the tobermorite group of calcium silicate hydrates (57). The structure of tobermorite is similar to that of some clay minerals, particularly vermiculite (43,61). All members of the tobermorite group, however, do not have precisely the same structure. These calcium silicate hydrates, in addition to the structural similarities, also have the small particle size, large surface area, and a number of other properties analogous to clay minerals (12,58).

Tobermorite

Tobermorite is a platy calcium silicate hydrate with a composition approximating $C_5S_6H_{0-9}$(57). There are several known discontinuous hydration states of tobermorite, each with a characteristic c-axis spacing. The mineral exists normally with a c-axis spacing of 11.3 Å which may be collapsed to 9.3 Å by heating. A 14 Å variety, presumably having an extra layer of water molecules between adjacent layers, has been found naturally and has been synthesized. Crystalline 10 Å and 12.6 Å varieties have also been found but these phases have not been fully investigated (57). The 11 Å tobermorite has been shown to be the major constituent of the binding material in most autoclaved cement-silica or lime-silica products (17,33, 34,45). A typical X-ray diffraction pattern of the 11 Å tobermorite (34)

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[1] It is customary in cement chemistry to denote the following compounds by short symbols; CaO = C; SiO_2 = S; Al_2O_3 = A; Fe_2O_3 = F; MgO = M; H_2O = H. Thus $nCaO \cdot pSiO_2 \cdot qH_2O$ is represented by CSH.

is shown in Table 1.

Table 1. Representative X-ray diffractometer d-spacings for the tobermorite group of calcium silicate hydrates

Synthetic tobermorite (34)[a]		CSH(I) (58)[a]		CSH(II) (23)[a]		CSH(gel) (7)[a]	
d-spa., Å	Int.[b]	d-spa., Å	Int.[c]	d-spa., Å	Int.[b]	d-spa., Å	Int.[c]
11.1	10	12.5	vs	9.8	9	3.05	s,vb
5.4	2	5.3	vvw	4.9	2	2.79	wb
3.62	<1	3.04	vs	3.07	10	1.82	wb
3.51	<1	2.80	s	2.85	5		
3.33	2	2.4	w,d	2.80	9		
3.08	6	2.1	w,d	2.40	4		
2.97	3	1.82	s	2.20	1		
2.81	3	1.67	mw	2.10	1		
2.52	<1	1.52	vw	2.00	6		
2.43	<1	1.40	w	1.83	9		
2.27	1			1.72	1		
2.12	1			1.62	1		
2.06	<1			1.56	5		
2.00	<1			1.40	4		
1.84	3						
~1.82	1						
1.75	<1						
1.65	1						

[a] Source of data.

[b] Relative intensities on an arbitrary numerical scale: 10 being the strongest.

[c] Relative intensity: s, strong; m, medium; w, weak; v, very; b, broad; d, diffuse.

Kalousek (32) and Diamond (12) have studied isomorphous substitutions in tobermorite. It was found that no significant change in the X-ray diffraction pattern of synthetic tobermorite was caused by the incorporation of considerable amounts of aluminum, magnesium or iron ions into the lattice of the material. It was presumed that these ions substituted for silicon in the tetrahedral coordination, rather than for calcium in the structure, although this violates Pauling's rules.

A shift of basal spacing from 11.2 Å to 11.5 Å was shown in the X-ray diffraction pattern of Al-substituted tobermorite in a sample having 15 percent replacement of SiO_2 by Al_2O_3. Except for this, there was no definite proof that the ions actually substituted in the silica chains. Kalousek first reported the appearance of a hydrogarnet phase (C_3ASH_4) in his compositions prepared with more than 11 percent nominal Al-substitution.

Diamond observed that some disorder in the c-axis direction resulted from substitution of magnesium and iron (the ionic radii of both being substantially larger than aluminum), because the basal intensities of the (002) and the (222) peaks are approximately halved, while the strong peaks due to reflecting planes entirely within the unit layer, i.e. the (220) and the (400), are essentially unchanged in intensity.

Diamond also observed that certain new peaks (2.7 Å, 4.2 Å) appeared with all the substituents including aluminum, while others (1.95 Å, 7.0 Å) appeared only with the substitution of the larger ions, iron and magnesium.

CSH(I)

Calcium silicate hydrate (I) has been called "CSH(B)", the "fibrous phase", or "C/S 0.80 - 1.33 hydrate", etc. by different investigators. The designation "CSH(I)" is now most generally used. This phase, while not known to occur naturally, may be produced in a variety of ways, either hydrothermally or by reaction at room temperature, through the reaction of silica or silica sol with calcium hydroxide solution or reaction of sodium silicate solution with calcium salts (34,58,59).

Recent studies by Diamond (12), Glenn (17), and Wang (66) have shown that CSH(I) can be readily formed by reaction between lime and clay minerals at both room and elevated temperatures.

CSH(I) is a poorly crystallized gelatinous precipitate which is related structurally to tobermorite, but the exact structure is not known. Its composition varies, the C/S ratio is probably between 0.8 and 1.33 (35); the lower limit is well established but the upper one is less definite, and higher values up to 1.5 or even farther, have been suggested (59). Taylor (57) arbitrarily sets 1.5 as the upper limit and regards the semi-crystalline tobermorites prepared at room temperatures having a higher C/S ratio as CSH(II). Furthermore, this product is metastable and eventually transforms to tobermorite or other phases depending on the composition (34).

Regardless of C/S ratio, the X-ray diffraction pattern resembles that of tobermorite except that only a few of the strongest reflections can be observed. These are mainly ones with (hk0) indices. "Typical" data obtained by Taylor (58) are given in Table 1; similar results have been obtained by other investigators (12,21,34,47). A basal spacing is sometimes present in the region 10-13 Å; some investigators report this line as "very strong", while some list it as "very weak, very broad", and in a few cases it is absent entirely. This disagreement is caused by the fact that this basal spacing is often not observable on diffractometer equipment, but can be observed by film camera diffraction technique, which permits long-time exposure and hence more certain recognition of peaks of overall weak intensity (66). Diamond (12) recently reported a CSH(I) X-ray pattern which exhibits only 3.25 Å (w), 3.02 Å (w), 2.78 Å (w), 1.8 Å (w), and 1.66 Å (vw) peaks.

Aluminum may also substitute in the CSH(I) structure. The evidence for this was found by Diamond (12) in his differential thermal analysis pattern of CSH(I).

CSH(II)

Calcium silicate hydrate (II) is commonly abbreviated CSH(II), but "C_2SH_2", "hydrate II", "1.8 C/S hydrate", "$C_7S_4H_n$", etc. have also been used as designations. It denotes a lime rich phase, having a C/S ratio of at least 1.5 and probably up to 2.0, and a low degree of crystallinity, comparable with that of CSH(I) (16,35,57,58).

CSH(II) is formed as an intermediate product by hydrothermal reactions, usually below 200°C, between lime and silica (34,35). It appears that this is true even when the overall C/S ratio of the mixture is low; in that case CSH(II) is formed first and later reacts with more silica to give lower C/S ratio products. Evidence of the formation of CSH(II) by reactions of lime with clay minerals have been reported recently (17,66).

The X-ray diffraction pattern resembles that of CSH(I) except that the basal spacing of CSH(II) appears to be comparatively strong and fairly consistent between 9.8 and 10.5 Å, and the (060) line at 1.67 Å, present in CSH(I) is not found in CSH(II), while a new 1.56 Å line characterizes the presence of CSH(II) (16,35,47,59). A representative pattern given by Heller and Taylor (23) is given in Table 1.

No data has been reported on lattice substitution of CSH(II).

CSH(gel)

Calcium silicate hydrate (gel) is commonly abbreviated CSH(gel) but it has sometimes been called "tobermorite (G)" (G for gel) to imply its structural resemblance to natural or synthetic tobermorite, even though the crystal structure of this phase is unknown. It is a relatively high-lime phase having a C/S ratio usually at 1.5 or higher (7,58).

CSH(gel) is very poorly crystallized, having an X-ray diffraction pattern normally consisting of three lines; a very strong and very broad reflection, with a maximum at 3.05 Å, and two much weaker broad lines at 2.79 and 1.82 Å (Table 1) (7). These three lines correspond to three strongest (hk0) lines of tobermorite. Recently, however, only two lines at 3.03 and 1.82 Å were observed by Diamond (12). Kantro *et al.* (36) observed only a single broad diffraction band with the maximum in the vicinity of 3 Å.

Calcium aluminate hydrates

Compared with the calcium silicate hydrates, the calcium aluminate hydrates are relatively well crystallized. They occur frequently as products of portland cement hydration, and of the reaction between lime and aluminum bearing clay minerals.

Table 2 gives a few selected X-ray diffraction lines for the calcium aluminate hydrates that have been found in lime-clay reactions.

C_3AH_6 is usually formed at temperatures slightly above 50°C and is thermodynamically stable at room temperature (58,67). Its structure may be related to that of garnet, $Ca_3Al_2(SiO_4)_3$, by replacement of each $(SiO_4)^{-4}$ by 4 $(OH)^-$, giving $Ca_3Al_2(OH)_{12}$ (58).

C_4AH_{13}, C_2AH_8, and CAH_{10} are formed easily under appropriate conditions at room temperatures. It has been found that when C_4AH_{13} is in contact with aqueous solution it is actually in the form of C_4AH_{19}. C_4AH_{19} dehydrates readily with moderate drying at room temperature to give a mixture of α and β forms of a 13 H_2O hydrate. Drying over $CaCl_2$ results in the formation of a phase of C_4AH_{11} (52).

Table 2. Selected calcium aluminate hydrates

Composition	Crystal system	d-spacing, Å				Source of data
		Longest	Strongest three			
C_3AH_6	Cubic	5.14	2.30 (10)[a]	5.14 (9)	2.04 (9)	(47)
C_4AH_{19}	Hexagonal	10.6		-[b]		(52)
αC_4AH_{13}	Hexagonal	8.2	8.2 (vs)[c]	4.1 (s)	2.9 (m)	(52,67)
βC_4AH_{13}	Hexagonal	7.92	7.92 (vs)	3.99 (vs)	2.87 (s)	(8,52)
C_4AH_{11}	Hexagonal	7.4		-[b]		(52)
C_4AH_7	Hexagonal	7.4		-[b]		(52)
αC_2AH_8	Hexagonal	10.7	10.7 (10)	5.36 (8)	2.86 (7)	(47,52,67)
βC_2AH_8	Hexagonal	10.4		-[b]		(52)
C_2AH_5	Hexagonal	8.7		-[b]		(52)
$C_3AH_{11} \cdot CaCO_3$	Hexagonal	7.57	7.57 (10)	3.78 (4)	2.86 (3)	(9)
CAH_{10}	Hexagonal	14.3	14.3 (10)	7.16 (10)	3.56 (7)	(47)

[a] Relative intensities on an arbitrary numerical scale; 10 being the strongest.

[b] Data not obtained.

[c] Relative intensity: v, very; s, strong; m, medium.

Several phases iso-structural with C_4AH_{13} have some of the hydroxyls replaced by a different anion. The dimension of the structural element and essential features of the structure are unaffected. A wide range of anions can be incorporated but the ones most important to cement chemistry are $(CO_3)^{-2}$ and $(SO_4)^{-2}$ (58). Two phases in which the anion is carbonate are known; a natural mineral, hydrocalumite, and calcium monocarboaluminate, $C_3A \cdot CaCO_3 \cdot 11\ H_2O$. The latter is formed very readily from aqueous suspensions or supersaturated solutions at or below room temperatures when small amounts of CO_2, such as normally exist in the atmosphere, are present (58).

C_2AH_8 is structually related to C_4AH_{13} with certain $Al(OH)_3$ substitution for H_2O in the latter (31). On drying over $CaCl_2$, C_2AH_5 is formed (52).

The structure of CAH_{10} and its relation to the calcium aluminate hydrate is not clear (31). It occurs primarily at temperatures below room temperature (47).

Hydrogarnet

Hydrogarnets are solid solutions within the area

$$\begin{tikzcd}
C_3FH_6 \arrow[r, dash] \arrow[d, dash] & C_3FS_3 \arrow[d, dash] \\
C_3AH_6 \arrow[r, dash] & C_3AS_3
\end{tikzcd} \quad (63).$$

They occur as natural minerals and have been prepared hydrothermally from mixtures of C_3A and C_3S, C_3AH_6 and calcium silicate hydrates, and lime and clay minerals (63,66).

The three strongest lines of the diffraction pattern of a typical hydrogarnet are given in Table 3 (3).

Table 3. X-ray data for a typical hydrogarnet (3).

d-spacing, Å	I^a
2.68	100
3.00	80
1.61	80

[a] Relative intensities on an arbitrary numerical scale, 100 being the strongest.

Time, Temperature, Strength Interrelationship

As long ago as 1886 it was recognized that there was some relationship between curing temperature, curing time and strength of portland cement and lime-sand cement (64). Since that time other investigators have studied the interrelation of strength, time and temperature of concrete (4,49,50,51,56). Three principal approaches to the problem have been made. Bergström (4) suggested a "maturity" rule such that any given concrete would attain the same strength if $A(T - \theta)$ were constant. In this expression,

A = time of curing

T = curing temperature (°C)

θ = the temperature at which no increase in strength occurs.

Plowman (50) modified this to the form:

$$\text{UCS} = \text{Constant} + \log A(T - \theta).$$

Rastrup (51), after studying the hydration process based his "maturity" rule on the form: $\text{UCS} = f(T_a)$

where

$$T_a = \int_0^A 2^{(T - \theta)/10} \, dA.$$

T_a is the "maturity" at curing temperature T, after a curing time A.

The effect of curing temperature on the strength of soil-lime mixtures has also been studied (13,46). It was found in these studies that the effect of increased curing temperature was to increase the strength of the soil-lime mixtures at the same age. Metcalf (46) also showed that although none of the "maturity" rules above hold exactly for soil-lime mixtures, his results most nearly follow the rule proposed by Rastrup.

Metcalf (46) assumed that the reaction between lime or cement and clay could be represented by the Arrhenius equation:

$$k = B\ e^{-E/RT}$$

where

k = the reaction rate

E = the activation energy

R = the gas constant

T = the temperature (in °Absolute) and

B = constant

then plotted his results on the basis:

$$\log\ (UCS) = B' - B''/T(^\circ\text{Absolute})$$

where

B' and B" are constants.

He found that the results of cement-stabilized soils plot a constant slope over the range 0-65°C, indicating that the hardening action in that temperature range is essentially similar and independent of the type of soil.

For lime-stabilized clays, however, Metcalf found that not only was the slope of the curves different for the different clays but that there was an abrupt change of slope in the vicinity of 45°C. He made no comment concerning the change of slope at 45°C but did conclude that the lime-clay reaction responsible for the strength of the lime-clay mixture is not the same for all clay minerals.

MATERIALS

Bentonite is a clay formed by decomposition of volcanic glass. The predominate clay mineral is usually montmorillonite (44). The clay used in this investigation was a Ca-saturated montmorillonitic clay commercially produced as the "Panther Creek Southern Bentonite" from White Spring, Mississippi by the American Colloid Company. This bentonite contains approximately 56% SiO_2, 20% Al_2O_3, 8% Fe_2O_3, and 3% MgO as its main constituents.[1] The S/A ratio is approximately 4.75. The chemical formula of a similar bentonite from Amoy, Mississippi is listed in AAPG Reference Clay Minerals (37) as $(Al_{1.40}Fe_{0.32}Mg_{0.31})(Al_{0.12}Si_{3.88})\ O_{10}(OH)_2$ $(Na_{0.02}\frac{Ca}{2}{}_{0.28})$.

Montmorillonite is composed of units made up of two silica tetrahedral sheets with a central aluminum hydroxyl octahedral sheet. All the tips of the tetrahedrons point toward the center of the unit. The tetrahedral and octahedral sheets combine so that the tetrahedrons of each silica sheet and one of the hydroxyl layers of the octahedral sheet form a common layer. The atoms common to both the tetrahedral and octahedral layer are O instead of OH. The layers are continuous in the a and b directions and are stacked above one another in the c direction.

The units are stacked with the O layers of each unit adjacent resulting in a very weak bond and excellent cleavage. The outstanding feature of this structure is that water and other polar molecules can enter between the unit layers causing the lattice to expand in the c direction (20).

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[1] Information furnished by the American Colloid Company.

Isomorphous substitution of Al for Si in the tetrahedral sheets and/or Mg, Fe, Zn, Ni, Li, etc., for aluminum in the octahedral sheets is quite common. As can be seen by the chemical formula of the material used in this investigation, there is indeed isomorphous substitution in both the tetrahedral and octahedral sheets.

The lime used in the investigation was a powdered analytical reagent grade calcium hydroxide.

All water used in the preparation of specimens and in testing procedures was distilled by a Barnstead Automatic Water Still, No. SLH-2.

METHODS OF STUDY

In order to reduce the variables to a minimum, only one ratio of lime to clay was examined, and the amount of water was held constant. A C/S ratio of approximately 1.0 was chosen for the study because Wang (66) had established that this C/S ratio produced a variety of reaction products over the curing times and temperatures to be studied. The clay used in the investigation was chosen because some information concerning its reaction with lime had already been developed by Wang (66).

In general, the procedure followed in the investigation was to prepare 1 in. high by 1/2 in. diameter samples of the lime-clay mixture, cure them at the selected temperature for the selected times, then test them for unconfined compressive strength. Following the strength testing, all the broken samples of the same curing time and temperature were placed in a container and vacuum dryed over a mixture of $CaCl_2$ and Ascarite for a period of at least forty-eight hours. Following the vacuum drying the samples were ground by hand until the powder passed the No. 200 sieve. Representative samples of each mixture cured under different conditions were then scanned by X-ray diffraction for evidence of reaction product formation. Other representative samples were tested to determine the amount of calcium hydroxide, silica, and alumina present in the cured samples. The techniques used are explained in greater detail in subsequent paragraphs.

Molding and Testing of Specimens

The utilization of 1 in. high by 1/2 in. diameter strength test specimens results in considerable savings of time and materials. The results obtained reflect the cohesive strength of the lime-clay system, and are sufficiently valid for comparative studies. The molding apparatus has been described in detail by Roderick (53); the lime-clay mixture is compressed by hand into a cylindrical mold through a lever arrangement, and density and moisture content are controlled in the molded specimens.

In the present investigation, the specimens were molded to constant density at optimum moisture content for maximum density. This optimum moisture content and maximum density were determined by use of the Harvard Miniature Mold. The procedure used is described in detail by Wilson (68). The procedure is similar to that described by ASTM Designation: D 698-58 T (2) for the moisture-density relation of soils.

Proper amounts of lime, clay and water were hand mixed until a uniform mixture was obtained, then the amount of material required to attain the maximum density was weighed out and placed in the mold. Five specimens were used in each testing condition. After completion of specified curing, the specimens were tested by a proving ring type of compression apparatus, accurate to ± 25 psi, and the average of the five specimens was reported as the unconfined compressive strength.

Curing

After molding, the samples were placed on a rack inside an airtight hard plastic Lustro-ware bowl in which distilled water had been placed such that the water was not allowed to come in contact with the specimens. The tops of the bowls, although very tight fitting, were further sealed with cellophane tape to prevent the entry of carbon dioxide and the loss of moisture, before being placed in the appropriate curing chambers.

Electric ovens were used as chambers for the 40°C, 50°C, and 60°C curing. The 23°C curing was performed in a temperature-controlled humidity room. The 5°C curing was done in a small laboratory refrigerator.

X-ray Diffraction

A General Electric XRD-5 diffractometer was used for general investigation of powder samples for the presence of crystalline products and for the determination of the calcium hydroxide content of the cured mixture. Nickel filtered copper Kα radiation was used. The powder samples were mounted in disc-shaped brass rings with a pressure of 1000 psi in order to obtain a dense packing, avoid effects of preferred orientation, and give good reproducibility (54). To further avoid the effects of preferred orientation the discs were continually rotated while in the X-ray beam (22).

Determination of Calcium Hydroxide Content

The quantitative determination of the calcium hydroxide content of the cured mixture was made using the internal standard method outlined by Klug and Alexander (39).

Quartz powder was used as the internal standard. The standard series of mixtures for use in preparation of the calibration curve was made up from finely ground quartz powder, calcium hydroxide, calcium carbonate and the clay. The mixtures were placed in four-dram glass vials with small pieces of rubber and mixed in a Spex Model 8000 vibratory mixer/mill for five minutes to assure thorough mixing. Five samples of each mixture were then examined by X-ray analysis and the intensities of the d = 2.62 Å (calcium hydroxide) and d = 2.45 Å (quartz) reflections were compared. Because of the linearity of the curves and the reproducibility of the data, it was believed unnecessary to use additional mixtures.

In the determination of the intensities, allowances were made for the background intensity. Figure 1 shows a composite chart of the X-ray traces of quartz, calcium hydroxide, montmorillonite, and tobermorite for copper Kα radiation from 32° to 40° 2θ; the background under the calcium hydroxide peak at approximately 34.1° was assumed to be equal to the background at around 39°. Similarly, the background under the quartz peak at 36.8° was taken as a straight line connecting the background at 38.2° and 35.9°. These observations were used in the calculation of the intensities of the quartz and calcium hydroxide peaks as shown in Figure 2. A line was drawn connecting the intensity at 38.2° to the intensity at 35.9° and the distance from the quartz peak to this line was considered the peak intensity of the quartz. Another line was drawn parallel to the intensity at 38.2° and the distance from the calcium hydroxide peak to this line was considered the peak intensity of the calcium hydroxide. The heights were measured rather than areas because observations showed that there was no appreciable differences in line broadening. The resulting calibration curve is shown as Figure 3.

The quantitative analysis of the cured mixtures was carried out under the same conditions as the preparation of the calibration curve. In this case, 0.5 grams of ground quartz was mixed with 2.5 grams of the ground cured sample and the calcium hydroxide content found by comparison of the ratios of the intensities of the lines indicated above with those of the

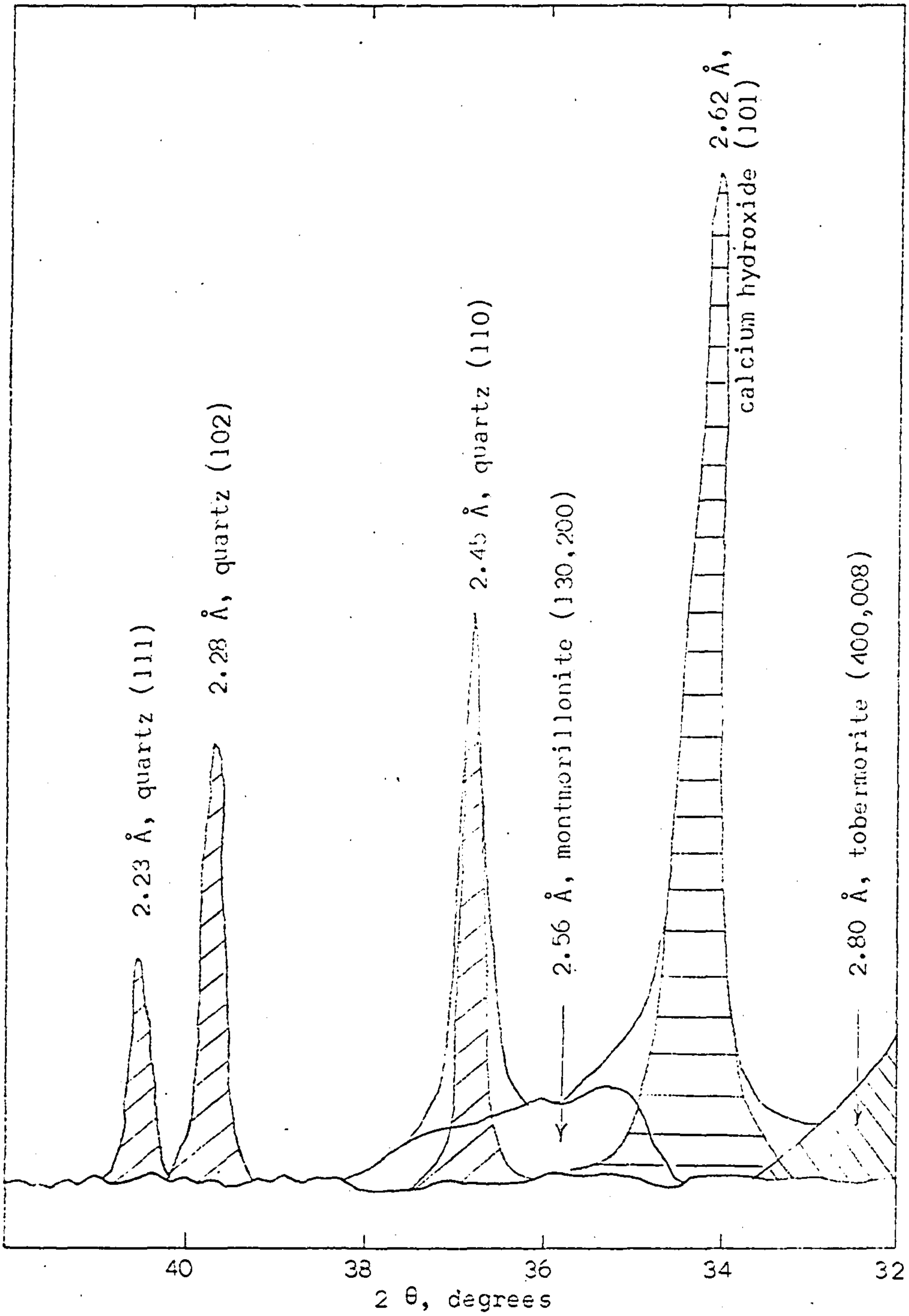

Figure 1. Composite chart of X-ray traces of quartz, calcium hydroxide, montmorillonite and tobermorite for copper Kα radiation from 32° to 40° 2θ

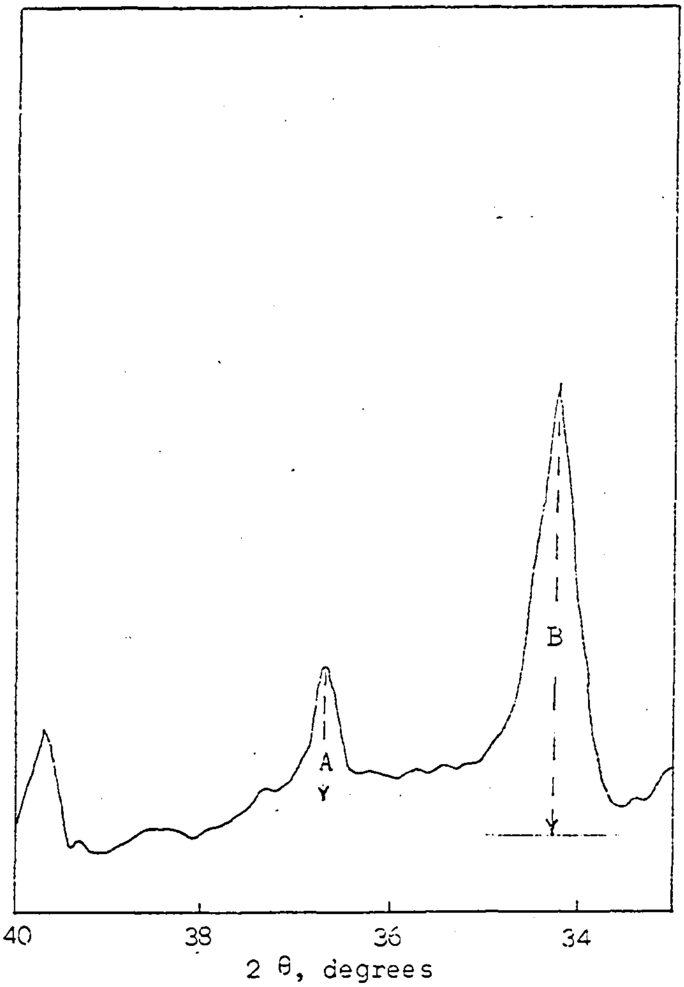

Figure 2. Example calculation of the intensities of the quartz and calcium hydroxide peaks

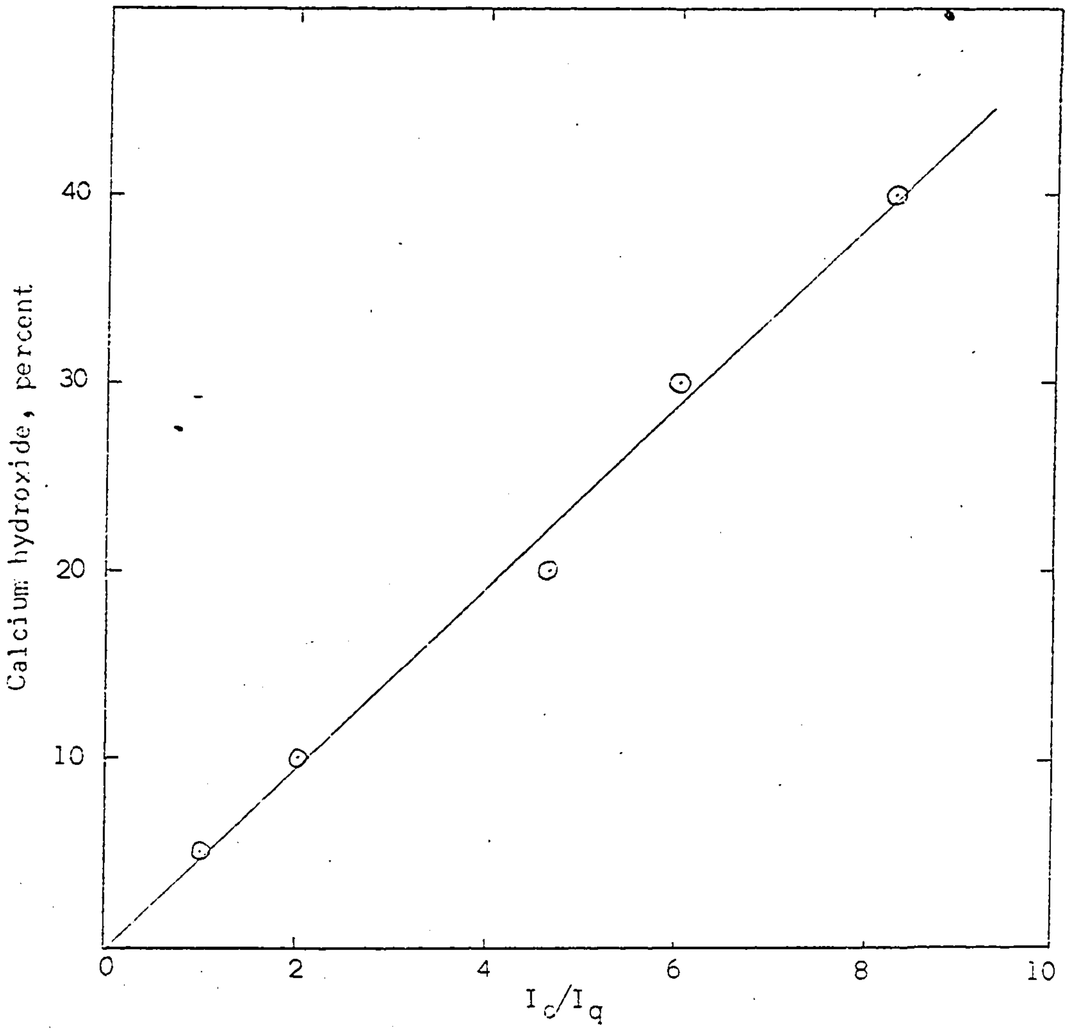

Figure 3. Calibration curve for determination of calcium hydroxide content of cured specimens by X-ray analysis

standard curve. The hygroscopic moisture content of the sample was determined and the calcium hydroxide content was reported as grams per 100 grams oven-dry mixture.

Determination of Silica and Alumina Content

The amounts of silicates and aluminates contained in the reaction products may be determined by chemical means because the reaction products are soluble in dilute HCl whereas the solubility of the clay mineral is negligible under certain conditions (40).

Preliminary tests for optimum conditions for extraction

Time of extraction   The procedure is designed to extract the maximum amount of Ca-silicates and aluminates formed but to cause the minimum dissolution of clay structure. Preliminary tests had shown that pure tobermorite prepared at 175°C in a saturated steam autoclave can be dissolved completely in a sufficient amount of 0.1 N HCl within 30 minutes by continuous shaking. It also has been shown that clay or soil samples are not subjected to any extensive breakdown under this condition.[1]

Proper Normality of HCl   The sample must be dissolved in HCl of such strength as to give a final supernatant pH of between 1 and 2. The pH is critical for two reasons. First, the rate of polymerization of silicic acid dissolved is a minimum in this pH range (29). Second, the aluminum ion is stable at this pH range, but slowly polymerizes and precipitates as $Al(OH)_3$ at a pH greater than 4. In addition, the strength

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[1] Ho, C., Soil Research Laboratory, Iowa Engr. Exp. Sta., Iowa State University of Science and Technology, Ames, Iowa. Solubility of Tobermorite in dilute HCl. Private communication. 1964.

of the HCl must be such that all the calcium silicates and aluminates are dissolved and at the same time a minimum amount of clay is dissolved. The optimum strength of the HCl used for extraction varies depending on the clay and the lime content of the lime-clay mixture. To determine the optimum acid strength for the lime-clay mixture used in the present investigation, a series of tests was made by shaking 0.5 grams of the sample in 50 ml HCl for 30 minutes. The results are shown in Table 4. The cured lime-clay mixture chosen for the determination had previously been determined to contain the least unreacted calcium hydroxide.

Table 4. Results of optimum HCl normality determination

Sample	HCl N	pH	SiO_2 dissolved gm/100 gm sample	Al_2O_3 dissolved gm/100 gm sample
Clay	0.00	6.0	0.018	0.000
Clay	0.10	1.5	0.018	0.094
Clay	0.15	1.4	0.220	0.189
Clay	0.20	1.1	0.180	0.265
Clay	0.25	1.1	0.200	0.472
Clay	0.30	1.0	0.250	0.510
Cured Lime-clay	0.00	11.7	0.200	1.965
Cured Lime-clay	0.10	3.7	7.70	3.250
Cured Lime-clay	0.15	2.0	12.70	5.442
Cured Lime-clay	0.20	1.6	12.20	5.442
Cured Lime-clay	0.25	1.45	12.00	5.744
Cured Lime-clay	0.30	1.3	12.70	5.744

From these data, after making allowances for possible experimental error, it was decided that an acid concentration of 0.20 N and a 30 minute shaking time best met all the criteria.

Sample extraction

A suspension of 0.5 grams of vacuum-dryed cured sample in 50 ml of

0.2 N HCl was placed in a 125 ml Erlenmeyer flask. The flask was placed on a vibratory shaker operated at approximately 400 rpm for 30 minutes. The residue was then immediately washed into a centrifuge tube and centrifuged at 16,000 rpm for 10 minutes to obtain a clear supernatant, which was then diluted to 100 ml with distilled water in a 100 ml volumetric flask.

Alumina determination

Modifying the procedure for determination of aluminum outlined by Vogel (65), a quantity of extract containing between 0.01 and 0.10 mg of aluminum in a 25 ml volumetric flask was diluted with 5 ml of a buffer solution. This buffer solution is made up of approximately 77 grams NH_4AC and 57 ml concentrated HAC per liter to give a pH of 4.5 (the amounts are given as approximate because they vary depending on the strength of the concentrated HAC). One ml of 0.2 percent Aluminon reagent was added and the mixture made up to 25 ml with distilled water and allowed to stand for 30 minutes before the color intensity was measured at 520 mμ on a Beckman Model B spectrophotometer. A calibration curve was prepared in exactly the same manner by using a standard solution made up of $AIK(SO_4)_2 \cdot 12\ H_2O$ to contain 0.01 mg/ml of aluminum. The aluminum content in each sample was determined from the calibration curve. The test gave the amount of dissolved aluminum but for ease in reporting and comparing the results this was converted to dissolved alumina. Correction for the hygroscopic moisture content of the sample was made and the results expressed in grams per 100 grams oven-dry mixture.

Silica determination

Following the procedure outlined by Govett (19), an aliquot of extract containing between 0.2 mg and 0.7 mg SiO_2 was added to a 25 ml volumetric flask, acidified with 5 ml of 1 N H_2SO_4 and further diluted with 5 ml of 0.3 M (with respect to $(MoO_4)^{-2}$) ammonium molybdate. The sample was then diluted to 25 ml with distilled water. The color intensity was measured at 400 mμ on a Beckman Model B spectrophotometer not sooner than two minutes nor later than ten minutes after the addition of ammonium molybdate. Calculation of the silica content was made by reference to a standard curve. The standard silica solution was prepared by dissolving sodium metasilicate ($Na_2SiO_3 \cdot 9\ H_2O$) in distilled water acidified with H_2SO_4 so that the final pH is about 1.5. Aliquots of the standard solution were used to prepare a standard curve up to about 1.0 mg SiO_2 per 25 ml. The silica content as determined from the standard curve was then corrected for the hydroscopic moisture content of the sample and the silica content reported in grams per 100 grams oven-dry mixture.

RESULTS AND DISCUSSION

Strength vs. Time and Temperature

Results

No significant loss of moisture was found in any of the samples cured at 5°C, 23°C and 40°C up to 56 days, 50°C up to 28 days and 60°C up to 14 days. Samples cured at 50°C for 56 days and at 60°C for 28 and 56 days seemed excessively dry and the containers were completely dry. This lack of excess water is believed to have critical effects on the strengths obtained and the formation of reaction products; therefore, data on the samples cured at those temperatures for those times were ignored.

Figure 4 shows the average and extreme unconfined compressive strengths as a function of curing time for the various curing temperatures. Except for the 3 day curve at 5°C, the figure shows an increase of strength with time at all temperatures with the greater rate of increase at the higher temperatures. This was as expected. The drop in strength for 3 day curing at 5°C appears to be due to experimental error.

Figure 5 shows the unconfined compressive strength as a function of log T_a; with $T_a = 2^{(T + 11.7)/10} A$, where T = curing temperature in °C and A = curing time in days. This function of time and temperature was chosen because Metcalf (46) showed that of all the "maturity" laws, this one gave the closest fit to the results of lime-caly stabilization. The T_a used in this expression is merely a simplification of Rastrup's (51) "maturity" rule, $T_a = \int_0^A 2^{(T - \Theta)/10} dA$, when the temperature at which the reaction ceases is considered to be - 11.7°C and the curing takes place at a constant temperature during the entire curing time. The temperature - 11.7°C

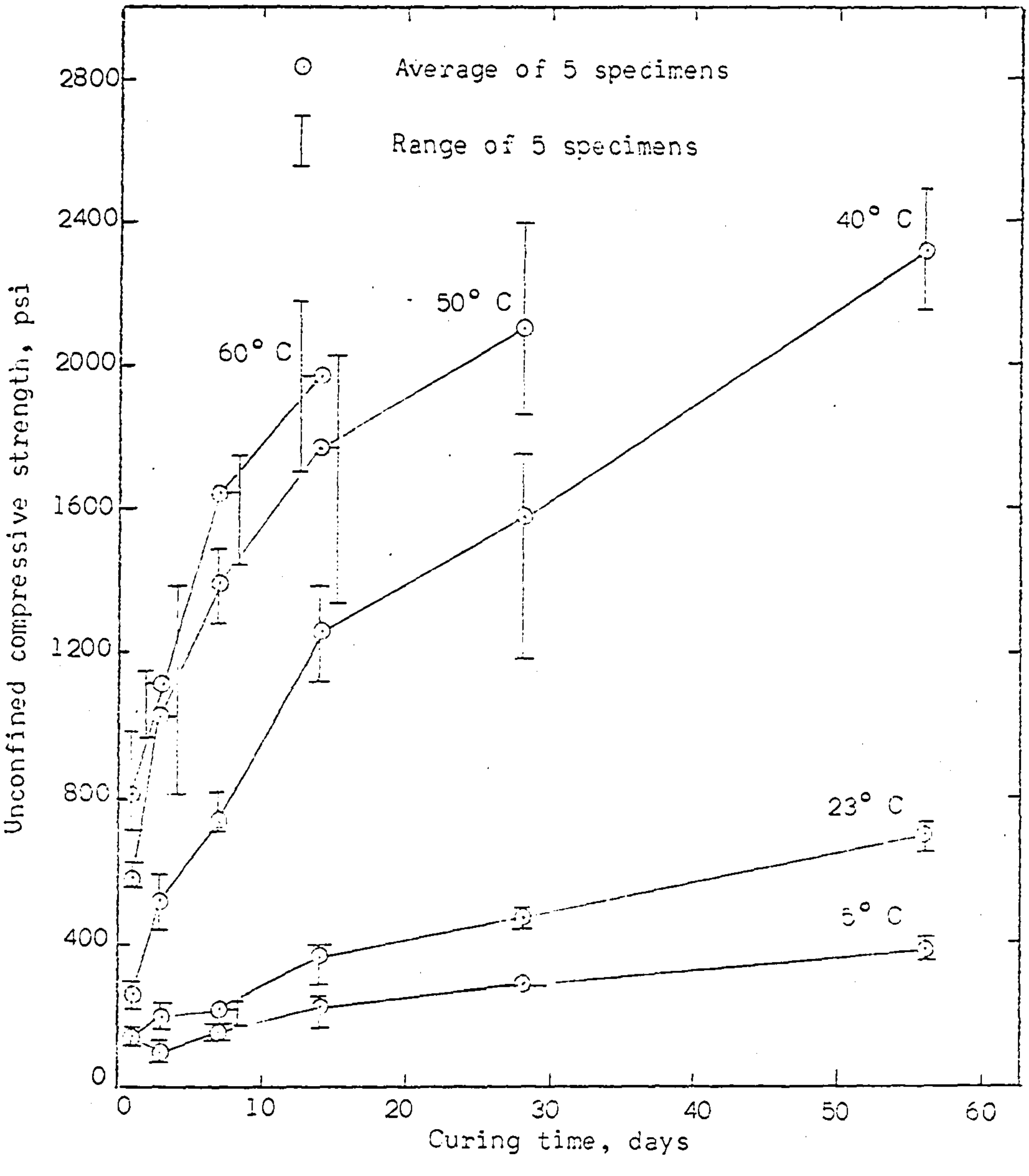

Figure 4. Relation of unconfined compressive strength to curing time for lime-clay mixtures cured at various temperatures

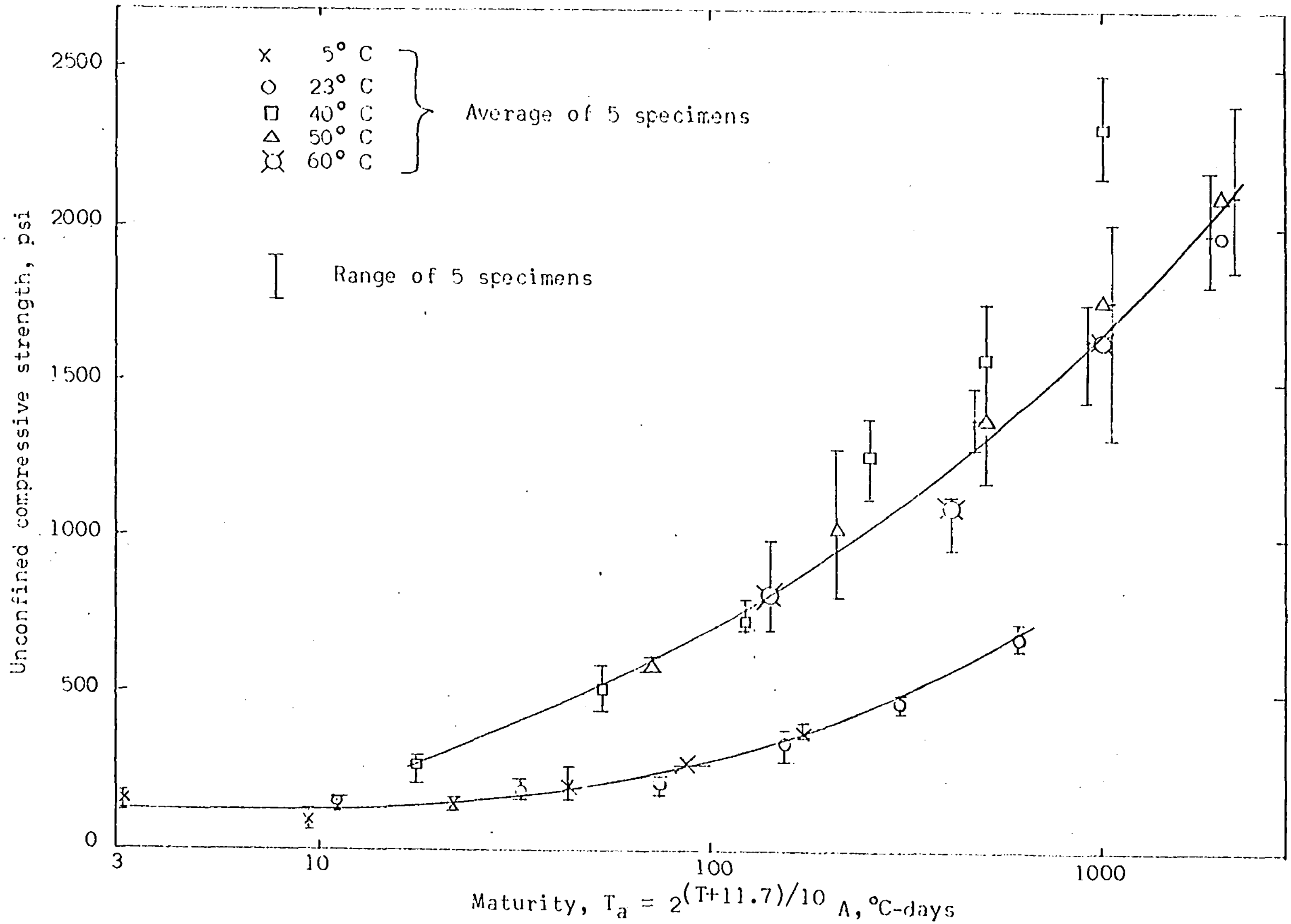

Figure 5. Relation of unconfined compressive strength to "maturity"

was chosen because Plowman (50) determined this temperature to be the datum temperature for concrete maturity calculations. Saul (56) had earlier chosen - 10°C for the datum on the basis of curve fitting. Plowman made his modification on the basis of direct measurements. A plot of the unconfined compressive strengths of the present investigation was made using - 10°C as the datum temperature and it was found that there was a great deal more scattering of points than when the - 11.7°C datum temperature was used. However, even with the increased scatter, the - 10°C datum temperature plot had all the characteristics of Figure 5.

Discussion

Examination of Figure 5 shows a grouping of points along two different lines. The lower line is formed by the unconfined compressive strengths of samples cured at 5°C and 23°C; the upper line by the unconfined compressive strengths of the samples cured at 40°C, 50°C, and 60°C. Plotting the average unconfined compressive strength as log (UCS) = B' - B"/T (°Absolute) in the fashion of Metcalf (46), Figure 6 shows a similar trend. If equal slopes are taken to indicate that the strength is due to a similar reaction, the following results: all curing times except 1 day curing produce the same reaction over the temperature range 5-23°C. For the 1 and 3 day curing this temperature range is extended to 40°C. In the range 40-60°C, 1 and 3 day curing produce another reaction. For the other curing periods a third reaction is responsible for strength development over the range 40-60°C. In the range 23-40°C either the second reaction or a combination of the first and third reactions is responsible for the strength development.

One tentative explanation is that a different reaction product is formed at different curing temperatures and that the cut-off temperature

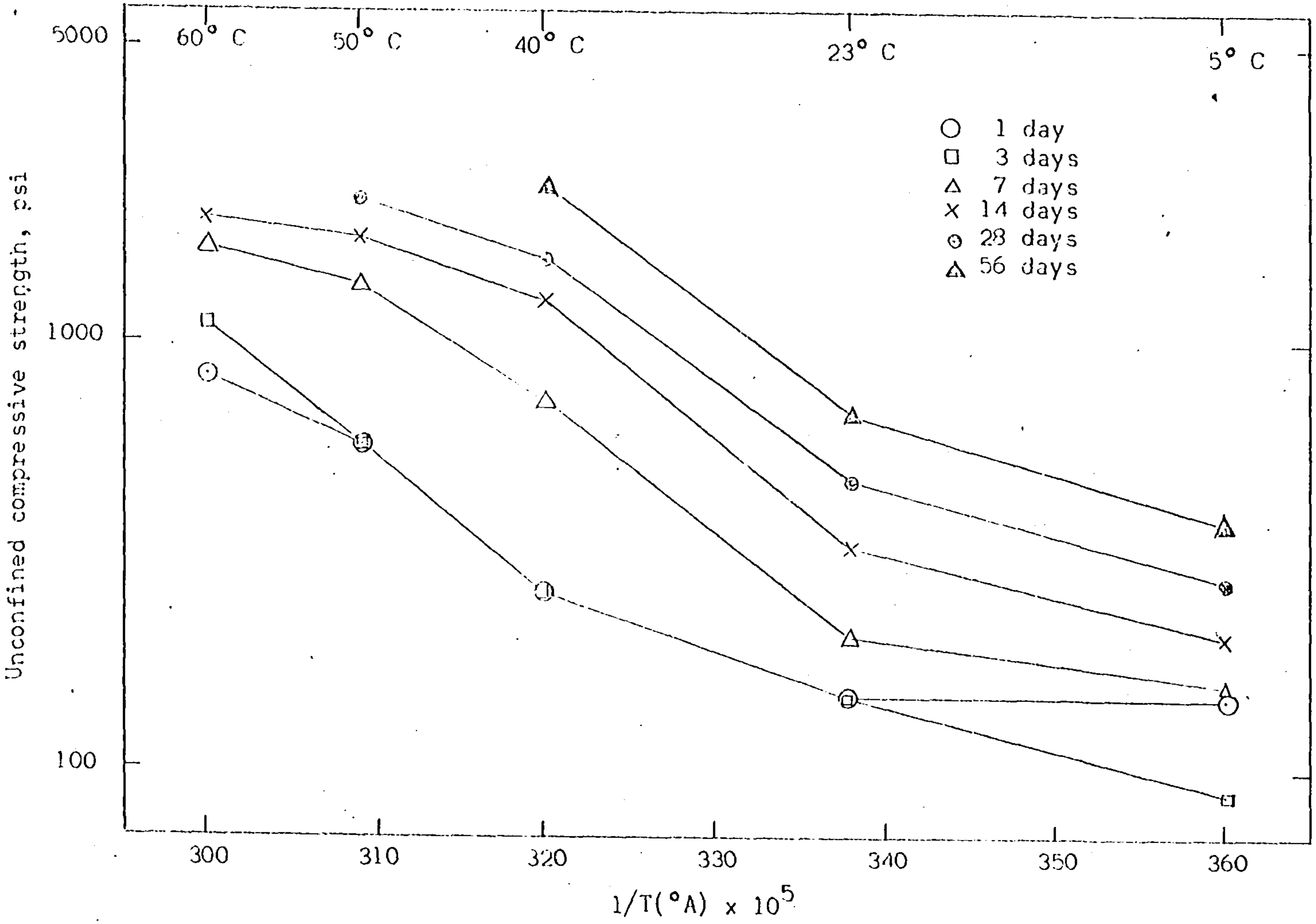

Figure 6. Relation of unconfined compressive strength to curing temperature after various curing times

lies between 23°C and 40°C. Wang (66) found with the same materials used in this investigation and C/S = 0.892, mixtures produced CSH(gel), CSH(I), hydrogarnet, and C_4AH_{13} when cured at 40°C for periods of 7 to 180 days, the products formed being dependent on the curing time. The same mixture composition cured at 23°C for periods of from 28 to 180 days produced only CSH(gel) and C_4AH_{13}. Glenn (17) also found, when investigating a similar bentonite-lime mixture with C/S = 0.69, that mixtures cured at room temperature for long periods produced C_4AH_{13}, CSH(I), CSH(gel), and possibly CSH(II). Mixtures of the same composition cured hydrothermally for short periods yielded; CSH(gel), CSH(I), and C_4AH_{13} at 40°C, and CSH(I), and possibly CSH(II) or aluminum substituted tobermorite at 80°C.

Another explanation is that a complex reaction is taking place. In support of this, Taylor (58) in discussion of lime-quartz paste reactions says that although many details of the reaction are obscure and others depend on the conditions of the investigation, the general picture seems to be clear: Reactions on the quartz surface initially give a lime-rich substance similar to CSH(II). When the overall C/S ratio is low, this reaction proceeds until all the lime is depleted; the CSH(II) then reacts with more quartz giving CSH(I), the C/S ratio of which eventually drops to 0.8. If the temperature and time are sufficient, the CSH(I) then recrystallizes to tobermorite. If the overall C/S ratio is below 0.8, the CSH(I) or tobermorite also reacts slowly with the unused quartz to give gyrolite.

If the lime-clay reaction is similar to the lime-quartz reaction, and on the basis of reaction products it appears that it is, then it would appear that a complex reaction is taking place. It also appears that this complex reaction is a consecutive reaction of the form $A + B \xrightarrow{k} C \xrightarrow{l} D$, in which k is the rate constant for the first step and l is the rate constant for the second step (38). With $l \geqq k$ no C will be formed, and if $l \ll k$ a negligible amount of D will be formed. Since k and l are temperature dependent, at some temperature where k is slightly larger than k, both C and D will be present. As time progresses the amount of D will build up whereas the amount of C will increase slower. Now if D contributes more to the strength of the mixture than does C, at some time when the amount of D in the mixture is great enough, the mixture will behave as though all of its strength was coming from D. At temperatures around room temperature and below only the first reaction would be taking place; at temperatures of 40°C and higher the second reaction will be taking place at relatively the same rate as the first, so that essentially there is very little if any of the first product formed.

In general, this consecutive reaction theory may be substantiated by data from Wang (66), who showed that CSH(gel) formed at low curing times and temperatures, and converted to another CSH phase with prolonged curing.

Figure 4 also confirms that even though it appears that the strength gain of the lime-clay mixtures cured at different temperatures is due to different phases of the complex reaction, it is possible to utilize accelerated curing methods to approximate the strengths of soil-lime mixtures cured at lower temperatures for longer times. However, the results of this investigation also point out that because of the differing reactions with lime and different soils, care must be exercised in the use of accelerated curing tests. Each soil that is to be subjected to accelerated curing should be investigated thoroughly to assure that disproportionate strengths are not achieved by accelerated curing.

Reaction Products

The analysis of the reaction products formed will be made on the basis of X-ray diffraction curves and data obtained from the spectrophotometer analysis of leachates. The results will be discussed according to the curing times.

Figure 7 shows the acid-soluble alumina after curing at various temperatures for various times, corrected for the 0.13 grams alumina per 100 grams oven-dry mixture found to dissolve from the natural clay. The alumina is expressed in grams Al_2O_3 per 100 grams oven-dry mixture.

Figure 8 shows the acid-soluble silica after curing at the various temperatures for various times, corrected for the 0.06 grams silica per 100 grams oven-dry mixture dissolved from the natural clay. The silica is expressed in grams SiO_2 per 100 grams oven-dry mixture.

<u>One day curing</u>

The X-ray diffraction curves for one day curing confirm that reaction products in the tobermorite hydrate group are formed at all temperatures, indicated by peaks at 3.07 and 1.82 Å. All curing temperatures also produce a slight amount of C_4AH_n, indicated by peaks in the regions of 7.5, 4.1, 3.99, and 2.88 Å. However, the mixture cured at 23°C gives the most definite peak in the region of 7.5 Å. The mixture cured at 60°C also has broad weak peaks at 3.03 and 1.97 Å. The additional peak at 3.03 Å probably indicates that there are two phases of the tobermorite group present in the cured mixture, i.e., CSH(II) and CSH(gel). The 1.97 Å peak

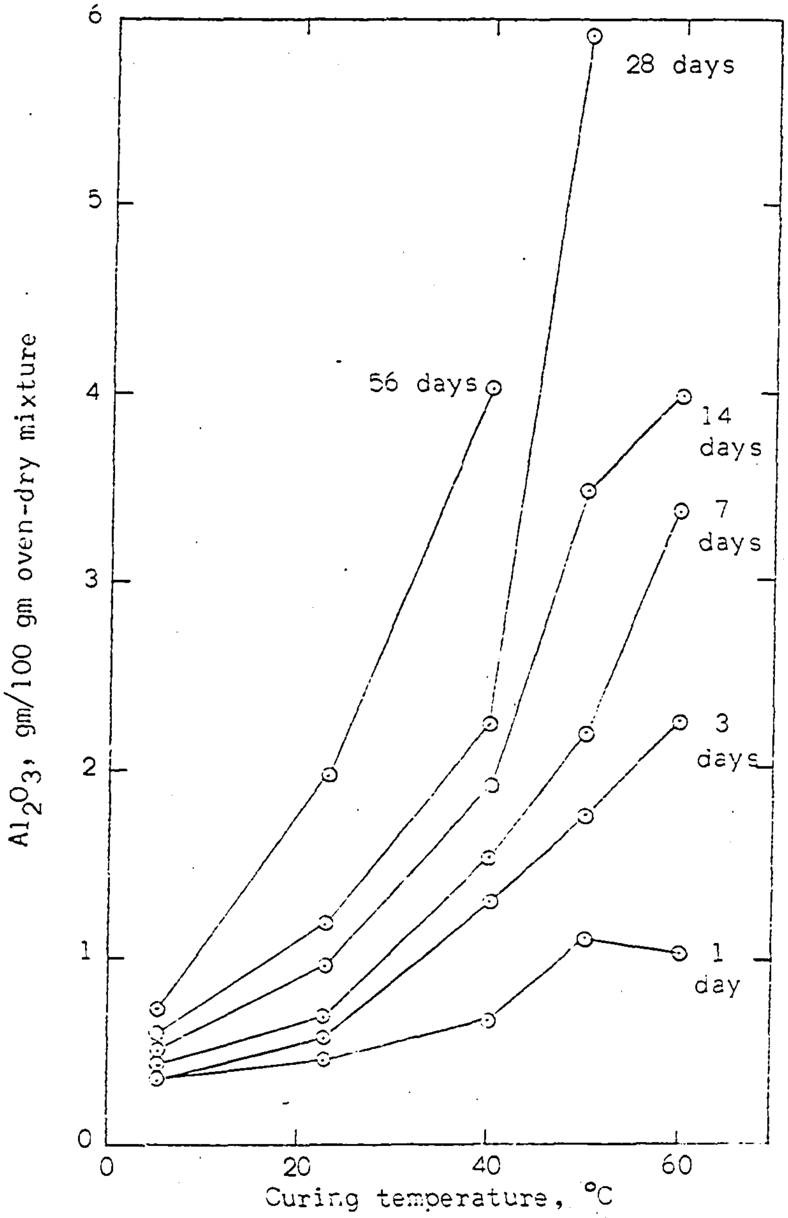

Figure 7. Acid-soluble alumina in specimens after curing at various temperatures for various times

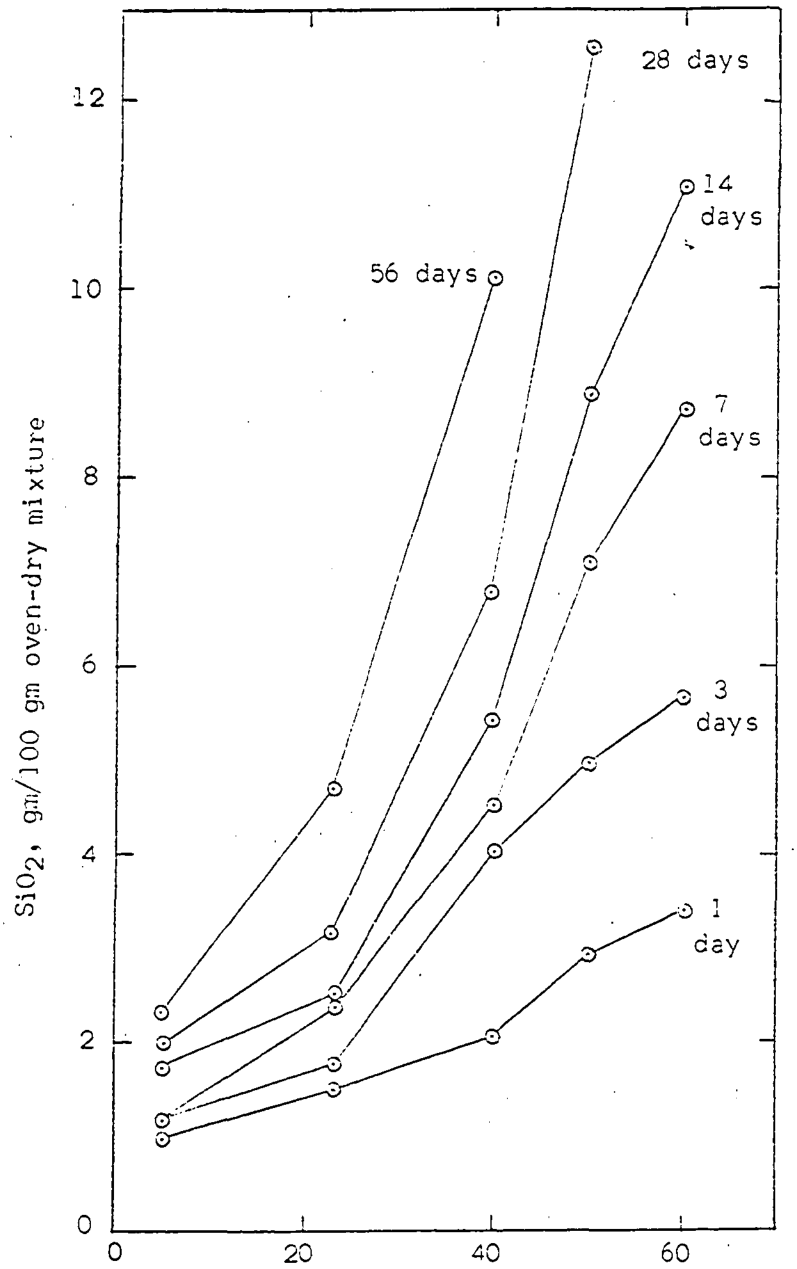

Figure 8. Acid-soluble silica in specimens after curing at various temperatures for various times

corresponds to a peak found by Diamond (12) in iron or magnesium substituted tobermorite; since no data are available on lattice substitution in CSH(II) or CSH(gel), this may indicate that some substitution is taking place in one or both of these.

At one day curing there is little difference in the amount of acid-soluble silica and alumina found after curing at 5°C and that found after curing at 60°C (Figures 7 and 8).

Three day curing

The X-ray diffraction curves for three day curing are essentially the same as those for one day curing, except that mixtures cured at all temperatures have weak peaks in the region of 10.5 - 9.8 Å, indicating the presence of CSH(II). The diagnostic 7.5 Å peak is missing from all curves but the other C_4AH_n peaks are still weakly present. The 1.97 Å peak does not appear in any of the curves but there is a broad hump in the region of 3.03 Å on all curves. The rate of increase of acid-soluble alumina and silica with respect to temperature is slightly greater for this curing time than it was for one day curing (Figures 7 and 8).

Seven day curing

The X-ray diffraction curves of this curing time are the same as those for three day curing, however, the 7.5 Å peak of C_4AH_n is quite evident at 50°C and 60°C curing temperature, but not at the lower temperatures. At these same curing temperatures the 1.98 Å peak indicating possible iron or magnesium substitution in the calcium silicate hydrate reappears. The rate of increase of acid-soluble alumina with respect to temperature is approximately constant between 23°C and 50°C but increases between 50°C and 60°C (Figure 7). The rate of increase of acid-soluble silica is constant from 5°C to 40°C but increases from 40°C to 50°C and then decreases slightly between 50°C and 60°C (Figure 8). The latter may be another indication of lattice substitution.

14 day curing

The X-ray diffraction curves again are the same as those for seven day curing. A noticeable feature though, is the change in shape of the curves for 50°C and 60°C curing temperatures at 3.07 Å. At shorter curing times this peak was relatively sharp, but now it has become very broad. At 60°C curing temperature additional peaks at 2.74 and 2.23 Å occur. The 2.74 Å peak is between a 2.78 Å peak reported by Diamond (12) for CSH(I) and a 2.7 Å peak also reported by him for aluminum substituted tobermorite. The 2.23 Å peak cannot be accounted for.

28 day curing

The diffraction curves for 50°C curing is the same as that of 60°C curing for 14 days, but the other curing temperatures do not exhibit any change from the 14 day curves. It should be noted that there is a great increase in the rate of increase of acid-soluble silica and alumina between 40°C and 50°C (Figures 7 and 8).

56 day curing

The X-ray diffraction curves for 56 day curing are the same as those for 28 day curing except that very distinct peaks appear on all curves in the region of 7.5 Å, indicating the definite formation of crystalline C_4AH_n.

Summary of X-ray data

No evidence of formation of hydrogarnet, ordinarily shown by peaks in the region of 2.68, 3.00, and 1.61 Å, was found in any of the X-ray diffraction curves.

A summary of the crystalline products diagnosed from X-ray diffraction are shown in Table 5. C_4AH_n is reported as present only where there are peaks in the region of 7.5 Å; at other times it is reported as probable, on the basis of other peaks.

Table 5. Summary of crystalline products observed from X-ray analysis

Curing Temp. °C	Curing Time					
	1 day	3 days	7 days	14 days	28 days	56 days
5	A?,G	A?,G,II	A?,G,II	A?,G,II	A?,G,II	A,G,II
23	A,G	A?,G,II	A?,G,II	A?,G,II	A?,G,II	A,G,II
40	A?,G	A?,G,II	A?,G,II	A?,G,II	A?,G,II	A,G,II
50	A?,G	A?,G,II	A,Ga,IIa	A,Ga,IIa	A,Ga,Ia,IIa	N.D.
60	A?,Ga,IIa	A,G,II	A,Ga,IIa	A,Ga,Ia,IIa	N.D.	N.D.

A - C_4AH_n

G - CSH(gel)

I - CSH(I)

II - CSH(II)

? - probable

a - probable lattice substitution

N.D. - not determined

At 5°C, 23°C and 40°C curing temperatures C_4AH_n, CSH(gel) and CSH(II) appear to be the stable phases. The same products appear at 50°C and 60°C curing temperatures, with probable lattice substitutions and CSH(I) appearing after several days of curing.

Examination of Table 5 also reveals that the X-ray diffraction curves gave supporting evidence to the theory advanced earlier, that the lime-clay reaction is a consecutive reaction:

$$\text{lime} + \text{clay} \rightarrow \text{CSH(gel)} \rightarrow \text{CSH(II)} \rightarrow \text{CSH(I)},$$

as evidenced by the trend indicated in the 50°C and 60°C curing; and that at any given time there may be more than one phase of the reaction present, depending upon the curing time and temperature.

C/S ratio of reaction products

Table 6 shows the apparent C/S ratio of the reaction products at the different curing times and temperature, based on the results of the X-ray diffraction determination of calcium hydroxide in the cured mixture, and the spectrophotometer determination of acid-soluble silica and alumina. These C/S ratios were computed after making these assumptions:

1. All the calcium hydroxide that disappears during curing is assumed to enter into the pozzolanic reaction.
2. All acid-soluble alumina is assumed to come from C_4AH_n reaction products.

The first assumption may be incorrect because as Hilt and Davidson (26) have shown, some of the lime is utilized in the modification of clay and hence does not enter into the pozzolanic reaction. Ho and Handy (27,28) have further shown that this lime does not show up on DTA curves, suggesting that the lime is adsorbed onto the clay structure. Since the exact amount of lime utilized in this manner could not be determined, the assumption was made to make a rough comparison rather than an exact determination of the reaction products' C/S ratio.

Table 6. C/S ratio of dissolved reaction products after assuming all acid-soluble alumina comes from C_4AH_n products and all calcium hydroxide that disappears is utilized in calcium silicate and calcium aluminate products

Curing Temp. °C	Curing Time					
	1 day	3 days	7 days	14 days	28 days	56 days
5	6.0	6.2	6.6	4.7	5.8	3.8
23	3.4	3.8	2.6	3.6	3.2	2.7
40	2.6	1.9	1.7	1.7	1.8	1.5
50	2.7	1.7	1.7	1.6	.9	-
60	2.9	1.8	1.2	1.3	-	-

The second assumption may also be in error because of the indication of lattice substitution in the reaction products. However, since the amount and type of substitutions that do occur cannot be accurately determined, the assumption was considered valid enough for comparison purposes. The assumption of formation of only C_4AH_n products seems valid on the basis of X-ray analysis and the fact that in this temperature range the tetracalcium aluminate hydrates are most likely to be formed (63).

The C/S ratios of the reaction products of the mixtures cured at 40°C, 50°C, and 60°C are all in the same range. Those of the mixtures cured at 5°C and 23°C are in an altogether different range. At this point it should be recalled that the C/S ratio of the tobermorite group of calcium silicate hydrates is in the range of 0.8 to 2.0 (60).

The validity of the first assumption is indeed questionable at low curing temperatures and short curing times, as the apparent C/S ratio is much higher than is believed possible for the tobermorite group (Table 6). Indeed, it is so much higher that it seems reasonable to take this as additional evidence that an appreciable amount of calcium is adsorbed onto the clay structure as suggested by Ho and Handy (27,28). At higher temperatures and longer curing times the effect of this erroneous assumption is reduced because of the dissolution of the clay and the accompanying release of the adsorbed calcium. It appears, however, that if allowances are made for errors due to lattice substitution and adsorbed calcium, that the apparent C/S ratios of the reaction products generally correspond to those expected from the X-ray analysis, i.e., of the order of 0.8 to 2.0.

S/A ratio of reaction products

Table 7 gives the ratio of acid-soluble silica to acid-soluble alumina at the different curing times and temperatures. Plots of these data against time, temperature, and unconfined compressive strength showed no consistent relationship except that all values of S/A are between 3.6 and 5.9 (Figure 9). The average is 4.76, or about identical with the S/A ratio of the clay, which is 4.75. This would suggest that at all temperatures the lime is reacting with the clay along edges of the sheets rather than on the flat surfaces, since if the reaction were taking place on the surface of the tetrahedral sheets the S/A ratio would be higher than 4.75. The close agreement of the S/A ratio of the dissolved reaction products to the S/A ratio of the clay also indicates that the chemical determination of the acid-soluble silica and acid-soluble alumina is valid.

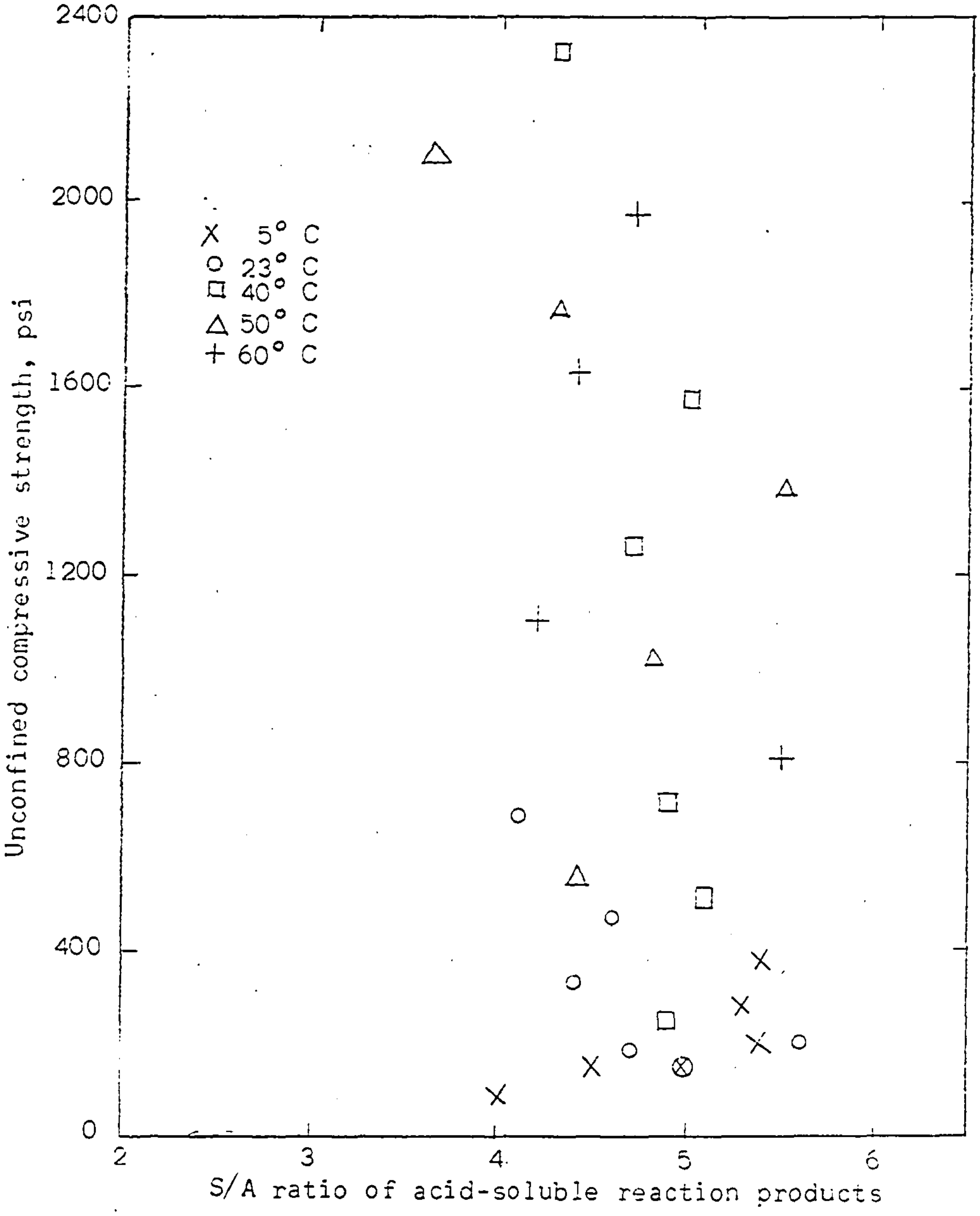

Figure 9. Relation of unconfined compressive strength to the S/A ratio of acid-soluble reaction products in cured specimens

Table 7. S/A ratio of dissoved reaction products at various curing times and temperatures

Curing Temp. °C	Curing Time						
	1 day	3 days	7 days	14 days	28 days	56 days	Avg.
5	5.0	4.0	4.5	5.4	5.3	5.9	5.02
23	5.0	4.7	5.6	4.4	4.6	4.1	4.73
40	4.9	5.1	4.9	4.7	5.0	4.3	4.82
50	4.4	4.8	5.5	4.3	3.6	-	4.52
60	5.5	4.2	4.4	4.7	-	-	4.70
Avg.	4.96	4.56	4.98	4.70	4.62	4.77	4.76

Relation of Strength to Reaction Products

Jambor (30) has shown that the compressive strength of a mixture is affected by the volume and by the kind and micro-structure of the cementitious hydration products developed. With this in mind let us examine the relationships, if any, of the various factors that have been determined in the investigation to the unconfined compressive strength of the cured mixtures.

As can be seen from Figure 9, the S/A ratio of dissolved reaction products has little or no effect on the strength of the cured mixture.

Figure 10 shows the unconfined compressive strength of the mixture as a function of the calcium hydroxide present in the cured samples. It is evident that the strength of the mixture is not a function of the calcium hydroxide alone, but that the temperature of curing has an effect on the strength of the mixture developed by the reaction of a given amount of calcium hydroxide. It is also evident that in the samples cured at 5°C and 23°C, the difference in temperature has little effect on the strength

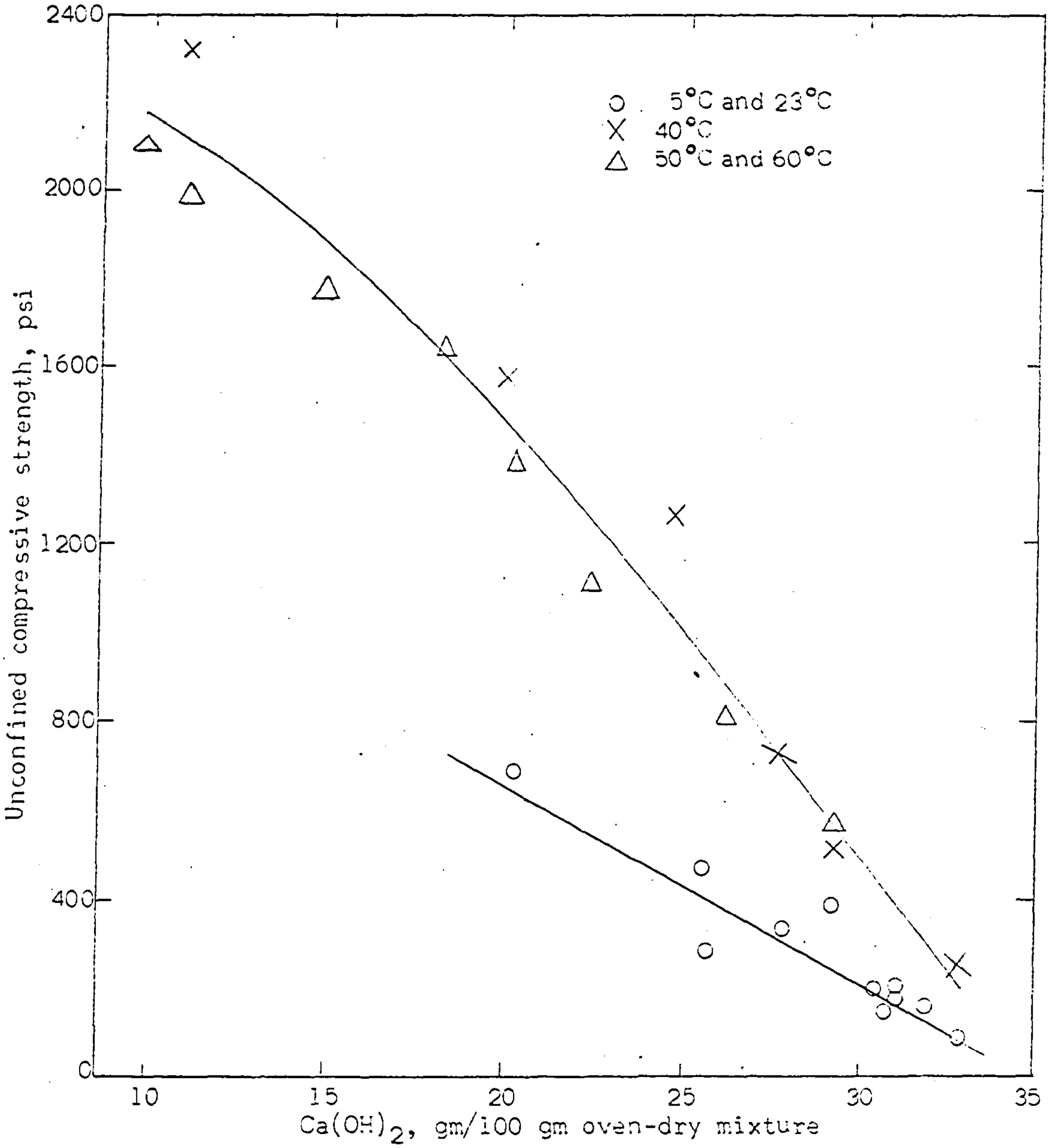

Figure 10. Relation of unconfined compressive strength to the calcium hydroxide in cured specimens. Prior to curing, the specimens all contained 41.6 gm Ca(OH)$_2$/100 gm oven-dry mixture, giving a C/S ratio of about 1.0

developed by the amount of disappearing calcium hydroxide. The same feature is noted in the samples cured at 40°C, 50°C, and 60°C. However, there is a noticeable difference in the strength developed by the disappearance of a given amount of calcium hydroxide between samples cured at 23°C and 40°C.

Figure 11 shows the unconfined compressive strength as a function of acid-soluble silica. Here again it appears that temperature plays a role in determining the strength developed by a given amount of silica. The samples cured at 5°C and 23°C follow one curve, the samples cured at 50°C and 60°C follow another, and the samples cured at 40°C follow still another.

Figure 12 shows the unconfined compressive strength as a function of acid-soluble alumina. The figure displays the same characteristics as Figure 11.

On the basis of these figures it can only be concluded that at a given curing temperature the cured sample that has the largest amount of acid-soluble silica or alumina, or the smallest amount of unreacted calcium hydroxide, will have the highest unconfined compressive strength. These figures also confirm that there is a different phase of the reaction responsible for strength development at 50°C and 60°C curing temperatures than at the 5°C and 23°C curing temperatures, but they do not explain the more efficient strength development in terms of acid-soluble silica and alumina with the intermediate 40°C curing temperature.

The average unconfined compressive strength as a function of apparent C/S ratio is shown in Figure 13. Although there is a large amount of scatter it is evident that for the production of high strengths it is

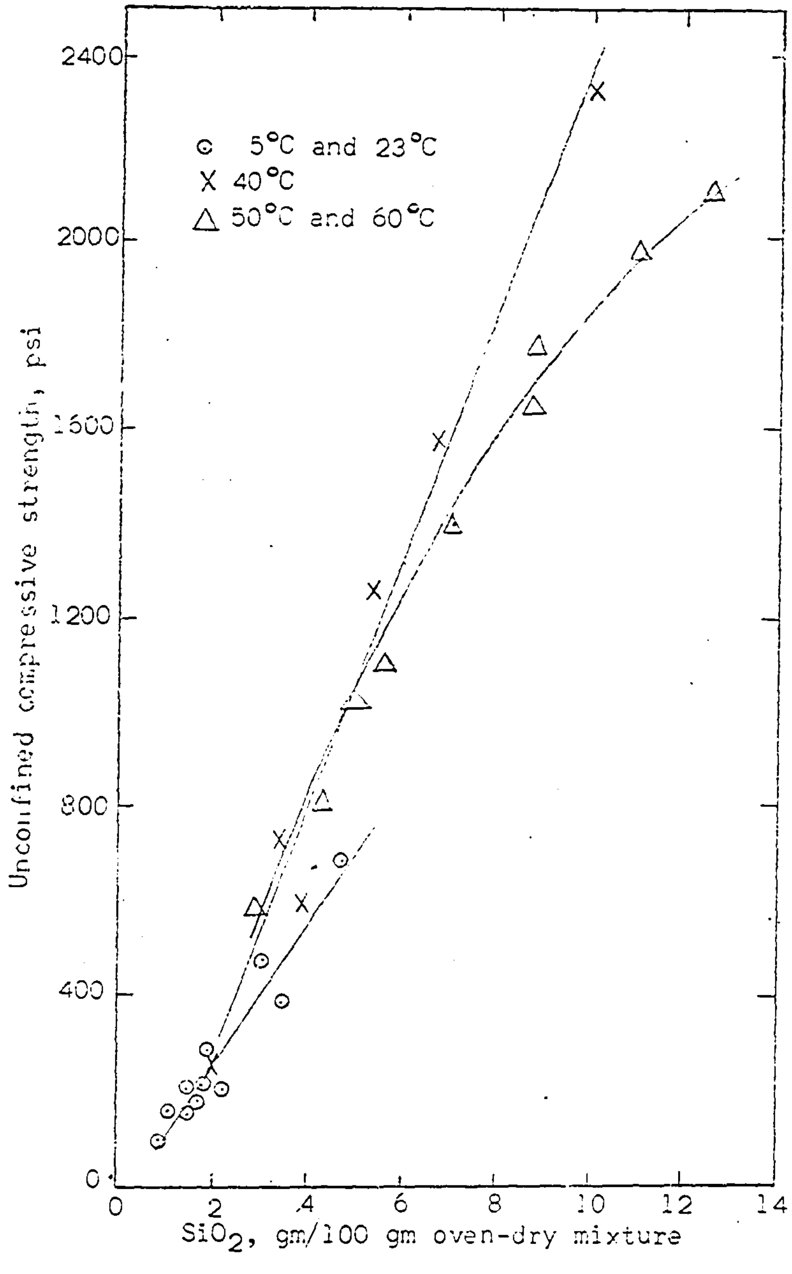

Figure 11. Relation of unconfined compressive strength to acid-soluble silica in cured specimens

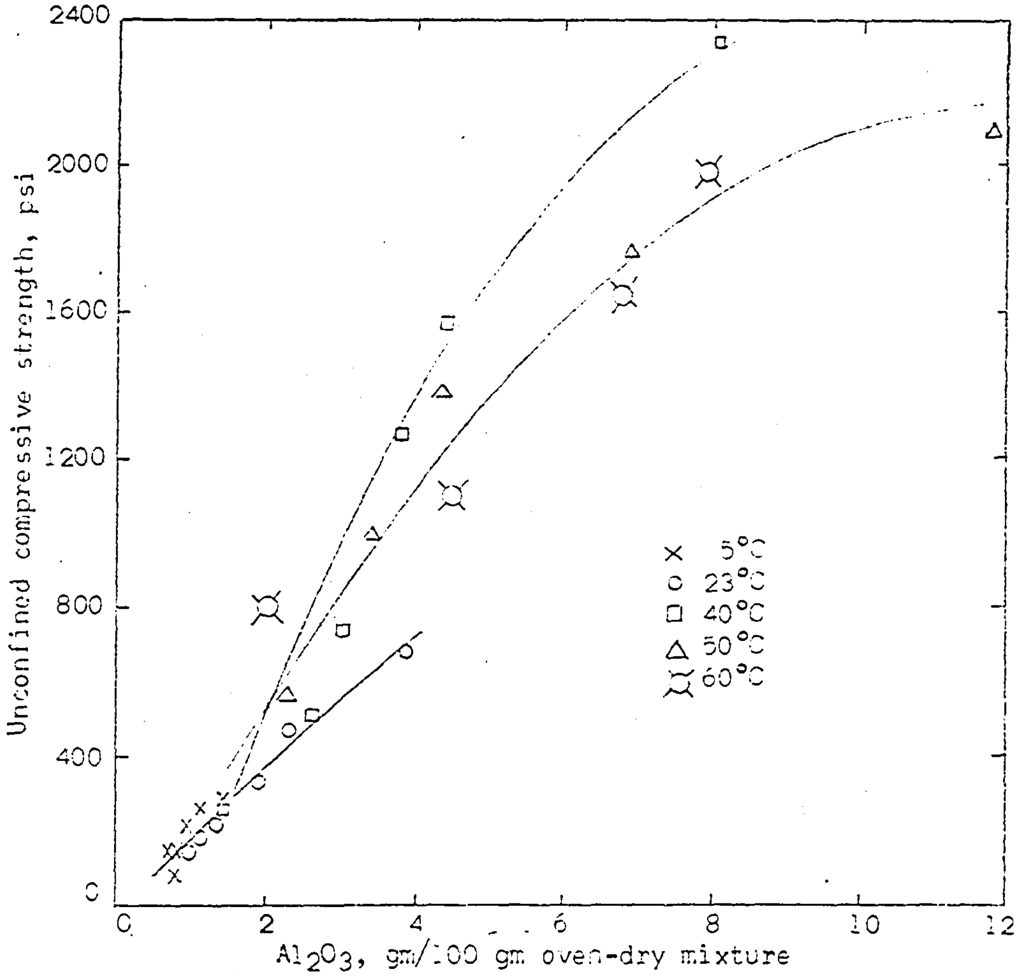

Figure 12. Relation of unconfined compressive strength to acid-soluble alumina in cured samples

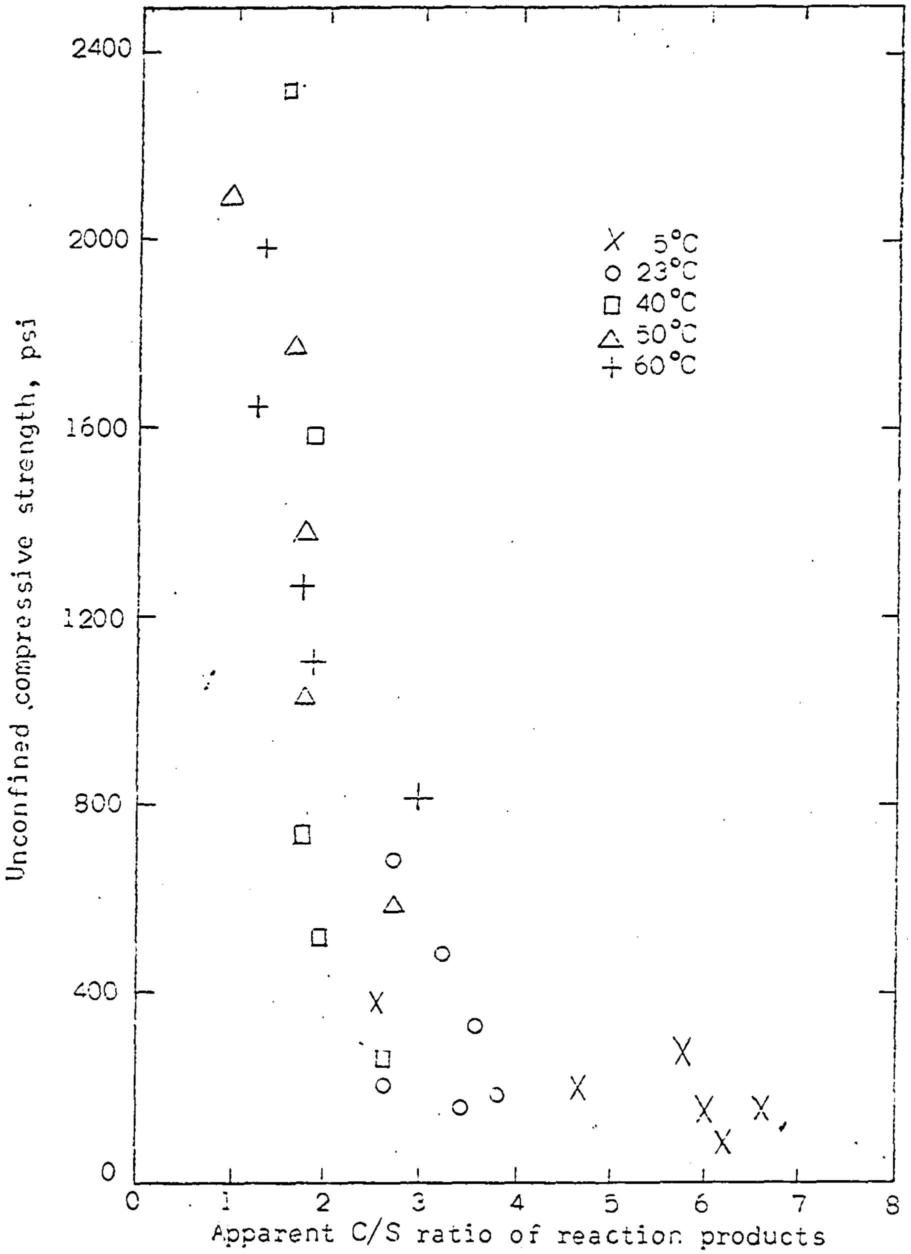

Figure 13. Relation of unconfined compressive strength to apparent C/S of reaction products in cured specimens

necessary to have an apparent C/S ratio less than two.

These low C/S ratios are produced at curing temperatures of 40°C and higher (Table 6). This probably accounts for the two distinct groupings of points in Figure 5.

It also appears that the farther the consecutive reaction proceeds the lower the C/S ratio becomes and the higher goes the unconfined compressive strength (Tables 5 and 6, Figure 4).

To summarize, the compressive strength of the mixture is affected by the crystalline structure as well as the amount of reaction products formed in the lime-clay reaction. This was evident from the more efficient strength development in terms of acid-soluble silica and alumina, and disappearing calcium hydroxide at the higher curing temperatures. This increased strength development was accompanied by a change in the number of crystalline reaction products detected by X-ray analysis. It appears that the S/A ratio of the reaction products has no apparent effect on strength developing potential of the reaction products, but the C/S ratio does.

CONCLUSIONS

Based on this investigation the following conclusions were reached:

1. The strength gain of lime-clay mixtures cured at different temperatures is due to different phases of a complex reaction.
2. This complex reaction is: lime + clay → CSH(gel) → CSH(II) → CSH(I) → tobermorite. The farther the reaction proceeds, the higher the strength.
3. At curing temperatures of 50°C and higher, lattice substitutions take place in the structure of the calcium silicate hydrates.
4. There is no consistent relationship between time, temperature, strength, and the S/A ratio of the reaction products.
5. The curing temperature has an effect on the strength developed by a given amount of silica in a cured lime-clay mixture.
6. At a given curing temperature the cured sample that has the largest amount of acid-soluble silica or alumina, will give the highest strength.
7. To achieve high strengths the apparent C/S ratio must be less than two.
8. Some calcium is adsorbed onto the clay structure rather than entering into a pozzolanic reaction as evidenced by abnormally high apparent C/S ratios at low curing temperatures.
9. The total S/A ratio of the lime-clay reaction products equals that of the clay mineral. This suggests that lime reacts with the clay along edges of the clay sheets rather than on the

flat surfaces.

10. Alumina in the reaction products occurs mainly in C_4AH_n at all curing temperatures; at curing temperatures of 50°C or higher, some alumina may substitute isomorphously in the calcium silicate hydrate structures.

11. It is possible to determine the amount of silica and alumina in lime-clay reaction products by spectrophotometer analysis with sufficient accuracy for comparison purposes.

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628