FOREWORD

Progress is being made in efforts to combat alkali-silica reaction in both new and existing portland cement concrete structures. Of the several viable methods that exist to prevent damage in concrete structures because of this significant durability problem, the use of lithium compounds has been recognized for more than 50 years. There has been renewed interest in recent years in using lithium compounds as either an admixture in new concrete or as a treatment of existing structures.

This report 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.

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Research and Development

NOTICE

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16. Abstract

Alkali-silica reaction (ASR) is a significant durability problem that has resulted in premature deterioration of various types of concrete structures in the United States and throughout the world. Although several viable methods exist to prevent ASR-induced damage in new concrete structures, very few methods mitigate further damage in structures already affected by ASR-induced expansion and cracking. Lithium compounds have been recognized for more than 50 years as effectively preventing expansion caused by ASR, and there has been renewed interest in recent years in using lithium compounds as either an admixture in new concrete or as a treatment of existing structures. This report 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 its use in repair and service life extension applications. This report replaces the previous report (*Guidelines for the Use of Lithium to Mitigate or Prevent ASR*, Folliard, et al., 2003) and includes significant changes, especially those related to recommendations for testing and specifying lithium compounds.

This report provides a basic overview of ASR, including information on mechanisms, symptoms of ASR damage in field structures, mitigation approaches, test methods, and specifications. A comprehensive summary of lithium compounds is provided, including information on their production, availability, and use in laboratory concrete studies and field applications (including a range of case studies). Guidelines for using lithium compounds as an admixture in new concrete and for treating existing structures suffering from ASR-induced damage are presented, including information on how to assess the efficacy of lithium compounds in laboratory tests. Some basic information also is provided on the economics of using lithium both in new concrete and as a treatment for existing structures. A summary of conclusions is included and identifies several technical and practical issues that should be considered for future laboratory studies and field applications.

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SI* (MODERN METRIC) CONVERSION FACTORS

APPROXIMATE CONVERSIONS TO SI UNITS

Symbol	When You Know	Multiply By	To Find	Symbol
LENGTH				
in	inches	25.4	millimeters	mm
ft	feet	0.305	meters	m
yd	yards	0.914	meters	m
mi	miles	1.61	kilometers	km
AREA				
in^2	square inches	645.2	square millimeters	mm^2
ft^2	square feet	0.093	square meters	m^2
yd^2	square yard	0.836	square meters	m^2
ac	acres	0.405	hectares	ha
mi^2	square miles	2.59	square kilometers	km^2
VOLUME				
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)				
^oF	Fahrenheit	5 (F-32)/9 or (F-32)/1.8	Celsius	^oC
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)				
^oC	Celsius	1.8C+32	Fahrenheit	^oF
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
AASHTO   American Association of State Highway and Transportation Officials
ACR   Alkali-Carbonate Reaction
AMBT   Accelerated Mortar Bar Test
ASR   Alkali-Silica Reaction
ASTM   American Society for Testing and Materials
BRE   Building Research Establishment
CPT   Concrete Prism Test
CSA   Canadian Standards Association
DOT   Department of Transportation
ECE   Electrochemical Chloride Extraction
EDL   Electrical Double Layer
FHWA   Federal Highway Administration
LANL   Los Alamos National Laboratory
NMSHTD   New Mexico State Highway and Transportation Department
SCM   Supplementary Cementitious Material
SHRP   Strategic Highway Research Program
SEM   Scanning Electron Microscopy
UK   United Kingdom

Chemical Notations
C-S-H   Calcium silicate hydrate
CaOH   Calcium hydroxide
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 flouride
$LiNO_3$ Lithium nitrate
LiOH   Lithium hydroxide
$LiOH•H_2O$ Lithium hydroxide monohydrate
Li_2CO_3 Lithium carbonate
Li_2SiO_3 Lithium silicate
Li_2SO_4 Lithium sulfate
M   molar
N   normal
Na_2O Sodium oxide
Na_2O_e Total sodium oxide equivalent
NaCl   Sodium chloride
OH^- Hydroxyl ion

Measurements

cm	centimeter
g	gram
GPa	gigapascal
kg	kilogram
kgf	kilogram force
L	liter
m	meter
mL	milliliter
MPa	megapascal
ppm	parts per million
w/cm	water-cementitious materials ratio

CHAPTER 1   INTRODUCTION

1.1   OVERVIEW

Alkali-silica reaction (ASR) is a major durability problem that has resulted in premature deterioration of various types of concrete structures in the United States and throughout the world. Although the potential for lithium compounds to control ASR-induced expansion has been known for about 50 years, there have been limited field applications with even less comprehensive performance monitoring. In the past 10 years, however, there has been renewed interest in using lithium as either an admixture in new concrete or as a treatment of existing structures. Because of the limited use of lithium compounds in laboratory research and field applications, guidelines have been lacking. This report presents recommendations for practitioners to test, specify, and use lithium compounds in concrete construction and repair applications.

1.2   SUMMARY OF REVISIONS AND MODIFICATIONS TO GUIDELINES

This report replaces the previously published lithium guideline report (*Guidelines for the Use of Lithium to Mitigate or Prevent Alkali-Silica Reaction (ASR)*, Folliard, et al., 2003). Substantial changes have been made, and the recommendations provided within the current document should be considered to be the most relevant and applicable to future applications of lithium. The following highlights some of the key modifications and revisions made to the current guideline document:

- Deleting the prescriptive recommendations for the use of lithium as an admixture in new concrete. The exact relationship between the amount of lithium required and the nature of the reactive aggregate is not clearly understood. As discussed in chapter 3, recent studies have shown that dosages higher than 100 percent of the standard dosage may be needed to suppress expansion for several major aggregate types. Consequently, it is not appropriate to specify a single dose for all reactive aggregates and the dose required has to be determined by testing individual aggregate sources with lithium.

- Deleting the modified accelerated mortar bar test (AMBT) in the performance specification. This test underestimates the amount of lithium required for the control of expansion with a number of reactive aggregate types.

- Updating summary of field studies to include recent applications of lithium.

- Updating literature review to include recent publications.

1.3   ORGANIZATION OF REPORT

This report is organized in seven chapters, including this brief introductory chapter. Major topics are summarized below.

Chapter 2 provides a basic overview of ASR, including information on mechanisms, symptoms of ASR damage in field structures, mitigation approaches, test methods, and specifications. The main objective of this chapter is to provide the reader with sufficient technical background on ASR, which is essential in understanding how lithium compounds affect the process.

Chapter 3 summarizes basic information on lithium compounds, including their production and availability. This chapter presents a comprehensive review of laboratory research on using lithium compounds to control ASR-induced expansion, including discussions on the proposed mechanisms by

which lithium additives suppress expansion. It also includes a brief discussion on specifications related to lithium usage as an admixture in new concrete.

Chapter 4 describes several major field applications of lithium compounds aimed to minimize or prevent ASR-induced expansion in new concrete and that treat field structures already showing signs of distress due to ASR. Relevant information on materials, mixture proportions, supporting laboratory data (if applicable), and field performance is provided for the selected case studies.

Chapter 5 presents recommendations for using lithium compounds as an admixture in new concrete and as a method of treating existing structures suffering from ASR-induced damage. The recommendations are aimed at helping practitioners test, specify, and use lithium in concrete construction applications. The guidelines are based on a comprehensive review of laboratory and field applications of lithium compounds and on a survey of relevant specifications.

Chapter 6 discusses the economic considerations of using lithium compounds in new concrete and to treat existing structures. This chapter presents various factors that should be taken into account when considering the use of lithium.

Chapter 7 summarizes some of the major conclusions from this report and identifies some technical and practical issues that should be considered for future laboratory studies and field applications.

CHAPTER 2   ALKALI-SILICA REACTION

2.1   INTRODUCTION

This chapter provides an overview of the fundamentals of ASR in concrete. The basic mechanisms of ASR are summarized, followed by discussions on ASR manifestations and symptoms in field structures, relevant test methods, methods of preventing ASR, and specifications. The use of lithium compounds to control ASR is covered only to a limited extent in this chapter but is discussed in detail in Chapter 3.

Alkali-aggregate reaction (AAR) was first identified as a cause of concrete deterioration more than 60 years ago (Stanton, 1940). Since this initial discovery, cases have been reported throughout the world. Of the two types of AAR, ASR and alkali-carbonate reaction (ACR), ASR is considerably more widespread and is of more significance in the United States. Incidences of ACR are relatively scarce and generally restricted to a few isolated regions; ACR will not be considered in this report. ASR-induced damage has become a widespread durability issue throughout the United States and has been implicated in virtually every State in the Nation.

ASR has been implicated in the deterioration of various types of concrete structures, including dams, pavements, bridges, and other structures. The manifestation of ASR in such structures is discussed later in this chapter. The impact of ASR on field structures is best understood in the context of its underlying mechanisms, which are presented below.

2.2   ALKALI-SILICA REACTION

2.2.1   Essential Components of ASR

The mechanisms governing ASR and expansion are quite complex; moreover, there are several schools of thought on which mechanisms are most important in field structures. This section starts with the well-documented and agreed-upon fundamentals of ASR and continues with a mechanistic discussion of the process.

It is widely accepted that the three essential components necessary for ASR-induced damage in concrete structures (as shown in Figure 1) are: (1) reactive silica (from aggregates); (2) sufficient alkalis (mainly from portland cement, but also from other constituent materials or external sources); and (3) sufficient moisture. Eliminating any one of the above components effectively will prevent damage resulting from ASR, as discussed next.
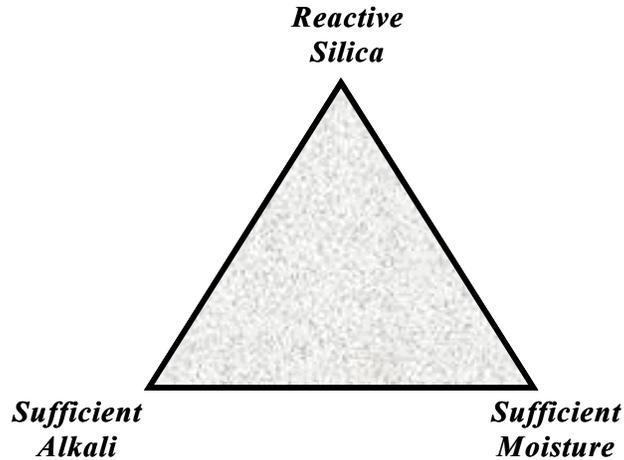
Figure 1. The Three Necessary Components for ASR-Induced Damage in Concrete.

Table 1. Rock Types and Reactive Minerals Susceptible to ASR (After CSA, 2000b).

Rocks	Reactive Minerals
Arenite	Crisobalite
Argillite	Cryptocrystalline (or microcrystalline) quartz opal
Arkose	Strained quartz tridymite
Chert	Volcanic glass
Flint	–
Gneiss	–
Granite	–
Greywacke	–
Hornfels	–
Quartz-arenite	–
Quartzite	–
Sandstone	–
Shale	–
Silicified carbonate	–
Siltstone	–

Reactive Silica

The presence of reactive aggregates or another reactive silica source in concrete is necessary for ASR to occur. The term *reactive* refers to aggregates that tend to breakdown under exposure to the highly alkaline pore solution in concrete and subsequently react with the alkalis (sodium and potassium) to form an expansive ASR gel. More detailed information on the specific mechanisms governing aggregate breakdown and subsequent gel formation is provided later in this section. Based on years of laboratory and field experience, a list of reactive minerals and typical rock types that are susceptible to ASR have been compiled, as summarized in Table 1. It is important to note that not all siliceous aggregates are prone to ASR. The inherent reactivity of aggregates depends on several factors, including aggregate mineralogy, degree of crystallinity, and solubility (of the silica in high-pH concrete pore solution). The rocks and minerals shown in Table 1 represent those that are most prone to ASR, but it does not suggest that these are always prone to ASR or that other rocks or minerals not listed in Table 1 are completely immune from ASR.

Sufficient Alkalis

The presence of sufficient alkalis is another required ingredient for ASR. While portland cement is considered the main contributor of alkalis, under certain conditions, other materials may provide additional alkalis that are available to the reaction. The source of alkalis can be from any of the following:

- Portland cement.
- Supplementary cementing materials (e.g., fly ash, slag, silica fume).
- Aggregates.
- Chemical admixtures.
- External sources (e.g., seawater and deicing salts).
- Wash water (if used).

The quantity of alkalis in portland cement typically is expressed as:

$$Na_2O_e = Na_2O + 0.658K_2O \tag{1}$$

Where: Na_2O_e = total sodium oxide equivalent (or equivalent soda), in percent by mass
Na_2O = sodium oxide content, in percent
K_2O = potassium oxide content, in percent

Although the percentage of alkalis in portland cement is relatively low (in the range of 0.2 to 1.1 percent) in comparison to other oxides or compounds, the bulk of the alkalis ultimately resides in the pore solution of concrete, and it is the associated hydroxyl (OH^-) concentration (necessary to maintain charge balance) that produces the inherent high pH in the pore solution (i.e., 13.2 to 14.0). Based on Stanton's early work (1940), it was proposed for many years that expansion resulting from the ASR reaction is unlikely to occur when the alkali content of the cement is below 0.6 percent Na_2O_e. This rule-of-thumb value has been cited in various specification limits and was adopted as part of American Society for Testing and Materials (ASTM) C 150. However, it is now recognized that limiting the alkali content of portland cement is not, by itself, an effective way of preventing ASR-induced damage, because this approach does not control the total alkali content of the concrete mixture. Therefore, limiting the maximum alkali content of concrete is the preferred approach when specifying alkali levels. Nixon and Sims (1992) reported that maximum permissible alkali contents between 2.5 and 4.5 kg/m^3 Na_2O_e have been specified by various countries and agencies, with the allowable alkali content sometimes varying depending on aggregate reactivity.

Figure 2 illustrates the effects of the alkali content on the expansion of concrete prisms stored over water at 38 °C (this and other tests are described later in this chapter). Using an expansion limit of 0.04 percent, the graph shows that laboratory concrete containing less than 3.0 kg/m^3 Na_2O_e generally resisted excess expansion, even after 2 years of testing. Although laboratory tests have shown that keeping the total alkali content below 3.0 kg/m^3 Na_2O_e is an effective method of limiting expansion, field structures have exhibited damage with even lower alkali loadings, especially when alkalis have also been contributed by the aggregates in the mixture or by external sources, such as deicing salts. Thus, when considering imposing a limit on the alkali content for a given concrete mixture, consideration should be given to the aggregate type and reactivity, exposure conditions, and nature of the structure (i.e., design life or relative importance).
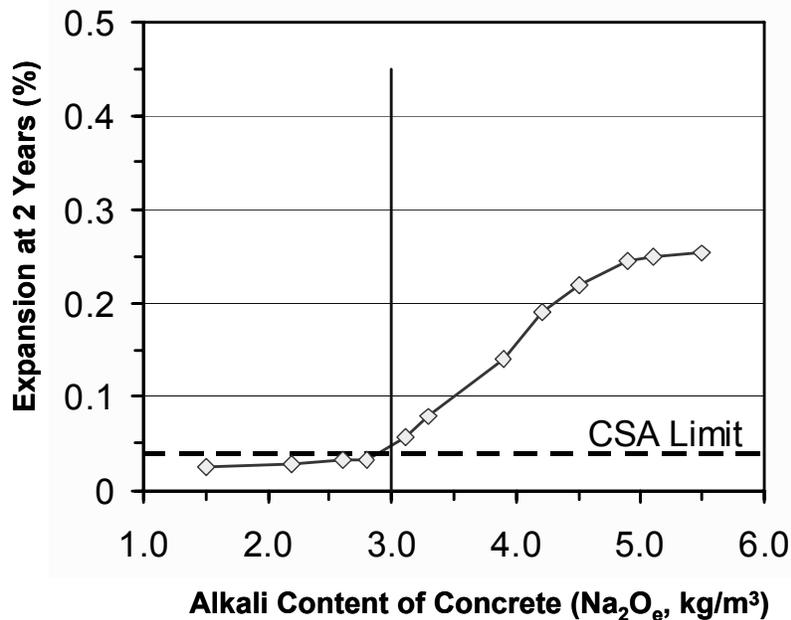
Figure 2. Effects of Alkali Content on Expansion of Prisms Stored Over Water at 38 °C
(After Thomas, 2002).

There has been significant debate regarding the impact of alkalis from supplementary cementitious materials (SCMs) on ASR. Specifically, different countries and agencies vary in how they treat SCMs when calculating the total alkali content of a given concrete mixture. Although an advanced discussion of this issue is beyond the scope of this report, readers are directed to the comprehensive review of current practice compiled by Nixon and Sims (1992). Some countries ignore the contribution of alkalis from SCMs, whereas others use the available alkali content (ASTM C 311) or a percentage of the total alkali content in calculating the total alkali loading of the mixture. Perhaps the most recent advice regarding the contribution of alkalis from fly ash and slag is included in the latest Canadian Standards Association (CSA) guidelines, where it is assumed that SCMs do not contribute any alkalis to concrete when computing total alkali loading. However, limits are placed on the total alkali content of the SCMs, and replacement levels (by mass of cement) are specified, based on the chemistry of the SCMs. Additional information on the mitigation of ASR with SCMs is provided later in this chapter, including information on relevant test methods.

As previously mentioned, alkalis also can be released from certain aggregates within concrete, thereby increasing the alkali content of the mixture (Thomas, et al., 1992; Stark and Bhatty, 1986, Gillott and Rogers 1994) and probably contributing to the increased expansion resulting from ASR (Durand 2000a). Stark and Bhatty (1986) reported that certain aggregates can release alkalis equivalent to a 10 percent alkali contribution from the portland cement under extreme conditions.

The total alkali content within a given concrete mixture may also be increased by the penetration of alkalis from external sources, such as seawater, ground water (containing sulfates), deicing salts, brackish water and industrial wastes. In addition, Nixon, et al. (1987) demonstrated that seawater (used as part of the batch water) increased the OH$^-$ concentration in the pore solution and resulted in higher concrete expansion values.

6

Sufficient Moisture

Available moisture is important when considering the potential for ASR-induced damage in field structures. Concrete mixtures comprised of highly reactive aggregates and high-alkali cements have shown little or no expansion in certain very dry environments. Likewise, local differences in moisture availability within the same structure have resulted in vastly different performance within that structure. Specifically, portions of the structure exposed to a constant or steady source of moisture (e.g., as a result of poor drainage or poor detailing) have exhibited significant ASR-induced damage, while other portions of the structure that remain essentially dry have shown little or no damage. Therefore, the exposure conditions, in general, and the availability of moisture, specifically, play key roles in the durability of field structures.
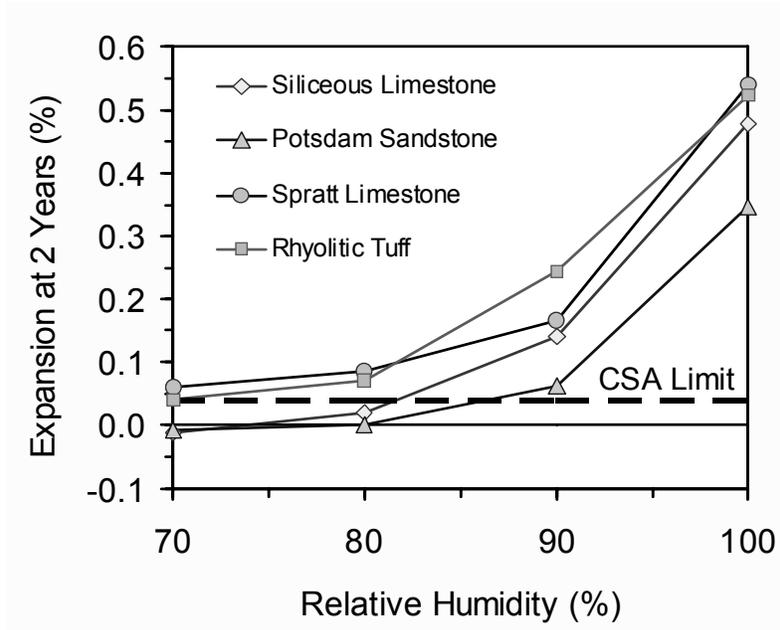
Figure 3. Effects of Relative Humidity on Expansion Using the ASTM C 1293 Storage Regime (Pedneault, 1996).

After the formation of the ASR gel, it is the subsequent imbibing of water that causes expansion within concrete, which ultimately can lead to tensile stresses and cracking. It is generally believed that a minimum relative humidity of 80 percent is required to cause significant expansion as a result of ASR. Data supporting the importance of moisture on expansion are shown in Figure 3, where four different reactive aggregates were stored under different moisture conditions, and the expansion of concrete prisms (similar to ASTM C 1293) was assessed (Pedneault, 1996). In this experiment, concrete that was maintained in an environment with less than 80 percent relative humidity had greatly reduced expansion (e.g., expansion in two of the four mixtures was less than 0.04 percent after 2 years).

Limiting the availability of external moisture in field structures is an effective way of reducing ASR-induced damage; however, it is often not feasible to reduce the moisture content below the critical threshold value (i.e., 80 percent relative humidity). However, any attempt at reducing available moisture, whether through proper detailing and design of drainage or through the use of low-permeability concrete, will improve the long-term durability of concrete.

2.2.2 Mechanisms of ASR

The previous sections described the major contributors to ASR in concrete, namely reactive silica, sufficient alkalis, and sufficient moisture. This section provides more detailed information on the specific mechanisms involved, including the chemical reaction that leads to the breakdown of reactive silica, the formation of the ASR gel, and the proposed mechanisms for subsequent expansion.

The term *alkali-silica reaction* is somewhat misleading—the reaction itself is actually between the hydroxil (OH⁻) ions in the pore solution and certain siliceous components of the aggregates. The alkalis, specifically sodium and potassium, do not actually attack the reactive silica. The importance of the alkalis is that their presence in high concentrations in the pore solution results in an equally high concentration of OH⁻ ions (to maintain charge equilibrium). It is this high OH⁻ concentration, and thus high pH, that leads to the initial breakdown of reactive silica components in the aggregates. The alkalis also ultimately contribute to the expansive ASR gel formation, as discussed later in this section.

There is general agreement by researchers regarding the specific chemical process governing the breakdown of reactive silica components by a highly alkaline solution, such as pore water inside concrete. When poorly crystalline hydrous silica is exposed to a highly alkaline solution, there is an acid-base reaction between the OH⁻ ions in solution and the acidic silanol (Si-OH) groups (Dent Glasser and Kataoka, 1981), as shown in equation 2. As additional OH⁻ ions penetrate into the structure, some of the stronger siloxane (Si-O-Si) linkages are also attacked, as shown in equation 3.

$$\equiv\text{Si-OH} \ + \ \text{OH}^- \ \rightarrow \ \equiv\text{Si-O}^- + \text{H}_2\text{O} \tag{2}$$

$$\equiv\text{Si-O-Si}\equiv \ + \ 2\text{OH}^- \ \rightarrow \ 2\,(\equiv\text{Si-O}^-) + \text{H}_2\text{O} \tag{3}$$
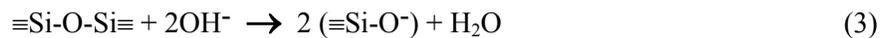
To maintain charge equilibrium, cations (Na^+ and K^+) diffuse into the structure to balance the negative charges present on the terminal oxygen atoms. The disruption of the siloxane linkages ultimately weakens the structure. Provided that sufficient amounts of alkali-hydroxides are available, this process continues, producing an alkaline silicate solution.
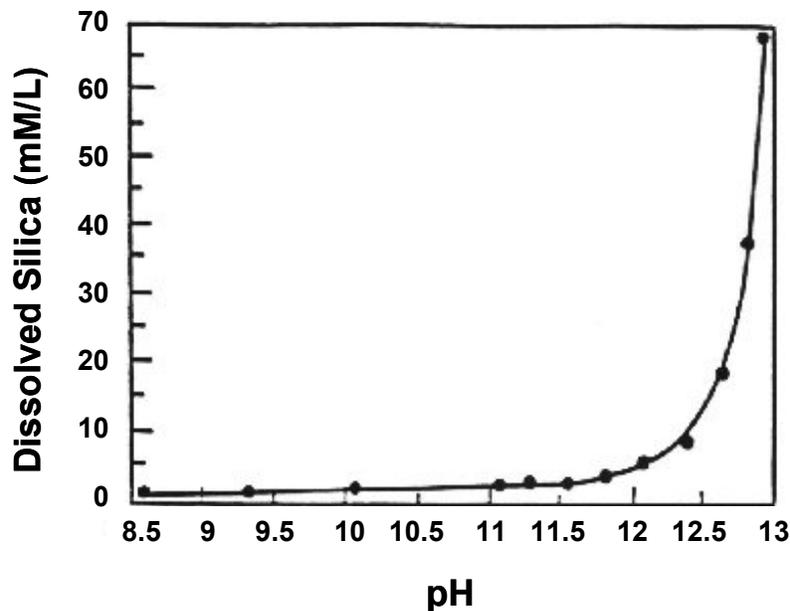
Figure 4. Effects of pH on Dissolution of Amorphous Silica (Tang and Su-Fen, 1980).

The chemical process described above results in the dissolution of the reactive silica components; the alkalinity of the pore solution and the structure of the silica govern the rate and/or amount of dissolution. Poorly crystalline or amorphous silica (e.g., opal, volcanic glass, cristobalite) is much more prone to ASR than well-crystallized or dense forms of silica (e.g., macrocrystalline quartz). One reason for this difference in behavior is that the solubility of amorphous silica increases significantly with pH, as illustrated in figure 4. Thus, aggregates composed of amorphous or poorly crystalline silica will tend to dissolve more readily in the inherently high-pH pore solution in concrete. Well-crystallized or dense forms of silica, such as quartz, are relatively inaccessible to alkaline hydroxide solution, and dissolution only occurs at the surface, at a very slow rate.

As previously mentioned, there is general acceptance of the chemical reactions governing ASR; however, there are several schools of thought regarding the mechanisms of expansion of ASR gel. It is beyond the scope of this publication to thoroughly examine the various proposed mechanisms; however, a basic overview of these mechanisms is provided.

Hansen (1944) proposed an osmotic theory, in which the cement paste surrounding reactive grains behaves like a semi-permeable membrane through which water (or pore solution) may pass but not the larger complex silicate ions. The water is drawn into the reacting grain, where its chemical potential is lowest. An osmotic pressure cell is formed and increasing hydrostatic pressure is exerted on the cement paste, inevitably leading to cracking of the surrounding mortar.

McGowan and Vivian (1952) disputed the osmotic theory proposed by Hansen on the basis that cracking of the surrounding cement paste membrane because of ASR would relieve hydraulic pressure and prevent further expansion. They proposed an alternative mechanism, in which water is physically absorbed into the alkali-silica gel, resulting in swelling of the gel. Tang (1981) later concurred with this water imbibition and swelling theory.

Other researchers, including Powers and Steinour (1955), proposed a compromise, in which pressures resulting from both osmotic pressure and water absorption may be generated, depending on the nature of the alkali-silicate complex, specifically whether it is a fluid or solid. Despite these theories' differences, the fundamental cause of expansion is essentially the same—the entry of water into a region where the effects of absorption or a solute reduces its free energy (Diamond, 1989).

One aspect involving ASR and expansion that has received renewed interest in recent years is the important role of calcium. Although early proposed mechanisms (Hansen, 1944; McGowan and Vivian, 1952) did not recognize calcium's role in ASR, later studies have identified the presence of calcium in the reactive system as being essential to the expansion process. Diamond (1989) proposed that, in the absence of calcium, silica simply dissolves in alkali-hydroxide solution and does not form alkali-silicate gel.

Further support of the solubility of silica in the absence of calcium is found in the work of Kilgour (1988). She found low-calcium ashes to be partially soluble (losing 20 percent soluble mass in 6 months) when exposed to alkali-hydroxide solution (1 g ash in 100 mL of 0.7M NaOH-KOH) in the absence of calcium. The principal soluble phase was analyzed as silica, which remained in solution (no evidence of gel formation). Under the same conditions, except with addition of CaOH, an increase in mass was observed and attributed to the formation of a reaction product analogous to ASR gel. Thomas, et al. (1991) found that gels that are low in calcium and high in alkali are relatively fluid and readily dispersed into cement paste, whereas gels higher in calcium are more viscous and less able to dissipate when they swell on contact with water.

2.2.3 Symptoms of ASR

This section briefly describes the symptoms of ASR in concrete, beginning first with the impact on the microstructure of concrete and concluding with the manifestation in concrete structures. Figure 5 shows a thin-section cut from concrete affected by ASR, which is viewed under transmitted-light microscopy. The reaction product of ASR gel is shown, as is a crack forming through the aggregate and extending into the surrounding cement paste. The crack itself also is filled with ASR gel in some locations. This type of damage is typical of ASR-induced deterioration at the microstructural level of concrete.
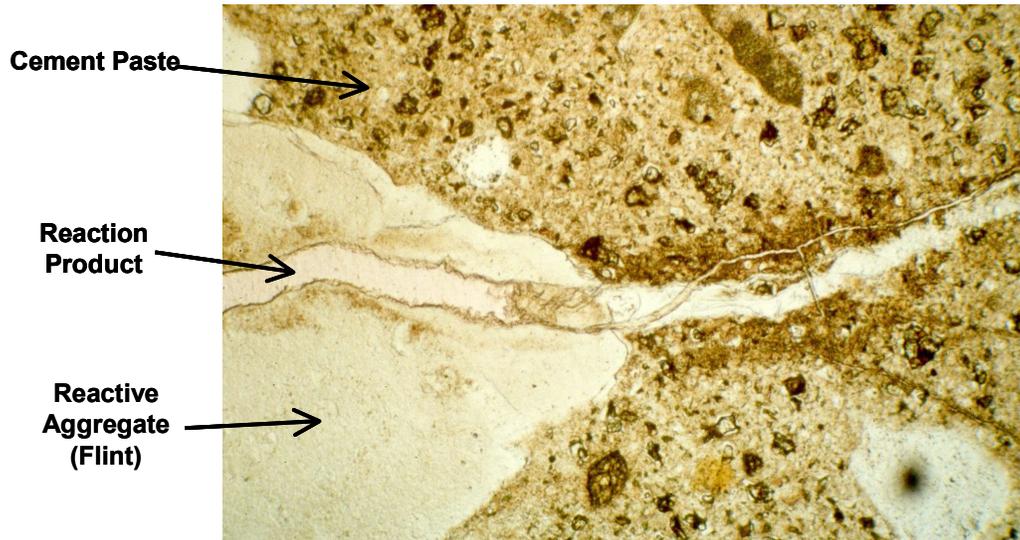
Figure 5. Thin-Section Cut of ASR-Damaged Concrete, Showing ASR Gel and Typical Crack Pattern (Through Aggregate and Into Surrounding Matrix).

Figure 6. ASR-Induced Damage in Unrestrained Concrete Element. Uniform Expansion in All Directions Results in Classic Map-Cracking.

The outward manifestation of ASR distress in actual concrete structures varies, depending on the severity of the attack, exposure conditions, type of structure, amount and direction of restraint (internal or external), and other factors. Perhaps the most important of these factors in determining the physical manifestation of ASR-induced damage in field structures is the role of restraint on subsequent crack patterns. Restraint may originate either from external sources, such as adjacent structural elements or applied loads, or internal sources, such as reinforcing steel (conventional, prestressed, or post-tensioned). Figure 6 shows typical ASR-induced damage in unrestrained concrete, resulting in classic map-cracking. Figure 7 shows similar damage in restrained concrete structures, where cracking tends to align itself in the direction of the main reinforcement (i.e., principal stress direction).

(a) Reinforced Concrete Column.   (b) Prestressed Concrete Girder.

Figure 7. ASR-Induced Damage in Restrained Concrete Elements, Including (a) Reinforced Concrete Column, and (b) Prestressed Concrete Girder.

When field structures suffer from excessive expansion because of ASR, significant misalignment (with respect to adjacent elements) may result, as shown in Figure 8. For pavements suffering from ASR, the subsequent expansion can lead to extrusion of joint-sealing material or even joint failure, as shown in Figure 9.

Figure 8. Misalignment of Adjacent Sections of a Parapet Wall on a Highway Bridge Due to ASR-Induced Expansion (Strategic Highway Research Program (SHRP)-315, 1991).

Figure 9. Extrusion of Joint-Sealing Material Triggered by Excessive Expansion Due to ASR.

2.3   LABORATORY TEST METHODS FOR ASSESSING ASR

This section provides an overview of available laboratory test methods to assess ASR of aggregates and to measure the effectiveness of various methods of mitigating ASR in new concrete, including SCMs. Limited information about testing lithium compounds in laboratory mixtures is also provided, but more information is provided in Chapter 3.

Table 2 lists several of the most commonly used standard test methods to assess ASR. The table also provides some basic information on each test, including pros and cons of using the test to predict field performance. Of the laboratory tests described, only two are recommended as suitable tests for assessing ASR: (1) ASTM C 1260 (Accelerated Detection of Potentially Deleterious Expansion of Mortar Bars Due to Alkali-Silica Reaction), and (2) ASTM C 1293 (Test Method for Concrete Aggregates by Determination of Length Change of Concrete Due to Alkali-Silica Reaction).

ASTM C 1260 is based on the method developed by Oberholster and Davies (1986) at the National Building Research Institute in South Africa. The test, often referred to as the accelerated mortar bar test, has been adopted by various countries and agencies, including the United States (ASTM and the American Association of State Highway and Transportation Officials (AASHTO)) and Canada. The test entails casting mortar bars containing the subject aggregate (either coarse or fine), which is processed to a standard gradation. The mortar bars are then removed from their molds after 24 hours and placed in water at room temperature. The temperature of the water is then raised to 80 °C in an oven, and the mortar bars are stored in this condition for the next 24 hours. After removing the bars from the water, they are measured for initial length and then submersed in a 1N NaOH solution at 80 °C, where they are then stored for 14 days. Length-change measurements are made periodically during this storage period. Total expansion at the end of the 14-day soaking period typically is used in specifications, although the expansion limits specified by different agencies vary. For example, the expansion criteria established by ASTM and CSA are:

ASTM C 1260 expansion criteria:
- < 0.10 percent is considered innocuous.
- 0.10 to 0.20 percent is considered potentially reactive.
- > 0.20 percent is considered reactive.

CSA A23.2-25A expansion criteria:
- > 0.15 percent (0.10 percent for limestones) is considered potentially reactive.
- < 0.15 percent (0.10 percent for limestones) is considered nonreactive.

Table 2. Available Standard Tests for Assessing Alkali-Silica Reactivity.

Test Method	Comments
ASTM C 227: Standard Test Method for Potential Alkali Reactivity of Cement-Aggregate Combinations (Mortar Bar Method)	- Mortar bar test (aggregate/cement = 2.25), intended to study cement-aggregate combinations. - Specimens stored in high-humidity containers at 38 °C. - Several reported problems with test, including excessive leaching of alkalis from specimens and its unreliable correlation to field performance.
ASTM C 289: Standard Test Method for Potential Alkali-Silica Reactivity of Aggregates (Chemical Method)	- Aggregate test in which crushed aggregate is immersed in 1M NaOH solution for 24 hours—solution is then analyzed for amount of dissolved silica and alkalinity. - Poor reliability. - Problems with test include: - Other phases present in aggregate may affect dissolution of silica (Bérubé and Fournier, 1992). - Test is overly severe, leading aggregates with good field performance to fail the test. - Some reactive phases may be lost during pretest processing.
ASTM C 295: Standard Guide for Petrographic Examination of Aggregates for Concrete	- Useful evaluation to identify many (but not all) potentially reactive components in aggregates. - Reliability of examination depends on experience and skill of individual petrographer. - Results should not be used exclusively to accept or reject aggregate source—findings best used in conjunction with other laboratory tests (e.g., ASTM C 1260 and/or ASTM C 1293).
ASTM C 856: Practice for Petrographic Analysis of Hardened Concrete	- Useful for analyzing concrete (from laboratory or field) and for identifying presence of reactive aggregates or reaction products. - Reliability of examination depends on experience and skill of individual petrographer. - Essential for relating aggregate reactivity to field performance.

Table 2. Available Standard Tests for Assessing Alkali-Silica Reactivity (cont.).

Test Method	Comments
ASTM C441: 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	• Mortar bar test, intended to assess effectiveness of SCMs in reducing ASR expansion. • Test uses high-alkali cement and Pyrex™ glass. • Test not very reliable because of the use of Pyrex glass, which is sensitive to test conditions and contains alkalis that may be released during the test. Test does not correlate well with data from concrete mixtures containing natural aggregates (Bérubé and Duchesne, 1992).
ASTM C 1260: Standard Test Method for Potential Alkali Reactivity of Aggregates (Mortar-Bar Method) • **Recommended Test**	• Mortar bar test, originally designed to assess aggregate reactivity. • Bars are soaked in 1N NaOH solution for 14 days. • Accelerated test suitable as screening test, but because of the severity of the test, it should not be used, by itself, to reject a given aggregate. If aggregate is tested using both ASTM C 1260 and ASTM C 1293, the results of ASTM C 1293 should govern. • Modified method (ASTM C 1567) has been used with success to evaluate effectiveness of SCMs to control ASR expansion (Thomas, et al., 2005). • Effectiveness of the method for testing lithium compounds has also been evaluated by adding lithium to the bar and/or soak solution; limited success to date (chapter 3).
ASTM C 1293: Standard Test Method for Concrete Aggregates by Determination of Length Change of Concrete Due to Alkali-Silica Reaction • **Recommended Test**	• Concrete prism test, generally regarded as best indicator of field performance, is conducted at high humidity (close to 100 percent) at 38 °C. • Uses high-alkali cement (raised to 1.25 percent Na_2O_e), with a cement content of 420 kg/m^3. • Originally intended as aggregate test (using nonreactive fine aggregate to test reactivity of coarse aggregate, and vice-versa); test can also be used to evaluate potential alkali-reactivity of job combinations of fine and coarse aggregates. • Test requires 1 year for completion. • Also can be used to test effectiveness of SCMs and lithium compounds, but test is then typically run for 2 years. • Widely accepted test method; however, long duration of test is major drawback.

In ASTM C 1260, these expansion limits are proposed in an appendix to the standard test method and are not a mandatory part of the standard, whereas in CSA, the limits form part of a standard practice for assessing reactivity and evaluating the effectiveness of preventive measures (e.g., the use of SCMs) (CSA A23.2-27A). Draft guidelines developed by the AASHTO Lead States Program recommend an expansion limit of 0.10 percent for all aggregates, except metamorphic aggregates, for which an expansion limit of 0.08 percent is recommended (AASHTO, 2000).

ASTM C 1260 is recognized as a very severe test method because of the extreme test conditions, specifically the use of a highly alkaline storage solution and high temperature. Because of this inherent severity, the test has been shown to identify some aggregates as being reactive, even though they have performed well in concrete prism testing (ASTM C 1293) and in field applications (Bérubé and Fournier, 1992). Therefore, an aggregate should not be rejected solely based on ASTM C 1260 results unless the reactivity is confirmed using ASTM C 1293. Whenever data are available from both ASTM C 1260 and ASTM C 1293, the ASTM C 1293 results should govern.

Although ASTM C 1260 was developed initially only to test aggregate reactivity, the test has been found to be a suitable method for assessing the efficacy of SCMs in reducing ASR expansion (Thomas and Innis, 1999; Thomas, et al., 2005), where an expansion limit of 0.10 percent at 14 days is typically used.

However, the test is not suitable for assessing cement alkalinity because the highly alkaline soak solution masks any effect of cement alkalinity. In addition, ASTM C 1260 is not suitable, in its present form, for testing lithium compounds because the sodium hydroxide soak solution dominates the beneficial effects of adding lithium to the mortar bars. Researchers have attempted to modify ASTM C 1260 to allow for testing lithium compounds; however, these attempts, described in chapter 3, have not yet yielded a rapid mortar bar test that accurately estimates lithium dosage requirements needed to suppress ASR in concrete.

ASTM C 1293, commonly referred to as the concrete prism test (CPT), is generally considered the most accurate and effective test in predicting the field performance of aggregates. In this test, concrete is cast with a cement content of 420 kg/m^3. The cement is required to have an equivalent alkali content between 0.8 percent and 1.0 percent, and additional alkalis (NaOH) are then added to the mixing water to obtain a total alkali content of 1.25 percent (by mass of cement), which equates to a total alkali content in the concrete mixture of 5.25 kg/m^3. Concrete prisms are cast, cured for 24 hours at 23 °C, and then stored enclosed over water at 38 °C. Expansion measurements are taken at regular intervals, and when testing plain concrete (without SCMs or chemical admixtures), the test typically is run for 1 year. When testing SCMs or lithium compounds, the test typically is carried out for 2 years. This relatively long period for conducting ASTM C 1293, either 1 or 2 years, has been the major drawback for the test and has somewhat limited its use.

In recent years, more countries and agencies have adopted the CPT as a standard method. An expansion limit of 0.04 percent (at the end of the 1- or 2-year test) is typically specified because this value has been reported to correlate well with the cracking of test prisms. This expansion limit (0.04 percent) is referenced in the appendix to ASTM C 1293. In a few rare cases, ASR has been evident as cracks, extruding gel, and spalls (or popouts) in test prisms that have expansions greater than 0.04 percent (Whiting 1999). Noting the appearance of the test prism is part of the test procedure recommended by ASTM C 1293. As part of the most recent guidance provided by CSA (2000a), the expansion limits for the CPT (CSA A23.2-14A) were delineated further to assess aggregate reactivity as follows:

CSA A23.2-14A expansion criteria:

- < 0.04 percent is considered nonreactive.
- 0.04 percent to 0.12 percent is considered moderately reactive.
- 0.12 percent is considered highly reactive.

ASTM C 1260 and ASTM C 1293 are the two recommended tests for ASR (ASTM C 1293 is generally considered to be more representative of field performance). To supplement these tests, a petrographic evaluation of a given aggregate (ASTM C 295) is also suggested, but not required. A thorough petrographic evaluation, performed by a skilled petrographer, provides useful information about the types and amounts of minerals present in an aggregate, and can be used to identify a wide range of reactive components. However, because of inherent difficulties in identifying all potentially reactive phases within an aggregate, petrographic analysis findings alone should not be used to accept or reject a given aggregate, but rather to supplement the findings of other laboratory evaluations. Field performance histories of aggregates, supplemented with petrographic analysis of field concrete (ASTM C 856) containing the subject aggregate, also can provide useful information when considering future use of selected aggregates in new construction. However, as in the case of petrographic analysis of aggregates (ASTM C 295), field performance evaluations should not be used solely to accept or reject a given aggregate for use in new structures.

2.4   METHODS OF MITIGATING ASR

This section briefly describes common methods of mitigating or preventing ASR in new and existing concrete structures. The main focus is on minimizing ASR expansion in new concrete, with less emphasis on methods of extending the service life of structures already affected by ASR.

2.4.1   Minimizing or Preventing ASR in New Concrete

The most common methods of minimizing the risk of expansion resulting from ASR are discussed next, including:

- Using nonreactive aggregates.
- Limiting the alkali content of concrete.
- Using supplementary cementing materials.
- Using lithium compounds.

Using Nonreactive Aggregates

Using nonreactive aggregates is certainly a viable method of preventing ASR-induced damage. However, to use this approach, one must have a very high level of confidence that the subject aggregates to be used are, in fact, nonreactive. To confirm nonreactivity, the aggregates must be tested strictly (e.g., using ASTM C 1260 and ASTM C 1293), good quality control ensured, and, preferably, field performance well-documented. If the above conditions are met, such aggregates may be used without special precautions. However, given that these conditions often are not met, and given that some aggregates that were believed to be nonreactive (based on testing methodologies available at the time of construction) have caused damaging ASR expansion in field structures, further precautions should be taken in some situations. Instances that warrant such extra caution, even when using aggregates believed to be nonreactive, include the design of critical structures (e.g., prestigious structures or those with an extended design life) and the construction of structural elements exposed to a very aggressive environment (e.g., structures exposed to seawater or deicing salts, which may provide an external source of alkalis). The use of a suitable SCM is an example of taking special precautions with aggregates presumed to be nonreactive.

Limiting the Alkali Content of Concrete

Limiting the alkali content of concrete mixtures below some threshold value is generally effective in preventing ASR-induced damage, but this approach is not always effective by itself. For example, aggregates that are durable at relatively low alkali contents may become more reactive when exposed to higher alkali contents under field conditions, where unanticipated high concentrations of alkalis may result from exposure to deicing salts, alkali release from aggregates, drying gradients (resulting in alkali migration), and other field effects. For example, Stark (1978) reported increases in soluble alkalis from 1.1 to 3.6 kg/m^3 Na$_2$O$_e$ close to the surface of some highway structures. Additional information on limiting the alkali content of concrete is provided in section 2.2.1.

Using Supplementary Cementing Materials

The use of SCMs to control ASR in concrete is the most common mitigation measure used in concrete construction. The benefits of properly using SCMs include not only ASR mitigation, but also improved resistance to other durability problems, including sulfate attack, corrosion of reinforcing steel, and freezing and thawing. The benefits related to ASR mitigation are both physical in nature, specifically by reducing permeability, and chemical, where SCMs affect pore solution alkalinity, alkali binding, and other parameters. This section briefly discusses minimizing the risk for ASR-induced damage by the prudent use of SCMs, including ASTM C 618 class C or F fly ash, ASTM C 989 ground-granulated blast-furnace slag (GGBFS), ASTM C 1240 silica fume, and combinations of SCMs (ternary blends). Other

industrial byproducts or natural pozzolans (e.g., rice husk ash, calcined clay, metakaolin, etc.) have also shown effectiveness in controlling expansion caused by ASR. However, their effectiveness should be evaluated through an appropriate testing program. CSA standard practice A23.2-28A is the only current standardized approach for evaluating the effectiveness of such materials.

Fly ash is one of the most commonly used SCMs in the world for several reasons, including the economic and technical benefits. To control ASR, the following issues affect the efficacy of a given fly ash:

- Dosage of fly ash (typically as a mass replacement of cement).
- Chemical composition of fly ash (especially lime (CaO) content and Na_2O_e content).
- Reactivity of the aggregate.
- Alkali content of the concrete (from portland cement).

Perhaps the most important parameter affecting the ability of fly ash to control ASR expansion is the CaO content of the ash (Shehata and Thomas, 2000). Generally, lower lime ashes are more effective than higher lime ashes in controlling ASR, mainly because of the higher alkali-binding capacity of concretes containing lower lime ashes (Shehata, et al., 1999). Specifically, fly ash lower in CaO contains more silica that contributes to a C-S-H structure with a lower calcium to silicon ratio, which imparts a negative surface charge, leading to the absorption of cations, especially alkalis (Glasser, 1992). In addition, low-calcium ashes are more effective in controlling ASR because the alkalis contained in the ash are generally not available to the pore solution (Diamond, 1981), whereas high-calcium ashes tend to have more readily available alkalis. Although higher lime ashes can still be used to combat ASR, significantly higher dosages may be needed, especially when using highly reactive aggregates.

GGBFS is also commonly used to mitigate ASR and is typically used in higher dosages than fly ash, typically 35 to 50 percent (by mass of cement) and, in some cases, in even higher dosages. The specific dosage needed to mitigate ASR in a given concrete mixture depends on the reactivity of the aggregate and the total alkali content of the concrete. Slag, which is high in silica, results in reduced formation of CH and produces C-S-H with a higher silica to calcium ratio (Odler, 2000), thereby increasing the alkali-binding capacity of concrete (similar to low-calcium fly ash); however, only limited research has been performed on this topic (Uchikawa, et al., 1989).

Silica fume has not been used as frequently as fly ash and slag to control ASR. Although the efficacy of silica fume in minimizing the risk of ASR-induced damage depends on the reactivity of the aggregate, it appears to depend more on the total amount of alkalis available within the concrete. Thus, dosing silica fume based on the total alkalis within a given concrete mixture has been proposed in recent years (Thomas and Bleszynski, 2000; CSA, 2004), with the required silica fume dosage ranging between the lower and upper limits shown below (based on required levels of prevention):

Lower limit: Minimum % SF = 2 x (alkali contributed by portland cement)
Upper limit: Minimum % SF = 3 x (alkali contributed by portland cement)

Where: % SF is the percentage of silica fume (by total mass of cementitious material)
the alkali contributed by portland cement is expressed as kilograms of Na_2O_e per cubic meter of concrete

For highly reactive aggregates, the amount of silica fume required to control ASR (e.g., 10 percent) may be in excess of the typical dosage used in concrete construction, making it difficult for use in field applications (mainly because of workability concerns, high water and superplasticizer demand, and shrinkage problems). For such cases, it generally is more effective to use silica fume in conjunction with

another SCM, such as fly ash or slag, to reduce the required amount of silica fume and to improve constructability attributes. The use of these combinations of SCMs, known as ternary blends, is discussed next.

Ternary blends of cementitious materials have gained in popularity in recent years, either through the use of a blended cement (type IP or IS) in conjunction with another SCM or through the use of plain cement with two SCMs. The benefits of such combinations may improve the economic situation, workability, early strength development, and durability properties. When considering ternary blends to control ASR, combining two or more SCMs may reduce the quantities that would otherwise be used individually as the combined effects are synergistic in their ability to control ASR. For example, concrete mixtures with relatively low quantities of silica fume (4 to 6 percent), combined with moderate levels of slag (20 to 35 percent) or fly ash (class F or class C), were found to be very effective in controlling the expansion of highly reactive aggregates (Bleszynski, et al., 2000; Shehata and Thomas, 2002), as illustrated in Figure 10.

Using Lithium Compounds

Using lithium compounds, especially $LiNO_3$, is a viable approach to controlling ASR-induced damage. Because Chapter 3 provides a comprehensive review of research performed on using lithium compounds to mitigate ASR, no additional discussion is provided in this section. Chapter 4 provides an overview of selected case histories where lithium compounds have been used for both new and existing concrete structures.
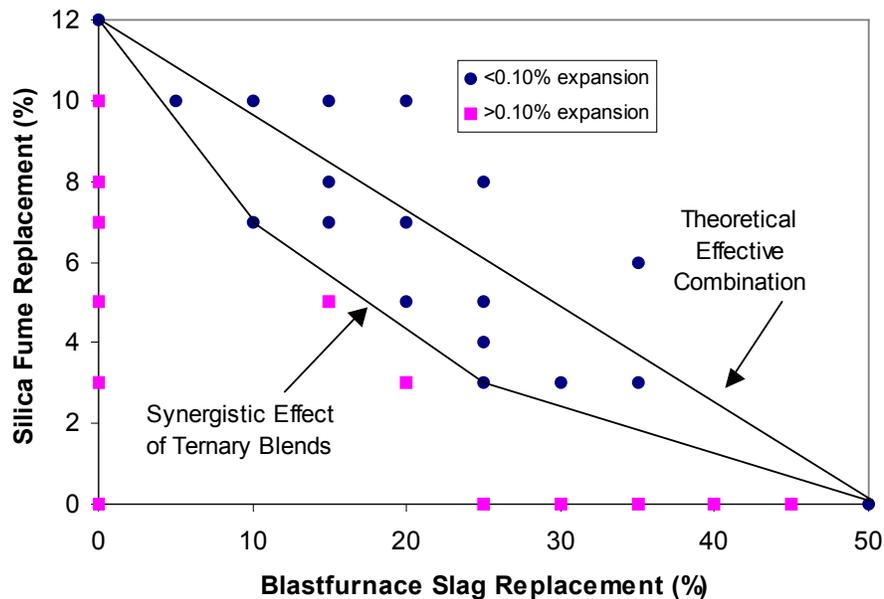
Figure 10. Synergistic Effects of Ternary Blends in Controlling ASR Expansion Using ASTM C 1260 (After Bleszynski, et al., 2000).

2.4.2   **Mitigating ASR in Existing Concrete**

When ASR-induced expansion and damage has already manifested itself in a field structure, there are some available techniques that can help extend the service life of the structure, as described in detail in CSA A684-00, *Guide to the Evaluation and Management of Concrete Structures Affected by Alkali-Aggregate Reaction*. To minimize future damage to such structures:

- Provide adequate or improved drainage (to minimize availability of moisture).
- Apply claddings or coatings to further limit ingress of moisture.
- Treat existing cracks to minimize future expansion (and direct ingress of moisture, deicing salts, etc.).
- Avoid future use of deicing salts that will increase alkali content within the structure.
- Restrain or confine expansion of structural element.
- Chemically suppress ASR using lithium compounds (see Chapter 4 for case studies and Chapter 5 for guidelines for mitigation techniques).

2.5 SPECIFICATIONS

There are numerous specifications, recommendations, and guidelines for avoiding ASR in new construction or managing it in existing structures, including national specifications from Canada, Australia, the Republic of South Africa, France, the United Kingdom (UK), and many other European nations. Within the United States, there are guidelines from the American Concrete Institute, a guide specification from the Portland Cement Association, and individual specifications from State highway agencies and other government bodies. A summary of all the above specifications is beyond the scope of this report; however, the overall approach to specifying preventive measures to control ASR in new concrete structures can be placed in two categories: (1) performance-based specifications, and (2) prescriptive specifications.

Performance-based specifications dictate what tests should be conducted on a given aggregate to determine its potential reactivity and usually what tests should be run to assess methods of mitigating aggregate reactivity, if needed. An example is a specification that states that aggregates must pass ASTM C 1260, ASTM C 1293, or both, where the term "passing" would be linked to specific expansion limits (e.g., 0.10 percent in ASTM C 1260 or 0.04 percent in ASTM C 1293). Many State highway agencies and other agencies and organizations use these types of specifications for ASR, although all do not currently specify the use of ASTM C 1260 and ASTM C 1293.

Prescriptive specifications actually dictate what materials (and mixture proportions) must be used to control ASR. For example, specifications of this type limit the alkali content of the cement or concrete mixture and specify minimum required dosages of SCMs or lithium compounds.

Various agencies and organizations use different combinations of performance and prescriptive specifications. Perhaps the most progressive and comprehensive specifications for ASR are those recently adopted by CSA, where the aggregates are categorized first according to their reactivity based on either ASTM C 1293 or C 1260. The risk of deleterious ASR expansion develops in the structure and the prevention level thus required (i.e., W (mild) to Z (exceptional), Table 3) is then established as a function of the aggregate reactivity, exposure condition, and size of the element and required service life of the structure. The guidelines are shown in Table 3, which includes the minimum dosages of SCMs required for specific risk levels. This approach considers key parameters previously described in this chapter, such as the CaO content of fly ash and the total alkali content of the mixture when dosing silica fume. The approach also allows for the use of natural pozzolans and ternary blends. Although lithium compounds are not included in the current CSA guidelines, it is expected that the next version of the specifications will allow for the use of lithium salts and will provide specific guidelines on prescribed dosages.

Table 3. CSA Guidelines for Controlling ASR in New Concrete (CSA, 2000a).

Type of SCM	Total Alkali Content of SCM (% Na$_2$O$_e$)*	Chemical Composition Requirement (% oxides)	Cement Replacement Level (% by mass)[a]		
			Prevention Level W (mild)	Prevention Level X (moderate)	Prevention Levels Y and Z (strong–Y) (exceptional–Z)
Fly Ash	< 3.0	CaO < 8%	≥ 15	≥ 20	≥ 25
		CaO = 8%–20%	≥ 20	≥ 25	≥ 30
		CaO > 20%	See note *b*	See note *b*	See note *b*
	3.0–4.5	CaO < 8%	≥ 20	≥ 25	≥ 30
		CaO = 8% - 20%	≥ 25	≥ 30	≥ 35
		CaO > 20%	See note *b*	See note *b*	See note *b*
	> 4.5		See note *b*		
Blast Furnace Slag	< 1.0[b]	None	≥ 25	≥ 35	≥ 50
Silica Fume	< 1.0[b]	SiO$_2$	2.0 x alkali content[c]	2.5 x alkali content[c]	3.0 x alkali content[c]
Natural Pozzolans	Natural pozzolans that meet the requirements of CSA A23.5 may be used provided that their effectiveness in controlling expansion due to ASR is demonstrated according to CSA Recommended Practice A23.2-28A.				
Ternary Blends	When two or more SCMs are used together to control ASR, the minimum replacement levels given in Table 5 of CSA, 2004 for the individual SCMs may be reduced partially, provided that the sum of the parts of each SCM is 1. For example, when silica fume and slag are combined, the silica fume level may be reduced to one-third of the minimum silica fume level given in Table 5, provided that the slag level is at least two-thirds of the minimum slag level given in Table 5.				

* Na$_2$O$_e$ = sodium oxide content = Na$_2$O + 0.658 * K$_2$O

a   To control the total alkali content of the concrete mixture, the maximum alkali content of the cement used in combination with any SCMs should be < 1.0 percent Na$_2$O$_e$.

b   In the presence of reactive or potentially reactive aggregates, blast furnace slag and silica fumes with alkali contents > 1.0 percent Na$_2$O$_e$, and fly ash with alkali contents > 4.5 percent Na$_2$O$_e$ and/or with CaO contents > 20 percent may be used when their effectiveness in reducing expansion due to ASR is demonstrated in accordance with CSA Recommended Practice. In this respect, test results have indicated that higher alkali fly ashes (but not high CaO ashes), when used in large quantities (e.g., > 50 percent as cement replacement by mass), can significantly reduce expansion due to ASR.

c   The minimum level of silica fume (as a percentage of material content) is calculated on the basis of the alkali content of the concrete (expressed as kg/m^3 Na$_2$O$_e$), but in cases where silica fume is the only SCM to be used, the silica fume content should be 7.0 percent by mass.

2.6   CONCLUSIONS

This chapter provided an overview of ASR in concrete, including basic mechanisms, relevant test methods, mitigation methods, and specifications. It provides the necessary background and technical basis for better understanding the role of lithium compounds in controlling ASR, as described in the remainder of this report.

CHAPTER 3   LITHIUM COMPOUNDS FOR CONTROLLING ASR

3.1   INTRODUCTION

This chapter reviews research to date on using lithium compounds to control ASR. Included are discussions on the basic chemistry and production of lithium compounds, and the mechanisms by which lithium compounds control ASR. It also provides a critical review of various laboratory evaluations of lithium, including the effects of lithium on ASR and on other concrete properties. Significant emphasis is placed on combining lithium technology with other more traditional materials, including fly ash and slag.

The information and data presented in this chapter are limited to laboratory evaluations using lithium compounds. Chapter 4 summarizes various case studies of actual field applications of lithium compounds to control or mitigate ASR in new and existing concrete structures. Guidelines are provided later in this report on how to efficiently test, specify, and use lithium compounds.

3.2   THE BASICS OF LITHIUM

Lithium is an alkali metal found in Group IA of the periodic table and has an atomic number of 3. Lithium is a soft, silver-white metal and is the lightest dense metal, with a density about half that of water (0.53 g/cm^3). Lithium is a very reactive metal because of its tendency to expel its outer electron (it has a valence of $+1$). It does not occur freely in nature, but rather it is bound in stable salts or minerals.

The most common sources of lithium are pegmatite rocks, which are coarse-grained granites composed of quartz, alkali feldspar, and possibly mica, and salt brine lakes. The main lithium-bearing minerals include spodumene, petalite, amblygonite, lepidolite, and eucrypite; the chemical compositions of these minerals are shown in Table 4. The table also includes the location of major mineral deposits, although other significant deposits have also been identified worldwide.

Table 4. Principal Lithium Minerals and Their Sources (After Lumley, 1997).

Mineral	Formula	Locations of Deposits (in alphabetical order)
Spodumene	$Li_2O \cdot Al_2O_3 \cdot 4SiO_2$	Australia, Brazil, Canada, China, Russia, United States
Petalite	$Li_2O \cdot Al_2O_3 \cdot 8SiO_2$	Australia, Brazil, Namibia, Russia, Sweden, Zimbabwe
Amblygonite	$LiAl(PO_4)(F,OH)$	Brazil, Canada, Mozambique, Namibia, Rwanda, South Africa, Surinam, Zimbabwe
Lepidolite	$K_2(Li,Al)_{5-6}\{Si_{6-7}Al_{2-1})_{20}\} (OH,F)_4$	Brazil, Canada, Namibia, Zimbabwe
Eucryptite	$Li_2Al_2O_3 \cdot 2SiO_2$	Zimbabwe

Of the minerals shown in Table 4, spodumene is the most common lithium ore. However, because extracting lithium from spodumene is an energy-intensive process (requires heating to approximately 1100 °C), most lithium production has shifted in recent years to the use of subsurface brine deposits (Ober, 2000). Lithium is extracted from brine sources by solar evaporation of concentrated brine, a process that is significantly less expensive than extracting lithium from ore deposits. Lithium is obtained from brine deposits found mainly in North and South America—Chile and Argentina are major sources (Ober, 2002).

Lithium carbonate (Li_2CO_3) is the most important lithium compound produced from brine and ore deposits, and in most cases, other lithium compounds require Li_2CO_3 as a feedstock for further processing (Ober, 2002). In addition to Li_2CO_3, other commonly produced lithium compounds include lithium nitrate ($LiNO_3$,) lithium hydroxide and monohydrate ($LiOH$, $LiOH \cdot H_2O$), lithium chloride ($LiCl$), lithium fluoride (LiF), and lithium sulfate (Li_2SO_4).

3.3 USING LITHIUM COMPOUNDS TO CONTROL ASR

3.3.1 History and Background

The use of lithium compounds to control expansion due to ASR was first reported by McCoy and Caldwell (1951). They conducted a comprehensive investigation on the potential use of chemical admixtures to prevent or minimize ASR-induced expansion and damage. More than 100 different compounds were included in this study, including metallic salts, acids, oils, organic chemicals, proteins and proprietary admixtures. McCoy and Caldwell conducted a series of ASTM C 277 mortar bar tests (using Pyrex glass as the reactive aggregate) and reported that the most promising candidates in reducing ASR expansion were lithium compounds ($LiCl$, Li_2CO_3, LiF, Li_2SiO_3, $LiNO_3$, and Li_2SO_4), which essentially eliminated expansion after 8 weeks storage at 38 °C, provided they were used in sufficient quantity.

For about 40 years after McCoy and Caldwell published the findings of their study, only a few studies were conducted on the effectiveness of lithium compounds to control ASR. In the past 10 years, however, there has been resurgence in the interest in lithium-bearing compounds. This is reflected in an increase in scientific publications on the topic and field applications of lithium-based products.

3.3.2 Mechanisms of ASR Suppression by Lithium Compounds

As previously mentioned, McCoy and Caldwell (1951) used mortar bars prepared with high-alkali cement and reactive glass aggregate to demonstrate the effectiveness of lithium additives in reducing expansion associated with ASR. These results and the results of more recent research (Chatterji, 1987; Sakaguchi, et al., 1989; Stark, 1992; Lumley, 1997; Ramachandran, 1998; Diamond, 1999; Thomas, et al., 2000, Collins, et al., 2004; Tremblay, et al., 2004), that show a reduction in expansion by ASR in the presence of lithium-containing additives, have generated much interest in using these compounds in concrete structures. While it is known that some lithium additives are effective at reducing expansion in concrete affected by ASR, the mechanism or mechanisms by which these additives reduce expansion are not clearly understood. Without understanding the control mechanism, it may be difficult to predict the effectiveness of a particular chemical additive or dosage, or to predict the duration of its control. However, several mechanisms have been proposed to describe the effect of lithium, including:

- Lithium may alter the ASR product composition, resulting in a less expansive product.
- Lithium may reduce silica dissolution.
- Lithium may decrease the repolymerization of silica and silicates.
- Lithium may reduce repulsive forces between colloidal ASR gel particles.

Proposed Mechanism: Formation of Less Expansive Product

Several researchers have proposed that a less expansive or nonexpansive product may form during alkali-silica reaction in the presence of lithium. Stark (1992) proposed that during the alkali-silica reaction, in the presence of a sufficient concentration of lithium, a lithium-alkali (and possibly calcium) silicate forms that has little or no capacity for expansion. Because the research suggests that a minimum lithium threshold content is required to inhibit expansion, Stark reasoned that the product must contain a minimum proportion of lithium to be nonexpansive. Similarly, Diamond and Ong (1992) showed that, as the amount of lithium present in the gel product increased in proportion to the amount of sodium and potassium present, mortar bar expansion decreased, confirming the work of Stark (1992).

Lawrence and Vivian (1961) suggested that a lithium silicate forms by ASR in the presence of lithium, and that this product is less soluble and more stable than the ASR product in the absence of lithium. Due

to its stability, it was proposed that the resulting LiOH silica complex may form an insoluble surface layer, protecting silica from further attack by other alkalis (Lawrence and Vivian, 1961).

Lawrence and Vivian (1961) also showed that silica gel tended to be less reactive with NaOH with increasing concentrations of LiOH, to 2N LiOH equivalent in 2N NaOH equivalent solution. By measuring lithium and alkali concentrations in expressed pore solutions from mortar bars, Sakaguchi, et al. (1989) found that the concentration of lithium decreased with time, while alkali concentrations remained nearly constant. In the absence of lithium, the alkali concentration of the expressed pore fluid decreased over time, suggesting that the lithium-silica reaction is more favorable than the sodium-silica or potassium-silica reaction in mortar bars. According to this theory, the formation of a nonexpansive lithium-containing product would be favored over the formation of a more expansive product containing relatively greater concentrations of the alkalis sodium and potassium.

Others (Chatterji, 1987), however, disagree, stating that the reaction of silica with sodium is favored over the reaction of silica with lithium. In a system containing Na^+, K^+, and Li^+, the alkalis compete for adsorption at negatively charged sites on the silicate surface. Since adsorption affinity increases with bare cation radius, it is expected that sodium adsorption will be preferential to lithium adsorption, in disagreement with Sakaguchi (1989). Kurtis, et al. (1998; 2003), however, have proposed that strong field exchange behavior, where cations are in direct contact with a surface, may account for the preference of the alkali-silica reaction gel for Li^+ as compared to Na^+ and K^+, as described by Sakaguchi (1989).

Ramyar, et al. (2004) reported the results of a study to determine the chemical and morphological characteristics of reaction products from mortar bars, with/without lithium (LiF, Li_2CO_3 used in the mixing water) or fly ash, subjected to ASTM C 1260 test conditions. The use of fly ash and lithium-based admixtures resulted in significant reduction in mortar bar expansion, while expansion seemed to stabilize after 14 days for Li-bearing mortar bars. Also, observations using scanning electron microscopy (SEM) and energy dispersive X-ray microanalysis confirmed that the morphology of the crystalline reaction products was changed by the use of Li-bearing admixtures.

Mei, et al. (2004) studied the properties of alkali-silica reaction products formed from the reaction of silica particles in LiOH, KOH, or NaOH test solutions. They found that the water absorption capacity of the reaction products, when further exposed to relative humidity ranging from 25 to 100 percent, always increased as follows: KOH > NaOH > LiOH. The authors also evaluated the expansion of concrete microbar incorporating a highly reactive zeolitized perlite aggregate after autoclave treatment (at 150 °C) for a few days in water, LiOH, KOH, or LiOH+KOH solutions. The authors found that the use of LiOH (in the bar and the soak solution) can inhibit ASR expansion and cracking. Reaction rims surrounding the reactive silica and secondary reaction products were observed in both systems; however, "textured" (approximately crystalline) lithium-based silicates were formed when LiOH was present in the system. The authors proposed that since the charge density of Li+ is much higher than that of K+, the ion binding force of Li-Si is stronger than that of Li-K, thus forming lithium silicates (L-S-H) of nonexpansive character surrounding and protecting the reacting silica from further deleterious reaction with K ions.

Kawamura and Fuwa (2003) reported that adding lithium to mortar mixtures decreased the CaO/SiO_2 ratio in ASR gel. This ratio was found to decrease with increasing lithium dosages until a threshold lithium concentration was reached, above which the gel composition became essentially insensitive to further increases in lithium concentration. The link between the CaO/SiO_2 ratio in gel products and expansion was not clearly established in this study, but the direct impact of lithium on gel composition may eventually shed light on expansion mechanisms.

Proposed Mechanism: Suppression of Silica Dissolution

In examining the effect of various alkali-hydroxides on silica dissolution rate, Lawrence and Vivian (1961) found that the dissolution rate increased in this order:

$$KOH > NaOH > LiOH \qquad\qquad (4)$$

Wijnen, et al. (1989) found that the rate of silica dissolution decreased in a similar order and proposed that this rate decreases with increasing hydrated ion radius of the alkali metal cations in solution surrounding a silicate surface. Considering lithium, sodium, and potassium, the rate of silica dissolution would, then, be slowest in the presence of lithium, which has a larger hydrated ion radius than sodium which is, in turn, larger than potassium. Chatterji, et al. (1987) proposed that the size of the hydrated ion radius was important in determining the extent of chemical reaction during alkali-silica reaction, supporting research findings that degree of chemical reaction increased from lithium to sodium to potassium.

These results suggest that lithium may act to decrease the rate of silica dissolution, which would then limit the rate of product formation and potential for expansion. Over time, however, the concentration of dissolved silica for each alkali-hydroxide concentration examined by Lawrence and Vivian (1961) approached the same value, independent of alkali type, suggesting that lithium may reduce the rate of dissolution, not the solubility of silica. In examining silica gel in model pore solution, Collins (2002), however, found that silica concentration in solution decreased with increasing lithium concentration over a period from 1 hour to 28 days. The results of Collins (2002) may demonstrate, again, the significance of dosage. If, as Sakaguchi's (1989) results suggest, the lithium reaction with the silica or ASR gel is preferential to the reaction with sodium and potassium cations, local concentrations of lithium near the silica may decrease the rate of dissolution, effectively decreasing the rate of formation of the expansive gel.

Qi and Wen (2004) proposed that lithium hydroxide reduces the dissolution of silica and results in a different morphology of reaction products. The authors reported that a layer of lithium silicate forms on the surface of reactive aggregates, thereby reducing subsequent dissolution. This work was based on observing gel products and measuring expansions in solution testing (sol-gel test) in the presence and absence of lithium hydroxide. It was shown that [Li]/[Na+K] ratios in excess of 0.8 were required to reduce the expansion of opal in sol-gel testing by approximately 90 percent.

Collins, et al. (2004) analyzed slurries of silica gel and alkali solution at various ages to determine changes in concentration of solution phase species (Si, Na, Ca, and Li). Quantitative analysis showed that sodium and lithium were bound in reaction products found within the slurries. It was also noted that lithium may have been preferentially bound over sodium in at least one of the reaction products. From this research, it appeared that lithium additives either decreased silica dissolution or promoted precipitation of a silica-rich product (some of which may be nonexpansive) as the dissolved silica concentration decreased with increasing dosage of lithium nitrate or lithium chloride. Slurries prepared with LiCl and $LiNO_3$ evidenced a decrease in silica dissolution with a corresponding increase in additive amount, whereas slurries prepared with LiOH showed an opposite trend. The increase in silica dissolution in the case of LiOH did not translate to an increase in expansion in mortar bars prepared with LiOH. Therefore, it was proposed that expansion due to ASR in the presence of lithium was most likely not dependant upon the quantity of dissolved silica. The authors purport that the reduction in expansion when lithium is present may be due to the formation of a nonexpansive lithium-silicate complex.

Proposed Mechanism: Decreased Repolymerization

Based upon microscopy, elemental analysis, and surface chemistry principles, Kurtis, et al. (1998, 2003) have suggested that, in addition to decreasing the rate of silica dissolution, lithium may limit repolymerization of dissolved silica species into a gel, effectively reducing the potential for expansion. Using x-ray microscopy to examine the reaction of silica in model pore solution in the presence and absence of lithium, Kurtis, et al. (1998, 2000, in press) observed that significantly more gel product formed in samples containing no lithium than in those containing lithium. Companion results from elemental analysis showing a decrease in silicon concentration in solution indicated that the presence of lithium decreased silica dissolution to some extent, but the concentration of silicon in solution in the presence of lithium was on the order of the concentrations observed in the absence of lithium. These results suggested that the differences in behavior observed with lithium may be due more directly to changes in the amount of product formed rather than in the degree of reaction. Kurtis and Monteiro (2003) also propose that lithium yields a reduction in surface charge density of ASR gel.

If, as the research of Sakaguchi (1982) suggests, adsorption of Li^+ is favored over Na^+ and K^+ adsorption, a physical mechanism for preventing gel repolymerization may exist. Iler (1956) postulates that the highly hydrated lithium ions are not adsorbed as near to the silicate surface as a cation which has a smaller hydrated radius, such as sodium or potassium. Thus, Kurtis, et al. (1998, 2000, in press) proposed that the net repulsion between the silicate particles remains high in the presence of lithium. As a result, it is theorized that when lithium is present in sufficient concentrations, repolymerization into a potentially expansive gel does not occur. The effect of the lithium should, then, depend upon its relative concentration in the solution as well as the favorability of the silica-lithium reaction.

Proposed Mechanism: Reduction in Repulsive Forces Within Product

Prezzi, et al. (1997) proposed the use of the electrical double layer (EDL) theory to explain the expansion of the ASR gel, and the theory was extended to describe a proposed mechanism by which chemical additives, including lithium salts, may inhibit expansion (Prezzi, 1998). Applying these principles, the ASR gel is assumed to act as a colloid composed of negatively charged particles. According to the theory, swelling of the gel is attributed to double-layer repulsion effects between the colloidal particles. According to EDL theory, the valence and hydrated radius of cations in the colloid are important factors in determining the expansion of the gel. The double-layer theory predicts that an ASR gel containing larger concentrations of cations with larger valences will exhibit less expansion. That is, higher proportions of trivalent (e.g., Al^{3+}) and bivalent (e.g., Ca^{2+}) cations relative to monovalent cations (e.g., Na^+, K^+, and Li^+) should result in less expansive gels. Results from a series of mortar bar tests performed by Prezzi, et al. (1998) agree with double-layer predictions according to cation valence. These tests showed expansion increasing with cation charge in the order:

$$Al^{+3} < Ca^{+2} < Mg^{+2} < Li^+ < K^+ < Na^+ \qquad (5)$$

However, it is important to recognize that the size of the hydrated ion radius also will affect expansion as predicted by EDL theory. As stated previously, the radius of the hydrated lithium ion is larger than those for sodium or potassium. Therefore, EDL theory predicts that lithium will produce greater expansion compared to these other monovalent cations, not reduce expansion, as is generally evident. Therefore, additional mechanisms may need to be considered to explain the reduction in gel expansion associated with the use of lithium additives.

According to Prezzi (1997, 1998), a decrease in surface charge density ($-\sigma$) effectively reduces the pressure (ΔP) generated by ASR gel expansion:

$$\Delta P = C_o RT \left(y_o + \frac{1}{y_o} - 2 \right) \tag{6}$$

Where: C_o is the bulk electrolyte concentration

R is the molar gas constant

T is the absolute temperature and

$$y_o^{0.5} = 4 \tan^{-1} \left[\frac{-\sigma}{2Fy_o} \left(\frac{\beta}{C_o} \right)^{0.5} \right] \tag{7}$$

Where: F is the Faraday constant

$\beta = 1.084 \times 10^{16}$ m/mol at 25 °C

σ is expressed per unit area.

The presence of bivalent and trivalent cations provided by chemical salts has been theorized to lower surface charge density of the ASR gel as compared to systems where more monovalent cations are present. Rodrigues, et al. (2001; unpublished) have performed potentiometric titrations to examine how the surface charge density of silicates, including ASR gel, is affected by the presence of various chemical salts, including LiCl. Their work showed that in a system with both sodium and lithium ions present, the surface charge density of opal (2001) and alkali-silica gel (obtained from an ASR-affected dam) (unpublished data) were decreased in the presence of LiCl, as compared to NaCl. A decrease in the repulsive forces between colloidal particles of ASR gel in the presence of lithium would reduce expansive pressure generated by swelling of the gel. However, Rodrigues (2001) also observed that KCl produced an even greater reduction in surface charge density than LiCl. These results do not coincide with the findings of Prezzi, et al. (1998) described above and suggest that further research is necessary.

3.3.3 Laboratory Studies Using Lithium to Control ASR: A Critical Review

This section reviews research to date on using lithium to control ASR, beginning with the initial investigation by McCoy and Caldwell and proceeding to recent studies. Because most of the laboratory (and exposure site) studies have dealt with lithium compounds as an admixture, only limited information is available on post-treating hardened concrete with lithium to mitigate further expansion.

Laboratory Research on Using Lithium as an Admixture

Many laboratory studies have focused on the use of lithium compounds to control ASR, some of which are discussed in section 3.3.2, as related to proposed mechanisms. The studies span more than 50 years and have used different test methods, lithium compounds, cementitious materials, and aggregates, making it somewhat difficult to compare one study directly to another. However, general comparisons are possible and trends in test results can be identified. These then can be synthesized and incorporated into guidelines and recommendations for efficiently testing, specifying, and using lithium to control ASR. Of particular interest in the review that follows is the documented dosage of lithium required to control ASR for aggregates of different levels of reactivity and for mixtures containing SCMs. Information is also provided on recommended methods of assessing lithium compounds in mortar and concrete, expanding upon the information provided in Chapter 2 on testing methodologies. At the end of this section, the main findings from the various studies will be summarized and incorporated into specific guidelines for using lithium in new concrete.

As previously discussed, McCoy and Caldwell (1951) were the first researchers to identify lithium compounds as effective admixtures in controlling ASR. Their study included the use of LiCl, Li_2CO_3, LiF, Li_2SiO_3, $LiNO_3$, and Li_2SO_4 at various dosages. Testing was performed according to ASTM C 227,

with Pyrex glass as the reactive aggregate. Each of the lithium compounds was found to be effective in minimizing expansion, provided that a high enough dosage was used.

Table 5. *Effects of Lithium Compounds on Mortar Bar Expansion (From McCoy and Caldwell, 1951).*contains the expansion data (at various ages) for mortar bars containing different lithium compounds, where the dosages listed are based on mass of cement. A more convenient and useful method of displaying this data is to express expansion as function of the lithium-alkali molar ratio. Figure 11. *Relative Expansion of Mortar Bars Containing Lithium Compounds (After McCoy and Caldwell, 1951).* shows the relative expansion of mortar bars containing lithium to a control without lithium (where a value of 1.0 reflects no effect on expansion), plotted against the lithium-alkali ratio (which is equal to the moles of lithium divided by the moles of sodium plus potassium). As the amount of lithium in mortar increased, the relative amount of expansion decreased. The data indicated that a molar ratio of lithium to alkali of 0.74 or above was sufficient to suppress expansion efficiently.

Table 5. Effects of Lithium Compounds on Mortar Bar Expansion (From McCoy and Caldwell, 1951).

Lithium Salts	% Addition (by mass of cement)	% Reduction in Expansion			
		2 weeks	4 weeks	6 weeks	8 weeks
Lithium Chloride	0.50	75	43	34	34
Lithium Chloride	1.00	90	91	90	88
Lithium Carbonate	0.50	89	68	67	62
Lithium Carbonate	1.00	94	94	93	91
Lithium Fluoride	0.50	92	92	89	82
Lithium Fluoride	1.00	97	99	98	98
Lithium Nitrate	1.00	81	72	31	20
Lithium Sulfate	1.00	88	72	53	48
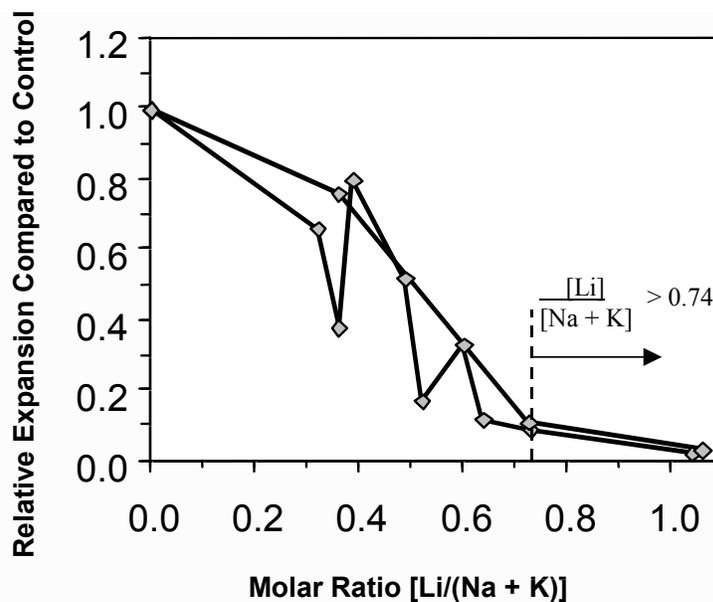
Figure 11. Relative Expansion of Mortar Bars Containing Lithium Compounds (After McCoy and Caldwell, 1951).

After the early findings of McCoy and Caldwell, it was approximately 40 years before research on controlling ASR with lithium compounds continued in earnest. A series of studies were initiated in the late 1980s and early 1990s, and more recent studies have been conducted or are still in progress. Several of these studies are reviewed briefly below. Most of these studies have used ASTM C 227 as the method of testing lithium, but some of the more recent investigations have used the CPT (ASTM C 1293) and a modified version of the accelerated mortar bar test (ASTM C 1260).

As described in section 3.3.2, Sakaguchi, et al. (1989) proposed that the formation of a nonexpansive lithium-containing product would be favored over the formation of a more expansive product containing relatively greater concentrations of the alkalis, sodium and potassium. Their study included the use of LiOH•H_2O, lithium nitrite ($LiNO_2$), and Li_2CO_3 in mortar bars containing Pyrex glass, and LiOH•H_2O in mortar bars containing a reactive pyroxene andesite sand from Japan. All of the lithium compounds were effective in reducing expansion, with increasing lithium dosages resulting in decreased expansion. For the tests performed using LiOH•H_2O with the reactive aggregate, the reductions in expansion are shown in Table 6. A molar ratio of 0.9 was sufficient to completely suppress expansion.

Table 6. Effects of Lithium Hydroxide Monohydrate on Mortar Bar Expansion
(After Sakaguchi, et al., 1989).

Dosage of LiOH•H2O (by mass of cement, %)	Molar Ratio [Li]/[Na+K]	Expansion after 1 Year (%)	Relative Expansion Compared to Control (%)
0.00	0	0.88	100
0.27	0.3	0.86	97
0.55	0.6	0.48	55
0.83	0.9	0.05	6
1.11	1.2	0.04	5

Ohama, et al. (1989) investigated the use of LiOH•H_2O, LiF, and Li_2CO_3 in mortar bars containing opaline amorphous silica as the reactive aggregate. The bars were cured for 1 day at 20 °C and 100 percent RH, then subjected to autoclave curing at 128 °C under a pressure of 2.5 kgf/cm^2 for 4 hours, after which the bars were cooled back to 20 °C and measured for expansion. Li_2CO_3 only slightly reduced expansion, whereas LiF and LiOH•H_2O at 0.5 percent and 0.7 percent (based on mass of cement), respectively, reduced the expansion to about half of that of the control. Because of the extreme conditions typical of high-temperature autoclaving, it may be difficult to relate these results to other laboratory investigations.

Considerable research on using lithium compounds to control ASR was performed under SHRP, with the relevant findings reported by Stark (1992) and Stark, et al. (1993). Because of the large scope of the SHRP study, only selected aspects of the study are discussed here. Stark and his coworkers produced and tested mortar bars according to ASTM C 227, using LiF and Li_2CO_3 and confirmed the efficacy of lithium in suppressing expansion, provided that a high enough dosage was used. Table 7 summarizes the results of these tests, which used a highly reactive natural aggregate (rhyolite). Expansion was essentially controlled at molar ratios (lithium to sodium plus potassium) of 0.6 for LiF and 0.92 for Li_2CO_3.

When testing the same rhyolitic aggregate as above and a less reactive granite gneiss, Stark, et al. (1993) reported that molar ratios in the range of 0.75 to 1 were needed to suppress expansion adequately when using ASTM C 1260 (and adding LiOH to the 1N NaOH soak solution). Stark also recognized a

pessimum effect, in which an insufficient dosage of lithium actually increased expansion (compared to a control). This was attributed to an increase in the alkalinity (OH$^-$ concentration) of the pore solution, which is triggered by the addition of lithium (especially LiOH). As discussed later in this section, other forms of lithium, such as LiNO$_3$, do not tend to raise the pH of the pore solution in concrete, thereby eliminating the pessimum effect.

Diamond and Ong (1992) reported several interesting findings when using LiOH in a series of mortar-bar tests. They reported that a substantial portion of the lithium (> 40 percent) added during mixing was removed rapidly from solution, presumably absorbed by the hydrating cement, and that this absorption was greater for lithium than for sodium or potassium. When mortar bars were cast and tested according to ASTM C 227, a [Li]/[Na+K] molar ratio of 1.2 was required to suppress expansion for mortar containing cristobalite as the reactive aggregate, but this dosage was not quite sufficient to suppress the expansion of similar bars containing beltane opal as the reactive aggregate. The amount of lithium required to suppress ASR-induced expansion was higher for this study than for other published studies, although the reasons for this difference are not clear. Diamond and Ong also confirmed the pessimum effect that was observed by Stark (1992), in which low and moderate amounts of LiOH actually increased expansion, compared to a control mortar without lithium.

Table 7. Effects of Lithium Compounds on Mortar Bar Expansion (After Stark, 1992).

Lithium Compound	Dosage of Lithium Compound (by mass of cement, %)	Molar Ratio [Li]/[Na+K]	Expansion After 1 Year (%)	Relative Expansion Compared to Control (%)	Expansion After 3 Years (%)	Relative Expansion Compared to Control (%)
Control	0	0	0.62	100	0.63	100
LiF	0.25	0.3	0.59	95	0.71	112
	0.50	0.6	0.06	10	0.06	10
	1.00	1.2	0.02	3	0.02	3
Li$_2$CO$_3$	0.25	0.23	0.61	98	0.63	100
	0.50	0.46	0.50	81	0.58	92
	1.00	0.92	0.04	6	0.05	10

In one of the few studies using LiNO$_2$, Qinghan, et al. (1995) tested mortar bars containing reactive andesite aggregate. The mortar bars were cured for 1 day at 20 °C, then placed in an autoclave under a pressure of 0.28 MPa for 4 hours. After they were removed from the autoclave, the bars were placed in a curing container at 20 °C for four months, then at elevated temperature (40 °C) for long-term measurements. A [Li]/[Na+K] molar ratio of 0.8 was found to reduce expansion significantly for mortars with very high alkali contents (2 percent by mass of cement), but more lithium (based on molar ratio) was needed for mortars with lower alkali contents.

Lumley (1997) used the CPT (ASTM C 1293) to assess the efficiency of LiOH•H2O, LiF, and Li$_2$CO$_3$ in reducing expansion due to ASR. A calcined flint cristobalite was used as the reactive aggregate, and researched a range of lithium dosages. The findings were in broad agreement with most published literature, suggesting that a ratio of equivalent Li$_2$O to equivalent Na$_2$O of 0.33 to 1 (by mass) or a [Li]/[Na+K] molar ratio of 0.62 was sufficient to inhibit expansion.

An important trend in recent years has been the emergence of LiNO$_3$ as the preferred lithium compound in controlling ASR. Stokes, et al. (1997) reported that a major advantage of LiNO$_3$ over other lithium compounds is that LiNO$_3$ does not increase the pH of the pore solution, thereby eliminating the risk of the

pessimum effect as described earlier. Using LiNO$_3$ avoids this effect because its addition to cement paste results in an increase in the lithium and nitrate ion concentrations of the pore solution with no significant increase in the hydroxyl ion concentration (Stokes, et al., 1997). The implication of this behavior was confirmed in this study in that all mortar bars containing LiNO$_3$, regardless of dosage, expanded less than the control, which was not the case for previous studies using other lithium compounds (e.g., LiOH). Another important advantage of using LiNO$_3$ as an admixture is that it is closer to a neutral pH than other lithium compounds, making it safer to handle.

Bérubé, et al. (2004) evaluated the influence of LiNO$_3$ or a Li-bearing glass on the chemistry of the pore solution in low- and high-alkali cement pastes stored in sealed containers at different temperatures. For the mixtures incorporating the Li glass, the [Li+] concentration was found to increase with time, temperature, glass fineness, and the [Na$^+$+K$^+$] concentration in the pore solution. However, lithium was found to be released at a slow rate while the pH of the pore solution increased slightly, which could explain the limited effectiveness of the lithium glass tested in controlling ASR expansion (Tremblay, et al., 2004). The use of LiNO$_3$ resulted in a slight decrease in pH of the pore solution. It was also found that Li in LiNO$_3$-bearing systems was incorporated into the cement hydrates in greater proportions than Na and K, with Na being always incorporated in greater proportions than K, even in the absence of Li. For all mixtures incorporating LiNO$_3$, the [Li]/[Na+K] molar ratio in the pore solution was usually between 0.30 and 0.45 (i.e., corresponding to only about half of the original amount (0.74) introduced in the system). The authors reported that the overall chemistry of the pore solution and the cement hydrates appeared to not be significantly influenced by temperature, at least in the investigated range of 23 to 60 °C.

A comprehensive study was initiated at the Building Research Establishment (BRE) in 1994 on using lithium compounds (LiOH and LiNO$_3$) to control ASR. Blackwell, et al. (1997) reported on the preliminary findings and Thomas, et al. (2000) gave a more recent update on the status of the project, which includes over 150 concrete mixtures, laboratory testing (using ASTM C 1260 and ASTM C 1293), and exposure block testing at an outdoor site located at BRE in the UK. The program involved the use of several reactive UK aggregates and also included the use of fly ash and slag. Figure 12 summarizes the 3-year expansion data for concrete prisms for the most reactive aggregate, plotted in a similar format to allow comparison with McCoy and Caldwell's findings (Figure 11). A lithium to alkali molar ratio of approximately 0.70 was sufficient to control expansion when using LiNO$_3$, and a higher dosage, around 0.85 (molar ratio) was required for LiOH, mainly due to the impact of LiOH on pore solution pH (as previously discussed). The study also illustrated that the efficacy of lithium in reducing expansion is a strong function of aggregate type and that using low-calcium fly ash in conjunction with lithium increased reductions.
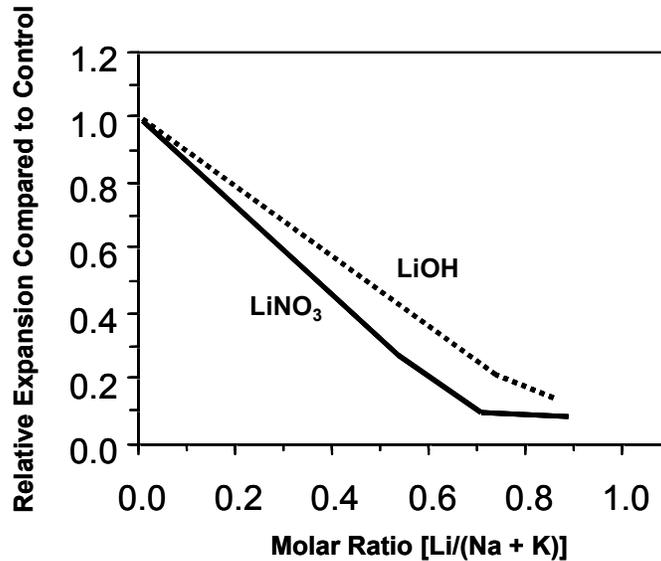
Figure 12. Relative Expansion of Concrete Prisms Containing Lithium Compounds.

Diamond (1999) provided further discussion of the work previously described by Stokes, et al. (1997), including additional insight into the role of $LiNO_3$ in suppressing ASR-induced expansion. He noted that $LiNO_3$ does not raise pore solution pH and demonstrated that the Li^+ ions in the pore solution were balanced mainly by NO_3^- ions and to a smaller extent by SO_4^{-2} ions. Diamond also illustrated that $LiNO_3$ tends to be removed from solution by hydration products, as do other lithium compounds, thus reducing the lithium available to suppress ASR expansion.

Collins, et al. (2004) studied the effect of three lithium additives ($LiNO_3$, LiCl, and LiOH) on the expansion of mortar bars made in accordance with ASTM C 227. While it was shown that all lithium additives were effective in reducing expansion below acceptable limits, different ratios of [Li]/[Na+K] were reported for each additive (i.e., approximately 0.6 for LiOH, 0.8 for $LiNO_3$, and 0.9 for LiCl).

Durand (2000) presented the results of extensive testing using $LiOH•H_2O$, LiF, Li_2CO_3, and $LiNO_3$ in concrete prisms following ASTM C 1293. Three different reactive aggregates from Canada (from Sudbury, Potsdam, and Sherbrooke) were used in conjunction with different dosages of the four lithium compounds. The results indicate that a molar ratio [Li]/[Na+K] of 0.83 was required to suppress expansion (below 0.04 percent at 2 years) for $LiOH•H_2O$, LiF, and Li_2CO_3 when using the Sudbury aggregate. A molar ratio of 0.72 was found to be sufficient when using $LiNO_3$ with the Sudbury aggregate. None of the lithium compounds, even when used at their highest dosages (1.66 molar ratio for $LiOH•H_2O$, LiF, Li_2CO_3 and 0.72 for $LiNO_3$), were able to reduce sufficiently the expansion of concrete containing the Sherbrooke aggregate (a metamorphic schist). The only lithium compounds (and dosages) that adequately controlled expansion of concrete containing Potsdam sandstone were $LiOH•H_2O$ and LiF, at molar ratios of 1.66. These findings confirm that the amount of lithium required to suppress expansion depends strongly on aggregate reactivity and also on the specific lithium compound used.

Thomas, et al. (2001) provided preliminary findings from a comprehensive study focusing on the combined use of lithium and fly ash to control ASR. Testing was performed using ASTM C 227 and ASTM C 441, using a highly reactive aggregate from New Mexico, and Pyrex glass. In addition, a modified version of ASTM C 1260 was used to investigate various combinations of lithium nitrate (30 percent solution), six fly ashes, and three cements. ASTM C 1260 was modified by adding $LiNO_3$ to the 1N NaOH soak solution to achieve the same lithium-alkali ratio as that used in the mortar mixture.

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However, recent unpublished studies have indicated that the results of this modified test method do not correlate well with the results of concrete expansion testing.

Tremblay, et al. (2004a, b, 2006a) presented the results of an extensive testing program using $LiNO_3$ in concrete prisms following ASTM C 1293. In that study, concrete prisms were made with 12 Canadian moderately to highly reactive aggregates of various petrographic natures at various alkali-to-lithium molar ratios. The authors found that the effectiveness of $LiNO_3$ against ASR was related more to the petrographic nature of the aggregate than to its degree of reactivity. Based on a 0.04 percent concrete prism expansion limit after 2 years at 38 °C and R.H. > 95 percent, the "efficient" molar ratios for $LiNO_3$ ranged from 0.56 to 0.74 for six aggregates, 0.93 to 1.11 for three aggregates, while a molar ratio of 1.11 (i.e., 150 percent of the standard dosage) was even found insufficient for three aggregates (Table 8).

Tremblay, et al. (2006b) evaluated the effectiveness of a modified version of the ASTM C 1260 (using various proportions of $LiNO_3$ in the soak solution, with/without lithium in the bar) for a selection of reactive aggregates of various types and reactivity levels from North America; their results are shown in Table 9, which is briefly outlined below:

- One-year concrete prism expansion obtained for the control concretes performed in accordance with the CPT Method CSA A23.2-14A (equivalent to ASTM C 1293).

- Fourteen-day expansion obtained for the control mortars performed in accordance with the Accelerated Mortar Bar Method CSA A23.2-25A (equivalent to ASTM C 1260).

- The minimum molar ratio ([Li]/[Na+K]) required to control ASR expansion based on CPT data (i.e., using a limit of 0.04 percent after 2 years of testing at 38 °C and R.H. > 95 percent).

- The minimum molar ratio ([Li]/[Na+K]) required to control ASR expansion based on modified ASTM C 1260 data (using two different limits, i.e., 0.10 percent or 0.08 percent after 14 or 28 days of immersion in 1N NaOH solution at 80 °C, respectively).

The limit of 0.08 percent at 28 days has been suggested by some as being a better indicator of the preventive effect of lithium nitrate against ASR. The results in Table 9 show that the minimum lithium-to-alkali molar ratio required from the CPT results ranges from 0.55 to greater than 1.11. Based on the modified ASTM C 1260 results (as purported in the previous version of the guidelines report), when no lithium is used in the bar, this ratio would vary from 0.23 to greater than 0.66 and from 0.33 to 0.73 using the 0.10 percent at the 14-day or 0.08 percent at the 28-day expansion limits, respectively. When 100 percent of the "standard" lithium dosage is used in the bar, the above ratios would vary from 0.18 to 0.45 and from 0.28 to 0.65 using, once again, 0.10 percent at the 14-day or 0.08 percent at the 28-day expansion limits, respectively.

The results in Table 9 show that for most aggregates tested and no matter which limit is used:

- The "modified" AMBT used significantly underestimate the amount of lithium required to control ASR compared to the values suggested by the CPT.

- There is a not a significant difference in the minimum lithium to alkali molar ratio to be added to the soak solution to control ASR expansion (i.e., bring expansion down to less than the limit used) whether no lithium or the standard dosage (e.g., 100 percent) is added to the mortar bar. It is the amount of lithium in the soak solution that controls the efficacy of lithium in the modified ASTM C 1260.

Considering that if one were to use the minimum molar ratio in the soak solution, as given in Table 9, to select the dosage of lithium required to control ASR expansion with the aggregates selected, as has been suggested/used by some organizations, this would result in the use of lithium dosages that are significantly lower than those suggested from the results of the CPT. Figure 14 further shows that there is no correlation between the minimum lithium to alkali molar ratios determined from the modified concrete prism and accelerated mortar bar test series performed so far by the authors. More work is currently in progress to evaluate additional modifications of the ASTM C 1260 for lithium-based admixtures.

Fournier, et al. (2003) reported the results of a comparative field and laboratory investigation on the use of SCM and lithium-based admixtures in controlling expansion due to ASR. Concrete mixtures incorporating three highly reactive aggregates of a different petrographic nature were made with LiOH and $LiNO_3$ at molar ratios ranging from 0.74 to 1.11. With the highly reactive NM (rhyolite) and Con (greywacke) aggregates, the use of a molar ratio of 0.74 for LiOH resulted only in a slight reduction in concrete prism and block expansions compared to the control; however, test specimens at a 1.11 molar ratio performed well in the laboratory and after 6 years of field exposure. For the highly reactive NM (rhyolite) aggregate, the use of $LiNO_3$ at molar ratios of 0.74 or 0.93 resulted in similar concrete prism expansions of about 0.031 percent at 2 years (mixtures without added alkalis); however, cracking was observed after 6 years of field exposure for the block with the 0.74 molar ratio. In the case of the highly reactive Sp (siliceous limestone) aggregate, a molar ratio of 0.93 for $LiNO_3$ suppressed concrete prism expansion and offered good performance after 6 years of field exposure.

Berra, et al. (1999) compared the effectiveness of lithium carbonate and lithium nitrate in concrete mixes (CSA test method) made with two natural siliceous aggregates. Also, the ultra-accelerated expansion test in alkaline solution at 150 °C was performed on concrete prisms. The results showed that lithium at the standard molar ratio of 0.74, combined with an alkali loading above 4.5 kg/m^3, was ineffective at reducing expansion in the CPT at 2 years below 0.04 percent for the more highly reactive siliceous aggregate in the study. For the second aggregate of lower reactivity, the dosage of lithium was greatly overestimated. While only two aggregate types were studied, the results confirmed that the efficacy of lithium was highly aggregate dependant. This study also stressed that as the alkali content of the concrete increases, the effective molar ratio of lithium to sodium plus potassium also increases significantly. Lithium carbonate was shown to be much less effective than lithium nitrate with the more highly reactive aggregate and was therefore not recommended as a form of lithium for mitigation. In cases where the alkali contents were above 4.5 kg/m^3, lithium carbonate was ineffective and, in some cases, especially when the lithium to alkali molar ratio was increased to above 0.74 and the alkali content was also above 4.5 kg/m^3, expansion in these prisms exceeded the expansion in the controls.

Perhaps the most promising information from this work was the use of an ultra-accelerated test that was outlined in a previous publication by the same authors (Berra, et al., 1999). In this test, concrete prisms are cast according to the CSA standard with varying molar ratios of [Li]/[Na+K]. After 1 day of curing, they are placed in cylindrical stainless steel containers and immersed in an alkaline solution mimicking that of the pore solution. In mixes using lithium, the soaking solution was also adjusted to yield the same initial alkali to lithium molar ratio as that of the concrete mixture. They showed a strong correlation between the effective dosages of lithium nitrate in this test at 21 days and the effective dosage of lithium nitrate predicted in the CPT at 1 and 2 years for both aggregates. While this represents a promising approach for a possible accelerated version of the test, a larger database will need to be developed that incorporates many types of aggregates before a conclusion as to its validity may be reached.

Mangialardi (2002) used a modified version of the ASTM C 1260 test for assessing the efficacy of lithium nitrate where lithium nitrate was added to both mortar specimens and the soaking solution. While traditional expansion results yielded varying predictions for the proper lithium dosage, the application of the kinetic model proposed by Johnston and Fournier (2000) removed these discrepancies. They also

pointed to the fact that although this method is promising, it needs to be applied to a greater variety of ASR-susceptible aggregates before it is relied upon without reservation.

McKeen, et al. (2000) studied the effect of fly ash and fly ash/lithium nitrate combinations on the expansion of mortar bars (the AASHTO T303-96 test, which is virtually identical to ASTM C 1260) for five aggregates from New Mexico. Lithium nitrate was added at 75, 100, and 125 percent of the standard dosage (0.74 [Li]/[Na+K]) in the bar, while no lithium was added to the soaking solution. The researchers measured the lithium concentration in the soaking solution after the bars had been immersed for 24 hours in water (prior to placement in 1N NaOH) and after the 14-day measurement (1N NaOH). They found that, on average, 43 percent of the lithium nitrate had leached out of the bars. They concluded that "some other method should be used to fairly evaluate the effect of $LiNO_3$ on ASR." However, most of the samples (three aggregates with three lithium and three fly ash dosages) exhibited expansions of less than 0.1 percent at 14 days, and these combinations would be said to have passed the test. As a result, a recommendation of a minimum of 25 percent class F fly ash or lithium nitrate at the manufacturer's standard dosage plus class F fly ash at a minimum dosage of 15 percent was made to the New Mexico State Highway and Transportation Department (NMSHTD).

The findings presented by Thomas, et al. (2001) suggest that the beneficial effects of using low-calcium fly ash and lithium together to control ASR are cumulative. Specifically, when either the $LiNO_3$ or low-lime ash were used individually and were unable to suppress expansion completely (e.g., less than 0.10 percent at 14 days in ASTM C 1260), the combined action often was found to be sufficient. The benefits of this approach include needing less lithium, thereby reducing cost, and less fly ash, thereby increasing the early strength development. The combination of lithium and high lime ashes (i.e., > 25 percent CaO) was not found to be synergistic.

Qian, et al. (2002) studied the expansion behavior of dolomite-bearing aggregates in LiOH and KOH solutions. The authors found that the use of LiOH can induce expansion due to alkali-carbonate reaction (ACR) but suppress that due to alkali-silica reaction (ASR), thus offering a mean of differentiating ASR from ACR contributions in the deleterious reaction/expansion of such aggregates.

Table 8 summarizes some of the information provided in this section on various laboratory studies using lithium compounds to suppress ASR expansion. The table particularly focuses on comparisons between the dosage of lithium needed to suppress expansion and does not include the combined use of SCMs with lithium. The findings, as summarized in Table 8, will be used in Chapter 5 to develop specific guidelines for using lithium in new concrete.

Other forms of lithium than those described in this section have also been investigated. For example, Thomas and Stokes (1999) investigated the potential use of decrepitated spodumene (a lithium-containing ore) as a preventive measure and reported that the material was effective when used in sufficient proportions. Cement kiln trials have been also been conducted using spodumene as part of the raw feed, thus producing a clinker rich in lithium (Stokes, et al., 2000a). A technology has been developed for producing a lithium-containing glass, which can be used as a concrete admixture or interground with portland cement, to suppress expansion due to ASR (Baxter, 2000). This approach of using lithium-bearing glass has been reported as a means of minimizing the uptake of lithium by hydration products, thereby resulting in more efficient use of the active lithium compound in controlling ASR-induced expansion.

Johnston, et al. (2003) has described a new approach for the interpretation of the data from ASTM C 1260 based on a modification of the kinetic model proposed by Kolmogorov-Avrami-Mehl-Johnston. The method has shown some promise in recognizing the potential alkali-reactivity of certain "challenging" aggregates and determining preventive mixtures incorporating supplementary cementing materials

(Johnston, et al., 2003); however, the method has yet to be applied to the evaluation of lithium-based admixtures to control ASR.

The findings summarized in this section have dealt exclusively with the effects of lithium compounds on expansion due to ASR. However, it is very important that there are no undesired side effects from any admixture added to concrete that impact other fresh or hardened concrete properties. Fortunately, it has been well-documented that lithium compounds, used in typical dosages to suppress ASR expansion, do not significantly affect other important concrete properties. Most of the more recent investigations have dealt specifically with $LiNO_3$, as it is the most common lithium compound being used today. Studies have shown that fresh concrete properties, such as air content, slump and setting time, and hardened concrete properties, such as strength and permeability, are not altered significantly by the use of $LiNO_3$, and that $LiNO_3$ is compatible with other chemical admixtures (Wang, et al., 1994; Wang and Stokes, 1996; McKeen, et al., 2000; Thomas, et al., 2002).

Table 8. Summary of Selected Research Findings Related to Lithium Dosages.

Study	Test Method	Reactive Aggregate	Lithium Compound(s)	Minimum Molar Ratio [Li]/[Na+K] Needed to Suppress Expansion*
McCoy and Caldwell (1951)	ASTM C 227	Pyrex glass	LiCl, Li_2CO_3, LiF, Li_2SiO_3, $LiNO_3$, Li_2SO_4	0.74
Sakaguchi, et al. (1989)	ASTM C 227	Pyrex glass, pyroxene andesite sand	$LiOH•H_2O$, $LiNO_2$, Li_2CO_3	0.90
Ohama, et al. (1989)	Autoclave test	Opaline amorphous silica	$LiOH•H_2O$, LiF, Li_2CO_3	0.5% (by mass of cement) for LiF 0.7% (by mass of cement) for $LiOH•H_2O$
Stark (1992); Stark, et al. (1993)	ASTM C 227 ASTM C 1260	Rhyolite Granite gneiss	$LiOH•H_2O$, LiF, Li_2CO_3	0.6 (LiF) 0.92 (Li_2CO_3) 0.75-1.00 (LiOH)
Diamond and Ong (1992)	ASTM C 227	Cristobalite Beltane opal	LiOH	1.2 (for cristobalite, more for opal)
Qinghan, et al. (1995)	Autoclave	Andesite	$LiNO_2$	0.8 (for high-alkali mortars only)
Lumley (1997)	ASTM C 1293	Cristobalite	$LiOH•H_2O$, LiF, Li_2CO_3	0.62
Blackwell, et al. (1997); Thomas (2000)	ASTM C 1293	Various UK aggregates	LiOH, $LiNO_3$	0.70 (for $LiNO_3$) 0.85 (for LiOH)
Durand (2000)	ASTM C 1293	Canadian aggregates (Sudbury – sandstone, quartzwacke; Potsdam – siliceous sandstone , and Sherbrooke – chloritic schist)	$LiOH•H_2O$, LiF, and Li_2CO_3, $LiNO_3$	0.72 (for $LiNO_3$ with Sudbury) 0.82 (for $LiOH•H_2O$, LiF, and $LiCO_3$ with Sudbury)
Collins, et al. 2004	ASTM C 227	Crushed, graded borosilicate glass	LiOH, $LiNO_3$, LiCl	0.6 (LiOH), 0.8 ($LiNO_3$), 0.9 (LiCl)
Fournier, et al. 2004	ASTM C 1293	Rhyolite (NM) Greywacke (Con) Siliceous limestone (Sp)	LiOH (NM, Con); $LiNO_3$ (NM, Sp)	LiOH: 1.11 with NM; ~1.0 with Con $LiNO_3$: ~ 0.74 with NM; 0.93 with Sp
Tremblay, et al. (2004a, b)	ASTM C 1293	Canadian aggregates (greywacke-argilite, dolostone, polygenic gravels, rhyolite, siliceous limestones, granite-gneiss)	$LiNO_3$	Agg. type (1-year CPT exp. %): Molar ratio ** • Granite/gneiss (0.029%): 0.56 • Chloritic schist (0.082%): > 0.94 • Greywacke/arg. (0.087%): 0.71 • Dolostone (0.100%): 0.61 • Gravel (0.101%): 0.58 • Gravel (0.103%): 0.91 • Gravel (0.113%): 0.97 • Gravel (0.122%): 0.66 • Greywacke (0.142%): > 1.11 • Gravel (rhyolite) (0.151%): 0.63 • Siliceous limestone (0.162%): 1.04 • Siliceous limestone (0.199%): > 1.11

*   Molar ratios are used unless otherwise noted.

**   The information given includes the aggregate (rock) type, the concrete prism expansion at 1 year for the control ASTM C 1293 concrete (data in brackets), and the minimum molar ratio needed to suppress expansion (i.e., to reduce concrete prism expansion to < 0.04 percent at 2 years according to Standard Practice CSA A23.2-28A).

Table 9. Comparison Between CPT and Accelerated Mortar Bar Test (AMBT) Results to Determine the Efficacy of Lithium-Based Admixtures to Control ASR Expansion.

| Aggregate Types | Expansion for Control Specimens | | Minimum [Li]/[Na+K] Required to Control ASR Expansion | | | | |
| | | | Modified | 0% Lithium in the Bar [2] | | 100% Lithium in the Bar [3] | |
	ASTM C 1293 Exp. (%) @ 1 year	ASTM C 1260 Exp. (%) @ 14 days	ASTM C 1293 [1]	Limit 0.10% @ 14 days	Limit 0.08% @ 28 days	Limit 0.10% @ 14 days	Limit 0.08% @ 28 days
Granite/gneiss	0.029	0.197	0.56	0.23	0.33	0.18	0.28
Chloritic schist	0.082	0.138	> 0.94	0.24	0.45	0.25	0.42
Greywacke/argilite	0.087	0.295	0.71	0.35	0.55	0.31	0.52
Gravel (mixed)	0.103	0.232	0.97	0.48	0.66	0.40	0.55
Gravel (mixed)	0.113	0.224	0.91	0.49	0.73	0.45	0.65
Gravel (mixed)	0.122	0.238	0.66	0.30	0.43	0.21	0.30
Gravel (mixed)	0.131	0.375	0.58	0.48	0.56	0.27	0.41
Greywacke	0.142	0.273	> 1.11	0.41	0.68	0.39	0.61
Rhyolite	0.151	0.414	0.63	0.25	0.45	0.21	NA
Siliceous limestone	0.162	0.305	1.04	0.52	0.65	0.42	NA
Siliceous limestone	0.199	0.246	> 1.11	0.32	0.52	0.25	0.40
Gravel (volcanic)	0.212 [4]	0.966	0.74	>>0.60	>>0.60	0.45	0.59
Sand (cherty)	0.590 [5]	0.656	0.55	0.63	0.70	0.36	0.47

[1] Minimum molar ratio ([Li]/[Na+K]) required to meet the 2-year 0.04 percent concrete prism expansion limit (as per CSA Standard Practice A23.2-28A).

[2] Minimum molar ratio ([Li]/[Na+K]) required in the 1N NaOH soaking solution to meet either the 14-day 0.10 percent or 28-day 0.08 percent accelerated mortar bar expansion limits, as per modified ASTM C 1260 (0 percent lithium in the bar).

[3] Minimum molar ratio ([Li]/[Na+K]) required in the 1N NaOH soaking solution to meet either the 14-day 0.10 percent or 28-day 0.08 percent accelerated mortar bar expansion limits, as per modified ASTM C 1260 (100 percent of the standard dosage of lithium in the bar).

[4] From Fournier, et al. (2003).

[5] From Folliard and Ideker (2005).
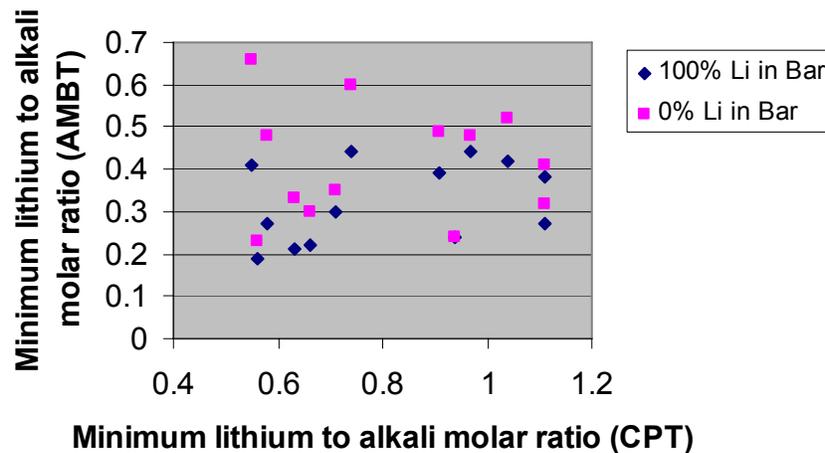
Figure 13. Comparison Between the Minimum Lithium to Alkali Molar Ratios to Control ASR Expansion Based on CPT and AMBT Results (Plot of Data in Table 9) (Tremblay, et al. 2005).

Laboratory Research on Using Lithium to Suppress Expansion in ASR-Damaged Concrete

In comparison to the number of studies on using lithium as an admixture in new concrete, there have been very few laboratory-based studies on post-treating hardened concrete to arrest expansion due to ASR. There have been several field applications, as described in the next chapter, but the following briefly summarizes laboratory research on the topic.

Sakaguchi, et al. (1989) allowed both high-alkali mortar bars (containing Pyrex glass) and concrete prisms (containing a reactive aggregate) to expand considerably (0.2 percent expansion for mortar, 0.1 percent for concrete), and then soaked the specimens in $LiNO_2$ or $LiOH \cdot H_2O$ solution. For both mortar and concrete, future expansion was essentially significantly retarded or, in some cases, prevented.

Stark, et al. (1993) confirmed that treating hardened mortar, previously subjected to ASR-induced expansion, by soaking it in LiOH solution was an effective method of suppressing further expansion. They noted that a key issue in field applications would be to ensure adequate LiOH penetration.

Recently, Stokes, et al. (2000b) reported on the development of a material for controlling future expansion of hardened concrete. The material is a lithium nitrate-based solution, but also contains a proprietary blend of surfactants to aid in penetrating hardened concrete. It was reported to be 50 percent more effective than $LiNO_3$, by itself, or three times more effective than LiOH, by itself. Stokes, et al. (2000b) also noted that the specific time of treating hardened concrete plays a major role in the subsequent efficiency of lithium compounds in controlling expansion, presumably because of increased permeability and damage of ASR-affected concrete.

3.3.4 Specifications for Using Lithium to Control ASR in Concrete

There is relatively little guidance provided in specifications related to the use of lithium in concrete. Current specifications within ASTM and CSA do not include guidance on using lithium compounds, although the next version of CSA specifications is expected to provide information on using lithium in new concrete. AASHTO (2000) has provided guidance on using lithium compounds in new concrete as part of the guide specifications developed by the Lead States Program. Several State highway agencies in the United States allow for the use of lithium in their specifications, including Delaware, Idaho, Maine, New Mexico, South Dakota, Texas, Washington State, and Wyoming.

The BRE (2002) has published guidelines recently for using lithium admixtures in concrete, as shown in Table 10. The BRE recommendations take into account aggregate reactivity, fly ash dosage (if used), type of lithium compound, and total alkali content of the concrete mixture. Table 10 is only applicable for concrete with a total alkali content of less than or equal to 5 kg/m^3. The classification of aggregates (high reactivity or normal reactivity) generally is based on mineralogy, as opposed to performance tests, but a test similar to ASTM C 1293 may be used if aggregate reactivity is in question. Guidance is not provided by BRE on using slag in conjunction with lithium compounds. When fly ash is used, the alkali contribution of the fly ash in calculating the total mixture alkali content is as follows:

- If fly ash content is greater than or equal to 25 percent (by mass of total cementitious materials)— the alkalis in fly ash are *not* included in calculating the total alkali content of the concrete.

- If fly ash content is 20 to 24 percent—*one-fifth* of the total fly ash in the alkalis are included in calculating the total alkali content of the concrete.

- If fly ash content is less than 20 percent—*all* of the alkalis present in the fly ash are included in calculating the total alkali content of the concrete.

Table 10. BRE (2002) Guidelines for Using Lithium in New Concrete.

| Aggregate Type | Lithium Compound | Fly Ash, % (by mass of cementitious materials) | Lithium Dosage | | Molar Ratio [Li]/[Na+K] |
			Mass Addition (kg per kg of Na$_2$O$_e$)	Volume Addition (L of solution admixture per kg of Na$_2$O$_e$)	
High Reactivity	LiOH•H$_2$O (solid)	0–14	1.30	–	0.96
		15–25	1.00	–	0.74
	LiNO$_3$ (30% solution)	0–14	5.95	5.00	0.80
		15–25	5.20	4.40	0.71
Moderate Reactivity	LiOH•H$_2$O (solid)	0–25	0.75	–	0.56
	LiNO$_3$ (30% solution)	0–25	3.75	3.15	0.51

For convenient comparison to data presented earlier in this chapter, the last column of Table 10 shows the molar ratio for each of the standard lithium dosages. For the same aggregate type and fly ash content, higher dosages of lithium (based on molar ratio) are recommended for LiOH·H$_2$O than for LiNO$_3$, which recognizes the superior performance of LiNO$_3$ in controlling expansion due to ASR.

3.4   CONCLUSIONS

This chapter has reviewed a wide range of research performed using lithium to combat ASR-induced expansion. The following are some of the key findings:

- Lithium compounds have been used in laboratory research to control expansion due to ASR for more than 50 years. The results generally showed that the effectiveness of lithium-based admixtures is a function of the alkali-to-lithium molar ratio in the mixture and of the petrographic nature of the reactive aggregate to the control.

- The mechanisms by which lithium controls ASR are not fully understood at this time.

- ASTM C 1293 (2-year test) is currently the only recommended test for assessing lithium compounds, as it possesses the strongest correlation to field performance over the other test methods currently in use. ASTM C 1260 (modified by adding lithium to the soak solution) has been used by several organizations; however, the method is *not recommended* because the modified ASTM C1260 test underestimates the amount of lithium to control damaging alkali silica reaction in concrete.

- Although the previous report noted that adding lithium at a molar ratio [Li]/[Na+K] of 0.74 was adequate to suppress expansion for most aggregates, recent investigations have shown that the efficient molar ratio can actually vary significantly from one aggregate to another (e.g., from as low as 0.56 to > 1.11).

- Lithium nitrate is more efficient at reducing expansion than other lithium compounds, mainly because it does not raise pore solution pH.

- Lithium compounds have been used for post-treating hardened concrete that has already expanded from ASR in an attempt to reduce or eliminate future expansion. However, a relatively small database exists to substantiate the efficacy of using lithium compounds as post-treatment options for ASR-affected structures. Monitoring of several of the treated sections outlined in this report, which is

currently in progress, in addition to long-term monitoring results from other treated structures, should provide critical information on the effectiveness of such treatments over the next few years.

CHAPTER 4   CASE STUDIES

4.1   INTRODUCTION

This chapter summarizes various case studies involving the use of lithium in both new and existing concrete. This comprehensive summary provides relevant information on materials, mixture proportions, supporting laboratory testing (if available), application techniques (for treating existing concrete), and field performance for each of the trials. Information gathered and lessons learned from these case studies are incorporated into the interim recommendations for using lithium (Chapter 5).

4.2   USING LITHIUM AS AN ADMIXTURE IN NEW CONCRETE

4.2.1   Lomas Boulevard, Albuquerque, NM (1992)

Construction of Experimental Pavement

An experimental pavement consisting of the westbound approach lanes to a bridge carrying Lomas Boulevard (State Route 352) over U.S. Interstate 40 in Albuquerque, NM, was constructed in June 1992. The three-lane pavement is 155 m long and 11 m wide. Eleven different concrete mixtures were used to construct the pavement, to evaluate different methods for preventing ASR. Reactive aggregate (sand and gravel) from two local sources, namely the Shakespeare and Placitas pits, were used in combination with either fly ash or LiOH as summarized in Table 11.

Table 11. Summary of Mixtures Used in Lomas Boulevard Experimental Pavement.

Source of Reactive Aggregate	Mix No.	Preventive Measure
Shakespeare Pit	1	1.0% LiOH
	2	0.5% LiOH
	3	Lomar^{TM} Admixture
	4	Class F Fly Ash
	5	Class C Fly Ash
	6	None (Control)
	7	Blend of Class F and C Fly Ash
Placitas Pit	8	Class F Fly Ash
	9	None (Control)
	10	1.00% LiOH
	11	Class C Fly Ash

The total cementitious material content of the concrete mixtures was nominally 395 kg/m^3 with five of the mixtures containing fly ash at a nominal replacement level of 20 percent. The cement was reported to have an alkali content of approximately 0.55 percent Na_2O_e (Stark, et al., 1993). The class F fly ash was from the Cholla Generating Station in Phoenix, AZ, and the class C fly ash was from the Tolk Generating Station in the Texas Panhandle. One mixture contained a 50-50 blend of class F and class C fly ash. In this case, the "C ash" was from the same source, but the "F ash" was from Escalente Generating Station

(according to mixture data sheets). The water-cementitious materials ratio (w/cm) of these mixtures was generally in the range of 0.40.

The lithium was added as a dry powder of lithium hydroxide monohydrate (LiOH•H_2O) and dosed at rates of either 0.5 percent or 1.0 percent by mass of portland cement. Assuming the alkali content of the cement to be 0.55 percent Na_2O_e these lithium doses yield lithium-alkali molar ratios of [Li]/[Na+K] = 0.67 and 1.34 in the concrete with 0.5 percent and 1.0 percent LiOH•H_2O, respectively.

To ensure adequate dispersion of the LiOH•H_2O powder, the mixing water and appropriate dose of powder were batched into the trucks the night before the concrete was placed. The use of LiOH had no discernable effect on the slump or air content of the concrete, nor did it impact the placing or finishing operations.

Subsequent to placing the experimental pavement, the aggregates were tested in combination with the fly ashes and low-alkali cement (0.18 percent Na_2O_e) using the accelerated mortar bar test (ASTM C 1260) yielding the results shown in Table 12. Aggregate-LiOH combinations were tested using ASTM C 227, but no data from these tests have been reported. The test data in Table 12 confirm the high reactivity of both aggregate sources and the inferior performance of class C fly ash compared to class F fly ash in controlling expansion.

Table 12. Results From the ASTM C 1260 Tests (Stark, et al., 1993).

Aggregate	Fly Ash	Expansion (%)	
		7 days	14 days
Shakespeare Pit	None	0.580	–
	None	0.502	–
	Class C	0.405	–
	Class F and C	0.052	0.125
	Class F	0.017	0.045
Placitas Pit	None	0.575	–
	None	0.511	–
	Class C	0.400	–
	Class F	0.015	0.055

Subsequent Investigations

Concrete cores were taken from the different sections after 2 and 3 years, and were tested to determine the elastic (static) modulus. The results from these tests, shown in Figure 14 do not indicate signs of progressive deterioration (i.e., there was no reduction in modulus between 2 and 3 years), although the static modulus of the concrete with class C fly ash and Shakespeare aggregate (mix #5) was significantly lower than the other mixtures.

Cores taken at 2 years were also subjected to limited petrographic examination, and a summary of the results is presented in Table 13. Only concrete containing class C fly ash showed any visual signs of damage when lapped samples were viewed under a stereobinocular microscope.
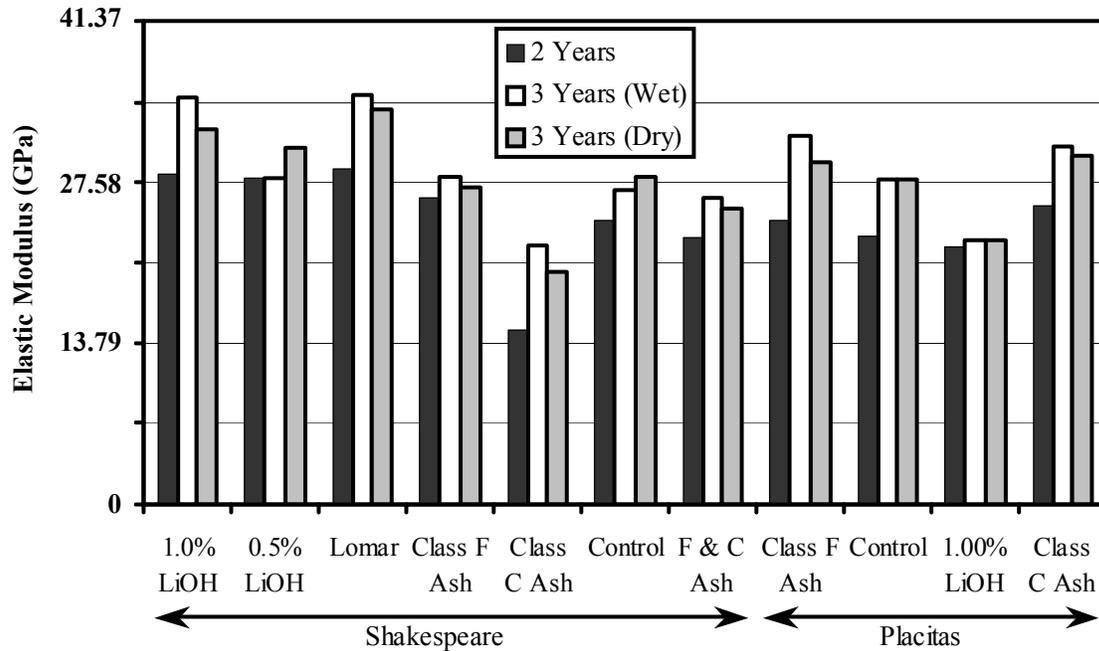
Figure 14. Elastic Modulus of Concrete Cores From Lomas Boulevard.

Table 13. Observations From Petrographic Examination of Cores.

	Cores at 2 Years		Cores at 4 Years			
Concrete Mixture	**Number of Reaction Sites**	**Damage**	**Uranyl Acetate**	**LANL Stain**	**Petrography**	**Overall**
Shakespeare Aggregate						
1. 1.0% LiOH	5	No	3	4	4	**11**
2. 0.5% LiOH	10	No	4	4	4	**12**
3. Lomar*	30	Yes	2	2	2	**6**
4. Class F Fly Ash	15	No	4	4	3	**11**
5. Class C Fly Ash	30	Yes	1	1	1	**3**
6. Control	5	No	4	3	3	**10**
7. Blend of F and C Ash	Many	Yes	3	3	3	**9**
Placitas Aggregate						
8. Class F Fly Ash	Many	No	2	2	3	**7**
9. Control	10	No	4	4	3	**11**
10. 1.00% LiOH	None	No	4	3	4	**11**
11. Class C Fly Ash	Many	Yes	1	2	2	**5**

* Lithium-containing high-range, water-reducing admixture

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Further cores were extracted in 1996 (at 4 years), and these samples were subjected to a detailed petrographic examination (Sherman and Krauss, 1997). Thin-section microscopy and staining techniques using uranyl acetate and Los Alamos National Laboratory (LANL) stain were used together with visual observations of the reacted particles, amount of gel and distress in the form of microcracking. The results of these studies are compared with the observations made at 2 years in Table 13. The observations made during the later examination were ranked using a numerical scale (see Table 13), which can be interpreted as shown in Table 14.

Generally, the mixtures containing class C fly ash showed the most signs of reactivity and those containing LiOH the least. However, the observations reported were largely qualitative, and it is not possible to provide a more objective ranking of the performance of the different mixtures.

Further visual inspections of the site were made in February 1999 and April 2001. Figure 15 shows a general view of the experimental pavement looking westward. Figure 16 through Figure 19 show the four sections with Placitas aggregate in February 1999. Significant cracking was evident in both the control section and the section with class C fly ash at this time, and the extent of damage appeared to be substantially more severe in the fly ash concrete. The concrete sections containing class F fly ash or 1 percent LiOH•H_2O appeared to be in good condition, with little visible cracking at the surface at the age of 7 years. However, after 2 more years, some cracking appeared on the surface of the fly ash concrete close to the sawn-cut edge of the slab (see Figure 20).

Table 14. Criteria for Assessing ASR Damage Based on Staining Techniques and Petrographic Analysis.

Rank	Uranyl Acetate	LANL Stain	Petrography
1 (Worst)	Highly positive	Much yellow stained gel and aggregate	Many reacted particles, much gel, and distress
2	Abundant glowing areas	Yellow stained gel and aggregate	Many reacted particles and much gel
3	Some glowing areas	Yellow aggregate	Some reacted particles and gel
4 (Best)	Mostly negative	Mostly negative	Few particles and little gel

The control concrete containing Shakespeare aggregate and the sections with either class C fly ash or a blend of F and C fly ash admixture all exhibited significant cracking when examined at 7 and 9 years. The concrete with the class F fly ash and either 0.5 percent or 1.0 percent LiOH•H_2O show no significant cracking at the same ages.

More cores were taken from the experimental pavement in December 2001 and were to be subjected to the following tests:

- Petrographic damage rating.
- Static modulus of elasticity.
- Tensile strength.
- Expansion testing.

There is no available funding to assemble, analyze, and publish data; therefore, the results are currently unavailable.

Figure 15. General View of Lomas Boulevard Experimental Pavement.

Figure 16. Control Section With Placitas—February 1999.

Figure 17. Section With Class C Fly Ash and Placitas—February 1999.

Figure 18. Section With Class F Fly Ash and Placitas—February 1999.

Figure 19. Section With 1 Percent LiOH and Placitas—February 1999.

Figure 20. Section With Class F Fly Ash and Placitas—May 2001.

In summary, the concrete mixtures containing LiOH (at both doses), together with highly reactive New Mexico aggregates, appear to be performing very well after 10 years of service. Although only small differences were observed between the visual appearance of these concrete mixtures and those containing approximately 20 percent of a class F fly ash, the lithium appears to have been slightly more effective in controlling cracking. However, continued monitoring of this site is required to determine whether the lithium continues to show improved performance over the class F fly ash.

All the mixtures without fly ash had a total cementitious material content of 350 kg/m^3. The fly ash mixtures contained 315 kg/m^3 of portland cement with varying amounts of fly ash. The water-cementitious material ratio of the mixtures was 0.44, except for mix #11, where w/cm = 0.42. Lithium hydroxide was added in the form of an aqueous solution containing 8.75 percent LiOH by mass to achieve the target lithium-alkali molar ratios. In mix #12, which contained LiOH in combination with class F fly ash, the lithium was dosed at the same rate as mix #2 (i.e., assuming the fly ash to contribute the same amount of alkali as the cement it replaced).

4.2.2   Lackawanna Valley Industrial Highway, PA (1997)

The Lackawanna Valley Industrial Highway is a new four-lane highway built in May 1997 in Lackawanna County in northeastern Pennsylvania. A section of this highway was constructed using reactive greywacke aggregate, high-alkali cement, and various preventive measures to assess SHRP recommendations for controlling ASR (Thomson and Stokes, 1999; Thomson, 2000). A photograph of the experimental pavement section is shown in Figure 21.

Figure 21. Lackawanna Valley Industrial Highway Experimental Section.

Twelve different concrete mixtures were used in the construction of the experimental section; one of these was a control mixture with high-alkali cement (0.86 percent Na$_2$O$_e$) and the remaining 11 mixtures used various approaches to mitigate expansion. The preventive measures adopted are summarized in Table 15. The different systems were tested using the Pyrex mortar bar test (ASTM C 441) and the accelerated mortar bar test (ASTM C 1260), and the test results are also included in Table 15.

The test data in Table 15 clearly indicate the coarse and fine aggregates to be potentially reactive and demonstrate that the use of sufficient levels of lithium, fly ash or slag are all effective in controlling damaging expansion. Note that the accelerated mortar bar test (ASTM C 1260), as it exists in its standard form, is not suitable for the purpose of evaluating lithium or low-alkali cement.

Table 15. Summary of Mixtures and Expansion Data Used in Lackawanna Valley Industrial Highway Experimental Pavement (Thomson, 2000).

Mix #	Preventive Measure	ASTM C 441	ASTM C 1260	
			Coarse Aggregate	Fine Aggregate
1	None (Control)	0.432	0.402	0.257
2	LiOH: [Li]/[Na+K] = 0.75	0.014	–	–
3	LiOH: [Li]/[Na+K] = 1.00	0.014	–	–
4	LiOH: [Li]/[Na+K] = 1.25	0.011	–	–
5	Low-alkali cement (0.37% Na_2O_e)	0.299	–	–
6	25% GGBF Slag	0.187	0.301	0.127
7	40% GGBF Slag	0.026	0.113	0.034
8	50% GGBF Slag	0.024	0.065	0.016
9	15% Class F Fly Ash	0.239	0.247	0.074
10	20% Class F Fly Ash	0.221	0.156	0.046
11	25% Class F Fly Ash	0.155	0.101	0.017
12	15% Class F Fly Ash + LiOH [Li]/[Na+K] = 0.75	0.008	–	–

Detailed visual inspection of the experimental pavement is conducted periodically. Figure 22 shows some very fine cracking developing on the 15 percent class F fly ash mix after 4 years. Several other sections showed similar cracking, however, all of the concrete was in generally excellent condition at this age. The conditions of the concrete also are being monitored using impact echo techniques (Figure 23); little significant change in response has been observed to date.

Figure 22. Lackawanna Valley Industrial Highway Experimental Pavement—15 percent
Class F Fly Ash (Mix #9)—May 2001.

Figure 23. Impact Echo Testing—Lackawanna Valley Industrial Highway Experimental Pavement.

4.2.3   U.S. I–90, Oacoma, SD (1996)

In June 1996, the South Dakota Department of Transportation (DOT) replaced a 13.36-km-long section of asphalt pavement with a continuously reinforced concrete pavement and jointed plain concrete pavement. A highly reactive sand and a slowly reactive quartzite coarse aggregate were used together with a series of 14 different concrete mixtures incorporating various measures to control expansion due to ASR (Johnston, 2001). Details of the mixtures are summarized in Table 16.

The cement used in all of the mixtures was a Type V low-alkali (0.55 percent Na_2O_e) cement. The test sections are being monitored by means of visual examination, impact echo, and modulus of elasticity (on cores). The LiOH and $LiNO_3$ were added as aqueous solutions containing 8.75 percent LiOH and 30 percent $LiNO_3$ by mass, respectively. Decrepitated spodumene represents an intermediate stage in the lithium extraction process of the ore spodumene. Spodumene ore normally is crushed and fired in a kiln to "untie" the lithium before its extraction. The material at this stage is known as decrepitated spodumene and is basically an amorphous alumino-silicate that contains significant quantities of available lithium. A detailed description of the material and its efficacy in controlling ASR in laboratory tests has been presented by Thomas and Stokes (1999).

Table 16. Summary of Mixtures Used in I–90 Oacoma Experimental Pavement.

Mix #	Cementitious Material (kg/m³)		Preventive Measure	
	Type V Cement	Class F Fly Ash	Type	Dose (L/m³)
1	356	–	LiOH Solution	9.90
2	356	–	LiOH Solution	12.87
3	356	–	LiOH Solution	15.84
4	356	–	LiNO₃ Solution	4.95
5	356	–	LiNO₃ Solution	7.43
6	356	–	LiNO₃ Solution	9.90
7	356	–	LiNO₃ Solution	12.38
8	303	66.4	LiNO₃ Solution	2.48
9	303	66.4	LiNO₃ Solution	4.95
10	356	–	Decrepitated Spodumene	10.9 kg
11	356	–	Decrepitated Spodumene	21.8 kg
12	303	66.4	Decrepitated Spodumene	10.9 kg
13	356	–	–	–
14	303	66.4	–	–

All of the concrete appeared to be in good condition when inspected in June 2001, and there has been no progressive change in the in situ response of the concrete to impact echo or in the static modulus of core samples. A photograph of the site is shown in Figure 24.

Figure 24. Experimental Pavement on I–90 Near Oacoma, SD.

4.2.4   Coyote Springs Bridge, NM (2000)

This bridge, shown in Figure 25, was built in 1999, using highly reactive aggregate from the Placitas quarry near Albuquerque, NM. The concrete was produced using a combination of class F fly ash and lithium.

During an inspection of the bridge in August 2001, cracking was observed on the surface of the deck. A photograph showing the nature of the cracking observed is shown in Figure 26. This type of cracking was visible on many parts of the exposed bridge deck. Although this type of random or map-pattern cracking with associated damp staining of the cracks is observed frequently in concrete structures affected by ASR, the feature is not reliably diagnostic of this form of deterioration. Such cracking may form due to other processes, such as plastic shrinkage during construction or drying shrinkage during the early stages of exposure. The role of ASR can be determined only by petrographic examination of the samples removed from the structure.

Two cores were taken from the structure for petrographic examination and chemical analysis to determine the lithium content. The average lithium content was determined to be 0.0097 percent and 0.0101 percent for the two cores. This equates to a lithium dosage of between 6.5 to 7.0 liters of $LiNO_3$ solution per cubic meter of concrete, assuming the solution to be 30 percent $LiNO_3$.

The petrographic examination revealed minor evidence of internal microfracturing of some aggregate particles and of reaction rims around other particles; however, there was no indication of an expansive reaction that could lead to internal microcracking of the concrete. To determine that ASR has led to the internal disruption of concrete requires evidence of sites of expansive reaction, i.e., the occurrence of features that provide direct evidence of reaction and production of expansive forces. Such features take the form of reactive aggregate particles showing cracking internally or at the cement/aggregate interface,

with cracks propagating into the surrounding matrix and cracks filled or partially filled with gel. No such features were evident in the sections examined. Indeed, very few cracks were found in the cement paste matrix, and these were largely confined to the exposed surface of the concrete. Spherical fly ash particles were found in the cement paste fraction of the cores, but no attempt was made to quantify the level of replacement. Further monitoring is required to determine whether there is progressive deterioration of the structure due to ASR.

Figure 25. Coyote Springs Bridge, NM.

Figure 26. Cracking on Deck Surface of Coyote Springs Bridge, NM.

4.2.5 Bridge Deck Overlay, Wilmington, DE (1999)

Delaware DOT specified the use of $LiNO_3$ in a concrete overlay for repairing a corrosion-damaged concrete bridge deck in Wilmington, DE. The contract involved the removal, by milling, of the concrete down to the top mat of reinforcing steel and placing a dense, low-permeability overlay containing 7 percent silica fume. The concrete bridge also was suffering from ASR, and there were concerns that the new concrete might provide an additional source of alkali to stimulate further reaction in the existing concrete. The cements available in Delaware are typically high in alkali. Lithium nitrate solution (30 percent $LiNO_3$) was sprayed onto the freshly milled surface prior to placing the overlay and was also used as an admixture in the concrete overlay. The sand used in the overlay was moderately reactive. The philosophy of this approach is to provide sufficient lithium to control ASR in the overlay and in the existing concrete. The latter is achieved by direct topical application of the $LiNO_3$ solution onto the substrate and also by migration of the lithium from the overlay into the substrate. Although the efficiency of penetration is not known, it is hoped that sufficient lithium will penetrate to control damaging reactions at the interface between the old and new materials, thus minimizing the risk of debonding. Figure 27 shows a photograph of the bridge deck, and Figure 28 provides a comparison of the new overlay concrete with the existing ASR-affected concrete.

Figure 27. Bridge Deck Overlay, Wilmington, DE.

Figure 28. Comparison of Existing ASR-Affected Concrete (at Left) With New
Overlay Concrete (at Right).

4.2.6   Bridge Deck Overlay, Lyman County, SD (2000)

Lithium nitrate solution was specified by the South Dakota DOT as an admixture for a number of
concrete bridge deck overlays placed during the repair of a 20.9-km stretch of highway in Lyman County,
SD (Figure 29). In addition, the bonding grout used between old and new concrete also contained $LiNO_3$.
The lithium was used for the same reasons as those discussed in the previous section (deck overlay in
Delaware).

Figure 29. Bridge Deck Overlay, Lyman County, SD.

The overlay concrete was produced using low-alkali cement, class F fly ash and 7.43 L/m^3 of 30 percent LiNO$_3$ solution, and both the sand and coarse aggregate were alkali reactive. As with the overlay placed in Delaware, the incorporation of LiNO$_3$ into the concrete mixture had no noticeable impact on the concrete properties or the placing schedule.

4.2.7 Utility Transmission Towers, Corpus Christi, TX (2000)

Lithium nitrate was used in transmission tower footings constructed for a 40.2-km length of transmission line near Corpus Christi, TX. The potential reactivity of the aggregates in the area called for some measure of ASR control, and the options available to the contractor were using lithium, class F fly ash, or importing nonreactive aggregates. Lithium was chosen, since the quality and availability of the fly ash in the region was questionable, and the costs associated with hauling aggregate were too high. The concrete mixture contained a low-alkali cement and 8.42 L/m^3 of 30 percent LiNO$_3$ solution together with moderately reactive coarse and fine aggregates. Figure 30 shows a photograph of the construction of one of the foundations.

Figure 30. Utility Transmission Tower Footing in Corpus Christi, TX.

4.2.8 Repair of Platte Winner Bridge, SD (1998)

Repair of the pile caps of the Platte Winner Bridge in South Dakota (Figure 31) became necessary after severe damage was caused by heavy river ice loads during a winter storm in 1997. Petrographic examination of the concrete revealed that ASR was occurring in the 30-year-old structure, and it was thought that this might have weakened the concrete, thereby exacerbating the storm damage. The concrete and grout used for repair were specified to contain LiNO$_3$ solution to prevent ASR in the new concrete and to provide a source of lithium to the existing concrete. The concrete mixture contained low-alkali cement, a fly ash with an intermediate calcium content, and 7.43 L/m^3 of 30 percent LiNO$_3$ solution, together with slowly reactive coarse, as well as highly reactive fine aggregates. The repair concrete had to be pumped over 60.9 m horizontally and then down 9.1 m from the bridge deck to the pile caps. The use

of the lithium admixture did not affect the concrete properties and was found to be compatible with the other admixtures.

Figure 31. Repair of Pile Caps on Platte Winner Bridge, SD.

4.3 USING LITHIUM TO SUPPRESS EXPANSION IN ASR-AFFECTED CONCRETE

4.3.1 Topical Applications

Rt. 14, Wolsey, SD (1995)

This roadway, which forms part of U.S. 14 near Wolsey, SD, and was constructed in 1981, is a two-lane, 185-mm-thick jointed plain concrete pavement. Damage due to ASR was first detected in 1989 and topical lithium application was completed in October 1995. A detailed description of the project is given in Johnston, et al. (2000).

The decision to use a $LiNO_3$ solution was based on concerns surrounding the possible pessimum effect associated with LiOH (i.e., if the quantity of LiOH introduced to the concrete was too low, it could have increased the potential for expansion by raising the pH of the concrete pore solution). However, it should be noted that the pessimum effect has only been observed when insufficient LiOH is added to new concrete, and there is no experimental evidence to suggest similar behavior when lithium is applied to hardened concrete. A 30 percent $LiNO_3$ solution containing a proprietary blend of surfactants (to reduce surface tension effects and aid penetration) was applied at a rate of 0.16 L/m^2. A photograph of the spray truck is shown in Figure 32. Three 150-m-long sections were treated once, twice, or three times, achieving total applications of 0.16, 0.32, and 0.48 L/m^2, respectively. Three sections of the same size were left untreated for comparison.

Figure 32. Topical Application of Pavement Near Wolsey, SD.

Monitoring of these sections included visual assessment, modulus testing of cores, and in situ impact echo soundings. In addition, samples were collected at different times to determine the depth of penetration of lithium into uncracked and cracked concrete. Modulus testing indicated little significant change in the stiffness of the treated or untreated sections 1 to 3 years after treatment. However, between 3 and 4 years, there was a sudden increase in the modulus of elasticity ($\sim$ 5 to 6 GPa) for the treated sections; no change was observed for the control sections. By contrast, the impact echo measurements made 2 years after treatment showed slightly reduced frequency values in the treated sections compared with the control sections, however, these differences could be due to small differences in the thickness of pavement. Interestingly, for the control sections, there was a significant reduction in the compression-wave velocity calculated from impact echo readings made on cores compared to in situ measurements made at the same location prior to coring. Differences between measurements made in situ and on cores were less pronounced for the treated concrete. This change in velocity was attributed to relaxation of internal stresses in the concrete when the cores were removed (Johnston, et al., 2000)—the greater change in the untreated sections may indicate increased ASR activity and, hence, internal stress. Chemical analysis to determine lithium concentration profiles showed little significant penetration of lithium into uncracked concrete below the surface 10 mm or so. However, larger quantities of lithium were detected at depths of 45 mm in concrete that was moderately cracked, although there was no correlation between the amount of lithium detected and the number of treatments.

Johnston, et al. (2000) concludes that the lithium appears to have had a positive effect by reducing the distress due to ASR. However, there is little visible difference between the treated and untreated sections at this time, and continued monitoring is required to confirm these preliminary findings.

I–68, LaVale, MD (1997)

In 1986, the decks and parapets to two bridges carrying opposite lanes of I–68 over a gorge in the Appalachian Mountains were replaced. Just 10 years later, ASR was detected in the new concrete in both structures, and lithium treatment was conducted in 1997. The treatment involved a single topical application to the structure carrying the westbound lanes; the other structure was left untreated as a control. A photograph of the bridge carrying the westbound lanes is shown in Figure 33. Figure 34 shows

a closeup of the deck surface and the slight to moderate ASR cracking apparent approximately 1 year after treatment. The surface condition of the untreated deck appeared relatively unchanged, and there appeared to have been little change in the appearance of either concrete (treated and untreated) since the time of treatment.

Figure 33. Bridge Carrying Westbound Lanes of I–68 Near LaVale, MD.

Figure 34. Cracking in 12-Year-Old Bridge Deck.

Electrical chemical injection of lithium into the deck was considered initially, but this option was later dismissed because the reinforcing steel was epoxy coated. The topical treatment involved a single pass using an application rate of 0.37 L/m^2 of 30 percent LiNO$_3$ solution. Three years after treatment, there was little visible difference between the condition of the treated and untreated sections. In addition to visual observations of the concrete, impact-echo monitoring is conducted periodically.

Rt. 1, Bear, DE (1998)

A 6.43-km section of Route 1 near Bear, DE, built in 1990, began to show signs of ASR just 7 years after construction. Treatment of two sections of the affected pavement began in 1998. One of the sections was at the southern end and one at the northern end of the project, and control sections were set aside for each project. The treatment involved a total of six spray applications (two per year), each at a rate of 0.24 L/m^2 using 30 percent LiNO$_3$ solution.

Monitoring included visual observations, testing of cores for modulus of elasticity, and in situ impact-echo testing. More recently, cores were taken from treated and untreated sections for the purpose of quantitative petrographic examination and determining the depth of lithium penetration.

Figure 35. Cracking of 11-Year-Old Untreated Section of Rt. 1 in Delaware.

Figure 35 shows the nature of the cracking observed on one of the untreated sections during an examination in the summer of 2001. The untreated section at the southern end of the project has undergone accelerated deterioration in the past few years, especially in the vicinity of the control joints. Consequently, frequent patch and partial-depth repairs of joints have been required on this section. The two treated sections and the second control section have required fewer repairs.

Figure 36 shows two photographs to compare the visual appearance of the treated and untreated sections located at the southern end of the project. The photographer stood at the point where the two sections meet. The picture to the left is the view north showing the treated concrete, and the picture to the right is

the view south showing the untreated concrete. The difference between the two sections is quite apparent. It is interesting to note that despite the differences in visual appearance in the treated and untreated concrete, little difference in behavior of the concrete has been detected by the physical testing (modulus and impact echo).

The untreated section of the southern end of the project was repaired with a hot-mix asphalt overlay in 2003, which will probably take the form of removing the deteriorated surface by milling and resurfacing with an asphalt overlay. The Delaware DOT views the lithium treatment as successful in terms of extending the life of the pavement (Pappas, 2001), as repairs of the treated sections do not require resurfacing at this time.

| (a) Treated Concrete. | (b) Untreated Concrete. |
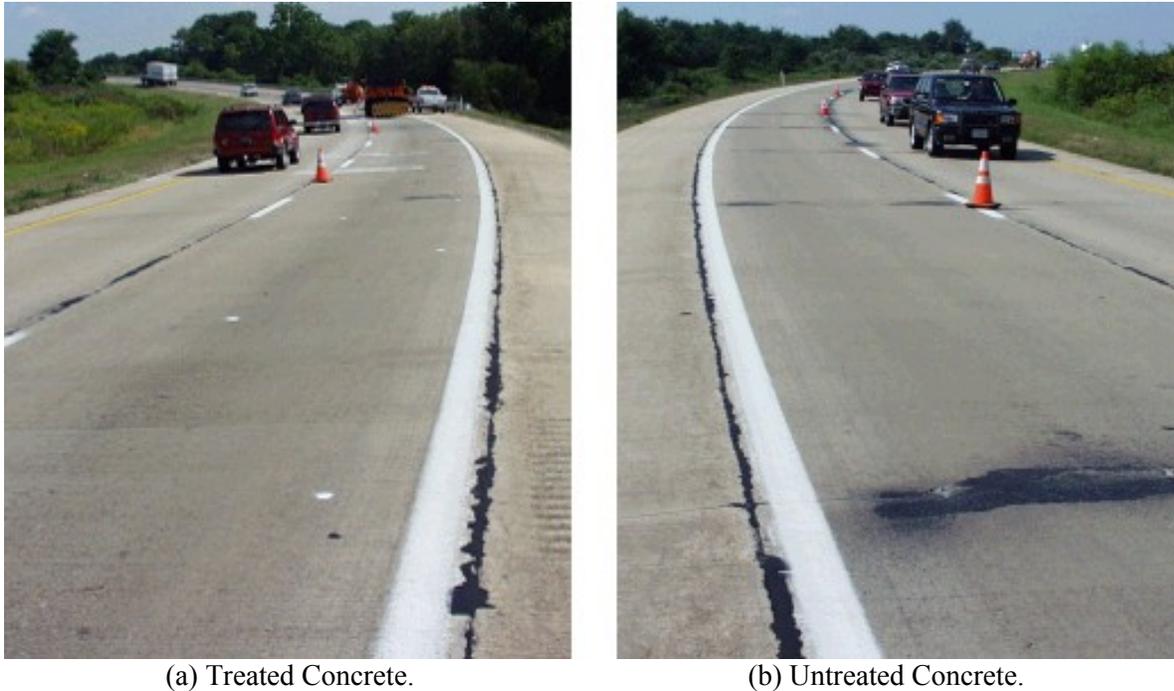
Figure 36. Sections of Rt. 1 Near Bear, DE.

I–84 Mountain Home, ID

In September 2004, a 5-km section of highway on I–84 in Mountain Home, ID was treated with 30 percent $LiNO_3$ solution at a rate of 0.24 L/m^2 (6 gal/1000 ft^2). Monitoring included taking core samples to establish depth of lithium penetration and determine the extent of damage using petrographic and stiffness damage rating techniques (Thomas et al, 2004). Treated and control sections were monitored by crack mapping and monitoring length changes (Figure 37). The pavement surface was very slippery immediately after application of the lithium, and some salt was observed to have precipitated out of solution. A decision was made to apply water about 1 hour after the lithium treatment to re-dissolve the salt to enable it to penetrate into the concrete. One further water application was required before the pavement was opened for traffic.

In May 2005, researchers traveled to Mountain Home for the second application to treat approximately two-thirds of the previously treated pavement. The section for lithium application was determined and subsequent measurement and monitoring was conducted on 20 pavement panels that were initially evaluated in September 2004. Instrumentation was added to 13 panel and/or shoulder combinations of the affected pavement. In this second application, lithium was applied at a rate of 0.23 L/m² (5.7 gal/1000 ft²),

just slightly less than manufacture recommendations. However, salting out of the lithium resulted in six applications of water to the surface of the pavement. The water was applied at a rate of 0.18 L/m² (4.5 gal/1000 ft²). This resulted in an even surface treatment of water with no visible runoff.

The third application of lithium nitrate was applied to approximately one-third of the originally treated pavement in September 2005. The section for lithium application was determined and subsequent measurement and monitoring of the previously instrumented and crack mapped pavement panels was conducted. The application rate was planned for 0.12 L/m² (3 gal/1000 ft²), but after calculations the rate was adjusted to between 0.089–0.10 L/m² (2.2–2.5 gal/1000 ft²). Minor salting out of the lithium occurred as compared to the second lithium treatment. Subsequently, no post-treatment with water was required. Traffic was reopened on the treated section the same day. This resulted in an even surface treatment of lithium solution with no visible runoff. Cores were taken from selected pavement panels to be used for lithium penetration profiling, as well as additional laboratory testing (potentially modified ASTM C 1293, stiffness damage index testing).

The team returned in May 2006, to monitor the treated section of pavement. Crack mapping and expansion measurements were performed on all instrumented panels. Humidity probes were installed in several panels for data collection, and additional cores were requested for further testing. Cores were extracted from the pavement and from previously removed slabs for further testing. The next monitoring visit is planned for fall 2006.

Summary and Other Projects

A summary of the above projects and a number of others is presented in Table 17. Two of the other projects listed are concrete pavements in New Ulm, MN, and High Point, NC. Both of these pavements were in a fairly advanced stage of deterioration when they were treated, and it has not been possible to discern any benefits due to lithium treatment. In fact, the rehabilitation of the pavement in North Carolina included an asphalt overlay following treatment with lithium that was applied to stabilize the underlying concrete. Two more pavement rehabilitation projects using a combined lithium treatment and asphalt overlay are planned in Delaware this year. Similarly, a lithium treatment under a methacrylate wearing surface is being placed on a bridge deck in Reno, NV.

Figure 37. Making Length-Change Measurements on a Treated Pavement in Mountain Home, ID.

Other projects involving topical applications of lithium have included pavements in Lexington and Selby, NC, Albuquerque, NM, Cheyenne, WY, and Dover, DE.

Table 17. Summary of Structures Treated With Lithium.

Date of First Application	Structure Type	Location	Application Rate (L/100 m^2)	No. of Appl.	Condition Prior to Treatment	Comments on Effectiveness
1995	Pavement	Rt. 14, Wolsey, SD	18.36, 36.72, 55.08	1	Fair	Little visible difference (controls and treated areas unchanged during evaluation period).
1997	Bridge deck	I–68, LaVale, MD	36.72	1	Good	Little visible difference (controls and treated areas unchanged during evaluation period).

Table 17. Summary of Structures Treated With Lithium (cont.).

Date of First Application	Structure Type	Location	Application Rate (L/100 m^2)	No. of Appl.	Condition Prior to Treatment	Comments on Effectiveness
1998	Pavement and bridge decks	Rt. 1, Bear, DE	24.48	6 (2 per year for 3 years)	Good to Fair	On southern end of project, treated areas faring better than control—no noticeable difference on northern end.
1998	Pavement	Rt. 15, New Ulm, MN	24.48	1, 2	Fair to poor	Second treatment done on portions. No noticeable improvement (controls and treated areas both continued to deteriorate about the same).
1999	Pavement	I–85, High Point, NC	12.24	1	Fair	Not evaluated—used as enhancement of durability of asphalt overlay.
2004	Pavement	I–84, Mountain Home, ID	24.48	1, 2, or 3 (third planned for fall 2005)	Fair to poor	Too early to determine. Ongoing monitoring includes expansion measurements and crack mapping.

4.3.2 Electrochemical Migration

Bridge Abutments, Latchford, Ontario (1992)

This arch bridge carries Highway 11 over the Montreal River just south of Latchford, in Northern Ontario (Figure 38). Electrochemical chloride extraction (ECE) was used to treat corrosion problems in the abutments, because concrete removal was not an option in the vicinity of the bearing seat of the steel arch. Lithium borate was used as the electrolyte in the ECE system to reduce the risk of exacerbating ASR, as the structure was thought to contain potentially reactive aggregates. The process of ECE results in the generation of hydroxyl ions at the embedded steel cathode, thus increasing the risk of ASR. Further augmentation of the alkalis may occur, as sodium borate is often used as the electrolyte. The use of a lithium-based anolyte should offset the effects of the increased pH.

Figure 38. Bridge Over Montreal River Near Latchford, ON.

This case has been discussed in detail elsewhere (Manning and Ip, 1994). Continued monitoring of the structure to determine the effectiveness of the treatment was planned, but it is not known if any such monitoring is taking place.

Bridge Deck, Arlington, VA (1995)

As with the bridge in Ontario described above, the main purpose of the electrochemical treatment of the bridge deck on I–395 in Arlington, VA, was the removal of chlorides and lithium borate was used as the electrolyte in response to concerns regarding the potential for ASR. Details of the project are given elsewhere (Whitmore and Abbott, 2000). The installation and operation of the system was typical of any other ECE application, with the exception that special measures were required to prevent run-off of the electrolyte from the sloping deck. The treatment lasted for eight weeks, and periodic analysis of the electrolyte during this period indicated a rapid decrease in the lithium concentration over time. Cores taken before and after treatment showed that the lithium penetrated a significant distance into the concrete. Lithium concentrations at a depth of 6 to 19 mm ranged from 315 to 343 ppm and at a depth of 19 to 32 mm the concentrations of lithium were in the range 203 to 265 ppm.

Bridge Deck, Seaford, DE (1997)

ECE treatment with lithium borate as an electrolyte was also applied on a 50-year-old bridge, classified as a heritage structure in Seaford, DE.

Pier Footings, New Jersey Turnpike, NJ (1999)

The remediation of five pier footings on the New Jersey Turnpike was likely the first time an electrochemical migration technique was used solely for the purpose of reducing the potential for ASR (Whitmore and Abbot, 2000). Figure 39 shows a photograph of the system during operation.

Figure 39. Application of an Electrochemical Lithium Migration Technique for a Pier Footing on the New Jersey Turnpike.

Repair of some of the larger cracks was carried out before lithium treatment and in such cases the mix water for the grout was a 10 percent $LiNO_3$ solution. The footings were massive sections (approximately 6 m by 6 m by 1.5 m deep), with a single mat of steel at a depth of approximately 1 m. The small amount of steel necessitated the use of a system of embedded anodes and cathodes. A series of vertical holes were drilled to a depth of just less than 1 m into the footing. Into some of these holes, steel cathodes were grouted in place and connected together with the reinforcing mat to the negative terminal of the rectifier. A titanium anode was inserted into other holes, and these were connected to a titanium mesh covering the top surface of the footing. The anodes were connected to the positive terminal of the rectifier. A lithium borate solution was used as an anolyte to fill the holes containing anodes and to pond the top surface of the footing.

Other Structures

Other structures that have been treated using electrochemical techniques include an overpass on I–29 in North Sioux City, SD, and the columns and piers of a bridge connecting Route 631 and I–64 in Charlottesville, VA.

4.3.3   Pressure Injection

Pressure injection techniques frequently are used to assist the penetration of grout materials into concrete. Such techniques generally are not recommended for concrete damaged by ASR, as the internal pressures may lead to disruption of the concrete.

4.3.4   Vacuum Impregnation

Vacuum impregnation is an alternative to pressure injection and has been used for increased grout penetration into cracked concrete. The authors are aware of three structures in the United States that have been treated using this technique. The vertical beams and columns on a structure carrying the New Jersey Turnpike over the Hackensack River in New Jersey were treated by vacuum impregnation in 2004. A 30

percent $LiNO_3$ solution was applied at an application rate of 1.6 L/m^2 through a vacuum created under a steel plate 1.2 by 2.4 m in size. The dose of $LiNO_3$ was targeted to provide a concentration of 100 ppm through the full depth of the elements. In 2003, a number of elements on the Prospect Avenue Viaduct in Johnstown, PA, were vacuum impregnated with 30 percent LiNO3 solution at a dose of 0.41 L/m^2; a total area of 474 m^2. In 2004, one trapezoidal prestressed bridge girder was treated by vacuum impregnation as part of a study of ASR-mitigation methods on five girders in Corpus Christi, TX.

In summer 2004, a series of five ASR-affected prestressed concrete box beams that had been rejected from a Texas DOT project because of cracking (confirmed by petrography to be the result of ASR) were treated with various strategies to control future expansion. The treatment options included a single application of lithium nitrate solution applied using vacuum impregnation and a topical application of lithium nitrate applied on four separate occasions. The beams were instrumented using mechanical, vibrating-wire, and fiber-optic strain gauges and embedded relative humidity probes. Data monitoring is scheduled to continue until fall 2008.

CHAPTER 5 APPROACH FOR USING LITHIUM IN NEW AND EXISTING CONCRETE STRUCTURES

5.1 INTRODUCTION

This chapter provides interim recommendations for the use of lithium compounds to inhibit expansion due to ASR in both new and existing concrete. These recommendations are based on a review and synthesis of laboratory studies, field applications, and existing specifications. The intention of these recommendations is to assist practitioners in testing, specifying, and using lithium to control ASR-induced expansion and damage efficiently. Relevant information on the economics of using lithium compounds is presented in Chapter 6.

5.2 USING LITHIUM COMPOUNDS IN NEW CONCRETE

This section focuses primarily on performance-based recommendations for using lithium compounds to mitigate ASR in new concrete. After presenting a method of evaluating and selecting lithium dosage based on laboratory testing, some information on a prescriptive approach is presented. However, it is not possible to propose the prescriptive dosages of lithium needed to control ASR due to the lack of data required to link aggregate mineralogy to requisite lithium dosage. This gap in understanding, described in chapter 4, extends beyond just aggregate-related issues, but also to combining lithium with SCMs. It is hoped that ongoing research on lithium technology will aid in the development of prescriptive guidelines for using lithium as an admixture in new concrete.

This chapter does not provide comprehensive recommendations regarding all the options available to mitigate ASR (i.e., SCMs, low-alkali concrete), as summarized earlier in Chapter 1, but rather provides practitioners who are interested in using lithium compounds with technical guidance on the topic.

5.2.1 Performance-Based Recommendations for Using Lithium in New Concrete

This section provides guidance on how to evaluate lithium compounds through laboratory performance tests. Emphasis is placed on determining the appropriate dosage of lithium to use in combination with a given reactive aggregate, either with or without the combined use of SCMs, especially fly ash and slag.

The previous lithium report (Guidelines *for the Use of Lithium to Mitigate or Prevent ASR*, Folliard, et al., 2003) recommended either the CPT (ASTM C 1293) or a modified version of the accelerated mortar bar test (ASTM C 1260) as tests to determine the requisite lithium dosages to suppress ASR-induced expansion. However, research since the time of the aforementioned report has shown that the proposed, modified version of ASTM C 1260 (where lithium-based admixtures is added to the soaking solution) tends to overpredict the efficiency of lithium in actual concrete mixtures. Research under Federal Highway Administration (FHWA) funding is currently assessing the mortar bar test and other rapid tests to determine if a quick test is able to accurately predict lithium behavior in field concrete. Until this has been achieved, *only* the CPT is being recommended as an accurate predictor of lithium performance for use in concrete.

ASTM C 1293

ASTM C 1293 generally has been recognized as the most accurate test in predicting field performance of aggregates (1-year test) and SCMs (2-year test). The test is less severe than ASTM C 1260 or other rapid tests, uses concrete (rather than mortar), and results in less leaching of alkalis than other tests. Its main drawback has been of the practical sort, rather than technical. Specifically, the long duration of the test

has been the major criticism. However, this longer test time provides a more realistic environment and results in better correlation with field performance.

Based on a review of published literature and a survey of current practice, ASTM C 1293 is recommended as the only reliable standard test for assessing lithium compounds. However, ASTM C 1293 does not currently provide guidance on using the test for this purpose. Following are recommendations for testing lithium compounds, by themselves or in combination with SCMs, using ASTM C 1293 as the basis.

To test lithium compounds (without SCMs) using ASTM C 1293:

- The same mixture proportions and methods described in ASTM C 1293 should be used, except lithium compound is added to the mixing water. If the lithium used is in the form of an aqueous solution (i.e., 30 percent $LiNO_3$ solution), the amount of water contained in the admixture should be removed from the calculated mixing water to maintain the target w/c ratio.

- The dosage of lithium used in the test may be varied, depending on specific objectives. It is expected that different aggregates will respond differently to lithium, and the actual amount needed to suppress expansion may vary considerably. Prior information or data on the aggregate of interest may help to guide the researcher in selecting relevant lithium dosages for laboratory evaluation.

- The test should be conducted for 2 years, with an expansion limit of 0.04 percent.

To test lithium compounds in combination with SCMs using ASTM C 1293:

- The same mixture proportions and methods described in ASTM C 1293 should be used, except for the following:

  - Add lithium compound to the mixing water. If the lithium used is in the form of an aqueous solution (i.e., 30 percent $LiNO_3$ solution), the amount of water contained in the admixture should be removed from the calculated mixing water to maintain the target w/c ratio.

  - Use SCM (or SCMs) as mass replacement of portland cement, maintaining a constant cementitious materials content of 420 kg/m^3.

  - Alkali (NaOH) should be added to the mix water to increase the alkali content of the portland cement component of the concrete to 1.25 percent Na_2O_e.

- The dosage of lithium used in the test may be varied, depending on specific objectives. The dosage should be calculated based on the alkalis present in the portland cement (and its corresponding added alkalis from NaOH), but not those alkalis present in the SCMs. For example:

  - A mixture containing 25 percent fly ash (by mass replacement of cement) would result in a portland cement content of 0.75 x 420 kg/m^3 = 315 kg/m^3. Given that the Na_2O_e of the cement is 1.25 percent (including alkalis added to the cement, as per ASTM C 1293), the total alkali contribution of the portland cement is 315 kg/m^3 x 1.25 percent = 3.94 kg/m^3. When using a 30 percent $LiNO_3$ solution, a molar ratio of 0.74, for example, yields a dosage of 4.6 L of solution per kg of alkalis. For this example, to assess a 0.74 molar ratio (based on

cement alkalis), the total amount of LiNO$_3$ solution added to the concrete would be 4.6 L x 3.94 kg/m^3 = 18.1 L/m^3. This example assumes a 0.74 molar ratio, but lower values may be sufficient to suppress expansion, especially if the SCM used is a low-calcium fly ash (Thomas, et al., 2001).

- When testing certain SCMs, such as silica fume or metakaolin, it may be necessary to incorporate a high-range water-reducing admixture in the concrete to improve the workability and enable proper compaction of the test specimens. In such cases, an admixture that does not contain alkalis (sodium or potassium) should be used.

    – The test should be conducted for 2 years, with an expansion limit of 0.04 percent.

ASTM C 1260

As previously mentioned, this updated recommendations report does not recommend ASTM C 1260, or modifications to the test, as a method of testing and selecting requisite dosages of lithium. Matching the [Li]/[Na+K] ratio of the mortar bar to the host solution tends to overestimate the beneficial effects of using lithium to control ASR-induced expansion. This overprediction of the efficacy of lithium would translate into inadequate dosages in field concrete.

More work is needed to develop a rapid test that best predicts the performance of lithium compounds in laboratory concrete (as per ASTM C 1293) or in concrete exposed to field conditions. This rapid test may be based on the accelerated mortar bar test, or may be entirely different. Regardless of the nature of the test, it should provide an accurate assessment of how lithium would perform in actual concrete mixtures.

5.2.2   Prescriptive Guidelines for Lithium in New Concrete

As previously mentioned, it is not possible at this time to provide prescriptive guidelines for using lithium compounds in new concrete. The previous version of this guideline report (*Guidelines for the Use of Lithium to Mitigate or Prevent ASR*, Folliard, et al., 2003) had recommended a minimum lithium dosage of 4.6 L of 30 percent lithium nitrate solution for every kilogram of Na$_2$O$_e$ contributed by the portland cement per cubic meter of concrete. However, since that time, research has shown that this dosage may not be sufficient for all aggregate types (Tremblay, et al., 2004). Furthermore, it is not possible to estimate how much additional lithium is needed for a given aggregate type as the relationship between inherent aggregate reactivity (e.g., expansion in ASTM C 1293) and requisite lithium dosage is not currently known. More research is needed to establish this relationship for a range of aggregate types. Furthermore, work is needed to determine appropriate lithium dosages when used in conjunction with SCMs. Ongoing FHWA-funded research is aimed at addressing these issues and developing prescriptive guidelines for lithium usage in new concrete.

5.3   USING LITHIUM IN EXISTING CONCRETE

Although the parameters that affect the efficiency of lithium-based compounds as chemical admixtures for controlling expansion due to ASR in new concrete have been established by laboratory studies and confirmed by field evaluations, the efficacy of these products in terms of treating existing ASR-affected concrete have not. It is clear from laboratory studies that treating small samples with lithium can reduce expansion (e.g., Stokes, et al., 2000b), but data are lacking from field cases. Although a number of structures have been treated in the field (especially topical applications of lithium to pavements and bridge decks) there is no unequivocal evidence to demonstrate that these treatments have been successful, or indeed, that the treatment has had any beneficial impact. In most cases this is due to the failure to implement appropriate monitoring programs to evaluate the effect of the treatment. Consequently, it is not

possible to develop guidelines for treating existing structures at this stage. However, certain procedures have been established empirically, and these are discussed below.

5.3.1 Topical Applications

The success of topical treatments of pavements and bridge decks with lithium compounds is likely to be influenced by a number of parameters, including:

- Lithium compound being used.
- Rate of application.
- Number of treatments.
- Temperature and moisture content of the concrete at the time of treatment.
- Quality of the concrete (e.g., permeability).
- Thickness of the element being treated.
- Extent of deterioration at the time of treatment.
- Presence of other deterioration process (e.g., freeze-thaw).

Many of these factors will, of course, affect the amount of lithium that infiltrates the concrete and the effective depth of penetration of the lithium.

Laboratory research has indicated that certain forms of lithium may exhibit a pessimum effect when used as an admixture for new concrete. This takes the form of increased expansion when an insufficient level of lithium is used, and the effect is ascribed to the increased pH resulting from the use of LiOH or other lithium compounds that react with $Ca(OH)_2$ to increase the concentration of OH ions in solution (e.g., $2LiCO_3 + Ca(OH)_2 \rightarrow 2LiOH + CaCO_3$). If such compounds are used to treat concrete, there is a possibility that the treatment may exacerbate the reaction if only a small amount of the compound penetrates the concrete. Lithium nitrate does not generally result in an increased pH due to the relatively high solubility of the calcium analogue; i.e., the nitrate ions stay in solution to balance the lithium rather than reacting with $Ca(OH)_2$ to release OH ions. For this reason, it is recommended that only solutions of $LiNO_3$ be used for topical treatments of existing ASR-affected concrete. Increased penetration may be achieved by incorporating a suitable surfactant into the solution (e.g., Stokes, et al., 2000b).

With regard to the application rate, there are two things to consider: (1) if the application rate is too high, the solution may run off the surface to be treated, resulting in waste (and possibly increasing environmental concerns), and (2) under certain conditions, solution ponded on the surface may evaporate, precipitating $LiNO_3$ salt on the treated surface, which may lead to reduced surface friction of trafficked surfaces. Experience has indicated that the optimum application rate for most cases is in the range of 0.16 to 0.40 liters of 30 percent $LiNO_3$ solution per square meter of concrete surface. A number of other controls may be necessary, and the following guidelines are reproduced from a recent specification to serve as an application:

- The surface shall be cleaned before treatment (e.g., by using a road sweeper).

- At the time of treatment the road surface shall be free of loose sand, debris, and similar materials, but need not be dry.

- Treatment shall not be applied during periods of rain or if rain is expected within 6 hours.

- Final coverage rate of the treatment shall not exceed 0.37 L/m^2 (3 gal/1000 ft^2).

- The application rate shall be adjusted to provide uniform surface coverage such that the material does not run off the surface.

- If a white residue covers more than 5 percent of the applied surface area due to evaporation, water shall be applied to the surface. If this precipitation at the surface results in a slippery surface, applications of water should continue until the pavement or bridge deck is deemed safe for vehicular traffic. The supplier and/or distributor of the lithium compound should be consulted in developing and implementing a strategy for safe and efficient topical treatment of pavements and bridge decks.

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 six individual treatments over a 3-year period.

It is expected that concrete with a high permeability that has been subjected to prolonged periods of drying prior to treatment will more readily absorb the solution applied to the surface. Also, a thin section with a high surface area to volume ratio will permit a greater volume of the concrete to be infiltrated by lithium compounds. However, these conditions clearly cannot be controlled.

The extent of deterioration of the concrete at the time of treatment will have an impact on the ease with which the lithium solution can penetrate the concrete. Cracking will clearly facilitate ingress of the solution. However, if the deterioration of the concrete has proceeded too far, it may be too late to treat the affected concrete. Johnston, et al. (2000) suggested that there is an optimum time to treat the concrete, in terms of the amount of deterioration, and explained the trade-off between cracking and lithium penetration by means of the schematic shown in Figure 40.
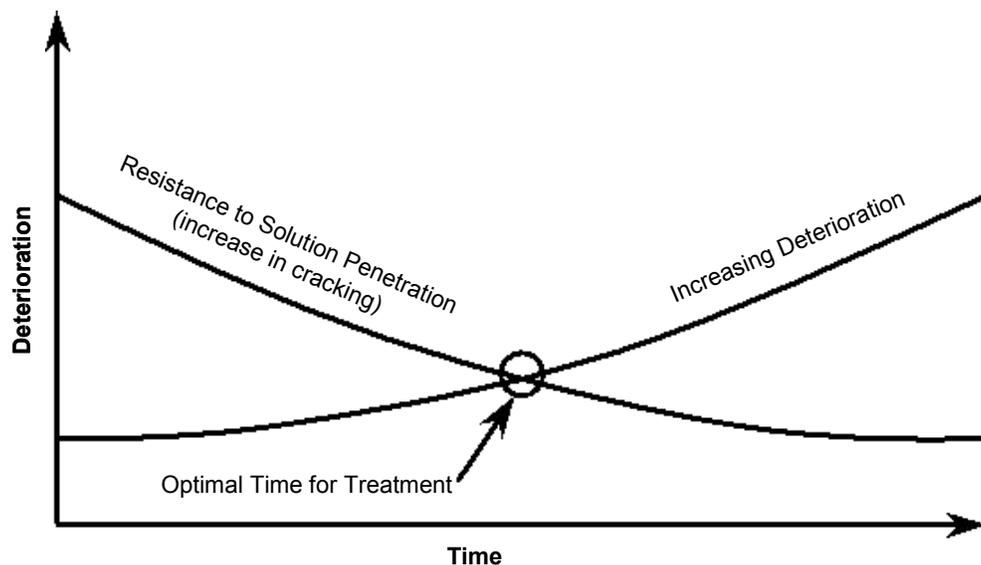
Figure 40. Optimal Time for Lithium Treatment Applied Topically (Johnston, et al., 2000).

Lithium treatment will only address the problems related to future ASR deterioration. Clearly it will not reinstate the concrete to its original condition, and if the deterioration present is likely to contribute to other deterioration processes, such as freeze-thaw or corrosion (by allowing access to chloride ions), then

these problems have to be addressed separately. This may be achieved by sealing the cracks or applying an overlay.

5.3.2   Electrochemical Migration

Electrochemical repair techniques used to drive lithium in concrete usually have been applied with the additional aim to remove chlorides (or realkalize the concrete). Regardless, these techniques are highly specialized, and it is likely that every case will involve design considerations specific to the individual job. As such, it is not possible to produce generic guidelines for the procedure. However, it is recommended that such techniques only be carried out by contractors with high levels of expertise and, if possible, with previous experience in using lithium-based materials such as the electrolyte.

5.3.3   Vacuum Impregnation

Since the writing of the first guideline document (*Guidelines for the Use of Lithium to Mitigate or Prevent ASR*, Folliard, et al., 2003), the Pennsylvania DOT and Texas DOT led efforts to vacuum impregnate bridge elements with lithium nitrate. Because there have only been limited field efforts involving vacuum impregnation, it is not possible at this time to provide specific guidelines for application. However, as long-term data become available from these two DOT trials and as more field structures are treated via vacuum impregnation, it is expected that specific guidelines will be developed and published.

CHAPTER 6   ECONOMIC CONSIDERATIONS OF USING LITHIUM COMPOUNDS

6.1   INTRODUCTION

This chapter discusses some of the economic considerations of using lithium compounds to control ASR-induced expansion in new concrete (when used as an admixture) or existing structures (when used as a post-treatment). Because of limited field applications of lithium to date, it is not possible to perform a comprehensive, quantifiable cost analysis of using the compounds to control ASR. However, some of the important factors to consider are discussed below.

6.2   ECONOMICS OF USING LITHIUM COMPOUNDS IN NEW CONCRETE

When considering using lithium nitrate as an admixture for concrete, the economics of this approach is often compared to other mitigation measures. The cost of lithium is probably higher than that of other technologies (e.g., fly ash, silica fume, low-alkali cement, etc.) typically used to control ASR-induced expansion. However, the delivered cost of concrete is just a part of the in-place cost of concrete, with the in-place cost depending on the type of structure, the amount of reinforcing steel, construction method, and other factors. For example, the in-place cost of concrete for a bridge deck may be as high as $450/m^3. Thus, one should regard direct comparisons of raw materials costs with caution because they do not reflect total delivered concrete or in-place concrete costs.

It is clear that adding lithium to concrete increases the cost of the raw materials and delivered concrete, and in many cases, other less-expensive alternatives are selected, such as using appropriate amounts of SCMs. However, when considering the use of lithium in new concrete, other factors must be taken into account:

- If the alternative is transporting nonreactive aggregates or low-alkali cement over a long distance, or if high-quality SCMs are not locally available, lithium becomes much more competitive.

- For some highly reactive aggregates, relatively high dosages of fly ash or slag may be required to control expansion, but these higher replacement levels would have a significant effect on early strength gain and related constructability issues. Using lower dosages of fly ash or slag, in combination with lithium, can then improve the early strength properties, which improve the economics of the situation.

- Some agencies and organizations have limited the maximum amount of SCMs mainly because of perceived concerns with salt scaling, and using lithium in these instances in combination with lower dosages of lithium becomes a viable alternative.

- For certain concrete structures (i.e., dams or airfield pavements), very little expansion can be tolerated before the expansion impacts performance or function of the structure. Using lithium in such structures, preferably in conjunction with SCMs, is a mitigation method worthy of consideration. Those designing and constructing these types of important or sensitive structures are generally more willing to spend additional money up front to ensure the desired function of the structure for the desired service life.

A critical factor identified above is the impact of materials selection on service life. For example, nondurable concrete that suffers from ASR (or other durability problems) may require significant repairs or even total replacement, and this has a major effect on the life-cycle cost of the structure. Recently, models have been developed to predict service life of reinforced concrete structures suffering from

corrosion. These models can be used to predict impact of different mitigation options (i.e., SCMs, corrosion inhibitors) on the service life and life-cycle cost of structures. However, models of this type are not currently available to predict the service life of structures suffering from ASR-induced damage. Nevertheless, it is clear that using lithium compounds, SCMs, or combinations of those will prolong the life of structures containing reactive aggregates significantly, thereby reducing the impact of initial material costs. As new models are developed that specifically address ASR, it will be possible to integrate life-cycle costs into initial strategies for controlling ASR, making the use of lithium compounds more attractive and competitive with other materials.

6.3   ECONOMICS OF TREATING EXISTING CONCRETE WITH LITHIUM

As discussed in sections 4.3 and 5.3 of this report, the effectiveness of treating existing ASR-affected concrete with lithium has not yet been established. Therefore, it is not possible to provide information on the economic viability of using this form of treatment. However, some discussion of the relevant economic considerations is warranted.

Lithium treatment of ASR-affected concrete is unlikely to be a lasting and complete solution to the problem. At best, such treatment may retard the process of deterioration and delay the time until more permanent repair or replacement becomes necessary. Also, lithium treatment will almost certainly only be considered when some level of deterioration is already present, and additional strategies may have to be considered to improve the existing condition of the concrete. However, extending the time to a more expensive repair or replacement option still may be a viable alternative. For example, consider the case of a pavement suffering from ASR. If it is predicted that, left untreated, the pavement will require some level of major rehabilitation (e.g., overlay or repair) at time T_1 with a cost of R_1, then the present worth of this option, P_1, is given by:

$$P_1 = \frac{R_1}{(1+i)^{T_1}}$$
(8)

Where: i = discount rate for the financial analysis

If the cost of applying a topical lithium treatment is R_2, and it is predicted that the lithium treatment will extend the time to major rehabilitation to time T_2, then the cost of the lithium treatment can be estimated as:

$$P_2 = R_2 + \frac{R_1}{(1+i)^{T_2}}$$
(9)

Both R_1 and R_2 should include the full cost to the user of implementing the rehabilitation strategy.

The comparative costs of the two options, P_1 versus P_2, are clearly a function not only of the cost of the lithium treatment, but also of the difference in the timing of the major rehabilitation, T_1 versus T_2. Without reliable information to predict how lithium will impact the timing of the repair schedule, it is not possible to perform an economic analysis. It is anticipated that an analysis of this type will be performed in the near future, using data obtained from the lithium treatment of pavement sections in Delaware.

CHAPTER 7   CONCLUSIONS AND RECOMMENDATIONS FOR FUTURE WORK

7.1   CONCLUSIONS

This report has reviewed the basics of ASR, summarized past research and field applications of lithium compounds in concrete construction, and presented revised recommendations for using lithium in new concrete and as a post-treatment for existing structures. Some of the main findings and conclusions from this report are:

- ASR is a significant problem in the United States and elsewhere, but there are several methods available for preventing ASR-induced expansion, including the use of nonreactive aggregates, low-alkali concrete, SCMs, and lithium compounds.

- The mechanisms by which lithium compounds suppress ASR expansion are not understood fully, but it is evident that lithium is incorporated into ASR gel, rendering the gel essentially nonexpansive. ASR gels still form in the presence of lithium; however, their altered structure (perhaps lithium substituting for calcium) inhibits water absorption and expansion.

- A variety of lithium compounds, including $LiCl$, Li_2CO_3, LiF, Li_2SiO_3, $LiNO_3$, $LiOH•H_2O$, $LiNO_2$, and Li_2SO_4 have been shown in laboratory studies to inhibit ASR-induced expansion effectively, provided that they are used at a sufficiently high dosage. $LiNO_3$ has been found to be the most efficient of the above compounds in controlling expansion because, unlike the other lithium salts, $LiNO_3$ does not increase pore solution pH.

- A substantial portion of lithium is absorbed in early hydration products, thereby requiring higher dosages of lithium compounds to offset this loss and to control expansion adequately. The development of a lithium-bearing glass has been reported as a means of minimizing this uptake of lithium by hydration products, thereby resulting in more efficient use of the active lithium compound in controlling ASR-induced expansion.

- The combined use of lithium and SCMs (especially fly ash and slag) is recommended to reduce the economic impact of using lithium and to produce low-permeability concrete that is more resistant to ASR and other deterioration mechanisms.

- The test method most recommended for assessing lithium compounds in the laboratory is ASTM C 1293, with a test duration of 2 years. Other more rapid tests are not currently available as an alternative to ASTM C 1293.

- Lithium compounds have proven to be effective in post-treating hardened mortar or concrete in the laboratory that has already expanded from ASR, thereby reducing or eliminating future expansion.

7.2   RECOMMENDATIONS FOR FUTURE WORK

As the availability of high-quality, low-reactivity aggregates continues to dwindle, the use of alternative means of controlling ASR certainly will become even more important. Given the past successes of using lithium compounds to inhibit expansion, both in the laboratory and in the field, the future of using lithium in concrete construction appears bright. However, there are several technical and practical issues that deserve further investigation:

- More mechanistic research is needed to define better how lithium compounds suppress expansion due to ASR. Several theories have been proposed, as described in Chapter 3, but gaining a better understanding of the underlying mechanisms will result in more efficient and cost-effective applications of lithium compounds in concrete construction.

- The uptake of lithium by hydration products reduces the amount of lithium available for ASR suppression. Research is needed to overcome this problem, thereby reducing the dosage of lithium needed to control expansion. Lithium-bearing glass has been reported to address this issue, but additional work on this material and new lithium-bearing products is recommended.

- Research is needed to establish correlations between aggregate mineralogy (and reactivity) and requisite lithium dosage to control expansion. Although it was initially proposed (*Guidelines for the Use of Lithium to Mitigate or Prevent ASR*, Folliard, et al., 2003) that a 0.74 molar ratio of lithium (e.g., manufacturer's 100 percent dosage) adequately controls expansion for all aggregates, it has since been shown that some aggregate require significantly more lithium to control expansion below typically prescribed limits (e.g., 0.04 percent expansion at 2 years in ASTM C 1293).

- Research is needed to refine available test methods (such as ASTM C 1260) to provide a more rapid method of assessing lithium compounds in mortar and concrete. Appropriate (and accurate) tests to assess lithium compounds in mortar and concrete must also be proposed for adoption by ASTM, AASHTO, CSA, and other organizations. The availability of these standard tests will help spur the development of specifications related to using lithium in concrete construction.

- Case studies have shown that lithium compounds, when used in new concrete or as a post-treatment for existing structures, are effective in inhibiting ASR-induced expansion. Long-term monitoring of the structures described in Chapter 4, as well as future field applications of lithium will be essential in relating laboratory tests to field performance, refining and improving the guidelines and recommendations provided in Chapter 5, and understanding the benefits of using lithium on service life extension (including economic considerations).

REFERENCES

American Association of State Highway and Transportation Officials, "AASHTO Guide Specification for Highway Construction, Section 56X, Portland Cement Concrete Resistant to Excessive Expansion Caused by Alkali-Silica Reaction," http://leadstates.tamu.edu/ASR/library/gspec.stm, 2000.

Baxter, S.Z., Stokes, D.B., Manissero, C.E., "Lithium-Based Pozzolans for ASR Control," *Proceedings of the 11th International Conference on Alkali-Aggregate Reaction (ICAAR),* Quebec, Canada, June 11–16, 2000, pp. 573–582.

Berra, M., Mangialardi, T., Paolini, A.E., "Rapid Evaluation of the Threshold Alkali Level for Alkali-Reactive Siliceous Aggregates in Concrete," *Cement and Concrete Composites,* Vol. 21, No. 4, 1999, pp. 325–333.

Bérubé, M.A., Duchesne, J., "Evaluation of Testing Methods Used for Assessing the Effectiveness of Mineral Admixtures in Suppressing Expansion Due to Alkali-Aggregate Reaction," *Proceedings of the Fourth International Conference on Fly Ash, Silica Fume, Slag, and Natural Pozzolans in Concrete*, (Ed. V.M. Malhotra), ACI SP132, Vol. 1, American Concrete Institute, Detroit, MI, 1992, pp. 549–575.

Bérubé, M.A., Fournier, B., "Accelerated Test Methods for Alkali-Aggregate Reactivity," *Advances in Concrete Technology* (Ed. V.M. Malhotra), CANMET/EMR, Ottawa, Canada, 1992, pp. 583–627.

Bérubé, M.A., Tremblay, C., Fournier, B., Thomas, M.D., Stokes, D.B. "Influence of Lithium-Based Products Proposed for Counteracting ASR on the Chemistry of Pore Solution and Cement Hydrates," *Cement and Concrete Research*, Vol. 34, 2004, pp. 1645–1660.

Bleszynski, R., Thomas, M.D.A., Hooton, D., "The Efficiency of Ternary Cementitious Systems for Controlling Expansion Due to Alkali-Silica Reaction in Concrete," *Proceedings of the 11th International Conference on Alkali-Aggregate Reaction (ICAAR)*, Quebec, Canada, June 11–16, 2000, pp. 583–592.

Building Research Establishment (BRE), "Minimizing the Risk of Alkali-Silica Reaction: Alternative Methods," Information Paper, BRE, London, United Kingdom, 2002.

Canadian Standards Association (CSA), "Standard Practice to Identify Degree of Alkali-Aggregate Reactivity of Aggregates and to Identify Measures to Avoid Deleterious Expansion in Concrete," CSA A23.2-27A, 2000a, Ontario, Canada, 2000.

Canadian Standards Association (CSA), "Guide to the Evaluation and Management of Concrete Structures Affected by Alkali-Aggregate Reactions," CSA A864-00, 2000b, Ontario, Canada, 2000.

Canadian Standards Association (CSA), "Standard Practice for Laboratory Testing to Demonstrate the Effectiveness of Supplementary Cementing Materials and Lithium-Based Admixtures to Prevent Alkali-Silica Reaction in Concrete," CSA A23.2-28A.C, Ontario, Canada, 2004.

Chatterji, S., Thalow, N., Jensen, A.D., "Studies of the Alkali-Silica Reaction, Part 4: Effect of Different Alkali Salt Solutions on Expansion," *Cement and Concrete Research*, 17, 1987, pp. 777–783.

Collins, C.L., "Examination of the Mechanism by Which Lithium Additives Inhibit Alkali-Silica Reaction Gel Expansion," M.S. Environmental Engineering Thesis, Georgia Institute of Technology, Atlanta, GA, 2002.

Collins, C.L., Ideker, J.H., Willis, G.S., Kurtis, K.E., "Examination of the Effects of LiOH, LiCl, and $LiNO_3$ on Alkali-Silica Reaction," *Cement and Concrete Research*, Vol. 34, No. 8, 2004, pp. 1403–1425.

Dent Glasser, L.S., Kataoka, N., "The Chemistry of Alkali-Aggregate Reactions," *Proceedings of the Fifth International Conference on Alkali-Aggregate Reaction,* Cape Town, South Africa, 1981, S252/23.

Diamond, S., "Effects of Two Danish Fly Ashes on Alkali Contents of Pore Solutions of Cement-Fly Ash Pastes," *Cement and Concrete Research,* Vol. 11, No. 3, 1981, pp. 383–394.

Diamond, S., "Unique Response of $LiNO_3$ as an Alkali-Silica Reaction-Prevention Admixture," *Cement and Concrete Research*, Vol. 29, 1999, pp. 1271–1275.

Diamond, S., "ASR—Another Look at Mechanisms," *Proceedings of the 8th International Conference on Alkali-Aggregate Reaction,* (Eds. K. Okada, S. Nishibayashi, and M. Kawamura), Kyoto, Japan, 1989, pp. 83–94.

Diamond, S., Ong, S., *Proceedings of the 9th International Conference on Alkali-Aggregate Reaction*, London, United Kingdom, July 1992.

Durand, B., "A Note About Alkali Contribution From Aggregates in Concrete," *Proceedings of the 11th International Conference on Alkali-Aggregate Reaction (ICAAR)*, Quebec, Canada, June 11–16, 2000a, pp. 169–177.

Durand, B., "More Results About the Use of Lithium Salts and Mineral Admixtures to Inhibit ASR in Concrete," *Proceedings of the 11th International Conference on Alkali-Aggregate Reaction (ICAAR)*, Quebec, Canada, June 11–16, 2000, pp. 623–632.

Fournier, B., Stokes D., Ferro A., "Comparative Field and Laboratory Investigations on the Use of Supplementary Cementing Materials (SCMs) and Lithium-Based Admixtures to Control Expansion Due to Alkali-Silica Reaction (ASR) in Concrete," *Proceedings of the Sixth CANMET/ACI International Conference on Durability of Concrete*, Thessaloniki, Greece, 2003, pp. 823–851.

Gillott, J., Rogers, C., "Alkali-Aggregate Reaction in Internal Release of Alkalies," *Magazine of Concrete Research*, Vol. 46, No. 167, 1994, pp. 99–112.

Glasser, F.P., "Chemistry of the Alkali-Aggregate Reaction," *The Alkali-Silica Reaction in Concrete* (Ed. R.N. Swamy)*,* Blackie, London, United Kingdom, 1992, pp. 96–121.

Hansen, W.C., "Studies Relating to the Mechanism by Which the Alkali-Aggregate Reaction Proceeds in Concrete," *Journal of the American Concrete Institute,* Vol. 15, No. 3, 1944, pp. 213–227.

Iler, R.K., *The Chemistry of Silica: Solubility, Polymerization, Colloid and Surface Properties and Biochemical of Silica,* John Wiley & Sons, New York, NY, 1979.

Johnston, D.P., "Mitigation of Potential Alkali-Silica Reactivity Using Lithium," *SHRP Strategic Highway Research Program Concrete and Structures ASR Showcase Test and Evaluation Project 34,* 2001.

Johnston, D., Fournier, B., "A Kinetic-Based Method for Interpreting Accelerated Mortar Bar Test (ASTM C 1260) Data," *Proceedings of the 11th International Conference on Alkali-Aggregate Reaction (ICAAR)*, Quebec, Canada, June 11–16, 2000, pp. 623–632.

Johnston, D.P., Stokes, D., Fournier, B., and Surdahl, R., "Kinetic Characteristics of ASTM C 1260 Testing and ASR-Induced Concrete Damage," *Proceedings of the 12th International Conference on Alkali-Aggregate Reaction in Concrete*, Beijing, China, Eds. Tang Mingshu and Deng Min, October 2003, pp. 338–346.

Johnston, D.P., Surdahl, R., Stokes, D.B., "A Case Study of a Lithium-Based Treatment of an ASR-Affected Pavement," *Proceedings of the 11th International Conference on Alkali-Aggregate Reactions,* (Eds. Bérubé, et al.), CRIB, Quebec, Canada, 2000, pp. 1149–1158.

Kawamura, M., Fuwa, H., "Effects of Lithium Salts on ASR Gel Composition and Expansion of Mortars," *Cement and Concrete Research*, Vol. 33, No. 6, June 2003, pp. 913–919.

Kurtis, K., "Transmission Soft X-Ray Microscopy of the Alkali-Silica Reaction," Doctoral Dissertation, University of California, Berkeley, CA, 1998.

Kurtis, K.E., Monteiro, P.J.M., Meyer-Ilse, W., "Examination of the Effect of LiCl on ASR Gel Expansion," *Proceedings of the 11th International Conference on Alkali-Aggregate Reaction (ICAAR)*, Quebec, Canada, June 11–16, 2000, pp. 51–60.

Kurtis, K.E., Monteiro, P.J.M., "Chemical Additives to Control Expansion of Alkali-Silica Reaction Gel: Proposed Mechanisms of Control," *Journal of Materials Science*, Vol. 38, 2003, pp. 2027–2036.

Lawrence, M., Vivian, H.F., "The Reactions of Various Alkalies With Silica," *Australian Journal of Applied Science*, Vol. 12, No. 1, 1961, pp. 96–103.

Lumley, J.S., "ASR Suppression by Lithium Compounds," *Cement and Concrete Research*, Vol. 27, No. 2, 1997, pp. 235–44.

Mangialardi, T., "Reconsideration of ASTM C1260 Test Results in the Light of a Recent Kinetic Model," *Advances in Cement Research,* Vol. 14, No. 2, 2002, pp. 51–60.

McCoy, W.J., Caldwell, A.G., "A New Approach to Inhibiting Alkali-Aggregate Expansion," *Journal of the American Concrete Institute*, Vol. 22, 1951, pp. 693–706.

McGowan, J.K., Vivian, H.E., "Studies in Cement-Aggregate Reaction: Correlation Between Crack Development and Expansion of Mortars," *Australian Journal of Applied Science*, Vol. 3, 1952, pp. 228–232.

McKeen, R.G., Lenke, L.R., Pallachulla, K.K., Barringer, W.L., "Mitigation of Alkali-Silica Reaction in New Mexico," *Transportation Research Record 1968*, National Research Council, 2000, pp. 9–16.

Mei, L.B., Lu, D., Deng, M., Tang, M.S., "Expansion of Siliceous Aggregate in LiOH Solution," *Proceedings of the 12th International Conference on AAR in Concrete*, Beijing, China, October 2004, pp. 399-406.

Nixon, P. J., Canham, I., Page, C. L., Bollinghaus, R., "Sodium Chloride and Alkali Aggregate Reaction," *Proceedings of the 7th International Conference on Concrete Alkali-Aggregate Reactions*, (Ed. P. E. Grattan-Bellew), Noyes, NJ, 1987, pp. 110-114.

Nixon, P.J., Sims, I., "RILEM TC106 Alkali Aggregate Reaction – Accelerated Tests Interim Report and Summary of Survey of National Specifications," *Proceedings of the Ninth International Conference on Alkali-Aggregate Reaction in Concrete*, Concrete Society, Slough, Vol. 2, 1992, pp. 731–738.

Ober, J.A., "Lithium," *United States Geological Survey (USGS) Minerals Yearbook*, Lithium, 2000.

Ober, J.A., *United States Geological Survey (USGS) Mineral Commodity Summaries*, 2002.

Oberholster, R.E., Davies, G., "An Accelerated Method for Testing the Potential Reactivity of Siliceous Aggregates," *Cement and Concrete Research*, Vol. 16, 1986, pp. 181–189.

Odler, Ivan, "Special Inorganic Cements," *Modern Concrete Technology Series*, Ed. E&FN Spon, Vol. 8 2000, pp. 115–133.

Ohama, Y., Demura, K., Kakegawa, M., "Inhibiting Alkali-Aggregate Reaction With Chemical Admixtures," *Proceedings of the Eighth International Conference on Alkali-Aggregate Reaction*, (Eds. K.Okada, S. Nishibayashi, and M. Kawamura), Kyoto, Japan, 1989, pp. 253–258.

Pedneault, A., "Development of Testing and Analytical Procedures for the Evaluation of the Residual Potential of Reaction, Expansion, and Deterioration of Concrete Affected by ASR," M.Sc. Memoir, Laval University, Québec City, Canada, 1996, 133 pp.

Powers, T.C., Steinour, H.H., "An Investigation of Some Published Researches on Alkali-Aggregate Reaction: I. The Chemical Reactions and Mechanism of Expansion," *Journal of the American Concrete Institute,* Vol. 26, No. 6, 1955, pp. 497–516.

Prezzi, M., Monteiro, P.J.M., Sposito, G., "The Alkali-Silica Reaction, Part I: Use of the Double-Layer Theory to Explain the Behavior of the Reaction-Product Gels," *ACI Materials Journal*, 94, No. 1, 1997, pp. 10–17.

Prezzi, M., Monteiro, P.J.M., Sposito, G., "The Alkali-Silica Reaction, Part 2: The Effect of Chemical Additives," *ACI Materials Journal*, Vol. 95, No. 1, 1998, pp. 3–10.

Qi, Z., Wen Z-Y., "Effects of Lithium Hydroxide on Alkali Silica Reaction Gels," *Proceedings of the 12th International Conference on Alkali-Aggregate Reactivity*, Beijing, China, October 2004, pp. 801–804.

Qian, G., Deng, M., Tang, M., "Expansion of Siliceous and Dolomitic Aggregates in Lithium Hydroxide Solution," *Cement and Concrete Research*, Vol. 32, 2002, pp. 763–768.

Qinghan, B., Nishibayashi, S., Xuequan, W., Yoshino, A, Hong, Z., Tiecheng, W., Mingshu, T., "Preliminary Study of the Effects of $LiNO_2$ on Expansion of Mortars Subjected to Alkali-Silica Reaction," *Cement and Concrete Research*, Vol. 25, 1995, pp. 1647–1654.

Ramachandran, V.S., "Alkali-Aggregate Expansion Inhibiting Admixtures," *Cement and Concrete Composites*, Vol. 20, Nos. 2–3, 1998, pp. 149–161.

Ramyar, K., Copuroglu, O., Andic, O., Fraaij, A.L.A., "Comparison of Alkali-Silica Reaction Products of Fly Ash or Lithium-Salt-Bearing Mortar Under Long-Term Accelerated Curing," *Cement and Concrete Research,* Vol. 34, No. 7, 2004, pp. 1179–1183.

Rodrigues, F.A., Monteiro, P.J.M., Sposito, G., "The Alkali-Silica Reaction: The Effect of Monovalent and Bivalent Cations on Surface Charge Density of Opal," *Cement and Concrete Research*, 31, 2001, pp. 1549–1552.

Sakaguchi, Y., Takakura, M., Kitagawa, Hori, T., Tomosawa, F., and Abe, M.., "The Inhibiting Effect of Lithium Compounds on Alkali-Silica Reaction," *Proceedings of the Eighth International Conference on Alkali-Aggregate Reaction*, Kyoto, Japan, 1989, pp. 229–234.

Shehata, M.H., Thomas, M.D.A., Bleszynski, R.F., "The Effect of Fly Composition on the Chemistry of Pore Solution," *Cement and Concrete Research*, Vol. 29, 1999, pp. 1915–1920.

Shehata, M.H., Thomas, M.D.A., "The Effect of Fly Ash Composition on the Expansion of Concrete Due to Alkali Silica Reaction," *Cement and Concrete Research*, Vol. 30, 2000, pp. 1063–1072.

Shehata, M.H., Thomas, M.D.A., "Use of Ternary Blends Containing Silica Fume and Fly Ash to Suppress Expansion Due to Alkali-Silica Reaction in Concrete," *Cement and Concrete Research*, Vol. 32, 2002, pp. 341–349.

Stanton, T.E., "Expansion of Concrete Through Reaction Between Cement and Aggregate," *Proceedings of the American Society of Civil Engineers,* Vol. 66, No. 10, 1940, pp. 1781–1811.

Stark, D., Morgan, B., Okamoto, P., Diamond, S., *Eliminating or Minimizing Alkali-Silica Reactivity*, SHRP-C-343, National Research Council, Washington, DC, 1993.

Stark, D., "Lithium Salt Admixtures – An Alternative Method to Prevent Expansive Alkali-Silica Reactivity," *Proceedings of the Ninth International Conference on Alkali-Aggregate Reaction in Concrete*, London, United Kingdom, July 1992.

Stark, D., Bhatty, M.S.Y., "Alkali-Silica Reactivity: Effect of Alkali in Aggregate on Expansion," *Alkalies in Concrete*, ASTM STP 930, American Society for Testing and Materials, Philadelphia, PA, 1986, pp. 16–30.

Stark, D., "Alkali-Silica Reactivity in the Rocky Mountain Region," *Proceedings of the Fourth International Conference on Effects of Alkalies in Cement and Concrete,* Publication No. CE-MAT-1-78, Purdue University, W. Lafayette, IN, 1978, pp. 235–243.

Stokes, D.B., Wang, H.H., and Diamond, S., "A Lithium-Based Admixture for ASR Control That Does Not Increase the Pore Solution pH," *Proceedings of the Fifth CANMET/ACI International Conference on Superplasticizers and Other Chemical Admixtures in Concrete*, SP-173, 1997, pp. 855–867.

Stokes, D.B., Manissero, C.B., Roy, D.M., Malek, R.I., and Roumain, J.C., "Portland Cement Manufacture Containing Lithium for ASR Control," *Proceedings of the 11th International Conference on Alkali-Aggregate Reaction (ICAAR)*, Quebec, Canada, June 11–16, 2000a, pp. 773–782.

Stokes, D.B., Thomas, M.D.A., and Shashiprakash, S.G., "Development of a Lithium-Based Material for Decreasing ASR-Induced Expansion in Hardened Concrete," *Proceedings of the 11th International Conference on Alkali-Aggregate Reaction in Concrete*, Eds. M.A. Bérubé, et al., CRIB, Quebec City, Canada, 2000b, pp. 1079–1087.

Strategic Highway Research Program, *Handbook for the Identification of Alkali-Silica Reactivity in Highway Structures*, SHRP C-315, 1991.

Tang, M.S., Su-Fen, H., "Effect of Ca(OH)$_2$ on Alkali-Silica Reaction," *Proceedings of the Eight International Congress of Cement Chemistry*, Paris, France, Vol. 2, 1980, pp. 94–99.

Tang, M., "Some Remarks About Alkali-Silica Reactions," *Cement and Concrete Research,* Vol. 33, No. 117, 1981, pp. 208–219.

Thomas, M.D.A., Bleszynski, R.F., "The Use of Silica Fume to Control Expansion Due to Alkali-Aggregate Reactivity in Concrete—A Review," *Materials Science of Concrete,* Eds. J. Skalny and S. Mindess, American Ceramic Society, Vol. 6, 2000.

Thomas, M.D.A., Innis, F.A., "Use of the Accelerated Mortar Bar Test for Evaluating the Efficacy of Mineral Admixtures for Controlling Expansion Due to Alkali-Silica Reaction," *Cement, Concrete, and Aggregates*, Vol. 21, No. 2, 1999, pp. 157–164.

Thomas, M.D.A., Nixon, P. J., Pettifer, K., "The Effect of Pulverized Fuel Ash With a High Total Alkali Content on Alkali-Silica Reaction in Concrete Containing Natural U.K. Aggregate," *Proceedings of the Second CANMET/ACI International Conference on Durability of Concrete,* Ed. V.M. Malhotra, American Concrete Institute, Detroit, MI, Vol. 2, 1991, pp. 919–940.

Thomas, M.D.A., Blackwell, B.Q., Pettifer, K., "Suppression of Damage From Alkali Silica Reaction by Fly Ash in Concrete Dams," *Proceedings of the Ninth International Conference on Alkali-Aggregate Reaction in Concrete,"* Concrete Society, Slough, London, United Kingdom, Vol. 2, Concrete Society, Slough, 1992, pp. 1059–1066.

Thomas, M.D.A., Fournier, B., Folliard, K.J., *Protocol for Selecting Alkali-Silica Reaction (ASR)-Affected Structures for Lithium Treatment*, Federal Highway Administration, Report No. FHWA-HRT-04-113, 2004.

Thomas, M.D.A., Hooper, R., Stokes, D., "Use of Lithium-Containing Compounds to Control Expansion in Concrete Due to Alkali-Silica Reaction," *Proceedings of the 11th International Conference on Alkali-Aggregate Reaction (ICAAR)*, Quebec, Canada, June 11–16, 2000, pp. 783–792.

Thomas, M.D.A., Stokes, D., "Use of a Lithium-Bearing Admixture to Suppress Expansion in Concrete Due to Alkali-Silica Reaction," *Transportation Research Record, No. 1668*, 1999, pp. 54–59.

Thomas, M.D.A, Baxter, S., Stokes, D., Hill, R., "The Combined Use of Fly Ash and Lithium for Controlling Expansion Due to Alkali-Silica Reaction," Presented at the International Center for Aggregate Research (ICAR) Symposium, Austin, TX, 2001.

Thomas, M.D.A., Personal communications, 2002.

Thomas, M.D.A., Stokes, D., Rodgers, T, "The Effect of Lithium-Based Admixtures on the Properties of Concrete," October 2003.

Thomas, M.D.A., Fournier, B., Folliard, K.J., Shehata, M., and Ideker, J.H., "Performance Limits for Evaluating Supplementary Cementing Materials using the Accelerated Mortar Bar Test," *Portland Cement Association,* R&D Serial No. 2892, Portland Cement Association, Skokie, IL, 2005, 22 pages.

Thomson, M.C., "Field Installation in Pennsylvania to Assess SHRP Recommendations for ASR Control, Part 2: Laboratory Testing of Job Material," *Proceedings of the 11th International Conference on Alkali-Aggregate Reactions,* Eds. Bérubé, et al., Quebec City, Canada, 2000, pp. 1215–1224.

Thomson, M.C., Stokes, D.B., "Field Installation in Pennsylvania to Assess SHRP Recommendations for ASR Control," *TRB Catalogue of 1999 Practical Papers, Design and Construction of Transportation Facilities*, Transportation Research Board, Paper No. 991190, Transportation Research Board, Washington, DC, 1999, pp. 29–30.

Tremblay, C., Bérubé, M.A., Fournier, B., Thomas, M.D.A., "Performance of Lithium-Based Products Against ASR: Effect of Aggregate Type and Reactivity, and Reaction Mechanisms," *Proceedings of the Seventh CANMET/ACI International Conference on Recent Advances in Concrete Technology (Suppl. Papers)*, Las Vegas, NV, May 2004a, pp. 247–267.

Tremblay, C., Bérubé, M.A., Fournier, B., Thomas, M.D.A., Folliard, K.J., "Use of the Accelerated Mortar Bar Test to Evaluate the Effectiveness of LiNO3 Against Alkali-Silica Reaction, Part 2: Comparison With the Concrete Prism Test Results," In preparation, to be submitted to the ASTM Journal of Testing and Evaluation, 2006b.

Tremblay, C., Berube, M.A., Fournier, B., Thomas, M.D.A., Stokes, D.B., "Performance of Lithium-Based Products Against ASR: Application to Canadian Reactive Aggregates, Reaction Mechanisms and Testing". 12th International Conference on Alkali-aggregate Reaction (AAR) in Concrete, Beijing (China), Proceedings edited by Tang, M. and Deng, International Academic Publishers, Beijing World Publishing Corp, October 2004b, Vol. 1, pp. 668-677.

Tremblay, C., Berube, M.A., Fournier, B. and Thomas, M.D.A., "Effectiveness of Lithium-Based Products in Concrete Made with Canadian Aggregates Susceptible to ASR", *8th CANMET/ACI International Conference on Recent Advances in Concrete Technology (*Proceedings of a Special Symposium honoring Prof. Marc-Andre Bérubé), Montréal (Canada), Proceedings published by CANMET, Ottawa, ON, Canada. May–June 2006a.

Uchikawa, H., Uchida, S., Hanehara, S., "Relationship Between Structure and Penetrability of Na Ion in Hardened Blended Cement Paste Mortar and Concrete," *Proceedings of the 8th International Conference on Alkali-Aggregate Reaction*, Eds. K. Okada, S. Nishibayashi, and M. Kawamura, Kyoto, Japan, 1989, pp. 121–128.

Wang, H.H., Tysl, S., Gillot, J.E., "Practical Implications of Lithium-Based Chemicals and Admixtures in Controlling Alkali-Silica Reaction," *Proceedings of the Fourth CANMET/ACI International Conference on Superplasticizers and Chemical Admixtures*, SP-148-20, 1994, pp 353–366.

Wang, H.H., Stokes, D.B., Tang, F., "Compatibility of Lithium-Based Admixtures With Other Concrete Admixtures," *Proceedings of the 10th International Conference on Alkali-Aggregate Reaction (ICAAR)*, Melbourne, Australia, August 18–23, 1996, pp. 884–891.

Whiting, N.M., "Comparison of Field Observations With Laboratory Test Results on Concretes Undergoing Alkali-Silica-Reaction," *Cement, Concrete, and Aggregates*, Vol. 21, No. 2, 1999, pp. 142–148.

Whitmore, D., Abbott, S., "Use of an Applied Electric Field to Drive Lithium Ions into Alkali-Silica Reactive Structures," *Proceedings of the 11th International Conference on Alkali-Aggregate Reaction in Concrete*, Eds. M.A. Bérubé, B. Fournier, and B. Durand, Quebec City, Canada, 2000, pp. 1089–1098.

Wijnen, P.W.J.G., Beelen, T.P.M., de Haan, J.W., Rummens, C.P.J., van de Ven, L.J.M., van Santen, R.A., "Silica Gel Dissolution in Aqueous Alkali Metal Hydroxides Studies by 29Si NMR," *Journal of Non-Crystalline Solids*, 1989, Vol. 109, 1989, pp. 85–94.