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COOPERATIVE HIGHWAY RESEARCH PROGRAM
REPORT **67-5**

Effects of Reactive Carbonate Aggregates on the Durability of Laboratory Concrete Specimens

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MISSOURI STATE HIGHWAY DEPARTMENT
BUREAU OF PUBLIC ROADS

EFFECTS OF REACTIVE CARBONATE AGGREGATES ON THE DURABILITY OF LABORATORY CONCRETE SPECIMENS

Prepared by

MISSOURI STATE HIGHWAY DEPARTMENT
Division of Materials and Research

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in cooperation with

U.S. DEPARTMENT OF TRANSPORTATION
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The opinions, findings, and conclusions expressed in this publication are not necessarily those of the Bureau of Public Roads.

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SUMMARY

The objectives of this study were to determine: (1) the relationship between rock prism and concrete expansions; (2) the effect of cement alkali content upon the expansion of concretes containing reactive rock; (3) the effect of various environments upon the rate of concrete expansion; and (4) the reduction in the alkali-carbonate reaction resulting from replacement of a portion of the cement with fly ash.

The results of these tests on concretes, made with carbonate rocks varying in reactivity to alkali, indicated that:

1. The expansion of the concrete tends to be directly related to the expansion of the rock prisms. The ratio of concrete expansion to rock prism expansion is small, and varies with (a) whether the maximum, average or minimum rock prism expansion is used, (b) the alkali content of the cement, (c) the environment to which the concrete is subjected, and (d) the length of the test periods.
2. An increase in the alkali content of the cement had no appreciable effect upon the expansions of concretes made with nonreactive rocks, or rocks exhibiting contraction in the prism test.
3. An increase in the alkali content of the cement appreciably increased the expansion of concretes made with reactive rocks, or rocks exhibiting expansion in the prism test.

4. Storage of concretes, containing reactive carbonate rocks, in a 4 percent solution of sodium chloride significantly increased the expansion.
5. The use of low alkali cement tends to offset the adverse effect of sodium chloride on concretes made with reactive rock and high alkali cement.
6. Storage of concretes containing reactive carbonate rocks, in a 4 percent solution of calcium chloride did not significantly effect the expansion.
7. Storage of concretes, containing reactive carbonate rocks, over water at 100°F significantly increased the expansion. The increased expansion was only slightly greater than that obtained with companion specimens stored in a 4 percent solution of sodium chloride.
8. The tests with fly ash were rather inconclusive. It would appear, however, that some benefit might be obtained when fly ash, similar to that used in this study, is used with mildly reactive carbonate rocks.

Although the observed increase in pattern cracking in some of the newer concrete pavements cannot presently be considered serious or proof of serious concrete deterioration in the future, it suggests that an undesirable amount of deterioration might ultimately develop as a result of the conbined deteriorating effect of the alkali-carbonate reaction and other factors. The possibility of an increase in concrete deterioration, resulting from the demonstrated ad-

verse effect of sodium chloride on concretes containing reactive aggregates, suggests that consideration should be given to the specified use of low alkali cement. Definitely these results indicate that the use of low alkali cement would tend to alleviate the adverse effect of the continuing increased use of sodium chloride as a de-icer. In addition, the specified use of low alkali cement would not only tend to reduce the need for control of the use of reactive aggregate, but it also should reduce the amount of needed testing if ultimately some control of the use of reactive aggregate is proven to be necessary.

Presently low alkali cement is not specified in Missouri, but little high alkali cement is being received or used. Consequently, a change in specifications does not appear to be warranted at this time. If, however, an appreciable increase in the use of high alkali cement should occur, a change to the specified use of low alkali cement would definitely follow.

As it is considered undesirable to continue subjecting concretes to several environments in future laboratory tests, it is recommended that, hereafter, the concretes should be stored over water in sealed containers at 100°F. Subjecting concretes to this storage condition at 2 or 3 days of age could reduce the necessary length of the test period to 30 or 60 days.

INTRODUCTION

Until the late 1930's most concrete technologists believed that concrete aggregates were either entirely or practically chemically inert. It was then discovered that some siliceous aggregates were sufficiently reactive to the alkali in the cement to cause serious concrete deterioration. Later, within the past decade, it has been established that some carbonate aggregates are also reactive to the alkali in the cement.

As a result of these discoveries, the Missouri State Highway Department conducted studies to determine the reactivity of siliceous and carbonate aggregates used in Missouri. The initial studies on the siliceous aggregates were made in the 1940's, and the results indicated no serious alkali-silica reactions. However, there would appear to be a possibility that even a slight amount of cracking from an alkali-aggregate reaction might tend to decrease the frost resistance of some concretes.

As previously stated the alkali-carbonate reaction was not recognized until the late 1950's, but prior to its recognition one Missouri carbonate rock had not been approved for use because laboratory concrete containing this rock had exhibited excessive early expansion. Later tests showed this carbonate rock to be highly reactive to alkali.

The recognition of the alkali-carbonate reaction caused concern in Missouri, because it was believed that (1) the excessive early expansion of the concrete, containing

the previously mentioned carbonate rock, was due to alkali-carbonate reaction, and (2) an increased amount of the newer PCC pavements was exhibiting a pattern cracking typical of alkali-aggregate reaction. This concern led to initiation of a study* designed to determine the location, description, and degree of reactivity of the reactive carbonate rocks being used in concrete.

The reactivity of the carbonate rocks to alkali was determined from the expansion of small rock prisms stored in a one normal solution of sodium hydroxide. The results of the prism tests indicated that some rocks were reactive to alkali, with the degree of reactivity varying from slight to appreciable. These results also indicated considerable variation in the reactivity of the rock within a single ledge, and showed that reactive rock could meet all currently used acceptance tests.

The results of the prism test have provided much information of value concerning the range in reactivity and the probable sources of reactive rock in Missouri. If or when control of the use of reactive carbonate rock is deemed necessary, the results of the prism test should be of great value.

Although much information was obtained from the prism test, it was recognized that other information was needed that could only be obtained from tests on concretes.

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*See paper, "Alkali-Carbonate Reactivity - An Academic Or a Practical Problem, "by E. O. Axon and Junior Lind, Highway Research Record No. 45, 114-125 (1964).

For example, it was believed that the use of de-icers was, in some manner, contributing to an increase in the rate and degree of the alkali-aggregate reaction in concrete and proof of this could not be obtained from the prism test. In addition, the relationship between the expansions of concretes and rock prisms needed to be studied, and the beneficial effect of various factors in reducing the alkali-aggregate reaction must be determined by tests on concrete.

Consequently, this report presents the results obtained in an exploratory study of the effect of the alkali-carbonate reaction upon concretes. The previously mentioned variability of the reactivity of the rock within a ledge prevented the procurement of large samples of rock of the desired reactivity. Although this prevented attainment of all of the objectives of the study, much information of value was obtained.

PROCEDURE AND MATERIALS

Scope:

Eight carbonate rocks, exhibiting a varying amount of expansion in the prism test, were tested in concretes. To facilitate testing, two sizes of concrete specimens were used, namely; 2 in. x 2 in. x 11.25 in. bars and 3.5 in. x 4.5 in. x 16 in. beams.

A total of 128 bars was made to be tested in accordance with the outline in Table 1.*

A total of 160 beams was made to be tested in accordance with the outline in Table 2.

Mix Design:

Requirements for the concretes used in this study were:

1. The maximum size of the coarse aggregates used in the bars and beams was 3/4 in. and 1¼ in. respectively.
2. The cement factor was approximately 1.52 barrels per cubic yard.
3. The volume of coarse aggregate was approximately 43 percent of the volume of the concrete.
4. The water-cement ratio was that required to maintain the slump, within the range of 2.5 to 3.5 inches.

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*All Tables and Figures are located at the back of this paper.

5. The desired air content was 5.5 percent.
6. In using fly ash, 20 percent of the cement was replaced by an equal weight of fly ash of 2.04* specific gravity. If the specific gravity of the fly ash differed from 2.04, the weight of fly ash was increased or decreased by the ratio of actual specific gravity of the fly ash divided by 2.04. This procedure insured that the volume of the fly ash would remain constant in the mix for all sources of fly ash.
7. The fine aggregate content was varied to compensate for differences in the volume of mixing water, fly ash, and air.

Cement:

A low alkali cement (0.51 percent total alkali as Na_2O) was used.

The high alkali cement (1.0 percent total alkali as Na_2O) was obtained by adding a sufficient quantity of a sodium hydroxide (NaOH) solution to the low alkali cement to increase the total alkali content to 1.0 percent.

Physical and chemical properties of the cement are shown in Table 3.

Fly Ash:

The fly ash used in this test was obtained from an operating plant in eastern Missouri. The physical and chem-

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*Available information indicated that the minimum specific gravity of fly ashes was or was near 2.04.

ical properties of the fly ash are shown in Table 4.

Fine Aggregate:

The fine aggregate was Missouri Rive sand obtained from the Jefferson City area. This sand was air dried and separated on a No. 16 sieve. The two sizes were recombined at the time of mixing by the following ratio:

30 percent by weight of plus #16 size and
70 percent by weight of minus #16 size,

thus meeting the required gradation of:

Percent Passing No. 4 sieve	95 to 100
Percent Passing No. 20 sieve	40 to 75
Percent Passing No. 50 sieve	5 to 30
Percent Passing No. 100 sieve	0 to 10

The actual gradation obtained was 99.0, 54.8, 11.5, and 0.4 percent respectively. The physical properties of this sand are shown in Table 5.

Coarse Aggregate:

Eight coarse aggregates from three geological formations were used. The first seven of these rocks were selected because they had exhibited rock prism expansions ranging from 0.12 to plus 4.0 percent. Stone 8 was obtained to represent nonreactive rock. All but stone 6 had been tested and approved for use in concrete. Although the ledges, from which stones 1, 2, and 4 were obtained, were once approved for use in concrete, these ledges were rejected the last time they were sampled. The rejection was due to failure to pass laboratory tests other than the prism test.

The design gradation for the coarse aggregate used in the bars was:

Percent Passing 3/4" sieve	100
Percent Passing 1/2" sieve	67.5
Percent Passing 3/8" sieve	35.5
Percent Passing #4 sieve	0 to 1.0

and the design gradation for the beams was:

Percent Passing 1¼" sieve	100
Percent Passing 1" sieve	87.5
Percent Passing 1/2" sieve	27.5
Percent Passing #4 sieve	0 to 1.0

The results of tests for bulk specific gravity (dry and saturated surface dry) and absorption are shown in Table 6.

The chemical analyses of the stones are shown in Table 8.

Vinsol Resin Solution:

A vinsol resin solution was used as an air-entraining agent for both the bars and beams. The solution was made according to instructions in the paper by H. F. Gonnerman in Volume 15, Number 6, June 1944, Journal of the American Concrete Institute, page 493:

45.4 grams of Vinsol Resin
6.8 grams of NaOH
Plus sufficient distilled water to make 2000 ml.

Mixing Water:

Tap water was used.

Calcium Chloride:

The chemical analysis of the Type 1 calcium chloride, used in preparing the solution for one of the storage environments is shown in Table 7.

This $CaCl_2$ was in a dry, flaky form and required slight heating during dissolution in distilled water. The strength of the solution used was initially 4.0 percent, but it was realized that due to evaporation and the addition of new solution to the storage jars, some slight change in the solution strength may occur. This same reasoning also applies to the sodium chloride solution.

Sodium Chloride:

The chemical analysis of the sodium chloride, used in preparing the solution for one of the storage environments, is shown in Table 7.

RESULTS OF TESTS ON FRESH CONCRETE

The results of the air content, yield, and slump tests, made on the fresh concretes immediately after mixing, are shown in Table 9. The air content for the bars was calculated as the percent difference in the design weight and the actual weight per cubic foot, as determined on a 0.03524 cubic foot sample of the fresh concrete. Some error is inherent in the values obtained because of the smallness of the sample. The air content for the beams was also calculated as the percent difference in the design weight and the actual weight per cubic foot, as determined on a 0.2064 cubic foot sample of the fresh concrete. Therefore, the results on the air tests for the beams should be more reliable.

DISCUSSION OF TESTS ON BEAMS AND BARS

Strength tests on concrete beams:

The results of the 7 and 28 day strength tests made on the concrete beams are shown in Table 10, along with the 28 day dynamic modulus of elasticity values. All of these concretes were cured and tested under the same conditions.

Concrete beams made with stone 6 had a low dynamic modulus, probably because of its very porous, lightweight, and highly absorptive nature.

The modulus values shown for the high alkali cement (part b, Table 10) compared fairly well with the values shown for the low alkali cements except for stones 1 and 2. This difference may be explained by the appearance of a faint pattern cracking on the surface of the beams containing these aggregates and the high alkali cement, as early as 14 days of age. The cracks were not visible but their presence was quite evident as the beams began to surface dry. The difference in the rate of drying between the cracked and the non-cracked areas gave a very distinct pattern of approximately 1" to 1½" square dry areas bounded by the darker meandering moist looking lines of approximately 1/8 inch in width.

Further evidence of this early cracking is also found in flexural strength values shown for stone 2 (parts a and b, Table 10). By comparing the 14" and 7" span length flexural tests at 28 days, the reduction in strength between

the low and high alkali cements is 23 and 18 percent respectively, or for practical purposes approximately 20 percent. The other stones tested (4, 5, and 8) did not show a significant loss in flexural strengths with increase in alkali content. The compressive strength values did not, as expected, reflect the same reduction in strength.

The third set of data (part c) included in Table 10, show the effects of fly ash, used as a partial substitute for the high alkali cement, on the strength properties of the concrete beams. Perhaps a better method of showing these results is in the percent reduction in strength caused by the fly ash as compared to the reduction caused by the use of high alkali cement only. In Table 11, the percent reductions in strength caused by cement alkali content and the fly ash is shown for the four aggregates tested. The low vs. high alkali cement (part a, Table 11) has been discussed previously. The data clearly show the difference in flexural and compressive strengths obtained.

The low alkali cement vs. high alkali cement plus fly ash (part b) again clearly shows a difference in strengths. The percent reductions in strength are considerably larger than those shown for low vs. high alkali cement only. The exceptionally large values for the reduction in flexural strength of concretes containing stone 2 are due primarily to the cracking of the specimens prior to testing. The addition of fly ash more than doubled the effects of the high alkali cement when used alone, as shown by comparison

of parts a and b in Table 11. The relative effects of the fly ash alone are shown in part c.

The high alkali cement vs. high alkali plus fly ash data (part c, Table 11) also have the 7 day strength values for comparison. The 7 day flexural strength differences are only slightly different between stones, averaging approximately 18 percent reduction. At 28 days the flexural strengths appear much the same as in part b. The 28 day compressive strengths, unlike the other data, show a fairly uniform reduction of approximately 18 percent. This is consistent with the literature concerning the slow rate of strength development of concretes containing fly ash. More information concerning the properties and behavior of concretes containing fly ash may be found in the Highway Research Board Bulletin 284, "Fly Ash in Concrete, An Evaluation".

With the limited amount of data presented on the early strength properties of these concretes, there is evidence that the use of high alkali cement did cause a significant reduction in flexural and compressive strengths with the expansive aggregates and did, to a lesser extent, reduce the flexural strength of the other concretes. The replacement of 20 percent of the cement with fly ash did not eliminate the loss in strength or control the reaction being studied. It did, however, more than double the percent reduction in flexural and compressive strength, over that caused by the high alkali cement alone.

The strength results indicate it would be beneficial to use low alkali cements with potentially expansive aggregates.

Change in Length of Bars:

The percent change in length of the bars is shown in Table 12. Also shown in this table is the 8-week, percent change in length of the 5/16 in. x 5/16 in. x 1½ in. rock prisms. The expansions of the prisms are used to arrange the aggregates in the order of maximum to minimum reactivity.

A study of the expansions of the bars in Table 12 reveals that:

1. The expansion of the concrete bars tend to vary directly with the expansion of the rock prisms. As expected, the expansions of the concrete bars, containing reactive rocks, are much less than the expansions of the rock prisms.
2. The expansions of companion sets of bars, during the 28 day moist curing, are very nearly the same. This is important because it shows that the variations in expansion of the bars after 28 days is due to difference in environment and not to variation in the reactivity of the rock within sets of bars.
3. The increase in the alkali content of the cement increased the 28 day expansion of bars made with all coarse aggregates except stone 8.

4. During the 28 day moist curing the expansion of bars, made with stones 1, 2, and 3 and cement of high alkali content, exceeded 0.05 percent. This value of 0.05 percent is believed to be the amount indicative of the presence of microcracks in concretes. As previously stated, pattern cracking was plainly visible on some of the beams at 14 days of age.

5. Storage of bars, made with stone 2, in environment B (4 percent solution of sodium chloride) greatly increased the rate of expansion over that obtained in environments A (saturated lime water) and C (4 percent solution of calcium chloride). However, storage of bars, made with stones 4 and 8, in environments B and C increased the expansions about equally. The reason for this apparent difference in the effect of the calcium chloride is unknown.

6. If the increased expansion of the concrete bars, made with the nonreactive stones 4 and 8 and subjected to environments B and C, is considered to be due to the effect of the chlorides on the cement hydration products, it is obvious that this effect cannot account for the large increase in expansion of the bars containing reactive stone 2 and stored in environment B. Very definitely these results indicate that sodium chloride contributes to the alkali-carbonate reaction.

7. Storage of bars in environment D (100 percent relative humidity at 100°F.) had approximately the same effect upon increased expansion as storage in environment B (4 percent sodium chloride solution).

8. Fly ash appears to be slightly beneficial in reducing the alkali-carbonate reaction. As the tests with fly ash were not exhaustive, it is impossible to evaluate the benefit that might be obtained by using fly ash with cement of low alkali content or with mildly reactive rocks.

Change in Length of Beams:

The percent change in length of the beams, initial measurement at 2 days, is shown in Table 13. The expansions of the rock prisms are used to arrange the aggregates from maximum to minimum reactivity, similar to Table 12.

A study of the beam expansions shown in Table 13 reveals that:

1. The expansions of the concrete beams show a fair similarity with that of the bars subjected to the lime water solution environment (A) as shown in Table 12. Again, as expected, the concrete expansions are less than the expansions of the rock prisms.

2. The effect of the increase in alkali content of the cement is evident when the expansions of beams made with stones 1, 2, 3, and 5 are studied. For

example, beams containing stone 2 showed an expansion in excess of 0.1 percent prior to 28 days with high alkali cement; whereas, comparable beams with low alkali cement required in excess of 240 days to reach 0.1 percent expansion. A similar benefit was obtained by the use of low alkali cement with stones 1, 3, and 5. Consequently, the expansions of the beams also clearly show that low alkali cement is very beneficial in reducing the rate of the alkali-carbonate reaction.

As these results, in general, tend to support those obtained with the bars, further discussion of them does not appear warranted at this time. Tests on these beams will be continued.

Dynamic Moduli of Bars and Beams:

When bars and beams were measured for change in length they were also tested sonically. As the results obtained merely tend to support the length change measurements, they are not included.

DISCUSSION OF ROCK PRISM VS. CONCRETE EXPANSIONS

One and perhaps the chief objective of this study was to determine the relationship between rock prism and concrete expansions. As previously stated, the expansion of the concrete tended to line up directly with the expansion of the rock prisms. Although this relationship exists, these data clearly show that the obtained relationship depends upon many factors. These factors and their effect upon the relationship were:

1. It will be noted in Table 12 that rock prisms varying apprecially in expansion were obtained from some of these rocks. The question immediately arises regarding which of the rock prism expansions should be used in determining the relationship with concrete expansions. The regression lines in Fig. 1 clearly show that different relationships are obtained with the maximum, average, and minimum prism expansions. Obviously, the relationship between rock prism and concrete expansions vary appreciably with the value of rock prism expansion used. Consequently, if one desires to insure that a specified amount of concrete expansion is not exceeded, it would appear mandatory to use the relationship between minimum rock prism and concrete expansions. This will be done in the following comparisons.

NOTE: This use of the minimum prism expansion is not intended to imply that this procedure should be

universally followed in determining the acceptability of the stone in a ledge. Actually, it is used here because, (1) there is some doubt regarding the sufficiency of the prism samples to establish an accurate average, and (2) the present objective is to establish a prism expansion which is indicative of the need for further tests. Actually, the use of minimum prism expansions would not be realistic in determining the acceptability of a rock in a ledge, because some ledges may contain both reactive and nonreactive rock. Such ledges may require extensive testing to determine the distribution and amount of reactive rock, and the probable average reactivity of the rock as produced.

2. The effect of the alkali content of the cement, upon the relationship between rock prism and concrete expansions, is clearly evident in Fig. 2. If the user places no control upon the alkali content of the cement, it would appear mandatory to use the relationship obtained with cement having the maximum alkali content that might be encountered. This would appear to be necessary even though the probability of using a cement of high alkali content with a particular rock may be exceedingly small. This could be prevented by specifying use of cement of low (maximum of 0.6 percent) alkali content.

3. The effect of the environment upon concrete expansion and the relationship between rock prism and concrete expansions is shown in Fig. 3. Maximum con-

crete expansions were obtained with environments B (in 4 percent sodium chloride after 28 days) and D (over water at 100°F. at 28 days). The regression lines in Fig. 3 are not exactly comparable because all eight stones were not tested in concretes subjected to each environment.

As environments B and D caused the maximum concrete expansions, environment D is indicated to be the desirable one for future tests. It is also suggested that concrete specimens be subjected to environment D at 2 days of age. If this suggestion is followed, the expected increased expansion could be offset by a reduction in length of the test.

4. The effect of the length of the concrete test period upon the relationship between rock prism and concrete expansions is shown in Fig. 4. As the concretes continue to expand with age, the length of the concrete test period has a definite effect upon this relationship. However, there is no apparent indication that an increase in length of the test period will make it less difficult to determine the acceptability of the rock. Consequently, these results indicate that there is little reason for subjecting the concretes to a lengthy test period. The problem is to establish acceptable concrete expansions for the length of test period used.

From the preceding there can be little doubt concerning the existence of a relationship between the expan-

sions of rock prisms and concretes. In fact there are many relationships. The effect of four factors upon the expansion of the concrete has been discussed. The effect of the length of test period upon rock prism expansions has not been discussed, but it also affects this relationship. It should, however, be very evident that concrete expansions are related to rock prism expansions. This fact is most encouraging, because it indicates that the cheaper and simpler rock prism tests may be used to minimize the number of concrete tests. Even though the acceptance or rejection of reactive rock may ultimately depend upon a concrete test, the prism test could be most valuable in determining which rocks need to be tested in concrete.

The problem is to specify the procedures for determining the relationship between rock prism and concrete expansions. The next problem is to establish an acceptable amount of concrete expansion. When these two problems have been solved, control of the use of reactive carbonate rock will be possible.

DISCUSSION OF CONCRETE EXPANSIONS

As stated in the preceding section, an acceptable amount of concrete expansion needs to be established before acceptable limits can be established for rock prism expansion. To do this one must be aware that a concrete expansion of near 0.05 percent is believed to be the amount indicative of microcracks in the concrete, and that visible cracking will be present at less than 0.10 percent expansion. For concrete deteriorated by frost action an expansion of as much as 0.10 percent is commonly considered as indicative of an unsatisfactory amount. This suggests that 0.10 percent should be set as the maximum amount of acceptable concrete expansion for the alkali-aggregate reactions.

There is a question, however, regarding the relative detrimentality of concrete expansions resulting from frost action and alkali-aggregate reactions. There presently appears to be an indication that expansion and/or cracking of the concretes in pavements is less detrimental when caused by alkali-aggregate reactions than when caused by frost action. The reason for this is unknown, but it may be due to a difference in the soundness and possibly the volume of the concrete between cracks. Undoubtedly the expansion and cracking places the concrete in pavements in compression, and this would tend to hold sound pieces of concrete tightly in place. If this is true, it would follow that relief of the compressive stress, by blow-ups or patching, could result in extensive and rapid deterioration of

the cracked concrete. Therefore, the unacceptable amount of alkali-aggregate reaction could be that which would result in sufficient concrete expansion to cause blow-ups.

The rate of the concrete expansion, or the time available for creep to reduce compressive stresses, may also be a factor in reducing the detrimental effect of alkali-aggregate reactions in concretes.

The fact remains, however, that there is some amount of concrete expansion caused by alkali-aggregate reactions which is unacceptable. The data presented in this report are of little value in establishing the acceptable amount of concrete expansion caused by alkali-carbonate reactivity. These data however, do show that under certain conditions excessive concrete expansions can be obtained. They also show the effect of various factors upon concrete expansions.

The curves in Fig. 2 show that if the excessive amount of concrete expansion of 0.10 percent at 91 days is permitted, this amount could be exceeded by using rocks with prism expansion in excess of 0.46 percent with cements having an alkali content of 1.0 percent, or by using rocks with prism expansions in excess of 2.8 percent with cements having an alkali content of 0.51 percent. Consequently, these results definitely show the advantage of specifying the use of cement of low alkali content, and indicate that rock having an average prism expansion in excess of approximately 2.4 percent should not be used even with low alkali cement.

If a safer and perhaps more realistic value for concrete expansion at 91 days of 0.05 percent be used, the curves in Fig. 2 indicate that rock having an average prism expansion in excess of approximately 1.0 percent should not be used even with low alkali cement. With no control on the alkali content of the cement and a maximum permissible concrete expansion of 0.05 percent at 91 days, the maximum permissible average rock prism expansion could be 0.2 percent or less. This comparison again shows the advantage of using low alkali cement.

Although the results obtained in this study cannot be used to determine the acceptable amount of concrete expansion, they rather emphatically point out the benefit to be derived from using cement of low alkali content. If a high proportion of the cement now used has an alkali content of less than or only slightly greater than 0.6 percent, a requirement that all cement be low alkali would not be expected to greatly decrease the amount of concrete deterioration caused by alkali aggregate reactions. The chief advantage of specifying low alkali content would be in determining the acceptability of reactive aggregate. For example, the possibility of obtaining rock having an average prism expansion in excess of 0.2 percent would be much greater than the probability of obtaining rock having an average prism expansion in excess of 1.0 percent. Consequently, the use of low alkali cement should greatly reduce the amount of testing required for control of the use of reactive rock, and should also tend to reduce the cost of producing rock.

If low alkali cement is not specified the acceptability of reactive rock should undoubtedly be established upon the assumption that each rock could be used with the cement of maximum alkali content. This would result in tighter control of the use of reactive rock, and undoubtedly increase the amount of testing needed. It could also result in the unnecessary rejection of some reactive rocks.

In considering whether low alkali cement should be specified, it should not be overlooked that these results, see Fig. 5, indicate that the use of low alkali cement would tend to offset the adverse effect of sodium chloride on concretes made with reactive rock and high alkali cements. Consequently, the specified use of low alkali cement might be expected to provide concrete performance approaching that obtained when high alkali cement was used with reactive rock prior to the use of sodium chloride as a de-icer. As the beneficial effect of low alkali cement could be largely or completely offset by the adverse effect of sodium chloride, the use of low alkali cement would not necessarily permit an increase in the reactivity of the stone.

Presently low alkali cement is not specified in Missouri, but little high alkali cement is being received or used. Consequently a change in specifications does not appear to be warranted at this time. If, however, an appreciable increase in the use of high alkali cement should occur, a change to the specified use of low alkali cement would definitely follow.

Actually the results obtained in this exploratory study leaves many questions that cannot be answered except by additional tests. Whether such tests are warranted depends to a large extent upon the probability of using rock of sufficient reactivity to cause excessive expansion of the concrete. This problem, however, is being investigated in another phase of this study and will not be discussed in this report.

Despite the exploratory nature of these tests, it is believed that the results not only tend to corroborate previously reported findings but they also provide some previously unreported indications.

Table 1

NUMBER OF CONCRETE BARS WITH INDICATED COARSE AGGREGATE, CEMENT, ADDITIVE, AND STORAGE ENVIRONMENT

Stone Ident. No.	Cement and Additive with Respect to Storage Environment[1]									Total Number of Bars
	High Alkali				Low Alkali			High Alkali and Fly Ash		
	A	B	C	D	A	B	C	A	B	
1	3[2]	-	-	-	3	-	-	-	-	6
2	3	3	3	3	3	3	3	3	3	27
3	3	-	-	-	3	-	-	-	-	6
4	3	3	3	-	3	3	3	3	3	24
5	3	3	-	3	3	3	-	3	3	21
6	3	-	3-	-	3	-	3	-	-	12
7	3	-	-	-	3	-	-	-	-	6
8	3	3	3	2	3	3	3	3	3	26
									Grand Total	128

(1) Storage environments after 28 days moist curing on shelves in moist room.

A - In saturated lime water
B - In 4 percent NaCl solution
C - In 4 percent $CaCl_2$ solution
D - Over water in sealed containers at 100°F.

(2) Each bar in each set made from a different batch of concrete.

Table 2

NUMBER OF CONCRETE BEAMS WITH INDICATED COARSE AGGREGATE, CEMENT, ADDITIVE, AND STORAGE ENVIRONMENT

Stone Ident. No.	Cement and Additive with Respect to Treatment[1]								Total Number of Bars
	High Alkali			Low Alkali		High Alkali and Fly Ash			
	A	B	C	A	C	A	B	C	
1	4[2]	-	-	4	-	-	-	-	8
2	4	4	4	4	4	4	4	4	32
3	4	-	-	4	-	-	-	-	8
4	4	4	4	4	4	4	4	4	32
5	4	4	4	4	4	4	4	4	32
6	4	-	-	4	-	-	-	-	8
7	4	-	-	4	-	-	-	-	8
8	4	4	4	4	4	4	4	4	32
								Grand Total	160

[1] Treatments:

A - Placed in Outdoor Test Pit after 28 days of moist curing
B - Broken in flexure at 7 days
C - Broken in flexure at 28 days

[2] Each beam in each set made from a different batch of concrete.

Table 3

PROPERTIES OF CEMENT

Specific Surface (Blaine)	3334
Autoclave Expansion, Percent	0.08
Specific Gravity	3.164
Air Content (Mortar), Percent	8.05
Time of Initial Set, Hours	3.58
Time of Final Set, Hours	5.67
Tensile Strength, 3 days, PSI	357
Tensile Strength, 7 days, PSI	420
Percent Silica	20.68
Percent Sulfur-Trioxide	2.48
Percent Calcium Oxide	62.30
Percent Magnesium Oxide	3.95
Percent Loss on Ignition	1.12
Percent Iron Oxide	3.35
Percent Aluminum Oxide	5.59
Percent Sodium Oxide	0.19
Percent Potassium Oxide	0.48
Percent Insoluble Residue	0.19
Percent Total Alkali (as Na_2O)	0.51

Table 4

PROPERTIES OF FLY ASH

Specific Surface (Blaine)	2079
Specific Gravity	2.333
Percent Moisture	0.25
Percent Silica	48.8
Percent Aluminum Oxide	21.2
Percent Iron Oxide	13.9
Percent Magnesium Oxide	1.0
Percent Sulfur Trioxide	1.2
Percent Loss on Ignition	2.98
Percent Total Alkali (as Na_2O)	0.3

Table 5

PROPERTIES OF FINE AGGREGATE

Bulk Specific Gravity (Oven-Dry)	2.607
Bulk Specific Gravity (Sat. Surface Dry)	2.614
Percent Absorption (24 Hrs.)	0.30
Percent Absorption (2 Hrs.)	0.20
Percent Moisture	0.20

Table 6

PROPERTIES OF COARSE AGGREGATE

Coarse Aggregate	Bulk Specific Gravity		Absorption Percent
	Dry	Sat. Surf. Dry	
1	2.662	2.692	1.2
2	2.656	2.694	1.4
3	2.604	2.654	1.9
4	2.644	2.669	0.9
5	2.688	2.713	0.9
6	2.207	2.371	7.5
7	2.652	2.677	1.0
8	2.603	2.627	0.9

* Obtained by soaking the air dried aggregates for two hours.

Table 7

PROPERTIES OF CHLORIDE SALTS

Calcium Chloride	
Percent Calcium Chloride	78.01
Percent Magnesium Oxide	0.03
Phenolphthalein end Point	1.20
Methyl Red end Point	3.62
Percent Sulfur Trioxide	0.00
Sodium Chloride	
Percent Sodium Chloride	96.30
Percent Calcium Oxide	1.45
Percent Magnesium Oxide	0.12
Phenolphthalein end Point	0.00
Methyl Red end Point	0.07
Percent Surfur Trioxide	2.04

Table 8

CHEMICAL ANALYSES OF STONES*

Component	Stone Ident. No. 1	2	3	4	5	6	7	8
Percent K_2O	0.31	0.54	0.52	0.34	0.18	0.33	0.08	0.01
Percent Na_2O	0.11	0.16	0.02	0.01	0.02	0.07	0.05	0.00
Percent Fe_2O_3	0.83	0.76	0.41	0.20	0.63	0.45	0.94	0.10
Percent Al_2O_3	3.15	2.54	2.53	1.52	0.71	1.61	1.88	0.18
Percent Loss on Ignition	40.66	38.32	38.08	39.32	42.42	41.98	41.69	43.26
Percent CO_2	40.91	38.59	37.34	39.24	42.59	40.76	42.29	44.09
Percent Insoluble	6.68	14.10	10.18	8.32	3.22	7.26	2.98	0.22
Percent SiO_2	0.83	10.60	9.46	7.70	2.88	6.62	2.30	0.22
Percent CaO	47.68	37.12	41.52	48.64	44.60	30.16	52.72	55.58
Percent $CaCO_3$	85.09	66.24	74.10	86.80	79.59	53.82	94.08	99.19
Percent MgO	3.21	8.68	4.34	0.99	6.96	15.67	0.85	0.44
Percent $MgCO_3$	6.71	18.15	9.10	2.07	14.56	32.77	1.78	0.92
Percent Dolomite (in carbonate fraction)	16.02	47.11	23.89	5.11	33.87	82.91	4.06	2.01

* Tests made according to ASTM Specification C114-61.

Table 9

RESULTS OF TESTS ON FRESH CONCRETE

Stone Ident. No.	Cement Alkali	With Fly Ash	Bars[1] W/C[5]	Bars[1] %Air	Bars[1] Wt/Cu Ft.	Beams[2] W/C[5]	Beams[2] %Air	Beams[2] Wt/Cu Ft.	Slump
1	High	No	0.63	7.7	141.7	0.63	7.2[4]	142.7[4]	3
	Low	No	0.65	7.2	142.1	0.63	6.4[4]	143.9[4]	2-3/4
2	High	Yes	0.60	7.5	140.0	0.60	6.8	142.1	2-1/2
	High	No	0.63	10.5	137.4	0.62	6.2	144.3	3
	Low	No	0.68	4.9	144.0	0.64	5.8[4]	144.7[4]	2-1/2
3	High	No	0.63	7.6	140.9	0.63	6.2[3]	143.3[3]	2-1/2
	Low	No	0.63	6.6	142.4	0.63	-	-	2-1/4
4	High	Yes	0.64	7.7	139.2	0.60	6.7	141.7	3
	High	No	0.63	10.0	137.5	0.63	6.2	143.5	3-1/4
	Low	No	0.63	8.6	139.6	0.63	7.3[4]	141.8[4]	2-3/4
5	High	Yes	0.64	7.8	140.3	0.61	7.0	142.3	2-3/4
	High	No	0.62	8.5	141.0	0.62	6.1	145.1	3
	Low	No	0.63	7.1	143.0	0.63	5.6[3]	145.5[3]	2-1/2
6	High	No	0.63	7.4	134.4	0.60	6.6[4]	135.5[4]	2-3/4
	Low	No	0.65	6.5	134.8	0.62	-	-	3
7	High	No	0.63	9.4	138.5	0.63	6.4[4]	143.5[4]	3-1/4
	Low	No	0.63	8.2	140.3	0.63	-	-	3
8	High	Yes	0.60	8.3	138.0	0.59	8.0	140.2	3-1/4
	High	No	0.63	9.8	136.8	0.62	7.0	142.7	3-1/4
	Low	No	0.63	8.2	139.1	0.63	7.5[4]	142.5[4]	3

(1) Each value is an average of three values.
(2) Each value is an average of four values except as otherwise noted.
(3) Average of two tests.
(4) One test only.
(5) By volume

Table 10

RESULTS OF TESTS ON CONCRETE BEAMS

Stone Ident. No.	Dynamic Modulus[1] 28 Days	Flexural Strengths[2] 7 Days 14" Span	7 Days 7" Span	28 Days 14" Span	28 Days 7" Span	Comp. Strength[2] 7 Days	Comp. Strength[2] 28 Days
a. - Cement Alkali Content = 0.51% as Na_2O							
1	5.08	-	-	-	-	-	-
2	5.00	-	-	773	795	-	3626
3	4.85	-	-	-	-	-	-
4	5.33	-	-	950	938	-	4804
5	5.71	-	-	889	970	-	5155
6	3.85	-	-	-	-	-	-
7	5.42	-	-	-	-	-	-
8	4.70	-	-	796	848	-	4709
b. - Cement Alkali Content = 1.0% as Na_2O							
1	4.42	-	-	-	-	-	-
2	4.21	660	670	597[3]	653	3307	3865
3	4.68	-	-	-	-	-	-
4	5.36	761	855	918	969	3548	4555
5	5.64	782	872	870	926	3496	4434
6	3.86	-	-	-	-	-	-
7	5.44	-	-	-	-	-	-
8	4.67	697	724	776	859	3175	4177
c. - Cement Alkali = 1.0% as Na_2O With Fly Ash Replacement of 20.0%, by Design Weight, of Cement							
1	-	-	-	-	-	-	-
2	3.93	530	571	440[3]	474	2407	3226
3	-	-	-	-	-	-	-
4	5.12	569	679	826	912	2643	3649[4]
5	5.30	669	676	725	759	2585	3637
6	-	-	-	-	-	-	-
7	-	-	-	-	-	-	-
8	4.41	602	582	748	796	2586	3364

(1) Average E values $X10^{-6}$ psi. for four beams.
(2) Average unit stress in psi. for four beams.
(3) Considerable cracking observed in these beams.
(4) Average of three beams only.

Table 11

RELATIVE STRENGTHS OF CONCRETE SPECIMENS
(PERCENT REDUCTION)

Stone Ident. No.	Flexural Strengths 7 Days 14" Span	Flexural Strengths 7 Days 7" Span	Flexural Strengths 28 Days 14" Span	Flexural Strengths 28 Days 7" Span	Comp. Strengths 7 Days	Comp. Strengths 28 Days
a. Low Alkali Cement vs. High Alkali Cement only						
2	-	-	23	18	-	+7*
4	-	-	3	+3*	-	5
5	-	-	2	5	-	14
8	-	-	3	+1*	-	11
b. Low Alkali Cement vs. High Alkali plus Fly Ash						
2	-	-	43	40	-	11
4	-	-	13	3	-	24
5	-	-	18	22	-	29
8	-	-	6	6	-	29
c. High Alkali Cement vs. High Alkali plus Fly Ash						
2	20	15	26	27	27	17
4	25	21	10	6	26	20
5	14	22	17	18	26	18
8	14	20	4	7	19	19

* Plus values indicate an increase in strength rather than reduction.

Table 12

EXPANSION RESULTS FOR THE 2 in. x 2 in. x 11.25 in. CONCRETE BARS

Stone Ident. No.	Rock Prism Expansions (1) (8 wk-Percent) Max.	Ave.	Min.	Cement (2)	Percent Expansion (3) 28 Days Moist Curing	Storage Environment (4)	Percent Expansion Moist Curing Plus Prolonged Storage (3 Total Age Days 91	238	441	728
2	6.66	4.75	2.83	HA	.230	A	.426	.523	.550	.561
	(2 samples)			HA	.219	B	.575	.890	1.017	1.064
				HA	.236	C	.444	.523	.535	.556
				HA	.240	D	.732	.954	1.054	1.106
				LA	.020	A	.060	.111	.137	.160
				LA	.020	B	.100	.291	.418	.494
				LA	.020	C	.068	.114	.134	.157
				HA+FA	.135	A	.291	.454	.500	.521
				HA+FA	.132	B	.345	.671	.869	.953
3	-	2.11	-	HA	.087	A	.161	.212	.256	.302
	(1 sample)									
				LA	.016	A	.026	.044	.066	.099
1	1.66	1.10	0.39	HA	.100	A	.237	.345	.385	.402
	(3 samples)									
				LA	.021	A	.049	0.87	.115	.136
5	0.34	0.27	0.20	HA	.017	A	.030	.043	.048	.061
	(2 samples)			HA	.019	B	.036	.056	.067	.082
				HA	.018	D	.052	.074	.079	.097
				LA	.008	A	.016	.023	.026	.039
				LA	.010	B	.021	.039	.048	.063
				HA+FA	.013	A	.022	.030	.036	.049
				HA+FA	.013	B	.025	.041	.054	.069

7	0.11 0.07 0.03 (3 samples)	HA	.019	A	.032	.046	.053	.063
		LA	.009	A	.014	.021	.026	.035
8	- -0.006 - (1 sample)	HA	.005	A	.006	.007	.008	.012
		HA	.005	B	.012	.020	.031	.051
		HA	.006	C	.014	.023	.026	.044
		HA	.006	D	.016	.031	.030	.049
		LA	.005	A	.008	.008	.009	.014
		LA	.006	B	.015	.022	.033	.048
		LA	.004	C	.016	.021	.030	.046
		HA+FA	.003	A	.005	.005	.004	.009
		HA+FA	.003	B	.009	.014	.025	.044
4	0.004 -0.012 -0.023 (3 samples)	HA	.004	A	.005	.006	.003	.010
		HA	.005	B	.010	.017	.021	.031
		HA	.005	C	.011	.016	.020	.030
		LA	.003	A	.005	.006	.003	.007
		LA	.003	B	.009	.016	.021	.031
		LA	.002	C	.010	.017	.021	.032
		HA+FA	.004	A	.004	.004	.002	.006
		HA+FA	.004	B	.007	.011	.013	.024
6	-0.013 -0.022 -0.031	HA	.011	A	.016	.024	.033	.046
		HA	.011	C	.027	.038	.050	.064
		LA	.005	A	.010	.013	.020(5)	.028(5)
		LA	.005	C	.021	.030	.040	.061

(1) Rock prisms were 5/16 in. x 1-1/2 in. in size taken perpendicular to bedding plane and stored in 1N NaOH solution (2 prisms per sample)
(2) Cement Identification: HA = High Alkali, LA = Low Alkali, HA+FA = High Alkali plus Fly Ash
(3) All values are the average of three specimens.
(4) Storage environments after 28 days moist curing on shelves in moist room
A - In saturated lime water
B - In 4 percent NaCl solution
C - In 4 percent $CaCl_2$ solution
D - Over water in sealed containers at 100°F.
(5) Average of two specimens only

Table 13

EXPANSION RESULTS FOR THE 3.5 in. x 4.5 in. x 16 in. CONCRETE BEAMS

Stone Ident. No.	Rock Prism Expansions[1] (8 wk-Percent) Max.	Ave.	Min.	Cement (2)	Percent Expansion[3] 28 Days Moist Curing	Percent Expansion Moist Curing Plus Outdoor Exposure[3] 91	240	440	818	959
2	6.66	4.75 (2 samples)	2.83	HA+FA	.134	.259	.332	.538	.587[4]	.610[4]
				HA	.138	.285	.369	.529	.515	.558
				LA	.026	.053	.082	.170	.269	.312
3	-	2.11 (1 sample)	-	HA	.059	.108	.142	.219	.271	.288
				LA	.015	.023	.028	.061	.099	.114
1	1.66	1.10 (3 samples)	0.39	HA	.108	.230	.328	.491	.553	.572
				LA	.021	.040	.048	.089	.132	.158
5	0.34	0.27 (2 samples)	0.20	HA+FA	.011	.021	.025	.047	.059	.065
				HA	.016	.034	.043	.071	.100	.112
				LA	.008	.014	.019	.036	.050	.056
7	0.11	0.07 (3 samples)	0.03	HA	.015	.029	.039	.062	.081	.093
				LA	.008	.014	.019	.032	.041	.050
8	-	-0.006 (1 sample)	-	HA+FA	.005	.009	.005	.014	.022	.026
				HA	.006	.010	.011	.024	.037	.044
				LA	.004	.007	.006	.022	.028	.034

4	0.004 -0.012 -0.023 (3 samples)	HA+FA	.003	.002	.002	.002	.001	.005
		HA	.005	.005	.004	.009	.010	.014
		LA	.005	.005	.002	.007	.010	.014
6	-0.013 -0.022 -0.031 (2 samples)	HA	.007	.017	.023	.041	.058	.065
		LA	.008	.014	.013	.026	.037	.043

(1) Rock prisms were 5/16 in. x 5/16 in. x 1-1/2 in. in size taken perpendicular to bedding plane and stored in 1N NaOH solution (2 prisms per sample)
(2) Cement Identification: HA = High Alkali, LA = Low Alkali, HA+FA = High Alkali plus Fly Ash
(3) All values are the average of four specimens with top and bottom measurements
(4) Average of three specimens only.

Fig. 1 - The Effect of Using the Minimum, Average, or Maximum 8 Week Rock Prism Expansions Upon the Relationship of Concrete Vs. Rock Prism Expansions. (Bars cured 28 days moist and 63 days in saturated lime water. Alkali content of cement, 1.0 percent. Data obtained from Table 12.)

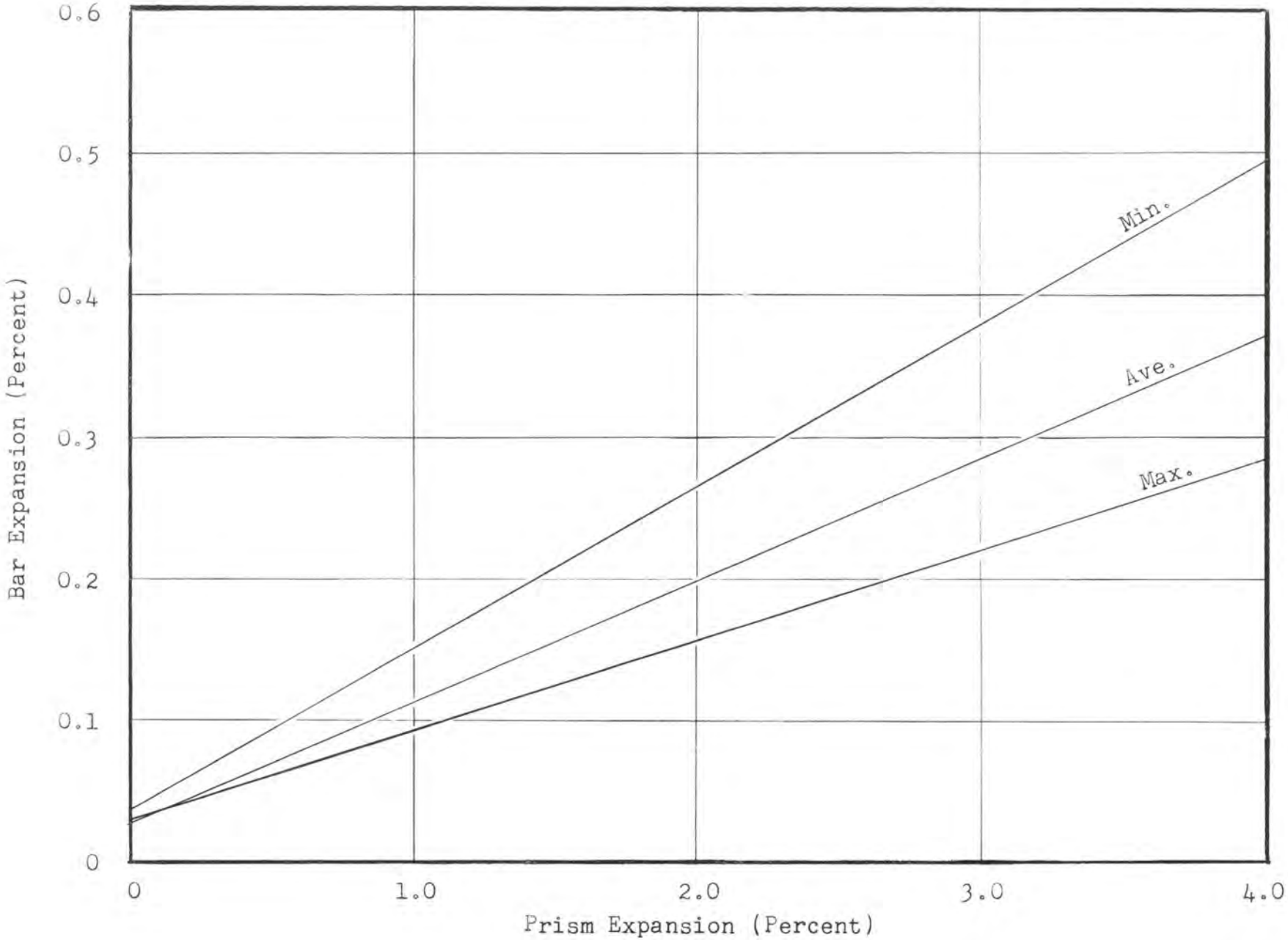
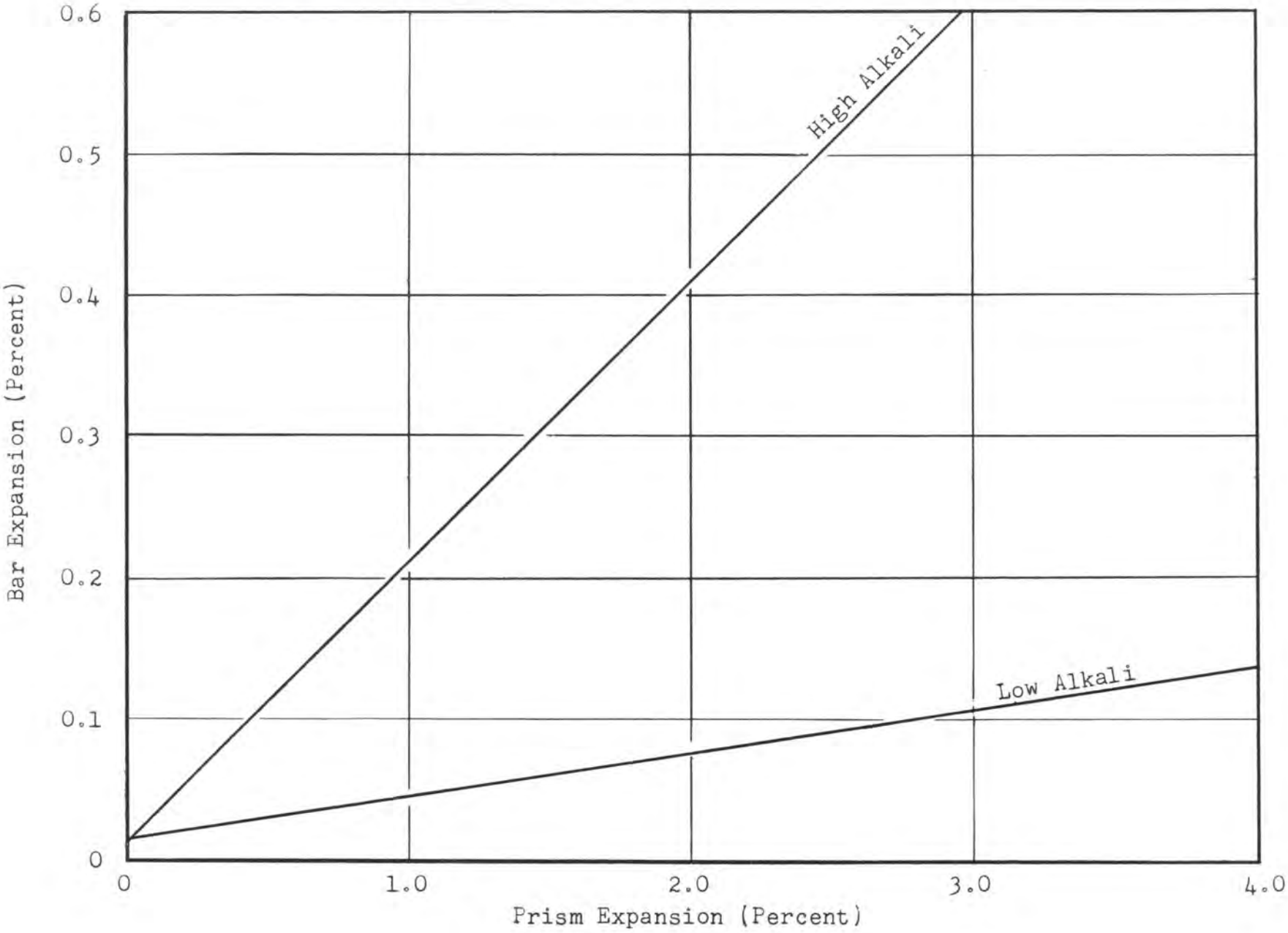


Fig. 2 - The Effect of High (1.0 percent) and Low (0.51 percent) Alkali Cement Upon the Relationship of Concrete Vs. Rock Prism Expansions. (Bars cured 28 days moist and 63 days in a 4.0 percent NaCl solution. Data obtained from Table 12.)



63 Days, Following 28 Days of Moist Curing, Upon the Relationship of Concrete Vs. Rock Prism Expansions. (Alkali content of cement 1.0 percent. Data obtained from Table 12.)

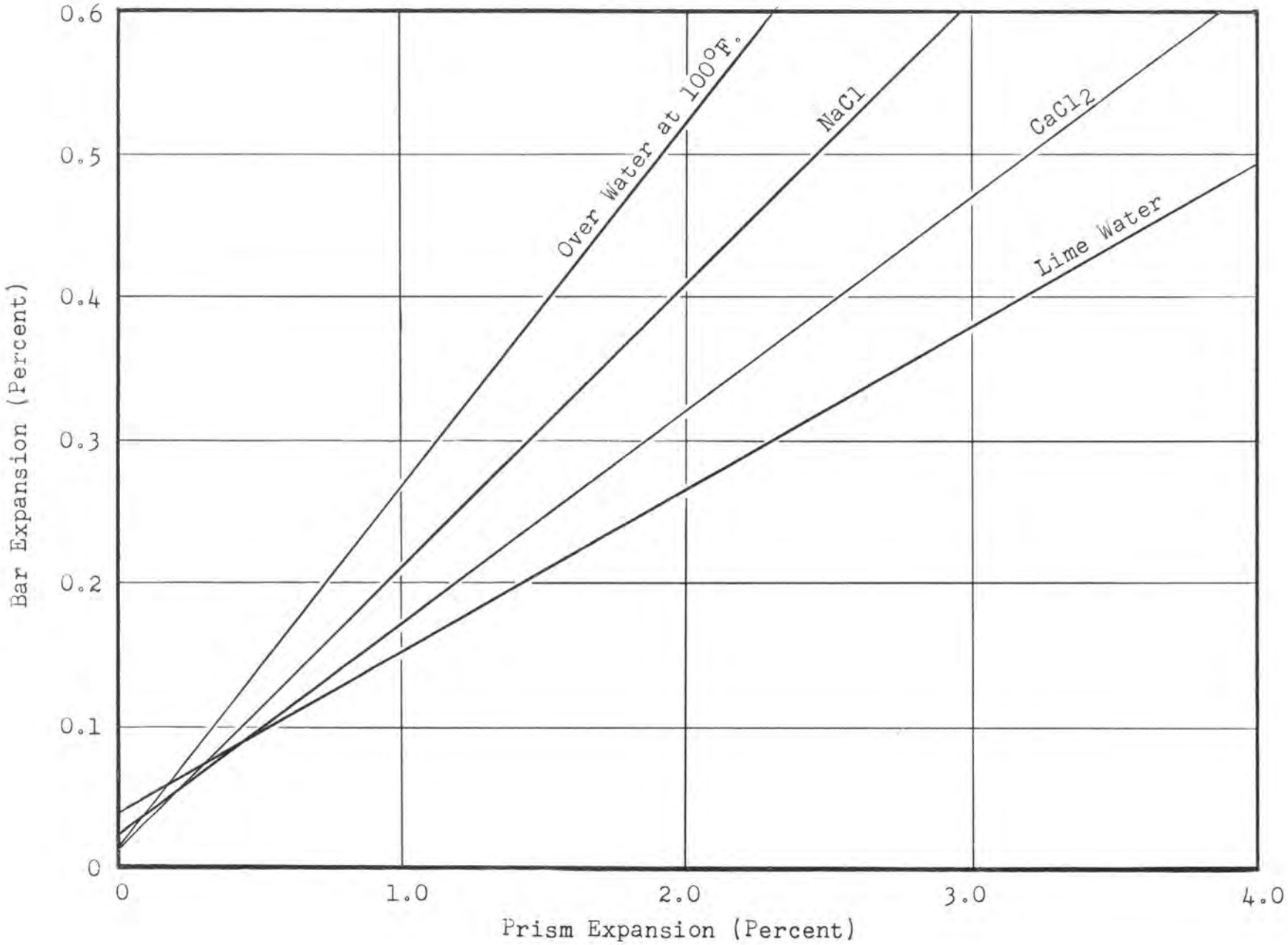


Fig. 4 - The Effect of the Length of Curing in Lime Water, After 28 Days of Moist Curing, Upon the Relationship of Concrete Vs. Rock Prism Expansions. (Alkali content of cement 1.0 percent. Data obtained from Table 12.)

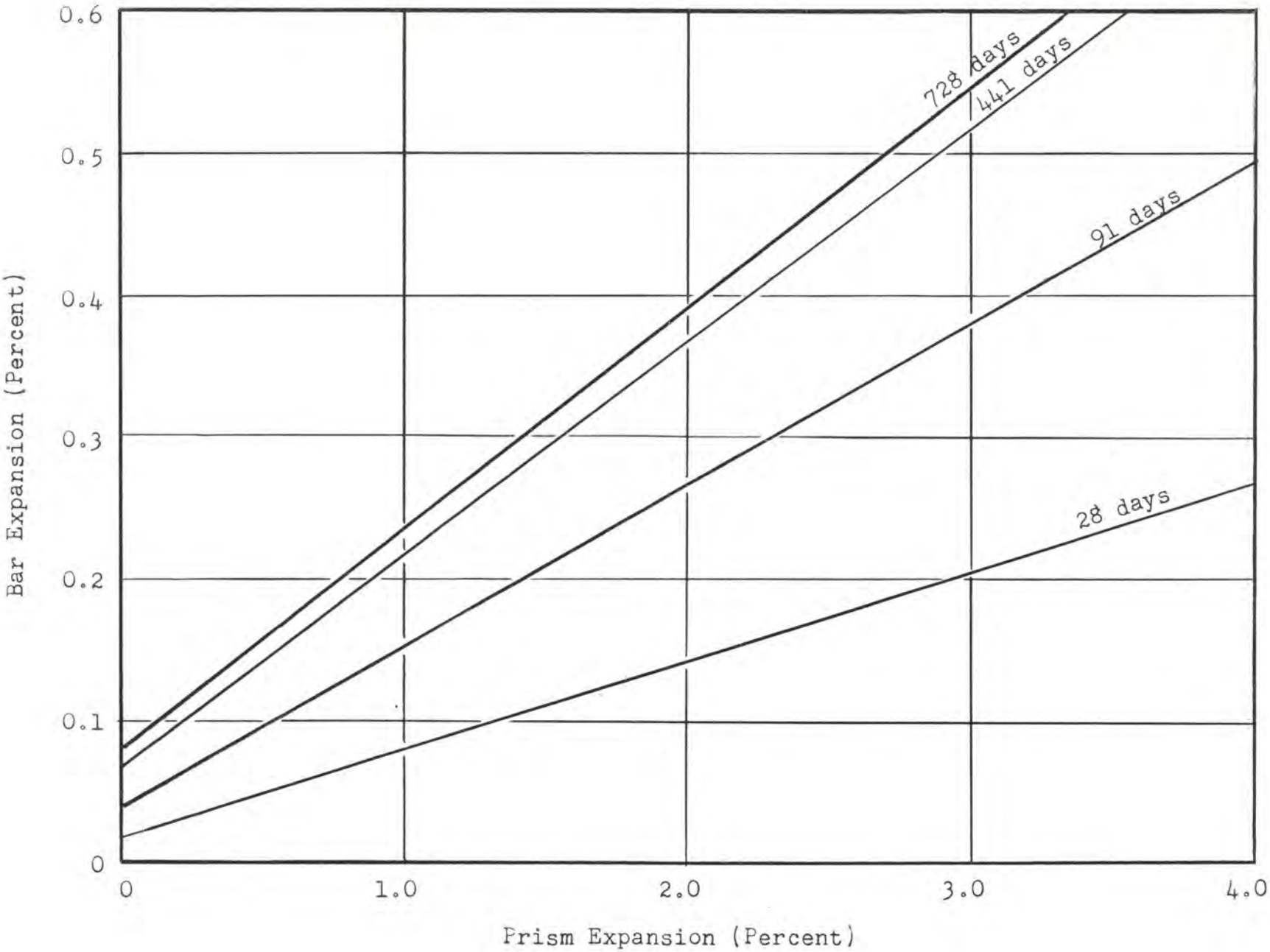
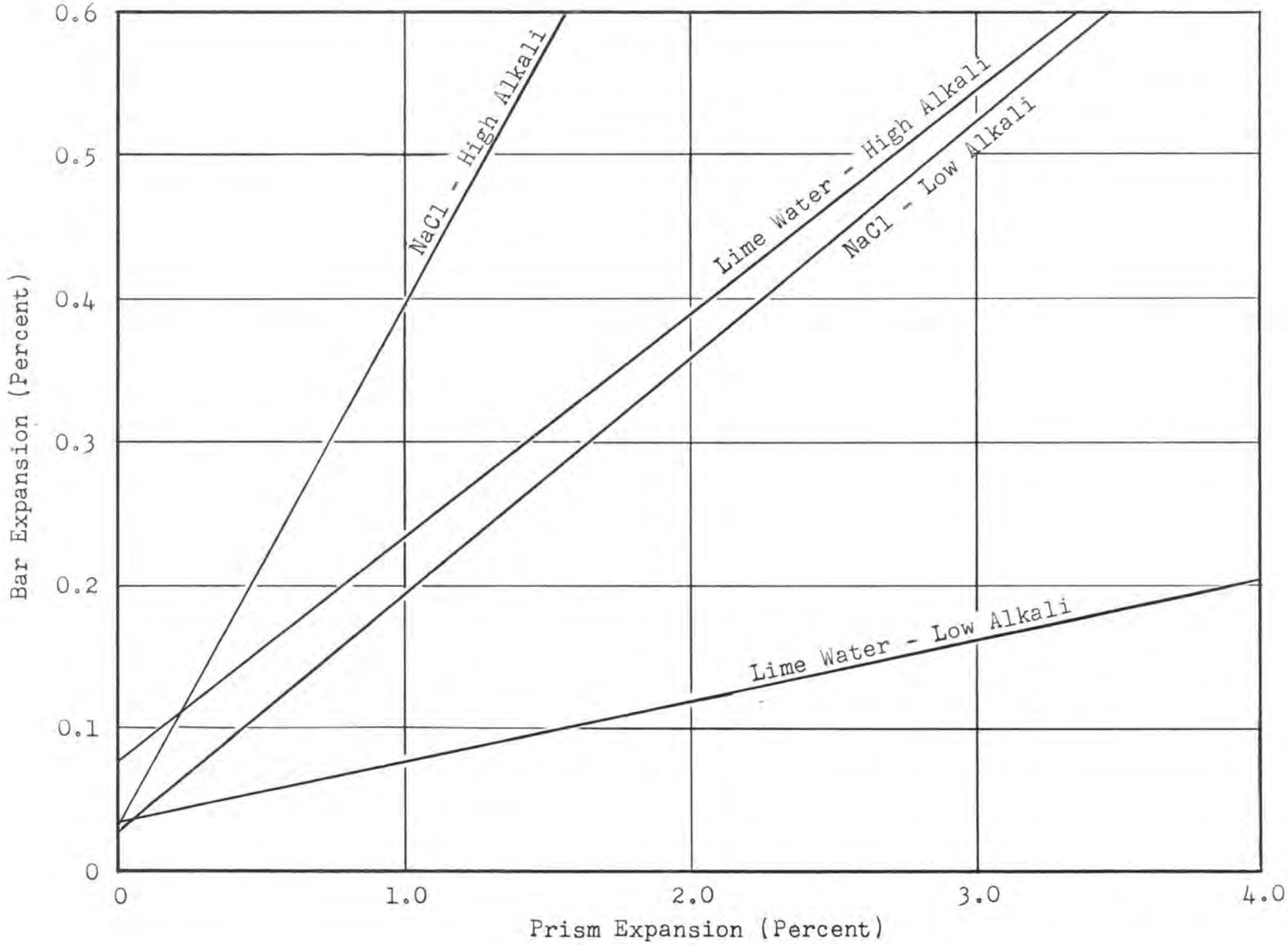


Fig. 5 - The Effect of High and Low Alkali Contents of Cement and Two (Lime Water and Sodium Chloride Solutions) Curing Environments, Upon the Relationship of Concrete Vs. Rock Prism Expansions. (Bars cured 28 days moist and 700 days in lime water or NaCl solution. Data obtained from Table 12.)



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