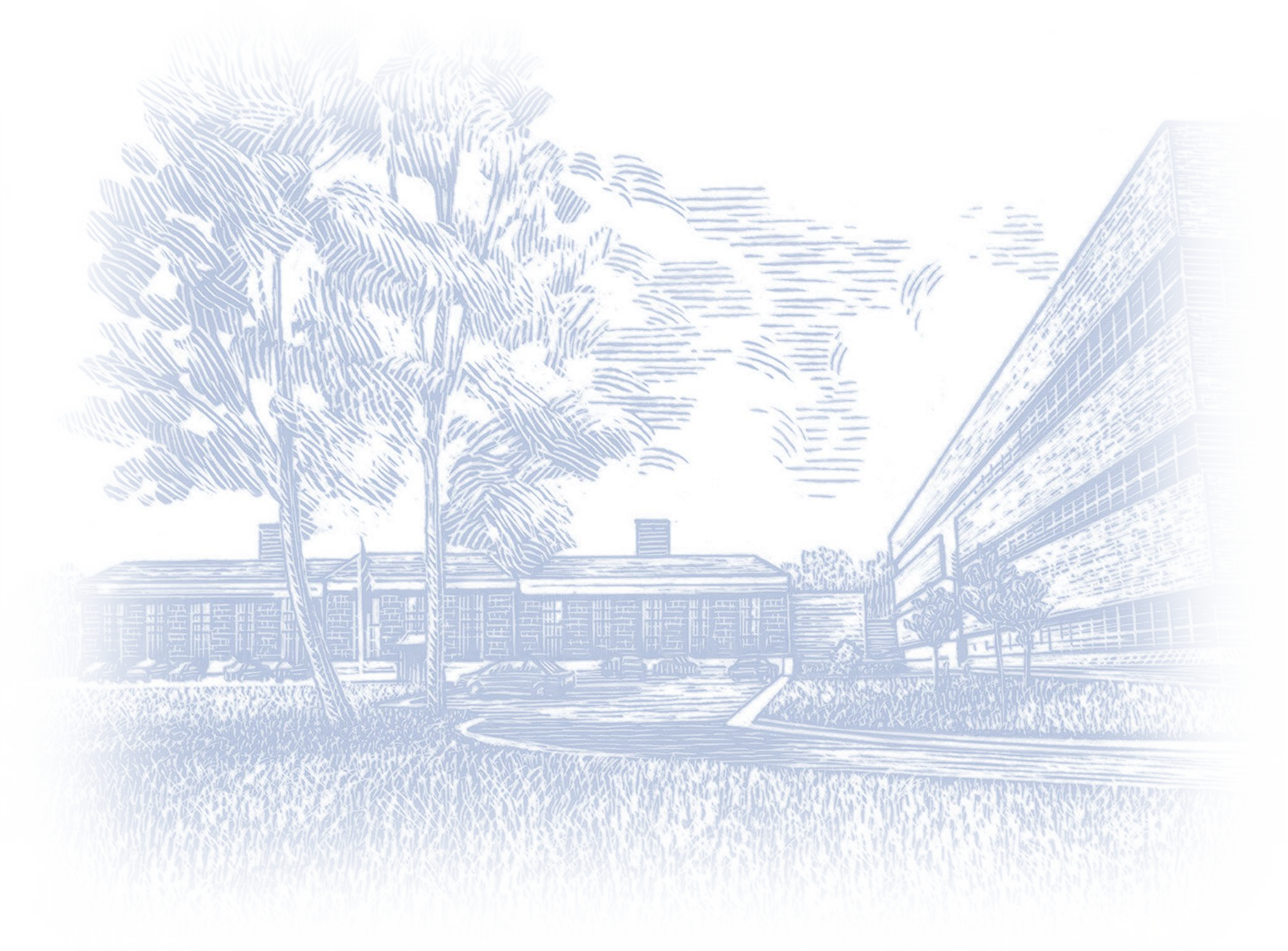
Guidelines for The Use of Lithium to Mitigate Or Prevent Alkali-Silica Reaction

Publication No.: FHWA-RD-03-047 **July 2003**



U.S. Department of Transportation
Federal Highway Administration

Federal Highway Administration
Turner-Fairbank Highway Research Center
6300 Georgetown Pike, McLean, VA 22101

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 due to this significant durability problem, the use of lithium compounds has been recognized for more than 50 years. In recent years, there has been renewed interest in using lithium compounds as either an admixture in new concrete or to treat 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 repair and extend the service life of existing concrete structures. This report will be of interest to engineers, contractors, and others involved in designing and specifying new concrete, as well as those involved in mitigating the damaging effects of alkali-silica reaction in existing concrete structures.

Sufficient copies of this report are being distributed to provide five copies to each Federal Highway Administration (FHWA) Resource Center, five copies to each FHWA Division, and a minimum of eight copies to each State highway agency. Direct distribution is being made to the division offices. Additional copies for the public are available from the National Technical Information Service (NTIS), 5825 Port Royal Road, Springfield, VA, 22161.

T. Paul Teng, P.E.
Director, Office of Infrastructure Research and Development

Notice

Technical Report Documentation Page

1. Report No.
FHWA-RD-03-047

2. Government Accession No.

3. Recipient's Catalog No.

4. Title and Subtitle
Guidelines for the Use of Lithium to Mitigate or Prevent ASR

5. Report Date

6. Performing Organization Code

7. Author(s)
Kevin J. Folliard, Michael D. A. Thomas, and Kimberly E. Kurtis

8. Performing Organization Report No.

9. Performing Organization Name and Address
The Transtec Group, Inc.1012 East 38 ½ StreetAustin, TX 78751

10. Work Unit No.

11. Contract or Grant No.
DTFH61-02-C-00051

12. Sponsoring Agency Name and Address
Office of Infrastructure R&D Turner-Fairbank Highway Research Center, HRDI-126300 Georgetown Pike, Room F-209McLean, VA 22101

13. Type of Report and Period Covered
Report

14. Sponsoring Agency Code

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

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 due to 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 in repair and service life extension applications.

This report first 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 next, 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 then 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. Finally, the report provides a summary of conclusions and identifies several technical and practical issues that should be considered for future laboratory studies and field applications.

17. Key Words
alkali-silica reaction, lithium, concrete durability, mitigation, fresh concrete, hardened concrete, case studies, laboratory

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

U.S. Department of Transportation
Federal Highway Administration

testing, field investigation, existing structures			
19. Security Classif. (of this report) Unclassified	**20. Security Classif. (of this page)** Unclassified	**21. No. of Pages** 86	**22. Price**

Form DOT F 1700.7 Reproduction of completed page authorized

Table of Contents

List of Figures

List of Tables

List of Acronyms and Abbreviations

Terms	
AASHTO	American Association of State Highway and Transportation Officials
ACR	alkali-carbonate reaction
ASR	alkali-silica reaction
ASTM	American Society for Testing and Materials
BRE	Building Research Establishment
CSA	Canadian Standards Association
DOT	Department of Transportation
ECE	Electrochemical chloride extraction

EDL	Electrical double layer
LANL	Los Alamos National Laboratory
SCM	Supplementary cementing material
SHRP	Strategic Highway Research Program

Chemical Notations

C-S-H	Calcium silicate hydrate
CaOH	Calcium hydroxide
KCl	Potassium chloride
K_2O	Potassium oxide
KOH	Potassium hydroxide
Li:(Na + K)	Molar ratio of lithium ions to the sum of sodium and potassium ions
$LiBO_2$	Lithium borate
LiCl	Lithium chloride
Li_2CO_3	Lithium carbonate
LiF	Lithium fluoride
$LiNO_3$	Lithium nitrate
LiOH	Lithium hydroxide
$LiOH \cdot H_2O$	Lithium hydroxide monohydrate
Li_2SiO_3	Lithium silicate
Li_2SO_4	Lithium sulfate
NaCl	Sodium chloride
Na_2O	Sodium oxide
Na_2O_e	Total sodium oxide equivalent
NaOH	Sodium hydroxide
OH^-	Hydroxyl ion
Si-O-Si	Siloxane
Si-OH	Acidic silanol

Measurements

cm	centimeter
g	gram
GPa	Gigapascal
kg	kilogram
kgf	kilogram (force)

L	liter
M	Molar
m	meter
ml	milliliter
mm	millimeter
MPa	Megapascal
N	Normal
ppm	parts per million
w/cm	water-cementitious material 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 use of lithium compounds has been known to be effective in controlling ASR-induced expansion for about 50 years, there have been only limited field applications. 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 for existing structures. Because of the limited use of lithium compounds in laboratory research and field applications, guidelines have been lacking. This report presents guidelines and recommendations to provide practitioners with the required tools to test, specify, and use lithium compounds in concrete construction and repair applications.

1.2 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. This chapter provides 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 salts suppress expansion. It also includes a brief discussion on specifications related to lithium usage as a concrete admixture.

Chapter 4 describes several major field applications of lithium compounds that 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 guidelines for using lithium compounds as an admixture in new concrete and as a method of treating existing structures suffering from ASR-induced damage. The guidelines are aimed at helping practitioners test, specify, and use lithium in concrete construction applications. The guidelines are based on a comprehensive review of past 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 was first identified as a cause of concrete deterioration more than 60 years ago (Stanton, 1940). Since this initial discovery, there have been reported cases throughout the world. Of the two types of alkali-aggregate reaction, 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. Figure 1 shows the distribution of some of the reported ASR cases in the United States. Each star in the figure represents a reported case of ASR.

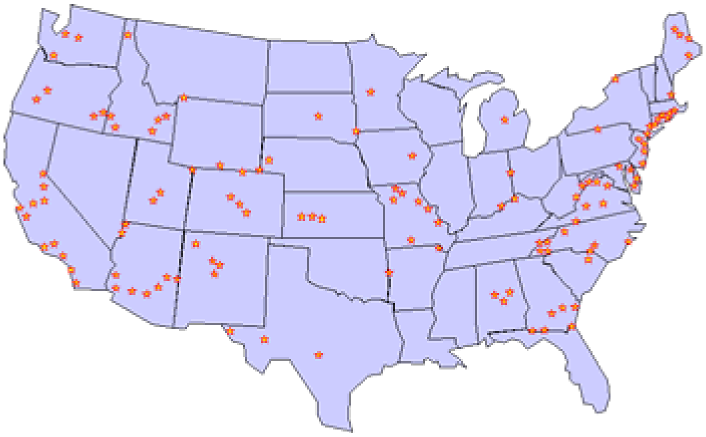


Figure 1. A Sample of Reported Cases of ASR in the United States.

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

2.2.1Essential 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 2) are: (1) reactive silica (from aggregates); (2) sufficient alkalies (mainly from portland cement, but also from other constituent materials); and (3) sufficient moisture. Eliminating any one of the above components effectively will prevent damage due to ASR, as discussed next.

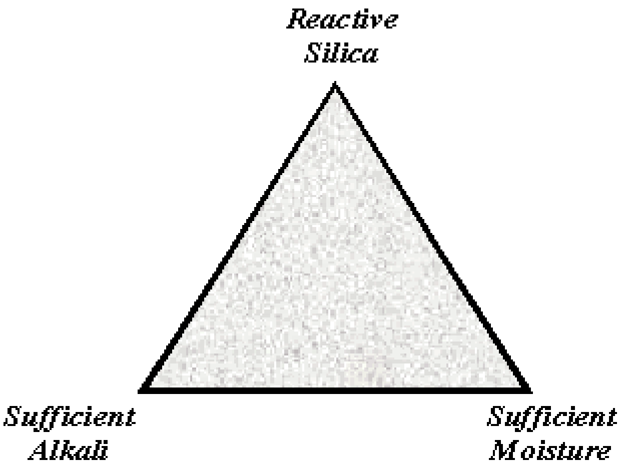


Figure 2. The Three Necessary Components for ASR-Induced Damage in Concrete.

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 use of reactive aggregates 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 alkali-hydroxides (sodium and potassium) to form 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, lists 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 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 Alkalies

The presence of sufficient alkalies is another required ingredient for ASR. The source of alkalies 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).

Of the above materials, portland cement is the main contributor of alkalies. The alkalies present in portland cement are in the form of potassium oxide (K_2O) and sodium oxide (Na_2O). The quantity of alkalies in portland cement is typically expressed as follows:

Equation 1:	$Na_2O_e = Na_2O + 0.658K_2O$
Equation 1. Total sodium oxide equivalent (or equivalent soda) in percent by mass is equal to the sodium oxide content in percent plus 0.658 times the potassium oxide content in percent.	

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 alkalies 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 alkalies 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 due to 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 the American Society for Testing and Materials (ASTM) standard 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 kilograms per cubic meter (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 3 illustrates the effects of the alkali content of concrete on expansion, using ASTM C 1293 (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 was generally resistant to 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 alkalies 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).

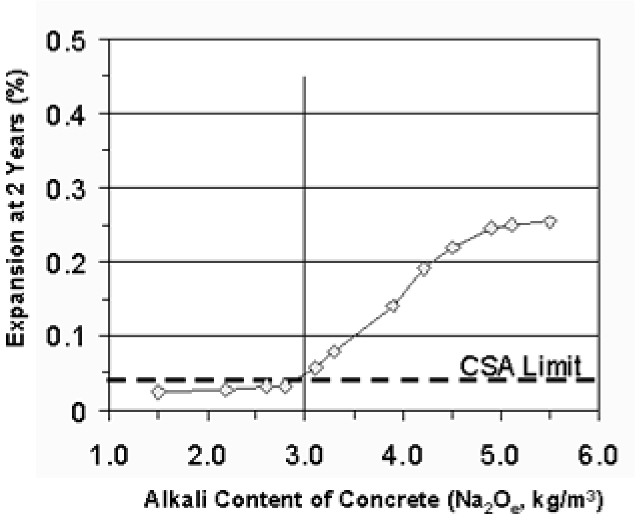


Figure 3. Effect of Alkali Content on Expansion Using ASTM C 1293 (after Thomas, 2002).

There has been significant debate regarding the impact of alkalies from supplementary cementing 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 alkalies 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 alkalies 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 alkalies 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, alkalies 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). Stark and

Bhatty (1986) reported that certain aggregates can release alkalies equivalent to 10 percent of the portland cement content under extreme conditions.

The total alkali content within a given concrete mixture may also be increased by the penetration of alkalies from external sources, such as seawater, ground water (containing sulfates), deicing salts, and brackish water. For example, Nixon et al. (1982) 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.

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., due to 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.

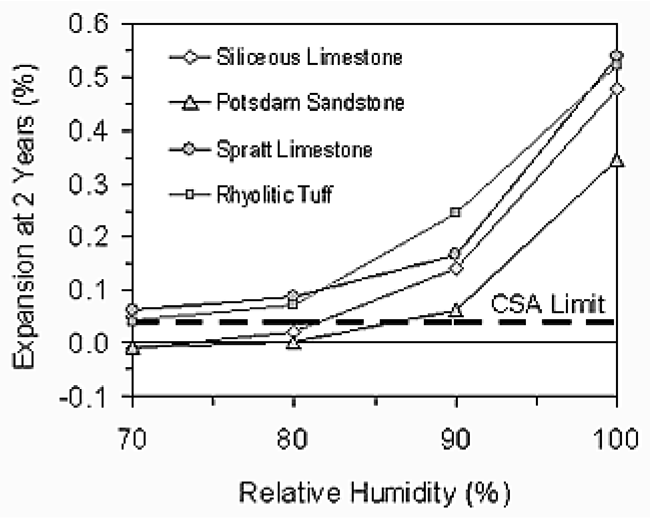


Figure 4. Effect of Relative Humidity on Expansion Using ASTM C 1293 (Pedneault, 1996).

After ASR gel forms, the subsequent water imbibing causes expansion within concrete, which ultimately can lead to tensile stresses and cracking. It generally is believed that a minimum relative humidity of 80 percent is required to cause significant expansion due to ASR. Data supporting the importance of moisture on expansion are shown in figure 4, where 5 different reactive aggregates were stored under different moisture conditions, and the expansion of concrete prisms (ASTM C 1293) was assessed (Pedneault, 1996). In this experiment, concrete that was maintained in an environment with less than 80 percent relative humidity did not undergo significant expansion (e.g., expansion 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, but 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 alkalies, 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 OH^- ions in the pore solution and certain siliceous components of the aggregates. The alkalies, specifically sodium and potassium, do not actually attack the reactive silica. The importance of the alkalies 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 alkalies 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 siloxane (Si-O-Si) linkages are also attacked, as shown in equation 3.

Equation 2: $\equiv\mathrm{Si\text{-}OH} + \mathrm{OH^-} \rightarrow \equiv\mathrm{Si\text{-}O^-} + \mathrm{H_2O}$

Equation 3: $\equiv\mathrm{Si\text{-}O\text{-}Si}\equiv + 2\mathrm{OH^-} \rightarrow 2\,(\equiv\mathrm{Si\text{-}O^-}) + \mathrm{H_2O}$

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.

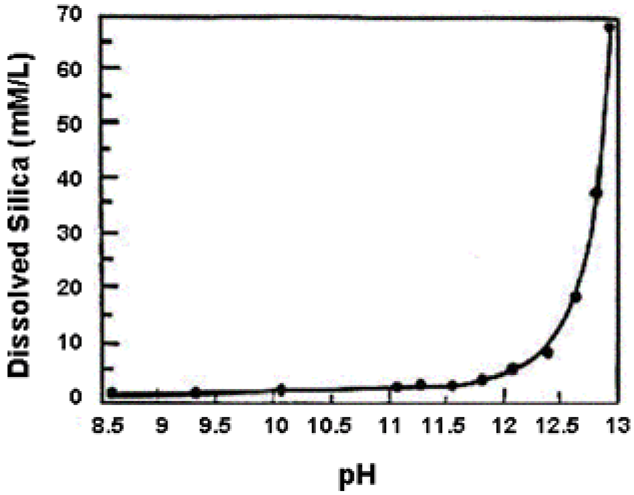


Figure 5. Effect of pH on Dissolution of Amorphous Silica (Tang and Su-fen, 1980).

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 governs the rate and/or amount of dissolution. Poorly crystalline or amorphous silica is much more prone to ASR than well-crystallized or dense forms of silica. One reason for this difference in behavior is that the solubility of amorphous silica increases significantly with pH, as illustrated in figure 5. 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 ASR gel expansion mechanisms. It is beyond the scope of this publication to examine thoroughly the various proposed mechanisms, but 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 semipermeable 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 due to ASR would relieve hydraulic pressure and prevent further expansion. They proposed an alternative mechanism, in which water is absorbed physically 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 due to 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. Kilgour (1988) supported this theory and showed that a low-calcium fly ash exposed to an alkali-hydroxide solution without the presence of calcium was partially soluble, losing up to 20 percent of its mass in 6 months. However, the same test performed in the presence of calcium hydroxide (CaOH) resulted in an increase in mass, and formed a reaction product similar in structure to ASR 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 gram (g) ash in 100 milliliters (ml) of 0.7 molar (M) sodium hydroxide (NaOH)-potassium hydroxide (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 6 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.

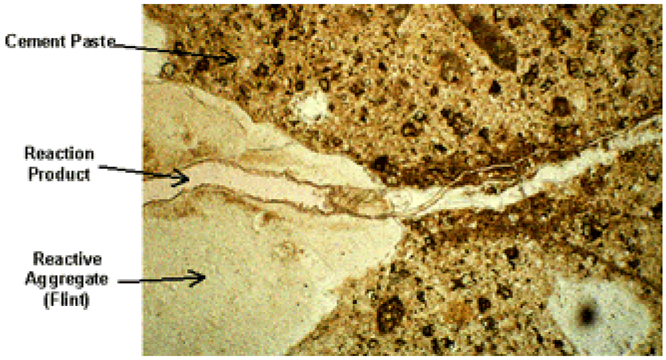
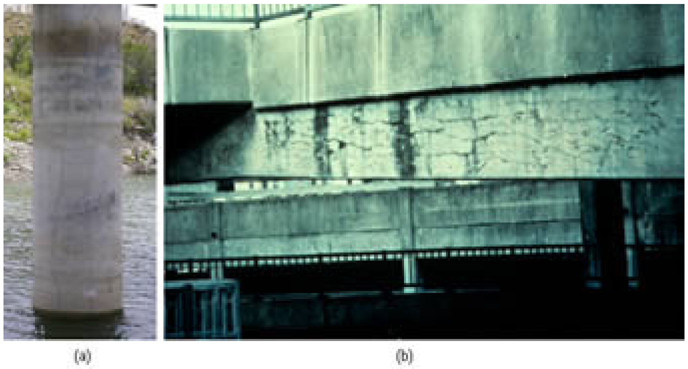


Figure 6. Thin-Section Cut of ASR-Damaged Concrete, Showing ASR Gel and Typical Crack Pattern (Through Aggregate and into Surrounding Matrix).

Figure 7. 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 posttensioned). Figure 7 shows typical ASR-induced damage in unrestrained concrete, resulting in classic map-cracking. Figure 8 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)

(b)

Figure 8. ASR-Induced Damage in Restrained Concrete Elements, Including (a) Reinforced Concrete Column, and (b) Prestressed Concrete Girder.

When field structures suffer from excessive expansion due to ASR, significant misalignment (with respect to adjacent elements) may result, as shown in figure 9. For pavements suffering from ASR, the subsequent expansion can lead to extrusion of joint-sealing material or even joint failure, as shown in figure 10.

Figure 9. Misalignment of Adjacent Sections of a Parapet Wall on a Highway Bridge Due to ASR-Induced Expansion (SHRP-315, 1994).

Figure 10. Extrusion of Joint-Sealing Material Triggered by Excessive Expansion from 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 measure the effectiveness of various methods to mitigate 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: ASTM C 1260 ("Accelerated Detection of Potentially Deleterious Expansion of Mortar Bars Due to Alkali-Silica Reaction") and 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 that contain 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 the bars are removed from the water, they are measured for initial length and then submersed in a 1 normal (N) NaOH solution at 80 °C, where they are then stored for 14 days. Length change measurements are made periodically during this storage period. The 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 as follows:

ASTM C 1260 expansion criteria:	CSA A23.2-25A expansion criteria:
< 0.10 percent is considered innocuous0.10 to 0.20 percent is considered potentially reactive > 0.20 percent is considered reactive	> 0.15 percent is considered reactive (all aggregates except limestones) > 0.10 percent is considered reactive (limestone aggregates only)

Table 2. Available Standard Tests for Assessing ASR.

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 alkalies from specimens.
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.
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 PyrexTM glass. - Test not very reliable because of the use of Pyrex glass, which is sensitive to test conditions and contains alkalies 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 severity of 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. - Test has shown promise in testing SCMs and lithium compounds, but the soak solution must be modified when testing lithium compounds (as discussed in 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%) at 38 °C. - Uses high-alkali cement (raised to 1.25% Na20e), 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 requires 1 year for completion. - Also can be used to test effectiveness of SCMs and lithium compounds, but then test typically is run for 2 years. - Widely accepted test method, but 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). 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), where an expansion limit of 0.10 percent typically is used. The test is not, however, suitable for assessing cement alkalinity, because the highly alkaline soak solution masks any cement alkalinity effect. In addition, ASTM C 1260 is not suitable for testing lithium compounds unless the soak solution is modified by adding lithium directly to the soak solution. Without this modification, significant lithium leaching would result. More specific information on proposed ASTM C 1260 modifications to assess lithium compounds is provided in chapter 3.

ASTM C 1293, commonly referred to as the concrete prism test, 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 alkalies (NaOH) then are 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 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 limited its use somewhat.

In recent years, more countries and agencies have adopted the concrete prism test as a standard method. An expansion limit of 0.04 percent (at the end of the 1- or 2-year test) typically is specified, as this value has been reported to correlate well with cracking of test prisms. This expansion limit (0.04 percent) is referenced in the appendix to ASTM C 1293. As part of the most recent guidance provided by CSA (2000a), the expansion limits for the concrete prism test (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 marginally 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 generally is 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 due to 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 alkalies). 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 alkalies 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 alkalies from 1.1 to 3.6 kg/m^3 Na_2O_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 fly ash, ground-granulated blast furnace slag, silica fume, and combinations of SCMs (ternary blends).

Fly ash is one of the most commonly used SCMs in the world, partly because it offers both 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 due to the higher alkali-binding capacity of concretes containing lower-lime ashes (Shehata et al., 1999). Specifically, fly ash lower in CaO produces a calcium silicate hydrate (C-S-H) structure with a lower calcium to silicon ratio, which imparts a negative surface charge, leading to the absorption of cations, especially alkalies (Glasser, 1992). In addition, low-calcium ashes are more effective in controlling ASR because the alkalies contained in the ash generally are not available to the pore solution (Diamond, 1981), whereas high-calcium ashes tend to make their alkalies more readily available. Although higher-lime ashes can still be used to combat ASR, significantly higher dosages may be needed, especially when using highly reactive aggregates.

Slag also is used commonly to mitigate ASR and typically is used in higher dosages than fly ash, generally 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 appears to increase the alkali-binding capacity of concrete (similar to low-calcium fly ash), but 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 alkalies available within the concrete. Thus, dosing silica fume based on the total alkalies within a given concrete mixture has been proposed in recent years (Thomas and Bleszynski, 2000; CSA, 2000a), with the required silica fume dosage ranging between the lower and upper limits shown below (based on required levels of prevention):

Equation 4: Lower limit: Minimum % SF = 2 x (alkali contributed by portland cement)

Equation 5: 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) alkali contributed by portland cement is expressed as kg of Na_2O_e per m^3 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 due to 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 constructibility 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 otherwise would be used individually, because the combined effects work together 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 11.

Using Lithium Compounds

Using lithium compounds, especially lithium nitrate ($LiNO_3$), 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.

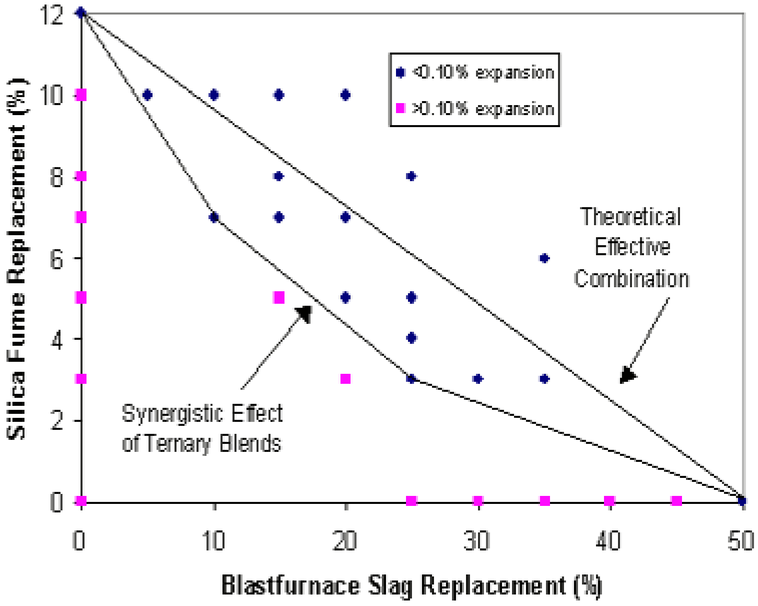


Figure 11. Synergistic Effects of Ternary Blends in Controlling ASR Expansion Using ASTM C 1260 (after Bleszynski et al., 2000).

2.4.2 Mitigating ASR in Existing Concrete

When ASR-induced expansion and damage already has 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 moisture ingress.
- Treat existing cracks to minimize future expansion (and direct moisture ingress, 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 mitigation technique guidelines).

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, 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, but the overall approach to specifying preventive measures to control ASR in new concrete structures can be placed in two categories: performance-based specifications and 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 not all 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 size of the structure and the environment to which it will be exposed are then considered, and the structure is placed within specified risk levels. The level of prevention and the preventive measures (if required) are determined based on the desired design life of the structure. The guidelines are shown in table 3, which includes 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.

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.

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

Type of SCM	Total Alkali Content of SCM (% Na_2O_e)*	Chemical Composition Requirement (% oxides)	Cement Replacement Level (% by mass)a		
			Prevention Level W	Prevention Level X	Prevention Levels Y & 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 CSA A23.5 requirements may be used, provided that their effectiveness in controlling expansion due to ASR is demonstrated according to CSA Recommended Practice.				
Ternary Blends	When two or more SCMs are used together to control ASR, the minimum replacement levels given in table 5 of the CSA Guidelines (CSA, 2000a) 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 this table, provided that the slag level is at least two-thirds of the minimum slag level given in the table.				

* Na_2O_e = sodium oxide content = $Na_2O + 0.658 * K_2O$

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% Na_2O_e.

b. In the presence of reactive or potentially reactive aggregates, blast furnace slag and silica fumes with alkali contents > 1.0% Na_2O_e, and fly ash with alkali contents > 4.5% Na_2O_e and/or with CaO contents > 20% 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% 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_2O_e), but in cases where silica fume is the only SCM to be used, the silica fume content should be 7.0% by mass.

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 test, specify, and use lithium compounds efficiently.

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/cubic centimeter (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 (Lumley, 1997). The table also includes the location of major mineral deposits, although other significant deposits also have been identified worldwide. Table 4. Principal Lithium Minerals and their Sources (after Lumley, 1997).

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	$K_2(Li,Al)_{5-6}\{Si6\text{-}7Al2\text{-}1)_{20}\}(OH,F)_4$	Brazil, Canada, Namibia, Zimbabwe
Eucryptite	$Li_2Al_2O3\cdot 2SiO_2$	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 ºC), 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 that 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 LiOH, lithium hydroxide (LiOH), lithium hydroxide monohydrate ($LiOH \cdot H_2O$), lithium chloride (LiCl), lithium fluoride (LiF), and 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. Over 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, lithium silicate (Li_2SiO_3), $LiNO_3$, and lithium sulfate (Li_2SO_4)), which essentially eliminated expansion after 8 weeks storage at 38 ºC, 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 a resurgence in the interest in lithium-bearing compounds. This is reflected in an increase in scientific publications and field applications on the topic.

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), 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 effectively reduce expansion in concrete affected by ASR, the mechanism or mechanisms by which these additives reduce expansion are not 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 the following:

- 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 ASR in the presence of lithium. Stark (1992) proposed that during the ASR, 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 attack by other alkalies (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 alkalies sodium and potassium.

Others (Chatterji, 1987) disagree, however, 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 alkalies 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; 2000; in press), however, have proposed that strong field exchange behavior, where cations are in direct contact with a surface, may account for the preference of the ASR gel for Li^+ as compared to Na^+ and K^+, as described by Sakaguchi (1989).

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:

Equation 6: $$\mathrm{LiOH} < \mathrm{NaOH} < \mathrm{KOH}$$

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 ASR, 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 silicon 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.

Proposed Mechanism: Decreased Repolymerization

Based upon microscopy, elemental analysis, and surface chemistry principles, Kurtis et al. (1998, 2000, in press) 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.

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 electrical double layer (EDL) theory to explain the expansion of the alkali-silica reaction 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 gel expansion. 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:

Equation 7: $$Al^{+3} < Ca^{+2} < Mg^{+2} < Li^{+} < K^{+} < Na^{+}$$

However, 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 (-s) effectively reduces the pressure (DP) generated by ASR gel expansion:

$$\text{Equation 8: } \Delta P = C_o RT\left(y_o + \frac{1}{y_o} - 2\right)$$

Where: C_o is the bulk electrolyte concentration
R is the molar gas constant
T is the absolute temperature and

$$\text{Equation 9: } y_o^{0.5} = 4\tan^{-1}\left[\frac{-\sigma}{2Fy_o}\left(\frac{\beta}{C_o}\right)^{0.5}\right]$$

Where:F is the Faraday constant
ß=1.084x1016m/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 a ASR-affected dam) (unpublished data) were decreased in the presence of LiCl, as compared to sodium chloride (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 potassium chloride (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 posttreating 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 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 12 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

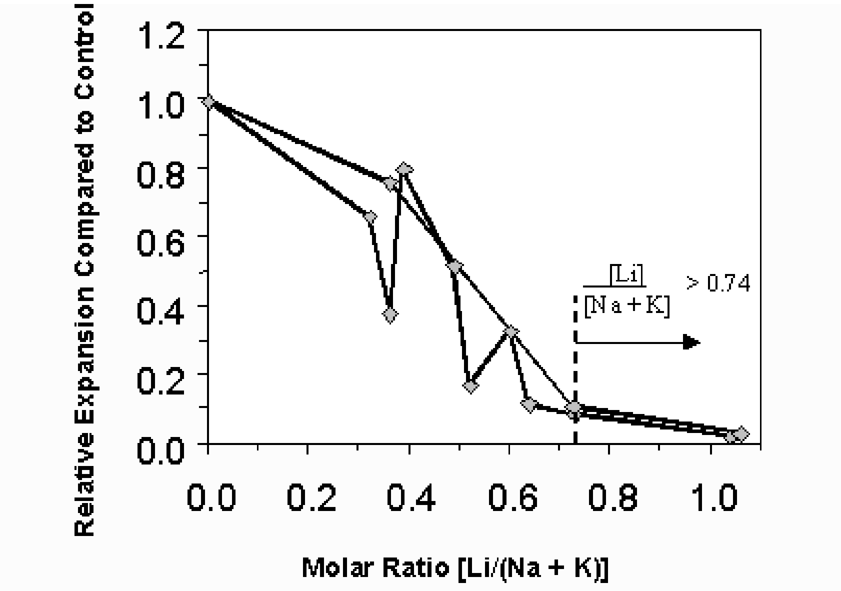


Figure 12. Relative Expansion of Mortar Bars Containing Lithium Compounds (after McCoy and Caldwell, 1951).

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 tests recommended for testing lithium compounds in chapter 2, specifically the concrete prism test (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 alkalies 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 $LiOH•H_2O$(by mass of cement,%)	Molar Ratio Li:(Na + K)	Expansion after 1 Year (%)	Relative Expansion Compared to Control (%)
0.00	0.0	0.88	100
0.27	0.3	0.86	97
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 relative humidity, then subjected to autoclaved curing at 128 °C under a pressure of 2.5 kilogram (force) (kgf)/cm_2 for 4 hours, after which the bars were cooled back to 20 cm^2 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 the Strategic Highway Research Program (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 essentially was 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 ofcement, %)	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_2CO_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 ºC, then placed in an autoclave under a pressure of 0.28 Megapascals (MPa) for 4 hours. After they were removed from the autoclave, the bars were placed in a curing container at 20 ºC for 4 months, then at an elevated temperature (40 ºC) for long-term measurements. A Li:(Na + K) molar ratio of 0.8 reduced 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 concrete prism test (ASTM C 1293) to assess the efficiency of $LiOH•H_2O$, LiF, and Li_2CO_3 in reducing expansion due to ASR. A calcined flint cristobalite was used as the reactive aggregate, and researchers covered a range of lithium dosages. The findings agreed with most published literature, suggesting that a ratio of equivalent Li2O to equivalent Na_2O 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 OH-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.

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 United Kingdom. The program involved the use of several reactive United Kingdom aggregates and also included the use of fly ash and slag. Figure 13 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 12). 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 reactivity (i.e., more reactive aggregates require more lithium), and that using fly ash in conjunction with lithium yielded synergistic reductions in expansion.

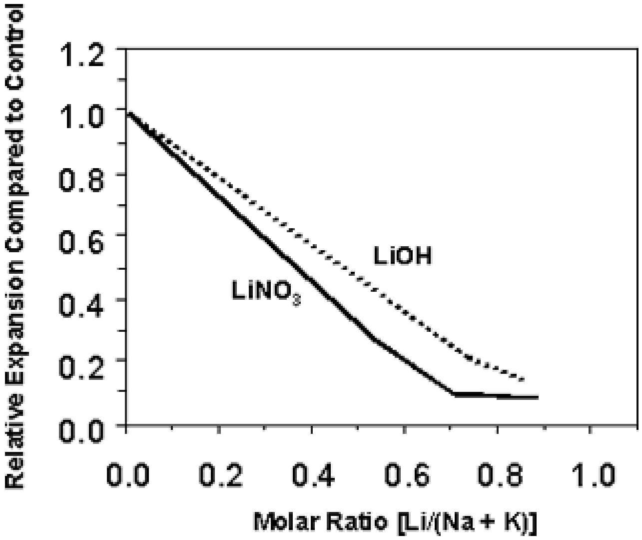


Figure 13. Relative Expansion of Concrete Prisms Containing Lithium Compounds.

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 SO4-2 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.

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 $LiLiOH•H_2O$ 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, with 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), 6 fly ashes, and 3 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. This is an important modification and is recommended whenever testing lithium compounds with ASTM C 1260 to prevent excessive leaching of lithium from the bars into the surrounding solution.

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. This approach requires less lithium, thereby reducing cost, and less fly ash, thereby increasing the early strength development. Although the combination of lithium and high-lime ashes (i.e., > 25 percent CaO) was not found to be synergistic, the combined use still sufficiently reduced expansion. Higher-lime fly ashes intrinsically are not as efficient as lower-lime ashes in controlling ASR expansion, and they require higher relative amounts to control expansion (Shehata et al., 1999). Using lithium in combination with such high-lime ashes helps control expansion, and also would provide other benefits in the field, including higher early strength (compared to low-lime ash), reduced permeability, and cost savings. It should also be noted that the lithium dose used by Thomas et al. (2001) was calculated on the basis of the portland cement alkalies alone, so even though the use of high-calcium fly ashes generally did not lead to a reduction in the dose rate (i.e. 75 percent to 100 percent of the recommended dose was needed), there is still less lithium added to these mixtures as they contain lower amounts of portland cement (due to replacement with fly ash).

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 (1998) 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 also have 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 increasing the efficiency of the active lithium compound in controlling ASR-induced expansion.

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 affect significantly 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 Relating 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	$LiOH \bullet H_2O$, $LiNO_2$, Li_2CO_3	0.90
Ohama et al. (1989)	Autoclave test	Opaline amorphous silica	$LiOH \bullet H_2O$, LiF, Li_2CO_3	0.5% (by mass of cement) for LiF0.7% (by mass of cement) for $LiOH \bullet H_2O$
Stark (1992); Stark et al. (1993)	ASTM C 227ASTM C 1260	RhyoliteGranite gneiss	$LiOH \bullet H_2O$, LiF, Li_2CO_3	0.6 (LiF)0.92 (Li_2CO_3)0.75-1.00 (LiOH)
Diamond and Ong (1992)	ASTM C 227	CristobaliteBeltane 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	$LiOH \bullet H_2O$, LiF, Li_2CO_3	0.62
Blackwell et al. (1997);Thomas (2000)	ASTM C 1293	Various United Kingdom aggregates	LiOH, $LiNO_3$	0.70 (for $LiNO_3$) 0.85 (for LiOH)
Durand (2000)	ASTM C 1293	Canadian aggregates (Sudbury, Potsdam, and Sherbrooke)	$LiOH \bullet H_2O$, LiF, and Li_2CO_3 ,$LiNO_3$	0.72 (for $LiNO_3$ with Sudbury)0.82 (for $LiOH \bullet H_2O$, LiF, and $LiCO_3$ with Sudbury)

* molar ratios are used, unless otherwise noted

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 posttreating 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 $LiOH \bullet H_2O$ 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 that was previously subjected to ASR-induced expansion by soaking it in LiOH solution effectively suppressed 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 novel material for controlling future expansion of hardened concrete. The material is a $LiNO_3$-based solution, but also contains a proprietary blend of surfactants to help penetrate hardened concrete. It was reported to be 50 percent more effective than $LiNO_3$, by itself, or 3 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, Texas, New Mexico, South Dakota, and Wyoming.

The BRE (2002) has published guidelines recently for using lithium admixtures in concrete, as shown in table 9. 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 9 is only applicable for concrete with total alkali content 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. BRE does not provide guidance 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 is as follows:

- If fly ash content is greater than or equal to 25 percent (by mass of total cementitious materials)-alkalies in fly ash are not included in calculating total alkali content of concrete.
- If fly ash content is 20 to 24 percent-one-fifth of the total fly ash alkalies are included in calculating total alkali content of concrete.
- If fly ash content is less than 20 percent-all of the alkalies present in the fly ash are included in calculating total alkali content of concrete.

Table 9. BRE (2002) Guidelines for Using Lithium in New Concrete.

Aggregate Type	Lithium Compound	Fly Ash, %(by mass of cementitious materials)	Lithium Dosage		
			Mass Addition(kg per kg of Na_2Oe)	Volume Addition(L of Solution Admixture per kg of Na_2Oe)	Molar Ratio Li:(Na + K)
High Reactivity	$LiOH \bullet H_2O$ (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
Normal Reactivity	$LiOH \bullet H_2O$ (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 9 shows the molar ratio for each of the recommended lithium dosages. For the same aggregate type and fly ash content, higher dosages of lithium (based on molar ratio) are recommended for $LiOH \cdot H_2O$ 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 successfully in laboratory research to control expansion due to ASR for more than 50 years.
- Although all the mechanisms are not understood fully, it is evident that lithium affects the nature of the ASR gel, essentially rendering it nonexpansive. The reaction product (gel) still forms, but lithium greatly hinders its ability to absorb water and expand.
- Two test methods are recommended for assessing lithium compounds. ASTM C 1293 (2-year test) is the preferred test, as it better relates to field performance. ASTM C 1260 (modified by adding lithium to the soak solution) is recommended, but should be used with caution due to the limited research to date using this modified test. Specific guidelines for performing these tests to assess lithium are provided in chapter 5.
- In general, adding lithium at a molar ratio Li:(Na + K) of 0.74 is adequate to suppress expansion for most aggregates, although highly reactive aggregates may require more, and some less reactive aggregates may need less.
- $LiNO_3$ reduces expansion more efficiently than other lithium compounds, mainly because it does not raise pore solution pH.
- Lithium compounds have proven to be effective in posttreating hardened concrete that has already expanded from ASR, thereby reducing or eliminating future expansion.

There is a general lack of guidance and specifications for properly using lithium to control ASR-induced expansion. It is hoped that this document will be useful in providing technical guidance to practitioners interested in using lithium for new and existing concrete structures.

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 guidelines 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 3-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 10.

Table 10. 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™ admixture
	4	Class F Fly Ash
	5	Class C 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_2Oe (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 $LiOH \bullet H_2O$ 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_2Oe, 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 $LiOH \bullet H_2O$, respectively.

To ensure adequate dispersion of the $LiOH \bullet H_2O$ 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.

After placing the experimental pavement, the aggregates were tested in combination with the fly ashes and low-alkali cement (0.18 percent Na_2Oe) using the accelerated mortar bar test (ASTM C 1260), yielding the results shown in table 11. Aggregate-LiOH combinations were tested using ASTM C 227, but no data from these tests have been reported. The test data in table 11 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 11. Results from 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 12. Only concrete containing Class C fly ash showed any visual signs of damage when lapped samples were viewed under a stereobinocular microscope.

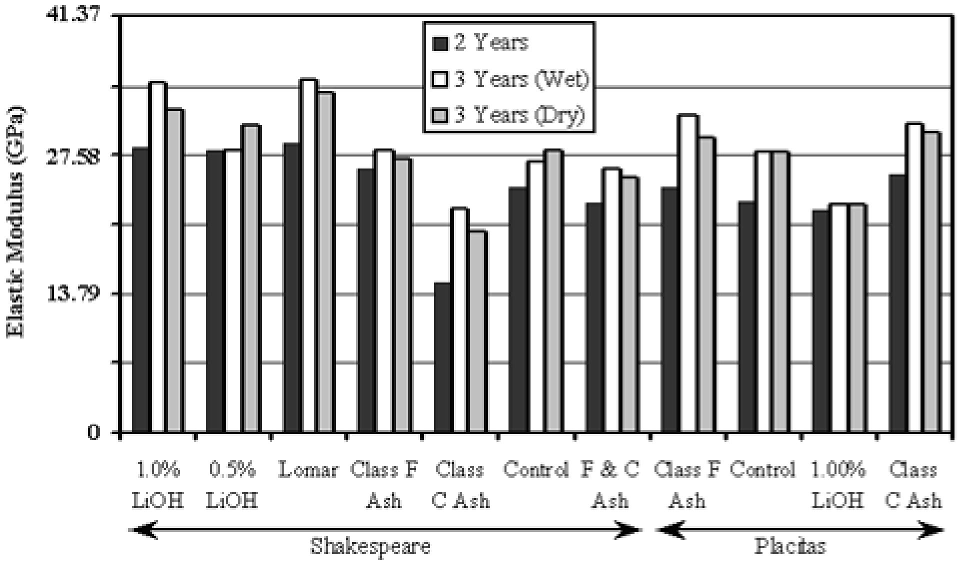


Figure 14. Elastic Modulus of Concrete Cores from Lomas Boulevard.

Table 12. Observations from Petrographic Examination of Cores.

Concrete Mixture	Cores at 2 Years		Cores at 4 Years			
	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

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, gel amount, and distress in the form of microcracking. The results of these studies, compared with the observations made at 2 years, are presented in table 12. The observations made during the later examination were ranked using a numerical scale (see table 12), which can be interpreted as shown in table 13.

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 different mixtures' performance.

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 4 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 13. 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 these will be subjected to the following tests:

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

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.

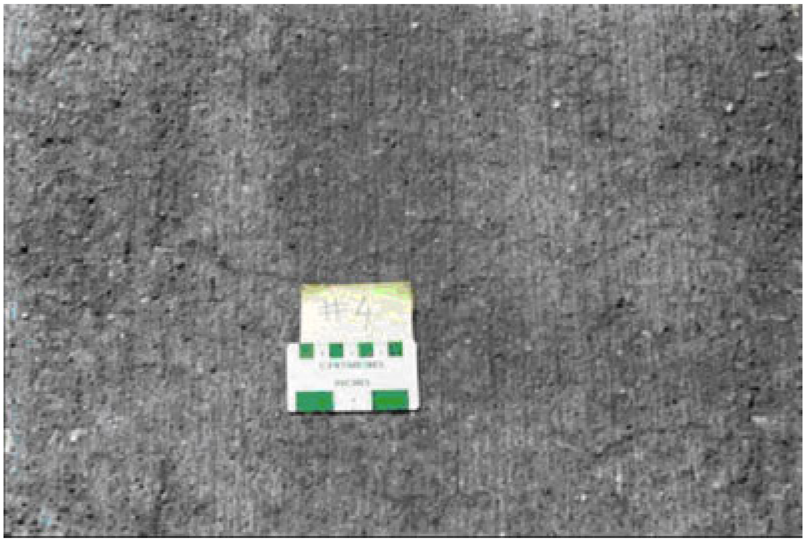


Figure 18. Section with Class F Fly Ash and Placitas-February, 1999.

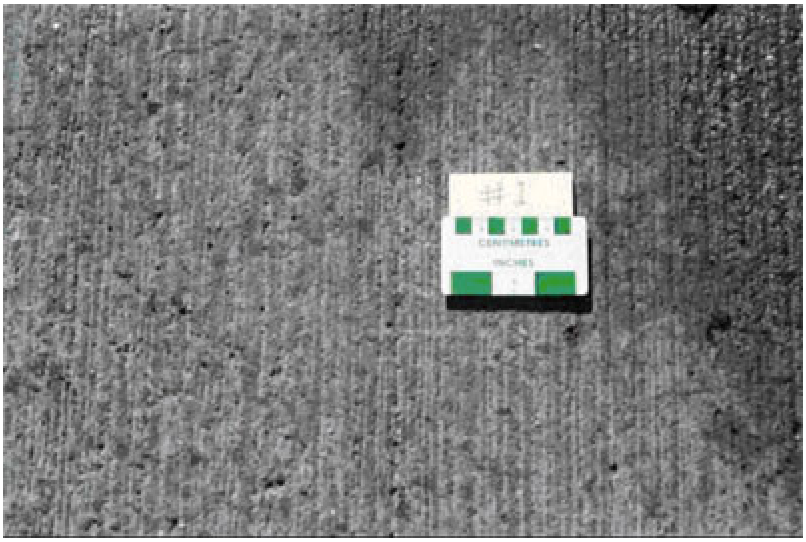


Figure 19. Section with 1 Percent LiOH and Placitas-February, 1999.

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 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 (w/cm) ratio of the mixtures was 0.44, except for mix #11 where w/cm = 0.42. LiOH 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 Lakawanna 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_2Oe) and the remaining 11 mixtures used various approaches to mitigate expansion. The preventive measures adopted are summarized in table 14.

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 14.

The test data in table 14 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 14. Summary of Mixtures Used in Lackawanna Valley Industrial Highway Experimental Pavement (Thomson, 2000).

Mix #	Preventive Measure	C 441	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% Na2Oe)	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.

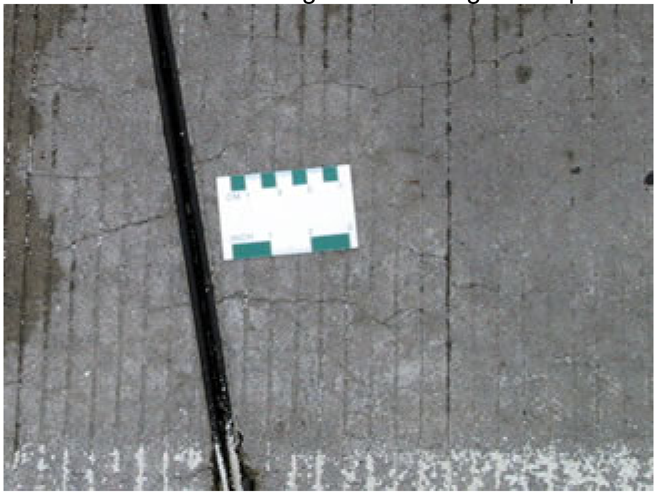


Figure 22. Lackawanna Valley Industrial Highway Experimental Pavement-15 percent Fly Ash (Mix #9)-May, 2001.

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 15.

The cement used in all of the mixtures was a Type V low-alkali (0.55 percent Na2Oe) 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 prior to its extraction. The material at this stage is known as decrepitated spodumene and is essentially 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 15. Summary of Mixtures Used in U.S. I-90 Oacoma Experimental Pavement.

Mix #	Cementitious Material (kg/m^3)		Preventive Measure	
	Type V Cement	Class F Fly Ash	Type	Dose (L/m^3)
1	356	-	LiOH Solution	9.90
2	356	-	LiOH Solution	12.87
3	356	-	LiOH Solution	15.84
4	356	-	$LiNO_3$ Solution	4.95
5	356	-	$LiNO_3$ Solution	7.43
6	356	-	$LiNO_3$ Solution	9.90
7	356	-	$LiNO_3$ Solution	12.38
8	303	66.4	$LiNO_3$ Solution	2.48
9	303	66.4	$LiNO_3$ 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 U.S. 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 2 cores. This equates to a lithium dosage of between 6.5 to 7.0 liters (L) 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 replacement 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, Delaware. The contract involved the remov ingal, 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 $LiNO_3$ 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 ly topical appl ying ication of the $LiNO_3$ solution onto the substrate and also by migrati ng on 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)

The South Dakota DOT specified Lithium nitrate$LiNO_3$ solution was specified by SDDOT 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).

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

The South Dakota DOT specified $LiNO_3$ solution was specified by SDDOT 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, South DakotaSD (figure 29). In addition, tThe 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 incorporatingion 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)

$LiNO_3$ was used in transmission tower footings constructed for a 40.2-km length of transmission line near Corpus Christi, Texas. 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 non-reactive aggregates. Lithium was chosen, because 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.

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

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

4.3 USING LITHIUM TO SUPPRESS EXPANSION IN ASR-AFFECTED CONCRETE

4.3.1 Topical Applications

U.S. Route 14, Wolsey, SD (1995)

This roadway, which forms part of U.S. Route 14 near Wolsey, SD, and was constructed in 1981, is a 2-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 $LiNo_3$ 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 the increased the potential for expansion by raising the pH of the concrete pore solution. However, 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 propriety blend of surfactants (to reduce surface tension effects and aid penetration) was applied at a rate of $0.16L/M^2$ A photograph of the spray truck is shown in figure 32. Three 150-m long sections were treated 1,2 or 3 times, achieving total applications of 0.16, 0.32, and $0.48\ L/m^2$. 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 different times to determine the penetration depth of lithium into uncracked and cracked concrete. Modulus testing indicated little significant change in the stiffness of the treated or untreated sections 1-3 years after treatment. However, between 3 and 4 years, there was a sudden increase in the modulus of elasticity (~5 to 6 Gigapascals 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 pavement 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 approximately 10 mm 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) conclude 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.

U.S. I-68, LaVale, MD (1997)

In 1986, the decks and parapets to two bridges carrying opposite lanes of U.S. 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 close-up 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 U.S. 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. In addition to visual observations of the concrete, impact-echo monitoring is conducted periodically. Three years after treatment, there was little visible difference between the condition of the treated and untreated sections.

S.R Rt. 1, Bear, DE (1998)

A 6.43-km section of S.R. Route 1 near Bear, Delaware, 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 to date has involved a total of 6 spray applications (2 per year), each at a rate of 0.24 L/m^2 using 30 percent $LiNO_3$ solution. Two more applications are scheduled for the year 2002.

Monitoring includes 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 to determine the depth of lithium penetration.

Figure 35. Cracking of 11-Year-Old Untreated Section of S.R. 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 2 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. 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, the physical testing (modulus and impact echo) has detected little difference in the 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 is scheduled for rehabilitation, 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), becauseas repairs of the treated sections do not require resurfacing at this time.

a) Treated Concrete b) Untreated Concrete

Figure 36. Sections of S.R. Rt. 1 near Bear, DE.

Summary and Other Projects

A summary of the above projects and two others is presented in table 16. The two 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 pavement 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 the state of Delaware this year. Similarly, a lithium treatment under a methacrylate wearing surface is being placed on a bridge deck in Reno, Nevada.

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

Table 16. Summary of Structures Treated with Lithium

Date of 1st Application	Structure Type	Location	Application Rate (L/100 m^2)	No. of Appl.	Condition Prior to Treatment	Comments on Effectiveness
1995	Pavement	U.S. 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	U.S. I-68, LaVale, MD	36.72	1	Good	Little visible difference (controls and treated areas unchanged during evaluation period)
1998	Pavement and bridge decks	S.R. Rt. 1, Bear, DE	24.48	6 (2/yr for 3 yrs)	Good to fair	On southern end of project, treated areas faring better than control-no noticeable difference on northern end
1998	Pavement	S.R. 15, New Ulm, MN	24.48	1)	Fair to poor	No noticeable improvement (controls and treated areas both continued to deteriorate about the same)
1999	Pavement	U.S. I-85, High Point, NC	12.24	1	Fair	Not evaluated - used as enhancement of durability of asphalt overlay

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 OntarioON (figure 37). 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 OH^- at the embedded steel cathode, thus increasing the risk of ASR. Further augmentation of the alkalies 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 37. Bridge over Montreal River near Latchford, ON Ontario.

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 U.S. I-395 in Arlington was to he remove al 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 electrolyte run-off of the electrolyte from the sloping deck. The treatment lasted for 8 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 parts per million (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 38 shows a photograph of the system during operation.

Figure 38. 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 prior to lithium treatment and in such cases the mix water for the grout was a 10 percent $LiNO_3$ solution. The footings were massive sections (approx. 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 required 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.

4.3.3 Pressure Injection

Pressure injection techniques frequently are used to help grout materials assist the penetrate ion 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. This technique should lend itself to applications where lithium impregnation is desired. There are no known cases involving the vacuum impregnation of lithium into concrete, however, at least three trials were scheduled for the summer of 2002.

CHAPTER 5 GUIDELINES FOR USING LITHIUM TO CONTROL ASR IN NEW AND EXISTING CONCRETE STRUCTURES

5.1 INTRODUCTION

This chapter provides guidelines for the use of lithium compounds to inhibit expansion due to ASR in both new and existing concrete. The guidelines are based on a review and synthesis of laboratory studies, field applications, and existing specifications. The intention of these guidelines is to help 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 GUIDELINES FOR USING LITHIUM COMPOUNDS IN NEW CONCRETE

Performance-based guidelines are presented first in this section, followed by prescriptive guidelines for using lithium admixtures in new concrete. Specific guidelines and details are provided on what laboratory tests and expansion limits should be considered when testing lithium compounds.

This chapter does not present comprehensive guidelines regarding all the options available to mitigate ASR (i.e., SCMs, low-alkali concrete), as summarized earlier in 0, but rather to provide practitioners who are interested in using lithium compounds with technical guidance on the topic. The performance-based guidelines allow for testing any lithium compound in the laboratory. The prescriptive guidelines only involve the use of $LiNO_3$, because it is the lithium compound most commonly used, does not exhibit a pessimum effect at lower dosages, and is safer to handle than other forms of lithium.

5.2.1 Performance-based Guidelines for Using Lithium in New Concrete

This section provides guidance on how to evaluate lithium compounds through laboratory performance tests. It emphasizes 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 two performance tests discussed in this section are ASTM C 1293 (concrete prism test) and ASTM C 1260 (accelerated mortar bar test). ASTM C 1293 is recognized as the best indicator of field performance and is preferred over ASTM C 1260 when assessing aggregate reactivity or the efficacy of SCMs in controlling expansion. In addition, based on past research, including the works reviewed in chapter 3, ASTM C 1293 is recommended as the best available test for assessing lithium compounds. Because ASTM C 1260 has several limitations, and because only limited testing has been performed using lithium compounds, caution should be taken when using it as the sole method of assessing a specific lithium/aggregate combination. Only limited testing has been performed to date to correlate ASTM C 1260 tests using lithium compounds to either ASTM C 1293 results or field performance. Whenever possible, ASTM C 1293 should be performed to gain the most reliable index of lithium performance.

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 alkalies 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 preferred 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.

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 lithium dosage of lithium used in the test may be varied, depending on specific objectives. Based on the literature review in chapter 3, a range of molar ratios Li:(Na + K) between 0.6 and 0.9 has been found to suppress expansion adequately for most aggregates. A molar ratio of 0.74 is the most commonly used value and is recommended by most lithium suppliers as a "100-percent dosage" of lithium.
- The test should be conducted for a duration of 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 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 por t land 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 alkalies present in the portland Portland cement, but not those alkalies present in the SCMs. For example:
    - A mixture containing 25 percent fly ash (by mass replacement of cement) would result in a portlan d 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 alkalies added to the cement, as provided in per ASTM C 1293), the total alkali contribution of the portland 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 yields a dosage of 4.6 L of solution per kg of alkalies. For this example, to assess a 0.74 molar ratio (based on cement alkalies), 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 alkalies (sodium or potassium) should be used.
    - The test should be conducted for a duration of 2 years, with an expansion limit of 0.04 percent.

ASTM C 1260

As described in chapter 3, the use of a modified version of ASTM C 1260 has shown promise in assessing the efficacy of lithium compounds in reducing expansion due to ASR. The modification entails the adding tion of lithium to the soak solution to minimize or prevent lithium leaching of lithium from the mortar bars. Although this approach appears to be technically sound, there are limited data correlating the test to either ASTM C 1293 or field performance. Therefore, caution should be exercised when interpreting the results from the modified version of ASTM C 1260, and if testing has been conducted on the same lithium-aggregate combination in ASTM C 1293, the data obtained from ASTM C 1293 should govern.

Following are recommendations for testing lithium compounds, by themselves or in combination with SCMs, using ASTM C 1260 (modified by adding lithium to the soak solution).

To test lithium compounds (without SCMs) using ASTM C 1260 (modified):

- Use the same mixture proportions and methods described in ASTM C 1260 should be used, except for the following modifications:
    - The portland cement used in the mortar bars must have an Na_2O_e of 0.90 ± 0.10 percent. The alkali content of the portland Portland cement currently is not specified in ASTM C 1260, because it has been demonstrated that the effects of solution alkalinity (1N NaOH) far outweigh any effect of cement alkalinity when testing aggregate reactivity. However, based on the past experience of the authors, cement alkalinity does affect the test results when testing SCMs or lithium compounds. As such, an alkali level of 0.90 ± 0.10 Na_2O_e percent is recommended, which is actually the value specified in the Canadian equivalent of ASTM C 1260 (CSA A 23.2-25A). Another reason for specifying a relatively high alkali cement is that the lithium dosages used in the test, as described later, are based on alkalies present in the Portland cement. Using a low-alkali cement (i.e., $Na_2O_e < 0.6$ percent) would result in an unusually low lithium content, which would then be overwhelmed by the 1N NaOH solution. Based on experience, this modified test can only be used with a degree of confidence when using a high-alkali cement, and when the main intention is to assess the performance of a given aggregate-lithium combination.
    - The desired dosage of lithium should be added to the mixing water, and 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 lithium dosage of lithium used in the test may be varied, depending on specific objectives, but the dosage should be calculated based on the Na_2O_e of the portland Portland cement (i.e., based on molar ratio of 0.74).
    - Lithium should be added to the soak solution to achieve the same molar ratio within the soak solution as that contained within the mortar bars. For example, if a 0.74 molar ratio (typical 100 percent manufacturers' recommended dosage) is selected for the mortar bars, a Li:Na ratio of 0.74 should also be maintained in the 1N NaOH soak solution. Without adding lithium to the soak solution, substantial leaching of lithium from the mortar bars would occur.
- After submerging the mortar bars in the modified soak solution, the testing regime is identical to the standard ASTM C 1260 test. An expansion limit of 0.10 percent at the conclusion of the test (after 14 days in the soak solution) should be used.

To test lithium compounds in combination with SCMs using ASTM C 1260 (modified):

- The same mixture proportions and methods described in ASTM C 1260 should be used, except for the following modifications:
    - The SCM (or SCMs) should be used as mass replacement of portland Portland cement, maintaining a constant cementitious materials content for all tests.
    - The portland cement used in the mortar bars must have an Na_2O_e of 0.90 ± 0.10 percent. The alkali content of the Portland cement is not currently specified in ASTM C 1260, because it has been demonstrated that the effects of solution alkalinity (1N NaOH) far outweigh any effect of cement alkalinity when testing aggregate reactivity. However, based on past experience, cement alkalinity does affect the test results when testing SCMs or lithium compounds (or in this case, both). As such, an alkali level of 0.90 ± 0.10

    Na_2O_e percent is recommended, which is actually the value specified in the Canadian equivalent of ASTM C 1260 (CSA A 23.2-25A). Another reason for specifying a relatively high-alkali cement is that the lithium dosages used in the test, as described later, are based on alkalies present in the portland Portland cement. Using a low-alkali cement (i.e., Na_2O_e < 0.6 percent) would result in an unusually low lithium content, which would then be overwhelmed by the 1N NaOH solution. Based on past experience, this modified test can only be used with a degree of confidence when using a high-alkali cement, and when the main intention is to assess the performance of a given aggregate-lithium combination.
    - The desired dosage of lithium should be added to the mixing water, and 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. The dosage should be calculated based on the alkali content (Na_2O_e)of the Portland cement, but not the alkalies contained in the SCMs.
    - Lithium should be added to the soak solution to achieve the same molar ratio within the soak solution as that contained within the mortar bars (based on cement alkalinity only). For example, if a 0.74 molar ratio (typical 100 percent manufacturer's recommended dosage) is selected for the mortar bars, a Li:Na ratio of 0.74 should also be maintained in the 1N NaOH soak solution. Without adding lithium to the soak solution, substantial leaching of lithium from the mortar bars would occur.
- This modified version of ASTM C 1260 is only appropriate for fly ash with a total alkali content less than 3 percent or for slag with an alkali content less than 1 percent. Fly ash or slag with higher total alkali contents greater than these values must be tested using ASTM C 1293.
- 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 alkalies (sodium or potassium) should be used.
- After submerging the mortar bars in the modified soak solution, the testing regime is identical to the standard ASTM C 1260 test. An expansion limit of 0.10 percent at the conclusion of the test (after 14 days in the soak solution) should be used.

5.2.2 Prescriptive Guidelines for Using Lithium in New Concrete

Prescriptive guidelines are intended to provide specific recommendations that can be followed without the need for performance tests. Examples of this approach when considering ASR would include specifying a minimum of 20 percent Class F fly ash or a minimum slag content of 35 percent. Prescriptive guidelines or specifications for SCMs are widespread and are used by many agencies and organizations with confidence because of the wealth of laboratory data and field-performance records available.

Because there is not the same magnitude of laboratory data and documented field performance for lithium compounds, recommending similar prescriptive guidelines is challenging. There are also sIn addition, some unresolved technical issues that have not been resolved that make it even more difficult to develop prescriptive guidelines for using lithium to control expansion due to ASR. Because of these limitations and concerns, the recommendations provided in this section tend to be more conservative. As the use of lithium compounds in concrete construction continues to evolve, more data and performance histories will become available, making future guidelines more directed and, perhaps, less conservative.

Before summarizing the prescriptive guidelines for using lithium compounds in new concrete, some background information on the factors influencing the performance of lithium compounds in concrete (e.g., effects on ASR-induced expansion) is presented. This information is intended to serve as a foundation for prescriptive guidelines and also is provided to show that the gaps in understanding and lack of field data warrant a conservative approach at this time. Of course, the performance testing described in the previous section, especially ASTM C 1293, provides practitioners with the necessary tools to determine lithium dosages required to suppress expansion and represents an alternative to prescriptive recipes.

As described in chapter 3, the efficacy of lithium in suppressing expansion due to ASR is dependent on the nature or reactivity of the aggregate, the form of lithium, and the availability of alkalies. Generally, aggregate reactivity is assessed by tests such as ASTM C 1260 and ASTM C 1293. The level of mitigation or protection against ASR is often based on the values obtained in these tests, with higher expansion values requiring higher dosages of fly ash or slag, for instance. The difficulty in applying this same approach for lithium compounds is that a clear correlation between a given aggregate's reactivity, as defined by ASTM C 1260 or ASTM C 1293, and the response of that aggregate to lithium (as a function of dosage) does not exist. For instance, research at BRE (Blackwell et al., 1997; Thomas et al., 2000) has demonstrated that some aggregates require more than a 0.74 molar ratio to control expansion, but some of these aggregates (i.e., siltstone) were not as reactive (as defined by ASTM C 1293) as other aggregates that responded more favorably to lithium compounds. In addition, research at the University of Texas at Austin (Folliard, unpublished data) has shown that an extremely reactive chert aggregate, which had an expansion greater than 0.6 percent in ASTM C 1260 and exceeded the 0.04 percent expansion limit in ASTM C 1293 in less than a month, responded very favorably to $LiNO_3$. Using $LiNO_3$, a molar ratio of 0.55 was found to suppress expansion with the highly-reactive chert aggregate, yet this aggregate was extremely difficult to mitigate using SCMs.

Clearly, there is not a trend between aggregate reactivity, as it is typically defined, and the response of an aggregate to lithium treatment, making it difficult to integrate aggregate reactivity into prescriptive guidelines. Based on a review of literature, a molar ratio Li:(Na + K) of 0.74 has been found to suppress expansion for the majority of aggregates, and a wider range of molar ratios, from 0.60 to 0.90, essentially brackets the range of lithium dosages needed to control expansion for the aggregate-lithium combinations reported in literature. For a given aggregate, a lower dosage of $LiNO_3$ is needed to control expansion, compared to other forms of lithium. As previously mentioned, the prescriptive guidelines provided later in this section only cover the use of $LiNO_3$. Because there are not enough data available to link $LiNO_3$ dosage or to show that dosages lower than 0.74 (molar ratio) are required to suppress expansion, a minimum $LiNO_3$ dosage of 0.74 will be recommended for all aggregates. Dosages higher or lower than this value may be used, provided that previous testing was performed using ASTM C 1293, as described under section 5.2.1.

Another issue that deserves attention is the role that alkalies present in SCMs should play in determining prescriptive dosages of lithium. As described in chapter 3, the BRE counts the alkalies present in SCMs to a varying degree, depending on the dosage of that SCM, and uses this alkali contribution in calculating the total alkali loading of the concrete. This alkali loading is then used to prescribe a lithium dosage (see section 3.3.4). The CSA guidance on using SCMs to control ASR actually does not actually use alkali contribution from SCMs in calculating the total alkali loading of the concrete, but CSA does recommend a tiered approach, where an SCM (i.e., fly ash) with higher alkali content requires a higher dosage of that SCM to adequately suppress expansion. There have been very few studies on the use of lithium combined with SCMs, and of these studies, the main focus has been on using SCMs with relatively low alkali contents. Because of the lack of available data on higher-alkali SCMs, the guidance provided in this section will only be valid for fly ashes with a total alkali content less than 3 percent or for slag with an alkali content less than 1 percent. If the alkali content of a specific fly ash or slag exceeds these limits, testing is required using ASTM C 1293 to determine the adequate lithium dosage. Prescriptive guidelines are not included in this section for SCMs other than fly ash and slag because of a lack of published information.

When combining the use of high-calcium fly ash (> 15 percent CaO) and slag with $LiNO_3$, the lithium dosage recommended as part of these prescriptive guidelines will be based on the alkali contribution from portland Portland cement only (e.g., 0.74 molar ratio based on Na_2O_e from cement). Therefore, the actual amount of lithium added to the concrete will be reduced, based on the replacement level of the fly ash or slag for portland cement, thereby treating the SCM essentially as a dilutent. No other reductions in lithium dosage, beyond this dilution effect, are prescribed for these higher-lime ashes and slag, because there are no published data to support such a reduction. It has been shown in chapter 3 that the beneficial effects of using low-calcium fly ash and lithium together to control ASR are cumulative. Thus, the guidelines provided later in this section allow for reduced lithium dosage (beyond the dilution effect) when combined with fly ash with a CaO content less than 15 percent. Although some studies have shown that a 50 percent reduction in lithium dosage (based on alkalies in the portland cement) may be possible with low-lime ashes (< 8 percent CaO), only moderate reductions in lithium dosage are proposed in these guidelines to be conservative.

Before summarizing the prescriptive guidelines, one last issue to be addressed is the total alkali loading of the concrete. Because most studies have dealt with moderate alkali loadings, the guidelines proposed in this section will be limited to concrete mixtures with alkali contents (based on alkalies from portland cement) of less than 5 kg/m^3, a limit that is consistent with the BRE guidelines. As previously described, the BRE guidelines include anywhere from zero to one hundred percent of the alkalies present in SCMs when calculating the total alkali loading for a given concrete mixture. However, because limits have been imposed on the alkalies in SCMs in the current recommendations (3 percent for fly ash, 1 percent for slag), and because relatively high dosages of fly ash and slag will be recommended in most cases, the contribution of alkalies from SCMs will not be included in calculating the alkali loading of concrete.

When considering the developing ment of prescriptive guidelines, the CSA approach is the most comprehensive and is highly recommended for assessing aggregate reactivity and the need for preventive measures (CSA, 2000a). The CSA guidelines cover a range of mitigation options (see table 3), including various SCMs and ternary blends, but they do not yet include guidance for lithium compounds. Consultation with the CSA guidelines is urged when seeking general guidance on testing, specifying, and using concrete that does not contain lithium. When considering the use of lithium, the guidelines presented below are recommended and can be compared to other available mitigation methods by following CSA A23.2-27A.

The ideal approach to developing prescriptive guidelines for lithium would be to follow the same methodology as the CSA guidelines. However, because of the limitations described in this section, including the difficulty in relating aggregate reactivity to lithium dosage, a more simplistic approach is necessary. CSA A23.2-27A dictates different levels of prevention based on aggregate reactivity, defined by ASTM C 1293 or ASTM C 1260, but as previously cited, this approach may not be valid for lithium. However, it is still possible to use ASTM C 1293 or ASTM C 1260 to determine if an aggregate even requires any preventive measure; that is, if the expansion in ASTM C 1293 is less than 0.04 percent (at 1 year), or if the expansion is less than 0.10 (after 14 days), no mitigation (i.e., SCMs, lithium) is required. As always, if data are available for a given aggregate from both ASTM C 1293 and ASTM C 1260, the data obtained from ASTM C 1293 should govern. Beyond determining whether an aggregate requires mitigation or not, it is not possible at this time to link aggregate reactivity or expansion values to required lithium dosages.

Because there is a general lack of field experience using lithium compounds, it is not currently feasible to adopt the CSA approach of selecting levels of protection (e.g., lithium dosages) based on the size of the concrete element and the nature of the surrounding environment. The approach currently proposed is to remain conservative in terms of specifying lithium dosage (either with or without SCMs).

The following are the proposed prescriptive guidelines for using lithium compounds in concrete, which summarize the key issues already discussed, including limitations and assumptions. For materials that are not explicitly covered in these prescriptive guidelines, such as lithium compounds other than lithium nitrate or SCMs other than fly ash or slag, the performance-based guidelines (section 5.2.1) should be followed.

Prescriptive Guidelines for Using Lithium Compounds in Concrete

- These guidelines only cover the use of $LiNO_3$.

- CSA A23.2-27A is recommended for assessing preventive measures other than lithium compounds.
- These guidelines are valid only for concrete mixtures with a total alkali content less than 5 kg/m^3.
- These guidelines are valid only for fly ashes with a total alkali content less than 3 percent and slag with a total alkali content less than 1 percent.
- When using concrete without SCMs, a molar ratio Li:(Na + K) of 0.74 should be used, unless previous testing (see section 5.2.1) has demonstrated that lower dosages are effective or higher dosages are necessary. A molar ratio of 0.74 equates to 4.6 L of 30 percent $LiNO_3$ solution per kg of Na_2O_e.
- When using concrete with high-calcium fly ash (CaO > 15 percent) or slag, a molar ratio of 0.74 is recommended, based only on the alkalies in the portland Portland cement. Thus, the total lithium dosage in the concrete will be reduced in proportion to the level of replacement of portland Portland cement.
- When using concrete with low-calcium fly ash (CaO £ 15 percent) and where the level of replacement of the fly ash is equal to or greater than 15 percent (by mass of total cementing materials), a molar ratio of 0.56 (75 percent of the typical 0.74 molar ratio) is recommended, based only on the alkalies in the portland Portland cement. Thus, the amount of lithium required is reduced not only by the dilution effect (replacing cement with fly ash), but also by the synergistic effect of combining low-lime ash with lithium. If the level of fly ash replacement is less than 15 percent, a molar ratio of 0.74 is recommended, based on the alkalies in the portland Portland cement.

5.3 GUIDELINES FOR 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., 2000), 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:

- The lithium compound being used.
- The rate of application.
- The number of treatments.
- The temperature and moisture content of the concrete at the time of treatment.
- The quality of the concrete (e.g. permeability).
- The thickness of the element being treated.
- The extent of deterioration at the time of treatment.
- The 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 lithium's effective penetration depth of penetration of the lithium.

Laboratory research has indicatesd 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., $2LiCO_3 + Ca(OH)_2 \longrightarrow 2LiOH + CaCO_3$). 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 nitrateLiNO3 generally 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^- 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., 2000).

There are two things to consider about the application rate: (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 L 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:

- Clean the surface before the treatment (e.g., by using a road sweeper).
- Ensure that the road surface is free of loose sand, debris, and similar materials, but it need not be dry.
- Do not apply the treatment during periods of rain, or if rain is expected within 6 hours.
- Do not exceed a final coverage rate of the treatment shall not exceed 0.37 L/m^2.
- Apply the treatment at least twice.
- Do not exceed Each application shall not exceed 0.20 L/m^2 with each application.
- Apply individual applications shall be applied at least 30 minutes apart.
- Adjust the application rate shall be adjusted to provide uniform surface coverage, such that the material does not run off the surface.
- Apply water to 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.

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 S.R. 1 in Delaware involved a total of 6 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 tobefore treatment will more readily absorb more readily 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. However, these conditions clearly cannot be controlled.

The extent of concrete 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 clearly will clearly facilitate ingress of the solution. However, if the concrete 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 in the schematic shown in figure 39.

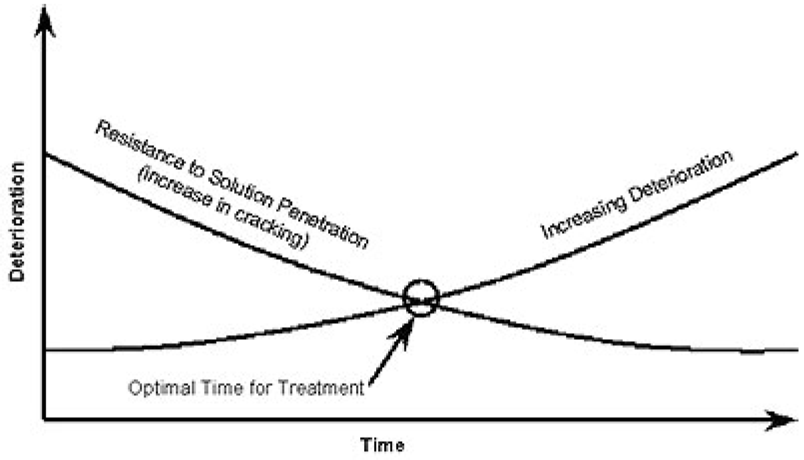


Figure 39. Optimal Time for Lithium Treatment Applied Topically (Johnston et al., 2000).

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 likely 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

At the time of writing, there were are no known cases involving the vacuum impregnation of lithium into concrete. Therefore, it is not possible to develop guidelines for this process.

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 posttreatment). 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 IN NEW CONCRETE

The cost of lithium is inherently quite high, compared to other concrete materials. Typical unit costs of selected raw materials are shown below:

Basic Materials -Approximate Cost

Type I portland Portland cement: $80/ton
Aggregates: approximately $7-10/ton

Selected aAdmixtures and SCMs -A approximate C cost

Fly ash: $25-30/ton
Slag: $25-35/ton
Silica fume: $600/ton
Calcium nitrite corrosion inhibitor: $1.50/L liter
High-range water reducer: approximately $3.25 per m^3 of concrete
$LiNO_3$ (30 percent% solution): ~ $3.50/L liter

The above estimates are based on typical values but do not reflect availability, differences in freight cost, local market trends, or other factors. The raw materials cost typically constitute approximately 50 to 75 percent of the delivered cost of concrete. For reference, a typical cubic meter of delivered concrete costs anywhere from around $60 to $120.

Assuming a delivered cost of concrete of $90/m^3, a cement content of 389 kg/m^3, and a cement alkali content (Na_2O_e) of 0.6 percent, the incremental cost of adding a typical $LiNO_3$ dosage (4.6 L of 30 percent solution per kg Na_2O_e) to this concrete would be approximately $38, resulting in a final delivered cost of approximately $128/m^3. This increase in cost is considerable, but can be somewhat offset by combining $LiNO_3$ with fly ash. Using the same example as above, but replacing 25 percent of the cement with low-lime fly ash and reducing the molar ratio (based on cement) to 0.54 (see section 5.2), the total cost of the concrete would be approximately $105/m^3. The above is just an example using assumed materials, mixture proportions, and costs. Specific cases should be evaluated independently to determine the potential economic impact of using lithium compounds, with or without SCMs. It is almost always the case that combining lithium with SCMs will make lithium more cost effective and will also produce higher quality, low-permeability concrete. If laboratory testing (based on ASTM C 1293) shows that the required lithium dosage, used in conjunction with an SCM, is even less than that recommended in section 5.2, it may be possible to reduce the lithium dosage, thereby further decreasing the cost of the mixture.

The delivered cost of concrete is also 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, direct comparisons of raw materials costs one should be regarded direct comparisons of raw materials costs with caution, as these comparisonsy 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 non-reactive 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 constructibility issues. Using lower dosages of fly ash or slag, in combination with lithium, can then improve the early strength properties, which improves 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 type 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, non-durable 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 theose 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 are developed, 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 deterioration process of deterioration and delay the time until more permanent repair or replacement becomes necessary. Also, lithium treatment usually will almost certainly only be considered only 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:

Equation 10: $$P_1 = \frac{R_1}{(1+i)^{T_1}}$$

where i = the 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:

Equation 11: $$P_2 = R_2 + \frac{R_1}{(1+i)^{T_2}}$$

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, is 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 performedis anticipated 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 guidelines (including economic considerations) for using lithium in new concrete and as a posttreatment for existing structures. Some of the main findings and conclusions from this report include:

- ASR is a significant problem in the United States and elsewhere, but there are several available methods available forof preventing ASR-induced expansion, including the use of non-reactive 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 non-expansivenonexpansive. ASR gels still form in the presence of lithium, but the ir 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, $LiNO_3$, $LiOH{\cdot}H_2O$, $LiNO_2$, 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.
- Adding lithium to concrete at a molar ratio Li:(Na + K) of 0.74 is adequate to suppress expansion for most aggregates, although certain aggregates may require more, and others may need less.
- 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. A modified version of ASTM C 1260 (modified by adding lithium to the soak solution) has shown promise as a rapid test for assessing lithium-aggregate combinations, but further research is recommended to correlate this rapid test with ASTM C 1293 and field performance.
- Lithium compounds have proven to be effective in posttreating hardened concrete 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 refine available test methods (such as ASTM C 1260) to provide a more rapid method of assessing lithium compounds in mortar and concrete. Modifying ASTM C 1260 by adding lithium to the soak solution appears promising, but more work is needed to correlate this version with the concrete prism test, and more importantly, with field performance. ASTM, AASHTO, CSA, and other organizations must propose for adoption aAppropriate (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 posttreatment 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 (2000). *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.

Baxter, S.Z., Stokes, D.B., and Manissero, C.E. (2000). "A lithium-based pozzolans for ASR control," *Proceedings of the 11th International Conference on Alkali-Aggregate Reaction (ICAAR)*, Quebec, Canada, June 11-16, 573-582.

Bérubé, M-A. and Duchesne, J. (1992). "Evaluation of testing methods used for assessing the effectiveness of mineral admixtures in suppressing expansion due to alkali-aggregate reaction." *Proceedings of the 4th 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, pp. 549-575.

Bérubé, M-A. and Fournier, B. (1992). "Accelerated test methods for alkali-aggregate reactivity." *Advances in Concrete Technology* (Ed. V. M. Malhotra), CANMET/EMR, Ottawa, Canada, pp. 583-627.

Building Research Establishment (2002). *Minimizing the risk of alkali-silica reaction: aAlternative methods*, Information Paper, Building Research Establishment, United Kingdom.

Qinghan, B., Nishibayashi, S., Xuequan. W., Yoshino, A, Hong, Z., Tiecheng, W., and Mingshu, T. (1995). "Preliminary study of the effects of $LiNO_3$ on expansion of mortars subjected to alkali-silica reaction," *Cement and Concrete Research*, 25:1647-1654.

Bleszynski, R., Thomas, M.D.A, and Hooton, D., (2000). "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, 583-592.

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

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

Chatterji, S., Thalow, N., and Jensen, A.D. (1987). "Studies of the Alkali-Silica Reaction Part 4: Effect of Different Alkali Salt Solutions on Expansion," *Cement and Concrete Research*, 17:777-83.

Collins, C.L. (2002). *Examination of the Mechanism by which Lithium Additives Inhibit Alkali-Silica Reaction Gel Expansion*, M.S.EnvE. Thesis, Georgia Institute of Technology, Atlanta, GA.

Dent Glasser, L.S. and Kataoka, N. (1981). "The chemistry of alkali-aggregate reactions." *Proceedings of the 5th International Conference on Alkali-Aggregate Reaction,* Cape Town, South Africa, S252/23.

Diamond, S. (1981). "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, pp. 383-394.

Diamond, S. (1999). "Unique response of $LiNO_3$ as an alkali-silica reaction-prevention admixture," *Cement and Concrete Research*, 29:1271-5.

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

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

Durand, B. (2000). "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, 623-632.

Glasser, F.P. (1992). " "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. (1944). "Studies relating to the mechanism by which the alkali-aggregate reaction proceeds in concrete." *Journal of the American Concrete Institute,* Vol. 15, No. 3, pp. 213-27.

Iler, R.K. (1956). *The Chemistry of Silica*, John Wiley & Sons, New York, NY.

Johnston, D.P. (2001). "Mitigation of potential alkali-silica reactivity using lithium." *SHRP Strategic Highway Research Program Concrete and Structures ASR Showcase Test and Evaluation Project 34*.

Johnston, D.P., Surdahl, R. and Stokes, D.B. (2000). "A case study of a lithium-based treatment of an ASR-affected pavement." *Proceedings of the 11th International Conference on Alkali-Aggregate Reactions,* (Ed. Bérubé et al.), CRIB, Quebec, Canada, pp. 1149-1158.

Kawamura, M. and Fuwa, D. (2001). "Effects of lithium salts on ASR gel composition and expansion of mortars," *Proceedings of the International Conference on Cement Microscopy*, 89-103.

Kurtis (1998). *Transmission Soft X-ray Mmicroscopy of the aAlkali-Ssilica Rreaction*, Doctoral Thesis, University of California, Berkeley, CA.

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

Kurtis, K.E. and Monteiro, P.J.M. (in press). "Chemical Additives to Control Expansion of Alkali-Silica Reaction Gel: Proposed Mechanisms of Control," *Journal of Materials Science*, accepted for publication.

Lawrence, M. and Vivian, H.F. (1961). "The reactions of various alkalies with silica" *Australian Journal of Applied Science*, 12, N.1, 96-103.

Lumley, J.S. (1997)., "ASR suppression by lithium compounds," *Cement and Concrete Research*, 27, n.2: 235-44.

McCoy, W.J. and Caldwell, A.G. (1951). "A new approach to inhibiting alkali-aggregate expansion," *Journal of the American Concrete Institute*, 47, 693-706.

McGowan, J.K. and Vivian, H.E. (1952). "Studies in cement-aggregate reaction: Correlation between crack development and expansion of mortars," *Australian Journal of Applied Science*, Vol. 3, pp. 228-232.

McKeen, R.G., Lenke, L.R., Pallachulla, K.K., and Barringer, W.L. (2000). "Mitigation of alkali-silica reaction in New Mexico," *Transportation Research Record 1698*.

Nixon, P.J. and Sims, I. (1992). "RILEM TC106 alkali aggregate reaction- - accelerated tests interim report and summary of national specifications,." *Proceedings of the 9th International Conference on Alkali-Aggregate Reaction in Concrete*, Vol. 2, p Published by The Concrete Society, Slough, pp. 731-738.

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

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

Oberholster, R. E. and Davies, G. (1986). "An accelerated method for testing the potential reactivity of siliceous aggregates," *Cement and Concrete Research*, Vol. 16, pp 181-189.

Ohama, Y., Demura, K. and Kakegawa, M. (1989). "Inhibiting alkali-aggregate reaction with chemical admixtures," *Proceedings of the 8th International Conference on Alkali-Aggregate Reaction*, (Ed. K.Okada, S. Nishibayashi, and M. Kawamura), Kyoto, Japan, pp. 253-258.

Pedneault, A. (1996). "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, 133p.

Powers, T.C. and Steinour, H.H. (1955). "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, pp. 497-516.

Prezzi, M., Monteiro, P.J.M., and Sposito, G. (1997). "The alkali-silica reaction-part I: U use of the double-layer theory to explain the behavior of the reaction-product gels," *ACI Materials Journal*, America Concrete Institute, 94, n.1:10-17.

Prezzi, M.; Monteiro, P.J.M.; and Sposito, G. (1998). "Alkali-Silica Reaction- Part 2: The Effect of Chemical Additives," *ACI Materials Journal*, America Concrete Institute, 95, n.1, 3-10.

Qinghan, B., Nishibayashi, S., Xuequan, W., Yoshino, A., Hong, Z., Tiecheng, W., and Mingshu, T. (1995). "Preliminary study of the effects of $LiNO_3$ on expansion of mortars subjected to alkali-silica reaction," *Cement and Concrete Research*, 25:1647-1654.

Ramachandran, V.S. (1998). "Alkali-aggregate expansion inhibiting admixtures," *Cement and Concrete Composites*, 20, N 2-3, 149-161.

Rodrigues, F.A., Monteiro, P.J.M., and Sposito, G. (2001). "The alkali-silica reaction: The effect of monovalent and bivalent cations on surface charge density of opal,", *Cement and Concrete Research*, 31:1549-52.

Sakaguchi, Y., Takakura, M., Kitagawa, A., Takahiro, H., and Fuminori, T. (1989). "The inhibiting effect of lithium compounds on alkali-silica reaction," *Proceedings of the 8th International Conference on Alkali-Aggregate Reaction*, Kyoto, Japan, 229-234.

Shehata, M.H., Thomas, M.D.A., and Bleszynski, R.F. (1999). "The effect of fly composition on the chemistry of pore solution," *Cement and Concrete Research*, Vol. 29, pp. 1915-1920.

Shehata, M.H. and Thomas, M.D.A. (2000). "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. and Thomas, M.D.A. (2002). "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, pp. 341-349.

Stanton, T.E. (1940). "Expansion of concrete through reaction between cement and aggregate," *Proceedings of the American Society of Civil Engineers,* Vol. 66, No. 10, pp. 1781-1811.

Stark, D., Morgan, B., Okamoto, P., and Diamond, S. (1993). "Eliminating or minimizing alkali-silica reactivity," *SHRP-C-343*, National Research Council, Washington, D .C.

Stark, D. (1992). "lithium Lithium salt admixtures - an alternative method to prevent expansive alkali-silica reactivity," *Proceedings of the 9th International Conference on Alkali-Aggregate Reaction in Concrete*, London, United Kingdom, July.

Stark, D. and Bhatty, M.S.Y. (1986). "Alkali-silica reactivity: effect of alkali in aggregate on expansion," *Alkalies in Concrete, ASTM STP 930*, American Society for Testing and Materials, Philadelphia, PA, pp 16-30.

Stark, D. (1978). "Alkali-silica reactivity in the Rocky mountain region," *Proceedings of the 4th International Conference on Effects of Alkalies in Cement and Concrete,* Publication No. CE-MAT-1-78, Purdue University, W. Lafayette, Indiana IN, pp. 235-243.

Stokes, D.B., Wang, H.H., and Diamond, S. (1997). "A lithium-based admixture for ASR control that does not increase the pore solution pH," *Proceedings of the 5th CANMET/ACI International Conference on Superplasticizers and Other Chemical Admixtures in Concrete*, SP-173, pp. 855-867.

Stokes, D.B., Manissero, C.B., Roy, D.M., Malek, R.I., and Roumain, J.C. (2000). "Portland cement manufacture containing lithium for ASR control," *Proceedings of the 11th International Conference on Alkali-Aggregate Reaction (ICAAR)*, Quebec, Canada, June 11-16, 773-782.

Stokes, D.B., Thomas, M.D.A., and Shashiprakash, S.G. (2000b). "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*, (Ed. M.A. Bérubé et al.), CRIB, Quebec City, Canada, pp. 1079-1087.

Strategic Highway Research Program, (1993). *SHRP C-315, Handbook for the Identification of Alkali-Silica Reactivity in Highway Structures*.

Tang, M. (1981). "Some remarks about alkali-silica reactions," *Cement and Concrete Research,* Vol. 11, pp. 477-478.

Thomas, M.D.A. and Bleszynski, R.F., (2000). "The use of silica fume to control expansion due to alkali-aggregate reactivity in concrete-a review," *Materials Science of Concrete* (Edited by Skalny and Mindess), Vol. 6, American Ceramic Society.

Thomas, M. D. A. and Innis, F. A. (1999). "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 (2), pp. 157-164.

Thomas, M. D. A., Nixon, P. J., and Pettifer, K. (1991). "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 2nd CANMET/ACI International Conference on Durability of Concrete,* (Ed. V.M. Malhotra), Vol. 2, American Concrete Institute, Detroit, pp. 919-940.

Thomas, M.D.A., Blackwell, B.Q. and Pettifer, K. (1992). "Suppression of damage from alkali silica r eeaction by fly ash in concrete dams," *Proceedings of the 9th International Conference on Alkali-Aggregate Reaction in Concrete*, (held in London, United Kingdom, 1992), Vol. 2 pPublished by The Concrete Society, Slough, pp. 1059-1066.

Thomas, M.D.A., Hooper, R., and Stokes, D. (2000). "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, 783-810.

Thomas, M.D.A. and Stokes, D. (1999). "Use of a lithium-bearing admixture to suppress expansion in concrete due to alkali-silica reaction,." *Transportation Research Record, No. 1668*, pp. 54-59.

Thomas, M.D.A, Baxter, S., Stokes, D., and Hill, R., (2001). "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.

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

Thomas, M.D.A., Stokes, D., and T. Rodgers, (2002). "The effect of lithium-based admixtures on the properties of concrete," to be published in October 2003.

Thomson, M.C. (2000). "Field installation in Pennsylvania to assess SHRP recommendations for ASR control: Part 2 l Laboratory testing of job material.,", *Proceedings of the 11th International Conference on Alkali-Aggregate Reactions (Ed. Bérubé et al.)*, Quebec City, Canada, pp. 1215-1224.

Thomson, M.C. and Stokes, D.B. (1999). "Field installation in Pennsylvania to assess SHRP recommendations for ASR control." *TRB Catalogue of 1999 Practical Papers, Design and Construction of Transportation Facilities*, Paper No. 991190, Transportation Research Board, Washington, D.C., pp. 29-30.

Uchikawa, H., Uchida, S. and Hanehara, S. (1989). "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,* (Ed. K.Okada, S. Nishibayashi and M. Kawamura), Kyoto, Japan, pp. 121-128.

Wang, H., Tysl, S., and Gillot, J.E. (1994). "Practical implications of lithium-based chemicals and admixtures in controlling alkali-silica reaction," *Fourth CANMET/ACI International Conference on Superplasticizers and Chemical Admixtures, SP-148-20*, pp 353-366.

Wang, H. and Stokes, D.B. (1996). "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, 884-891.

Wijnen, P.W.J.G., Beelen, T.P.M., de Haan, J.W.,; Rummens, C.P.J., van de Ven, L.J.M., and van Santen, R.A. (1989). "Silica gel dissolution in aqueous alkali metal hydroxides studies by 29Si NMR," *Journal of Non-Crystalline Solids*, 109:85-94.