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Lithium Salt Admixtures— An Alternative Method to Prevent Expansive Alkali-Silica Reactivity

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by David C. Stark*

ASTM C 227 and P 214 mortar bar tests were run to determine the capability of several lithium salts to inhibit expansive ASR. Both type and dosage of salt were evaluated in the presence of different alkali (hydroxyl ion) concentrations and highly and slowly reactive aggregate. Analyses are based on expansion measurements.

Introduction

Traditional methods of preventing abnormal expansion due to alkali-silica reaction (ASR) in concrete include reducing cement alkali levels, avoiding the use of potentially reactive aggregates, and utilizing pozzolans such as fly ash and natural (volcanic) glass. Each, however, has its limitations. In requiring lower cement alkali levels, for example, the level to which the alkali content must be reduced to prevent abnormal expansion often is not known. Simply prescribing low alkali cement, that is, cement with not more than 0.60% alkali as equivalent sodium oxide (Na_2O), commonly is not an adequate requirement. Avoiding the use of reactive aggregates also may not be feasible, or possible, for economic reasons. Furthermore, whether an aggregate is actually innocuous may be based on inadequate laboratory tests and uncertain field service records for which not all of the essential information is available. Finally, utilizing pozzolans such as fly ash may be questionable because of test limitations for suitability, or local or regional availability may not exist. In addition, fly ashes of acceptable composition may become scarcer because of possible stricter pollution controls. Although they can be extremely effective in inhibiting expansive ASR, natural pozzolans are available only in limited production at very few locations.

Accordingly, the need exists for alternative methods of preventing expansive ASR. One promising option appears to be the use of certain lithium salts as admixtures to the

fresh concrete. Only very small quantities appear to be necessary for this use, perhaps less than equimolar ratios of lithium oxide (Li_2O) to equivalent Na_2O in the cement. This paper describes results of tests conducted to determine requirements to inhibit expansive ASR utilizing different lithium salts.

Previous work

The concept of utilizing lithium salts to inhibit expansive ASR was first reported by McCoy and Caldwell in 1951^{(1)**}. In these studies, they used cement with 1.15% equivalent Na_2O , Pyrex glass as aggregate per ASTM C 227-50T gradation, and a fixed water-cement ratio. Lithium chloride, lithium carbonate, and lithium fluoride, used as 1.0% additions by weight of cement, were found to be the most effective agents inhibiting expansion due to ASR in mortars. Reductions in expansion in these cases were 90 to 97% at 14 days storage over water in sealed containers at 38°C (100° F), and about these same levels after 56 days of testing. Expansions of the control specimens without the lithium salts increased from 0.30% at 14 days to 0.54% at 56 days. Thus, the lithium salts were effective inhibitors for the duration of the test as expansive ASR progressed in the control mortars.

Lawrence and Vivian⁽²⁾ reported results in 1961 utilizing lithium hydroxide (LiOH) as the inhibitor. These studies included comparisons of lithium, sodium, and potassium reactions of a more fundamental nature than those of McCoy and Caldwell. The Lawrence and Vivian studies confirmed the effectiveness of LiOH in preventing abnormal ASR expansion up to one year when added at rates of 0.5, 1.0, or 1.5% by weight of cement, expressed as equivalent sodium hydroxide. These authors further concluded that the silica reaction product in the presence of lithium ion is different than that when only sodium or potassium is present. That is, the lithium silicate product appeared to be less soluble and more stable when LiOH was allowed to react with silica gels. Also, increasing LiOH concentrations up to 2N LiOH equivalent in 2N NaOH solution resulted in greatly decreased tendency for NaOH to react with silica gels.

Sakaguchi, et al.⁽³⁾ confirmed the conclusions of McCoy and Caldwell, and Lawrence and Vivian, regarding the

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** Numbers in superscript refer to references listed at the end of this report.

effectiveness of a lithium salt in inhibiting expansions due to ASR. In this case Pyrex glass and a known reactive andesite were used as aggregates. Sakaguchi, et. al. also found from expression of pore solutions from mortar bars made with lithium nitrate that the concentration of lithium ion decreased with time while that of sodium and potassium remained nearly constant. The latter was in contrast to other results, in which sodium and potassium (and hydroxyl) ion concentrations decreased when no lithium salt was used.

Results of previous laboratory investigations thus are quite convincing that lithium salts can be effective inhibitors of expansive ASR.

Present Investigations

Test Procedures

Two different test procedures were used to determine the capability of lithium salts to prevent abnormal expansion due to ASR. The ASTM* C 227 (*Standard Test Method for Potential Alkali Reactivity of Cement-Aggregate Combinations (Mortar Bar Method)*) test was used to evaluate lithium fluoride (LiF) and lithium carbonate (Li_2CO_3) salts. Test storage was over water in sealed containers held for three years at 38°C (100°F). Length changes were measured at 1, 3, 6, 9, 12, 18, 24, 30, and 36 months of testing.

ASTM P 214 (*Proposed Test Method for Accelerated Detection of Potentially Deleterious Expansion of Mortar Bars Due to Alkali-Silica Reaction*) was used in tests to evaluate LiOH as an inhibitor. This procedure is based on that developed by Heinz and Oberholster,⁽⁴⁾ in which mortar bars are immersed in 1M NaOH solution at 80°C (176°F) for a period of 14 days after fabrication. In the present series, solutions of different mixed concentrations of NaOH and LiOH, as well as separate solutions, were utilized. In all tests, cement with 0.18% alkali as equivalent Na_2O was used so that essentially all ASR could be attributed to alkali in the storage solution. After stripping from the molds at one day, the mortar bars were transferred, after measurement, directly to the test solution. Tests were run for 28 instead of the prescribed 14 days to better clarify prolonged inhibiting effects.

Materials

A highly reactive, commercially available, natural fine aggregate was used in both the C 227 and P 214 tests. Aggregate from this source is known to have reacted deleteriously in field structures when used with portland cements with alkali contents as low as 0.50% as equivalent Na_2O . The reactive components in the aggregate are weathered cryptocrystalline to glassy volcanic materials of andesitic to rhyolitic composition. A sample of slowly reactive crushed granite gneiss coarse aggregate also

was used in the P 214 tests. This aggregate is known to have reacted deleteriously in highway structures where cement alkali levels were in the range of 0.7 to 0.9% as equivalent Na_2O .

Two portland cements, each meeting ASTM C 150 (*Standard Specification for Portland Cement*) Type I requirements were used for all tests. Chemical and physical properties of these cements are given in Table 1. The cement with 0.92% alkali as equivalent Na_2O was used for the C 227 mortar bar test, while the cement with 0.18% alkali was used for the P 214 tests.

Scope of Tests

Different proportions of lithium salt admixtures were used in each test series to determine their effects on expansions due to ASR. In the C 227 mortar bar tests, LiF and Li_2CO_3 each were used in proportions of 0.25, 0.50, and 1.00% by weight of cement. Since both are virtually insoluble in water, they were added to the mixture in powder form.

In the P 214 expansion tests, LiOH was incorporated into test solutions in two different series of tests. In one series, increasing amounts of LiOH were added to 1M NaOH solutions in proportions corresponding to 0.33M, 0.67M, and 1.00M LiOH. That is, the most concentrated solution was 1M NaOH plus 1M LiOH.

In the second P 214 series, the OH^- concentration resulting from addition of NaOH and LiOH remained at the level corresponding to 1M NaOH, but with lithium substituted for sodium in the ratios of 0.33:1.0, 0.67:1.0, and 1.0:1.0. That is, the 1M concentration of the 1.0:1.0 solution was maintained by equal percentages, on a molar basis, of Na and Li. Individual 1M NaOH and 1M LiOH solutions also were utilized.

Test Results

Results of C 227 mortar bar tests up to three years of age are summarized in Figs. 1 to 3. Figure 1 shows results for the various dosages of LiF admixture compared with no dosage for the control mix. Here, it is seen that the 0.25% dosage by weight of cement provided no meaningful reduction at ages up to 18 months and, in fact, resulted in slightly greater expansion between 18 and 36 months. When the dosage of LiF was increased to 0.50% and 1.00%, expansions were reduced to about 0.06% and 0.02%, respectively, at 36 months. This represents 10-fold and 33-fold decreases in expansion and reductions to levels considered to be innocuous.

Similar data for Li_2CO_3 are shown in Fig. 2. In this case dosages of 0.25% and 0.50% by weight of cement resulted in only minor reductions in expansion, all of which remained in the range considered to represent highly expansive reactivity. Only when the dosage of Li_2CO_3 was increased to 1.00% did a significant reduction in expansion result. In the latter case, a 14-fold decrease brought expansions into a range considered to be innocuous.

A greater percentage of Li_2CO_3 than LiF was needed to reduce expansions to a safe level probably because LiF contains a greater proportion of lithium ion.

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Thirty-six-month expansions for all dosages of both lithium salts are plotted in Fig. 3. Also, shown is the 36-month expansion for mortar bars containing the same cement-aggregate combination but with 25% of the cement replaced by an ASTM C618 (*Standard Specification for Fly Ash and Raw or Calcined Natural Pozzolan for Use as a Mineral Admixture in Portland Cement Concrete*) Class F fly ash which has been used successfully in pavement concrete with aggregate from the same source. The results suggest a threshold dosage above which the lithium salts effectively suppress expansive ASR. For LiF and this cement-aggregate combination, this level appears to be about 0.50% by weight of cement. For Li_2CO_3 the level appears to be approximately 1.00%. For both salts, these levels resulted in expansions less than that indicated for the mix with 25% weight replacement of cement by fly ash. These levels, however, probably would vary with the particular cement alkali level or, perhaps, the cement-aggregate combination, exposure condition, and interaction with other admixtures in the concrete.

Twenty eight-day results of P 214 tests are summarized in Figs. 4 and 5. Fig. 4 summarizes expansions for mortar bars immersed in constant 1M NaOH solution with added LiOH. Results for both aggregates showed progressive reductions in expansion as greater amounts of LiOH were added to the 1M NaOH solutions. With equal proportions of Na and Li (molar basis), expansions were reduced to less than the 0.10% failure criterion. Thus, introduction of the lithium ion more than offset increased expansive reaction tendencies resulting from increased OH^- ion concentrations.

It should be noted that with no lithium in solution, expansions for both aggregates exceeded 1.0%, which was the limit measurable by the comparator.

Figure 5 summarizes results for solutions where OH^- ion concentration, corresponding to that of 1M NaOH, was maintained as lithium substituted for sodium. These data indicate that once the Li:Na molar ratio reached at least 0.67:1.0, expansion due to ASR appeared to have been totally suppressed, regardless of whether the highly reactive volcanic sand or the slowly reactive granite gneiss was utilized as aggregate.

Discussion and Conclusions

Results of this investigation shed additional light on earlier studies that showed that certain lithium salts are very effective inhibitors of expansive ASR. It was found that threshold levels apparently exist below which dos-

ages of lithium salts are ineffective in preventing expansion. Above those levels, these salts are as effective, or more so, than a 25% weight replacement of cement by a fly ash used successfully in field concrete to prevent deleterious ASR.

The mechanism by which lithium salts inhibit expansion due to ASR has not been elucidated. However, it appears at this point that a lithium-bearing silicate product forms which precipitates and has little or no capacity to expand. This product may be mixed lithium-alkali (and possibly calcium) silicate which consumes alkali without causing measurable expansion. The existence of threshold levels to inhibit expansion suggests that the reaction product must contain at least a certain proportion of lithium to be non-expansive. Other explanations, perhaps involving viscosity characteristics, blockage of further reaction, etc., are possible.

At the present time, LiOH has been used in one highway installation in the United States where highly reactive volcanic aggregate was utilized. This experimental installation contained other test selections in which fly ashes were used to inhibit ASR. This pavement will be closely monitored in the future.

Acknowledgement

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TABLE 1. Properties of Cements Used in Tests

Parameter - %	Cement for C 227 Tests	Cement for P 214 Tests
SiO ₂	20.9	20.5
Al ₂ O ₃	5.1	4.8
Fe ₂ O ₃	4.8	2.5
CaO	61.4	63.0
MgO	3.1	3.6
SO ₃	1.8	2.7
Na ₂ O	0.06	0.11
K ₂ O	1.30	0.11
Total alkali as Na ₂ O equiv.	0.92	0.18
Loss on Ign.	1.4	1.6
Insol. Residue	0.06	--
C ₃ S	41	55
C ₂ S	29	17
C ₃ A	5	10
C ₄ AF	15	7
Spec. Density	3.17	3.20
-325 mesh	90.7	93.0
Blaine fineness cm ² /g	3700	4040

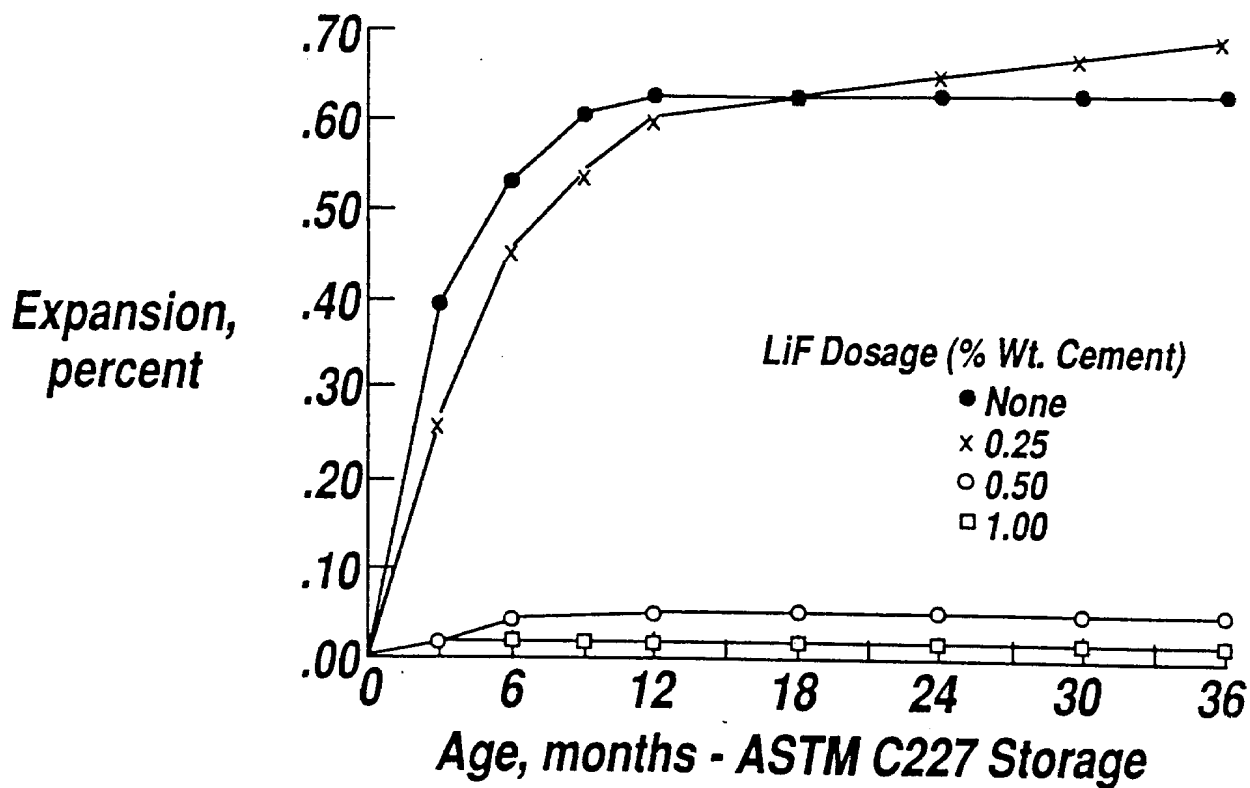


Fig. 1. Expansion of specimens made with lithium fluoride admixture.

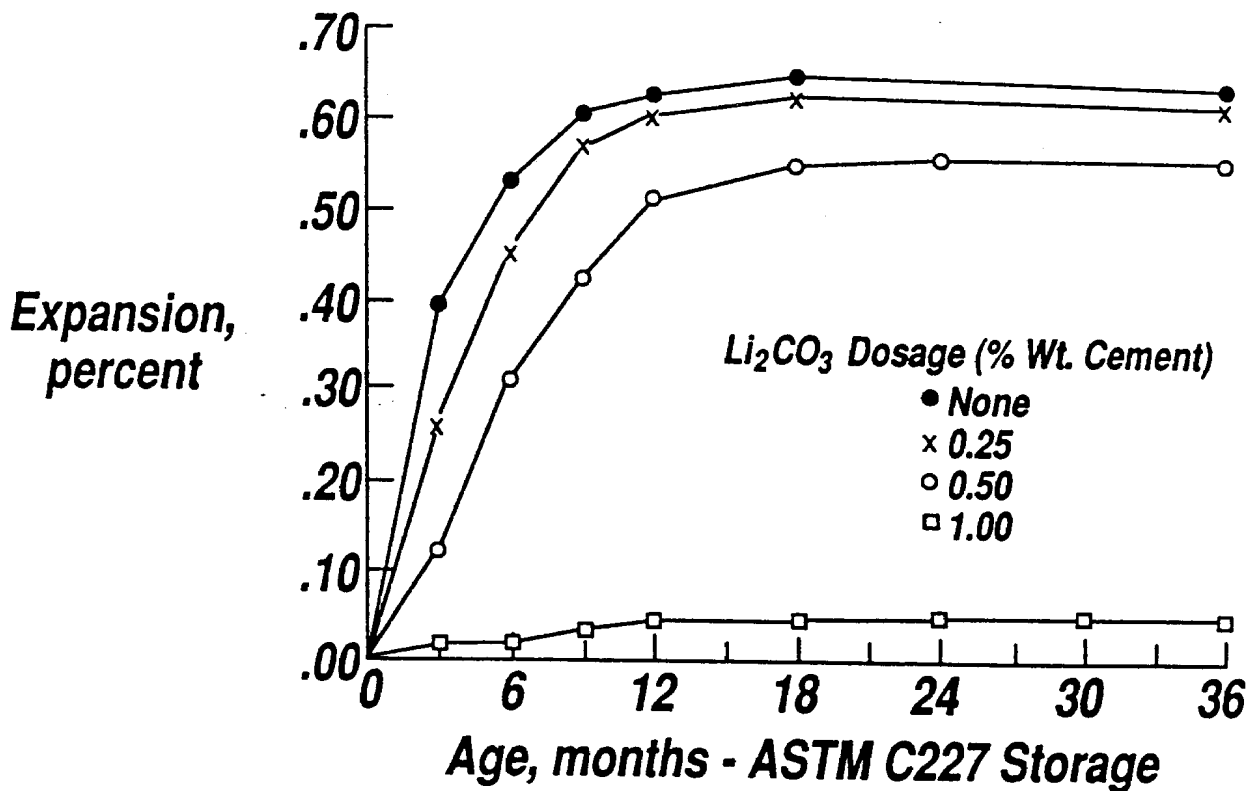


Fig. 2. Expansion of specimens made with lithium carbonate admixture.

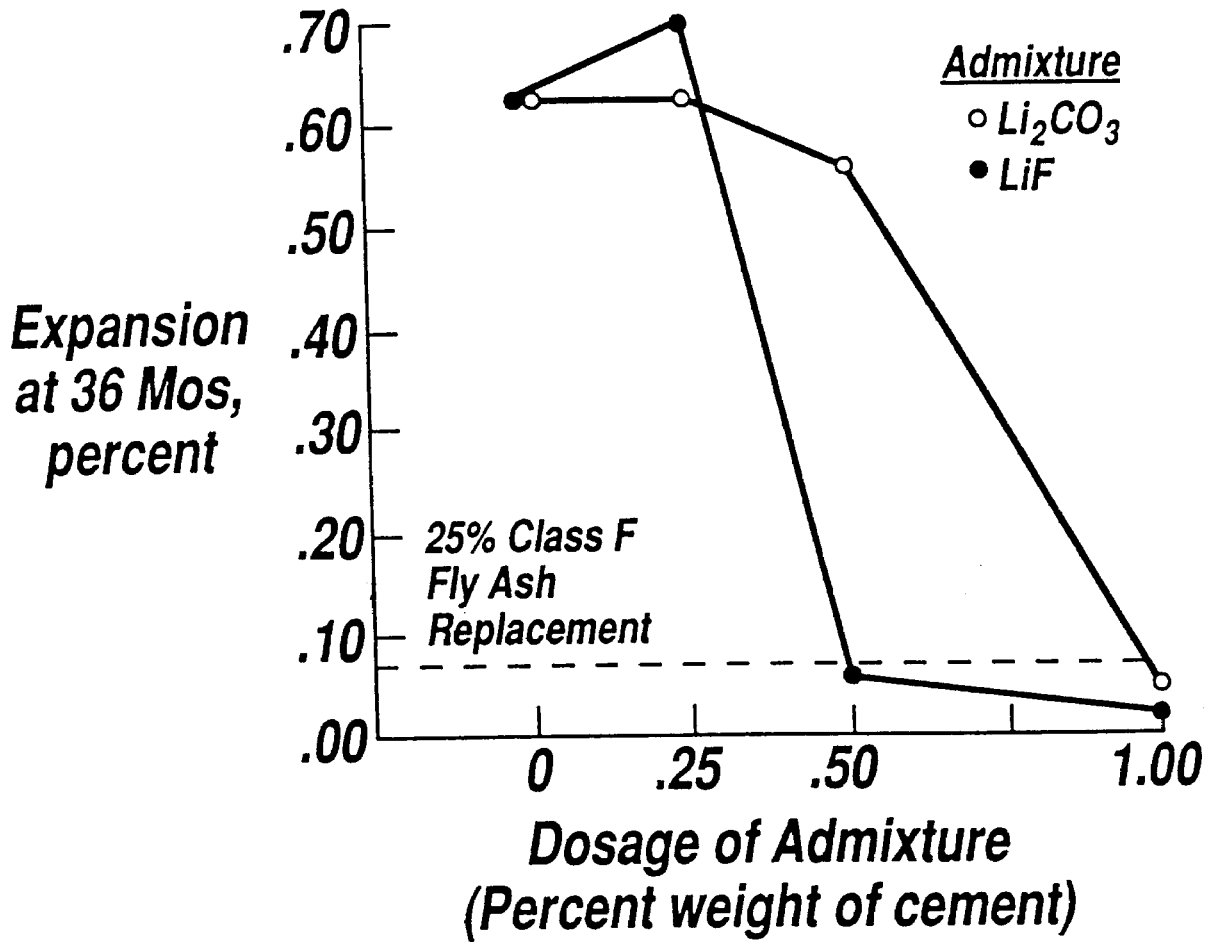


Fig. 3. Effects of dosage of admixture on expansion at 36 months.

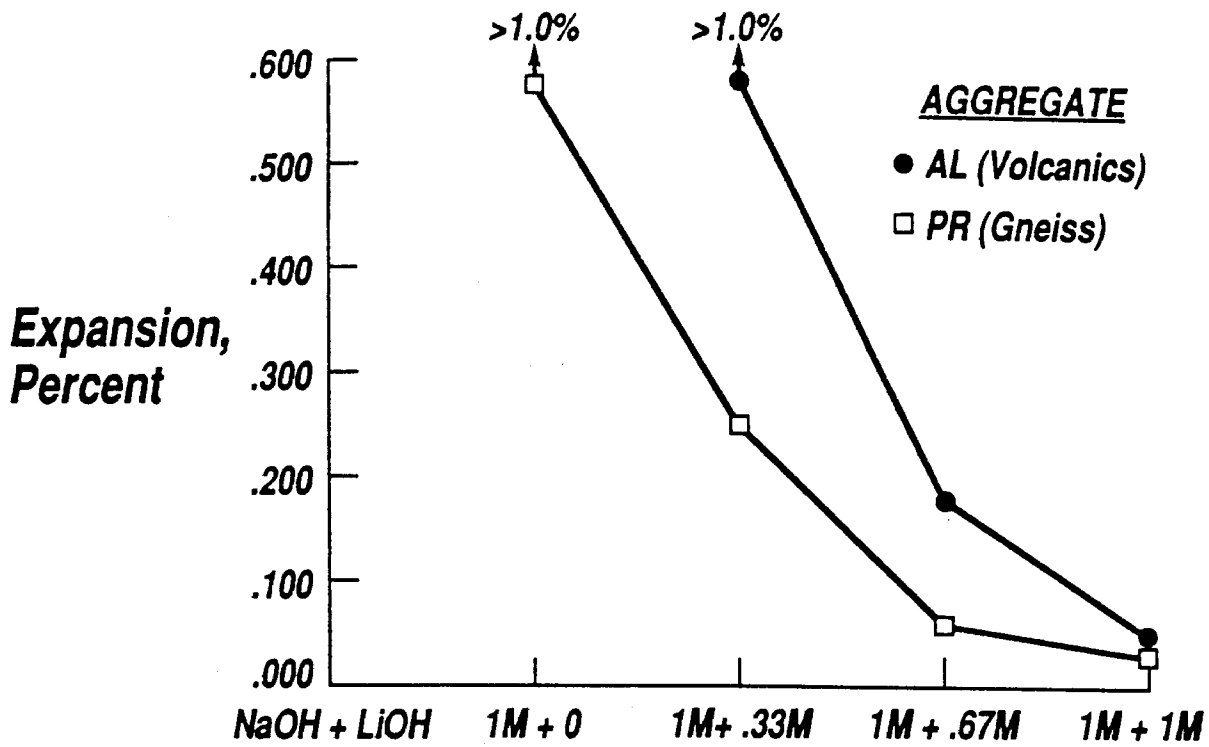


Fig. 4. Effect on 28-day expansions of increasing LiOH in solution of constant NaOH (1M).

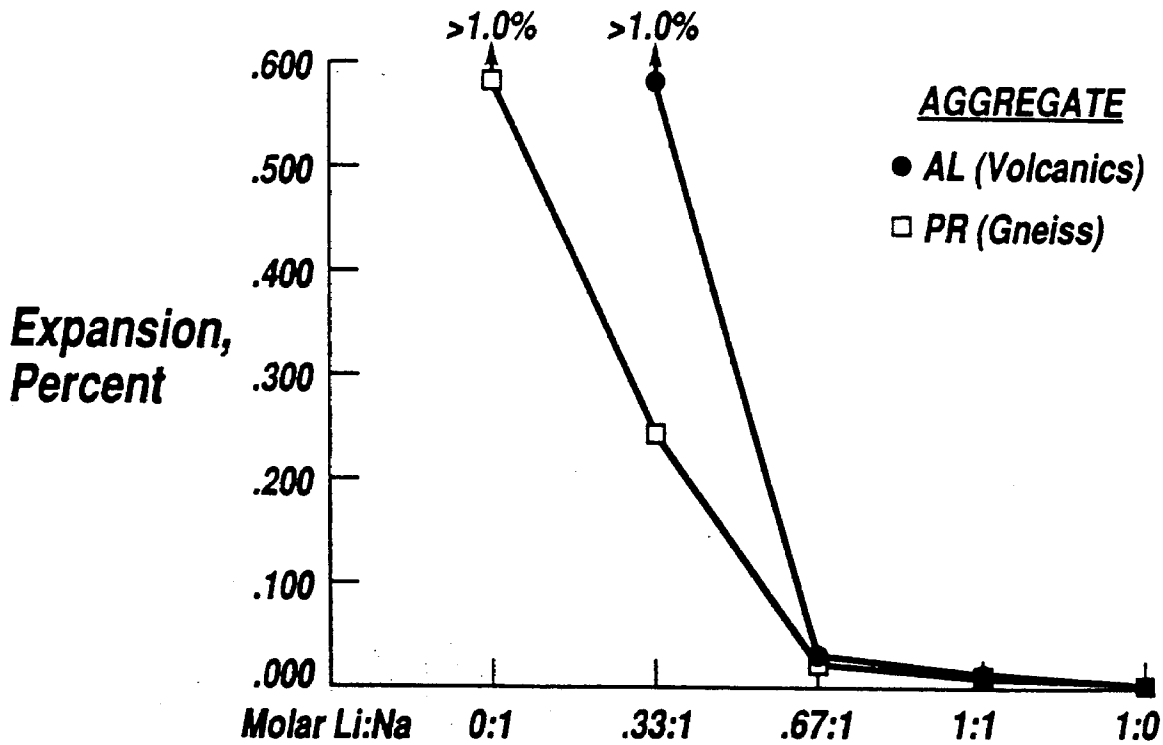


Fig. 5. Effect on 28-day expansions of increasing Li:NA in solution of constant OH ion concentration corresponding to 1M NaOH.

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