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Alkali-Silica Reaction in Concrete

Leslie J. Struble

U.S. DEPARTMENT OF COMMERCE
National Bureau of Standards
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Final Report

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U.S. DEPARTMENT OF COMMERCE, Malcolm Baldrige, *Secretary*

NATIONAL BUREAU OF STANDARDS, Ernest Ambler, *Director*

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Reaction in concrete between alkalies from the cement
and reactive silica in the aggregate may cause expansion
and cracking, and occasionally may cause significant
weakening of the structure. The mechanisms involved
in this reaction are not well understood, and this
program was undertaken to contribute to a better
understanding of the mechanisms. The objective of
this program is to determine whether there is any
influence of the alkali mineralogy in the cement on
the expansion of mortar due to alkali-silica reaction.

The experimental approach consisted of determining
the distribution of alkalies within a group of commercial
portland cements with a variety of alkali mineralogies,
and measuring expansion of mortar bars prepared using
these cements and various reactive aggregates.

In some cases, differences were observed in both level
and rate of expansion for cements differing in alkali
mineralogy. The differences were substantial with
cements high in alkali and with opal as the reactive
constituent. The results support our hypothesis that
the specific alkali mineralogy of the cement affects
the expansion due to alkali-silica reaction.

1.   Introduction

This report describes progress during the last 14 months of
a two-year research program on alkali-silica reaction in concrete.
The first progress report, covering work at Martin Marietta
Laboratories, is included as Appendix A.

Reaction in concrete between alkalies from the cement and reactive
silica in the aggregate may cause expansion, cracking, and
occasionally significant weakening of the structure. The mechanisms
that control this reaction are not well understood, and measures
to prevent or control the reaction are largely based on empirical
considerations. The work described in this report was undertaken
in order to improve our understanding of the mechanisms controlling
alkali-silcia reaction.

The objective of the program was to study whether the alkali mineralogy in the cement influences the expansion of mortar due to alkali-silica reaction. In order to meet this objective, we selected cements with various alkali mineralogies for the study, and determined their alkali distributions. Mortar bars were prepared from each cement and a reactive aggregate, and expansions of the bars due to alkali-silica reaction were measured over a period of several months.

One study initiated as part of this program is an evaluation of materials for possible use as a standard reactive aggregate. ASTM C441 [1][1] specifies pyrex[2] glass as a standard reactive aggregate, in order to test the effectiveness of pozzolanic materials in preventing expansion due to alkali-silica reaction. However, it appears that this glass will no longer be available as a lump cullet [2], so experiments have been initiated to find an alternative material.

2. Experimental Progress

2.1 Materials

The materials used in this study (described in Appendix A) included eight cements, designated A through G, and four aggregates -- limestone, opal, quartzite, and gneissic granite. An additional cement (designated I) and several aggregate materials have been used in the experiments aimed at identifying a standard reactive aggregate. The aggregates tested as possible standards were selected for potential reactivity and suitability as a standard. Thus far, we have tested the opal and quartzite already mentioned, a rhyolite sand, and three commercial glasses -- pyrex glass (presently specified in C441 [1]), vycor glass, and a porous silica glass.

2.2 Analysis of Cements for Alkali Distributions

Two techniques were used to analyze cements for their alkali distributions: qualitative X-ray diffraction (described in Appendix A), and selective extractions of cement minerals with chemical analyses of the extracted portions. Two extractions were used: a water extraction to determine alkalies present as alkali sulfate, and extraction in solution of salicylic acid in methanol to determine alkalies combined in the calcium silicate

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[1]Numbers in brackets indicate literature references at the end of the report.
[2]Certain trade names and company products are identified in order to specify adequately the experimental procedure. In no case does such identification imply recommendation or endorsement by the National Bureau of Standards, nor does it imply that the products are necessarily the best available for the purpose.

phases (C_3S[3] and C_2S). Alkalies combined in the calcium aluminate phases (C_3A and C_4AF) were calculated as the difference between the alkalies insoluble in the salicylic acid methanol extraction and the alkalies soluble in the water extraction.

Maintaining selectivity of the extractions required particular care. Hydration of the cements was a problem, because hydration would modify the alkali distributions determined using the extractions. Not unexpectedly, hydration occurred in several of the cements. Therefore, all extractions were carried out on freshly ignited samples, to prevent error due to hydration.

During previous experiments (Appendix A), occasional evidence of C_3A dissolution during a 10 minute water extraction was observed. This could be a source of error in determining alkalies present as alkali sulfate phases. Therefore, the water extractions were repeated using shorter extraction times in order to prevent, if possible, dissolution of C_3A. Extraction procedures generally followed Section 17.2 of ASTM C114 [3] for determination of water-soluble alkalies in cement. Samples of ignited cement were mixed with water (0.4 g with 10 ml) for durations of 5 seconds, 1 minute, or 10 minutes (the duration specified in ASTM C114 [3]). Samples were vacuum filtered using Whatman No. 50 paper, and sodium (Na) and potassium (K) concentrations in the liquid portions measured by atomic absorption (AA).

Table 1 lists the concentrations of alkalies dissolved from each cement during these extractions. It appears from these results that the alkalies dissolved during the 5 second extraction are equivalent to the alkalies dissolved during the 1 minute extraction. However, in some cases the alkalies dissolved during the 10 minute extraction, which had been shown to allow occasional dissolution of C_3A, were significantly higher. Therefore, the results from the 1 minute extraction, rather than the 10 minute extraction specified in ASTM C114 [3], were used in this study to estimate the level of alkali present as alkali sulfate minerals, $(K,Na)_2SO_4$ and $K_2Ca_2(SO_4)_3$.

[3]The following abbreviations, common in cement and concrete literature, are used in this report: C for CaO, S for SiO_2, A for Al_2O_3, and F for Fe_2O_3.

Table 1. Alkalies dissolved during water extractions[a]

(percent of ignited cement)

Cement	K_2O			Na_2O		
	5 sec	1 min	10 min	5 sec	1 min	10 min
A	1.26	1.21	1.26	0.24	0.22	0.39
B	0.54	0.55	0.61	0.07	0.02	0.08
C	0.87	0.96	0.96	0.16	0.13	0.14
D	0.58	0.63	0.65	0.05	0.01	0.06
E	0.14	0.15	0.16	0.04	0.03	0.08
F	0.26	0.30	0.28	0.05	0.00	-0.11
G	0.22	0.20	0.22	0.02	-0.02	0.03
H	0.06	0.08	0.15	0.00	0.06	0.07
I	0.94	0.98	0.97	0.19	0.19	0.18

[a]Determined by atomic absorption analysis. Negative results
are attributed to analytical error.

Extraction in a solution of maleic acid and methanol was explored
for the determination of alkalies combined in the calcium silicates.
The extraction, whose procedure is described elsewhere [4],
selectively dissolves C_3S and C_2S. However, during preliminary
experiments it became apparent that methanol was often contaminated
by water, such that water-soluble phases could dissolve during
the extraction. In order to prevent even partial dissolution
of water-soluble phases, the methanol had to be rigorously dried
prior to the extraction. Furthermore, it became apparent that
the solution of maleic acid and freshly dried methanol formed
a gel upon addition of ignited cement, causing the procedure
to be unsuitable for selective extraction. An alternative
extraction, using salicylic acid and methanol, did not form
a gel, and therefore was used for these experiments. A paper
describing the effects of water on the extractions has been
submitted for publication [4].

Because it was not possible to analyze the salicylic acid/methanol
extract directly by AA, alkalies were determined in the extraction
residue, and alkalies dissolved in the extraction calculated
by difference from the total. Both unextracted cements (for
total alkali) and residues from salicylic acid/methanol extractions

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were analyzed according to ASTM C114 [3], dissolving each sample in acid and determining by AA the concentrations of Na and K in solution.

Table 2 lists the distributions of alkalies determined by the various selective extractions. The extractions demonstrate quantitatively, as was shown qualitatively by XRD (Appendix A), that the cements for this program covered a suitable range of alkali distribution, a principal objective when selecting the cements. Some cements, particularly A, I, and C, have high levels of alkali sulfate phases [$(K,Na)_2SO_4$ and $K_2Ca_2(SO_4)_3$]. Other cements, particularly B and H, have high levels of alkali in the calcium aluminate phases (C_3A and C_4AF). Finally a few cements, particularly D, have high levels of alkali in the calcium silicate phases (C_3S and C_2S).

Table 2. Alkali distributions[a]
(percent of ignited cement)

Cement	Total		Water Soluble (alkali sulfates)		SA/M Soluble[b] (calcium silicates)		Insoluble[c] (calcium aluminates)	
	Na_2O	K_2O	Na_2O	K_2O	Na_2O	K_2O	Na_2O	K_2O
A	0.36	1.29	0.24	1.26	0.14	0.06	-0.02	-0.03
B	0.24	1.05	0.07	0.54	0.20	0.26	-0.03	0.25
C	0.25	1.00	0.16	0.87	0.19	0.07	-0.10	0.06
D	0.06	1.24	0.05	0.58	0.06	0.56	0.00	0.10
E	0.21	0.43	0.04	0.14	0.17	0.21	0.00	0.08
F	0.10	0.64	0.05	0.26	0.06	0.33	-0.10	0.05
G	0.14	0.50	0.02	0.22	0.07	0.21	0.05	0.07
H	0.32	0.29	0.00	0.06	0.25	0.15	0.07	0.14
I	0.29	0.98	0.19	0.94	0.12	0.07	-0.02	-0.03

[a] Determined by atomic absorption analysis. Negative results are attributed to analytical error.
[b] Soluble in a solution of salicylic acid in methanol. Determined by difference between total alkali and SA/M insoluble alkali.
[c] Determined by difference between SA/M insoluble alkali and water soluble alkali.

2.3 Mortar Bar Expansions

Mortars, as described in Appendix A, were prepared by mixing cement, water, and graded aggregate. A limestone was used as

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the inert aggregate, and each reactive material was substituted for some portion of the limestone.

The expansion tests involved measuring length changes of mortar bars while stored over water for a period of several months, as described in Appendix A. All bars were stored at room temperature except the bars prepared to explore reactive aggregates for ASTM C441 [1], which were stored at 37.8°C.

Figure 1 presents the expansion data obtained thus far for Cement I and the various candidate materials for a standard reactive aggregate. As this work is in progress, no conclusions have been made.

Figure 2 presents expansion data for Cement A with various levels of opal. This figure demonstrates the pessimum proportion, an important phenomenon in alkali-silica reaction. Pessimum proportion is a term that describes the occurence of maximum expansion at an intermediate proportion of reactive aggregate. For instance, in figure 2 the highest expansion is exhibited by Cement A with 4% opal, while expansions are substantially lower both with 8% opal and with 2% opal.

Although a pessimum proportion was observed for most combinations of cement and aggregate tested, the opal was unique in that its pessimum proportion was quite low, occuring at approximately 2% or 4% opal for all eight cements tested. Furthermore, each pessimum curve for opal was quite sharp, i.e., high expansion occurred over only a narrow range of opal level. Mortar bars prepared with opal at levels only slightly more or less than the pessimum level showed little or no expansion. In practical terms, such sharp pessimum curves require that each pessimum level be precisely determined if the expansion results are to be meaningful.

Expansion results for each reactive aggregate shown in figures 3 through 6. In some cases, significant differences were observed for both level and rate of expansion. In particular, the four high alkali cements with opal showed substantial differences in expansion (fig. 3). The four low alkali cements with opal, on the other hand, showed little difference in expansion (fig. 4). The four high alkali cements with quartzite showed slight differences in expansion (fig. 5), and the four high alkali cements with gneissic granite showed little or no difference in expansion (fig. 6).

The observed differences in expansion may tentatively be explained in terms of alkali distributions within the cements. In particular, expansions with opal were highest and most rapid for cements A and C, which contain the highest levels of alkali sulfate phases. Expansion with opal was lower and less rapid for cement B, which contains the highest level of alkali combined in calcium aluminate phases. Finally, expansion with opal was lowest and most slow for cement D, which contains the highest level of

alkali combined in the calcium silicate phases. Cement D also
showed the lowest and most slow expansion with quartzite (fig.
5).

These results tend to support our starting hypotheses, that
the specific alkali mineralogy of a cement affects the expansion
due to alkali-silica reaction. A full understanding of this
effect, however, requires further experimental work.

3. Conclusions

The following have been concluded from this study:

> 1) In order to determine the level of alkalies present
> as alkali sulfate minerals using a water extraction,
> an extraction duration of 1 minute is preferred over
> the 10 minute extraction presently specified in ASTM
> C114 [3].
>
> 2) In order to prevent partial dissolution of water-soluble
> phases during the selective extraction of calcium silicates
> in a solution of salicylic acid and methanol, it is
> necessary to use freshly dried methanol. Maleic acid
> may not be used with dried methanol, as the solution
> forms a gel when the sample is added.
>
> 3) For the eight cements tested, pessimum proportions
> of opal occurred between approximately 2% and 4%, and
> pessimum curves were very sharp. Such sharp pessimum
> curves require that the pessimum levels be precisely
> determined in order for the expansion results to be
> meaningful.
>
> 4) The specific alkali mineralogy of a cement affects
> its expansion due to alkali-silica reaction.

In order to understand more fully how the cement mineralogy
affects alkali-silica expansion, and thus understand more fully
the mechanism of the reaction, further experimental work is
required.

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4. References

1.   American Society for Testing and Materials. Standard
      test method for effectiveness of mineral admixtures
      in preventing excessive expansion of concrete due to
      the alkali-aggregate reaction. ASTM C441 in Concrete
      and Mineral Aggregates, Vol. 04.02 of Annual Book of
      ASTM Standards, 1984.

2.   Personal Communication from A. Flood, Corning Glass
      Works, to L. Struble, NBS, June 29, 1984.

3.   American Society for Testing and Materials. Method
      for chemical analysis of hydraulic cement. ASTM C114
      in Cement; Lime; Gypsum, Vol. 04.01 of Annual Book
      of ASTM STandards, 1984.

4.   Struble, L. The effect of water on maleic acid and
      salicylic acid extractions. Accepted for publication,
      Cem. Concr. Res. 1985.
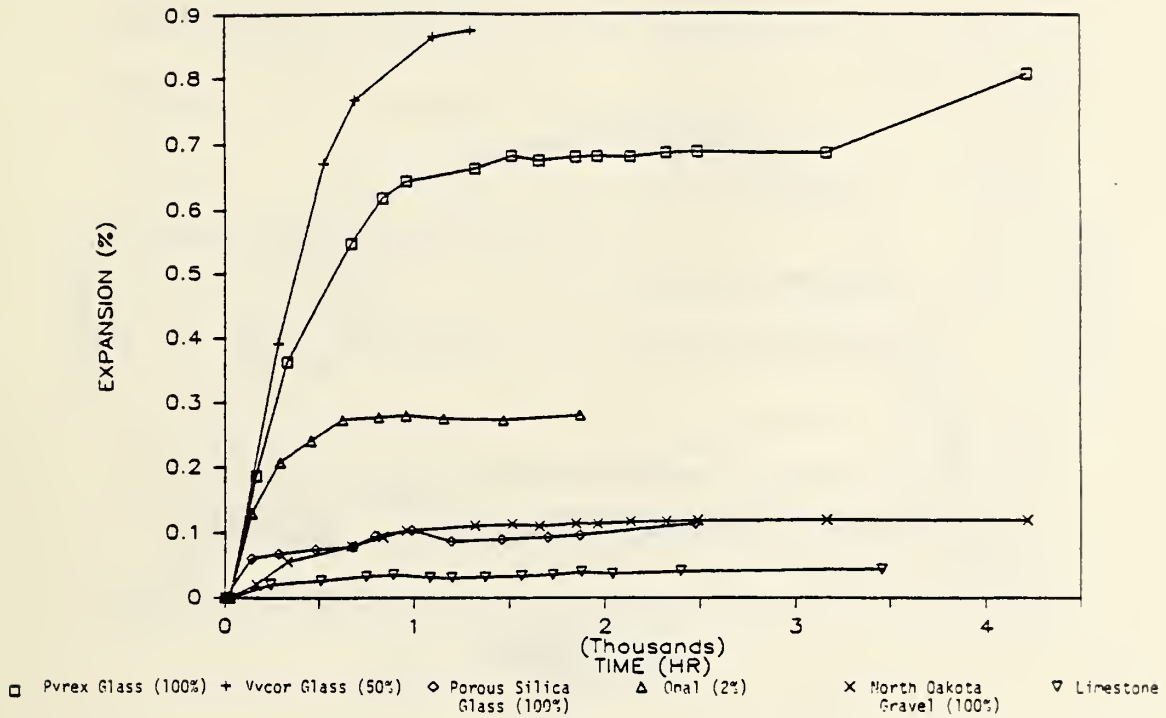
Figure 1. Mortar bar expansion for cement I and various aggregates, each aggregate replacing limestone at approximately its pessimum level.

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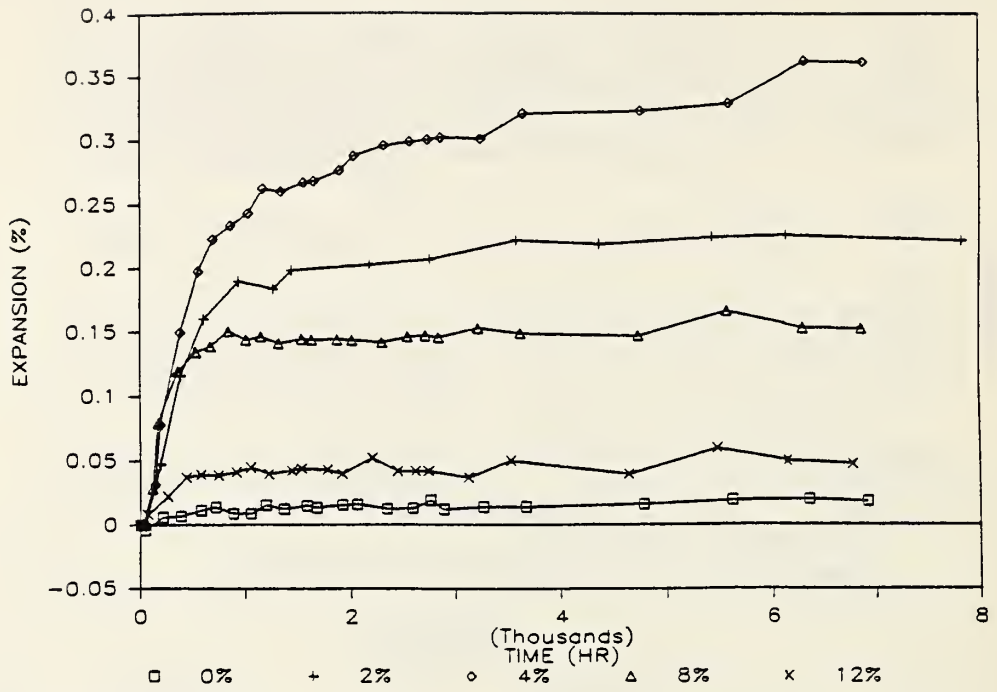
Figure 2. Mortar bar expansion for cement A and opal, with
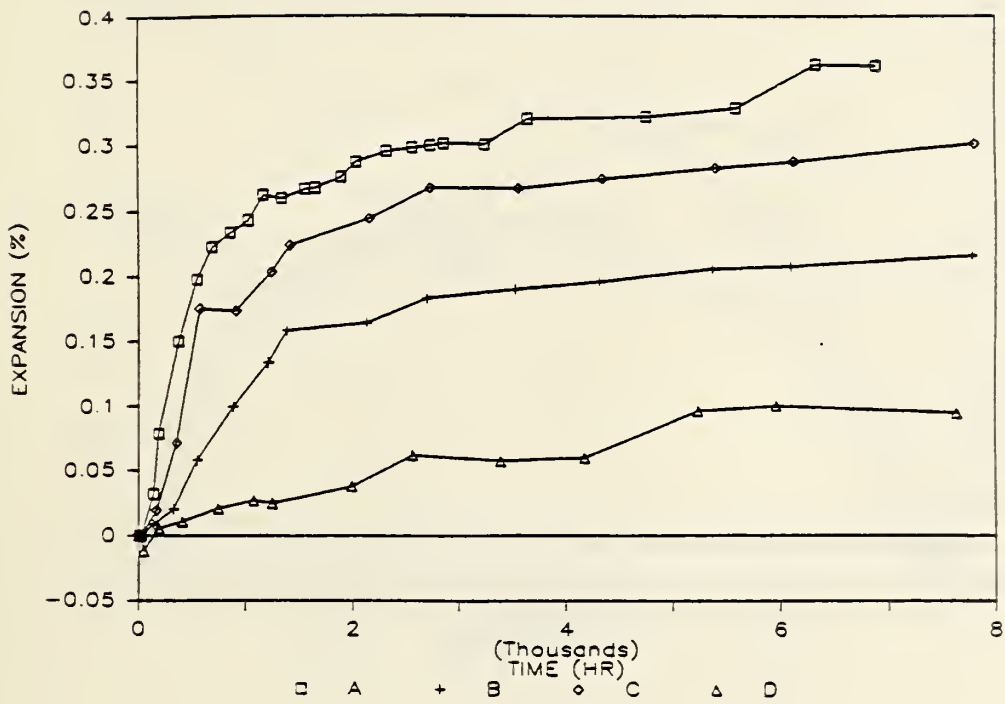opal replacing various levels of limestone.

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Figure 3. Mortar bar expansion for the high alkali cements
(A-D) and opal, with opal replacing limestone at approximately
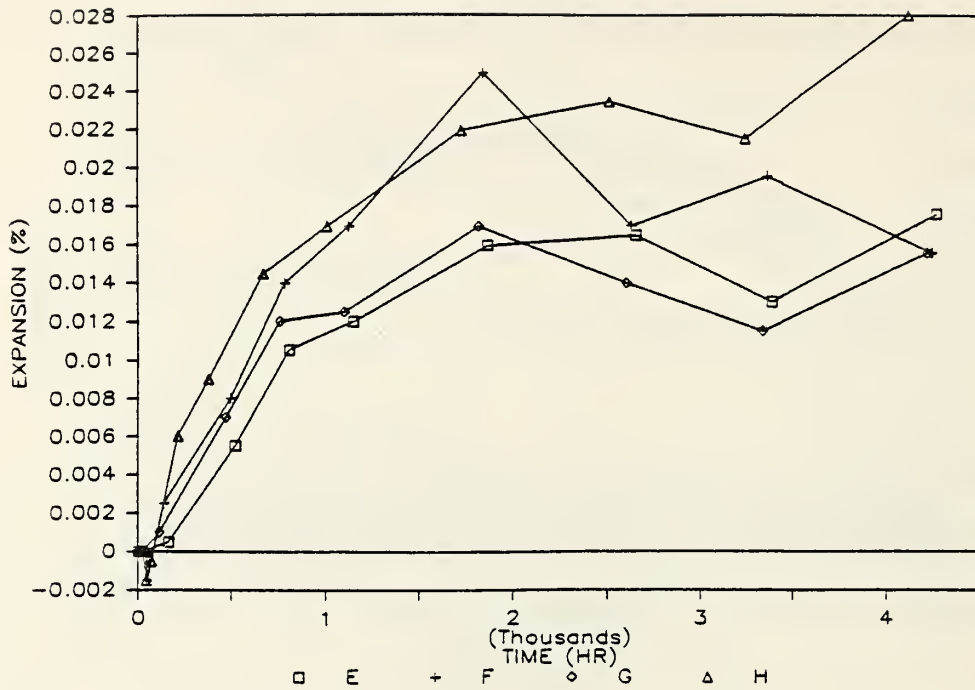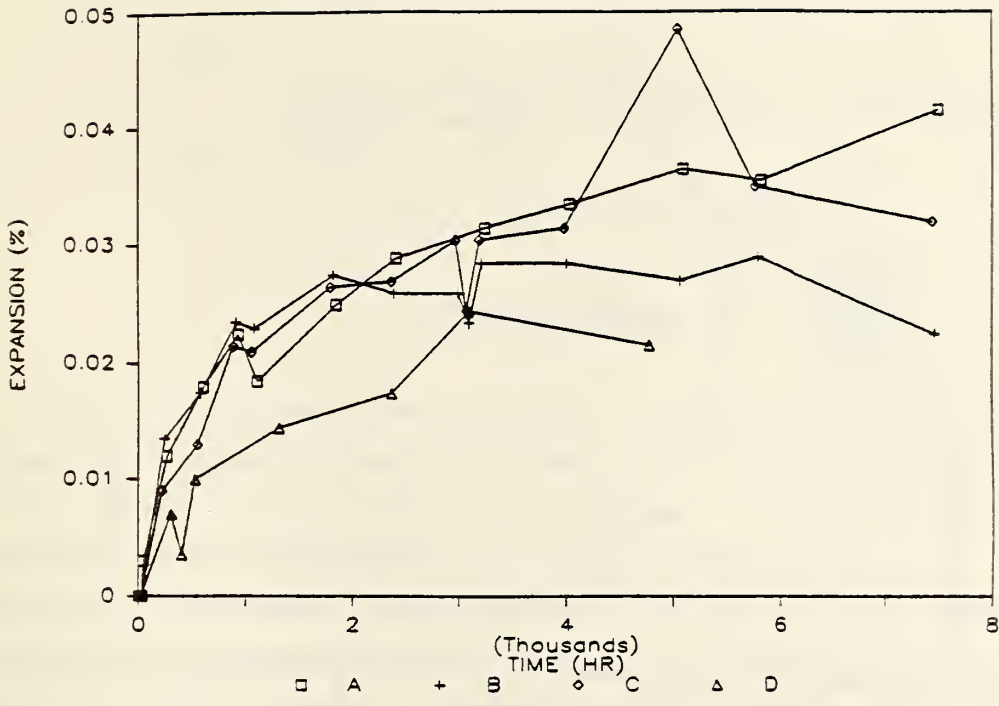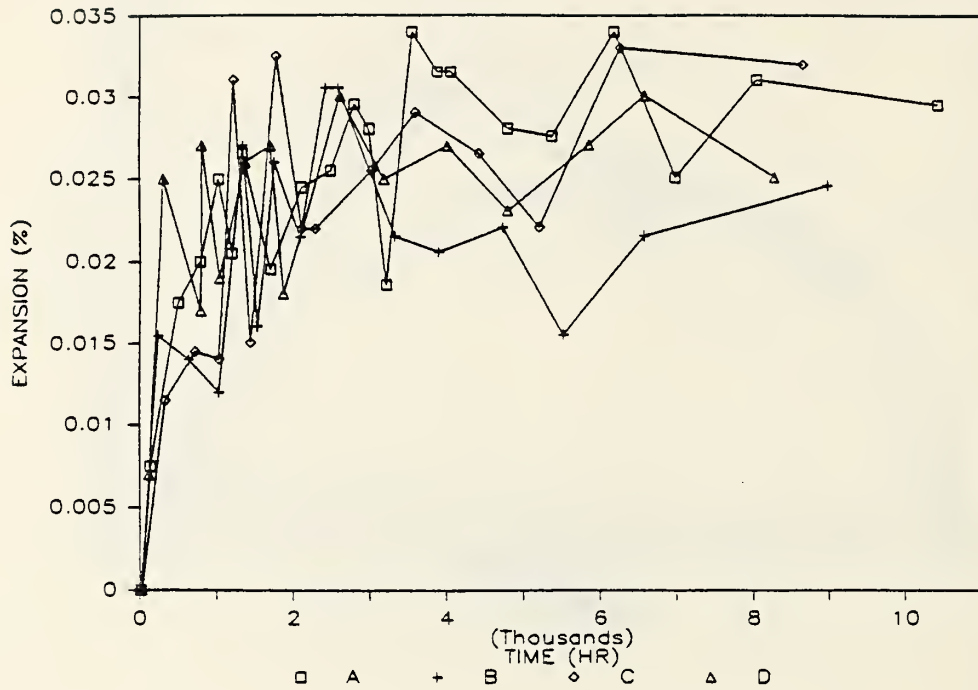its pessimum level for each cement.

Figure 4. Mortar bar expansion for the low alkali cements (E-H) and opal, with opal replacing limestone at approximately its pessimum level for each cement.

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Figure 5. Mortar bar expansion for the high alkali cements (A-D) and quartzite, with quartzite replacing limestone at approximately its pessimum level for each cement.

Figure 6. Mortar bar expansion for the high alkali cements
(A-D) and gneissic granite, each cement with 100% granite.

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Appendix A

PROGRESS REPORT ON NSF GRANT NO. CEE 8210791,

ALKALI-SILICA REACTION IN CONCRETE

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Leslie Struble

Martin Marietta Laboratories

I. INTRODUCTION

This progress report describes the first ten months of a two-year
program on alkali-silica reaction in concrete. Although not required
until the end of the first year of the program,   this report is being
prepared two months early because the grantee, Martin Marietta
Laboratories, is presently requesting that the program be transferred with
the Principal Investigator from Martin Marietta Laboratories to the
National Bureau of Standards. It was felt that a progress report should
be prepared early in order to assist the National Science Foundation in
deciding on this request.

II. CRITICAL ISSUES

This is an empirical study, designed to show whether there is an
influence of cement alkali mineralogy on the expansion of concrete or
mortar containing reactive silica. Such an influence is expected from
mechanistic considerations, and if we find an influence, a follow-up
proposal to NSF is planned to pursue mechanistic studies.

The reaction between alkalies and silica, a major concern in the
production of durable concrete, can lead to expansion, cracking, and even
significant weakening of the concrete structure. Although the reaction
has been studied for many years, the mechanisms that control the reaction
are not yet known. These mechanisms must be understood if the reaction is
to be adequately controlled or prevented.

We expected that alkali mineralogy influences expansion based on our proposal that the expansion is directly controlled by the composition of the pore solution in the concrete or mortar. This control is two-fold: the pH of the pore solution controls the rate of dissolution of silica, and the chemical composition of the pore solution controls the composition of the alkali-silica reaction product, which is best described as an alkali silica gel. Finally, the potential of the gel to sorb water and swell is thought to depend directly on its chemical composition -- especially on its relative proportions of alkali and silica.

The cement mineralogy, specifically the alkali mineralogy, is expected to control the chemical species dissolved in the pore solution, including its pH. In the absence of alkalies, the cement pore solution is saturated with Ca^{++} and OH^-, at a pH of approximately 12.6. However, with dissolved alkalies, the solution converts to a sodium or potassium hydroxide solution, with a much higher pH. Therefore, it is the level of dissolved alkalies from the cement that is the critical factor in both composition and pH of the pore solution.

The rate of alkali dissolution is expected to depend directly on the alkali mineralogy -- alkalies from the soluble sulfate phases will dissolve quite rapidly, but alkalies derived from the other clinker phases are expected to dissolve only as each phase hydrates. The hydration of these phases proceeds at vastly different rates -- C_3A undoubtedly hydrates most rapidly, followed by C_3S, and C_2S and C_4AF hydrate quite slowly. Therefore, for rapidly reactive silica, we expect cements with high levels of alkali sulfate or calcium langbeinite to be much more expansive than cements with alkali concentrated in the calcium silicates or C_4AF. In the case of more slowly reactive aggregate, however, it is possible that cements with high levels of alkali sulfate or calcium langbeinite will be less expansive than cements with alkali concentrated in the calcium silicates or C_4AF. Our experiments are designed to resolve these issues.

III. EXPERIMENTAL PROGRESS

The proposed technical approach consists of two sets of experiments:

1) Selection and characterization of cements. In order to determine whether there is an effect of alkali mineralogy, we proposed in the early part of the program to collect cements with a variety of alkali mineralogies and to determine the alkali partitioning for each cement.

2) Determination of expansion due to alkali-silica reaction. Expansions of mortar bars with the selected cements and either a rapidly reactive or a slowly reactive aggregate are to be tested throughout most of the program.

A. SELECTION AND CHARACTERIZATION OF CEMENTS

In order to carry out these experiments, we sought commercial cements with as high a total alkali content as possible (> 0.60% equivalent Na_2O), and to include sufficient cements such that various levels of all alkali minerals were included. Table 1 lists the selected cements, and their alkali contents and mineralogies. The distribution of mineralogies throughout the selected cements is quite good -- cements are included that contain either high or low levels of each alkali mineral (alkali sulfate, calcium langeinite, alkali-modified C_3A, and alkali-modified C_2S). In order to achieve this distribution, it was necessary to select several cements whose total alkali levels were lower than desired. Lower alkali levels mean that mortar bar expansions will be significantly lower.

Selective extractions of cement minerals with chemical analyses of the extracted portion constitute our primary method of determining the partitioning of alkalies in each cement. Both the total alkalies and the water soluble alkalies have already been measured (Table 2), in order to determine the levels of alkali derived from alkali sulfate and calcium

langbeinite. In addition, we plan to carry out extractions in a salicylic acid-methanol solution (to extract calcium silicates) and in ethylene glycol (to extract alkali sulfate).

XRD analysis of the residues from the water extractions (ASTM C114, Section 17.2), however, suggest that the alkali solubility do not always measure only alkali sulfate and calcium langbeinite. In many cases, a significant portion of C_3A dissolved during the extraction. Thus, alkali sulfates and calcium langbeinite estimated by water extraction may be in significant error. We will pursue the selective extractions very care- fully, continuing to analyze residues by XRD to determine what phases are dissolving. It is hoped that the water extraction can be modified to provide a better indication of the levels of alkali sulfates and calcium langbeinite.

Qualitative XRD analyses have been carried out on all cements -- including analysis of residues from the salicylic acid-methanol extrac- tion, to facilitate identification of alkali sulfates, calcium langbeinite, and alkali-modified C_3A, and analysis of residues from an extraction in an aqueous potassium hydroxide-sugar solution, to determine alkali-modified C_2S. This qualitative XRD work provided the basis for the alkali mineralogies listed in Table 1.

Certain of the proposed cement characterizations have not yet been carried out. The proposed experimental schedule has been modified some- what, in that the mortar bar tests (described below) were started earlier in the program, and cement characterizations were delayed until later in the program. QXRD analyses, SEM-EDS analyses, and further selective extractions will be carried out during the second year of the program.

B. AGGREGATES

Aggregates were to include one nonreactive aggregate to serve as matrix and control, and two aggregates containing reactive silica, one a rapidly reactive silica and the other a slowly reactive silica. We selected a limestone as the nonreactive aggregate, Beltane opal as the rapidly reactive aggregate, and both a quartzite, and a gneissic granite as slowly reactive aggregates. The Beltane opal is a hydrous silica,

known to be highly reactive in mortar, and is used in many laboratories as a standard reactive rock in studies of alkali-silica reaction. The quartzite (novaculite) is a high purity, very fine-grained silica. The gneissic granite is a commercial aggregate from Camak, Georgia, a coarse-grained granite composed primarily of quartz, feldspar, and mica, which was recommended for this program by A. Buck, U.S. Army Corps of Engineers.

In order to confirm that the aggregates, which were selected based on petrographic evidence, would have the intended rates of reactivity, they were tested for potential alkali reactivity according to ASTM C289. This is a chemical test to determine the extent of reaction in a 1 N NaOH solution for 24 hours at 80°C. Both the concentration of dissolved silicon and the reduction in hydroxyl ion concentration are measured. The test results (Table 3) were as expected: the opal is quite highly reactive, the novaculite moderately reactive, and the Camak only slightly reactive. The limestone, while providing no soluble silica, did significantly reduce the alkalinity of the solution.

There is a particular proportion of reactive aggregate -- actually, a particular ratio of reactive silica to total alkali -- which causes maximum expansion of mortar or concrete (called the pessimum proportion). Available evidence suggests that the pessimum for opal will be approximately 4% (by weight of total aggregate), and the pessimum for Camak granite will be approximately 80%. Based on the results of the chemical test (Table 3), the pessimum for novaculite is expected to be approximately 25%. We are preparing mortars with reactive aggregate replacing various proportions of limestone, such that these pessimum proportions are bracketed.

C. MORTAR BAR EXPANSIONS

The following procedures are used for the mortar bar expansion tests (generally according to ASTM C227): use a graded aggregate, a sand-to-cement ratio of 2.25 (by weight), and a single water-to-cement ratio of 0.49 (by weight) -- a constant ratio, rather than the variable ratio specified in ASTM C227; prepare two 10"x1"x1" bars from each mortar,

demold the bars at an age of 24 hours, and store the bars over water at room temperature -- bars are stored in brass racks in sealed plastic containers lined with blotter paper, a procedure presently under consideration by ASTM Subcommittee C09.02.02; periodically measure the length of each bar using a dial gage.

Expansion measurements are presently in progress for 76 bars. These include all the control bars (limestone only), most opal bars (at 4%, 8%, and 12% opal), and a few bars with novaculite or Camak. Additional tests are planned for some cements with 2% opal, and for most cements with either novaculite or Camak.

Expansion results for each cement at each level of opal are shown in Figs. 1-8. Tests with many Cements -- A, B, C, D, and G -- have been in progress for more than 1000 hours, and in most cases the expansions have leveled off. All these cements show high to moderate expansion (0.27% to 0.04), and a clear pessimum proportion of approximately 4% opal. The remaining lower alkali Cements -- E, F, and H -- have been in progress for less than 600 hours and expansions are much lower (< 0.01%). These cements do not show a clear pessimum proportion, so we intend to test them with 2% opal.

In order to compare results for cements with similar alkali levels, expansions at a single level of 4% opal are shown separately for higher alkali cements (Fig. 9) and for lower alkali cements (Fig. 10). It is too early in the tests to draw conclusions regarding the lower alkali cements, but expansions with opal of the higher alkali cements show clearly that many cements with similar levels of total alkali have significantly different expansions. Furthermore, in general the higher expansions with opal are produced by cements whose alkali is concentrated in more rapidly soluble forms. For instance, the highest expansion, 0.27%, was obtained with Cement A, which has 1.12% equivalent alkali, largely present as potassium sulfate. The next expansion level, 0.15%, was obtained with Cement C, which contains 0.90% alkali, largely as calcium langbeinite. The two cements with much lower expansions of 0.04% have similar alkali levels, Cement B, alkali with 0.92%, largely concentrated in C_3A, and Cement D with 0.81%, primarily as potassium sulfate. Thus these first

results are generally as we expected, with the exception of Cement D, whose expansion is much lower than expected.

D. ALKALI DISSOLUTION

One paper, partially supported by this program, was prepared in collaboration with Dr. I. Jawed and J. Epp of the Laboratories. Copies of this paper have already been sent to NSF, in accordance with the contract reporting requirements. The paper was presented at the Sixth International Conference on Alkalies in Concrete, held in Denmark in June, 1983, the proceedings of which will be published.

The paper describes the dissolution and hydration of C_3A - Na_2O solid solutions, including direct determinations of the rate of alkali dissolution from each C_3A phase. Through this work, we confirmed that the alkali goes into solution directly as the C_3A phase hydrates. Furthermore, we found no significant affect of Na_2O level on the rate of hydration of the C_3A - Na_2O solid solutions. Additional studies of this nature, to determine the rate of alkali dissolution from other alkali-containing minerals, will undoubtedly be included in our planned follow-up proposal.

IV. CONCLUSIONS

Good experimental progress has been made during the first 10 months of this program: cements have been selected, their characterizations are in progress, and a significant portion of the mortar bar tests are already in progress.

Hydration studies of several C_3A - Na_2O solid solutions shows that sodium dissolution occurs directly as the phase hydrates, which supports our hypothesis that alkali concentration and pH in the pore solution are controlled by cement alkali mineralogy.

Expansion tests are far enough along to conclude that there are, as expected, significant differences in expansion with opal between cements of different alkali mineralogy. In general, expansions are highest for cements whose alkali occurs in more rapidly soluble phases.

One paper already submitted for publication was partially supported by this grant. In addition, two presentations are planned in the near future — one in December at a Federal workshop on concrete durability at the National Bureau of Standards, and the other in January, 1984, at the annual meeting of the Transportation Research Board.

TABLE 1

Cements

Cement	Total Alkali (% eq. Na_2O)[1]	Alkali Mineralogy[2]
A	1.12	o largely K_2SO_4 o some $K_2Ca_2(SO_4)_3$ o some alkali-modified C_3A o some alkali-modified C_2S
B	0.92	o largely alkali-modified C_3A o some K_2SO_4 o some alkali-modified C_2S
C	0.90	o predominantly $K_2Ca_2(SO_4)_3$
D	0.81	o predominantly K_2SO_4
E	0.53	o largely alkali-modified C_2S o some K_2SO_4 o some $K_2Ca_2(SO_4)_3$
F	0.50	o some K_2SO_4 o some $K_2Ca_2(SO_4)_3$ o some alkali-modified C_2S
G	0.45	o some $K_2Ca_2(SO_4)_3$ o some alkali-modified C_3A o some alkali-modified C_2S
H	0.44	o largely alkali-modified C_3A

1 Eq. Na_2O is the sum of the Na_2O plus the Na_2O – molecular equivalent of the K_2O.

2 Determined by XRD.

TABLE 2

Cement Alkali Levels

Cement	Total		Water Soluble[1]	
	% Na_2O	% K_2O	% Na_2O	% K_2O
A	0.33	1.20	0.23	1.08
B	0.21	1.08	0.05	0.51
C	0.21	1.05	0.14	0.84
D	0.06	1.14	0.01	0.54
E	0.21	0.48	0.03	0.12
F	0.09	0.63	0.01	0.21
G	0.11	0.51	0.02	0.17
H	0.24	0.30	0.03	0.07

1 Water soluble alkali is derived largely from alkali sulfates, though there is some contribution from alkali-modified C_3A.

TABLE 3

Results of Chemical Test for Potential Reactivity
of Aggregates (ASTM C289)[1]

Sample	[Si] moles/liter	[OH$^-$] moles/liter
Blank	< 0.006	0.74
Opal	1.154	0.15
Novaculite	0.186	0.82
Camak	0.015	0.82
Limestone	< 0.006	0.40

1 Dissolved [Si] and reduction in [OH] due to reaction and dissolution of
   aggregate in an aqueous 1 N NaOH solution for 24 hours at 80°C.
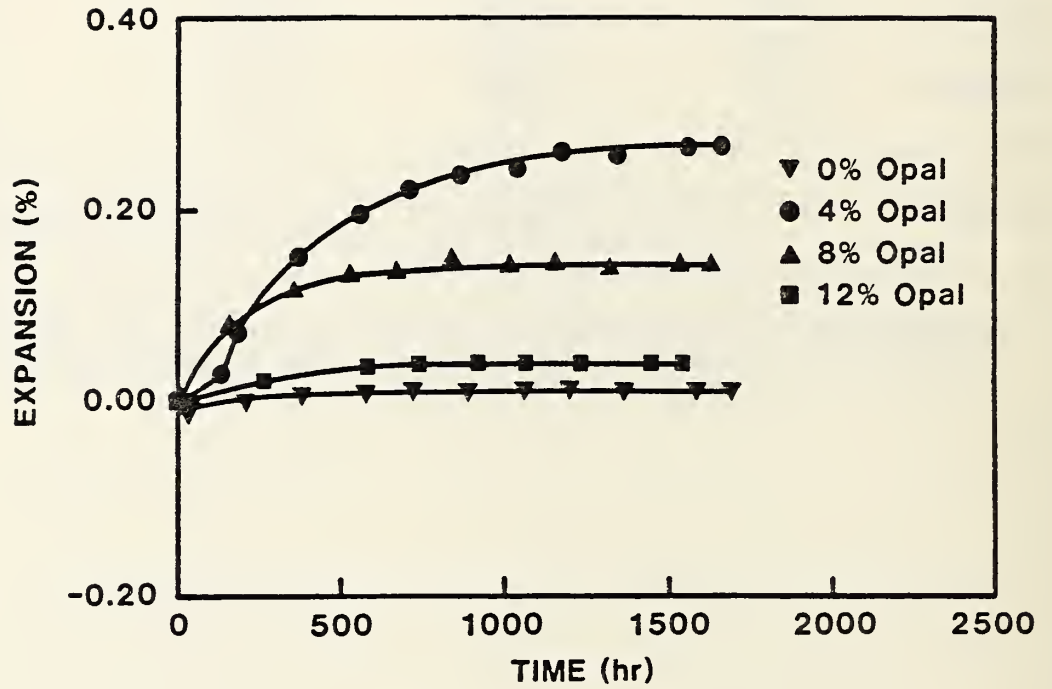
Figure 1.   Mortar bar expansions for Cement A with various levels of opal
(tests in progress).
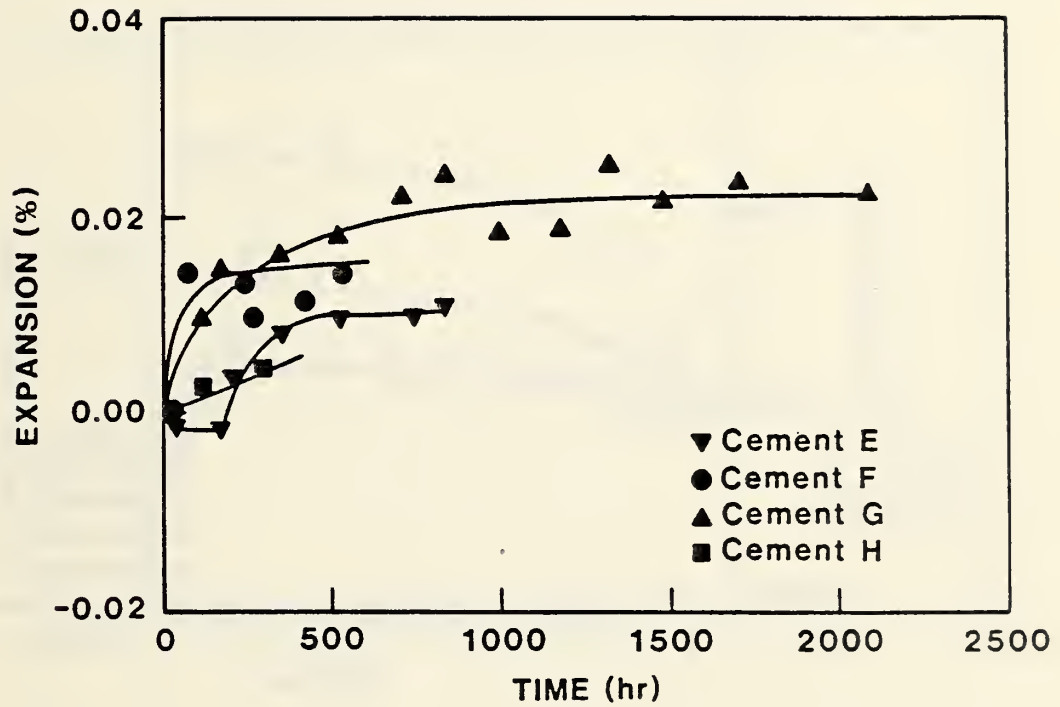
Figure 10. Mortar bar expansions for all low alkali cements with 4% opal (tests in progress).
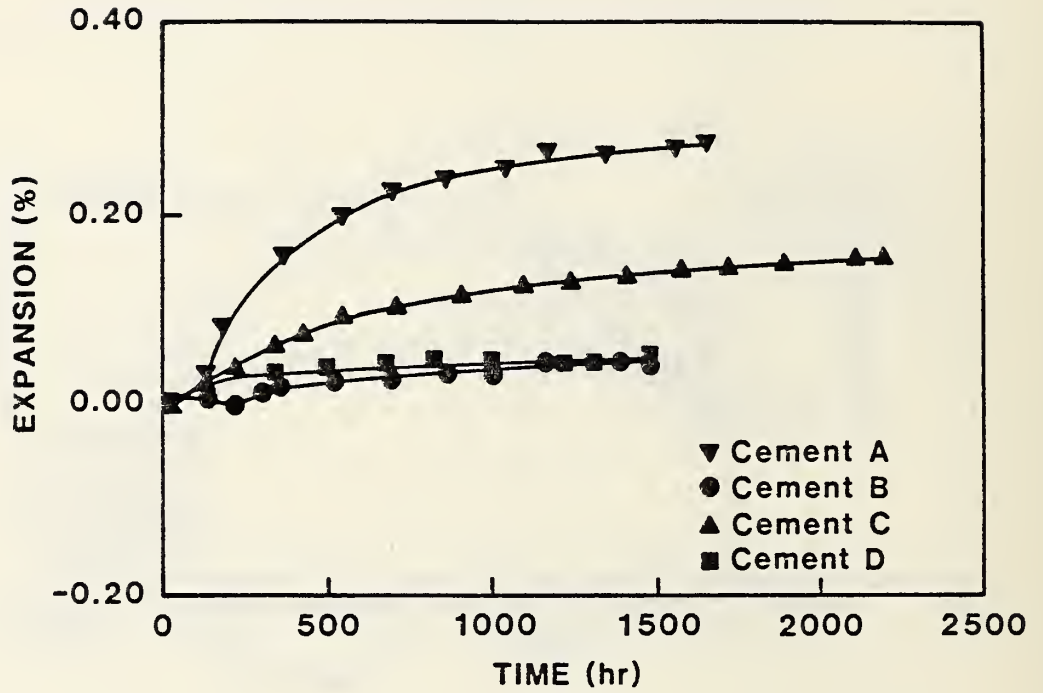
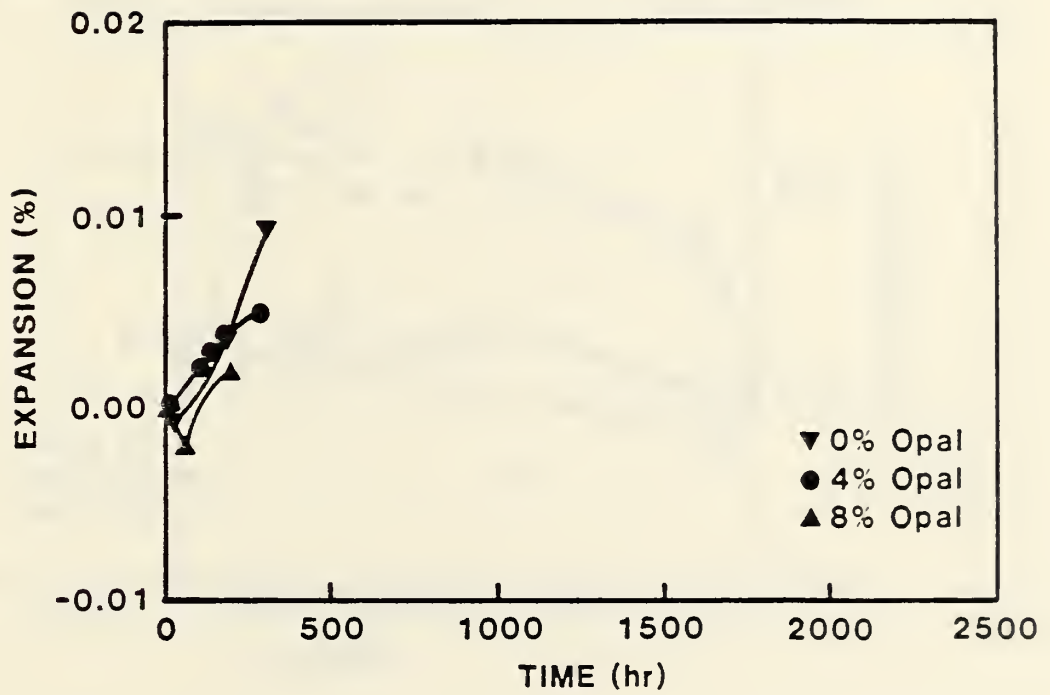Figure 9. Mortar bar expansions for all high alkali cements with 4% opal (tests in progress).

Figure 8. Mortar bar expansions for Cement H with various levels of opal (tests in progress).
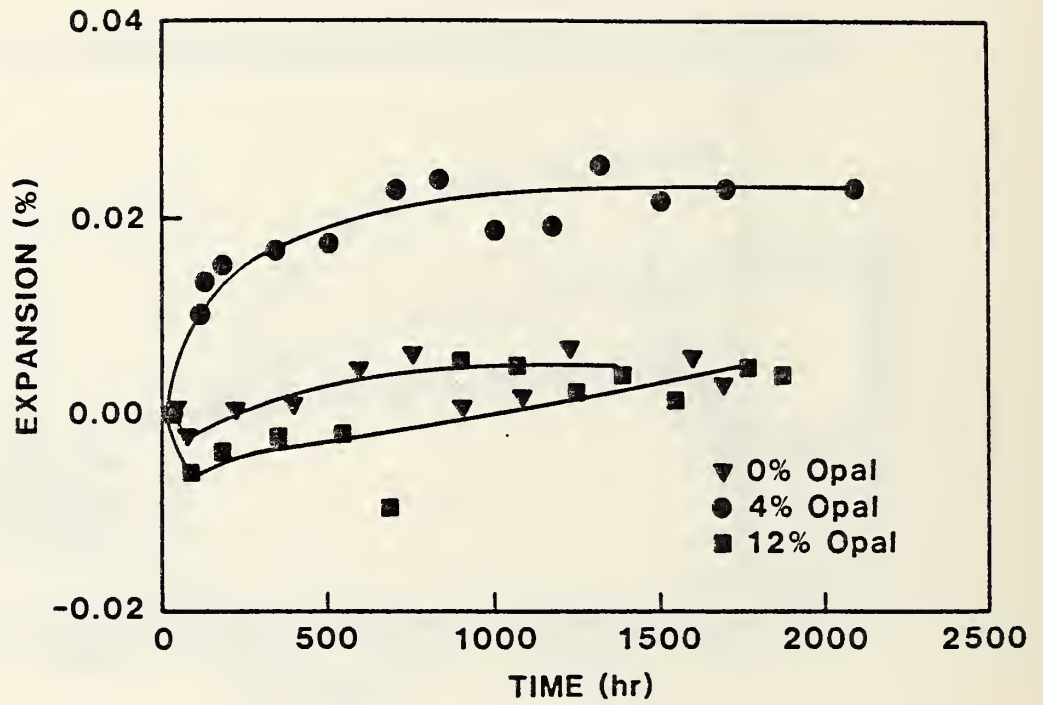
Figure 7.   Mortar bar expansions for Cement G with various levels of opal
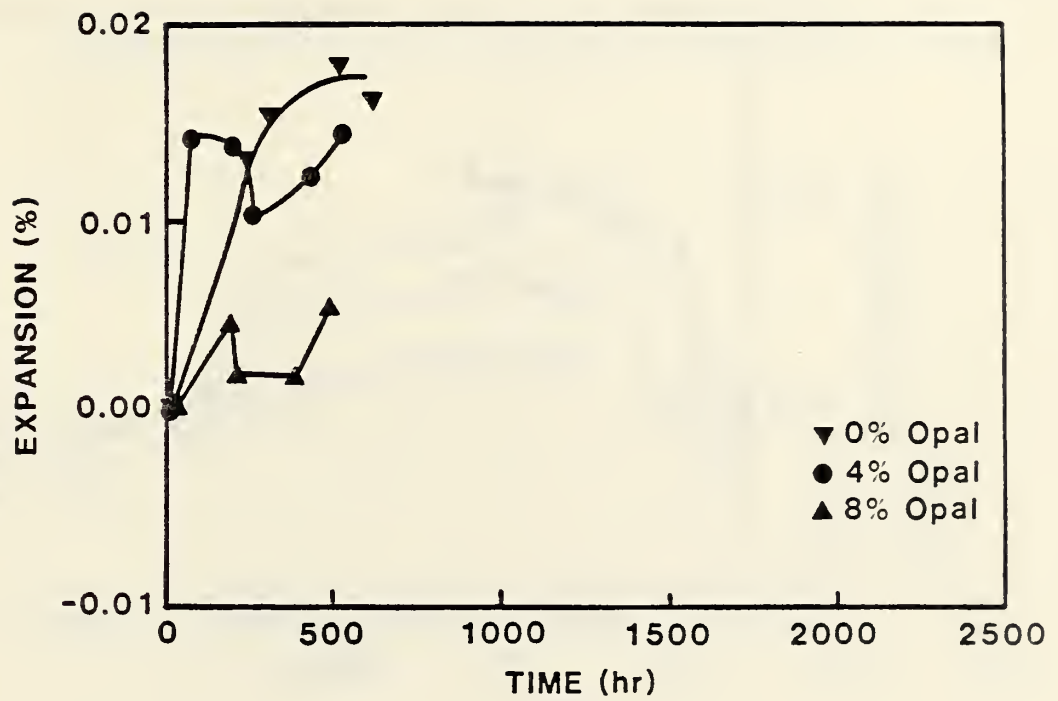(tests in progress).

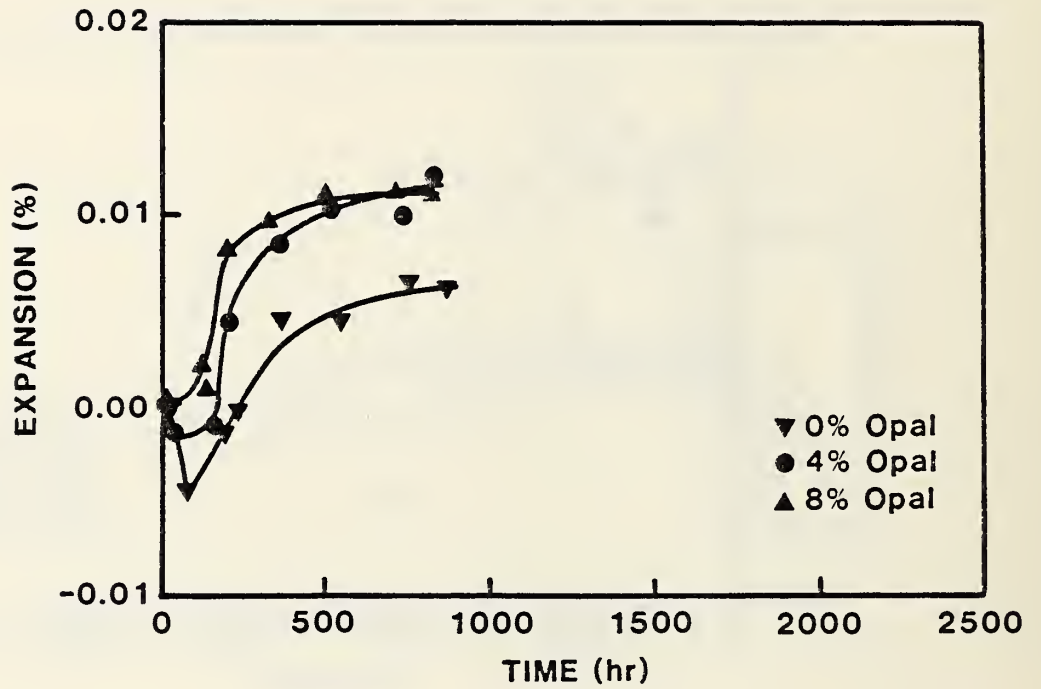Figure 6. Mortar bar expansions for Cement F with various levels of opal (tests in progress).

Figure 5.   Mortar bar expansions for Cement E with various levels of opal
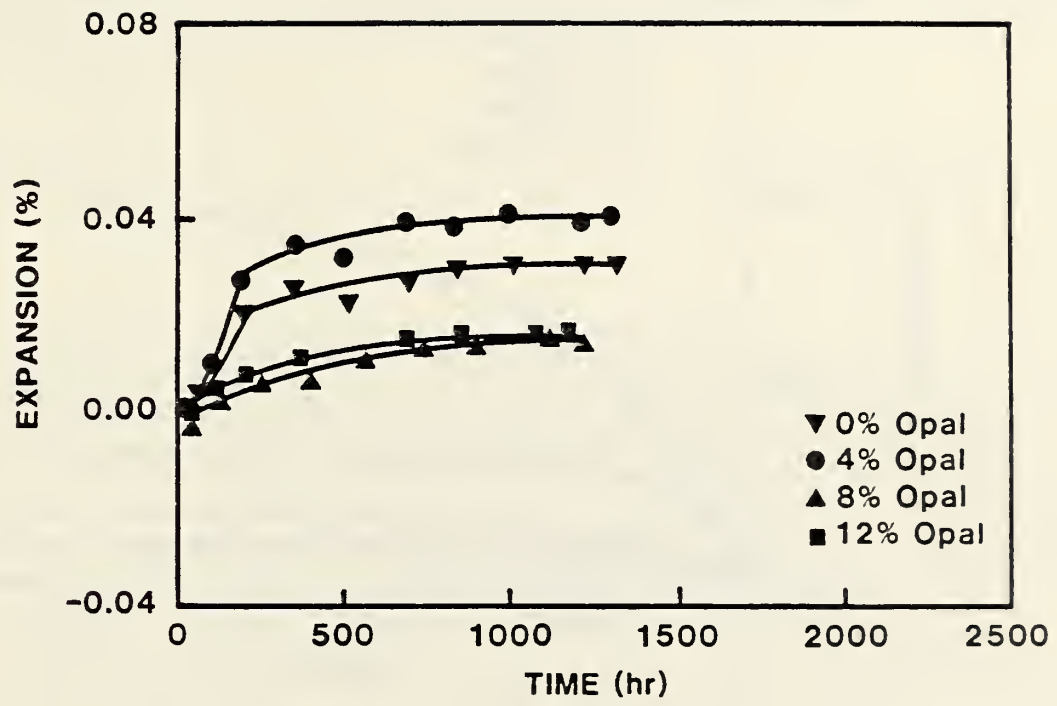(tests in progress).

Figure 4.   Mortar bar expansions for Cement D with various levels of opal
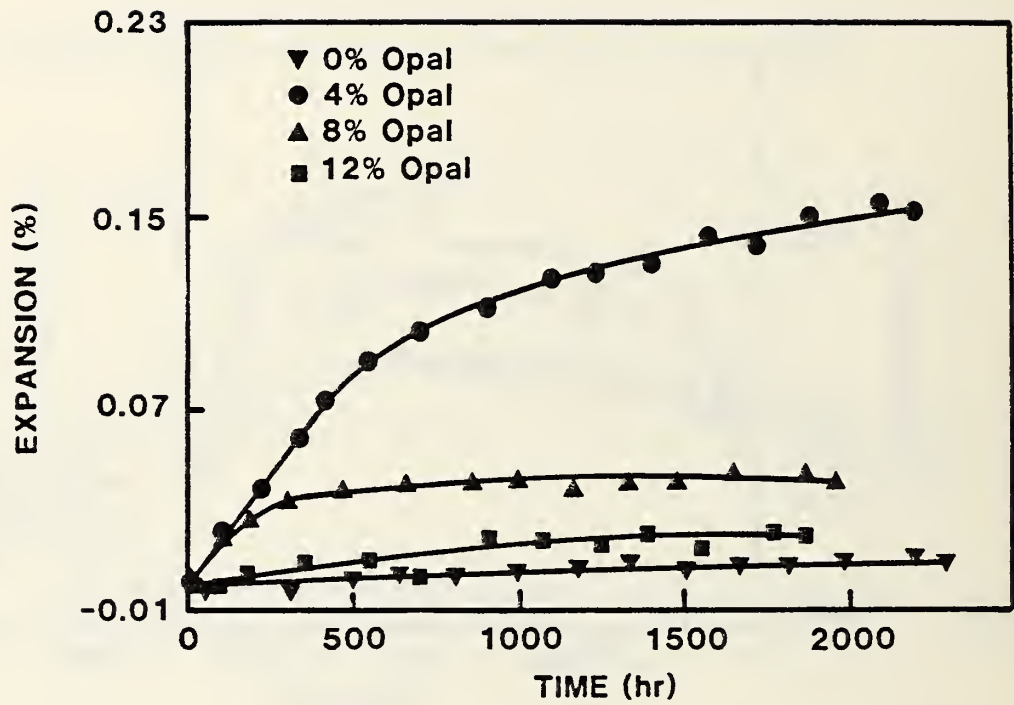(tests in progress).

Figure 3.   Mortar bar expansions for Cement C with various levels of opal (tests in progress).

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10. SUPPLEMENTARY NOTES

☐ Document describes a computer program; SF-185, FIPS Software Summary, is attached.

11. ABSTRACT *(A 200-word or less factual summary of most significant information. If document includes a significant bibliography or literature survey, mention it here)*

Reaction in concrete between alkalies from the cement and reactive silica in the aggregate may cause expansion and cracking, and occasionally may cause significant weakening of the structure. The mechanisms that control this reaction are not well understood, and this program was undertaken in order to improve our understanding. The objective of this program is to determine whether there is any influence of the alkali mineralogy in the cement on the expansion of mortar due to alkali-silica reaction. The experimental approach consisted of determining the distribution of alkalies within a group of commercial portland cements with a variety of alkali mineralogies, and measuring expansion of mortar bars prepared using these cements and various reactive aggregates. In some cases, differences were observed in both level and rate of expansion for cements differing in alkali mineralogy. The differences were substantial with cements high in alkali and with opal as the reactive constituent. The results support our hypothesis that the specific alkali mineralogy of the cement affects the expansion due to alkali-silica reaction.

12. KEY WORDS *(Six to twelve entries; alphabetical order; capitalize only proper names; and separate key words by semicolons)*

Alkali; alkali-silica reaction; cement; concrete; selective extraction; soluble alkali

13. AVAILABILITY ☒ Unlimited ☐ For Official Distribution. Do Not Release to NTIS ☐ Order From Superintendent of Documents, U.S. Government Printing Office, Washington, D.C. 20402. ☒ Order From National Technical Information Service (NTIS), Springfield, VA. 22161	14. NO. OF PRINTED PAGES 37
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