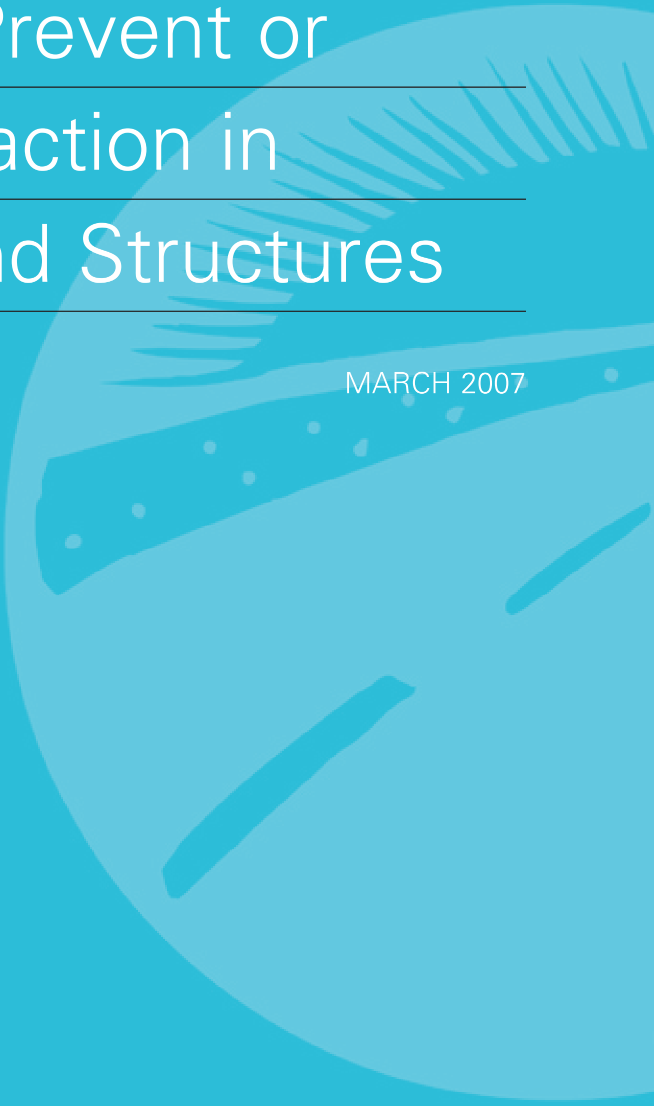
The Use of Lithium to Prevent or Mitigate Alkali-Silica Reaction in Concrete Pavements and Structures

PUBLICATION NO. FHWA-HRT-06-133

MARCH 2007



U.S. Department of Transportation
Federal Highway Administration

Research, Development, and Technology
Turner-Fairbank Highway Research Center
6300 Georgetown Pike
McLean, VA 22101-2296

Foreword

Progress is being made in efforts to combat alkali-silica reaction in portland cement concrete structures—both new and existing. This facts book provides a brief overview of laboratory and field research performed that focuses on the use of lithium compounds as either an admixture in new concrete or as a treatment of existing structures.

This document is intended to provide practitioners with the necessary information and guidance to test, specify, and use lithium compounds in new concrete construction, as well as in repair and service life extension applications. This report will be of interest to engineers, contractors, and others involved in the design and specification of new concrete, as well as those involved in mitigation of the damaging effects of alkali-silica reaction in existing concrete structures.

Gary L. Henderson, P.E.
Director, Office of Infrastructure
Research and Development

Notice

Quality Assurance Statement

Technical Report Documentation Page

1. Report No.
FHWA-HRT-06-133

2. Government Accession No.

3. Recipient's Catalog No.

4. Title and Subtitle
The Use of Lithium To Prevent or Mitigate Alkali-Silica Reaction in Concrete Pavements and Structures

5. Report Date
March 2007

6. Performing Organization Code

7. Author(s)
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8. Performing Organization Report No.

9. Performing Organization Name and Address
The Transtec Group, Inc.
6111 Balcones Drive
Austin, TX 78731

10. Work Unit No.

11. Contract or Grant No.
DTFH61-02-C-00097

12. Sponsoring Agency Name and Address
Office of Infrastructure R&D
Turner-Fairbank Highway Research Center, HRDI-11
6300 Georgetown Pike, Room F-209
McLean, VA 22101

13. Type of Report and Period Covered
Final Report

14. Sponsoring Agency Code

15. Supplementary Notes
Contracting Officer's Technical Representative: Fred Faridazar, HRDI-12

16. Abstract
Alkali-silica reaction (ASR) was first identified as a form of concrete deterioration in the late 1930s (Stanton 1940). Approximately 10 years later, it was discovered that lithium compounds can be used to control expansion due to ASR. There has recently been increased interest in using lithium technologies to both control ASR in new concrete and to retard the reaction in existing ASR-affected structures.

This facts book provides information on lithium, its origin and properties, and on its applications. The mechanism of alkali-silica reaction is discussed together with methods of testing to identify potentially alkali-silica reactive aggregates. Traditional methods for minimizing the risk of damaging ASR are presented; these include the avoidance of reactive aggregates, controlling the levels of alkali in concrete and using supplementary cementing materials such as fly ash, slag and silica fume. The final two sections of the facts book discuss the use of lithium, first as an admixture for new concrete construction and second as a treatment for existing concrete structures affected by ASR.

17. Key Words
alkali-silica reaction, lithium, concrete durability, mitigation, fresh concrete, hardened concrete, case studies, laboratory testing, field investigation, existing structures

18. Distribution Statement
No Restrictions. This document is available to the public through the National Technical Information Service; Springfield, VA 22161

19. Security Classif. (of this report)
Unclassified

20. Security Classif. (of this page)
Unclassified

21. No. of Pages
47

22. Price

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mi	miles	1.61	kilometers	km
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ft^{2}	square feet	0.093	square meters	m^{2}
yd^{2}	square yard	0.836	square meters	m^{2}
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mi^{2}	square miles	2.59	square kilometers	km^{2}
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fl oz	fluid ounces	29.57	milliliters	mL
gal	gallons	3.785	liters	L
ft^{3}	cubic feet	0.028	cubic meters	m^{3}
yd^{3}	cubic yards	0.765	cubic meters	m^{3}
		NOTE: volumes greater than 1000 L shall be shown in m^{3}		
		MASS		
oz	ounces	28.35	grams	g
lb	pounds	0.454	kilograms	kg
T	short tons (2000 lb)	0.907	megagrams (or "metric ton")	Mg (or "t")
		TEMPERATURE (exact degrees)		
^{o}F	Fahrenheit	5 (F-32)/9 or (F-32)/1.8	Celsius	^{o}C
		ILLUMINATION		
fc	foot-candles	10.76	lux	lx
fl	foot-Lamberts	3.426	candela/m^{2}	cd/m^{2}
		FORCE and PRESSURE or STRESS		
lbf	poundforce	4.45	newtons	N
lbf/in^{2}	poundforce per square inch	6.89	kilopascals	kPa

APPROXIMATE CONVERSIONS FROM SI UNITS

Symbol	When You Know	Multiply By	To Find	Symbol
		LENGTH		
mm	millimeters	0.039	inches	in
m	meters	3.28	feet	ft
m	meters	1.09	yards	yd
km	kilometers	0.621	miles	mi
		AREA		
mm^{2}	square millimeters	0.0016	square inches	in^{2}
m^{2}	square meters	10.764	square feet	ft^{2}
m^{2}	square meters	1.195	square yards	yd^{2}
ha	hectares	2.47	acres	ac
km^{2}	square kilometers	0.386	square miles	mi^{2}
		VOLUME		
mL	milliliters	0.034	fluid ounces	fl oz
L	liters	0.264	gallons	gal
m^{3}	cubic meters	35.314	cubic feet	ft^{3}
m^{3}	cubic meters	1.307	cubic yards	yd^{3}
		MASS		
g	grams	0.035	ounces	oz
kg	kilograms	2.202	pounds	lb
Mg (or "t")	megagrams (or "metric ton")	1.103	short tons (2000 lb)	T
		TEMPERATURE (exact degrees)		
^{o}C	Celsius	1.8C+32	Fahrenheit	^{o}F
		ILLUMINATION		
lx	lux	0.0929	foot-candles	fc
cd/m^{2}	candela/m^{2}	0.2919	foot-Lamberts	fl
		FORCE and PRESSURE or STRESS		
N	newtons	0.225	poundforce	lbf
kPa	kilopascals	0.145	poundforce per square inch	lbf/in^{2}

*SI is the symbol for the International System of Units. Appropriate rounding should be made to comply with Section 4 of ASTM E380. (Revised March 2003)

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LIST OF ACRONYMS AND ABBREVIATIONS

Terms

AAR	alkali-aggregate reaction
ACR	alkali-carbonate reaction
ASR	alkali-silica reaction
ASTM	American Society for Testing and Materials
CSA	Canadian Standards Association
DEMEC	demountable mechanical
FHWA	Federal Highway Administration
ppm	parts per million
SASW	spectral analysis of surface waves
SCM	supplementary cementitious material
w/cm	water-cementitious material ratio

Chemical Notations

C-S-H	Calcium silicate hydrate
Ca	Calcium
$CaCO_3$	Calcium carbonate
$Ca(NO_3)_2$	Calcium nitrate
$Ca(OH)_2$	Calcium hydroxide
OH^-	Hydroxyl ion
K	Potassium
K_2O	Potassium oxide
KCl	Potassium chloride
[Li]/[Na+K]	Molar ratio of lithium ions to the sum of sodium and potassium ions
LiCl	Lithium chloride
LiF	Lithium fluoride
$LiNO_3$	Lithium nitrate
LiOH	Lithium hydroxide
$LiOH \bullet H_2O$	Lithium hydroxide monohydrate
Li_2CO_3	Lithium carbonate
Li_2SiO_3	Lithium silicate
Li_2SO_4	Lithium sulfate
M	molar
N	normal
Na	Sodium
Na_2O	Sodium oxide
Na_2O_e	Total sodium oxide equivalent
NaCl	Sodium chloride
NaOH	Sodium hydroxide
Si	Silicon
SiO_2	Silicon dioxide

CHAPTER 1. INTRODUCTION

Alkali-silica reaction (ASR) was first identified as a form of concrete deterioration in the late 1930s (Stanton 1940). About 10 years later, it was discovered that lithium compounds could be used to control expansion due to ASR. Recently there has been increased interest in using lithium technologies both to control ASR in new concrete and to retard the reaction in existing ASR-affected structures.

This book provides information on lithium, its origin and properties, and its applications. The mechanism of alkali-silica reaction is discussed together with methods of testing to identify potential alkali-silica reactive aggregates. Traditional methods for minimizing the risk of damaging ASR are presented; these include the avoidance of reactive aggregates, controlling the levels of alkali in concrete, and using supplementary cementing materials such as fly ash, slag, and silica fume.

The final two sections of the book discuss the use of lithium, first as an admixture for new concrete construction, and second as a treatment for existing concrete structures affected by ASR.

The information in this document was obtained primarily from the FHWA publication *Interim Recommendations for the Use of Lithium to Mitigate or Prevent Alkali-Silica Reaction (ASR)* (Publication No. FHWA-HRT-06-073). For further information, the reader should refer to the above publication.

CHAPTER 2. LITHIUM—PROPERTIES AND PRODUCTION

Lithium is the third element in the periodic table (see figure 1) and is denoted by the chemical symbol "Li." Its atomic number is 3 and its atomic mass is 6.941 grams (g), making it the third lightest element on earth after hydrogen (H) and helium (He).

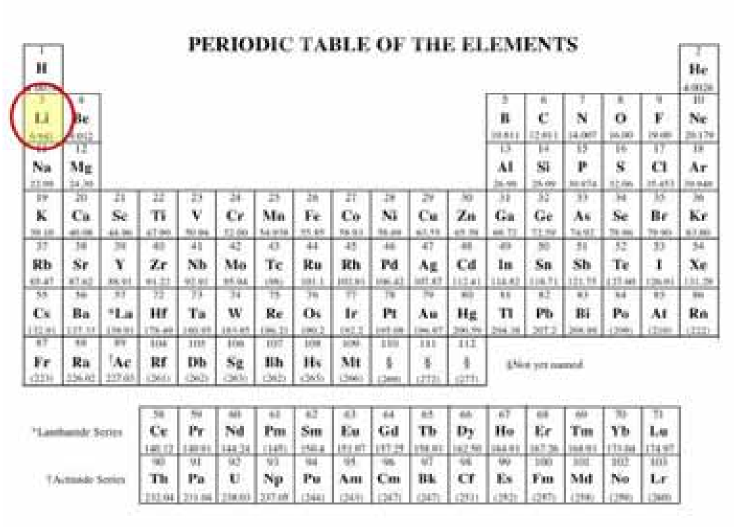


Figure 1. Periodic table showing the position of lithium.

As a pure element, lithium is a soft, silver-white metal and belongs in the Alkali Metal Group together with sodium (Na), potassium (K), rubidium (Rb), cesium (Cs), and francium (Fr).

Lithium has only one electron in its outer shell (i.e., valence = +1) which makes the pure metal very unstable and reactive to moisture. Stable lithium compounds can be manufactured for commercial use; examples are lithium carbonate (Li_2CO_3), lithium chloride (LiCl), lithium sulfate (Li_2SO_4), and lithium nitrate ($LiNO_3$).

Lithium metal does not occur naturally in the environment, and lithium is most commonly found in lithium-bearing minerals such as spodumene ($LiAlSi_2O_6$) in pegmatite rocks or as dissolved salt such as lithium chloride (LiCl) in brines (see figures 2 and 3). Table 1 provides a list of common lithium-containing minerals.

Figure 2. Photograph of lithium metal.

Figure 3. Photograph of the lithium-bearing mineral spodumene.

Table 1. Principal lithium minerals and their sources (after Lumley, 1997).

Mineral	Formula	Locations of Deposits (in Alphabetical Order)
Spodumene	$LiAlSi_2O_6$	Australia, Brazil, Canada, China, Russia, United States
Petalite	$LiAlSi_4O_{10}$	Australia, Brazil, Namibia, Russia, Sweden, Zimbabwe
Amblygonite	$(Li,Na)Al(PO_4)(F,OH)$	Brazil, Canada, Mozambique, Namibia, Rwanda, South Africa, Suriname, Zimbabwe
Lepidolite	$K(Li,Al)_3(Si,Al)_4O_{10}(F,OH)_2$	Brazil, Canada, Namibia, Zimbabwe
Eucryptite	$LiAlSiO_4$	Zimbabwe

Spodumene is the most abundant of the lithium-containing minerals from which lithium is extracted. To extract lithium in this process, spodumene ore concentrate is first heated in a rotary kiln at about 1,000 °Celsius (C) (1,832 °Fahrenheit (F)) to decrepitate the spodumene. This clinker is then roasted with sulfuric acid at about 250 °C (482 °F) to leach out an aqueous extract of lithium sulfate. This lithium sulfate is then converted to lithium carbonate, the primary compound from which other lithium compounds are manufactured.

Processing ore deposits is energy-intensive, but less expensive lithium extraction methods exist. For instance, much of the lithium produced today is extracted from subsurface salt brine deposits. The largest deposits of lithium-containing brines are found in Argentina and Chile. Solar evaporation is used to precipitate the salts, which are then processed chemically to separate the lithium (as Li_2CO_3) from the other compounds; figures 4 and 5 show aerial views of these deposits.

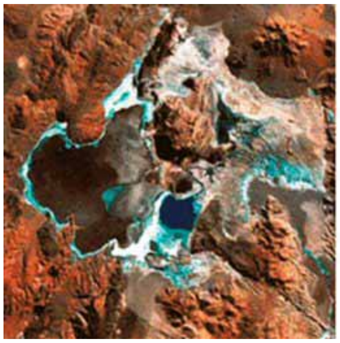


Figure 4. Aerial view of lithium-bearing brines in Argentina (Salar del Hombre Muerto).

Figure 5. Aerial view of lithium-bearing brines in Chile (Salar de Atacama).

Lithium carbonate (Li_2CO_3) is used as a feedstock for other processes to produce a variety of lithium compounds which are then used in a wide range of applications. Table 2 provides a list of common lithium compounds and different applications.

The main application for lithium in the construction industry is in the formulation of chemical admixtures for concrete. Various lithium compounds (Li_2CO_3, $LiOH$, Li_2SO_4) are used in the formulation of set accelerators for calcium-aluminate-cement concrete and both lithium hydroxide monohydrate ($LiOH•H_2O$) and lithium nitrate ($LiNO_3$) have been used to control ASR in portland cement concrete.

Table 2. List of lithium compounds and applications for lithium.

Forms of Lithium	Common Applications
Lithium metal (Li) Lithium carbonate (Li_2CO_3) Lithium nitrate ($LiNO_3$) Lithium hydroxide (LiOH) Lithium hydroxide monohydrate ($LiOH \bullet H_2O$) Lithium chloride (LiCl) Lithium fluoride (LiF) Lithium sulfate (Li_2SO_4)	Air treatment Alloys Batteries Construction (e.g., chemical admixtures or treatment of ASR-affected structures) Fine chemicals Glass and ceramics Greases and lubricants Pharmaceuticals Polymers Pool water treatment Other specialty applications

CHAPTER 3. ALKALI-AGGREGATE REACTION

3.1 Terminology

Alkali-aggregate reaction (AAR) is a reaction in concrete between the alkali hydroxides, which originate mainly from the portland cement, and certain types of aggregate. Two types of AAR are currently recognized; these are alkali-silica reaction (ASR) and alkali-carbonate reaction (ACR). As the names imply, these types of reaction differ in that they involve reactions with either siliceous or carbonate phases in the aggregates (table 3). ASR is far more widespread than ACR and is the focus of this document. ACR will not be discussed further, however, it should be noted that the measures used to control ASR have generally shown limited effectiveness in controlling ACR.

Table 3. Terminology for alkali-aggregate reactions (CSA A23.1-04).

Alkali-Aggregate Reaction (AAR)	Chemical reaction in either concrete or mortar between hydroxyl ions (OH^-) of the alkalies (sodium and potassium) from hydraulic cement or other sources and certain constituents of some aggregates; under certain conditions deleterious expansion of concrete or mortar may result.
Alkali-Carbonate Reaction (ACR)	Chemical reaction in either concrete or mortar between hydroxyl ions (OH^-) of the alkalies (sodium and potassium) from hydraulic cement or other sources and certain carbonate rocks, particularly calcitic dolostone and dolomitic limestones, present in some aggregates; the reaction causes dedolomitization and expansion of the affected aggregate particles, leading to abnormal expansion and cracking of concrete in service.
Alkali-Silica Reaction (ASR)	Chemical reaction in either concrete or mortar between hydroxyl ions (OH^-) of the alkalies (sodium and potassium) from hydraulic cement or other sources and certain siliceous rocks and minerals, such as opal, chert, microcrystalline quartz, and acidic volcanic glass, present in some aggregates. This reaction and the development of the alkali-silica gel reaction product can, under certain circumstances, lead to abnormal expansion and cracking of the concrete.

3.2 Mechanisms of ASR

Concrete is a porous material (typically about 10 percent of the volume of concrete is occupied (by pores) and, in saturated concrete, the pores contain a solution composed of alkali hydroxides (NaOH and KOH). The origin of the sodium (Na) and potassium (K) is, principally, the portland cement. Table 4 shows an oxide analysis of a typical portland cement.

Table 4. Typical chemical analysis for portland cement.

Oxide	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	Na_2O	K_2O	SO_3	LOI
Percent	20.55	5.07	3.10	64.51	1.53	0.15	0.73	2.53	1.58

It is convenient to convert the potassium oxide to an equivalent amount of sodium oxide using a molar ratio and to express the alkalies in terms of the equivalent alkali content of the cement; which is defined as:

$$\text{Equivalent Alkalies, } Na_2Oe = Na_2O + 0.658 \text{ x } K_2O \tag{1}$$

For the analysis given in table 4, the equivalent alkali content is calculated as follows:

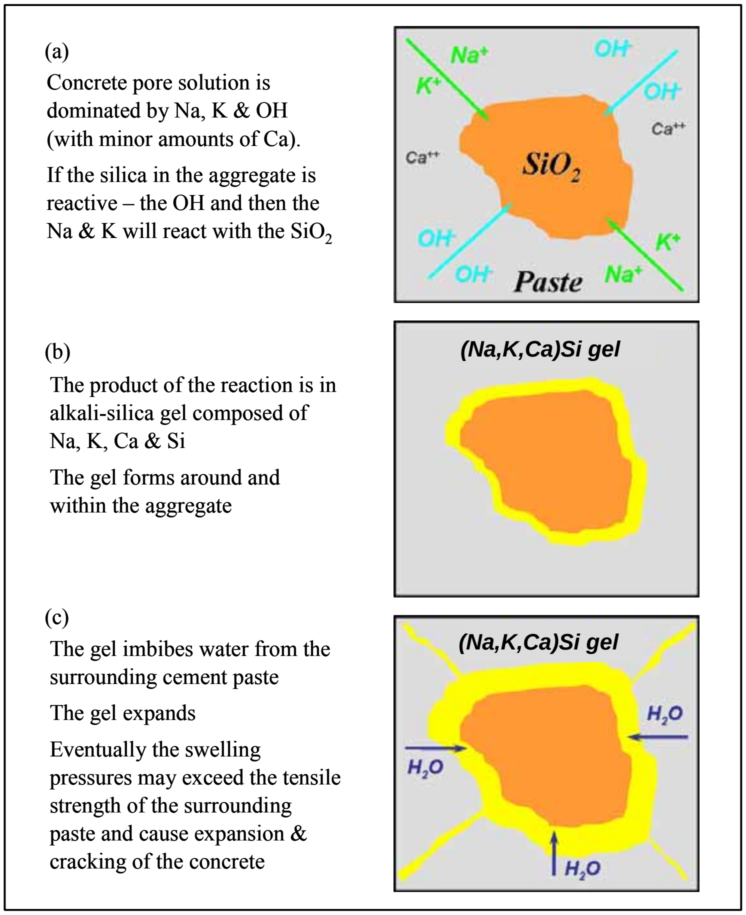
$$Na_2Oe = 0.15 + 0.658 \text{ x } 0.73 = 0.63\% \tag{2}$$

The equivalent alkali content of portland cements produced in or imported into North America typically ranges from 0.20 to 1.20 percent Na_2Oe.

Although the alkalies represent a small fraction of the portland cement, they dominate the pore solution of the concrete, which, as a result, is highly alkaline with a pH in the range of 13.2 to 13.8. Diamond (1989) indeed found a direct correlation between the cement alkali content and the pH of the pore solution.

Figure 6 summarizes the sequence of ASR in concrete. Some forms of silica (SiO_2) found in some aggregates are unstable at high pH and react with the alkali hydroxides to form an alkali-silica gel. This gel has the propensity to absorb large quantities of water and swell. Under certain conditions, the swelling pressures can cause expansion and, eventually, cracking of the concrete.

Figure 6 demonstrates the sequence of alkali-silica reaction (ASR) in concrete.



(a)

Concrete pore solution is dominated by Na, K & OH (with minor amounts of Ca).

If the silica in the aggregate is reactive – the OH and then the Na & K will react with the SiO_2

(b)

The product of the reaction is in alkali-silica gel composed of Na, K, Ca & Si

The gel forms around and within the aggregate

(c)

The gel imbibes water from the surrounding cement paste

The gel expands

Eventually the swelling pressures may exceed the tensile strength of the surrounding paste and cause expansion & cracking of the concrete

Figure 6. Sequence of alkali-silica reaction (ASR) in concrete.

Not all forms of silica are reactive in concrete. The reactivity depends on the crystal structure of the silica rather than its chemical composition. For example both quartz and opal are silica minerals and are predominantly composed of silica (SiO_2); i.e., they are of similar composition (although opal has varying proportion of water, usually 3 to 9 percent). Quartz has a well-ordered crystal structure (figure 7) and is very stable in concrete at normal temperatures. Opal, on the other hand, has an internal structure consisting of more-or-less densely packed aggregate of spheres of silica (cristobalite and/or tridymite) and is highly reactive in concrete.

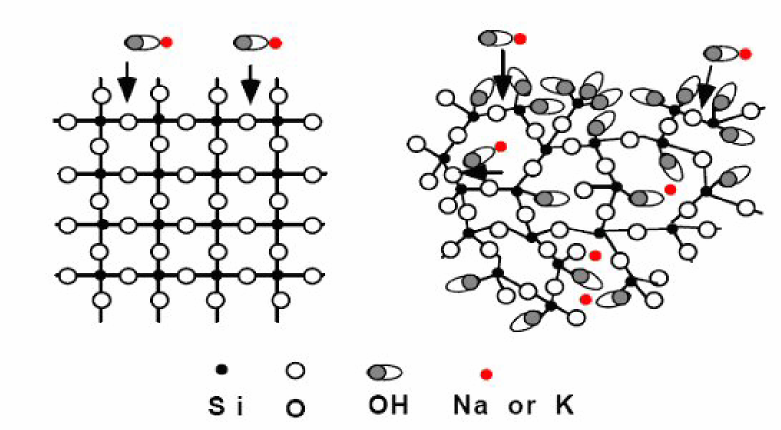


Figure 7. Schematic showing difference in crystal structure of quartz (left) and opal (right).

Table 5 contains a list of reactive silica forms and the rock types in which they may be found. Not all sources of these rock types are reactive in concrete. Damaging reaction will only occur if these rock types contain sufficient quantities of the reactive silica. For example, many granites are not deleterious reactive in concrete and make excellent concrete aggregates. However, if the granite contains a sufficient quantity of strained or microcrystalline quartz, the use of the rock may result in ASR when used in concrete, unless appropriate precautions are taken to control the reaction (sufficient alkali and moisture are also required to sustain the reaction—see figure 8 below).

Table 5. Table of alkali-silica reactive minerals and possible rock types in which they may be found.

Rock Types		Reactive Minerals and Glass
Andesite Arenite Argillite Arkose Basalt Chert Flint Gneiss Granite Greywacke	Hornfels Quartz-arenite Quartzite Rhyolite Sandstone Shale Silicified carbonate Siltstone Tuff	Cristobalite Cryptocrystalline (or microcrystalline) quartz Opal Strained quartz Tridymite Volcanic glass

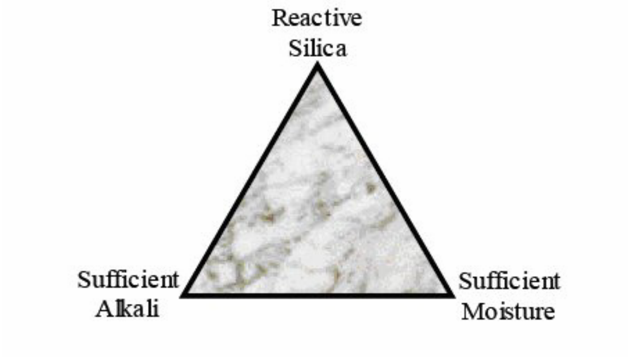


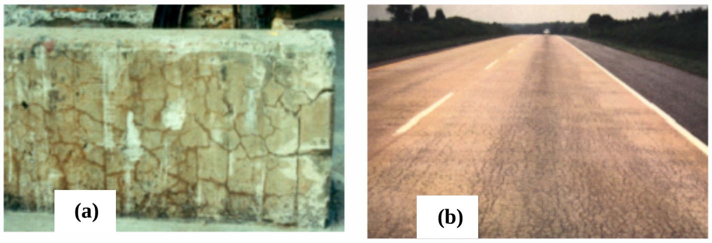
Figure 8. Three essential requirements for deleterious ASR.

3.3 Symptoms of ASR

Common symptoms of ASR in affected structures include (figure 9):

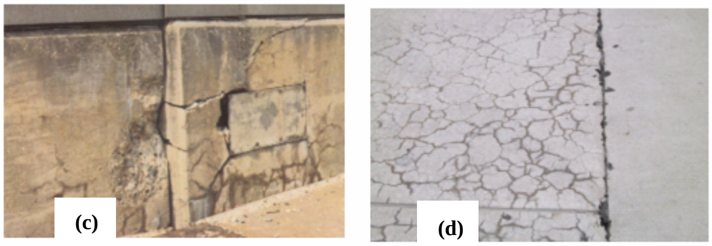
- Cracking which may be random in direction (i.e., map or pattern cracking) or may show preferred orientation if expansion is restrained in one direction.
- Discoloration around cracks.
- Gel exudation from cracks.
- Misalignment of adjacent sections.
- Closing of joints, extrusion of joint sealant and crushing/spalling of concrete around joints.
- Pop-outs over reactive aggregate particles.
- Operation difficulties (e.g., jamming of sluice gates in dams).

Field symptoms of ASR in concrete structures have been described and illustrated in a number of documents, including SHRP 315 (1995), CSA A864 (1992), and BCA 1992.



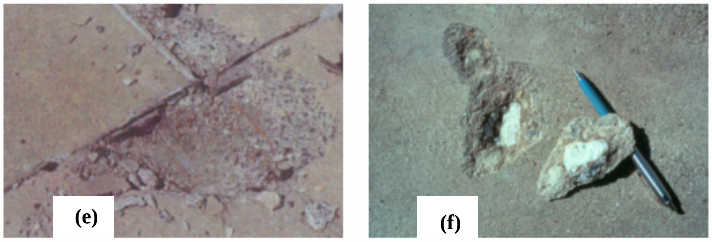
(a) Random (map or pattern) cracking

(b) Preferred alignment of cracks



(c) Misalignment of adjacent sections

(d) Extrusion of joint sealant



(e) Crushing of concrete at joints

(f) Pop-out over reactive aggregate

Figure 9. Typical symptoms of ASR.

3.4 Methods of Evaluating Potential Reactivity of Aggregates

3.4.1 Field Performance

Field performance survey of concrete structures can be used to determine the potential alkali-reactivity of concrete aggregates (CSA A23.1). When field performance is used for that purpose (CSA A23.1):

- The structure examined should have similar or higher cement/alkali contents compared to the new structure to be built.
- The concrete examined should be at least 10 years old.
- The exposure conditions of the structure examined should be at least as severe as those likely to affect the new structure to be built.
- In the absence of documentation, a petrographic report should confirm that the aggregates used (existing structure) and for use (new structure) are identical.
- The possibility that supplementary cementitious materials (SCMs) have been used should be considered / investigated so that if present SCMs for use (new structure) are as close to identical as possible in the structure under investigation.

Evaluating potential alkali-reactivity from field performance requires the involvement of an engineer and/or scientist with experience of assessing ASR in concrete structures.

3.4.2 ASR Testing in the Laboratory

A wide variety of standard test methods is available for identifying potentially reactive aggregates. Table 6 lists the tests that have been standardized by ASTM. Only the concrete prism test (ASTM C1293) and the accelerated mortar bar test (ASTM C1260) are currently recommended for use in identifying reactive aggregates. Petrographic examination of aggregates (ASTM C295) is often seen as the essential first step of an ASR testing program; however, it should not be used to accept an aggregate source without expansion testing in concrete or mortar. (ASTM C1105 is recommended for evaluating alkali-carbonate reactive rocks). ASTM C 1567 is used to test the efficacy of pozzolans and slags for controlling concrete expansion due to ASR rather than to identify reactive aggregates.

Table 6. ASTM test methods related to alkali-aggregate reaction.

C1293-05 Standard Test Method for Concrete Aggregates by Determination of Length Change of Concrete Due to Alkali-Silica Reaction[1,3]

C1260-05a Standard Test Method for Potential Alkali Reactivity of Aggregates (Mortar Bar Method)[1]

C227-03 Standard Test Method for Potential Alkali Reactivity of Cement Aggregate Combinations (Mortar Bar Method)

C289-03 Standard Test Method for Potential Alkali-Silica Reactivity of Aggregates (Chemical Method)

C1105-05 Standard Test Method for Length Change of Concrete Due to Alkali-Carbonate Rock Reaction

C295-03 Standard Guide for Petrographic Examination of Aggregates for Concrete[2]

C1567-04 Standard Test Method for Determining the Potential Alkali-Silica Reactivity of Combinations of Cementitious Materials and Aggregate (Accelerated Mortar-Bar Method)[3]

C441-05 Standard Test Method for Effectiveness of Mineral Admixtures or Ground Blast Furnace Slag in Preventing Excessive Expansion of Concrete Due to the Alkali-Silica Reaction

[1] Only the concrete prism test (ASTM C1293) and the accelerated mortar bar test (ASTM C1260) are currently recommended for use in identifying reactive aggregates.

[2] Often seen as the essential first step of an ASR testing program; however, it should not be used to accept an aggregate source without expansion testing in concrete or mortar.

[3] Only the modified version of the concrete prism test (ASTM C 1293) and the ASTM C 1567 are recommended for evaluating the efficacy of pozzolans and slag for controlling expansion due to ASR.

The concrete prism test is generally considered to be the most reliable laboratory test in its ability to predict field performance. In this test, concrete prisms are stored in sealed containers over water at 38 °C (100 °F). Figure 10 shows the test setup, and figure 11 provides the length change measurements. The test uses the following parameters:

- Aggregate is tested in a concrete mixture containing 420 kilograms per cubic meter (kg/m^3) (705 pounds per cubic yard (lb/yd^3)) of cement.
- Cement alkalies are raised to 1.25 percent Na_2Oe from a cement with an alkali content of 0.9 ± 0.1 percent Na_2Oe.
- Concrete is molded into prisms measuring 75 millimeters (mm) by 75 mm by minimum 250 mm gauge length (3 inches by 3 inches by minimum 10 inches).
- Concrete prisms are stored over water in sealed containers at 38 °C (100 °F).
- Length change is measured for 12 months to determine aggregate reactivity and 24 months to determine efficacy of preventive measures (CSA A23.2-27A).

The appendices to ASTM C1293 (the standard test method) and ASTM C33 (the specification for aggregates) consider aggregates that produce expansions greater than or equal to 0.04 percent at 1 year to be potentially deleteriously reactive. In Canada, in a test almost identical to ASTM C1293 (CSA A23.2-27A), the expansion after 12 months is used to classify the aggregate as (i) nonreactive (expansion < 0.04 percent), (ii) moderately reactive (expansion between 0.04 and 0.12 percent) or (iii) highly reactive (expansion > 0.12 percent). This test method can also be used to evaluate preventive measures (see section 3. 5).

Figure 10. Concrete prism test—prisms stored over water in sealed containers.

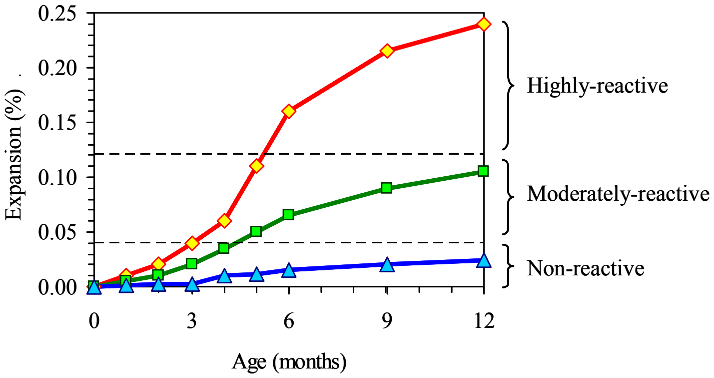


Figure 11. Concrete prism test—length change measurements (ASTM C1293)[1].

The accelerated mortar bar test yields results in as little as 16 days. In this test, mortar bars containing the aggregate under test are immersed in an alkaline solution at elevated temperature (1 N NaOH at 80 °C (176 °F)) and the length change of the bars is monitored. The test uses the following parameters:

- Aggregate is tested in mortar mixture.
- Coarse aggregates must be crushed to pass 5-mm (number 4) sieve, washed, dried and combined in the proper gradation to meet the requirements of the test.
- Mortar is molded into prisms measuring 25 mm by 25 mm by minimum 250 mm gauge length (1 inch by 1 inch by minimum 10 inches).
- Mortar bars are stored at laboratory temperature for 1 day and then demolded and immersed in tap water and raised to 80 °C (176 °F) for 1 day.
- After the second day, mortar bars are removed from water and the initial length reading is taken.

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[1] Note that the expansion limits shown in the graph are based on CSA recommendations.

- Mortar bars are then immersed in 1 N NaOH already at 80 °C (176 °F), and length change is monitored periodically.
- If expansion is greater than 0.10 percent after 14 days in the alkaline solution, the aggregate is considered to be potentially reactive, and the reactivity should be confirmed by testing in concrete (i.e., ASTM C1293).
- If expansion is less than or equal to 0.10 percent after 14 days in the alkaline solution, the aggregate is considered to be innocuous.

ASTM suggests the following interpretation of expansion results:

- Expansions of less than 0.10 percent at 16 days after casting are indicative of innocuous behavior in most cases.
- Expansions of more than 0.20 percent at 16 days after casting are indicative of potentially deleterious expansion.
- Expansions between 0.10 percent and 0.20 percent at 16 days after casting include both aggregates that are known to be innocuous and deleterious in field performance. For these aggregates, it is particularly important to develop supplemental information as described in Section 3.3. In such a situation, it may also be useful to take comparator readings up to 28 days.

However, other parties have suggested extending the immersion period to 28 days and using the same or a lower expansion limit (i.e., 0.08 percent). Details of the test are shown in figure 12. The accelerated mortar bar test can also be used to evaluate preventive measures in accordance with ASTM C1567 (see section 3.5). ASTM C1567 follows identical procedures in terms of storage conditions and measurements as ASTM C1260; the only difference is the incorporation of SCMs in the mortar mixture.

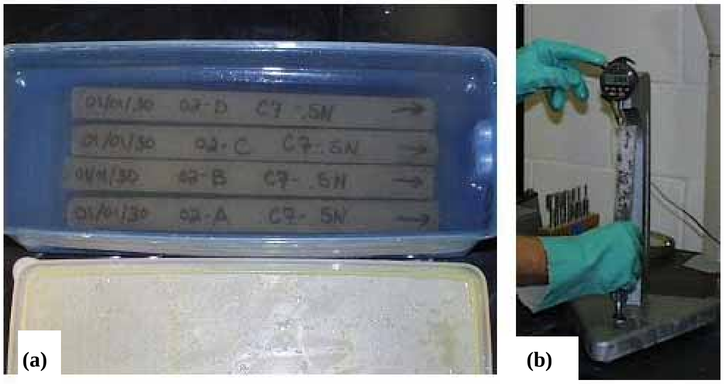

Figure 12. Accelerated mortar bar test (ASTM C1260): (a) view from the top of four rectangular concrete samples, under water in a blue rectangular container; (b) measuring a concrete sample for length change using a digital comparator.

3.5 Measures To Prevent ASR

The risk of damage due to ASR in new concrete can be minimized by following one or more of the following strategies:

- Avoid the use of reactive aggregates.
- Limit the alkali content of the concrete mixture.
- Use a sufficient quantity of effective SCM(s).
- Use of lithium-based compounds—see chapter 4.

The use of nonreactive aggregate is the most obvious measure for preventing damaging alkali-silica reaction. Aggregates that do not cause deleterious expansion when tested in accordance with ASTM C1293 and ASTM C1260 are unlikely to cause damage due to ASR when used in the field. However, because there is a small risk of ASR even when aggregate sources have been shown to be "nonreactive" by testing, some agencies still specify that additional precautions be taken (e.g., use of SCM or limiting the alkali content of the concrete). Furthermore, in some locations "nonreactive" aggregates may be scarce and potentially reactive aggregates can be used safely when appropriate preventive measures are taken.

The risk of damage due to ASR when potentially reactive aggregate is used increases as the alkali content of the concrete increases. Figure 13 shows the relationship between expansion of concrete prisms and the alkali content of concrete containing a reactive siliceous limestone. It can be seen that, in laboratory specimens, deleterious expansion only occurs with this aggregate when the alkali content exceeds 3.0 kg/m^3 (5 lb/yd^3) Na_2Oe. The alkali content of portland cement concrete is calculated by multiplying the cement content by the alkali content of the cement, as shown in table 7.

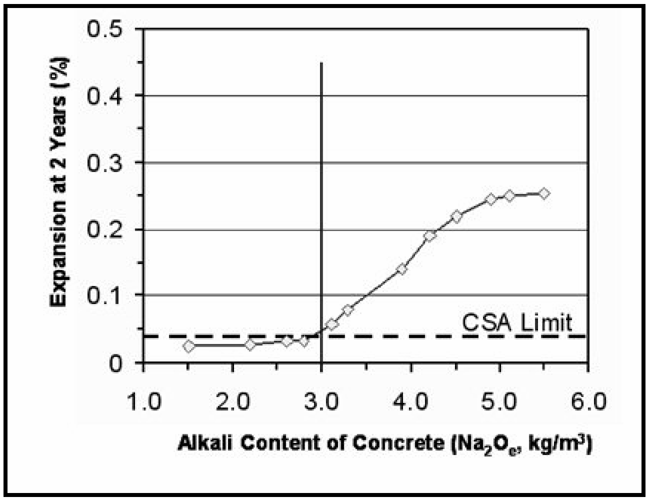

Figure 13. Effect of the alkali content of concrete on the expansion of prisms.

Table 7. Calculation for alkali content of portland cement concrete.

$$\begin{aligned}&\text{Alkali content of concrete (kg/m}^3\,\text{Na}_2\text{Oe)}\\&= \text{Cement content of concrete (kg/m}^3\text{)}\\&\times\ \text{alkali content of cement (percent Na}_2\text{Oe)}/100\end{aligned} \tag{3}$$

For example, the alkali content of a concrete mixture containing 350 kg/m^3 of Portland cement which has an alkali content of 0.91 percent Na_2Oe is:

$$350\ \text{kg/m}^3 \times 0.91\ \%\ \text{Na}_2\text{Oe} / 100 = 3.19\ \text{kg/m}^3\ \text{Na}_2\text{Oe} \tag{4}$$

$$588\ \text{lb/yd}^3 \times 0.91\ \%\ \text{Na}_2\text{Oe} / 100 = 5.35\ \text{lb/yd}^3\ \text{Na}_2\text{Oe} \tag{5}$$

It should be noted that expansion may occur in the field at lower alkali contents than that found necessary to cause expansion in the laboratory. The reason for this is that a portion of the alkalies may be lost through leaching under the conditions of the concrete prism test (Thomas et al., 2005). For example, the aggregate for which expansion data are presented in section 3.4.2 caused expansion and cracking of field-exposed concrete blocks (approximately 0.6 by 0.6 by 2.0 m (2 by 2 by 6 ft.)) with an alkali content of just 1.9 kg/m³ (3.2 lb/yd³) Na_2Oe (Rogers et al., 2004).

Limits on alkali contents in national specifications vary between different countries with values in the range of 2.5 to 4.5 kg of Na_2Oe per cubic meter (4.2 to 7.6 lb of Na_2Oe per cubic yard) being used (Nixon and Sims 1992). In Canada (CSA A23.1-27A), a range of alkali limits are specified depending on the level of prevention required; these are presented in table 8.

Table 8. Range of alkali limits (CSA A23.1-27A).

Level of Prevention Required	**Alkali Limit (Na_2Oe)**	
	kg/m³	lb/yd³
Mild	3.0	5.0
Moderate	2.4	4.0
Strong	1.8	3.0
Exceptional	1.8 + SCM	3.0 + SCM

In Standard Practice CSA A23.2-27A, the level of prevention required is determined by considering the reactivity of the aggregate proposed for use, the exposure condition, the size of the element and the design life of the structure to be built. As indicated in table 8, the required levels of prevention vary from “mild” to “exceptional” as a function of the above factors, with corresponding alkali limits for prevention purposes. For example, “mild” preventions (e.g., maximum total concrete alkali content of 3 kg/m^3 (5 lb/yd^3)) are required for massive concrete elements incorporating a moderately reactive aggregate (i.e., inducing a concrete prism expansion greater than 0.04 percent but less than 0.12 percent) in a dry environment (e.g., interior elements of buildings). The level of prevention would increase to “moderate” (maximum total concrete alkali content of 2.4 kg/m^3 (4 lb/yd^3)) if such a moderately reactive aggregate were used in an exposed structure with a design life of less than 75 years (e.g., sidewalk or pavement), or “strong” (maximum total concrete alkali content of 1.8 kg/m^3 (3 lb/yd^3)) if used in an exposed structure with a design life of greater than 75 years (e.g., a bridge or a dam). An “exceptional” level of prevention would be required when a highly reactive rock is used in the same type of structure. For the latter, it is recommended not only to limit the total concrete alkali content at less 1.8 kg/m^3 (3 lb/yd^3), but also to use a sufficient amount of SCM.

Specifying the use of low-alkali cement (< 0.60 percent Na_2Oe) or limiting the total alkali content in concrete under a certain level, as a means for preventing ASR when reactive aggregates are used, may however not be sufficient / effective in all cases. There have been a number of cases of ASR in concrete structures built with low-alkali cement. For example, a concrete with 400 kg/m³ (~670 lb/yd^3) of cement with an alkali content of 0.55 percent Na_2Oe will have a total alkali content of 2.2 kg/m³ (3.7 lb/yd^3) Na_2Oe, which is sufficient to produce ASR damage with some aggregates. Also, limiting the alkali content in concrete may not provide sufficient protection if the concrete is exposed to external sources of alkalies (e.g., deicing chemicals, seawater, etc.)

One of the most efficient means of controlling ASR in concrete containing reactive aggregates is the appropriate use of supplementary cementing materials (SCM). Such materials include pozzolans (e.g., fly ash, silica fume, calcined clay, or shale) and ground-granulated blast furnace slag. Almost any SCM can be used for this purpose provided it is used in sufficient quantity (figure 14). The amount of SCM required generally increases as:

- Reactivity of the aggregate increases.
- Alkali content of the concrete increases.
- Available alkali content of the SCM increases.
- Calcium-to-silica ratio (CaO/SiO_2) of the SCM increases.

Pozzolans, such as silica fume, which have a high content of reactive silica and low levels of calcium and alkali tend to be very efficient in controlling ASR and can be used at relatively low levels of replacement (typically 7 to 15 percent[2]) for this purpose. On the other hand, SCM with relatively high levels of calcium and lower amounts of silica, such as Class C fly ash or slag, generally need to be used at replacement levels of 35 percent or more. Low-calcium Class F fly ash is relatively more efficient (i.e., can be used at lower replacement levels) than Class C fly ash or slag, but has to be used at higher replacement levels than silica fume. Figure 14 shows typical expansion behavior of concrete containing high-alkali cement (see note below), reactive aggregate, and different types of SCM.

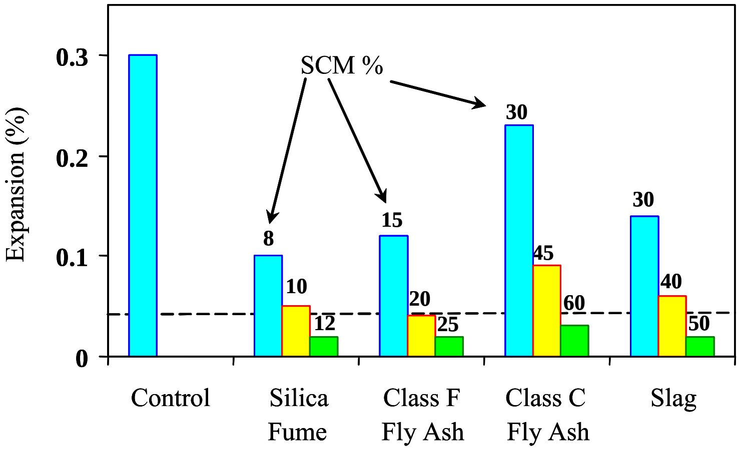

Figure 14. Effect of SCM on the expansion of concrete (using concrete prism test).

Ternary cement blends, which contain three different cementing materials (portland cement plus two SCMs) have been found to be very effective in controlling ASR, especially blends containing silica fume plus either Class F fly ash or slag. Relatively low levels of silica fume (3 to 5 percent) together with moderate levels of Class F fly ash (15 to 20 percent) or slag (25 to 35 percent) have been shown to be effective (Shehata and Thomas, 2002; Bleszynski et al., 2002).

The concrete prism test (ASTM C1293) can be modified to determine the amount of SCM required to control expansion with a particular reactive aggregate. The method is described in CSA A23.2-28A-04. When testing SCM, the portland cement component of the mixture is partially replaced with the SCM. Various replacement levels can be used to determine the minimum level required to suppress expansion. The alkali content of the portland cement component of the mixture should be maintained at 1.25 percent Na_2Oe (by adding NaOH, usually in liquid form, to the mixing water) to a cement with 0.90 ± 0.10

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[2] Note that SCM replacement levels are expressed as the mass percentage of the total cementitious material content of the concrete. For example, 10-percent silica fume means that 10 percent of the total mass of cementitious material is comprised of silica fume, the remaining 90 percent being portland cement.

percent Na_2Oe). When evaluating preventive measures, the test period should be extended to 2 years and the measure shall be considered effective if the expansion at this age is not greater than 0.04 percent.

The accelerated mortar bar test (ASTM C1567) can also be used to determine the amount of SCM required to control expansion with a particular aggregate. The portland cement component of the mix is partially replaced with the SCM under test; different replacement levels can be used to determine the minimum level of SCM required to control expansion. The preventive measure is considered effective if the expansion after 2 weeks immersion in the alkaline solution is not greater than 0.10 percent (Thomas et al., 2005). This test is generally not considered to be as reliable as the concrete prism test for evaluating SCM, and it is recommended that the results of the accelerated test be confirmed by the longer-term concrete test.

3.6 Treating Existing ASR-Affected Pavements and Structures

Methods for mitigating the effects of ASR can be divided into two categories: (1) mitigating the symptoms of distress and (2) addressing the cause of distress.

Methods for *mitigating the symptoms* include filling cracks; cutting joints to allow further expansion to take place, thereby relieving internal stresses within the concrete or pressures on adjacent members or structures; and providing restraint to further expansion.

Caulking cracks with an epoxy grout (or similar compound) can help protect embedded reinforcement and reinstate the integrity of the cracked concrete. However, it will not significantly retard the rate of reaction and expansion, and new cracks will inevitably form with time if the reaction is allowed to proceed.

Cutting joints to allow for expansion to take place has been used in a number of hydraulic structures, with the principal aim in these cases being to relieve stresses on embedded mechanical equipment such as sluice gates or turbines. Joints can also be cut to isolate expanding structures from adjacent structures or to relieve internal stresses in pavements. Providing space for expansion does not deal with the reaction, and it is likely that the expansion and cracking will continue.

Providing restraint in the form or rock anchors or post-tensioned tendons also has been used in hydraulic structures to prevent unwanted expansion and distortion of the structure. Fiber-reinforced polymers (FRPs) have been used to wrap elements such as columns.

The only two practical means for *addressing the cause* of damage (i.e., to retard or prevent further reaction), are to either dry the concrete to eliminate the moisture required to sustain ASR or to change the nature of the reaction by introducing lithium compounds.

Silane sealers have been used successfully to reduce the relative humidity in ASR-affected concrete piers (Kojima et al., 1992), railway sleepers (Oberholster et al., 1992) and median barriers (Bérubé et al., 1998). Silanes applied to concrete render the surface of the concrete hydrophobic and prevent the ingress of liquid water into the concrete. However, water vapor can still exit through the layer, reducing the moisture content, and hence reducing the relative humidity, with time. Figure 15 shows a photograph of silane-treated and untreated sections of a barrier wall in Quebec.

The use of lithium compounds to treat ASR-affected concrete structures is discussed in chapter 5.

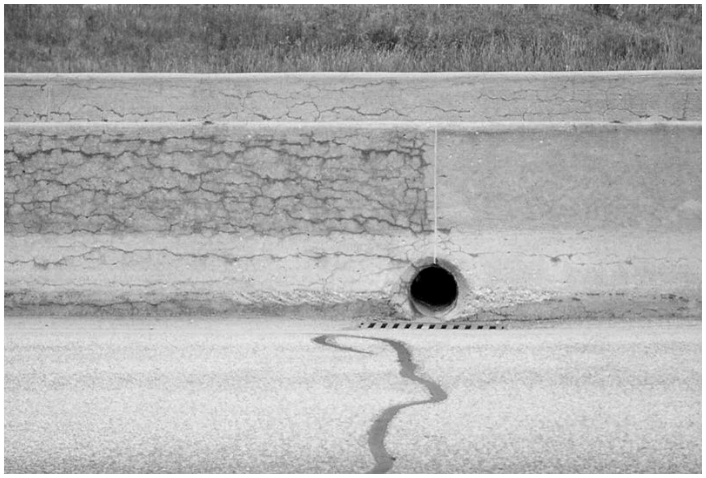


Figure 15. Barrier wall in Quebec—the section of the wall to the right of the picture has been treated with a silane sealer.

CHAPTER 4. USING LITHIUM TO PREVENT ASR IN NEW CONCRETE

4.1 Laboratory Studies

In 1951, McCoy and Caldwell published data showing that the incorporation of various lithium compounds (LiCl, Li_2CO_3, LiF, Li_2SiO_3, $LiNO_3$, and Li_2SO_4) in mortars (ASTM C227) containing highly reactive Pyrex® glass could control damaging alkali-silica reaction provided the lithium was present in sufficient quantity. Although little work was conducted in the 40 years that followed the publication of this paper, there has been renewed interest in the use of lithium as an admixture, starting with the work conducted under the SHRP program (SHRP-C-343), and the last 15 years has seen the publication of numerous papers on the subject. Detailed reviews of the literature have been published elsewhere (Folliard et al., 2005; Feng et al., 2005).

The amount of lithium required to suppress expansion depends upon the form of lithium, the nature of the reactive aggregate, and the amount of alkali in the concrete. Many studies have shown that the expansion of concrete for a given aggregate depends on the amount of lithium relative to the amount of sodium plus potassium in the mortar or concrete mixture. This has led to the use of the molar ratio [Li]/[Na+K] for expressing the lithium dose in mortar and concrete mixtures, where [Li] is the number of moles of lithium and [Na+K] is the sum of the moles of sodium plus the moles of potassium present in the mixture.

McCoy and Caldwell's (1951) data showed that expansion was largely eliminated if the lithium-to-sodium-plus-potassium ratio was equal to or greater than 0.74; i.e., $[Li]/[Na+K] \geq 0.74$. A number of recent laboratory studies have confirmed this finding, and $[Li]/[Na+K] = 0.74$ has become the "standard dose" for controlling ASR in concrete containing reactive aggregate.

At the time of writing this guideline, the only commercially available lithium compound for use as a concrete admixture is a solution containing 30 percent lithium nitrate ($LiNO_3$). To achieve a molar ratio of $[Li]/[Na+K] = 0.74$ requires the addition of 4.6 L of 30-percent $LiNO_3$ solution for every 1.0 kg of Na_2Oe in the mixture (0.55 gal of solution for every 1.0 lb of Na_2Oe), as shown in table 9.

Table 9. Example showing calculation of [Li]/[Na + K] molar ratio.

Alkali	Molecular Weight	Compound	Molecular Weight
Li	7	$LiNO_3$	69
Na	23	$LiOH \cdot H_2O$	42
K	39	Na_2Oe	62

Moles of lithium in 1 L of 30 % $LiNO_3$ solution

Specific gravity of 30% $LiNO_3$ solution = 1.2
Mass of 1 L of 30% $LiNO_3$ = 1,200 g
Mass of $LiNO_3$ in 1 L = 30/100 x (1,200) = 360g
Number of moles of $LiNO_3$ = 360/69 = 5.217 moles

Moles of sodium + potassium in 1 kg of Na_2Oe

Number of moles of Na_2Oe in 1 kg of Na_2Oe = 1,000/62 = 16.13 moles
Number of moles of Na = 2 x 16.13 = 32.26

Volume of 30 % $LiNO_3$ solution required for [Li]/[Na+K] = 0.74

Molar ratio for 1 L of 30% LiNO3 solution per 1 kg of Na2Oe = 5.217/32.26 = 0.162
Volume of 30% LiNO3 solution for molar ration of 0.74 = 0.740/0.162
= 4.6 L per 1 kg of Na2Oe

1 g = 0.035 ounce
1 Liter (L) = 0.26 gallon
1 kilogram (kg) = 2.20 lbs

Prior to the use of lithium nitrate, lithium hydroxide monohydrate ($LiOH \bullet H_2O$) was used in both laboratory testing and in a number of concrete structures (see section 4.3). To achieve a molar ratio of [Li]/[Na+K] = 0.74 requires the addition of 1 kg of $LiOH \bullet H_2O$ for every 1 kg of Na_2Oe in the mixture (1 lb $LiOH \bullet H_2O$ for every 1 lb of Na_2Oe).

$LiOH \bullet H_2O$ is somewhat less effective than $LiNO_3$ (see figure 16) as it introduces additional hydroxyl ions into the concrete. Furthermore, $LiOH \bullet H_2O$ may exhibit a pessimum behavior with some aggregates, with low doses actually increasing expansion. Other lithium compounds such as Li_2CO_3 and LiCl may also increase the concentration of hydroxyl ions because of reaction with $Ca(OH)_2$ in the paste as follows:

$$Li_2CO_3 + Ca(OH)_2 \rightarrow 2\,LiOH + CaCO_3 \tag{14}$$

Lithium nitrate does not produce this effect because of the high solubility of $Ca(NO_3)_2$.

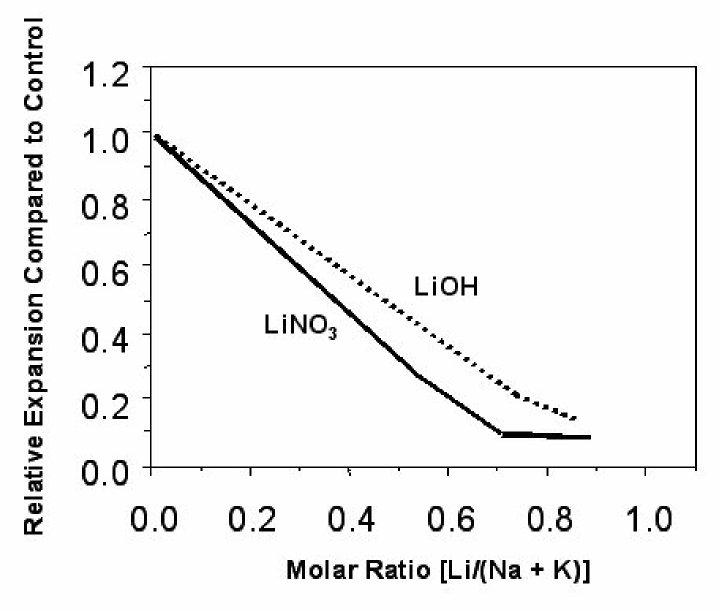


Figure 16. Relative expansion of concrete prisms (ASTM C1293) containing lithium compounds and reactive siltstone aggregate (Thomas et al., 2000).

Although the "standard dose" of [Li]/[Na+K] = 0.74 appears to be sufficient to control expansion with a great many aggregates, it is not sufficient for all aggregate types (Lane, 2000; 2002; Durand, 2000; Tremblay, 2004), and higher doses are required. With some aggregates, a dose of 1.5 times the standard dose, i.e., [Li]/[Na+K] = 1.11, may still not be sufficient to suppress damaging ASR (Tremblay, 2004).

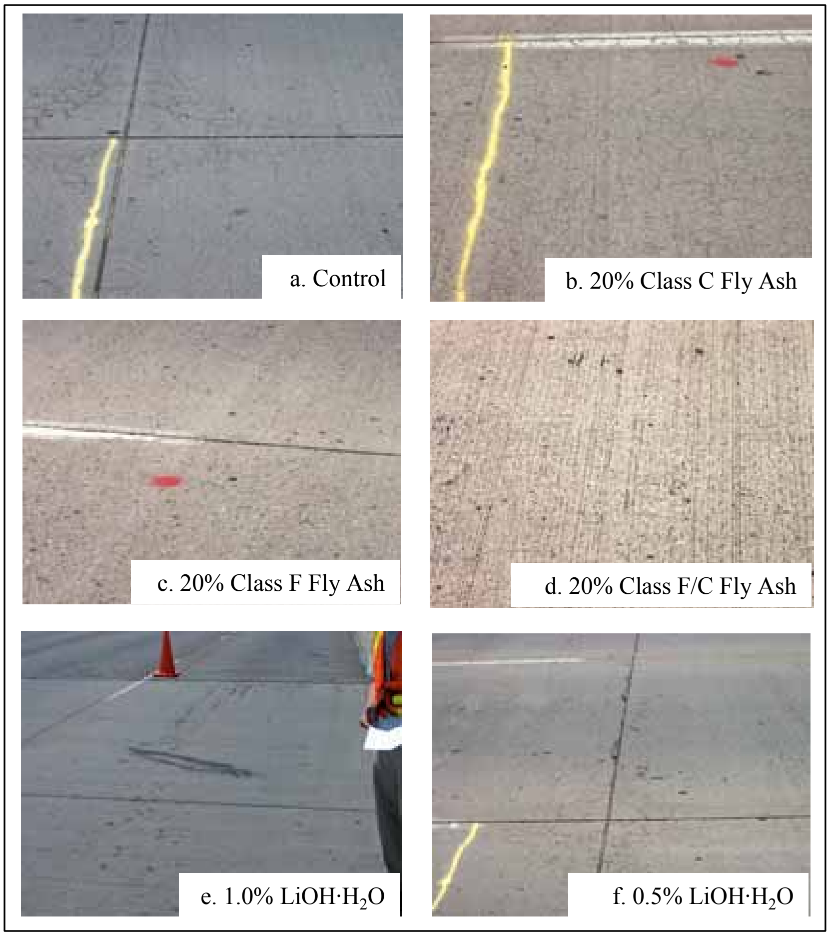
It would appear that lithium is more effective with rapidly reacting aggregates where the reactive phase is opal, chert, or volcanic glass, and less effective with slowly reacting aggregates which contain microcrystalline or strained quartz as the reactive phase. However, it is difficult to assess whether lithium will be effective or to determine the appropriate dose based purely on the mineralogy of the aggregates.

At this time, it is recommended that amount of lithium required to control expansion with a particular aggregate is determined by appropriate testing methods (see section 4.3).

4.2 Field Applications

The first field application of lithium as an admixture in concrete containing reactive aggregate was in the construction of an experimental pavement in Albuquerque, NM, in 1992. Two local sources of highly reactive sand and gravel were used together with low-alkali cement (0.55 percent Na_2Oe) and a range of preventive measures, which included lithium hydroxide monohydrate. Two doses of lithium were used; these were 0.5 percent and 1.0 percent $LiOH•H_2O$ by mass of cement, which yielded lithium-to-sodium-plus- potassium molar ratios of [Li]/[Na+K] = 0.67 and 1.34 (i.e., 91 percent and 182 percent of the standard dose), respectively. Figures 17 and 18 show selected sections of this pavement after 12 years of service. As shown in figure 17, cracking has occurred in the control section, the section with 20 percent Class C fly ash, the section with 20 percent of the blended Class F plus Class C fly ash, and in the section with 0.5 percent $LiOH•H_2O$ (lower dose lithium: [Li]/[Na+K] = 0.67). The section with the higher lithium dose ([Li]/[Na+K] = 1.34) is still performing well. These sections were constructed with the aggregate from the Shakespeare pit that contained mixed volcanic aggregates. Figure 18 shows the section with the higher dose of lithium and the aggregate from the Placitas pit, in Albuquerque that also contained mixed volcanics and is also in good condition after 12 years. There is no formal monitoring program tracking the long-term behavior of these pavements, and the only evaluation has been periodic visual inspections conducted by members of the research team or others.

Since the early 1990s, lithium compounds have been used in a variety of concrete structures across the United States, and some of these have been described in detail by Folliard et al., 2003. There have been no reports of ASR in these structures at the time of writing this report.



a. Control

b. 20% Class C Fly Ash

c. 20% Class F Fly Ash

d. 20% Class F/C Fly Ash

e. 1.0% $LiOH \cdot H_2O$

f. 0.5% $LiOH \cdot H_2O$

Figure 17. Photographs of 12-year-old pavement sections reactive aggregate from Shakespeare pit in Albuquerque, NM (photos taken in 2004).

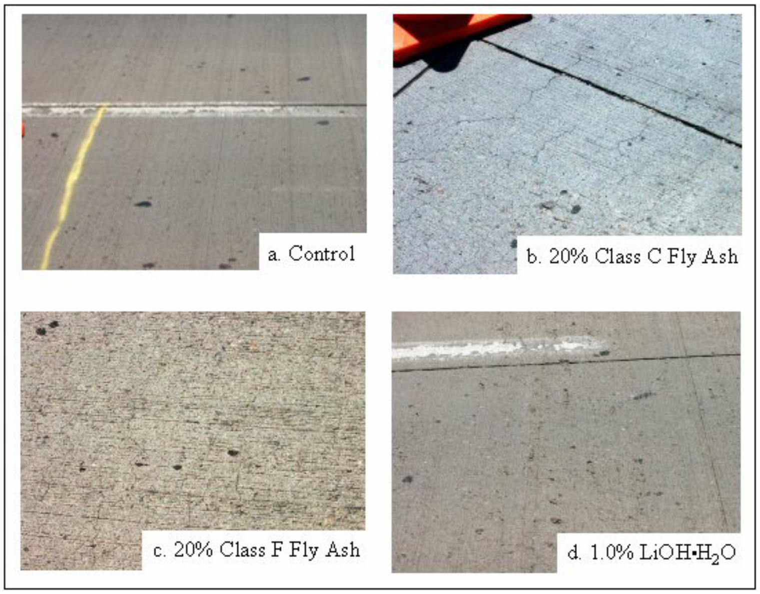


Figure 18. Photographs of 12-year-old pavement sections reactive aggregate from Placitas pit in Albuquerque, NM.

4.3 Laboratory Testing To Determine the Amount of Lithium Required

To determine the amount of lithium required to control ASR with a specific aggregate, it is recommended that the combination of materials be tested using a modification of the concrete prism test (ASTM C1293). The only modifications necessary are to add the required amount of lithium nitrate solution to the mix water and to correct the total water content for the water contained in the lithium nitrate solution. The test should be conducted at a range of different lithium doses to determine the minimum amount required to control expansion (< 0.040 percent at 2 years) with the aggregate under consideration. Table 10 provides an example of calculation for concrete prism testing using a standard dose (i.e., [Li]/[Na+K] of 0.74) of $LiNO_3$.

Table 10. Proportioning mixtures with lithium for the concrete prism test.

Control Mixture

420 kg/m^3 portland cement, NaOH added to mix water to raise cement alkalies to 1.25 percent:

Total alkalis in concrete = 420 x 1.25/100 = 5.25 kg/m^3 Na2Oe (15)

Water-to-cement ratio,

W/CM = 0.42 to 0.45 (16)

Mixture with [Li] / Na + K] = 0.74

420 kg/m^3 portland cement, NaOH added to mix water to raise cement alkalies to 1.25 percent:

Total alkalis in concrete = 420 x 1.25/100 = 5.25 kg/m^3 Na2Oe (17)

Add:

30-percent $LiNO_3$ solution at 4.6L per kg of Na_2Oe = 4.6 x 5.25 = 24.15L (18)

Water-to-cement ratio,

W/CM = 0.42 to 0.45 (19)

include water in 30-percent $LiNO_3$ solution.

Calculate as follows:

Mass of solution = volume x density = 24.15 L x 1.2 kg/L = 28.98 kg/m^3 (20)

Water present in solution = 70-percent of mass = 70/100 x 28.98 = 20.29 kg (21)

This water should be included in the calculation of W/CM (i.e., it should be subtracted from the water content used in the control mixture).

The accelerated mortar bar test (ASTM C1260) cannot be used to evaluate lithium without significant modification. Immersion of the mortar bars in the high temperature alkaline solution overwhelms the mortar bar with alkali and changes the [Li]/[Na+K]. Proposed modifications have included adding lithium to both the mortar mixture and the soak solution using the same [Li]/[Na+K] ratio. However, there is currently little information available to confirm whether the lithium dose determined using a modified version of the accelerated mortar bar test is similar to that determined using the longer-term concrete prism test and field experience.

4.4 Effect of Lithium on the Properties of Concrete

The use of lithium nitrate solution, at the levels of addition necessary to effectively control expansion due to ASR, has no adverse effect on the properties of fresh and hardened concrete, even at dosages in excess of 10 liters per cubic meter. The use of lithium nitrate may slightly enhance the workability of concrete (i.e., there is a small water-reducing effect) and lead to small decreases in the setting time (i.e., slight set-accelerating effect).

CHAPTER 5. USE OF LITHIUM TO TREAT EXISTING ASR-AFFECTED STRUCTURES

5.1 Laboratory Studies

A number of laboratory studies (Stark et al., 1993; Stokes et al., 2000) have demonstrated that treating ASR-affected concrete with lithium compounds can reduce or eliminate future expansion due to ASR (e.g., figure 19). Typically, such studies have used laboratory-sized specimens with relatively small cross-sections and it has not yet been demonstrated that lithium treatment is effective with larger specimens that are more representative of elements of concrete structures.

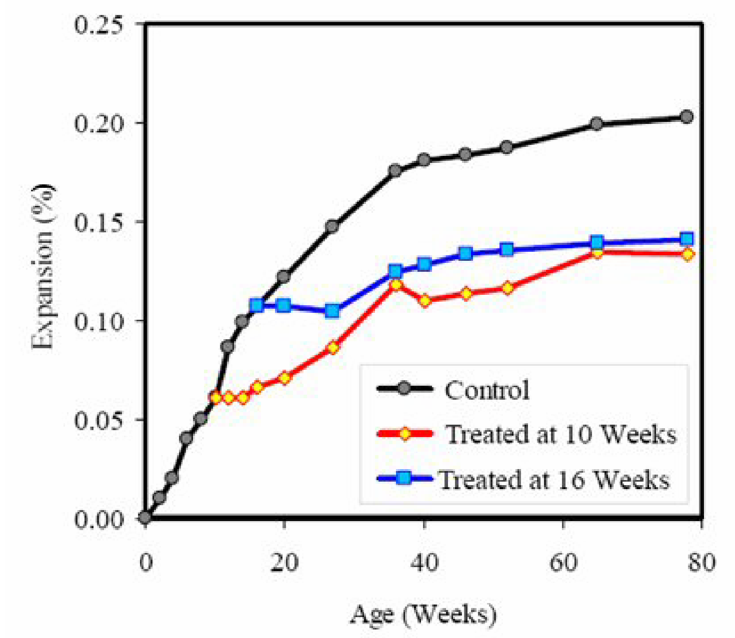


Figure 19. Expansion of concrete prisms after treatment with lithium at 10 weeks (expansion = 0.061 percent) and 16 weeks (expansion = 0.107 percent) (Thomas and Stokes, 2004).

5.2 Field Applications

5.2.1 Topical Treatment with Lithium

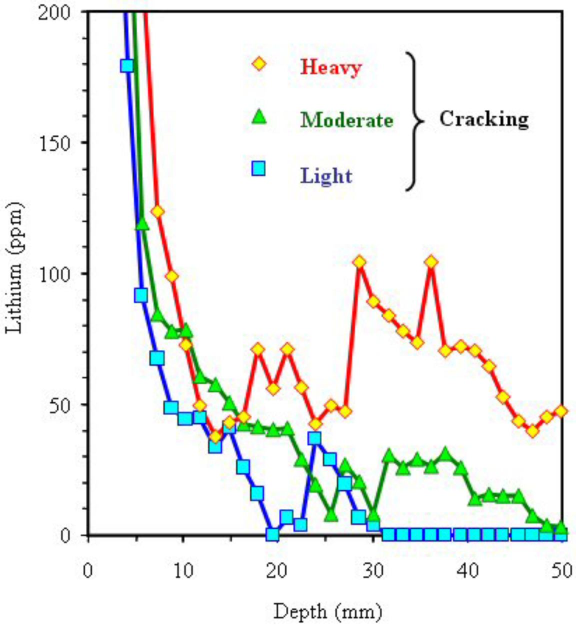
Numerous structures have been treated by spraying the surface of the structure with a solution of lithium (both $LiNO_3$ and LiOH have been used). These structures have included pavements, bridge decks and other bridge components, and median barriers. The solution has been applied by either truck-mounted spraying systems (figure 20) or hand-held pressurized spray bottles (figure 21).

Figure 20. Spraying 30 percent $LiNO_3$ solution with a tanker truck on a concrete pavement near Mountain Home, ID.

Figure 21. Spraying 30-percent $LiNO_3$ solution with handheld spray applicator on barrier wall near Leominster, MA.

Typical application rates have been in the range of 0.12 to 0.24 liters per square meter (L/m^2) (3 to 6 gallons per square feet (gal /1000 ft^2)). The most commonly used lithium compound for this purpose is a 30 percent $LiNO_3$ solution. Commercially available solutions contain a proprietary surfactant to enhance penetration.

There are few data available regarding the depth of lithium penetration following lithium treatment. Figure 22 shows lithium concentration profiles in concrete cores cut from a pavement after six treatments (one treatment in each of spring and fall for 3 consecutive years) of 0.24 L/m² (6 gal/1000 ft²). The depth of lithium penetration is clearly dependent on the extent of cracking.



1 mm = 0.039 inch

Figure 22. Lithium concentration profiles for concrete pavement after six treatments (at approximately 6-month intervals) of 0.24 L/m^2 (6 gal/1000 ft^2) (Stokes et al., 2002).

Figure 22 indicates that very little lithium penetrates below 25 to 50 mm (1 to 2 inches) unless the concrete is heavily cracked. Even in heavily cracked concrete, the lithium concentration at this depth is low, and its ability to suppress ASR is questionable[3].

Most of the structures that have been treated topically with lithium have not been monitored properly (i.e., other than by simple visual inspection) to confirm whether the treatment has been effective in terms of suppressing ASR expansion.

5.2.2 Electrochemical Lithium Impregnation

Electrochemical impregnation techniques have been used to increase lithium penetration on a number of structures (Whitmore and Abbot, 2000). A typical setup (i.e., for a bridge deck) is shown in figure 24 and includes the following parameters:

- Technique is based on electrochemical chloride extraction technique.
- Electrode (anode) applied to concrete surface.
- Lithium-bearing electrolyte ponded at surface.
- D.C. voltage (~40 volts) applied between surface anode and embedded steel (cathode).

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[3] If lithium were added to concrete containing 4 kg/m^3 (6.7 lb/yd^3) Na_2Oe at the standard dose of 4.6 Liters of 30 percentLiNO$_3$ solution per 1 kg Na_2Oe (0.55 gal of solution for every 1.0 lb of Na_2Oe), the lithium concentration in the concrete would be approximately 280 ppm.

- Positively charged lithium ions are repelled by the positively charged anode and are drawn towards the negatively charged cathode (steel reinforcement).
- Duration of treatment is typically 4 to 8 weeks.

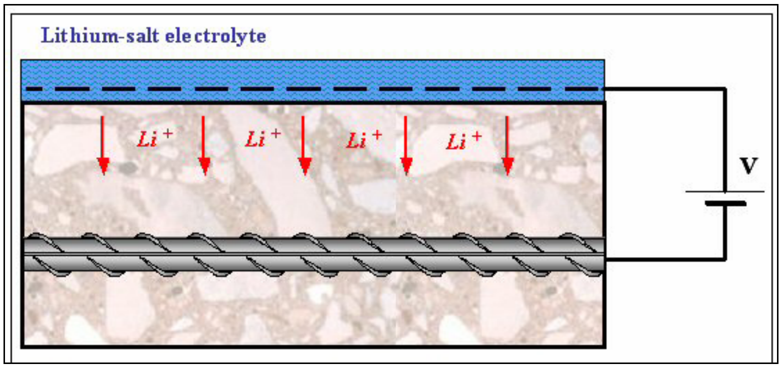


Figure 23. Electrochemical lithium impregnation.

Two such cases of using this electrochemical technology have been documented in the literature; these are two bridge decks, one in Arlington, VA, the other in Seaford, DE. In both cases, lithium borate was used as the electrolyte. Cores were taken from the deck in Virginia after 8 weeks of electrochemical treatment. Slices taken from the cores and subjected to chemical analysis revealed the data shown in table 11.

Table 11. Penetration of lithium after electrochemical treatment of bridge deck.

Depth of slice (mm)	Lithium (ppm)
6–19	315–343
19–32	203–265

1 mm = 0.039 inch

The data indicate that significant lithium penetrates to a depth of at least 19 to 32 mm (0.75 to 1.25 inches), and these dosages are theoretically high enough to have a beneficial effect on reducing ASR-induced expansion (see footnote 2 in chapter 3).

In March 2006, two columns in Houston, TX, were selected for electrochemical treatment as part of the Federal Highway Association Lithium Implementation Technology Program. Figure 24 shows the process of the treatment for one of the columns. The entire treatment was completed mid-May of 2006.

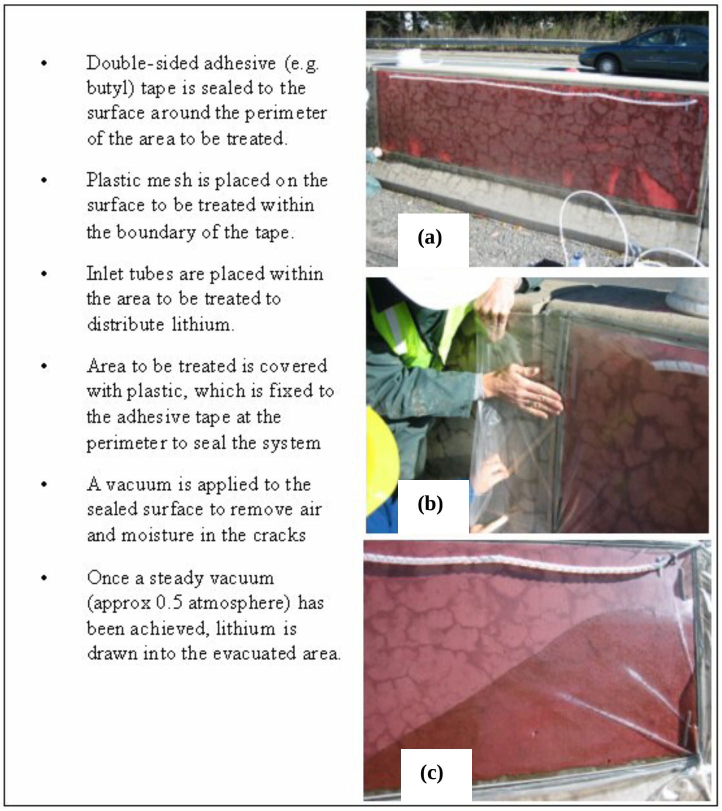
(a) (b) (c)

Figure 24. Electrochemical lithium treatment process. (a) irrigation tubes, wood splices, and metal strips are placed on the column. The metal strips are attached to titanium mesh that runs inside holes drilled into the sides of the column. (b) A cellulose layer is applied to the side of the column, and (c) plastic sheeting is placed on all sides of the column. The gutters under the sheeting collect excess lithium for reuse.

5.2.3 Vacuum Impregnation With Lithium

Vacuum impregnation is an alternative to pressure injection and has been used to increase grout penetration into cracked concrete. A number of structures have been treated with lithium using this technique; these include several substructure elements (beams and columns) of the New Jersey Turnpike, a number of elements on the Prospect Avenue Viaduct in Johnstown, PA, a trapezoidal prestressed bridge girder (treated by vacuum impregnation as part of a study of ASR-mitigation methods on 5 girders in Corpus Christi, TX), and sections of a barrier wall on Highway 2 near Leominster, MA (figure 26).

At the time of writing, no data were available concerning the depth of lithium penetration as a result of vacuum impregnation.



- Double-sided adhesive (e.g. butyl) tape is sealed to the surface around the perimeter of the area to be treated.
- Plastic mesh is placed on the surface to be treated within the boundary of the tape.
- Inlet tubes are placed within the area to be treated to distribute lithium.
- Area to be treated is covered with plastic, which is fixed to the adhesive tape at the perimeter to seal the system
- A vacuum is applied to the sealed surface to remove air and moisture in the cracks
- Once a steady vacuum (approx 0.5 atmosphere) has been achieved, lithium is drawn into the evacuated area.

Figure 25. Typical vacuum impregnation setup.

5.3 Recommendations for Treating ASR-Affected Structures with Lithium

Before treating a structure with lithium-based compounds, an investigation should be conducted to ensure that the structure meets the following criteria:

- The main cause of damage is alkali-silica reaction. Lithium treatment is unlikely to "cure" any other deterioration processes such as freeze-thaw damage, corrosion of embedded steel or even alkali-carbonate reaction. Proper diagnosis involves extracting samples for petrographic analysis and other testing in the laboratory.
- There remains potential for further expansion and damage due to ASR.

Lithium treatment will not "repair" any damage that has already occurred. A protocol for selecting structures that may be suitable for lithium-treatment is available from FHWA (FHWA-RD-04-113).

Treating structures with lithium is a technology that is still under development and, at this time, recommended protocols for selecting the type of treatment (e.g., topical, electrochemical, or vacuum impregnation) or methodologies for performing the treatment do not exist. Electrochemical and vacuum impregnation require specialized knowledge and equipment, and should be conducted only by an experienced contractor. Topical applications are relatively simple to perform, and a few general guidelines are provided in table 12. Figure 26 shows examples of $LiNO_3$ precipitation after application.

Table 12. General guidelines for topical lithium treatment.

Treatment Procedure
• Clean surface (e.g., road sweeper) prior to treatment. • Do not treat if rain is forecast within 6 hours. • Keep single application rate ≤ 0.12 L/m^2 (3 gal /1,000 ft^2). • Minimum two applications. • Applications at least 30 minutes apart. • Ensure uniform surface coverage and no runoff. • If precipitate forms over > 5 percent of surface, re-wet the surface to dissolve the precipitate. If surface becomes slippery, applications of water should continue until the surface is safe for vehicular traffic.
The number of individual treatments that can be applied to a structure will be governed by economics and other aspects of the repair strategy. For example, if the structure is being treated prior to the application of a concrete or asphalt overlay, there may only be time for a single treatment. For pavements or bridge decks that remain exposed after treatment, additional treatments may be considered at appropriate intervals. For example, the treatment of State Route 1 in Delaware involved a total of 6 individual treatments over a 3-year period.

As the efficacy of lithium treatment has yet to be established, it is recommended that treated structures are tested and monitored properly. Some suggestions for monitoring are provided in table 13. Figure 27 shows crack mapping and length change monitoring.

The authors are not aware of any studies aimed at evaluating the effect of lithium nitrate on the environment.

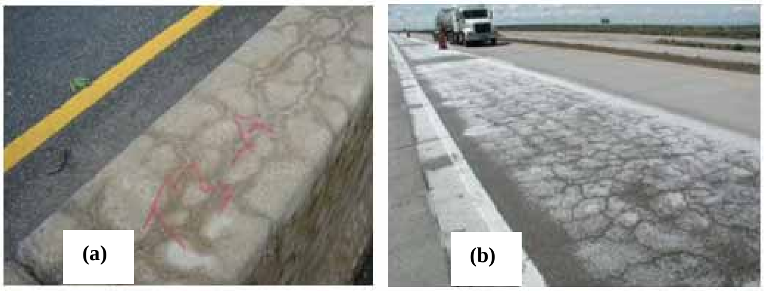


Figure 26. Precipitation of LiNO3 from solution (a) on barrier wall and (b) on pavement.

Table 13. Suggestions for monitoring lithium-treated structures.

Monitoring Guidelines
• Take core samples to determine depth of lithium penetration. • If possible, maintain untreated control section to compare performance with treated section. • Monitor length change of concrete. There are a wide variety of techniques available; one of the simplest being to embed stainless steel reference pins and monitor the change in length between the pins using a demountable mechanical (DEMEC) strain gauge (see figure 27b). • Crack mapping techniques can be used to follow damage accumulation. • Consider use of non-destructive techniques such as spectral analysis of surface waves (SASW). • There are a number of technologies available for performing condition surveys of roads and bridges. Some of these have been employed to follow the progress of damage due to ASR.

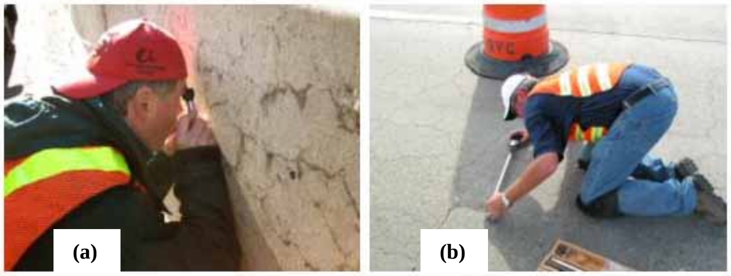


Figure 27. Monitoring techniques—(a) crack mapping of a barrier wall and (b) measuring length changes on concrete pavement with a DEMEC gauge.

CHAPTER 6. SUMMARY

1. Lithium-based admixtures can be used to control expansion due to ASR provided they are used in sufficient quantity. The amount of lithium required increases as the amount of alkali in the concrete increases. $LiNO_3$ is more efficient (i.e., can be used in lesser amounts) than other lithium compounds.

2. Some aggregates require higher doses of lithium than others for efficiently controlling deleterious expansion due to ASR. It would appear that lithium is more effective with rapidly reactive aggregates containing opaline silica, chert, or volcanic glass as the reactive component, and that lithium is relatively less efficient (at similar dosages) with more moderately reactive aggregates that contain microcrystalline or strained quartz as the reactive phase.

3. At this time, it is recommended that the lithium dose required to control ASR with a specific aggregate be determined by testing using the concrete prism test, with an expansion limit of 0.04 percent at 2 years.

4. Laboratory testing has shown that ASR-affected concrete specimens can be treated topically using lithium-based compounds to slow down the rate of expansion.

5. Many structures have been treated with lithium using either a simple topical application or electrochemical or vacuum impregnation techniques to increase lithium penetration.

6. The extent to which lithium penetrates hardened concrete or controls expansion in the field structures has not been unequivocally established.

7. It is recommended that treated structures be monitored and tested to provide information on the efficacy of lithium treatment.

ACKNOWLEDGEMENTS

A special thank you goes to the FHWA Expert Panel for their assistance reviewing this document and providing useful feedback that was integrated into the final printed version of this facts book.

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