

*STUDIES OF VOLUME CHANGE
IN EXPANSIVE CEMENTS*

*FEBRUARY 1965
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by
T. J. AYLWARD

*Joint
Highway
Research
Project*

PURDUE UNIVERSITY
LAFAYETTE INDIANA

Final Report

STUDIES OF VOLUME CHANGE IN EXPANSIVE CEMENTS

TO: K. B. Woods, Director
Joint Highway Research Project

February 4, 1965

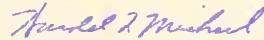
FROM: H. L. Michael, Associate Director
Joint Highway Research Project

Project: C-36-47J
File: 4-6-10

A final report "Studies of Volume Changes in Expansive Cements" by Thomas J. Aylward is attached. The research was conducted under the direction of Professor W. L. Dolch and the report was also used by Mr. Aylward in partial fulfillment of the requirements for the MSCE degree.

The plan of study for this research was approved by the Board on July 1, 1963. The report is submitted for the record as completion of the approved research.

Respectfully submitted,



Harold L. Michael, Secretary

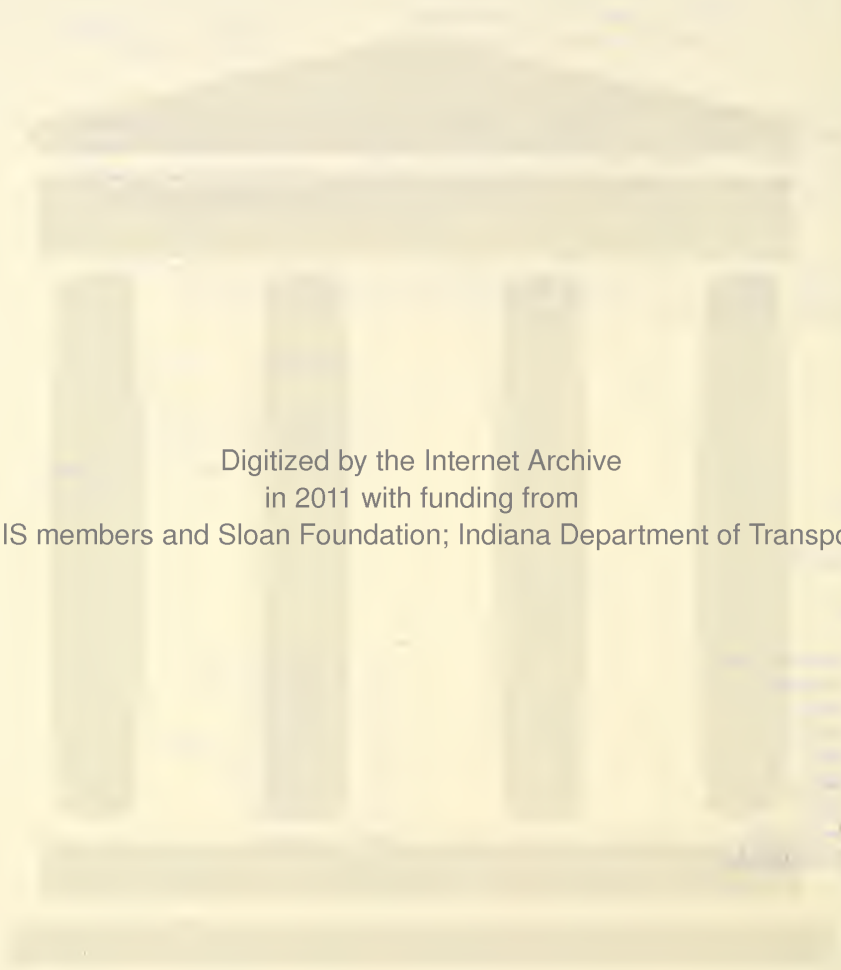
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by

Thomas J. Aylward
Graduate Assistant

Joint Highway Research Project

Project: C-36-47J

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Purdue University

Lafayette, Indiana

February 4, 1969

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Mr. Robert Nako performed a number of sample preparations and X-ray analyses.

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ABSTRACT

Aylward, Thomas John. M.S.C.E., Purdue University, January 1965.

Studies of Volume Change in Expansive Cements. Major Professor:

W. L. Dolch.

Expansive cements containing proportions of Portland cement, high-alumina cement, and gypsum were prepared. Pastes were made with these mixtures at two different water contents. The pastes were molded into small cylinders which were kept immersed in water. These cylinders were tested to determine their linear expansion, change in weight, and content of tricalcium aluminate trisulfate (ettringite) at various times. The ettringite was determined by quantitative X-ray diffraction.

The amount of ettringite, in general, increased very rapidly in the first few hours and then became more or less constant for a similar period. If the mixture contained sufficient gypsum the ettringite contents increased further after either the stripping of the mold or the onset of visible surface cracking.

The expansion was negligible at first and gradually became progressively greater to the point of disintegration of the sample. Visible surface cracking occurred at about two percent linear expansion, but the specimen remained intact to about ten percent expansion. The weight gain was of the same nature and relative extent as the expansion.

The results indicate that greater expansions are associated with greater amounts of real and potential ettringite and with

greater water contents, but the association is not simple. Much, but not all, of the relatively large amount of initially-formed ettringite is non-expansive in character. Limitation of water is probably an important factor in limiting the production of ettringite. Ingress of curing water to form additional ettringite is probably an important cause of expansion in these cementitious systems.

INTRODUCTION

Statement of the Problem

Several cement compositions have been used to produce concrete possessing expansive characteristics. These materials generally have been composed of certain combinations of Portland cement, gypsum, lime, blast-furnace slag, and high-alumina cement (HAC). By varying the proportions of the constituents it is possible to obtain a material that has no net volume change after shrinkage or one that is expansive and can be used in a self-stressing application.

Understanding of these materials has been hampered because the work performed to date has been largely empirical in a effort to find useful and economical applications. Factors influencing the magnitude and rate of the expansion include chemical composition of the components, fineness of the reacting phases, ratio of water to cementing materials, conditions of curing, and degree of restraint.

The nature of the changes that take place during expansion has been in question from the beginning of the use of expansive cements. The chemical and physical composition of the products formed, the kinetics of their formation, the changes that take place on drying, and the role of water are all topics necessary to the adequate understanding of these cements.

It is generally agreed that the expansion of these materials, whether of the desirable sort expected in anti-shrinkage or self-

stressing applications or the undesirable sort associated with sulfate attack on concrete, is brought about by the production of ettringite, $3\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot 3\text{CaSO}_4\cdot 32\text{H}_2\text{O}$.

The rate of ettringite production during early stages of hydration is presumably an important factor in the volume change characteristics of these cements. The purpose of this investigation was to determine the relationships between the volume change of expansive cement combinations during the early stages of hydration and the production of calcium sulfoaluminate therein.

Literature Review

This review is an outline of previous work in the field of expansive cements. It is intended to give the reader insight into the mechanisms associated with both detrimental and useful effects of these materials.

In this paper the conventional abbreviations of the chemical formulae of the compounds found in cements will be used. They are as follows: C = CaO, S = SiO₂, A = Al₂O₃, F = Fe₂O₃, M = MgO, K = K₂O, N = Na₂O, H = H₂O, $\bar{\text{C}}$ = CO₂, $\bar{\text{S}}$ = SO₃. In this notation tricalcium silicate, Ca₃SiO₅ or 3CaO·SiO₂, is C₃S; hydrated tetra-calcium aluminate, 4CaO·Al₂O₃·13H₂O, is C₄AH₁₃, etc.

Expansive cements are directly associated with the problem of sulfate unsoundness and its associated excessive volume change. This unsoundness, or slow expansion due to the cement phase in concrete, can be attributed to three causes (1). Crystalline magnesium oxide can cause large expansions when present in excessive amounts in cements. Since MgO reacts slowly with water this expansion

may not develop until considerable time has elapsed. An excess of hard-burned lime can also cause this same effect. As with magnesium oxide, hard-burned lime reacts slowly with water, causing the concrete to crack after it has thoroughly set. In contrast, soft-burned lime reacts rapidly while the concrete is still plastic and causes no adverse effects.

The third and most common cause of unsoundness is an excess of sulfate. This material causes expansion by the formation of hydrated calcium sulfoaluminates, mainly ettringite. Ettringite has a high molecular weight (1254) and a large water content (44-46%). It is commonly found in long, needle-shaped crystals. Calcium sulfate is always present in Portland cement since gypsum is interground with almost all Portland cement to control the set. This material has no destructive effect under ordinary conditions. The quantity present is small (less than 5%) and calcium sulfoaluminate is formed mostly while the concrete is still plastic. Difficulty arises when the concrete is exposed to sulfate-bearing waters. The sulfate from these waters then combines with calcium and aluminate constituents present in the cement and may bring about the destructive formation of ettringite. This reaction can be of such magnitude that complete disruption of the concrete will occur.

The problem of sulfate attack was first recognized in Europe in the last century. It was, however, during the 1880's before products were developed to combat the problem. These resembled the present day high alumina cements (2) and were prepared by a process of reacting bauxite, siliceous materials, and lime in a kiln. In 1918 the French

manufactured the first successful commercial product. Although it was primarily developed for sulfate resistance, it possessed the additional property of rapid hardening. These cements have, however, the undesirable properties of high shrinkage, low strength under hot, wet conditions, high heat evolution and low resistance to alkalis.

It might seem that high alumina cements (HAC) should have low resistance to sulfate action, since they have a high aluminate content and a molar lime to alumina ratio of approximately one. Such cements would therefore have readily available lime and alumina to combine with sulfate and form ettringite. Such, however, is not the case, and high alumina cements have proven their resistance to sulfates in soils, sea water, and industrial liquors. According to Lea (3) various theories have been offered to explain these phenomena. One factor may be an absence of free calcium hydroxide in hydrated HAC in contrast with the situation for Portland cement.

Lafuma (3) has proposed that direct combination of a cement compound in the solid state with a substance in solution leads to expansion, but when the cement compound passes first into solution, reacts, and then precipitates as a solid, no expansion occurs. Lafuma further proposed that calcium sulfoaluminate formation in Portland cement due to the action of sulfate solutions is a reaction of the first type. This explanation is plausible because free calcium hydroxide in hydrated Portland cement paste renders hydrated calcium aluminates insoluble. The hydrated calcium aluminates in high alumina cements are slightly soluble in water when free lime

is not present and therefore the reaction may be of the second type in such cements.

The primary reason for the resistance to sulfate action of HAC, however, appears to be that the aluminate compounds are simply immune to attack, rather than any difference in the type of reactions. This is substantiated by the fact that chemical analysis of concrete in a sulfate environment shows very little sulfate present (3). This can be explained by the presence of alumina gel which forms a protective film around the hydrates which is not readily dissolved (3).

Of the three possible mechanisms for producing expansion, only sulfoaluminate will produce a controllable expansion (4) and is the reaction of which advantage is taken in the production of "expansive" cements. In these materials calcium sulfoaluminate, mainly ettringite, is produced during the early stages of hydration while the paste is still plastic (5). The paste can, therefore, undergo expansion without harmful effects.

The useful application of these cements come from the ettringite production after set. By controlling composition, water content, and curing conditions (4) it is possible to obtain a concrete that has an initial expansion about equal to the shrinkage that is normally associated with concrete on drying, thereby creating a material with a low volume change. It is also possible to obtain an overall expansive material that is suitable as a "self-stressing" agent for prestressed concrete.

Lossier is credited with the commercial development of expansive cements. According to Lafuma (6) the cement of Lossier is made by

intergrinding 70% Portland cement clinker with 20% granulated blast furnace slag and 10% "calcium sulfoaluminate cement." The last material was obtained by burning a finely-ground mixture of 25% chalk, 50% gypsum and 25% bauxite. The resulting product consisted of about 38% calcium sulfate, 38% aluminates, ferrites and aluminoferrites, and 20% gamma-dicalcium silicate, with smaller amounts of other substances. Lafuma also commented that this sulfoaluminate cement is essentially made up of the same components as a mixture of HAC and gypsum. Blast furnace slag is said to act as a stabilizing agent that absorbs excess sulfoaluminate.

This cement, as do all cements using the formation of ettringite for expansion, requires an abundance of water during the initial curing period. Such French cements have been in use since 1940 and are said to possess sulfate resistance superior to ordinary Portland cement and about the same as that of high-alumina cement. This material has a lower heat of hydration than HAC, and does not suffer the loss in strength associated with HAC when cured up to 50°C. Klein in his review (7) stated that this is not the case, and that these cements have poor resistance to waters containing sulphates. Furthermore, he said that aggregates used should contain no soluble sulfates. These cements may be difficult to control.

Commercial expansive cements are now manufactured in the Soviet Union, where extensive research has been conducted (5). The Russians have grouped these cements into two general categories - waterproofing and self-stressing expansive cements.

According to Mikhailov (5) the principal uses of waterproofing

manufactured the first successful commercial product. Although it was primarily developed for sulfate resistance, it possessed the additional property of rapid hardening. These cements have, however, the undesirable properties of high shrinkage, low strength under hot, wet conditions, high heat evolution and low resistance to alkalis.

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expansive cements are for caulking, patching, and other repair work where watertightness must be assured.

It is stated that layers as little as 3.5 cm. thick can be placed directly on damp surfaces and will promptly stop water seepage. The waterproofing quality of these cements may be due to the disruptive effect of ettringite growth that effectively destroys the natural pore system of the concrete. These cements were first developed in 1942, and are made by dry grinding artificial hydrocalumite, gypsum, and HAC. The first compound, artificial hydrocalumite (C_4AH_{13}) was obtained by joint hydration of high-alumina cement and lime, followed by drying and grinding. It should be noted that this synthesis of C_4AH_{13} could not be repeated in the present study using HAC manufactured in the United States. Stoichiometric amounts of Lumnite HAC (assumed mostly CA) and lime were reacted, and the product was oven dried and ground. The resulting product, when examined by X-ray analysis, contained a large amount of free lime and some C_3AH_6 and C_4AH_{13} .

The expansion process of these cements is caused by rapid formation of calcium sulfoaluminate during the early stages of hydration, which levels off after the paste is set. The expansion after set is at a rate that compensates for normal shrinkage. According to Mikhalov (5) these cements are rapid-setting, reach a high strength in several hours and withstand high hydrostatic pressure without any signs of water transmission. He also stated that the degree of expansion is largely regulated by a change in the proportions of the components.

Waterproofing but non-expansive cements are another type in the general class that is now manufactured in the U.S.S.R. This material has a lower gypsum and higher C_4AH_13 content than the expansive type. According to Mikhailov (5) this material gives little expansion in humid storage and is characterized by rapid setting and hardening, instantaneous watertightness, and relatively low strength.

Self-stressing cements were more recently developed in the Soviet Union. These cements are composed of finely-ground Portland cement clinker, high-alumina cement, and gypsum. Again according to Mikhailov (5), this material, cured under the proper conditions, acquires sufficient strength and expands against the restraint of the reinforcement and thereby creates a self-stressed condition. Any Portland cement in amounts of from 60 to 70% to which high alumina cement and gypsum have been added in the proper proportions is said to make self-stressed cement. As in all expansive cement, the water-cement ratio and curing conditions are important. These cements are made with 25 to 30% water and cured at elevated temperatures to accelerate sulfoaluminate formation and hydration of the silicate components. They therefore have a higher strength with less expansion than samples cured in the usual way.

In the United States Klein and Torxell (7) developed an expansive cement suitable to prestress concrete containing high strength steel. This material consists essentially of a blend of Portland cement of high C_3S and low C_3A content with an expansive component obtained by grinding a clinker of calcium sulfoaluminate composition. The latter is produced by burning calcite, gypsum and bauxite.

Klein, Karby and Polivka (8) have investigated these materials and stated that free lime and low water-cement ratio are essential in the initial formation of ettringite. These factors insure that the solution will remain supersaturated during the initial stages of ettringite production and expansion. Klein, Karby and Polivka in this same study investigated Klein's expansive cement under various conditions of restraint. They found that this material can produce self-stress when properly restrained, even with the reduction in strength accompanying expansion.

Klein and Lin (9) have published a recent article in which they reported tests of pressure pipes and one- and two-way slabs made with Klein's expansive admixtures. They conclude that structural behavior of these materials can generally be predicted by the elastic and plastic theories of structural analysis. These cements, as well as the French and Soviet expansive cement are subject to aeration and must be packaged in moisture-proof bags to prevent deterioration of their useful properties.

Monfore (4) recently reported investigations of certain properties of expansive cements composed of Portland cement, gypsum and HAC. These compositions are of the general type of the Russian "self-stressing" cements. In Monfore's work, mortars were used to evaluate effects of composition, water-cement ratio, curing time and temperature of curing water on strength, free expansion, shrinkage and development of stress in restrained specimens. The greater the rate of expansion, the greater was the maximum expansion. Expansion decreased as the specimen cross-section increased. He also stated

that mixes with high gypsum and HAC contents had a low expansion when cured in water at 160°F, presumably because most calcium sulfoaluminate was produced while the material was still plastic. Expansion decreased with increasing water-cement ratio between 0.25 and 0.30. Bars cured at 73°F showed a substantially higher expansion than did bars cured at 170°F for 24 hours and then cured further at 73°F. Bars made with 4-6% gypsum and 4-10% Lumnite HAC had relatively the same shrinkage after the maximum expansion was reached, even though this expansion varied from 0.12 to 1.88%. The shrinkage was comparable to that of mortar bars made from ordinary Type I Portland cement under the same curing conditions. Tests were also conducted on the self-stressing abilities of these materials, and it was found that the stress built up to a value of 350 psi at 88 days and then fell off to 150 psi after two years. This result indicates that the material undergoes creep.

Various other investigations have been conducted in the field of expansive cements, mainly by Russian workers. Owing to the language barrier and difficulty in obtaining literature, only a brief outline of these works is presented from information obtained from Chemical Abstracts.

Kozielski (10) described four Russian high-expansive cements and their methods of manufacture. The first class has been previously discussed, and are known as waterproofing expansive cements. He describes another cement made by adding 30% gypsum to high-alumina cement composed mainly of CA and $C_{12}A_7$. This mixture is said to have less tendency to form cracks. Another composition is described

composed of 70 to 80% blast-furnage slag, 8 to 9% Portland clinker, 3 to 5% HAC and 5 to 15% hemihydrate. This cement is said to be especially suited for pressure grouting and oil wells. A fourth cement is made by burning at 800 to 900°C a mixture composed of 3 to 7% dolomite, 31% lime, and 21% magnesium oxide, and adding this material to self-stressing or waterproofing expansive cements. This material is said to have the advantage of ease in application and of low cost.

Skramtaev and Kravchenko (11) conducted a 5 year-long testing program on gypsum-alumina expanding cements. This paper is noteworthy since they stated that a 1:2 mortar would withstand 130 freezing cycles while a 1:2:5 concrete could withstand 170 and retain more than 82% of the original strength. They also stated that corrosion of the reinforcing bars, produced in the first 3 to 7 days, did not increase on further storage for five years.

Budnikov and Kozyriva (12) described a cement that expands without the formation of calcium sulfoaluminate. This material is prepared by adding calcined dolomite (containing MgO) as the expanding agent to hydraulic cement. Guizburg and Veseseojug (13) made tests to determine the effects of water-cement ratio, storage conditions and additives on cement mixes made with gypsum and expanding cements. Mchedlov-Petrosyan and Filatov (14) described a cement made by adding 0.01% aluminum powder and a small amount of sulfite waste to ordinary Portland cement, with the sulfite waste serving as a retarder of the lime-alumina reaction. This material is said to give a small amount of swelling but has a low initial strength. The author also described

a similar cement, but with the addition of 2% calcium chloride and 2% aluminum sulfate.

Budnikov (15) patented an expansive cement made with a hydraulic binder and an expanding material composed of clay or kaolin burned at 700-800°C, lime and Portland cement. The dry ingredients were then mixed with water, and after hardening and drying, ground and mixed with an equal amount of hemihydrate.

Approach Used in this Work

Pastes and mortars made with gypsum, Type I Portland cement and Lumnite HAC were used in this work. Length changes were measured by means of a micrometer caliper on small cylindrical bars. X-ray diffraction samples were obtained at various times from paste bars identical to those used for length change determinations. A quantitative X-ray analysis was performed on these samples, using a quartz internal standard, to determine the amount of ettringite formed. Weight changes were also determined on similarly prepared paste bars.

EXPERIMENTAL WORK

Materials

Type I Portland cement (laboratory designation 317), Lumnite high alumina cement, and reagent grade calcium sulfate dihydrate (gypsum) were used as the major constituents of the samples. The chemical analyses of the Portland and Lumnite cements are given in Appendix A. The gypsum was finely ground to break up lumps that were originally present in the material. Graded Ottawa sand (ASTM Designation: C 109) was used for all mortars.

Synthetic ettringite was used to prepare a calibration curve for the determination of the amounts of this material in the hydrated paste samples by quantitative X-ray diffraction analysis. Ettringite was prepared by a method similar to that described by Lea and Desch (17). Stoichiometric amounts of reagent aluminum sulfate and calcium hydroxide were added to a large excess of water. The solution was rolled in a glass bottle on a roller mill for approximately four hours. It was then allowed to stand for twenty-four hours, was filtered, and the residue was dried with acetone and ether. At the time the calibration curve was determined an ignition loss was performed on the ettringite. This time was approximately three weeks after the material was prepared. It was found that the ettringite contained 28 moles of water rather than the 32 of the usual formula. Fresh ettringite was prepared that had an ignition loss indicating 32 moles of water. Various points on the standard calibration curve were checked with this fresh material, and it was found that there was no change in the curve.

Fine quartz used as an internal standard was prepared by a sedimentation process. An amount of finely ground silica was allowed to settle in a large volume of water for thirty-three minutes. At this time the top four and one half inches of solution was drawn off. This material had a theoretical maximum size of 8.3 microns as determined by the usual Stokes law calculation. The suspension was evaporated to dryness, and the residue was ground to break up loosely held aggregates that formed during heating.

Sample Preparation

Various proportions of Portland cement, Lumnite cement, and gypsum were used to make paste and mortar bars. These bars were then investigated to determine their expansive characteristics. The compositions used and the numbers assigned thereto are shown in Figure 1 and Table 1.

The dry materials for paste samples were mixed for one minute with a laboratory stirrer. Distilled water was then added, and the paste was mixed by hand for one minute and by the stirrer for an additional minute. The paste was then placed in the molds and vibrated on a vibrating table for approximately 30 seconds to remove entrapped air. Molds were placed directly in water which was at a temperature of $20^{\circ}\text{C} \pm 2^{\circ}\text{C}$.

Molds used to make specimens are shown in Figures 2, 3 and 4, and consisted essentially of three parts. A small cylinder of plastic was split longitudinally into two equal sections and pinned at two opposite corners to promote stability. The two sections were then held together by means of an adjustable hose clamp. The bottom disk

MIX DESIGNATION	PHASE - COMPOSITION - PERCENT		
	PORTLAND	LUMNITE	GYPSUM
1	92	4.75	3.25
2	73	16	11
3	66	20	14
4	59	24	17
5	42	34	24
6	66	26	8

TABLE I.

MIXES USED IN THE TESTING PROGRAM.

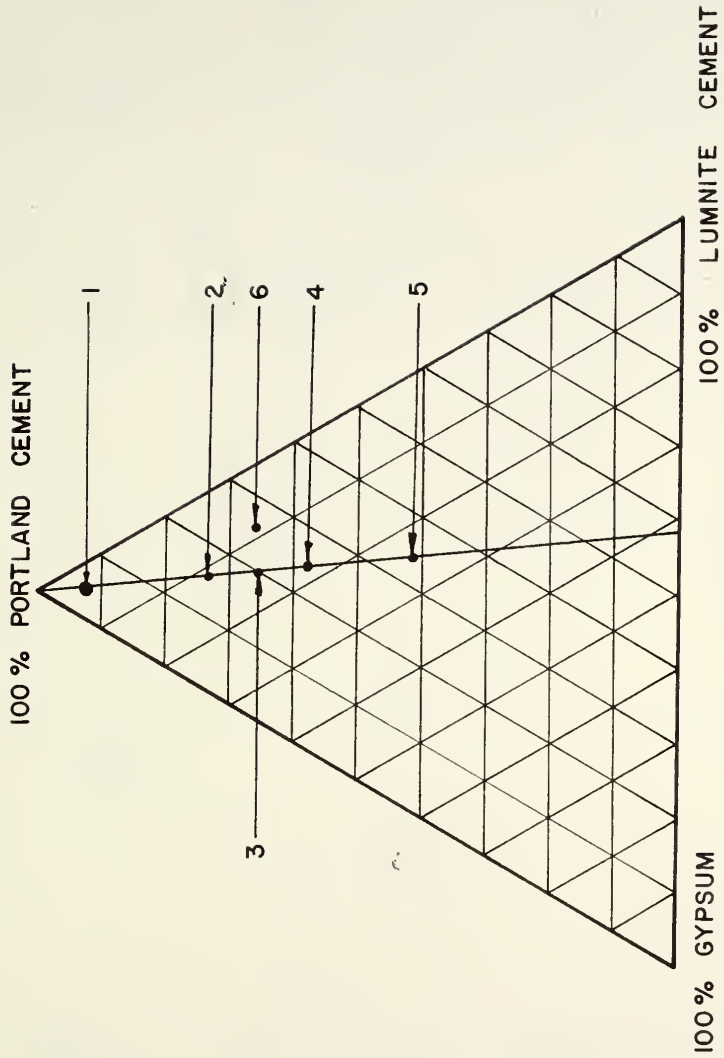
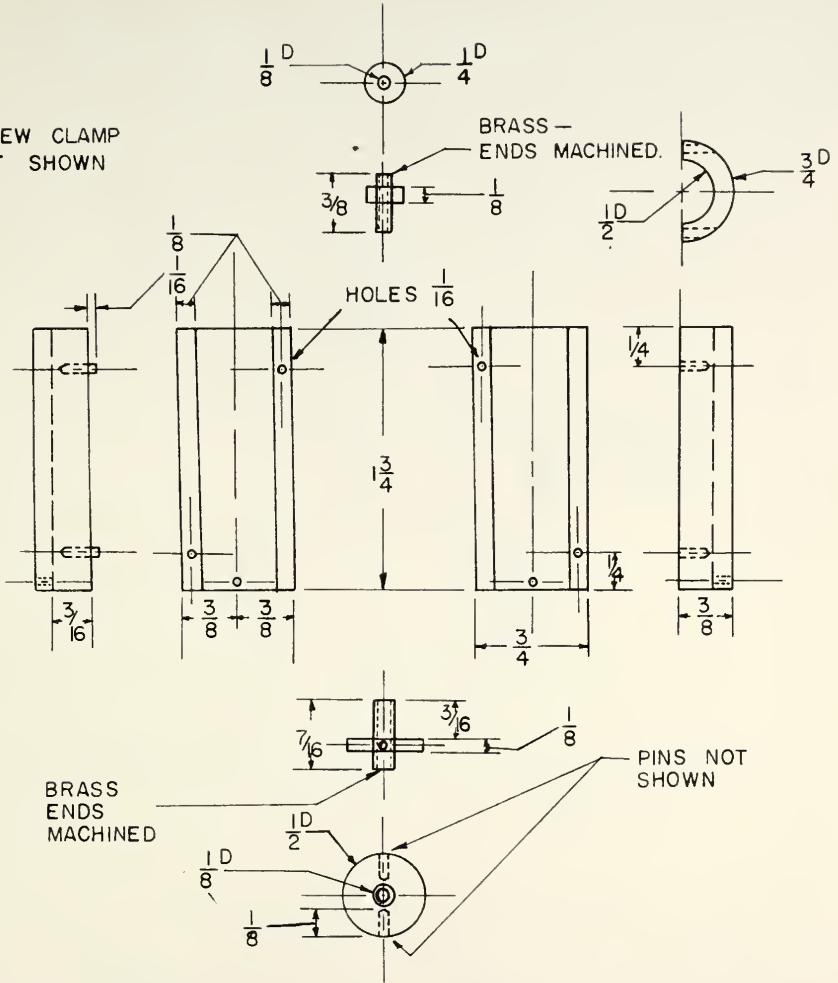


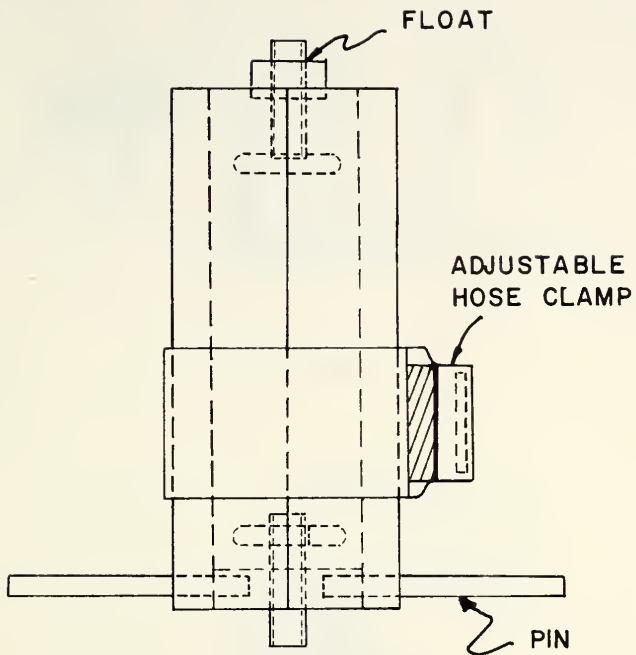
FIG. 1 TERNARY DIAGRAM SHOWING MIXES USED IN THE TESTING PROGRAM.

SCREW CLAMP
NOT SHOWN



SCALE 1:1

FIG. 2 BAR MOLD (DETAIL)



SCALE 2:1

ASSEMBLED BAR MOLD

FIG. 3



Component Parts



Assembled

Figure 4. Bar Mold

was machined to fit loosely inside the split cylinder. The disk was drilled and tapped in the center and a 1/8-inch diameter threaded brass stud was inserted so that approximately 3/16 of an inch of the stud would be surrounded by paste or mortar. The other end provided a point for length change measurements. The bottom disk was held in place by two steel pins that were inserted through the surrounding cylinder into either side of the disk. The split cylinders and bottom disks were consecutively numbered for alignment and recording purposes.

The top section was designed to "float" on the sample in the mold and thereby permit measurement of length changes. The "float" consisted of a 1/4-inch diameter and 1/8-inch thick disk that was drilled in the center. Through this hold a 1/8-inch diameter threaded brass stud was inserted. Approximately 1/8-inch of the stud extended into the mix while 1/16-inch remained above the disk to provide the other point for measuring the length changes. All stud ends were machined flat for measurement purposes. Unless otherwise stated all parts of the mold were made of clear plexiglass. The pins were lubricated for ease in the stripping operation.

A total of eleven molds were prepared for each paste composition. Two paste bars were prepared for length change measurements, two for weight measurements, five for X-ray analysis, and two mortar bars for length change measurements. For X-ray and weight change samples, the top "floating" section was not inserted.

Mortar samples were prepared in the same way except that sand was added after the fine materials had been blended. After sand (twice the weight of the fine materials) was added the total mix was again blended for one minute. Mortar samples had a w/c ratio of 0.40.

At various times during the course of hydration, portions of the paste bars were taken for X-ray analysis. The paste was ground under acetone in an agate mortar to terminate hydration, and was then air dried overnight. Twenty-five percent of fine silica by weight of the dry paste was then added. It was observed that the silica tended to form lumps. To break up these lumps and to facilitate thorough mixing the mixture of dried paste and silica was ground under acetone in a small glass jar on a roller mill using stainless steel balls.

The samples were then air dried overnight, ground with a mortar and pestle and bottled.

The samples used to prepare the X-ray analysis calibration curve consisted of various known proportions of ettringite, fine quartz as an internal standard, and Lumnite cement as a diluent. Various proportions of the materials were weighed out and ground and mixed for approximately one-half hour in the roller mill, as was previously described.

Apparatus and Procedure

Length Change Measurements

All tests were made on small cylindrical bars. Relatively small specimens were made to obtain as rapid an equilibrium with ambient conditions as possible.

After the mix had been placed in the mold the top floating section was inserted, centered and "set." The initial length readings were taken during this "setting" operation. All length readings were taken by means of a friction thimble micrometer caliper cali-

brated to ± 0.0001 of an inch. Since the specimens were about 2 in long the accuracy of strain values is about 0.01%. The initial "setting" of the "float" was done by placing the micrometer so that the anvil was resting directly against the end of the lower stud while the micrometer spindle was close to the upper ("float") stud, and then adjusting the micrometer until there was no rebound of the float when the micrometer spindle was backed off. This reading was taken as the zero point of strain. After the initial readings were taken all samples were placed in a nearly vertical position in water to hydrate.

Most samples were stripped after 16 hours of hydration. This operation consisted of removing the hose clamp, pulling the two pins that stabilized the bottom disk and prying apart the split cylinder. The bottom disk and top "float" remained with the bar.

The bars were marked so that all readings would be taken with the bars in the same position. Length measurements were then taken at the time the bars were stripped and at intervals until the bars were completely disrupted or until length changes ceased.

Quantitative X-Ray Analysis

The amount of ettringite in the paste samples was determined by quantitative X-ray diffraction. The general procedure was to mix the sample with a known amount of finely-divided quartz, to determine the ratio of the X-ray diffraction counts for the 9.73 \AA ettringite peak and the 3.34 \AA quartz peak. The amount of ettringite present was then determined by reference to a calibration curve that

had been prepared using known amounts of synthetic ettringite, quartz and HAC. The HAC was chosen as a diluent for the calibration samples because its X-ray absorption approximates that of the pastes that were the other samples.

Analyses were performed on a GE XRD-5 diffractometer using Cu-K α radiation at 40 KV and 16 ma. One-degree beam and 0.2-degree detector slits were used. The data were taken, for the most part, on a cumulative printer.

Powder mounts were made by a slight variation of the McCreery method (16), which minimizes preferred orientation. The equipment used is shown in Figure 5. The sample holder was a small plate of aluminum 1 1/2 x 1 x 1/8-inch in size with a 9/16-inch hold drilled through the center. The cell-filling procedure was as follows:

(1) A piece of typing paper the size of the plate was placed on the plate and then a glass microscope slide was placed over the paper. The assembly was bound firmly at each end with scotch tape.

(2) An excess of the powdered sample was placed into the cavity in the plate.

(3) The powder was tapped gently with the point of a spatula in two directions perpendicular to each other.

(4) This procedure was repeated with the blade of the spatula across the top of the cavity in the plate.

(5) Excess powder was removed to leave approximately 1/16 inch of material above the top of the cavity. A glass slide was then pressed against the sample to compact the material.

Figure 5. Powder Mount Equipment



(6) More sample was added, and steps 4 and 5 were repeated.

(7) After the last compaction the slide used was taped to the plate and the exposed sample.

(8) The tape holding the other slide and the piece of paper was then cut, and the face of the sample was exposed. The result was a flat powder face with a minimum of preferred orientation.

A minimum of five powder mounts were made and X-rayed for each sample. Each mount was X-rayed with the goniometer scanning speed set at 0.2 degree 2 θ per minute while recording the pattern on the recorder and the counts on the digital printer. The following procedure was used: the goniometer was set at 8.4 $^{\circ}$, 2 θ and a 100-second count was taken to determine the background. The goniometer then was allowed to travel through one degree 2 θ , and both the background counts and counts due to ettringite were recorded. The goniometer was then set at 9.4 $^{\circ}$ and another 100 second count was taken. From the two 100 second counts it was possible accurately to determine the average background intensity. This value was subtracted from the total counts obtained to get the counts due to ettringite alone. The same procedure was used to determine the counts from the quartz internal standard by allowing the goniometer to travel from 26.0 $^{\circ}$ to 27.0 $^{\circ}$ 2 θ and taking 100 second counts at the two end points. The ratio I_E/I_Q , the intensity of the ettringite peak to that to the quartz peak, was then calculated.

The ratio, I_E/I_Q was determined for each of the five powder mounts. The average value of the ratio and the standard deviation were computed. These data were statistically analyzed by standard

methods (18, 19) to determine readings not belonging to the population. The average values thus obtained were then multiplied by the appropriate factor determined from the standard calibration curve to determine the amount of ettringite in the paste (20).

Weight Change Measurements

Weight change data were obtained from paste bars prepared and cured in the same way as those used for X-ray analysis and for strain measurements. The bars were surface dried with a damp cloth and weighed on an analytical balance. The first weight was measured just after stripping the molds. The zero-time weight was extrapolated from a plot of weight vs. time.

Data

The proportions of the various mixtures of Portland cement, HAC and gypsum are shown in Table 1 and Figure 1. In the data and figures to follow the mixtures are designated by prefix numbers 1, 2, etc. and the water to "cement" or, rather, fine materials ratio is designated by the following number. For example, the designation 3-30 means mix proportions No. 3, as shown in Figure 9, and a w/c ratio of 0.30. Designation 2-45 means mix proportions No. 2 and w/c = 0.45, etc. In what follows w/c refers to the ratio by weight of the mix water finely divided solids, i.e. the sum of the Portland cement, HAC, and gypsum.

Expansion and ettringite content data were obtained for all 6 mixes with a w/c = 0.30. These data are given in Figures 6, 7, 9, 12, 14 and 16. Additional data were obtained for mixture Nos. 2, 3

and 4 made with $w/c = 0.45$; these data are shown in Figures 8, 10 and 13. Figure 11 shows expansion strain data obtained for mix No. 3 with w/c of 0.30, 0.35 and 0.45, respectively. Figure 15 shows additional data for mix No. 5; expansion curves are shown for paste bars stripped after both four and sixteen hours of hydration. Figures 17, 18 and 19 show summary strain data for both water contents.

Weight change data were obtained for the paste bars. Data obtained for mixtures Nos. 1-6 made with a w/c of 0.30 are presented in Figure 20. Figure 21 shows the same data obtained for mixes Nos. 2, 3 and 4 made with 45 percent water. Two to one (graded Ottawa sand to "cement") mortars were prepared for all six mixes with a w/c ratio of 0.40. Expansion data obtained from these mortar bars are presented in Figures 22 and 23.

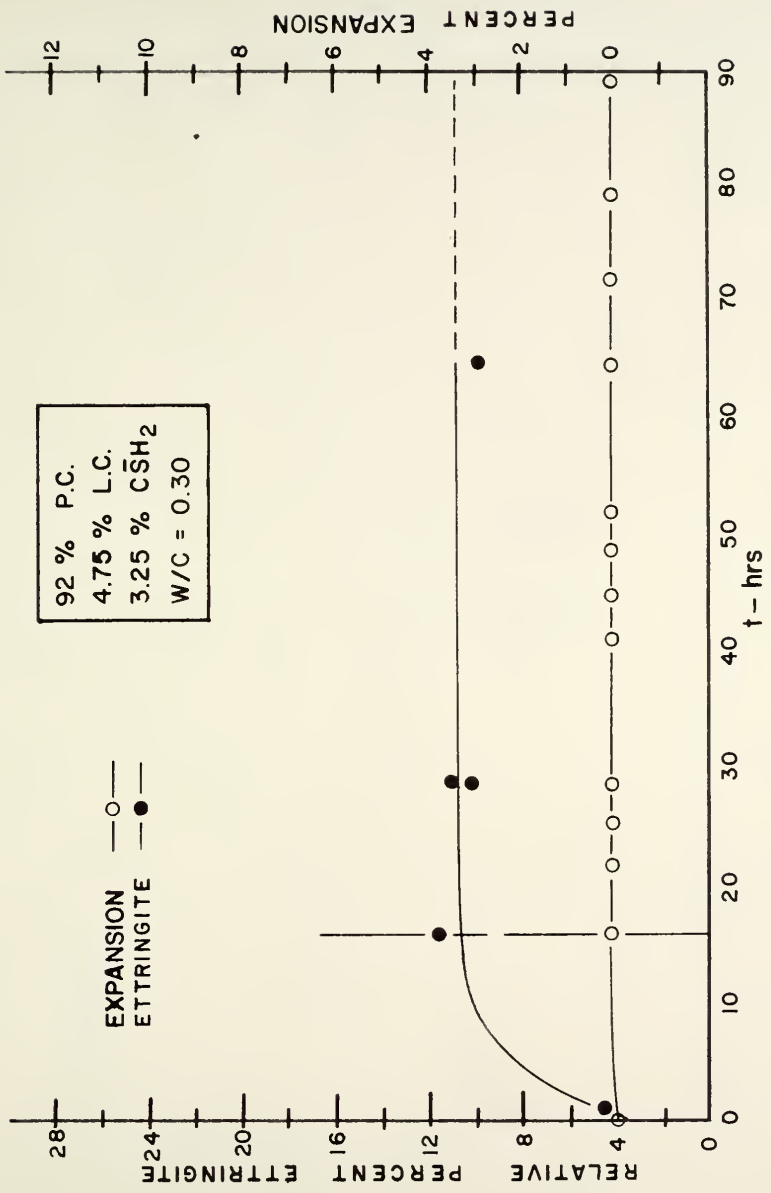


FIG. 6 MIX I-30 (PASTE) VARIATION OF RELATIVE PERCENT ETTRINGITE AND PERCENT EXPANSION WITH TIME

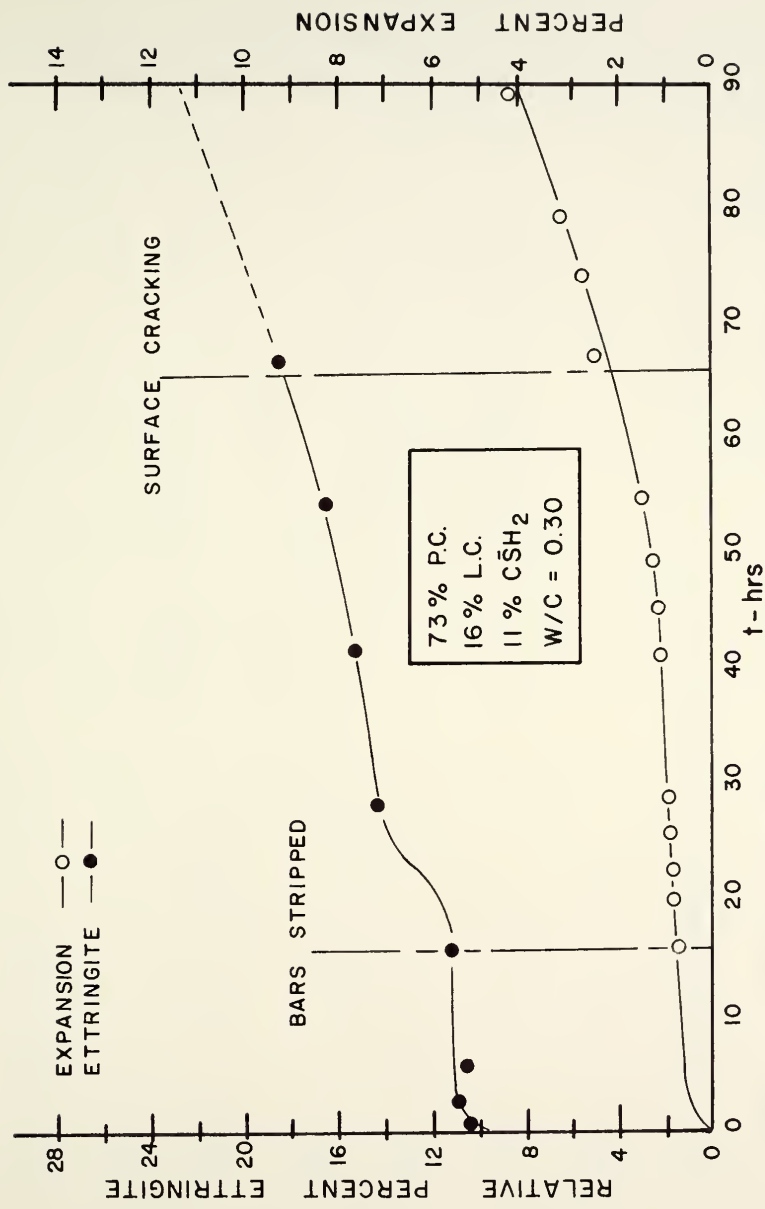


FIG. 7 MIX 2-30 (PASTE) - VARIATION OF RELATIVE PERCENT ETTRINGITE AND PERCENT EXPANSION WITH TIME.

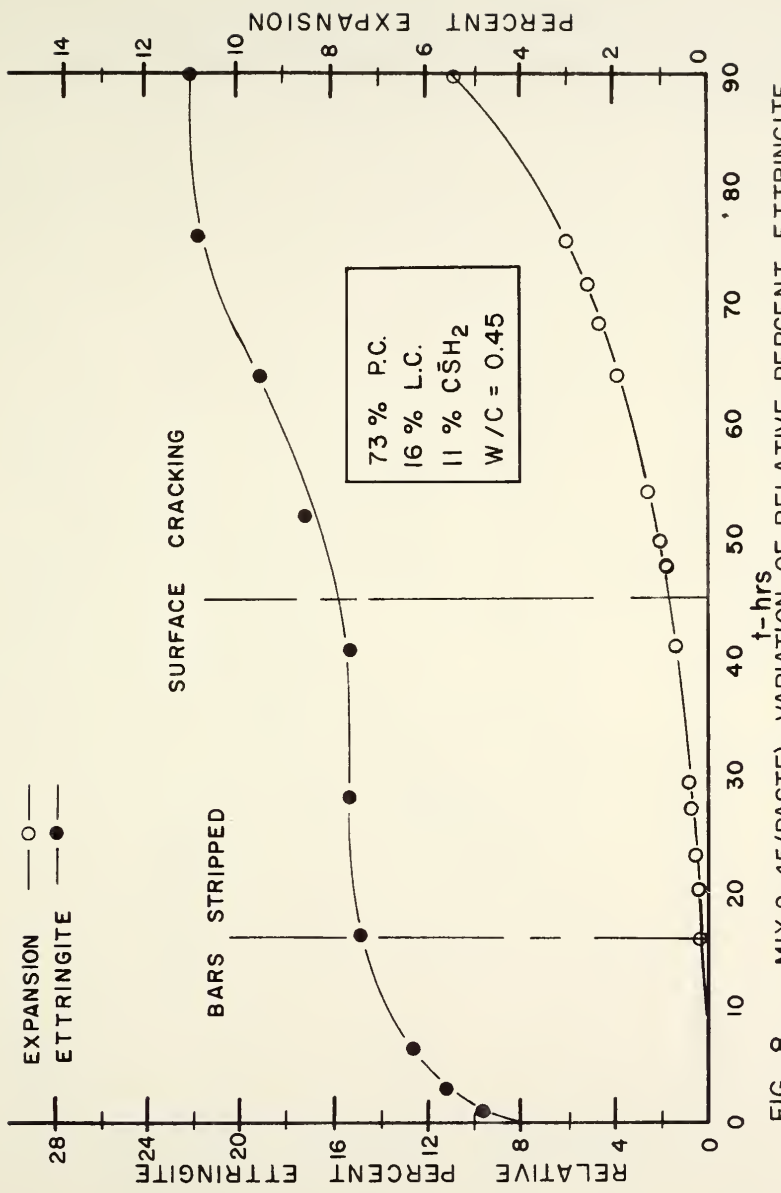


FIG. 8 MIX 2-45(PASTE) VARIATION OF RELATIVE PERCENT ETTRINGITE AND PERCENT EXPANSION WITH TIME.

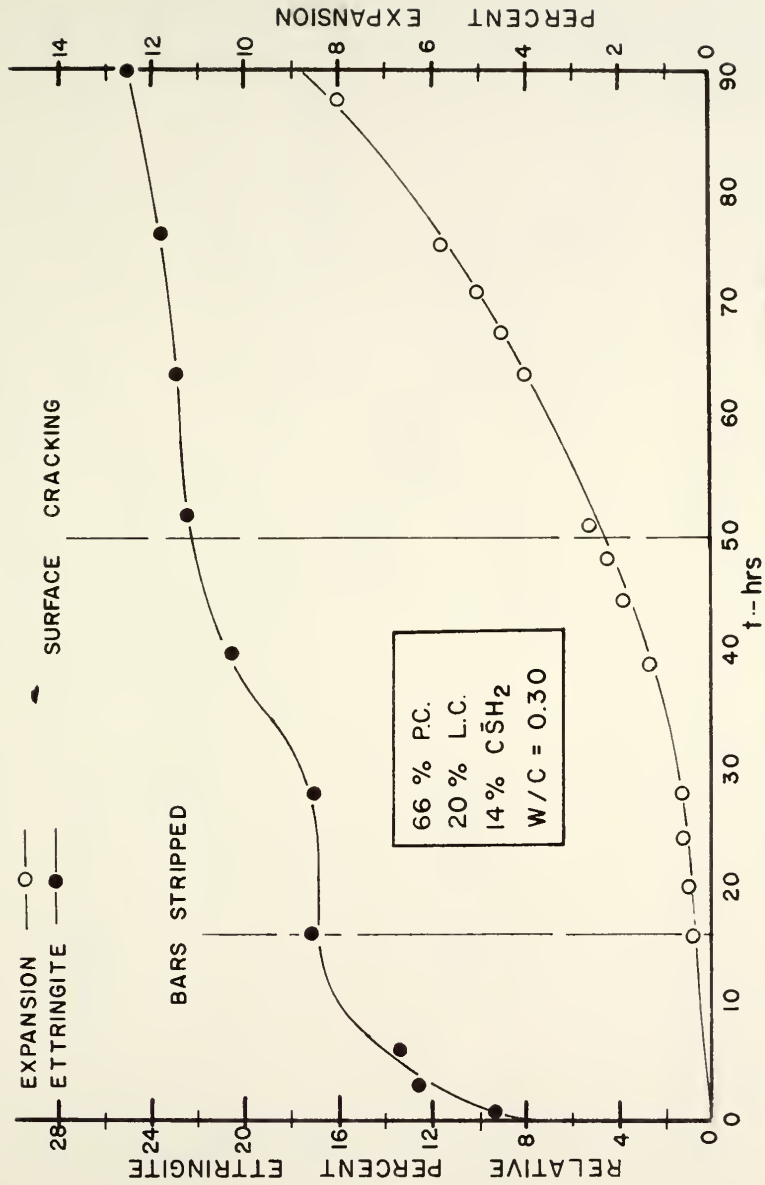


FIG. 9 MIX 3-30(PASTE) VARIATION OF RELATIVE PERCENT ETTRINGITE AND PERCENT EXPANSION WITH TIME.

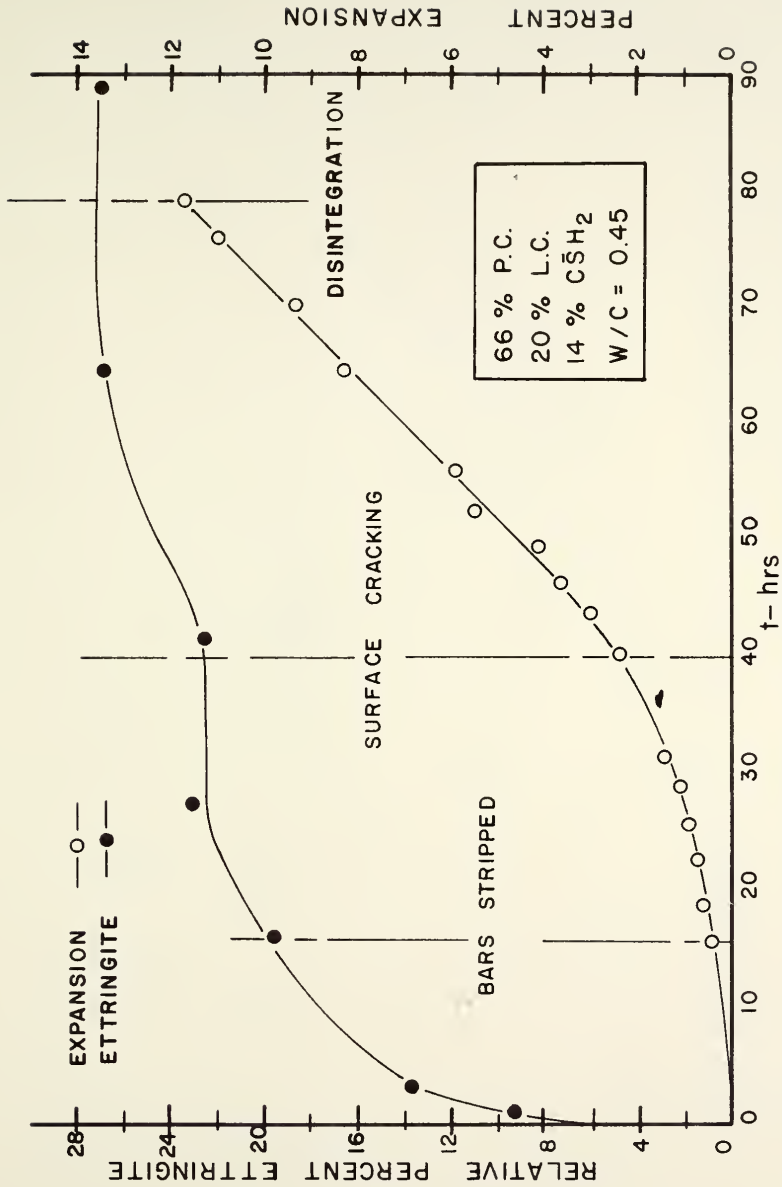


FIG. 10 MIX 3-45 (PASTE) VARIATION OF RELATIVE PERCENT ETTRINGITE AND PERCENT EXPANSION WITH TIME.

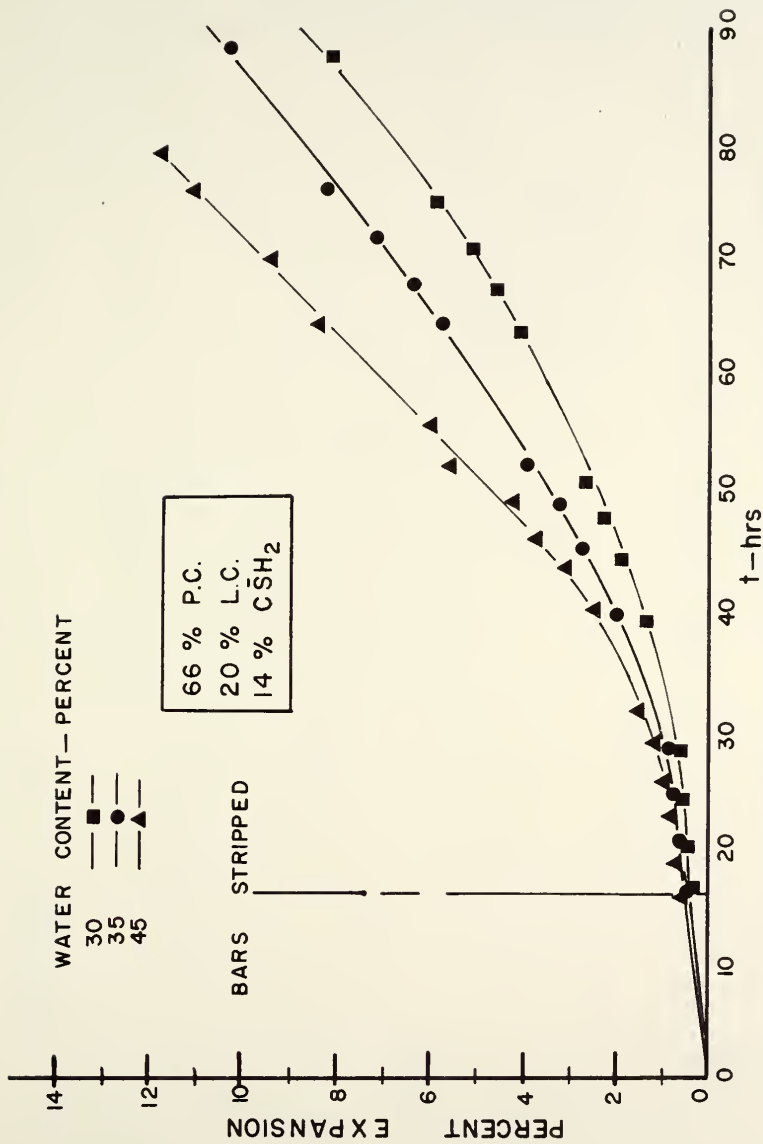


FIG. 11 VARIATION OF PERCENT EXPANSION WITH TIME FOR MIX 3 WITH 30, 35 AND 45 PERCENT WATER.

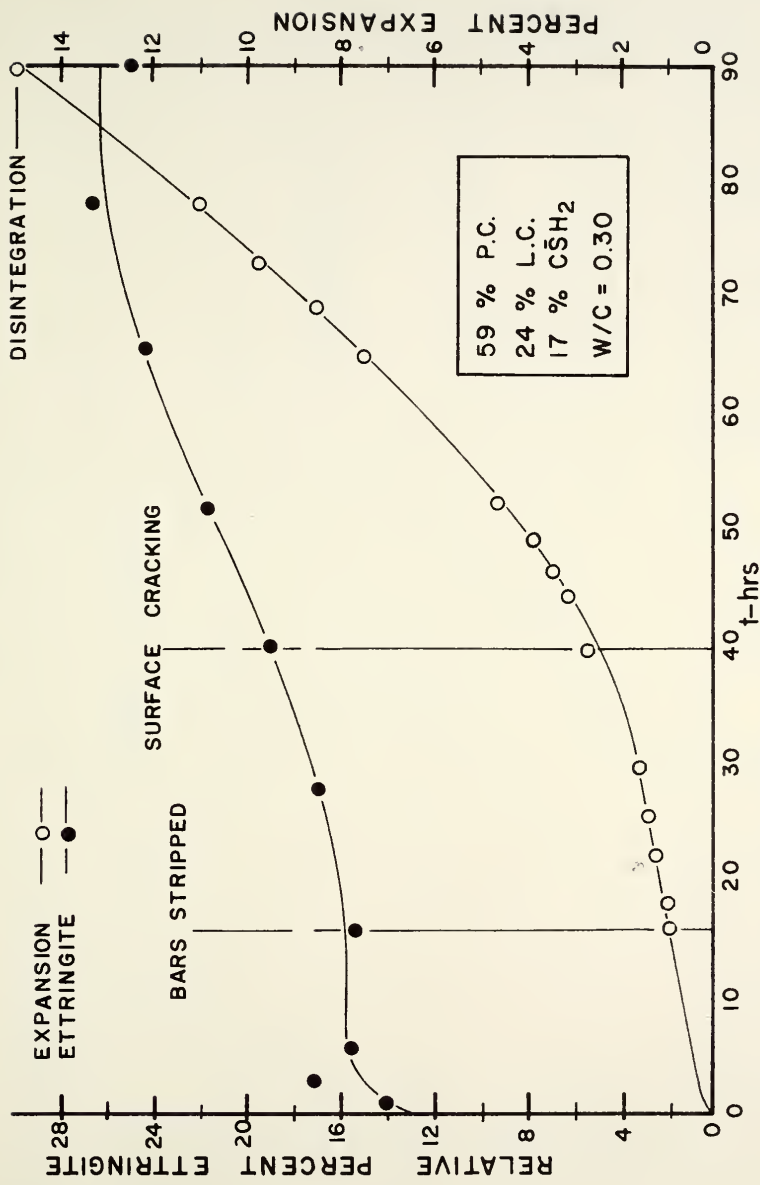


FIG. 12 MIX 4-30(PASTE) VARIATION OF RELATIVE PERCENT ETTRINGITE AND PERCENT EXPANSION WITH TIME.

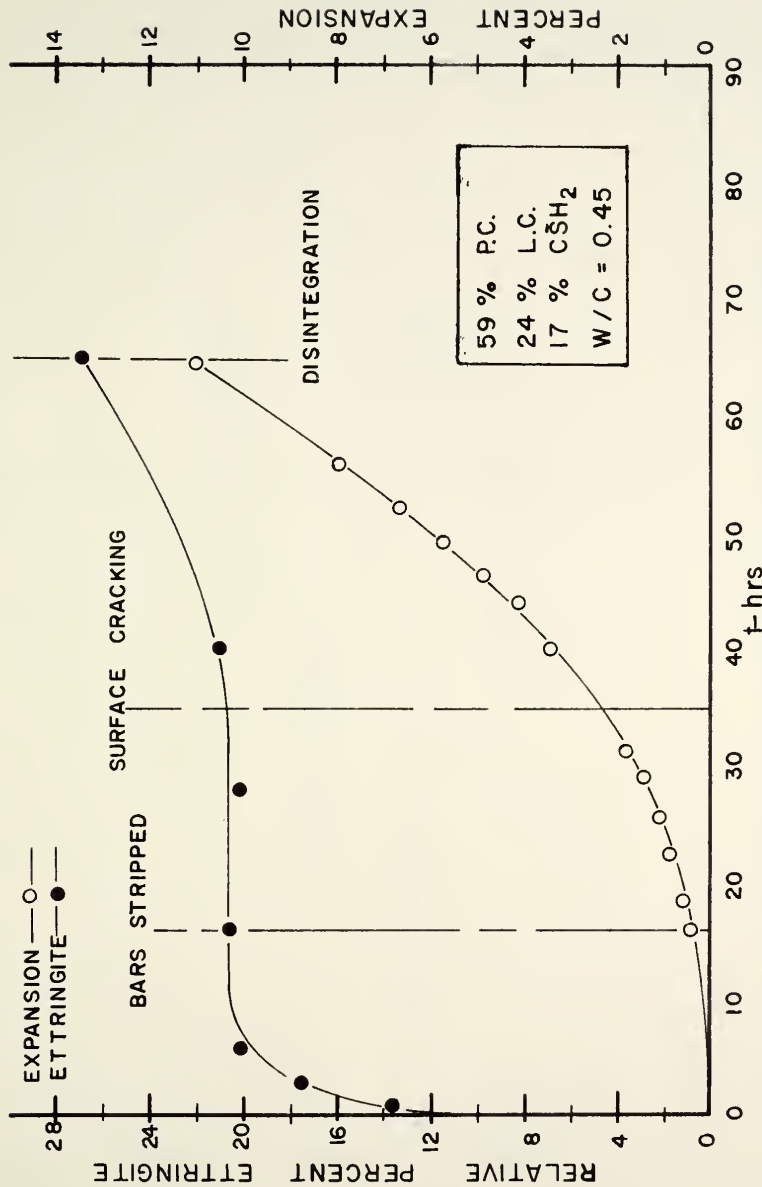


FIG. 13 MIX 4-45(PASTE) VARIATION OF RELATIVE PERCENT ETTRINGITE AND PERCENT EXPANSION WITH TIME.

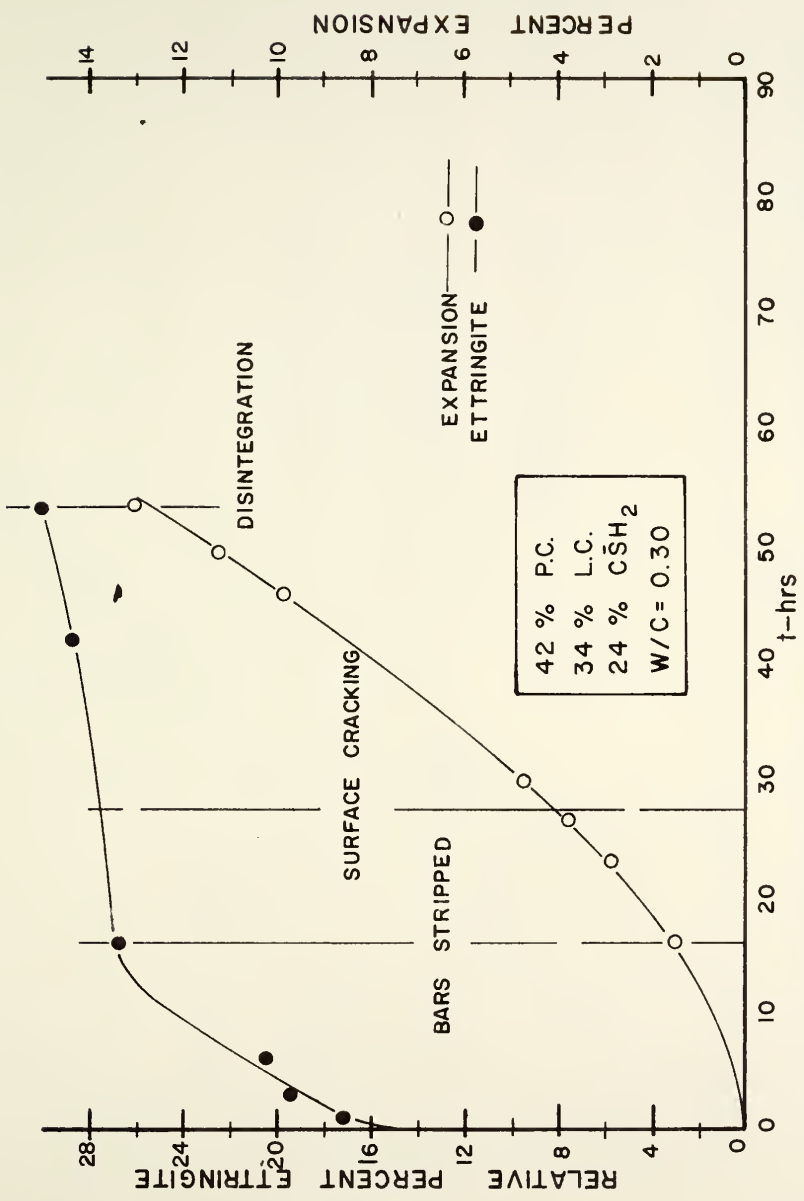


FIG. 14 MIX 5-30(PASTE) VARIATION OF RELATIVE PERCENT ETTRINGITE AND PERCENT EXPANSION WITH TIME.

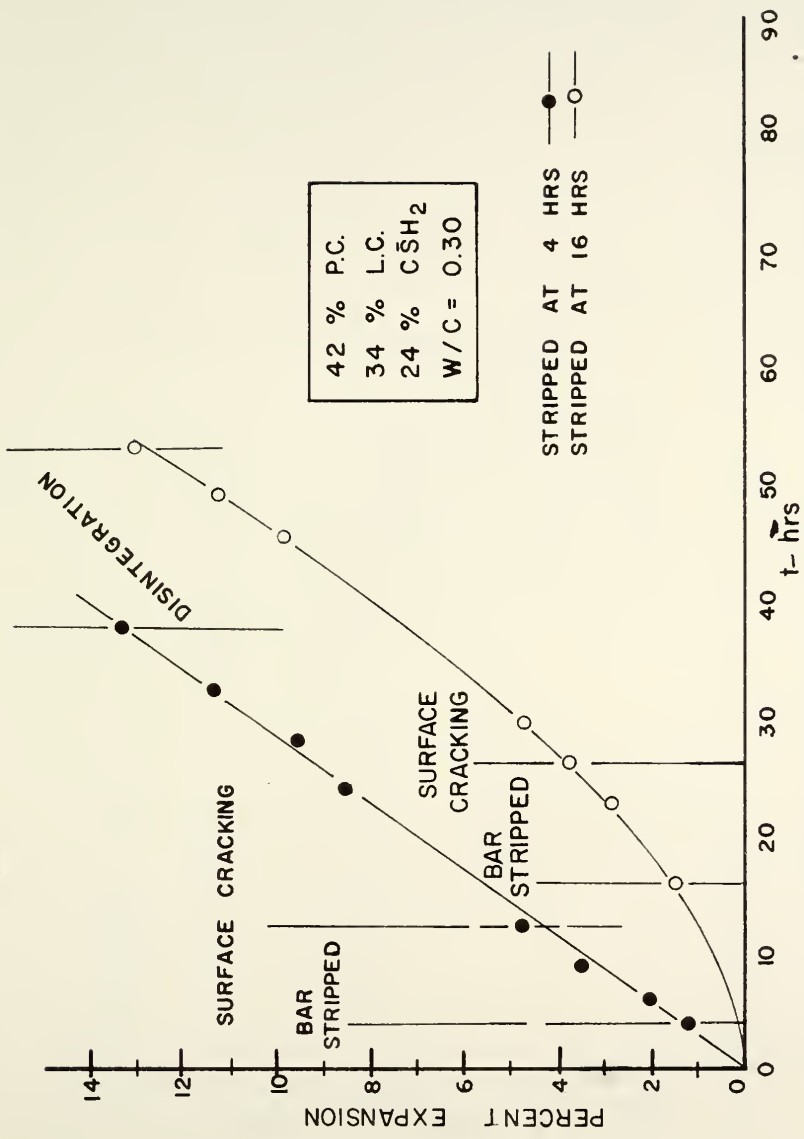


FIG. 15 MIX 5-30(PASTE) VARIATION OF PERCENT EXPANSION WITH TIME FOR IDENTICAL BARS STRIPPED AT DIFFERENT TIMES.

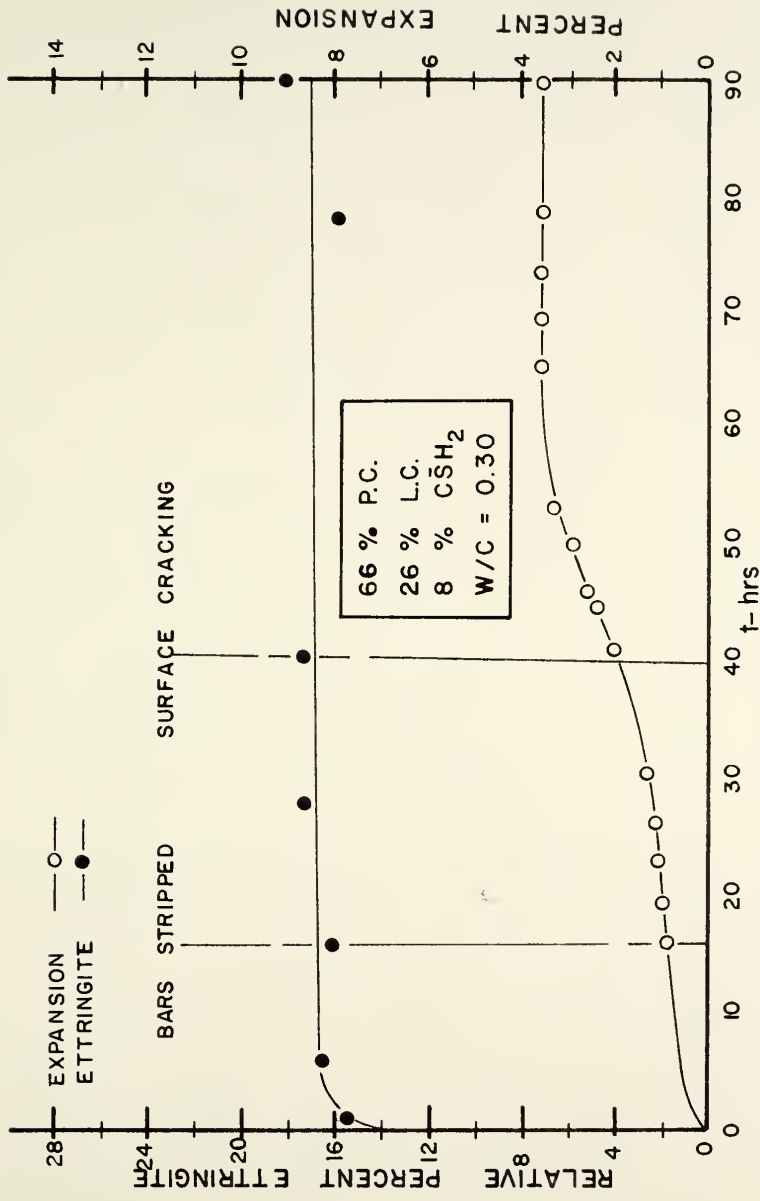


FIG. 16 MIX 6-30(PASTE) VARIATION OF RELATIVE PERCENT ETTRINGITE AND PERCENT EXPANSION WITH TIME.

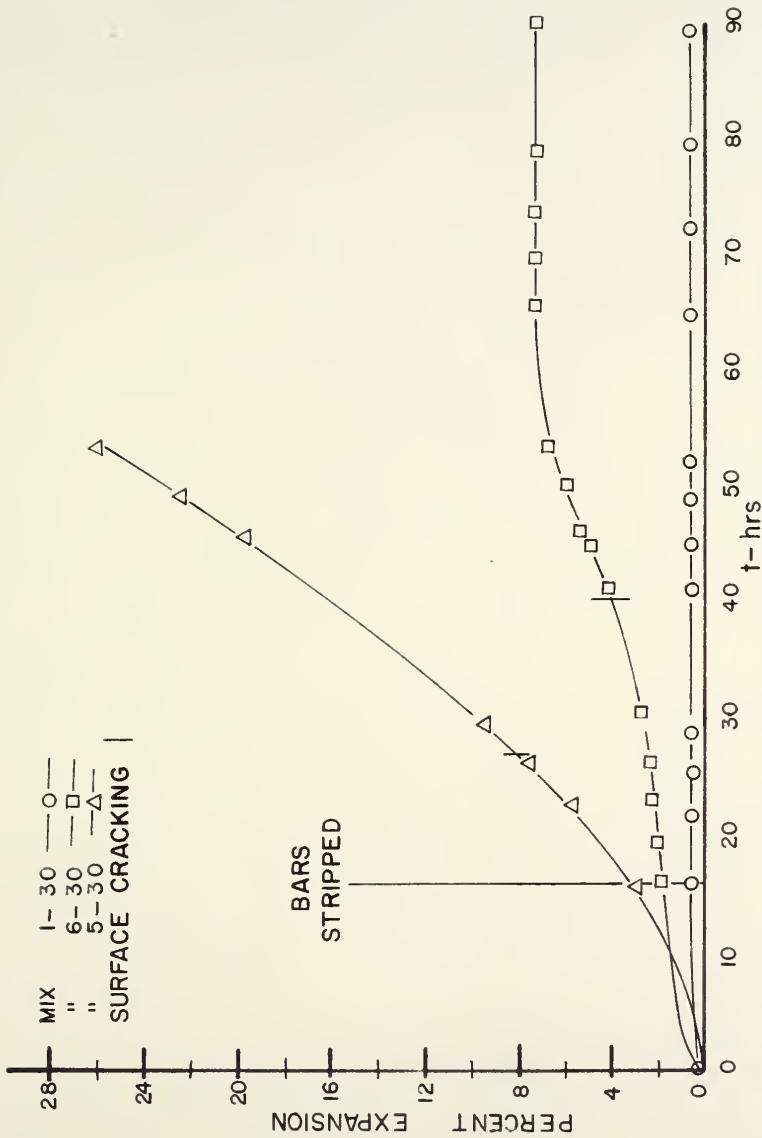


FIG. 17 VARIATION OF PERCENT EXPANSION WITH TIME FOR MIXES 1-30, 5-30 AND 6-30.

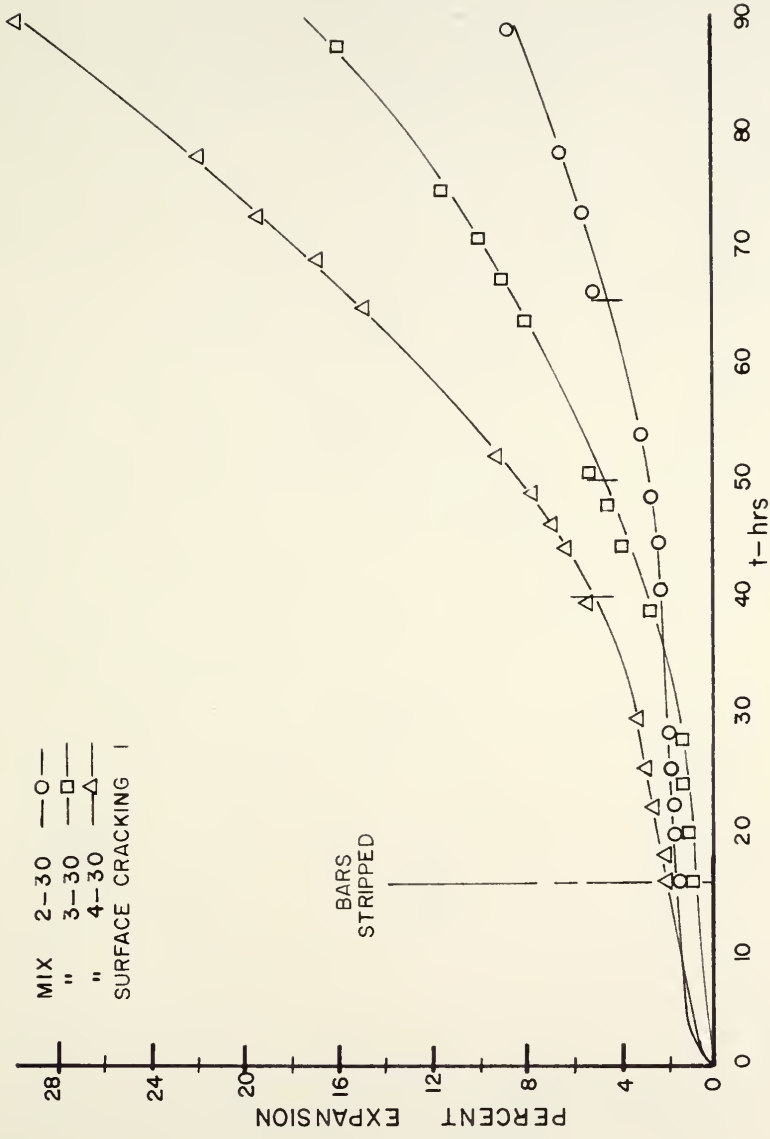


FIG. 18 VARIATION OF PERCENT EXPANSION WITH TIME FOR MIXES 2-30, 3-30 AND 4-30.

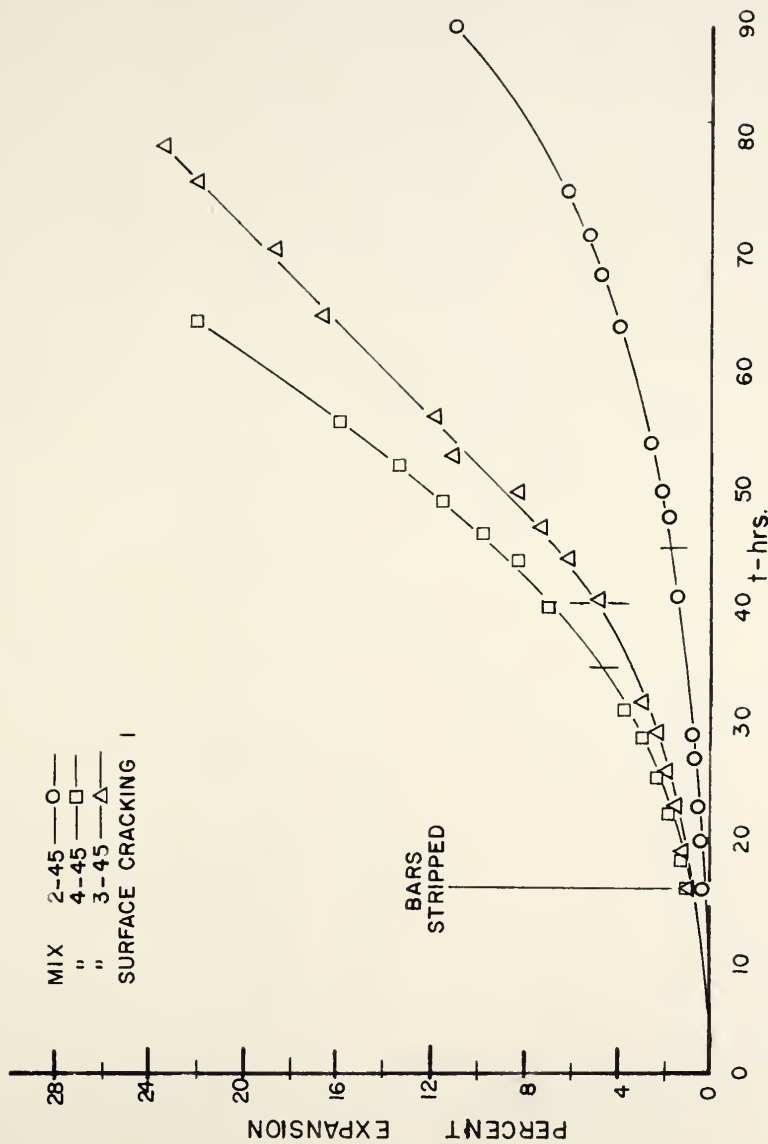


FIG. 19 VARIATION OF PERCENT EXPANSION WITH TIME FOR MIXES 2-45, 3-45 AND 4-45.

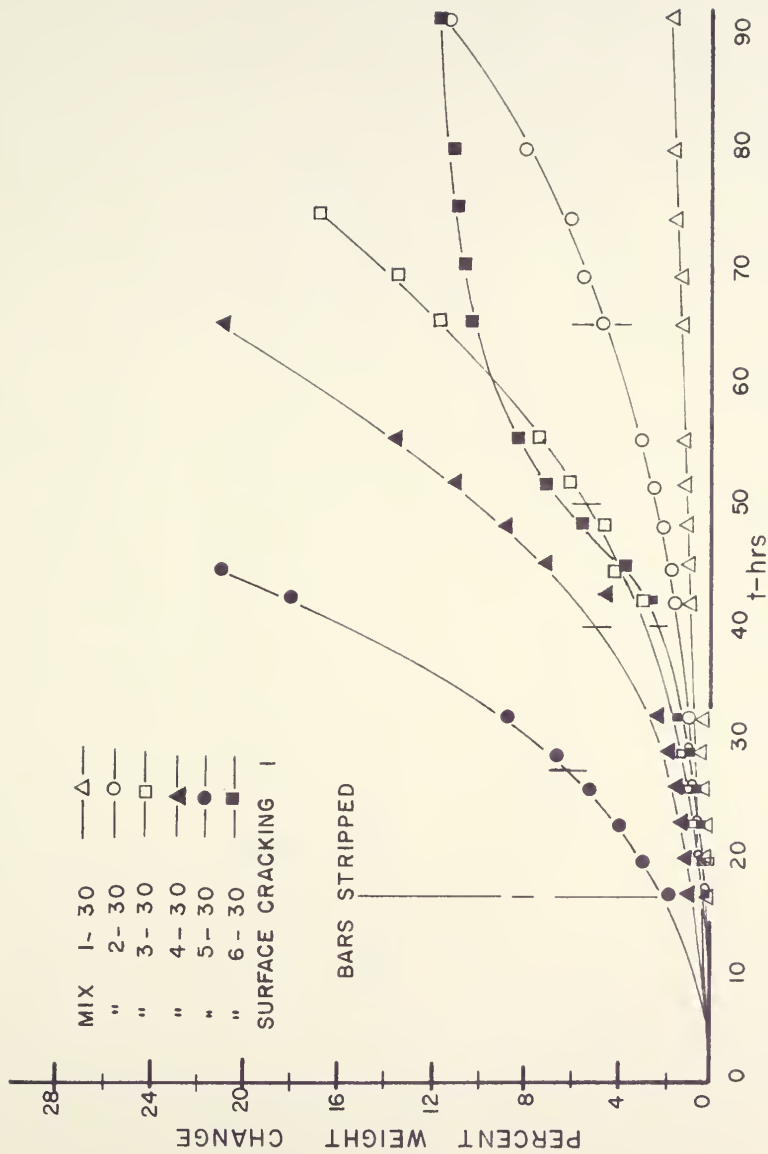


FIG. 20 VARIATION OF PERCENT WEIGHT CHANGE WITH TIME FOR MIXES CONTAINING 30 PERCENT WATER.

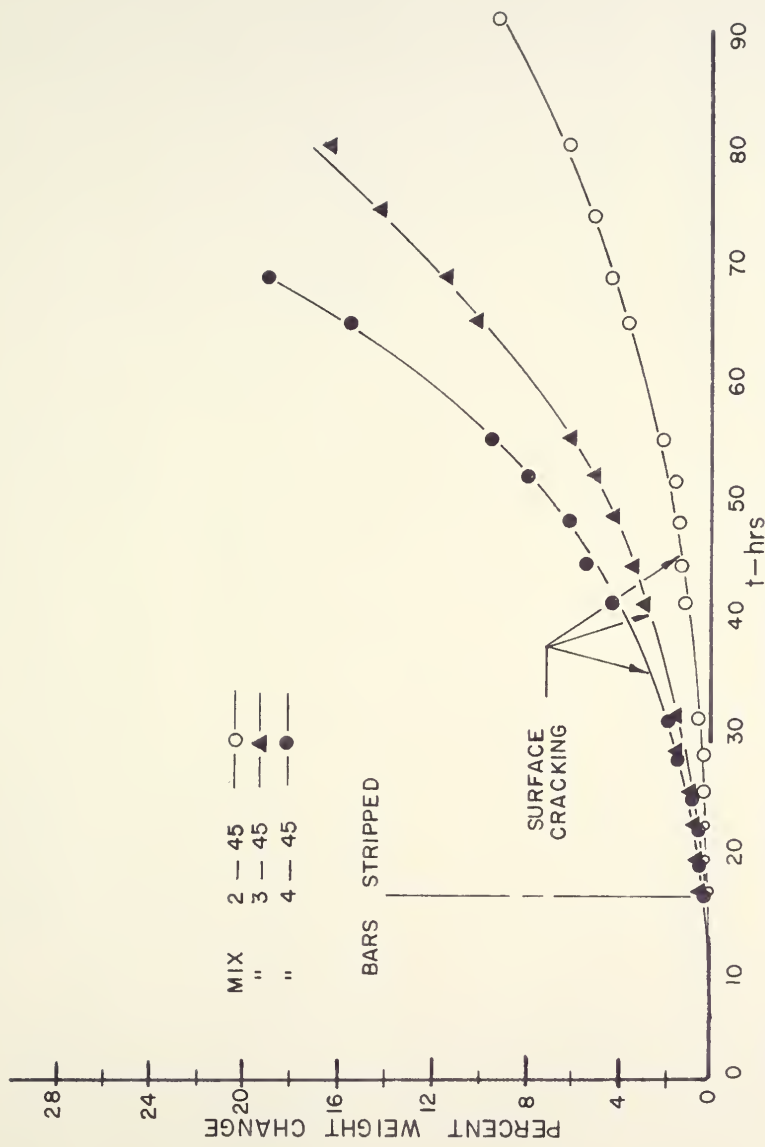


FIG. 21 VARIATION OF PERCENT WEIGHT CHANGE WITH TIME FOR PASTE MIXES CONTAINING 45 PERCENT WATER .

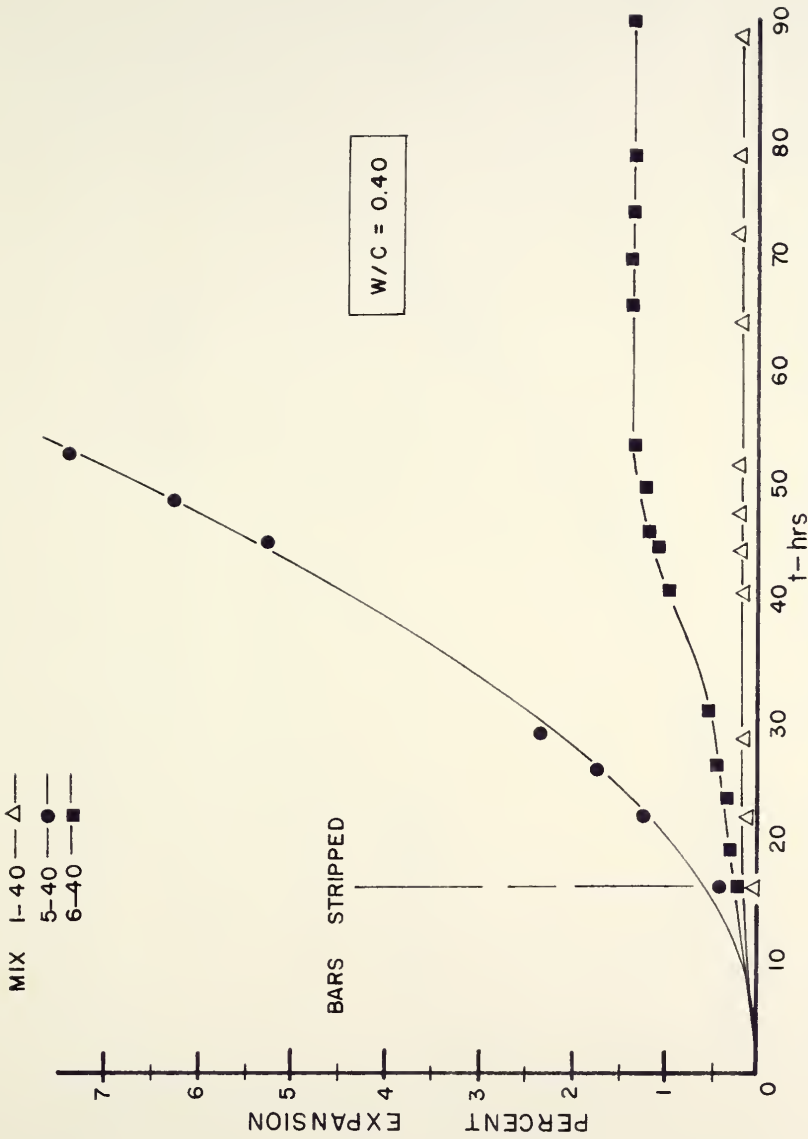


FIG. 2.2 VARIATION OF PERCENT EXPANSION WITH TIME FOR MORTARS PREPARED FROM MIXES 1, 5 AND 6.

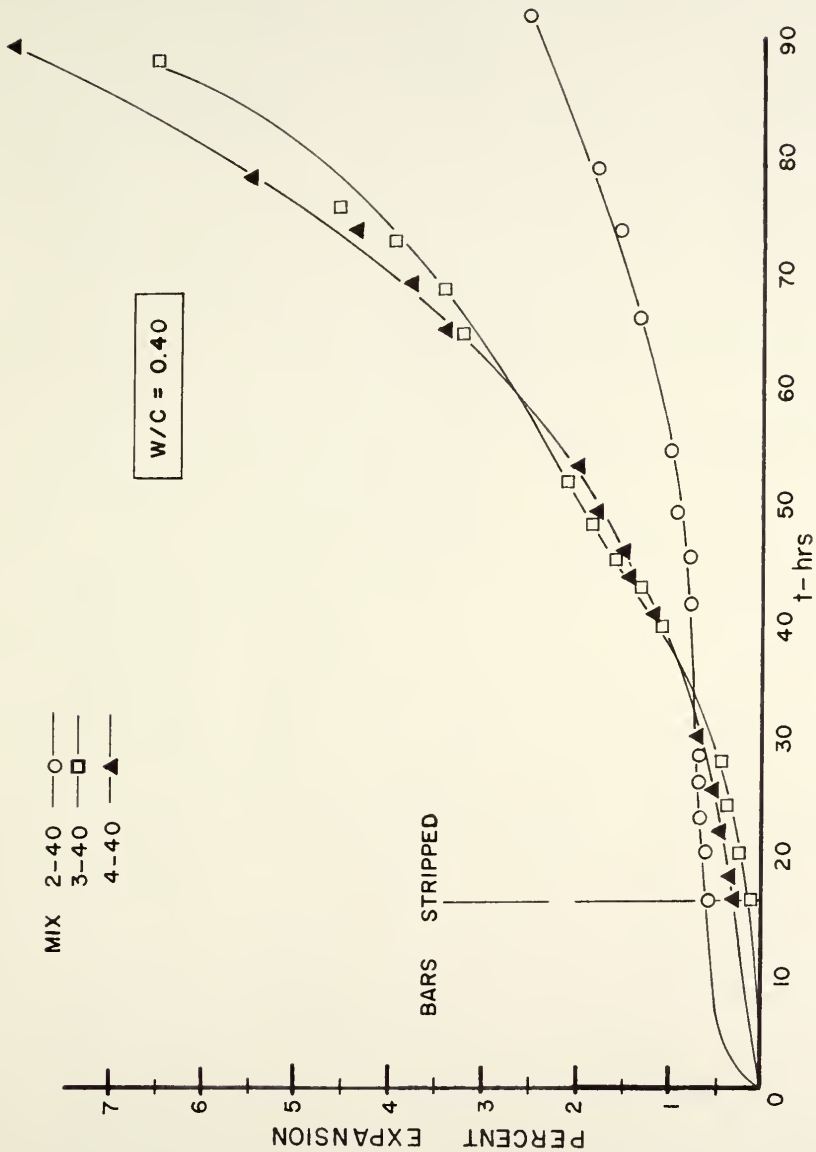


FIG. 23 VARIATION OF PERCENT EXPANSION WITH TIME FOR MORTARS PREPARED FROM MIXES 2, 3 AND 4.

DISCUSSION

• The purpose of this work was to investigate the relationships between the production of ettringite by a particular type of expansive cements and the dimensional changes of pastes or other mixtures made with these cements. If ettringite is indeed responsible for expansion, there should be some relationships between the amount of ettringite and expansion. This was found to be true, but the relationships are not simple ones, and there are other factors involved. Before these relationships are gone into in detail, there are characteristics of the data that should be pointed out.

With respect to the cement mixture compositions, the critical factor with respect to the potential production of ettringite was in all mixtures the amount of gypsum. This statement is based on the fact that the Lumnite HAC was composed mostly of CA, which was the conclusion based on X-ray diffraction analysis of the HAC. The potentiality for the production of ettringite varied from a small amount (Mix No. 1) to a very large amount (Mix No. 5). See Figure 1 and Table 1.

Mix No. 1 corresponded most closely to a pure Portland cement since the amounts of gypsum and HAC present were only about four percent. Figure 6 shows the production of ettringite to be complete after the first ten hours of hydration. Since the amount of gypsum was small, it would be expected that the production of ettringite would be small. The strain data show that there was a very small

initial expansion during the first few hours of hydration. This expansion had ceased by the time the bars were stripped, and no further volume change was observed during the course of the test.

Expansion and ettringite production data for mix No. 2 made with a w/c of 0.30 are shown in Figure 7. Initially there was a rapid production of ettringite followed by a dormant period that lasted until after the molds were stripped from the bars. At this point more ettringite was again produced for a few hours. The rate then decreased and continued at a slower rate during the remainder of the test.

Figure 8 shows expansion and ettringite contents for mix No. 2 made with 45 percent water. The ettringite production curve shows an initial rise comparable to the value obtained for the drier mix (Fig. 7). Ettringite increase continued, however, until it ceased after approximately twenty hours of hydration. Ettringite production resumed again after about 40 hours of hydration, just before surface cracking of the specimens was noticed.

Comparison of Figures 7 and 8, shows that ettringite production did not cease before stripping of the molds of the wetter mixture. There was no increase in the amount of ettringite present in the wetter paste after stripping. Between 40 and 65 hours the two curves look much the same. Comparison of the expansion curves from the same two figures shows there was no rapid initial strain in the first few hours for the wetter mix but there was a small one for the drier mix. Strain increase rates were greater for the wetter mix. Surface cracking was noticed about twenty hours earlier for the drier mix.

In Figure 9 are shown data obtained from mix No. 3 with a w/c of 0.30. The ettringite production curve shows a rapid increase during the first hour of hydration. The amount of ettringite increased until about fifteen hours, when production ceased. After about twenty-eight hours there was again a rapid increase in the amount of ettringite present. After approximately forty hours ettringite production slowed and continued at a reduced rate during the remainder of the test. The strain curve shows an initial small linear expansion during the first thirty hours or so of hydration. After this time expansions increased progressively.

Figure 10 shows data obtained for mix No. 3 with a w/c of 0.45. The ettringite production curve shows an initial rapid rise. After thirty hours of hydration ettringite production ceased and did not begin again until surface cracking was observed. Production of ettringite again leveled off when disintegration of the paste was nearly complete. Expansion increased progressively until after approximately forty hours of hydration. After this time the strain rate remained constant until disintegration was complete.

When Figure 10 is compared with Figure 9, it is seen that again there was no leveling off of ettringite production before stripping in the wetter mix, but there was in the drier mix. Surface cracking occurred ten hours earlier for the wetter mix. Also there was no distinct rise in the ettringite production curve of the drier mix at the time of surface cracking.

Figure 12 shows data obtained from bars made with mix No. 4 at a w/c of 0.30. The ettringite production curve shows an initial

rapid production that ceased after approximately six hours. Production resumed after stripping of the molds and continued until disintegration was nearly complete.

Figure 13 shows data for the same mix but with a w/c of 0.45. There was a large initial production of ettringite that ceased after nine hours of hydration. There was no further increase of ettringite until surface cracking was first noticed. After this time production was progressively greater until disintegration was complete. The strain data show that expansion increased progressively until the bars were destroyed.

Comparison of Figure 13 with Figure 12 shows that the production of ettringite during the first hour leveled off at approximately the same time in both mixes (9 hours), but that the amount of ettringite produced during this time was much greater in the wetter mix. Ettringite production in the wetter mix was not affected by stripping while production in the drier mix did not appear to be affected by the onset of surface cracking. The ultimate percentage of ettringite in the two samples was about the same. The ultimate strain was greater for the drier mix. Disintegration and surface cracking occurred earlier in the wetter mix.

Figure 14 shows data obtained from mix No. 5 with a w/c of 0.30. There was a large initial production of ettringite during the first hour or so of hydration. This was followed by a further large production. At stripping, production of ettringite ceased but soon resumed at a slower rate until disintegration occurred. The expansion data show an increasing expansion during the life of the bar.

Mix No. 6 was the only one that did not have a Lumnite cement to gypsum ratio of 1.43. This mix contained the same amount of Portland cement as did mix No. 3 but had a larger Lumnite HAC and a smaller gypsum content. It can be seen from the ettringite production curve (Fig. 16) that there was a large initial increase during the first few hours of hydration. The production leveled off, and only a very slight change was observed during the remainder of the testing program. The expansion data show that strains increased until approximately ten hours after surface cracking was observed. Strains slowed until no further expansion was observed during the remainder of the test.

Figures 17-19 show that the expansion rates increased as the original Portland cement contents decreased for all cases where the Lumnite to gypsum ratio was 1.43. Expansion rates were greater in the wetter mixes than for the corresponding drier mixes.

Weight change data were obtained from paste bars prepared identically to those used for the other measurements. The bar weight at zero time was obtained by extrapolation from a plot of weight vs. time. The bars were first weighed after they had hydrated for 16 hours and were stripped from the molds. Figure 20 shows weight change data for Nos. 1-30, 2-30, 3-30, 4-30, 5-30 and 6-30. The relative weight gain of the bars was larger for those compositions initially lower in Portland cement. Figure 21 shows the weight change data for mixes Nos. 2-45, 3-45 and 4-45. Here again, as the initial Portland cement contents were made smaller the relative weight gain of the bars became larger. The amount of weight increase was less

for the mixes with a higher water content. The slope of the weight curves increased rapidly after surface cracking was observed.

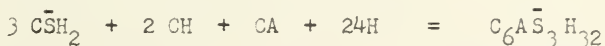
In all instances, $\bar{C}\bar{S}H_2$ was present at the end of the run, as indicated by the X-ray diffraction pattern with the exception of mixtures Nos. 1 and 6. As can be seen from Figures 6 and 16, these samples had no production of ettringite after the initial amount presumably because the supply of gypsum was exhausted. Gypsum was present in all stages of ettringite production for all other samples. The leveling out of ettringite production observed in Figures 6-10, 12, 13, 14, and 16 must therefore be due to some cause other than gypsum exhaustion. One other possible cause was the exhaustion of the water initially present in the mix. Ettringite has much water of crystallization (nearly 50% by weight). If water is no longer available, production of ettringite will cease regardless of the availability of other constituents. This seems to have occurred even though the samples were water-cured at all times. During the time the bars were in the molds, water had access only through the small space at the top. Some water probably did get in, but not enough to fill the great demand. A sample calculation was made, based on a hydration period of a one day since this was the time at which most of the ettringite plateaus occurred. This calculation assumed that 50 percent of the Portland cement had hydrated, $2/3$ of the Luninite had gone to CAH_{10} , and a non-evaporable water content of 0.2 and a gel water content of 0.15 g/g of Portland cement that hydrated. This calculation, although crude, showed that there was not nearly enough water originally present in the mix to form all the ettringite capable of being formed. It also showed that there was not even

enough water to form the ettringite that was found. This point will be discussed further.

There are characteristic features from all the curves that should be pointed out. Initially there was a very large production of ettringite that was not accompanied by any substantial expansions. The initial expansions observed in some cases were relatively insignificant compared with the expansions that occurred at later times. For this reason, if no other, there is no simple relationship between ettringite and expansion.

This result is also the basis for the assumption that much of the original ettringite production occurred by a "through-solution" as opposed to a "solid-state" mechanism.

If one assumes that the production of ettringite in these particular cement compositions occurred according to the following stoichiometry:



then a sample calculation shows a volume decrease for this reaction. The lime, of course, is provided by the hydrating Portland cement. If this reaction is accommodative in the sense of a smaller volume of products than that of reactants, one would expect no expansion of a system undergoing this reaction if it takes place in such a way as to use effectively the space formerly occupied by reactants for the deposition of the products. It is logical to assume that a solution process would so use the space because of the inherent mobility of dissolved species and the consequent ability of such a

process to deposit products in the pore space available. On the other hand, if the reaction proceeds by an attack on a particular solid component with its conversion to the final product more or less in situ, then such a process might well result in a non-use of available pore space and a resultant expansion because the physical geometry of the reactants would tend to determine that of the products. This question has been examined by Lea (3) and others.

These considerations are the basis for the statement that the large ettringite production in all these samples, which was not accompanied by expansion, points to a "through solution" mechanism for its formation. Even if this conclusion is true, however, the data point to some other action also. This point is discussed later.

In spite of the lack of relationships between early ettringite formation and expansion there are relationships between potential ettringite and changes that were observed in the curves in Figures 6-10, 12, 13, 14 and 16. The larger the potential ettringite, the larger was the amount formed at any comparable stage of hydration. (It was determined from the calibration curve that the ettringite values were probably accurate to $\pm 1\%$.) It was also observed that the larger amount of potential and indeed actual, ettringite, the larger was the observed expansions, expansion rates, weight gain and weight gain rates at any comparable stage. The rates and amounts of expansions and increases in weight were more rapid after surface cracking was observed. It can, therefore, be argued that there is a correlation between ettringite production, expansion and weight gain, but not a direct or simple relationship since there is no obvious relationship

between early ettringite production, expansion and weight gains.

The importance of w/c ratio in all concrete technology is well known. To gain additional information on the effects of water content on these expansive materials mix Nos. 2, 3 and 4 were also made with a w/c ratio of 0.45 (Figures 8, 10 and 13). Mix Nos. 1, 5 and 6 were not tested with a higher w/c ratio.

If the notion that water was the essential ingredient in limiting early ettringite production, more water initially available in the mixes should bring about a larger initial production of ettringite. This was indeed the case. At any comparable stage of hydration more ettringite was produced in the higher water content mixes. Mixes containing the higher water contents also gave greater expansions at any given point. Figure 11 shows expansion data for mix No. 3 made with three different water contents. This figure shows a clear influence of w/c ratio on the amount of expansion at any given time. There was also an influence of w/c ratio on the weight gains but in a reverse direction to that of the expansions, although the general shape of the curves is the same.

The influence of water on expansion may simply be that more ettringite was formed and therefore it would be logical to assume that more expansion would be expected. It may also be that higher water contents make the cementing cohesive components physically weaker. Most of the expansion occurred after surface cracking was observed and was therefore part of a progressive disintegration, although the samples could be handled until much later times. Expansions were far larger than those that would be expected from

any elastic or creep mechanisms. It must therefore be assumed that micro-cracking occurred before the surface cracking was noticed. This micro-cracking influence was probably more prevalent in the mixes containing 30 percent water since their demand for water was higher. Affinity for water probably was greater for these mixes and it would be expected that cracking may have occurred due to additional ettringite being produced in the outer layers. This progressive cracking would allow water to penetrate deeper into the structure. This phenomenon, if real, was probably not as important in the mixes containing 45 percent water because, even though the amounts of ettringite were higher in all cases and the samples were probably weaker, the ettringite was probably more dispersed throughout the medium and its effects less localized. The increased weight gain observed in the lower water mixes was probably due to water filling these micro-cracks as well as to water combining chemically to form ettringite.

General trends are observable between the 30 and 45 percent water mixes (Figures 6-10, 12, 13, 14 and 16). The amount of ettringite tended to increase after stripping in the mixes with $w/c = 0.30$ and its production was not changed by visible surface cracking. Conversely, in the mixes of $w/c = 0.45$, there was no change in the amount of ettringite on mold stripping but its production resumed again about when surface cracking was noticed.

When the molds were stripped a larger area was available for water ingress and ettringite was probably produced again at least in the surface layers. This is what seems to have happened in 2-30,

4-30 and 5-30 but mix No. 3 was a little different. Although the data were rechecked, the ettringite production in mix 3-30 did not increase as soon as stripping occurred, but there was a time lag. In the case of the mixes containing 45 percent water it would be logical to assume that they were less sensitive to stripping because the water initially available is more adequate to sustain ettringite production. These ettringite production curves also leveled out, however, which fact indicates the exhaustion of water to be not the only factor operating. Other factors involved may be coatings of the reactant particles and diffusion of water through such barriers. Such a mechanism is the one invoked to explain the retarding action of gypsum in ordinary cement by the coating of C_3A grains by ettringite. There is no reason to think it is not partially operative in other similar systems.

In spite of relatively large differences in potential ettringite and water contents, surface cracking took place at about 2 percent linear strain in most instances. Surface cracking occurred at a later time in every case for mixes made with 30 percent water and did not appear to be accompanied by increases in ettringite. It may be that surface cracking did increase the ettringite production but that this increase is part of the general increase that began after stripping of the drier mixes.

As was previously noted, initial large ettringite production was not accompanied by volume change and probably not by a weight change. Weight changes occurring before 16 hours of hydration are questionable since the weight at zero time was extrapolated from a

plot of weight vs. time. In certain instances there did seem initially to be a small jump in expansion, but this expansion was small relative to the large increases that occurred at later times. Initial expansions could perhaps have been due to experimental error. This would be possible if the "float" was initially set too low and rebounding upward or if the paste swelled up around the float without moving it. Either of these errors is unlikely since two bars were used for each expansion test. Also, no swelling was observed around the "float" and the pastes stiffened too quickly for it to occur.

It appears from Figure 6 that ettringite, in amounts up to about 10 percent, can form with no expansion occurring. If the bar tended to expand, it was contained elastically by the large Portland cement content present. The sample from mix No. 1 was firm, stable, and did not disintegrate. The converse is also observed in mix No. 6 (Fig. 16) where an appreciable expansion was observed at a time when no additional ettringite was produced beyond the initial amount. In this mix, however, the ettringite produced was half again as much as that in mix No. 1 and the Portland cement content was less. Both these factors would tend to contribute to a tendency toward a volume change. The weight gain curve shows the same general shape as the volume change curve. Expansions did not occur until long after ettringite production had ceased and the bars did not disintegrate. The observed expansion must therefore have been the result of a long-term process since, at the time of the expansions, no ettringite was being produced. The samples acted as if they had some sort of a coiled "spring" inside it. This "spring" caused the volume to

increase until after surface cracking occurred. When the "spring" became fully extended expansion ceased. The nature of the "spring" is largely speculative but deformations of the same nature as creep could be due to stored elastic stresses inherent to ettringite. It would be necessary, however, to postulate larger stresses than are normally stored residually in elastic materials.

This "spring" mechanism could also be brought about by a change in the water of hydration of ettringite. It has been observed that ettringite can exist with less than 32 moles of water, depending on the temperature (35). It may be that ettringite produced when little water is available for hydration may form in a "dry" phase. It is possible to have ettringite with 20 moles of water and still observe no change in the X-ray pattern (35). It is therefore possible that the initially formed ettringite may have contained fewer than 32 moles of water. Part of the volume and weight increases may then be due to the ettringite absorbing additional water. This explanation is supported some by the calculations that showed that there was not enough water initially available in the 30 percent water mixes to form the ettringite that did indeed form if 32 moles of water per mole of ettringite were required. If some such effects operated in mix No. 6, there is no reason to believe that they did not operate in other mixes showing expansion and secondary ettringite production.

Figure 15 shows expansion data for two bars made from mix No. 5-30 but stripped at 4 and 16 hours respectively. These data show that expansion increased much more rapidly for the bar stripped at 4 hours. This increase was, furthermore, at a constant rate. Ultimate expansion

was approximately the same for the two bars, although the value was reached ten hours later for the bar that was stripped after 16 hours of hydration. These data are consistent with the "spring" mechanism since it means that the spring constant was decreased by keeping the bars in the molds longer. It also means that the "spring" was the same "size" in the two bars since the expansions were the same at disintegration.

Mortar bars were prepared for each of the six test mixtures. A water to fine material ratio of 0.40 was used for all bars. Figures 22 and 23 show that the expansion strain rates increased as the Portland cement contents originally present in the mix decreased. The mortar expansion curves also showed the same general shape as the paste curves except that there was less expansion due to restraint by the aggregate. This is the same effect observed in other mortar and concrete systems.

Chatterji and Jeffery have postulated that the mechanism responsible for expansion due to sulfate attack on cementitious systems, where the sulfate ions are brought in from outside the system, is the conversion of C_4AH_13 to low calcium sulfoaluminate which in turn goes to ettringite (21). Although the system investigated in this paper was different from these, no C_4AH_13 or monosulfate was found in the samples at any time and the data that were obtained does not support this mechanism.

SUMMARY

Expansive cements containing proportions of Portland cement, high-alumina cement, and gypsum were prepared. Pastes were made with these mixtures at two different water contents. The pastes were molded into small cylinders, which were kept immersed in water. These cylinders were tested to determine their linear expansion, change in weight, and content of tricalcium aluminate trisulfate (ettringite) at various times. The ettringite was determined by quantitative X-ray diffraction.

The amount of ettringite, in general, increased very rapidly in the first few hours and then became more or less constant for a similar period. If the mixture contained sufficient gypsum the ettringite contents increased further after either the stripping of the mold or the onset of visible surface cracking.

The expansion was negligible at first and gradually became progressively greater to the point of disintegration of the sample. Visible surface cracking occurred at about two percent linear expansion, but the specimen remained intact to about ten percent expansion.

The weight gain was of the same nature and relative extent as the expansion.

The effects of larger aluminous cement and gypsum contents (more "potential" ettringite) and smaller Portland cement contents

of the original mixtures were:

1. The amount of ettringite formed at any comparable stage in the process was greater.
2. The expansion at any comparable stage was greater, as was the weight gain.
3. The rate of expansion and weight gain in the later stages was greater.
4. If the gypsum content was so small that it was exhausted early in the process, no further ettringite was formed.

The effects of higher water contents of the pastes were:

1. More ettringite was formed at any comparable stage in the process.
2. More expansion occurred at any comparable stage.
3. Less weight gain occurred at any comparable stage.
4. The resumption of production of ettringite after the initial large production and its cessation was related to the onset of surface cracking in the higher water content samples and to stripping of the molds in the lower.

The relationships between the production of ettringite and expansion were:

1. The initial very large production of ettringite was not accompanied by an expansion of any magnitude compared with later changes.
2. A large amount of ettringite was formed in some samples with no resultant volume change at any time.

3. Expansion occurred in some samples long after the initial ettringite was formed and at a time when no further ettringite was being produced.

No tricalcium aluminate monosulfate or C_4AH_{13} was observed in X-ray diffraction patterns.

Earlier stripping of molds caused earlier and greater expansion.

CONCLUSIONS

Based on the samples tested and the tests performed the following conclusions seem reasonable. They obviously apply only to the particular composition of expansive cements used in this study and not necessarily to other compositions or systems.

1. Relatively large amounts of ettringite in cementitious systems can be determined with reasonable accuracy by X-ray diffraction procedures.

2. Results of experiments with highly expansive cements depend to a large degree on experimental details of specimen preparation and treatment.

3. Greater expansion of these cement systems is associated with larger amounts of potential ettringite in the mixture, greater amounts of ettringite actually formed, and with greater water contents. The relationships between these factors are not simple.

4. A large amount of ettringite in these cements forms very rapidly and in a way that does not cause concurrent expansion. An accomodative process, such as a through-solution mechanism, is indicated. Some of the initially-formed ettringite, probably a minor portion, does have an expansive potential and brings about expansion at relatively long times after its formation.

5. Exhaustion of water is probably an important factor in limiting production of ettringite. It is not, however, the only factor so operating.

6. Ingress of water to cause formation of more ettringite is a principal cause of expansion of these cements. This ingress can be facilitated by removal of molds or partial cracking of the sample.

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APPENDIX A

APPENDIX A

Chemical Analysis of Materials

A. Type I Portland Cement (317)

SiO ₂	21.76 percent
Al ₂ O ₃	5.41
Fe ₂ O ₃	1.97
CaO	65.30
MgO	1.11
SO ₃	2.43
Loss	1.78
Total	99.66
Free Lime	0.72
Insol. Res.	0.27

Compound Composition (Calculated)

C ₃ S	51.20
C ₂ S	23.83
C ₃ A (C ₂ F)	11.00
C ₄ AF	5.99
C ₃ H ₂	5.23
Na ₂ O	0.08
K ₂ O	0.46
Total Alkalies (as Na ₂ O)	0.38

B. Luminite Cement

SiO ₂	10.55 percent
Fe ₂ O ₃ & FeO	10.25
Al ₂ O ₃	41.02
CaO	35.60
MgO	1.89
Total	99.31

Compound Composition (Calculated)

C ₂ AS	38.5
CF	13.9
CA	47.6

