FINAL REPORT

**LABORATORY INVESTIGATION OF LITHIUM-BEARING
COMPOUNDS FOR USE IN CONCRETE**

D. S. Lane
Senior Research Scientist

DISCLAIMER

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ABSTRACT

Lithium nitrate and lithium hydroxide were evaluated in the laboratory to examine their effectiveness in controlling expansions resulting from alkali-silica reaction and their effect on concrete properties. The lithium compounds were more effective in highly accelerated tests using Pyrex as the aggregate than in concrete prism tests using a reactive Virginia aggregate. The effective dosage of lithium nitrate in the concrete prism test was higher than that typically recommended. Lithium nitrate had a benign effect on the concrete properties of strength, electrical resistance, drying shrinkage, and resistance to freezing and thawing. Similar results were obtained with lithium hydroxide, with the exception of a retarding effect on strength development.

Additional research is needed to delineate an appropriate protocol for determining the dosage of lithium admixture needed for effective control of a given concrete mixture. Current sources of fly ash and slag provided more effective means of addressing the Virginia Department of Transportation's problems with alkali-silica reaction than lithium admixtures.

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INTRODUCTION

Research in the early 1950s found that lithium compounds were effective in preventing the expansion expected from alkali-silica reactions (ASR) (McCoy and Caldwell, 1951). Interest in the use of lithium in preventing ASR was renewed by studies performed in the Strategic Highway Research Program (SHRP) (Stark et al., 1993). The results of recent work on lithium compounds has been promising, and thus the potential exists for the use of these materials in concrete as an alternative to other measures for preventing damage resulting from ASR. Because the availability of mineral admixtures effective in preventing ASR may be limited on a regional basis and hence demand may exceed local supply, the use of lithium admixtures should be evaluated.

The mechanism by which lithium compounds prevent ASR-related expansions is believed to be different from that of mineral admixtures. Mineral admixtures function by reacting with the hydroxide in the pore solution, thus lowering its concentration sufficiently to prevent significant dissolution of silica present in the aggregates. In the case of the lithium compounds, Li^+ is believed to incorporate into alkali-silica gels, resulting in an insoluble lithium silicate with little or no potential for absorbing water and swelling. This raises particular concerns about the use of lithium with respect to ASR.

Although lithium compounds prevent expansion of ASR gels, the potential exists for continued deterioration of aggregate particles because of the elevated hydroxide ion concentration of the pore solution that occurs with certain lithium compounds. If this occurs, such degradation of aggregates could adversely affect the mechanical properties of the concrete. Mineral admixtures have the collateral benefit of significantly reducing concrete permeability, thus providing protection from other deterioration mechanisms, in particular, chloride-induced reinforcement corrosion. Thus, the use of lithium compounds should be considered not simply as a function of their effect on ASR-induced expansions but within the context encompassing total concrete durability.

Certain lithium compounds may serve to activate mineral admixtures through the elevated hydroxide ion concentration, making the mineral admixture function more efficiently and thus providing construction benefits. For instance, some research (Lane and Ozyildirim, 1995) indicates that 35% replacement of portland cement having an alkali content (Na_2Oeq) of 0.92% may be necessary to provide adequate resistance to ASR. The use of lithium in

conjunction with fly ash in such a case may reduce the amount of fly ash needed or mitigate some of the negative aspects of using such high dosages of fly ash.

As an extension of the SHRP studies, the Federal Highway Administration's Expert Task Group on ASR has been monitoring field studies involving the use of lithium in New Mexico and Nevada. Field studies are proceeding in Pennsylvania, South Dakota, and New Hampshire. The task group also conducted an interlaboratory testing program in part to evaluate the use of the American Association of State Highway & Transportation Officials' (AASHTO) rapid immersion test (AASHTO TP 14) (AASHTO, 1995) to determine the necessary dosage of lithium hydroxide monohydrate necessary to prevent excessive expansions with a particular aggregate. Results of an earlier study (Lane, 1996) suggest that American Society for Testing and Materials (ASTM) tests such as ASTM C 1293 or ASTM C 441 (ASTM, 1996) are better suited than the rapid immersion test to evaluate the effectiveness and required dosage rates of lithium.

This research investigated the effects of lithium compounds on the mechanical and transport properties (i.e., those properties that control the movement of fluids and ions) of concrete and their effect on ASR by testing concretes containing natural aggregates under controlled laboratory conditions.

PROBLEM STATEMENT

Achieving long-term durability of concrete structures and pavements is one of the primary goals of the transportation community. Much success has been realized in recent years through the use of mineral admixtures to produce low-permeability concretes resistant to ASR. However, a sufficient supply of these materials is not available in all regions nationwide, and future demands or environmental constraints may outstrip their supply on a local basis. The SHRP work on ASR renewed interest on the use of lithium compounds but focused only on its ability to prevent ASR-related expansions under limited testing parameters. There exists a need for a more comprehensive laboratory evaluation of the effects of lithium compounds in concrete on permeability, mechanical properties, ASR, and interactions with mineral admixtures.

PURPOSE AND SCOPE

The purpose of this research was to investigate the effects of lithium compounds on ASR involving natural reactive aggregates; the mechanical properties of concretes; the permeability of concretes; and any synergistic behavior with mineral admixtures. The results will permit the development of guidelines for the use of lithium compounds in concrete. The mixing, curing, and testing of concretes and mortars was performed under controlled laboratory conditions.

METHODS AND MATERIALS

This study used a comparative design plan wherein the results of tests conducted on experimental mixtures were compared to the results obtained for control mixtures and, where applicable, to absolute measures of acceptability. The tests selected consisted of those used to measure the most important properties of concrete and its resistance to particular deterioration mechanisms. Tests were conducted on mortars or concretes depending on the specific test method.

Experimental Mixtures

Experimental mixtures were prepared with lithium compounds at selected dosages, and control mixtures were prepared using ordinary portland cement (OPC) and combinations of OPC with a fly ash or a ground slag. The chemical parameters of the cementitious materials are shown in Table 1. The fly ash tested was a low-lime content ASTM C 618 Class F material and the term "fly ash" as used in this report pertains only to materials of similar chemical and physical characteristics. The slag used was an ASTM C 989 Grade 120 material.

Two lithium compounds were evaluated in this study:

1. lithium hydroxide monohydrate ($LiOH \cdot H_2O$) (LH)

2. lithium nitrate ($LiNO_3$) (30% by mass in aqueous solution) (LN).

Table 1. Chemical and Physical Analysis of Cementitious Materials (% by mass)

Analysis	OPC1	OPC2	OPC3	Fly Ash	Slag
SiO_2	19.1	20.1	22.1	47.0	37.6
Al_2O_3	5.7	4.8	5.3	23.4	3.3
Fe_2O_3	2.2	2.1	2.5	16.9	0.4
CaO	61.5	62.7	65.4	4.6	17.6
MgO	2.5	3.7	3.8	---	11.2
SO_3	4.4	3.5	2.9	1.0	1.94
Na_2O	0.41	0.25	---	0.26	0.22
K_2O	0.95	0.99	---	0.17	0.34
Na_2Oeq	1.04	0.90	0.75	0.37	0.44
C_3S	50.6	49.0	51.1	---	---
C_2S	16.7	20.4	24.7	---	---
C_3A	11.7	11.4	10.0	---	---
C_4AF	6.7	5.3	7.5	---	---
LOI	1.6	1.6	0.8	4.8	---
Blaine (m^2/kg)	372	400	393	---	540
+45 μm	3.1	---	---	25.3	---

LH received the primary attention in SHRP's ASR research (Stark et al., 1993). However, because its extreme caustic nature confounds its effectiveness in mitigating ASR and presents safety issues, a neutral pH formulation containing LN was developed (Diamond, 1999).

As with any material being used to produce specific effects, it is necessary to determine the effective dosage of the material. Although suggested dosage guidelines based on limited trials have been developed (AASHTO Lead States, 1999), it is recognized that dosage should be tailored to the reactivity of the specific set of the cementitious and aggregate materials. Guidelines for LH dosage (Stark et al., 1993) and LN dosage (AASHTO, 1999) suggest the following levels based on the alkali content ($Na_2Oeq.$) of the mixture:

- LH: 1:1 ratio, LH to Na_2Oeq by mass

- LN: 4.6 L/kg Na_2Oeq.

These dosages provide a 0.74 lithium to alkali molar ratio ($Li^+/Na^+ + K^+$).

Tests

Two test methods were used to evaluate the effects on ASR-related expansions, ASTM C 441-97, a mortar test, and ASTM C 1293-95, a concrete test. ASTM C 441 is a rapid method standardized for evaluating the effectiveness of pozzolans or slag in preventing ASR expansions. It is currently used by VDOT to ensure that cementitious materials used are not conducive to ASR. The method measures the expansion of mortar bars stored over water at 38° C in containers with wicking material. Because the primary factor affecting lithium dosage is believed to be the alkali content of the portland cement, the use of ASTM C 441 would seem to be a good option for determining dosages because it is a rapid method that does not rely on adding alkali to the system for acceleration. Acceleration is provided by Pyrex glass, a very alkali-reactive material that is used as the aggregate. Because Pyrex is much more reactive than the construction aggregates used in Virginia, it provides a conservative estimate of the effectiveness of pozzolans or slag in mitigating ASR (Lane, 1999a, 1999b).

ASR Mortar Tests

In the ASTM C 441 tests, controls were made with portland cements having alkali contents of 1.0% and 0.75% Na_2Oeq (OPC controls). Additional controls were made containing fly ash or slag replacements on a percentage by mass basis. Experimental mixtures containing LN and LH were made with OPC, fly ash, and slag mixtures.

Dosages of LN and LH were based in all cases on the alkali content of the mixture contributed only by the OPC portion of the mixture. For the LN and LH mixtures with OPC, dosages were factored by 1 and 0.5. In LN and LH mixtures with fly ash or slag, the dosage was

factored by 0.5. Each mixture was replicated, and three mortar bars were cast from each batch. The mixture specifics for the ASTM C 441 testing are shown in Table 2.

Another issue with the use of Pyrex glass is its reactivity relative to that of aggregates being used in concrete. In cases where the Pyrex is more reactive than the aggregates, it provides a conservative measure of effectiveness. Although conservatism is desirable in cases where long-term durability is needed; extreme conservatism may result in inefficient or impractical use of materials. The reactive constituents in Virginia aggregates are microcrystalline and strained quartz, materials considerably less reactive than Pyrex.

Table 2. Mixture Proportions for ASTM 441 Testing

ID	OPC (%)	FA (%)	S (%)	Na_2Oeq (g)	LN (ml)	LH (g)
1.0	100	---	---	4.14	---	---
1.0FA	65	35	---	2.70	---	---
1.0S	50	---	50	2.07	---	---
1.0LN	100	---	---	4.14	19	---
1.0LN0.5	100	---	---	4.14	9	---
1.0LH	100	---	---	4.14	---	4.14
1.0LH0.5	100	---	---	4.14	---	2.07
1.0FA15LN0.5	85	15	---	3.50	8	---
1.0FA35LN0.5	65	35	---	2.70	6	---
1.0FA15LH0.5	85	15	---	3.50	---	1.66
1.0FA35LH0.5	65	35	---	2.70	---	1.35
1.0S35	65	---	35	2.70	---	---
1.0SLN	75	---	25	3.10	7	---
1.0SLH	75	---	25	3.10	---	1.55
0.75	100	---	---	3.00	---	---
0.75FA20	80	20	---	2.40	---	---
0.75LN	100	---	---	3.00	14	---
0.75LN0.5	100	---	---	3.00	7	---
0.75LH	100	---	---	3.00	---	3.00
0.75LH	100	---	---	3.00	---	1.50
0.75FALN	85	15	---	2.55	6	---
0.75FALH	85	15	---	2.55	---	1.28

ASR Concrete Tests

Series 1 Tests

The concrete prism test (ASTM C 1293-95) was used to evaluate the lithium compounds directly with a set of Virginia aggregates.   Because the test evaluates the construction aggregates directly, it is considered to provide a more reliable result (Fournier and Malhotra, 1999; Lane, 1999a, 1999b; Lane and Ozyildirim, 1999; Thomas and Innis, 1999). A modification of the standard method is used to incorporate preventive materials into the mixtures (pozzolans or slag

on a percentage by mass basis). Other variations related to the testing of specific materials are described later.

The coarse aggregate used in the concretes is a crushed metarhyolite from Hylas, Virginia; the fine aggregate is a natural siliceous sand from Richmond, Virginia. Both aggregates have been associated with deleterious alkali-silica reactivity in concrete structures (Lane, 1994) and have been used in a similar program evaluating the effectiveness of pozzolans and slag (Lane and Ozyildirim, 1999). When tested in accordance with ASTM C 1260, the metarhyolite yields 14-day expansions of 0.39%, and the sand 0.19%. The results for the metarhyolite aggregate are the highest encountered thus far in testing Virginia aggregates, thus this aggregate is presumed to be the one of the most highly alkali-silica reactive aggregates commonly used in Virginia. It was selected for use in these tests under the premise that materials that control its susceptibility to ASR will also be effective with aggregates of lesser inherent reactive potential.

No chemical admixtures (except lithium compounds) were used in the concretes. Concrete batches were mixed in the laboratory using a mixture design based on Virginia Department of Transportation (VDOT) Class 30 concrete: 378 kg/m^3, 0.45 water-cement ratio (w/cm), and No. 57 coarse aggregate. Concretes for evaluating ASR resistance were not air-entrained. In the primary series of tests, OPC 1, having an alkali content of 1.0% Na_2Oeq was used. Mixture proportions are shown in Table 3.

Table 3. Mixture Proportions (per m^3)[a] for Series 1 ASR Concrete Prism Tests

ID	OPC (%)	FA (%)	Slag (%)	Na_2Oeq (kg)[b]	LN (L)[c]	LH (kg)[c]
1	100	---	---	3.8	---	---
2	100	---	---	3.8	21.7	---
3	100	---	---	3.8	10.9	---
4	100	---	---	3.8	---	4.7
5	100	---	---	3.8	---	2.4
6	85	15	---	3.2	---	---
7	85	15	---	3.2	7.4	---
8	85	15	---	3.2	---	1.6
9	65	35	---	2.5	---	---
10	65	35	---	2.5	5.7	---
11	65	35	---	2.5	---	1.3
12	75	---	25	2.8	---	---
13	75	---	25	2.8	6.5	---
14	75	---	25	2.8	---	1.4
15	51	---	50	1.9	---	---
16	50	---	50	1.9	4.4	---
17	50	---	50	1.9	---	1.0

[a]All mixtures had a cementitious materials content of 378 kg/m^3, a coarse aggregate content of 1108 kg/m^3, a fine aggregate content of 645 kg/m^3, and a w/cm of 0.45.
[b]Based on OPC portion only.
[c]LN and LH dosages are 1.25 and 0.625 times the manufacturer's recommended dose.

Three beams to determine length changes were cast from each mixture and subjected to the standard ASTM C 1293 curing regime (in containers over water stored at 38°C) after the initial curing. The progression of ASR was evaluated by measuring changes in length, where expansion in excess of 0.04% has been established as indicative of the onset of damage (ASTM C 1293). Length change measurements were made at 7 days, 28 days, 56 days, 6 months, and thereafter at 6-month intervals.

Concrete cylinders were also cast from each mixture to examine the mechanical (100 x 200 mm cylinders) and ionic-transport (100 x 100 mm cylinders) properties of the concretes. Strength specimens were cured under either under the standard conditions (moist at 23°C) or the ASR conditions (over water at 38°C). Compressive and tensile strength tests were conducted at 28 days, 6 months, and thereafter at 6-month intervals in accordance with ASTM C 39 and ASTM C 496, respectively. Ionic-transport specimens were cured under standard conditions (moist at 23°C), an accelerated curing procedure (7 days moist at 23°C followed by 21 days moist at 38° C), or the ASR conditions. Tests were conducted at 28 days, 6 months, 1 year, and 2 years in accordance with ASTM C 1202.

Series 2 Tests

A limited series of ASR concrete tests was conducted on concretes having an alkali content of 4.7 kg/m^3 as was used in a previous study of pozzolans and slag (Lane and Ozyildirim, 1999). The (used in these concretes had an alkali content of 0.90% Na$_2$Oeq (OPC2), and the alkali content was artificially raised by adding NaOH as described in ASTM C 1293 to simulate a cement alkali content of 1.25% Na$_2$Oeq. The aggregates used in these concretes were the same as those used in the Series 1 tests as were the cement, coarse, and fine aggregate contents, and the w/cm. Proportions for this series are shown in Table 4.

Three 75 x 280 mm specimens were fabricated from each mixture to determine changes in length. Specimens were stored and measured in accordance with ASTM C 1293. Storage conditions were over water at 38°C, and length change measurements were made at 3, 6, 12, 18, and 24 months. Concrete strength and permeability were not examined in the Series 2 tests.

Table 4. Mixture Proportions (per m^3) [a] **for Series 2 ASR Concrete Prism Tests**

OPC (%)	Na$_2$Oeq[b]	LN (L)[c]	LH (kg)[c]
100	4.7	---	---
100	4.7	27.2	---
100	4.7	13.6	---
100	4.7	---	5.9
100	4.7	---	3.0

[a]All mixtures had a cementitious materials content of 378 kg/m^3, a coarse aggregate content of 1108 kg/m^3, a fine aggregate content of 645 kg/m^3, and a w/cm of 0.45.
[b]Based on OPC portion only.
[c]LN and LH dosages are 1.25 and 0.625 times the manufacturer's recommended dose.

Strength Tests

Specimens for determining strength were moist cured at $23^{o}C$ and $38^{o}C$ until testing. The compressive strength of mixtures was determined using 100 x 200 mm specimens in accordance with ASTM C 39. In lieu of sulfur-mortar capping, the compressive strength specimens were tested using neoprene pads in steel retaining rings because of the convenience afforded by this procedure. Tensile strength was determined using 100 x 200 mm specimens in accordance with ASTM C 469.

Electrical Resistance Tests

Electrical resistance of the concrete mixtures was determined using 50 x 100 mm specimens in accordance with ASTM C 1202. The current passing through the specimen during the 6-hour test is measured in coulombs. High electrical resistance in this test is considered to indicate low ionic-transport properties of the concrete. Electrical resistance specimens were moist cured at $23^{o}C$ and tested at 28 days and 1 year. Two additional sets of specimens were subjected to accelerated curing: (1) 7 days moist cured at $23^{o}C$ followed by 21 days moist at $38^{o}C$, used to indicate 1-year values at 28 days (Lane and Ozyildirim, 1999), and (2) moist cured at $38^{o}C$ until testing following the ASR storage procedures.

Drying Shrinkage and Resistance to Freezing and Thawing and Deicer Scaling Tests

Air-entrained concretes were batched to evaluate the effect of the lithium compounds on drying shrinkage and resistance to freezing and thawing. The proportions of these concretes are shown in Table 5. Compressive strength and air content (gravimetric) were also measured.

Drying shrinkage tests were conducted on 75 x 75 x 280 mm specimens. The specimens were moist cured at $23^{o}C$ for 28 days before being subjected to the drying (50% relative humidity at $23^{o}C$) environment. Measurements were made in accordance with ASTM C 157.

Table 5. Mixture Proportions (per m^3)[a] for Drying Shrinkage and Freezing and Thawing Tests

OPC (kg)	Na$_2$Oeq[b]	LN (L)[c]	LH
378	3.4	---	---
378	3.4	15.6	---
378	3.4	11.7	---
378	3.4	---	3.4
378	3.4	---	2.6

[a]All mixtures contained a coarse aggregate content of 1108 kg/m^3, a fine aggregate content of 630 kg/m^3, an air-entraining admixture dosage of 0.5 ml/kg cement, and a w/cm of 0.45.
[b]Based on OPC portion only.
[c]LN and LH dosages are 1.0 and 0.75 times the recommended dose.

Freezing and thawing durability was evaluated on 75 x 100 x 405 mm specimens moist cured for 14 days at 23°C. Freezing and thawing was performed in accordance with ASTM C 666 Procedure A (in water) with 2% NaCl by mass added to the water. The dynamic modulus of elasticity and loss of mass were monitored during the test.

RESULTS AND DISCUSSION

ASR Tests

Results of the ASR mortar tests are shown in Figures 1 through 4. Current VDOT requirements for cementitious materials limit expansion to 0.1% at 56 days. In Figures 1 and 3, the 0.5X dosages of LN and LH with OPC1 and OPC3 delay expansion only slightly compared to the OPC controls. With OPC3, the ultimate expansion of the 0.5X LN and LH exceeded that of the OPC control. With OPC1, the 1X dosages of LN and LH adequately limited expansions, although the LH had a slight tendency for continued expansion. With OPC3, the 1X dosage was adequate for LN but not LH.

Combinations of 0.5X dosages of lithium admixtures with low amounts of fly ash or slag are shown in Figures 2 and 4. In Figure 2, with OPC1, none of these combinations should be considered effective although the 0.5X LH with FA met the 56-day expansion limit since it subsequently expanded quite rapidly. In Figure 4, with OPC3, the combinations were more effective; however, the fly ash and slag were used at about their effective amounts.
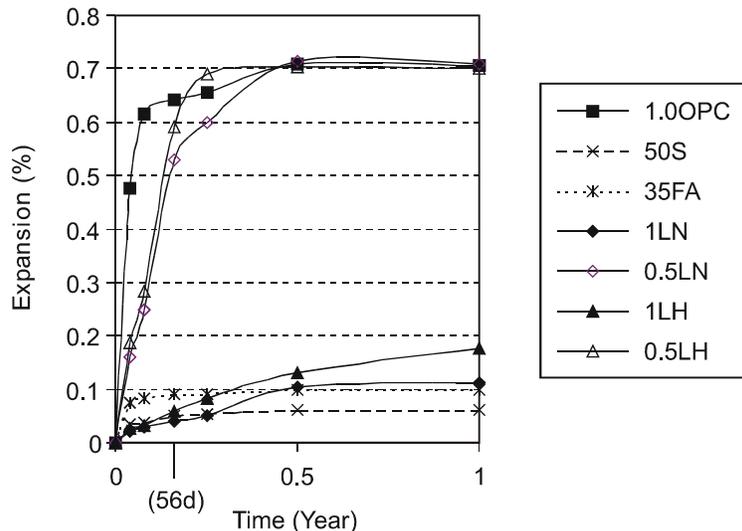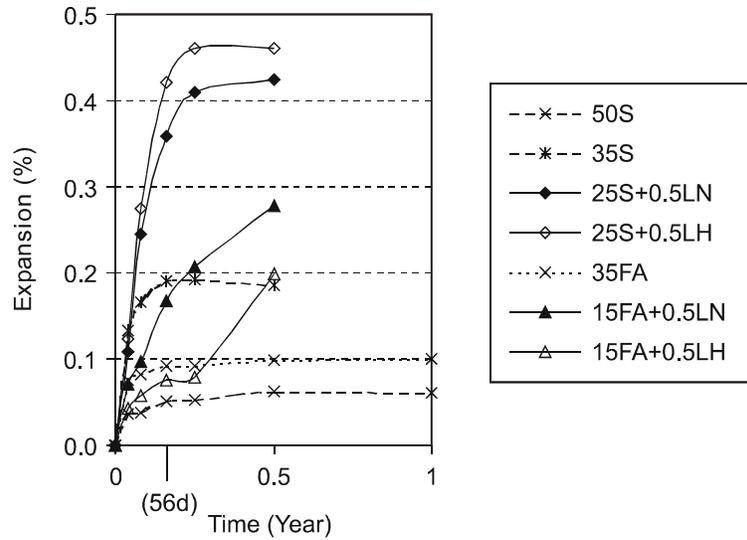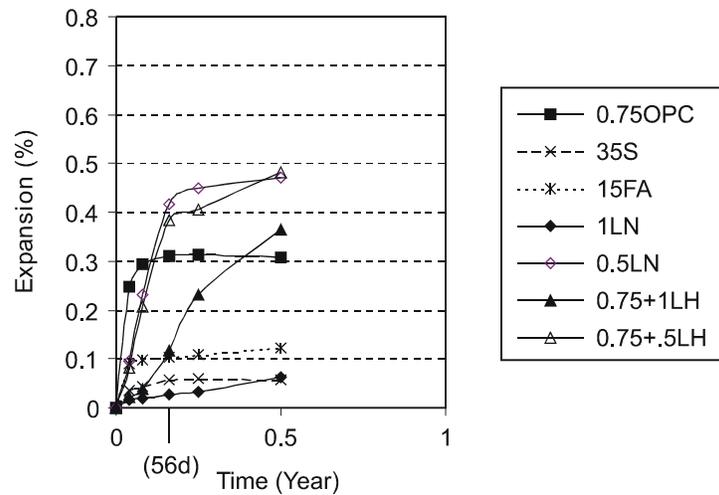

Figure 1. Expansions with OPC1 with Lithium Admixtures, Fly Ash, or Slag (ASTM C 441).
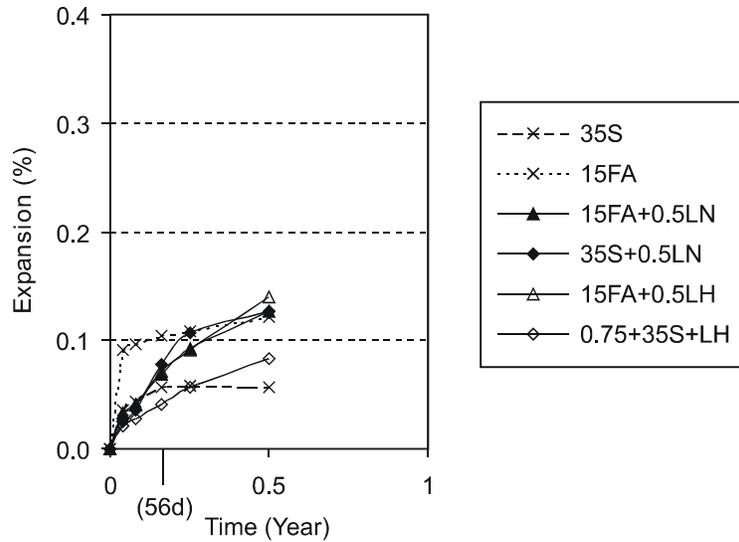
Figure 2. Expansions of OPC1 with Combinations of Lithium Admixtures and Fly Ash or Slag (ASTM C 441).

Figure 3. Expansions of OPC3 with Lithium Admixtures, Fly Ash, or Slag (ASTM C 441).

The results of ASTM C 441 suggest that the LN admixture when used at about the recommended dosage of 4.6L/kg Na_2Oeq is effective in controlling ASR expansions. Results with the LH were somewhat mixed, showing greater effectiveness with the higher alkali content cement (OPC1) than the lower alkali cement (OPC3). This may be a function of the increased pore solution pH when LH is introduced (Diamond, 1999), leading to increased reactivity and expansion. It suggests that the effective dosage for lithium compounds that increase pore solution pH (i.e., LH, lithium carbonate, lithium fluoride) is inversely proportional to the cement alkali content.

Figure 4. Expansions of OPC3 with Combinations OF Lithium Admixtures, Fly Ash, and Slag (ASTM C 441).

In Figures 5 and 6, the expansion results of the concrete ASR Series 1 tests are shown. These concretes had a control alkali content of 3.8 kg/m^3. A maximum expansion of 0.04% is generally applied to this test. When mitigation techniques are evaluated, a test period of 2 years is recommended (Thomas et al., 1997) and was used in a previous study of pozzolans and slag (Lane and Ozyildirim, 1999). However, in that study, a control alkali content of 4.7 kg/m^3 was used. Figure 7 shows the expansion results of the Series 2 tests that used a control alkali content of 4.7 kg/m^3. OPC control expansion was about 0.15% expansion at 1 year compared to 0.05% with that of the 3.8 kg/m^3 loading. This comparison shows the accelerating effect of the higher alkali loading and indicates that a long test period may be advisable for tests at the lower alkali content.

In Figure 5, the 1.25 dose of LH held expansion slightly below that of the control OPC concrete but exceeded the 0.04% limit just beyond 1 year. The 1.25 LN expansion remained slightly below 0.04% at 2 years. At 3 years, the 1.25 LN and 15% fly ash control expansions were just at the 0.04% limit whereas the 25% slag control remained lower, seemingly indicating somewhat marginal protection in light of the reduced acceleration of these concretes. The 0.65 doses of LN and LH produced expansions greatly in excess of that of the OPC control. This phenomenon was expected with LH because it is known to raise the alkalinity of the pore solution, but not with LN (Diamond, 1999). The results suggest that it is critical to avoid underdosing when using lithium compounds.

Based on these results, a dosage of at least 1.25 times the recommended dosage or a 0.925 lithium to alkali molar ratio would be needed with these aggregates when LN is used as the sole mitigation. Although the 0.74 molar ratio on which the recommended dosage is based has received considerable publicity, this work and others (Durand, 2000) have reported on aggregates that require higher levels of lithium to suppress expansion.
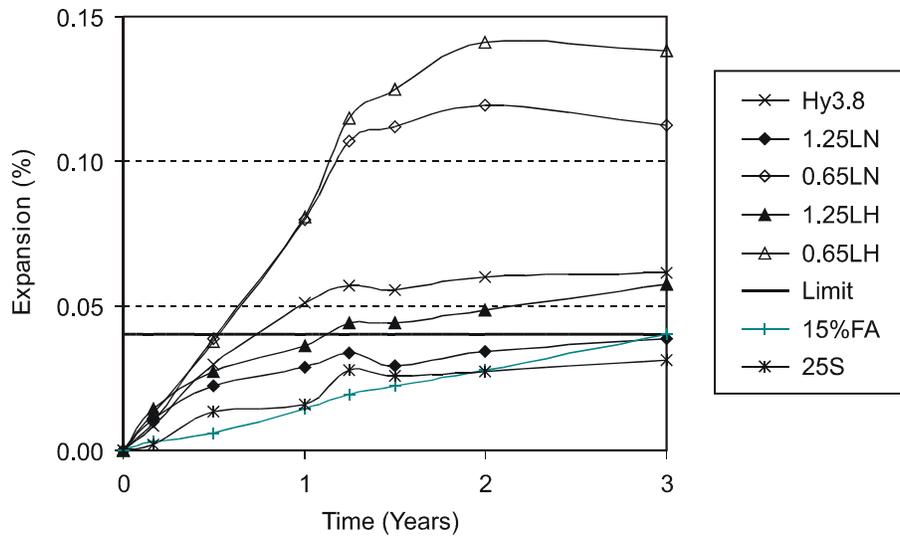
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Figure 5. Expansions with Lithium Admixtures and Controls, Series 1 Concretes (ASTM C 1293).
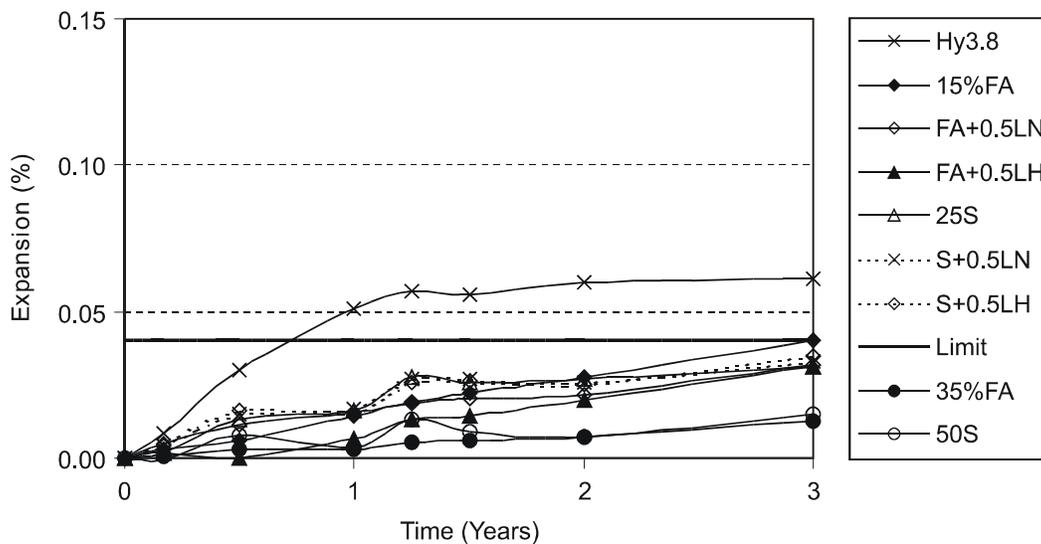

Figure 6. Expansions with Combinations of Lithium Admixtures and Fly Ash or Slag, Series 1 Concretes (ASTM C 1293).

Expansion results of 0.5 dosages of LN and LH combined with FA or slag are shown in Figure 6. All of the combinations were effective in controlling expansion. However, the fly ash (15%) and slag (25%) controls were equal in effectiveness to the lithium combinations and higher replacements, fly ash (35%), slag (50%) were more effective. These results suggest that with this aggregate combination, there is no benefit to be gained by combining lithium compounds with fly ash or slag with regard to ASR suppression.

The lithium admixtures appear more effective in the Pyrex mortar tests than in the concrete tests. This can be explained by the difference in reaction rates with the two test

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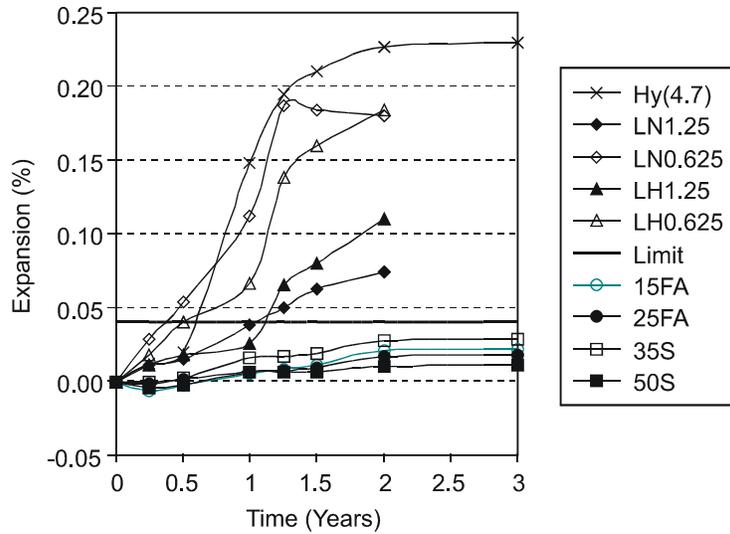
Figure 7. Expansions with Lithium Admixtures, Series 2 Concretes (ASTM C 1293). The fly ash and slag data shown are from a previous study (Lane and Ozyildirim, 1999).

methods. To suppress expansion, the lithium ion must be present in the pore solution while the silica is reacting. Pyrex reacts rapidly, producing reaction product at a rate equivalent to that of the production of cement hydrates. In the slower concrete tests, the ASR proceeds at a much slower rate than with cement hydration. Lithium ions are incorporated into the cement hydrates (Diamond, 1999) and are thereby unavailable to complex with AS reaction product that forms at later stages.

In field concrete, this rate differential will be even greater and should be considered when accelerated tests are used to establish an effective dosage of lithium admixtures. Another factor that should be considered is the manner in which dosage is translated from the accelerated test to the production level. General guidelines for determining lithium admixture dosage base the dosage on the alkali content of the concrete being produced. When tests are accelerated through added alkali, the test concrete contains a particular amount of lithium per unit volume of concrete. Translating the effective test dosage on a mass alkali basis results in a reduced field concrete admixture dosage when viewed on a volumetric basis. If the admixture is more effective in the accelerated test than under actual field conditions, this reduction in dosage results in a further erosion of the safety margin.

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Concrete Properties

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Compressive Strength

Compressive strength results for the Series 1 concretes are shown in Figure 8. All concretes underwent the typical increase in strength expected from 3 to 28 days. The lithium nitrate admixture did not significantly affect concrete strengths. Lithium hydroxide, however, depressed strengths at all ages, reflecting the reports of its retarding effect on cement hydration
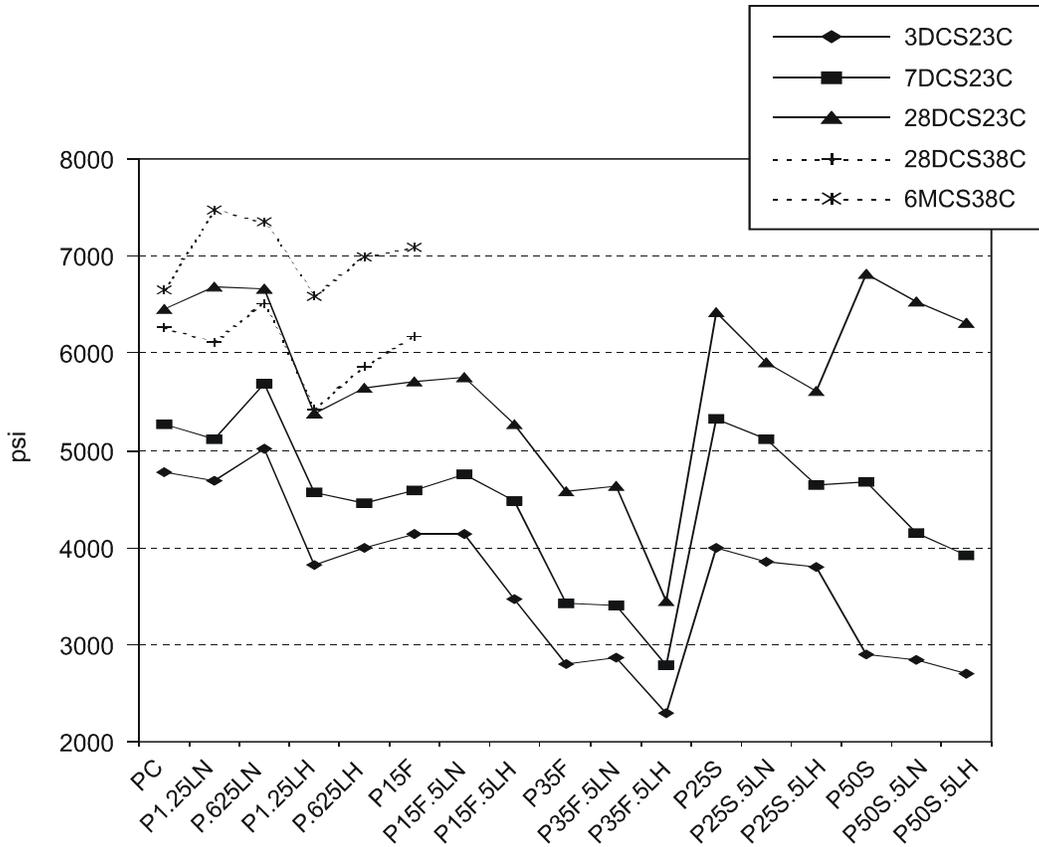
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Figure 8. Compressive Strength Results, Series 1 Concretes.

(Wang et al., 1996). Interestingly, this effect also occurred in the concretes containing fly ash and slag. It was initially suspected that the use of lithium hydroxide might serve to activate fly ash or slag, thus negating their tendency to retard concrete strength gain. No such beneficial response was noted in these results.

Tensile Strength

Tensile strength results for Series 1 concretes are presented in Figure 9. Specimens tested after curing for 1 year at 23°C serve as a (relatively) non-reactive control to the specimens stored at 38 $^{\circ}$C for 1 and 1.5 years as illustrated by the results for the PC mixture. Similar strength reductions occurred for the 62.5% dosages of LN and LH.
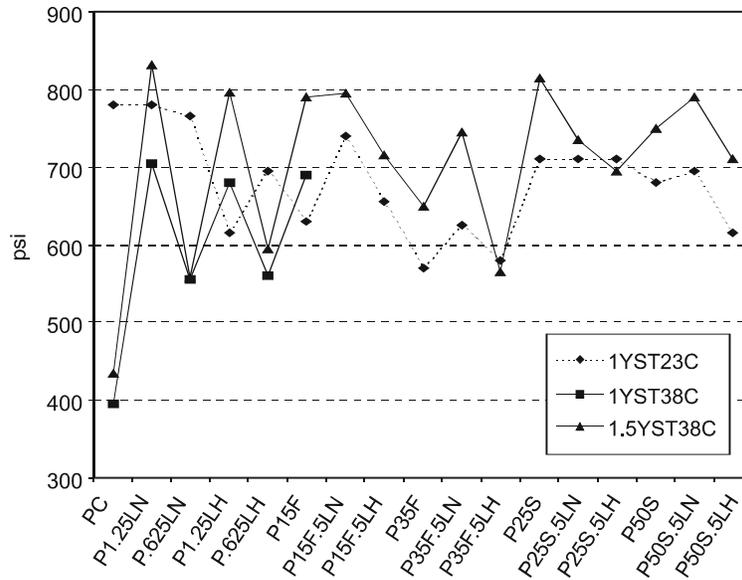
Figure 9. Split Tensile Test Results, Series 1 Concretes.

Electrical Resistance

The results of the electrical resistance tests are presented in Figure 10. The tests were conducted on specimens cured for 28 days and 1 year at 23 $^{\circ}$C and 28 days, 6 months, and 1 year at 38 $^{\circ}$C. Most notable are the beneficial effects of fly ash and slag on later-age electrical resistance, indicating these concretes provide good resistance to ionic transport and the deterioration mechanisms that rely on them (Lane and Ozyildirim, 1999). A slight benefit was noted in mixtures containing lithium compounds.
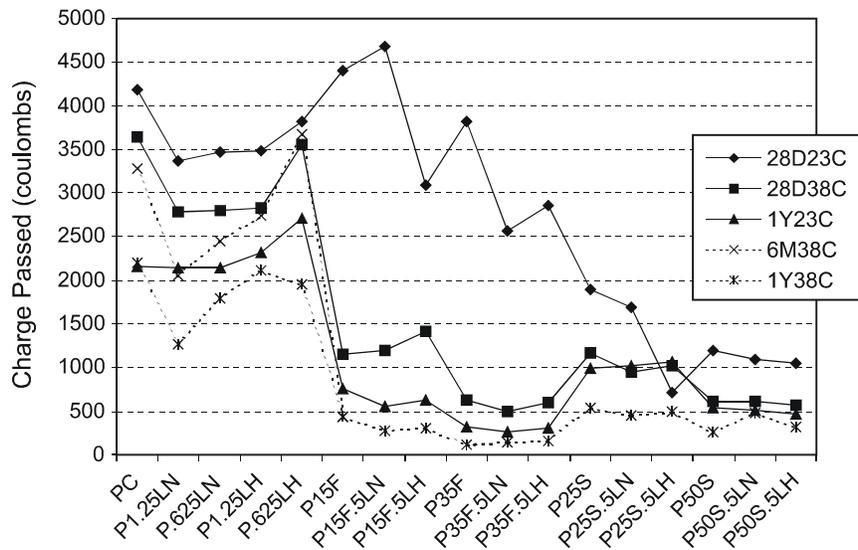

Figure 10. Electrical Resistance Results, Series 1 Concretes.

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Air-Entrained Concretes

The air content, compressive strength, and results of drying shrinkage and freezing and thawing tests are presented in Table 6. The results indicate that the lithium compounds did not affect the air-void parameters of the concretes and all mixtures had excellent resistance to freezing and thawing. Similarly, the lithium compounds had no effect on the drying shrinkage of the concretes.

Table 6. Results of Tests on Air-Entrained Concretes

Mixture	1: OPC	2: 1XLN	3: 0.75XLN	4: 1XLH	5: 0.75XLH
Air content (%)	4.0	4.2	4.4	5.4	6.1
3d compressive strength (psi)	3520	3540	3660	3290	3070
7d compressive strength (psi)	4260	4380	4060	3760	3610
28d compressive strength (psi)	5040	5160	5000	4770	4410
90d compressive strength (psi)	5230	5810	5660	4870	4890
1yr drying shrinkage (%)	0.06	0.06	0.06	0.06	0.06
F-T durability factor	101	101	99	98	99
F-T weight loss (%)	-0.10	-0.17	0.03	0.20	0.20

CONCLUSIONS

- Lithium nitrate admixture has a benign effect on concrete strength, electrical resistance, drying shrinkage, and resistance to freezing and thawing.

- Lithium hydroxide has a benign effect on electrical resistance, drying shrinkage, and resistance to freezing and thawing but a retarding effect on concrete strength.

- Lithium compounds are more effective in preventing expansions resulting from ASR in the more accelerated test.

- The effective lithium dosage is affected by factors such as aggregate type and concrete alkali content.

- The effective dosage of lithium nitrate in the less accelerated concrete prism test for the aggregates tested is 1.25 times the current manufacturer's recommendation.

- The amounts of fly ash or slag needed to control expansion in the less accelerated concrete prism test are less than VDOT currently requires.

- Using current sources of fly ash and slag is more effective in addressing VDOT's problems with ASR than is using lithium admixtures.

RECOMMENDATIONS

1. Do not use highly accelerated tests to determine the effective lithium admixture dosage.

2. Focus future work on establishing a well-defined protocol for determining the effective dosage of lithium nitrate admixture that provides an adequate engineering margin of safety for a given concrete mixture.

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