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Alkali-Silica Reaction and Delayed Ettringite Formation in Concrete: A Literature Review

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TABLE OF CONTENTS

CHAPTER 1 – INTRODUCTION 1		
СНА	PTER 2 – ALKALI-SILICA REACTION	
2.1	MECHANISMS	
2.1.1	REACTION	
2.1.2	Alkalies	
2.1.3	SILICA	
2.1.4	MOISTURE	
2.1.5	ТНЕ АТТАСК	
2.2	TEST METHODS	
2.2.1	ASTM C 1260	
2.2.2	ASTM C 1293	
2.3	MITIGATION METHODS10	
2.3.1	LOW-ALKALI CEMENT/CONCRETE	
2.3.2	FLY ASH 11	
2.3.3	SLAG	
2.3.4	SILICA FUME	
2.3.5	LITHIUM SALTS	
2.3.6	TERNARY BLENDS	
2.4	SPECIFICATIONS	
2.4.1	Agency Test Specifications	
2.4.2	SPECIFIED MITIGATION METHODS	
2.5	FIELD STUDIES	
2.5.1	PARAMETERS TO MONITOR	
2.5.2	MONITORING METHODS	
2.5.3	ASR FIELD STUDIES	

CHA	APTER 3 – DELAYED ETTRINGITE FORMATION	41
3.1	MECHANISMS	41
3.2	TEST METHODS	43
3.3	MITIGATION METHODS	46
3.4	SPECIFICATIONS	47
3.4.1	AGENCY TEST SPECIFICATIONS	47
3.4.2	2 Specified Mitigation Methods	48
3.5	FIELD STUDIES	49
3.5.1	DEF IN TEXAS	49
3.5.2	2 HIGH MAST ILLUMINATION POLE FOUNDATION ON US 59	50
3.5.3	3 CAST-IN-PLACE BENT CAPS AND COLUMNS ON IH 37	51
3.5.4	PRESTRESSED CONCRETE TYPE IV BEAM ON IH 45	52
CHA	APTER 4 – SYNERGISTIC EFFECTS BETWEEN ASR AND DEF	53
CHA	APTER 5 – CONCLUSIONS AND RECOMMENDATIONS	55
BIB	LIOGRAPHY	57

LIST OF FIGURES

FIGURE 1	ASTM C 1260 SPECIMENS SHOWING THE ABILITY OF	
	FLY ASH TO CONTROL CRACKING	11
FIGURE 2	ASTM C 1260 Specimens Showing the Ability of	
	SLAG TO CONTROL CRACKING	12
FIGURE 3	ASTM C 1260 Specimens Showing the Ability of	
	SILICA FUME TO CONTROL CRACKING	14
FIGURE 4	ASTM C 1260 Specimens Showing the Ability of	
	LITHIUM NITRATE TO CONTROL CRACKING	15
FIGURE 5	ASTM C 1260 Specimens Showing the Ability of	
	A TERNARY BLEND TO CONTROL CRACKING	16
FIGURE 6	AASHTO FLOWCHART FOR ASR PREVENTION	23
FIGURE 7	PCA/ACPA FLOWCHART FOR ASR PREVENTION	24
FIGURE 8	GLOBAL APPROACH FOR THE SELECTION OF PREVENTIVE	
	MEASURES AGAINST ASR	26
FIGURE 9	DIFFERENT TYPES OF MECHANICAL GAGES USED IN	
	THE SANEF PROJECT	38
FIGURE 10	THE SEVERITY OF CRACKING CAUSED BY ASR ON	
	THE SUSAN RIVER BRIDGE	39
FIGURE 11	FU METHOD TO ASSESS DEF	45
FIGURE 12	KELHAM METHOD TO ASSESS DEF	45
FIGURE 13	PREMATURE CRACKING IN THE END REGION OF A	
	6-YEAR-OLD BOX BEAM DUE TO DEF	49
FIGURE 14	HIGH MAST ILLUMINATION FOUNDATION WITH	
	PREMATURE CRACKING FROM DEF	50
FIGURE 15	A CAST-IN-PLACE BENT CAP WITH	
	PREMATURE CRACKING FROM DEF	51
FIGURE 16	PREMATURE CRACKING IN PRESTRESSED	
	I-SHAPED BEAMS FROM DEF	52

LIST OF TABLES

TABLE 1	TEST METHODS USED BY SELECTED AGENCIES	17
TABLE 2	MAXIMUM ACCEPTED LIMITS BY AGENCY	20
TABLE 3	VDOT ALKALI LIMITS FOR MINERAL ADMIXTURES	28
TABLE 4	CSA GLOBAL APPROACH FOR ASR PREVENTION	30
TABLE 5	MINERAL REQUIREMENTS FOR SELECTED AGENCIES	31
TABLE 6	METHODS TO DETERMINE HUMIDITY IN CONCRETE	33
TABLE 7	METHODS FOR DETERMINING ELASTIC PARAMETERS	34
TABLE 8	METHODS FOR CRACK ANALYSIS	34
TABLE 9	METHODS FOR INTERNAL AND EXTERNAL DEFORMATIONS	35
TABLE 10	INTERNATIONAL ACCELERATED CURING SPECIFICATIONS	48

Chapter 1 – Introduction

Recently in Texas, there has been significant damage of field structures resulting from concrete durability problems. Alkali-silica reaction (ASR) and delayed ettringite formation (DEF), or combinations of the two, have been found to be the main causes of these problems. The term Premature Concrete Deterioration (PCD) has been adopted to refer to problems associated with ASR and DEF because it is often difficult to distinguish between them. The Texas Department of Transportation (TxDOT) has designated six mitigation options that are available to prevent or minimize PCD-related problems. Research is currently underway to document the performance of concrete using these mitigation options in the laboratory and in the field. One of the objectives of this research is to review the state of the art regarding ASR and DEF, with particular attention to mechanisms of damage, appropriate test methods, specifications, and performance-related issues.

ASR was first discovered as a concrete durability problem in the early 1940s. During the past several decades, there has been significant research conducted concerning ASR. DEF arose as a problem in heat-cured concrete during the early 1980s. Methods to prevent ASR and DEF in new concrete have been developed and incorporated into numerous specifications. ASR is sensitive to the specific materials used in concrete, as well as the location and condition of the concrete. DEF is sensitive mainly to the temperature of the concrete and the surroundings during placement, but also to constituent materials and mixture proportions. For these reasons, it is critical to have available valid test methods that can be used to assess the potential for ASR or DEF in concrete. It is also necessary to have test methods to determine the effectiveness of different mitigation methods. Over time, a variety of test methods have been developed and later modified to produce more convenient and accurate results. Yet there still remain unanswered questions concerning these tests and the precise mechanisms that take place in ASR and DEF. More research needs to be done to develop feasible mitigation techniques that satisfy economical, practical, and technical issues.

There is a large amount of information available about ASR, yet some earlier research findings have been disproved, or in some cases merely clarified, based on more current findings. There is less information available about DEF, yet in the past few years more emphasis has been

placed on this durability problem, especially the synergistic effects it may have with ASR. This report outlines the latest research and developments in the field of ASR and DEF. There are five main areas examined concerning these problems. The first topic is the mechanism of the reaction that occurs for each of these durability problems to be present in concrete. Having a clear understanding of the reaction that takes place, as well as the necessary ingredients and conditions, is essential to conducting good research. The second area concerns the most recent developments in test methods, mainly ASTM C 1260 and ASTM C 1293 for ASR. The two main test methods for DEF are the Fu Method and the Kelham Method. The third area reviewed is mitigation techniques; today these include a wide variety of mineral and chemical admixtures and even certain combinations of materials. The current state and federal specifications that have been conducted are presented. ASR and DEF are often found in concrete together. Current information about the synergistic effects of these two reactions is also included in this report. Conclusions and recommendations are included based on the information collected from past and ongoing research.

Chapter 2 – Alkali-Silica Reaction

2.1 Mechanisms

2.1.1 Reaction

The alkali-silica reaction occurs between the alkalies in the cement paste and reactive silica found in aggregates. The three necessary ingredients for ASR expansion are the following:

- 1. Reactive forms of silica
- 2. Sufficient alkali (usually from the cement)
- 3. Sufficient moisture within the concrete

The expansion leading to deterioration from ASR will be prevented if any one of these ingredients is removed from the concrete. ASR can be simplified into a two-step process:

 $Alkali+Silica \rightarrow Alkali-Silica Gel Reaction Product$ $Gel Reaction Product + Moisture \rightarrow Expansion$

Alkalies (Na₂O and K₂O) in the concrete pore solution react with reactive siliceous minerals and form an alkali-silica gel product. When the gel absorbs water, it expands and eventually can result in cracking of the surrounding paste. If this cracking progresses to the concrete surface, it provides an entrance for additional moisture and chemicals that can produce more gel expansion or cause corrosion. The permeability of the paste is important when cracking does not create direct channels for moisture. The gel reaction product can be produced with very little water, but it will not produce damaging expansion if excess water is not available or cannot penetrate the paste. A high-quality, low water-to-cementious ratio paste will add some protection but is not sufficient to prevent damage on its own (Rear et al.1994).

2.1.2 Alkalies

The aggregates in concrete exist in a matrix of the cement paste; this paste has interconnected microscopic pores that water or ions in solution can easily migrate through. Hydrated Portland cement is a very alkaline material with a pore solution pH typically greater than 12. This type of environment is an ideal place for silica to react. Alkali hydroxides in solution will react readily with reactive forms of silica in an aggregate. As the aggregate reactivity increases, the gel reaction product can be formed with lesser concentrations of alkali. With highly reactive aggregates the use of low-alkali cements alone may not be adequate to control ASR.

The alkali content of cement is given as the weighted average of potassium and sodium ions according to the following equation:

$$Na_2O_e = Na_2O + (.658) * K_2O$$

Low-alkali cement is defined in ASTM C 150 as having an equivalent sodium oxide content of no more than 0.6 percent. Concrete made with low-alkali cement may still exhibit ASR expansion if the aggregate used is extremely reactive; if alkalies are provided by admixtures, aggregates, or mixing water; if moisture movement concentrates the alkalies in one location; or if the total alkali content of the concrete is high because of high cement content.

As the pH, or alkalinity, of the pore solution increases, the potential for ASR increases. At higher concentrations of alkali hydroxides, even more stable forms of silica are susceptible to attack. If the alkali concentration is great enough, the alkali hydroxides break stronger silicon bonds found in less-reactive aggregates to form the gel reaction product.

Repeated cycles of wetting and drying can cause high localized concentrations of alkalies. As moisture travels through concrete, dissolved alkalies move in the solution remaining when the moisture evaporates. Alkali migration can cause high alkali concentrations at an evaporative surface even when the overall concrete alkali is low (Farny and Kosmatka 1997).

The volume stability of C-S-H is very good compared with the volume stability of most alkali-silica gels. All Portland cements contain some quantity of sodium and potassium, so the C-S-H will actually be a combination of calcium sodium/potassium silicate hydrate, C-Na/K-S-H. The more calcium, the more stable the gel; the more sodium or potassium, the less stable the gel, and the more likely the gel will be deleteriously expansive.

In the presence of moisture and calcium or calcium hydroxide, the reactive silica in a pozzolan will form C-S-H. The calcium hydroxide is available in the paste as a by product of the hydration of Portland cement. Pozzolans can act as sacrificial silica to react with the alkalies in the pore solution of the concrete before the silica in the aggregate can react. The gel produced by reaction with pozzolans is more stable because of the higher calcium content of the paste. The

gel is more dispersed and is less likely to create deleteriously expansive stresses even if it does swell (Leming 1996).

2.1.3 Silica

The reactivity of silica (silicon oxide) in an aggregate depends on the type and forms of silica that are present in the aggregate. When silica is completely crystalline it is chemically and mechanically stable, although there are some exceptions. There are a few forms of crystalline silicon dioxide: quartz, tridymite, and crystobalite. Quartz is stable unless it is microcrystalline or highly strained.

Completely amorphous silica is more porous and very reactive. An aggregate that is poorly crystalline, amorphous, glassy, and micro-porous, and that has many lattice defects presents a large surface area for reaction and is susceptible to attack from alkali hydroxides. Quartz silica is impermeable and reacts only on the surface of the crystal, where the silicon and oxygen bonds are broken. The surface area per unit volume of quartz is low, so the reactivity is also low.

In certain volcanic aggregates the silica has melted and cooled quickly without recrystallizing: it has a very low state of crystallization and will be very reactive in an alkaline solution.

It is possible for a large amount of strain energy to be stored in the crystal lattice of crystalline silica that has been transformed by heat and pressure. The presence of this higher energy will make the silica more likely to react. Even in a stable silica mineral, such as quartz, it is possible for deleterious alkali-silica reactivity to occur because the silica is in a strained state; however, the rate of reaction is generally much slower than that of aggregates composed of glassy or amorphous silica. Aggregates that are primarily crystalline have very high surface energies between the crystals, which contribute to alkali sensitivity (Leming 1996).

The potential reactivity of an aggregate is a function of both the degree of crystallization of the silica in the aggregate and the amount of energy stored in the crystal structure. The surface area per unit volume of the reactive silica will affect the rate of reaction: a larger area of reactive silica will have more opportunity to react. The reactivity of an aggregate is also influenced by the silica content. Aggregates containing the following constituents in the quantities listed are considered potentially reactive:

- opal more than 0.5% by mass
- chert or chalcedony more than 3.0%
- tridymite or cristobalite more than 1.0%
- optically strained or microcrystalline quartz more than 5.0%
- natural volcanic glasses more than 3.0% (Farny and Kosmatka 1997)

2.1.4 Moisture

Deleterious ASR does not occur in concrete that remains dry throughout its service. The presence of sufficient moisture allows the migration of alkali ions to reaction sites, and the reaction product gel absorbs moisture, leading to expansion. Expansive ASR can occur in concrete that has a relative humidity above 80 percent. A reduction in permeability through the use of a low water-cement ratio, supplementary cementing materials, or other means, reduces the movement of moisture and alkalis into and within the concrete. It has been found that lower water-cement ratio (0.35) concretes expand significantly less than higher water-cement ratio concretes at ages up to 19 months (Farny and Kosmatka1997), but at later ages, ASR has been known to even in low w/cm plain concrete mixtures.

2.1.5 The Attack

There are two mechanisms of attack by alkalis upon reactive silica in aggregates. The first involves aggregates that are very reactive. A large quantity of hygroscopic, expansive gel may be created, which can cause cracking of the concrete, the aggregate, or both. Alkalies such as sodium and potassium will attach to the silica-oxygen bonds, breaking the bonds and opening the crystal structure to accommodate alkali ions and water. The sodium ion is generally the more reactive of the two.

The alkali-silica reaction product gels that are composed primarily of sodium silicate hydrate can absorb a substantial amount of water and create swelling pressures that can exceed the tensile capacity of the paste, mortar, or concrete, resulting in cracks. These cracks permit more water to penetrate the gel, which creates more swelling and more cracking. This type of reaction occurs fairly rapidly, and map cracking may appear within several years.

The other mechanism of deterioration is more typical of metamorphic aggregates in which the silica is only moderately reactive, or in aggregates that do not contain a large quantity

of reactive silica. The low quantity of reactive silica at the surface of the aggregate means that a more stable gel will be created because of the presence of significant quantities of calcium hydroxide at the paste-aggregate interface. If the aggregate is porous, the alkalies can penetrate the aggregate, move into an area away from the calcium hydroxide, and create a less stable, low-calcium gel. This has the effect of softening the outside of the aggregate.

The effects on the mechanical properties of the concrete are typically much slower and may be less obvious with this reaction. Expansion may be limited, but cracks can develop through the paste and through the softened aggregate particles. When the concrete is under load there is more stress on the paste, because of the softening of the aggregate. Although the service life may be longer than that of the highly reactive silica aggregates, some deterioration may be expected eventually, depending on the amount of available moisture (Leming 1996).

The role of silica content may be understood by considering a given alkali content in a concrete containing an aggregate that is composed of various quantities of reactive silica. At very low reactive silica contents, not enough gel is produced to cause deleterious expansion or softening of the aggregates. At very high reactive silica contents, the expansive gel may be dispersed over a large volume. Because local calcium hydroxide content is dispersed, it may be adequate to stabilize the gel. At some intermediate silica content there is the potential for the worst possible combination of reactive silica for a given alkali content; the pessimum silica content may produce rapid deterioration (Hobbs, 1988).

2.2 Test Methods

2.2.1 ASTM C 1260

An accelerated mortar bar test method was developed to respond to the need for a quick method to measure the potential reactivity of aggregates to ASR in concrete. In the early 1980s, Oberholster and Davies at the National Building Research Institute (NBRI) in South Africa developed a means of accelerating the expansion of mortar bars by storing them in sodium hydroxide solution at high temperatures. The American Society for Testing and Materials (ASTM) adopted draft test procedures for this test in 1989. The Canadian Standards Association (CSA) did so in 1988. Both CSA and ASTM formally adopted this test in 1994 (CSA A23.2-25A, ASTM C 1260) (Rogers 1999).

In the Accelerated Mortar Bar Test (ASTM C 1260), the mortar bars are demolded after 24 hours of curing and placed in water that is then heated to 80 °C. After 24 hours, the bars are measured for length and immediately placed in 1N NaOH solution preheated to 80 °C. They are stored at 80 °C in the solution for 14 days. Expansion is measured periodically over the 14 days, and again on the 14th day, by quickly removing the bars from the solution, measuring their length, and returning them to the solution. This length of time has proven sufficient to determine whether the aggregate is deleteriously expansive, although sometimes the test is carried out 28 days or longer.

The 14-day expansion criteria, according to ASTM, are as follows:

- < 0.1% =non-reactive
- 0.1% to 0.2% = potentially reactive
- > 0.2% = reactive (CSA specifies an expansion limit of 0.15%)

The high temperature of the solution and the high alkalinity of the soak solution create an extremely aggressive environment for the mortar specimens. These conditions are necessary to speed up the alkali-silica reaction, although for some aggregates the severe conditions may lead it to show expansive behavior, when in actual field conditions, that aggregate could be very durable. The accelerated mortar bar test has been known to indicate certain aggregates to be reactive despite satisfactory performance in the field and in the concrete prism test (ASTM C 1293). Interpretation of the results is not simple. Aggregates should not be rejected but can be accepted based solely on the accelerated mortar bar test results (Thomas et al. 1999b).

The accelerated mortar bar test was initially intended for testing only the reactivity of aggregates. In recent years, the test has been modified to test the effectiveness of mineral and chemical admixtures. A recent study was conducted by CANMET to evaluate the use of the accelerated mortar bar test for testing mineral admixtures. Only a few of the mixtures tested failed the accelerated test and passed the concrete prism test. Therefore, the researchers concluded that the accelerated method can be used to test the long-term effectiveness of mineral admixtures in controlling ASR (Fournier and Malhorta 1999). The accelerated mortar bar test can also be used to determine the effect of different cements. For testing the reactivity of cements, the normality of the soak solution is altered to represent different alkali levels of

cement. However, some problems have been observed with this approach, especially for aggregates that exhibit higher expansions at lower soak normalities.

2.2.2 ASTM C 1293

ASTM C 1293, The Standard Test Method for Concrete Aggregates by Determination of Length Change of Concrete Due to Alkali-Silica Reaction, tests fine or coarse aggregates with or without admixtures for reactivity resulting from ASR. The expansion limit is 0.04 percent, measured at 1 year for mixtures without admixtures and 2 years for mixtures with admixtures.

ASTM C 1293 is probably a more accurate test but is undesirable because of the lengthy test period. "The ASTM C 1293 test offers the advantage of testing the aggregates that are proposed to be used in construction and, thus, takes into consideration the inherent reactivity of the aggregates" (Lane 1999). It is well known that in tests of aggregates using both ASTM C 1260 and ASTM C 1293, the results of ASTM C 1293 should govern, because the findings correlate better with field performance. Canada recognizes this, and Canadian specifications state that concrete prism test data should supersede results obtained from accelerated mortar bar tests (Thomas and Innis 1999).

Thomas and Innis (1998) note that expansion of concrete prisms (CSA A23.2-14A) with slag continues after 2 years. Therefore, a longer time period may be necessary to yield accurate results. Fournier and Malhorta (1999) agree that a period of more than 2 years is needed in tests containing silica fume. However, the CSA recognizes that CSA A23.2-14A (ASTM C 1293) is a harsh test with high alkali content, temperature, and humidity, so the test should be reliable at 2 years if close attention is paid to expansion at the end of the test. Thomas and Innis (1998) found that slag reduces the expansion of concrete prisms and mortar bars made with reactive aggregates, and that the effectiveness increases with increasing levels of slag.

Fournier and Malhorta (1999) found that 30 or 56 percent Class C fly ash is generally acceptable. For highly reactive aggregates, 30 percent Class F fly ash is needed (Fournier and Malhorta 1999). Specimens with 50 and 65 percent slag passed the prism test, 35 percent slag did not pass with highly reactive aggregates, although it may be good with moderately reactive aggregates (Fournier and Malhorta 1999). All expansion limits were met with 12.5 percent silica fume, while 7.5 to 10 percent met the limits for moderately reactive aggregates (Fournier and Malhorta 1999).

Lane's concrete prism test results suggest that a minimum of 10 percent silica fume, 15 percent fly ash, and 35 percent slag replacement are needed to suppress ASR. These values are much lower than those suggested by the accelerated mortar bar tests. According to Lane, "the 2-year test period might reasonably be considered to reflect 20-years' field service" (Lane 1999). Lane (1999) cautions that the results from ASTM C 1293 need to be correlated to actual field results to determine whether the test is valid.

Whiting (1999) suggests that expansive criteria may not be enough to determine the reactivity of an aggregate. When testing the fine aggregate, she noticed that "the shales in the sand are reacting, forming gel, cracking, and causing pop-ups and spalls on the surface of the concrete prisms" even though the expansions were relatively low (Whiting 1999). Fournier et al. (2000a) state that an aggregate that shows reactivity in the concrete prism test may not expand in the field if the critical level of alkalis is never reached. They also suggest that testing at 100 °F and relative humidity greater than 95 percent accelerates the time required for field structures to reach an equivalent expansion by a factor of 8 to 14 depending how reactive the aggregate is (Fournier et al. 2000a). For example, a given aggregate may fail in ASTM C 1293 in one year but may take 8 to 14 years to fail in outdoor exposure blocks, using a 0.04 percent expansion limit.

2.3 Mitigation Methods

2.3.1 Low-Alkali Cement/Concrete

The use of low-alkali cement is a method of suppressing ASR because alkalis are needed for the reaction to occur. Limiting the cement content of the mix will also lower the total available alkalis in the concrete. Higher alkali contents result in more ASR reaction product, which can lead to more expansion (Leming and Nguyen 2000). It has been suggested that the total available alkali content of the concrete should be limited to less than about 5 lb per cubic yard (pcy) (Duchesne and Berube, 1994). However, Leming and Nguyen (2000) found that no deleterious ASR expansion occurred when the alkali content of the concrete, expressed as Na₂Oeq, was less than 2.5 pcy. When this value was greater than 3.4 pcy, deleterious ASR occurred (Leming and Nguyen 2000). Leming and Nguyen (2000) suggest that one should base specifications on the total alkalis per volume of concrete rather than placing limits on only the alkali content of the cement. Limiting the alkali content is a problem in certain areas, as Rogers points out, because of the climate and availability. "Reducing cement contents and, hence, alkali levels is often not practical because of the severe Canadian climate, which generally requires low water/cement ratio, air-entrained concrete for all exposed work" (Rogers 1993). For durability purposes, the Canadians require a cement content of 550–750 pcy. Therefore, the location and the surrounding conditions may not allow low cement contents and/or low-alkali cements to be used. Low-alkali concrete can still expand from ASR if moisture movement causes the alkalis to concentrate (Farny and Kosmatka 1997). However, if the conditions permit the use of low-cement content and/or low alkali cements, both will help reduce the damaging effects of ASR.

2.3.2 Fly Ash

"One of the mechanisms by which fly ash controls alkali-silica reaction is by increasing the alkali binding capacity of the hydrates and thus reducing the alkalinity of the pore solution" (Thomas et al. 1999a). According to Thomas et al (1999a), the increased binding capacity of cement fly ash hydrates has been linked to the lower Ca/Si ratio of the hydrates compared to Portland-cement pastes without fly ash" (Thomas et al. 1999a).



Figure 1 - ASTM C 1260 Specimens Showing the Ability of Fly Ash to Control Cracking

2.3.3 Slag

Slag is effective in limiting expansion from ASR, but there is not a consensus on what the minimum amount required should be. This minimum level is a function of the aggregate and the alkali level in the concrete. The CSA recommends a minimum of 50 percent replacement, which is difficult to achieve in practice because of low early strength concerns and resistance to deicing

salts (Thomas and Innis 1998). The beneficent effects of slag are seen in the results of concrete prism tests. "Slag affects a reduction in the rate and ultimate magnitude of expansion; the effect increases with the level of slag" (Thomas and Innis 1998). The reductions of ionic mobility and water permeability are the means by which slag is able to reduce ASR expansion (Thomas and Innis 1998). The level of slag needed depends on the type of aggregate and the amount of alkalis in the concrete mix. Thomas and Innis (1998) suggest that concrete specifications should be flexible regarding the minimum amounts of slag needed, basing it on the alkali content of the concrete and reactivity of the aggregate.



Figure 2 - ASTM C 1260 Specimens Showing the Ability of Slag to Control Cracking

2.3.4 Silica Fume

Silica fume can help reduce expansion caused by ASR through several mechanisms:

- 1. Reducing the pore solution alkalinity
- 2. Reducing ionic diffusion and water permeability
- 3. Consuming Ca(OH)₂
- 4. Improving Ca(OH)₂ distribution at the interface (Thomas 1996)

Examinations of pore solutions determined that silica fume reduces the amounts of Na^+ , K^+ , OH^- ion concentrations of concrete samples (Durand et al. 1990). Silica fume also decreases the permeability of concrete, implying a reduction in the mobility of ions in the pore solution that

helps control ASR (Durand et al. 1990). "Substituting silica fume into concrete promotes a pozzolanic reaction with calcium hydroxide and alkaline hydroxides, thereby forming a C-S-H with a low CaO/SiO² (C/S) and high density, and consequently reducing the empty space and leading to a reduction in permeability" (Hasparyk et al. 2000). By forming more alkalientrapping C-S-H (low C/S increases the capacity to entrap alkalis), silica fume leaves fewer alkalis available for ASR (Durand et al. 1990).

Silica fume slows and reduces expansion caused by ASR but does not completely eliminate it (Ferraris et al. 2000). Concrete prism tests show that silica fume protects concrete against ASR expansion for 2 years or more, but the results show that the expansion limit will be exceeded in time (Thomas 1996). Studies show that when silica fume or other pozzolans are used, the alkali concentrations increase and then decrease, reaching equilibrium level after about 20 to 30 days (Ferraris et al. 2000). When no admixtures are used, the alkali concentration increases continuously over time (Ferraris et al. 2000).

If silica fume is not properly mixed, it may cause ASR rather than prevent it because of the reaction of undispersed agglomerates (Shayan 1997). Another problem with silica fume is that there is not a consensus about the amounts needed to control ASR. Studies in South Africa suggest that 15 percent silica fume is needed to prevent long-term deleterious expansions (Thomas 1996), while Shayan (1997) states that for silica fume to be successful, it must be used in large enough quantities (10 percent), be in well-dispersed form, and have low alkali content.

There is not enough field data to verify the conclusions reached in laboratory tests (Thomas 1996). "Expansion decreases with increasing silica fume content, although pessimum behavior has been observed in some studies at levels of replacement of 5 percent silica fume" (Thomas 1996). However, at normal levels of use (5–10 percent), silica fume retards the rate of expansion from ASR, with the reduction becoming greater with larger amounts of silica fume (Thomas 1996).



Figure 3 - ASTM C 1260 Specimens Showing the Ability of Silica Fume to Control Cracking

2.3.5 Lithium Salts

"Research has shown that introducing a lithium ion may further reduce the expansion caused by the alkali and silica reaction" (Barringer 1999). Lithium salts can eliminate expansion caused by ASR, but some, such as lithium hydroxide, also increase the concentration of OH ions in the mix (Shayan 1997). Therefore, lithium hydroxide must be used in the correct amount (based on the Na₂O equivalent of the concrete) in order to avoid this pessimum effect.

Lithium hydroxide has been shown to produce a lithium containing ASR gel that has a very low rate of expansion or none at all (Farny and Kosmatka 1997). Lithium nitrate, the most commonly used lithium salt, was tested under the procedures listed in AASHTO T303 (which is the same as ASTM C 1260 except for a water-to-cement ratio of .5) but it did not control expansion enough under the manufacturer's recommended dosages (McKeen et al. 2000). An average of 43 percent of the lithium nitrate was leached from the bars when they were placed in the water, which is probably to blame for the excessive expansion (McKeen et al. 2000). This is why it is hard to use ASTM C 1260 to test the effectiveness of lithium salt mixtures. When lithium is combined with fly ash, it reduces expansions more than lithium would alone (Barringer 1999). However, the specific amounts of lithium and lithium-fly ash combinations required must be determined by testing (McKeen et al. 2000).

CONTROL	X
NITRATE	

Figure 4 - ASTM C 1260 Specimens Showing the Ability of Lithium Nitrate to Control Cracking

2.3.6 Ternary Blends

It may not be feasible to use high amounts of Class C fly ash or silica fume (Thomas et al. 1999b). A fly ash/silica fume ternary blend may be the solution to this problem. "Combinations of lesser amounts of these materials have been shown to be very effective in controlling ASR expansion" (Thomas et al. 1999b). CSA prism tests containing 5 percent silica fume and 20 to 30 percent Class C fly ash met the .04 percent expansion limit at 2 years using the reactive Spratt aggregate and high-alkali cement (Thomas et al. 1999b). It was found that the combination of fly ash and silica fume works better than the addition of individual expansion reductions (Thomas et al. 1999b). Pore solution examinations cannot explain why the ternary blend is more effective at reducing ASR expansion. "Pastes containing 5% silica fume and either 20% or 30% high CaO fly ash have a higher concentration of OH⁻ than pastes with 10% silica fume only. In spite of this, the ternary blends are more effective in controlling ASR expansion than 10% silica fume used on its own" (Thomas et al. 1999b). This is most likely due to the ability of silica fume to bind alkalis at early ages and fly ash or slag to do the same at later stages. More research is needed to determine how ternary blends work to reduce ASR expansion.

	CONTROL	
-1-1-27	「ゴートートー	J'L
		1
	5% SILICA FUME	
	20% CLASS 'L' FLY ASH	

Figure 5 - ASTM C 1260 Specimens Showing the Ability of a Ternary Blend to Control Cracking

2.4 Specifications

2.4.1 Agency Test Specifications

Widespread knowledge has been obtained during 60 years of research pertaining to ASR mechanisms, specific minerals within aggregates that are susceptible, and methods of mitigating the reaction. The industry still lacks, however, both adequate test methods that accurately quantify the level of reactivity of aggregates in field performance, and methods to repair and control affected concrete in the field (ACI 221.1R-98 1998).

Because no "perfect" test method has been established to adequately quantify the reactiveness of all types of aggregates susceptible to ASR, many agencies are specifying different methods. "None of these standard methods can be relied upon independently or collectively to provide an unquestionably definitive answer as to whether an aggregate is deleteriously reactive" (USACE 2000).

We performed a review of some of the larger agencies involved in the area of ASR research to determine which test methods were being used most frequently, and which mitigation alternatives were being presented as acceptable methods of eliminating or mitigating the reactivity of the aggregates in question.

Test Methods				
ASTM Designation	Test Description	Agencies Recommending this Method		
C 227	Mortar-bar method; samples above water @ 38 °C; minimum 12-month test; used to test cement only	U.S. Army Corps of Engineers		
C 289	Quick chemical test; finely crushed aggregate is soaked in NaOH for 24 hrs; tests for dissolved silica and alkalinity reduction	U.S. Army Corps of Engineers		
C 295	Petrographic analysis of fine and coarse aggregate	PCA/ACPA, U.S Army Corps of Engineers		
C 441	Method and procedure is the same as ASTM C 227; allows testing of mineral admixtures	TxDOT, VDOT, AASHTO, PennDOT, PCA/ACPA		
C 856	Petrographic examination of hardened concrete	PCA/ACPA		
C 1260	Accelerated mortar-bar method; samples in IN NaOH solution @ 80 °C; 12-day test	TxDOT, CSA, PCA/ACPA, AASHTO, PennDOT		
C 1293	Concrete prism method; samples stored above water @ 38 °C; 12-month test with no admixtures, 24-month with admixtures	TxDOT, CSA, PCA/ACPA, AASHTO		

 Table 1 - Test Methods used by Selected Agencies

2.4.1.1 Determination of Field Performance

According to the Portland Cement Association/American Concrete Pavement Association and the American Association of State Highway and Transportation Officials, monitoring the field performance of an aggregate is the best method of determining its susceptibility to ASR. When evaluating the field performance of an aggregate, the following should be considered (PCA/ACPA 1998):

- 1. Are the cement content of the concrete, the alkali content of the cement, and the watercement ratio of the concrete the same or higher than proposed for future use?
- 2. Is the field concrete at least 15 years old?
- 3. Are the exposure conditions of the field concrete at least as severe as those proposed for future use?
- 4. Were pozzolans used in the field concrete?

Additionally, the aggregate within the field concrete and the current aggregate supply should be tested petrographically to ensure that they remain similar in mineralogy.

2.4.1.2 Laboratory Testing

Petrographic Examination

For aggregates with a field history, PCA/ACPA and AASHTO recommend a petrographic analysis (ASTM C 856) and a visual examination be performed on the structure. AASHTO goes further in recommending petrographic evaluations of at least five structures that have been in service for a minimum of 10 years. Researchers should be cautious in concluding that an aggregate is nonreactive based on evaluations of structures that are less than 20 years old, because the reaction may not have had adequate time to show its effects (ASR Lead State Team 2000).

If the field history of the aggregate is not available, AASHTO, USACE, and PCA/ACPA recommend that a petrographic analysis be performed on the proposed aggregates using ASTM C 295. The types and amounts of potentially reactive minerals within aggregates can be

determined. This is a very valuable tool to use in determining whether an aggregate contains alkali-silica reactive minerals.

ASTM C 295 Maximum Accepted Limits for Nonreactive Aggregates		AASHTO	PCA/ACPA	USACE
1	Optically strained, microfractured or microcrystalline quartz	5.0%	5.0%	N/A
2	Chert or chalcedony	3.0%	3.0%	5.0%
3	Tridymite or cristobalite	1.0%	1.0%	1.0%
4	Opal	0.5%	0.5%	0.0%
5	Natural volcanic glass (acid or intermediate glass for Army Corps)	3.0%	3.0%	3.0%
6	More than 15% of particles of graywacke, argilit, phyllite, or siltstone containing any finely divided quartz of chalcedony	N/A	N/A	15%

 Table 2 - Maximum Accepted Limits by Agency

The test cannot, however, discern between minerals that will produce deleteriously expansive gels and those that will not. Because of this lack in knowledge, the test recommends "additional petrographic chemical, physical, or geological investigations that may be required to evaluate adverse properties that are indicated by the petrographic examination that has been performed" (ASTM C 295).

<u>ASTM C 289</u>

Of the agencies studied, only the USACE uses ASTM C 289 as a means of identifying alkali-silica reactivity in aggregates. The quick chemical method has numerous limitations, including: grinding the sample too fine can lead to flawed results, aggregates containing certain rock mineralogy can also lead to flawed results, and vague details are provided for potentially reactive aggregates.

<u>ASTM C 227</u>

As with the test previously mentioned, only the USACE uses ASTM C 227, which has been in use since 1950 (Stark 1994). The test method is an adequate evaluation of highly reactive aggregates' susceptibility in producing deleteriously expansive gels, but because of the mild testing environment, slowly-reacting aggregates may not show expansive traits within the 12-month test period. This test method is accepted for the testing of cement and aggregate combinations only; no mineral admixtures are permitted in this test method. There is less need for this test method because of the development of ASTM C 1260, which gives more rapid results (ACI 221.1R-98 1998).

<u>ASTM C 441</u>

This test method is modeled after ASTM C 227, with the added ability of testing the effectiveness of mineral admixtures in mitigating the expansion. The Virginia Department of Transportation (VDOT) is using this test method exclusively for the assessment of the efficacy of mineral admixtures. Some also question this test method, as the Pyrex glass used contains alkalis that may be released into the pore solution and is sensitive to test conditions (ACI 221.1R-98 1998).

<u>ASTM C 1260</u>

This test method was developed by the NBRI in South Africa to provide rapid and reliable test results, and it went through extensive testing before being adopted by ASTM. The test is usually used by agencies as a "screening" test in conjunction with other test methods to reliably determine the aggregates' potential reactivity. The severe environment of the test can lead to false positives, showing certain aggregates to be deleteriously expansive when in field structures, the aggregates display durable performance.

The practice of determining the efficacy of mineral admixtures using either ASTM C 1260 or C 441 is questioned because of the uncertain mechanism that causes the decrease in expansion. "Within the length of the test period used in both of these tests, the pozzolans or slags used are unlikely to react to an extent that replicates the actual mechanism that occurs in field concretes" (ACI 221.1R-98 1998).

<u>ASTM C 1293</u>

The concrete prism test, ASTM C 1293, is similar to that of ASTM C 227 with the exception that the bars are concrete instead of mortar. This provides a testing scenario that is more realistic than ASTM C 227 or C 1260 for an aggregate's susceptibility to deleterious reactivity (ACI 221.1R-98 1998). This method may be used to test the reactivity of a fine or coarse aggregate, assuming that the other aggregate has been determined to be innocuous. When using this test to evaluate the effectiveness of mineral admixtures, researchers are advised to allow a minimum of 2 years of testing. The concrete prism test is very useful in confirming ASTM C 1260 results for aggregates that have been shown to be slowly reactive with alkalis. However, questions have risen regarding the leaching of the alkalis from the bars, which ultimately stops the reaction.

2.4.1.3 Flowcharts

AASHTO and PCA/ACPA have developed detailed flowcharts that help in the analysis of an aggregate. The charts outline very similar paths and use the same test methods.



Figure 6 - AASHTO Flowchart for ASR Prevention (after ASR Lead States Team 2000)



Figure 7 - PCA/ACPA Flowchart for ASR Prevention (after PCA/ACPA 1998)
The CSA has recently released its new proposed approach to preventing the risk of deleterious expansion in concrete from ASR. Under these new guidelines, the aggregates are categorized according to their reactivity based on either ASTM C 1293 or C 1260. The size of the structure and the environment it will be exposed to are then considered, and the structure is placed within specified "risk levels." The level of prevention and the measures that need to be taken are determined based on the desired design life of the structure. The guidelines include a table that gives minimum proportions of mineral admixtures that are required for specific risk levels.



Figure 8 - Global Approach for the Selection of Preventive Measures Against ASR (after Fournier et al. 2000b)

2.4.2 Specified Mitigation Methods

If an aggregate shows no sign of potential deleterious reactivity, it should not be required to be used with any mitigation methods. But with uncertainty in the test methods used to determine such reactivity, some agencies are requiring mitigation options regardless of how the aggregate performs in the test methods. TxDOT requires that all contractors in the state of Texas use one of the following options regardless of the reactivity of the aggregates used (TxDOT Special Provision 421, 1995):

- 1. When using cement only, the total alkali contribution from the cement in the concrete shall not exceed 4 lb/yd^3 .
- 20 35 percent of the cement shall be replaced, by absolute volume, with Class F fly ash.
- 3. 35 50 percent of the cement shall be replaced, by absolute volume, with ground granulated blast furnace slag (GGBFS).
- 35 50 percent of the cement, by absolute volume, may be replaced with a combination of Class F fly ash, GGBFS, or silica fume. However, no more than 35 percent may be fly ash and no more than 10 percent may be silica fume.
- 5. Type IP or IS cement shall be used. Up to 10 percent of Type IP or IS, by absolute volume, may be replaced with Class F fly ash, GGBFS, or silica fume.
- 6. The contractor shall also have the option of the following as long as the mix does not exhibit an expansion greater than 0.10 percent at 14 days in accordance with ASTM C 1260:
 - a. Using Class C ash in lieu of Class F ash, except when Type II is specified.
 - b. Substituting a lesser percentage of fly ash and/or GGBFS for the cement.
 - c. Using a cement-only mix with a total alkali contribution greater than 4 lb/yd^3 .

Most agencies examined, including PennDOT, VDOT, PCA/ACPA, AASHTO, CSA, and USACE, require that no mitigation methods be required for aggregates shown to be nonreactive.

2.4.2.1 Low-alkali Cements

The trend of limiting the amount of alkalis in a concrete mix is meant to specify a maximum limit on the percentage of alkalis in the cement. VDOT currently specifies a maximum cement alkali, depending on the combination of cementitious materials (VDOT Sec. 405.07, 1998):

Combination of Cementitious Materials	Maximum Cement Alkali		
Cement Only	0.45%		
Cement with Minimum 15% Class F Fly Ash	0.60%		
Cement with Minimum 20% Class F Fly Ash	0.68%		
Cement with Minimum 25% Class F Fly Ash	0.75%		
Cement with Minimum 30% Class F Fly Ash	0.83%		
Cement with Minimum 25% Slag	0.60%		
Cement with Minimum 35% Slag	0.90%		
Cement with Minimum 50% Slag	1.00%		
Cement with Minimum 3% Silica Fume	0.60%		
Cement with Minimum 7% Silica Fume	0.90%		
Cement with Minimum 10% Silica Fume	1.00%		

Table 3 - VDOT Alkali Limits for Mineral Admixtures

This method of only considering alkali cement levels has come into some scrutiny lately, because pre-casters usually use high sack mixtures, which can bring the total amount of alkalis above a critical level.

CSA and TxDOT have dealt with this problem by specifying the total amount of alkalis by weight be below certain values. TxDOT requires that the total amount of alkalis be below 4 lb/yd³, and CSA requires that they be below 5.1 to 3.0 lb/yd³, depending on the level of prevention determined in their method.

The use of low-alkali concrete is the last mitigation method specified by PCA/ACPA, following the use of blended cements and mineral admixtures, to promote the use of mineral admixtures. The use of mineral admixtures is the preferred approach of PCA/ACPA (PCA/ACPA 1998).

2.4.2.2 Mineral Admixtures

The use of mineral admixtures to mitigate or eliminate the deleterious expansion of ASR is the method recommended by most industry standards. The advantages gained in terms of reduced permeability and reduced cost in materials are not offered with other mitigation methods.

CSA has developed a detailed approach to selecting the amount of mineral admixture required. The flowchart, shown in Table 4, considers the total alkali content of the admixture, its chemical composition, and replacement percentages for different prevention levels.

PennDOT requires that the amount of slag or fly ash used be enough to produce a 50 percent minimum reduction in mortar expansion when tested using ASTM C 441. Minimum amounts are specified, while allowing larger amounts if AASHTO T 303 shows expansion amounts of > 0.40 percent. PennDOT also limits the use of silica fume to an experimental basis only, until sufficient experience is gained (PennDOT, 2000).

	Type of SCM	pe of SCM Cement Replacement Level (% by mass) ^a				% by mass) ^a
		Total Alkali	Chemical			
		Content of	Composition			
		SCM (%	Requirement (%			
		Na ₂ Oeq)*	oxides)			
		2		Prevention	Prevention	Prevention
				Level W	Level X	Level Y & Z
			CaO < 8%	<u>> 15</u>	<u>></u> 20	<u>> 25</u>
		< 2.0				
		< 5.0	CaO = 8% - 20%	<u>></u> 20	<u>> 25</u>	<u>></u> 30
	Fly Ash		CaO > 20%	See ^b	See ^b	See ^b
			CaO < 8%	<u>></u> 20	<u>></u> 25	> 30
		3.0 - 4.5	CaO = 8% - 20%	<u>> 25</u>	<u>></u> 30	<u>></u> 35
			CaO > 20%	See ^b	See ^b	See ^b
		> 4.5			See ^b	
	Blast Furnace					
	Slag	< 1.0 b	None	<u>> 25</u>	<u>></u> 35	<u>></u> 50
	Silica Fume					
		< 1.0 b	$SiO_2 > 85$	2.0 x alkali	2.5 x alkali	3.0 x alkali
				content ^c	content ^c	content ^c
	Natural	Natural pozzol	ans that meet the req	uirements of CSA	A A23.5 may be us	sed, provided that
	Pozzolans	their effectiver	ness in controlling ex	pansion due to A	SR is demonstrate	d according to
		CSA Recomme	nded Practice (12).			
	Ternary Blends	When two or n	nore SCMs are used to	ogether to contro	ol ASR, the minim	um replacement
		levels given in	Table 5 for the indiv	idual SCMs may l	be partially reduce	d, 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 fum				imum silica fume
	level given in Table 5, provided that the slag level is at least two-thirds of the minimu				s of the minimum	
		slag level given in Table 5.				
ł	$Na_2Oeq = sodium$	n oxide content	$= Na_2O + 0.658 * K_2C$)		
3	In order to contr	rol the total alka	ali content of the con	ncrete mixture, th	e maximum alkal	i content of the
	cement used in combinition with any SCMs should be $< 1.0\%$ Na ₂ O _{eq}					
b	In the presence of reactive or potentially reactive aggregates, blast furnace slag and silica fumes with				a fumes with	

Table 4 - CSA Global Approach for ASR Prevention (after Fournier, et. al, 2000 b)

In the presence of reactive or potentially reactive aggregates, blast furnace slag and silica fumes with alkali contents > 1.0% Na2Oeq, and fly ash with alkali contents > 4.5% Na2Oeq 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 (12). 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 (13,14).

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/m3 Na2Oeq), but in cases where silica fume is the only SCM to be used, the silica fume content should be 7.0% by mass.

d Blended cements may be used, provided that the proportions of the supplementary cementing materials in the blend meet the requirements of Tables 4 and 5.

	Cementitious Material Percentage (by mass)			
Mineral Admixtures	AASHTO (minimum)	TxDOT	PCA/ACPA	USACE
Fly Ash - Class F	15%	20% - 35%	Must meet ASTM C 1260 or C 441 expansion limits	Must meet ASTM C 441 expansion limits
Fly Ash - Class C	30%	Must meet ASTM C 1260 or C 441 expansion limits	"	"
Ground Granulated Blast Furnace Slag	25%	35% - 50%	"	"
Silica Fume	5%	< 10%	"	"

Table 5 - Mineral Requirements for Selected Agencies

2.4.2.3 Chemical Admixtures

The only specification studied that deals specifically with addition rates of chemical admixtures is AASHTO, which discusses numerous lithium compounds. TxDOT and PCA/ACPA also allow the addition of lithium nitrate to be used in the mix, provided it is included in the effectiveness test in the anticipated proportions for use on the job.

2.4.2.4 Other

Decreasing the available water (low w/c) and decreasing the amount of reactive aggregate ("aggregate sweetening") are also given as options by USACE.

2.5 Field Studies

2.5.1 Parameters to Monitor

There are several factors that, if monitored correctly, should provide clues to the behavior of ASR in field structures. These factors are the environment inside and outside a concrete structure, and deformations of the structures.

The environmental measurements taken inside and outside of a concrete beam that can help describe the behavior of ASR are the following:

- Chemical content
- Temperature
- Relative humidity
- Wind exposure
- Moisture exposure

The chemical composition (including pore solution analysis) and temperature inside concrete determine the rate at which an aggregate is broken down and ASR gel forms. The amount of moisture inside the beam is important in the expansion of the ASR gel. To determine the available moisture of the structure, the researchers can measure the relative humidity, wind exposure, and moisture exposure of the structure.

The measurements taken pertaining to the interior and exterior deformations are as follows:

- Internal strains
- Internal cracks
- Exterior strains
- Exterior cracks
- Overall deflection of the structure

The measurements of strains and cracks at different areas of the structure show the areas where expansion is occurring. Strains represent small deformations in the structure, and cracks represent areas where the tensile capacity of the concrete has been exceeded because of induced strains. This external cracking of the structure usually causes serviceability issues rather than structural issues. The overall deflections of the structure, aesthetically unpleasant cracking, or other durability problems can arise because of ASR distress.

2.5.2 Monitoring Methods

Several methods have been developed to measure the crucial factors discussed above. The following tables, adapted from a conference paper by Siemens and Gulikers at the 11th ICAAR conference, Quebec (2000), discuss different techniques and advantages and disadvantages related to each.

Method	Advantages	Disadvantages
electrical	• well developed	• only possible in areas of no cracks or
resistance	• simple and cheap	reinforcement (profiles only available in
		the cover zone)
multiple ring	• reasonably	• measurements done in injected grout
sensors	developed	instead of the concrete
	• relatively simple	
	 inexpensive 	
di-electrical	• imaginary and real	• still under development
constant	signal can be	• interpretations still need a model for
	measured	concrete
microwave	• reasonably	• inaccurate with high humidity
sensors	developed	 measurements restricted to 25 mm
	• quick and simple	• not available commercially
	• affected by salt,	
	cracks, and	
	reinforcing	
Radar	• reasonably	 very specialized
	developed	high initial cost
	 continuous profiles 	restricted depth
		interpretation problems
Radiography	• reasonably	• very specialized
	developed	high initial cost
	 continuous profiles 	restricted depth
		• interpretation problems
		strict safety requirements
nuclear	• less sensitive to salt	under development
magnetic	and cracks	• cast-in-place application still experimental
resonance		high initial cost
		• currently confined to a restricted depth
infrared	• well developed	 only superficial measurements
reflection	• able to measure large	• relationship between humidity and cracks
	areas	unclear
humidity of	• simple	• measurements only between 85% and
wooden		100%
dowels		• relationship between wood and concrete
		questionable
		• wood will rot when humidity is lower than
		30%
		• each individual probe requires a different
		calibration

Table 6 - Methods to Determine	e Humidity in Concrete
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Method	Advantages	Disadvantages
ultrasonic pulse velocity	 well developed quick and simple sensitive to local changes 	• influences of compression zone and reinforcement difficult to eliminate
spectral analysis of surface waves	• potential to provide a lot of information	underdevelopeddifficult interpretationhigh initial cost
vibrations/ mechanical impedance	 well developed very sensitive to changes 	• difficult with complex geometry

 Table 7 - Methods for Determining Elastic Parameters

Table	8 -	Methods	for	Crack	Analysis
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Method	Advantages	Disadvantages	
radar/ active	• reasonably	resolution is poor	
acoustic	developed	• very specialized	
emission	• internal structure can		
	be developed		
radiography	 reasonably 	resolution is poor	
	developed	• very specialized	
	• internal structure can	• use of contrast fluid	
	be developed		
infrared	• well developed	• only exterior cracks are measurable	
reflection	• quick and simple	• variations in humidity are unclear	
	• low costs		
Video-	• well developed	• only exterior cracks are measurable	
records	• simple		
	• low costs		
Passive	• reasonably	• resolution is poor	
acoustic	developed	• very specialized	
emission	• internal cracking can	• pre-loading necessary	
	be determined		

Method	Advantages	Disadvantages
mechanical gages	well developedquick and simplelow cost	• only local measurements are available
vibrating wire gages	well developedquick and simplelow cost	• only local measurements are available
inductive gages	well developedquick and simplelow cost	• only local measurements are available
strain gages	well developedquick and simplelow cost	• only local measurements are available
glass fiber	• many simultaneous measurements	 experimental and under development expensive equipment
Moiré Method	 2D technique stress type is determined 	 only elastic deformations ruled incorrect by computer simulations
Photogrammetry	• 3D technique	 under development relatively expensive equipment specialized accuracy still unclear
speckle correlation	• 3D technique	 under development relatively expensive equipment specialized accuracy still unclear

Table 9 - Methods for Internal and External Deformations

2.5.3 ASR Field Studies

Field studies usually have been created to monitor a bridge or a dam after it has already shown some sign of damage from ASR. Instrumentation is typically used in these field studies to monitor how ASR continues to behave after it has caused damage. Instrumented field studies also have been conducted to monitor the effects of certain repairs designed to relieve the damage created by ASR.

2.5.3.1 Gel Fluorescence Test

In this method, a sample that is suspected of ASR damage is coated with uranyl ions. These ions cause ASR gel to fluoresce once a UV light is shined on them. Tests show that this method provides good results in showing whether ASR is present in a structure. However, this test method does not predict whether expansion will take place (Natesaiyer 1993).

A study by Mitchell and Leming took the gel fluorescence test to an advanced level by using an electronic camera in conjunction with an image-processing program to analyze the fluorescence. With this equipment the researchers hoped to be able to determine a magnitude of the ASR gel in different areas of the structure. The idea was that larger amounts of ASR gel would be found in areas of severe ASR damage and lower amounts would be found in other areas. No results were given in this publication (Mitchell and Leming 1998).

In another project, the gel fluorescence test was used to analyze cores taken from a 17year-old bridge in North Carolina. The study found that significant amounts of ASR were found only in the cores taken from ASR-damaged sections of the bridge and that no ASR gel was found at the bottom of the cores. This shows that the concentration of ASR gel varies with the depth of the structure. These findings show that this method does a good job of showing the concentrations of ASR gel in areas of ASR damage. This method could be used to monitor structures before ASR damage happens. This method would especially be useful to predict the areas that are in the most danger (Leming and Nguyen 2000).

There has been recent debate over the ability of the technique to accurately assess the type and amount of ASR gel in structures. There have also been environmental concerns raised over the use of uranyl acetate.

2.5.3.2 Ultrasound Tomography

This method uses vibrations to measure the bulk properties of concrete. The induced waves are altered when they travel through damaged concrete areas. By comparing the vibrations from concrete that is undamaged to those from damaged concrete, researchers can compare several material parameters. Calculations have been made to correlate the values of different vibration waves to dynamic modulus of elasticity, mass density, Poisson's ratio, and dynamic shear modulus. These equations, however, were developed for homogenous, isotropic, linear-elastic material. Concrete is none of these. The main problem of the method is that small defects

of the concrete can be interpreted as damage. However, if thick enough sections of concrete are compared to another, then satisfactory results can be obtained (Thomas 1995).

The ultrasound tomography method was used to monitor the repairs of the Coniston main dam in Ontario, Canada. The dam previously had some ASR problems, which had been repaired by replacement of the damaged concrete, placement of moisture membranes, reinforcing with concrete buttresses, and replacement of the concrete deck on the structure. Initial readings were then taken, and most values obtained were in the range between 3,600 m/s and 4,600 m/s. The repairs were monitored with the ultrasound tomography, and all have remained in good condition (Read and Thomas 1995).

2.5.3.3 Mechanical Gages

Mechanical gages have been used in quite a few different projects to measure the effects of ASR. These gages are good because they give a physical reading of the dimension changes. There are several different methods of using these gages. The main concern in the use of these gages is whether the deformations measured are a good representation of what is happening to the structure because of ASR.

A structure that is extensively damaged by ASR will show cracking on the exposed concrete faces. A project by the Societe des Autoroutes du Nord et de l'Est de la France (SANEF) is monitoring the ASR remediation steps taken for seven bridges on highway A26 in the northeastern part of France. The steps taken to repair the bridge were to add a waterproofing membrane and a thin cement-polymer coating to the damaged areas of the bridge. To determine how well these remediation steps were responding, the researchers set up instrumentation to monitor the existing exterior cracks in the structure. Two different types of sensors were used to measure the cracks. One sensor was used to monitor single cracks, while another sensor was used to measure the overall length change of members within the structure. Some thermocouples were also used in the system to remove the effects of temperature change. SANEF claims that there was no significant increase in the crack widths or the beam dimensions. Therefore, SANEF has concluded that its remediation methods were successful (Baillemont et al. 2000).



Figure 9 - Different Types of Mechanical Gages Used in the SANEF Project (Baillemont et al. 2000).

In 1988, there were eight cases of severe ASR damage found in prestressed bridges in Australia. A study then began to monitor the cracking of the structures after almost 10 years of service life in order to determine whether the deformations increased. Four of these bridges were monitored with Huggenberger gage points. These points are glued to the exterior of the bridges in several orientations, and their displacement is measured periodically with a reading device. The study used a gage length of 250 mm and corrected all the measurements to a temperature of 25 °C. If Huggenberger gages are attached correctly, they will move as the structure deforms. Since these bridges were more than 10 years old, the only expansion measured should have been due to either temperature changes or ASR. The study found that two of the bridges that used reactive river gravel were still very active in ASR expansion. A note should be made that an unfortunate design detail in the prestressed girders led to a larger amount of internal humidity. This might affect the amount of total expansion seen by this type of bridge when compared to others (Carse and Dux 1990).



Figure 10 - The Severity of Cracking Caused by ASR on the Susan River Bridge (Carse and Dux 1990)

The Beauharnois Power Plant was built in 1928. The dam was instrumented in 1979 and 1991 while some remediation work was completed on the dam to fix some deformation problems at the junction of the dam and a water intake structure. The method used to instrument the dam was to place vibrating wire gages in a 3-D pattern inside of cores that were taken out of the dam to monitor the concrete strengths. A total of forty-eight cores were instrumented at various places in the dam. The principle stresses were monitored in the dam to see how they changed over time. No results were given regarding the efficiency of the repairs or the expansion resulting from ASR (Gocevski 1995).

2.5.3.4 Visual Inspection

Another way to monitor ASR is by visual inspection. This method has been used in a project on sections of State Route 352 in Albuquerque, New Mexico. Several different mixes were used to try to control the expansion of ASR caused by the reactive coarse and fine aggregates. The project was started in June 1992 and inspected at regular intervals. A reference to the project is made in the SHRP-C-343 report. At the writing of this report, no other published references have been made; however, Dr. Mike Thomas has been contracted to finish the project.

Chapter 3 – Delayed Ettringite Formation

3.1 Mechanisms

Delayed ettringite formation, DEF, is defined as the formation of ettringite and associated expansion observed after heat curing at temperatures that are too high. A large number of experiments have shown that pastes, mortars, and concrete exposed during the hardening process to overly high temperatures exhibit expansion and cracking when subsequently exposed to moist conditions. These observations may be explained as follows.

Comprehensive laboratory studies have indicated that ettringite (AFt) in hydrated Portland cement products can be fully or partially destroyed when the materials are cured at a temperature hotter than 158 °F for a few hours. That is why it is generally agreed that during setting at temperatures hotter than 158 °F any ettringite (AFt) formed upon hydration will become thermodynamically unstable and will decompose to hydrated calcium monosulphoaluminate (AF_m), releasing sulfates to the pore solution. Moreover, at this high temperature, the sulfates released by the cement do not react completely with the tricalcium aluminate (C_3A) , and therefore they become available to the pore solution (Yang et al. 1996).

Kalousek (1941), Odler (1980), and Fu (1996) postulate that these available sulfates are trapped by physical adsorption on the surfaces of the calcium silicate hydrate (C-S-H gel), whose hydration has been accelerated as a result of heat curing (Divet et al. 1998).

Many studies have indicated that some mortars cured at temperatures around 176 °F to 194 °F can expand during subsequent storage in water. In addition, it has been noted that during water storage, ettringite, absent after the heat curing process, forms over time. The explanation for this comes from the fact that, during the storage or service at ambient temperature and moisture, the C-S-H gel will start slowly releasing the trapped sulfates and making them available to the pore solution again (Scrivener et al. 1999).

Sulfate ions, after release from the C-S-H gel, will diffuse into the nearest microcrack and react with the Al-bearing materials (C_3A most likely) in the crack to form ettringite, which will expand and crack the concrete. At this stage, there exist uncertainties regarding the exact mechanism by which ettringite expands. Many theories have been developed about this issue,

although there are two schools of thought that seem to be the most representative: Cohen's Crystal Growth Theory, and Mehta's Swelling Theory (Fu 1996).

Cohen proposes that expansion is the result of the growth of ettringite crystals forming on the surfaces of the Al-bearing particles and in solution. The growth of these crystals causes expansion through generation of crystallization pressure in regions of limited space (mainly crack tips) (Fu 1996).

Mehta postulates that expansion is the result of the swelling of ettringite colloidal particles. These gel-like particles have a large specific surface area analogous to the C-S-H gel and absorb water, resulting in overall expansion. The formation of this swelling gel occurs by a through solution mechanism due to the reaction between the expansive particles and the surrounding solution (Fu 1996).

At this point, it is important to identify some crucial parameters that affect DEF. One of the most important factors for ettringite formation and expansion is porosity, especially microcracking. Microcracking is essential for DEF-related damage, and it may be caused during manufacturing or because of ASR, freezing and thawing, or other causes including those related to steam curing. In concrete, microcracks are most likely to be found in the aggregate-paste interface (or *transition zone*) and at the steel-paste interface (Fu 1996).

These microcracks appear to be nucleation sites where secondary ettringite can grow and produce damage. Most petrographic examinations have shown that if one wishes to find ettringite in a deteriorated concrete, the first place one should look is the transition zone. Following this reasoning, it is obvious that DEF is not such a big problem in pastes, although this does not mean that it is not possible.

Another very important parameter for DEF is cement composition. Heinz and Ludwig postulate that the composition of cement is very important in determining whether expansions will occur. In particular, the main influence derives from the SO_3/Al_2O_3 ratio of the cement. However, the sulfate proportion appears to have a higher weight in determining behavior; therefore, Heinz and Ludwig suggest that the ratio $(SO_3)^2/Al_2O_3$ is a parameter that shows the strongest correlation to subsequent effects of secondary ettringite formation. They suggest a "safe ratio" of 2.0 – cements with a smaller ratio than 2.0 are not susceptible to secondary ettringite attack. Prior to this research, a SO_3/Al_2O ratio of 0.67 had been proposed as the limit (Day 1992).

Similarly, it is also known that alkalis accelerate the hydration process; therefore, the presence of alkalis accelerates the formation of ettringite.

In conclusion, the following factors are considered essential for DEF-related damage:

- Temperatures exceeding 158 °F
- Microcracks caused during manufacturing or because of ASR or other causes, including those related to steam curing
- Exposure to wetting-drying cycles
- Late sulfate release from the cement clinker or other sources.
- Migration of reactant ions (SO₄²⁻, Al³⁺, Ca²⁺) through the pore aqueous solution of concrete exposed to water or saturated air
- Ettringite deposits inside existing microcracks and subsequent crack opening by ettringite swelling or crystal growth (Collepardi 1999)

3.2 Test Methods

There are no standard ASTM or AASHTO test methods to assess the potential for DEF in laboratory samples. Nonetheless, efforts have been made by researchers to develop test methods capable of assessing the effect of DEF on laboratory samples. One of the first tests to be extensively used was the Duggan test. As originally devised, the Duggan test involves the following procedure:

- Concrete cores (a minimum of five) are taken from a structure or from laboratory-cast prisms or cylinders. The cores are 25 mm in diameter and at least 65 mm long and are to be cut to 50 mm lengths. The ends are ground smooth and parallel.
- Initial length measurements are taken with a comparator just before the start of heat treatment. In later tests by Duggan and Scott and in tests by Gillott this measurement was used as the zero point from which other strain readings were taken.
- Cores are soaked for 3 days in distilled water at 70 °F in a closed container.
- Cores are then placed in a dry-air oven at 180 °F for one day.
- Cores are removed from the oven, allowed to cool for 1 hour, and then placed back in distilled water for 1 day.
- A second 1-day heating, 1-day soaking cycle is performed.

- A third cycle is performed, but this time the cores are left in the oven at 180 °F for 3 days.
- At the end of the third heating cycle, the cores are removed from the oven and allowed to cool for 1 hour, and then length measurements are taken relative to a steel standard. In the early tests by Duggan and Scott this measurement was used as the zero point for further strain readings.
- Cores are placed in distilled water at 70 °F.
- Length measurements are taken relative to the steel standard at intervals of 3 to 5 days (Day 1992).

The test was initially thought to be an accelerated means by which the potential alkaliaggregate reactivity of various cement/aggregate combinations could be assessed. However, Gillott, through careful experimentation, was able to determine that DEF was the major cause of expansion of cements and concretes exposed to the Duggan test (Day 1992).

This test has raised several concerns among researchers about the adequacy of the heating regime. In fact, Lawrence pointed out that the heating cycle proposed by Duggan does not represent practical heating regimes; furthermore, the heating program is very severe and may result in the rejection of cements that may perform adequately in practice. For these reasons, the Duggan test has been progressively abandoned and new, improved tests like the Fu Method and the Kelham Method have been developed. Figures 11 and 12 show the procedures for both methods (Day 1992).



Figure 11 - Fu Method to Assess DEF (Thomas, Personal Communication, 2000 after Fu 1996)



Figure 12 - Kelham Method to Assess DEF (Thomas, Personal Communication, 2000 after Fu 1996)

3.3 Mitigation Methods

The published data indicates a critical early age temperature of approximately 158 $^{\circ}$ F, below which no expansions are observed (Heinz, Kelham). With increasing temperatures, cement composition starts to be an important factor on mortar expansions. At a higher temperature of 194 $^{\circ}$ F, factors such as cement fineness, levels of alkali, C₃A, C₃S, MgO, and SO₃ become very important (Fu 1996).

Similarly, Kelham concluded that the susceptibility of a cement to expansion attributed to DEF increased with the following:

- cement fineness
- equivalent Na₂O
- C₃A content
- C₃S content
- MgO
- SO₃

Obviously, a perfect mitigation technique would involve the use of cement with limited amounts of the above components. However, in some cases acceptable cements may not be available, or there may be insufficient time available for testing.

Preventive measures to reduce or eliminate the deleterious expansion of a cement product from DEF are desirable. Fu analyzed the effect of some mineral additives on the expansion of mortars containing a DEF-suspect cement. The mineral additives included ground granulated blast furnace slag (GGBFS), Class F fly ash, Class C fly ash, silica fume, and natural zeolite. Since microcracking plays an important role in the expansion from DEF, natural wollastonite was also used to control microcracking. The results of these tests yielded the following conclusions:

- Class F fly ash and GGBFS were the most effective mineral additives for eliminating expansion in Portland cement mortars resulting from DEF.
- Silica fume was also good for this purpose; however, the addition of silica fume was limited to 15 percent by mass of cement in the test because of its adverse effect on workability.

- Natural zeolite and Class C fly ash were relatively less effective in reducing the expansion than GGBFS, Class F fly ash, and silica fume.
- The expansion of the cement mortar due to DEF was greatly decreased by using wollastonite microfiber (Fu 1996).

Similarly, Heinz also showed that mortars containing blends of fly ash (30 or 40% percent) or GGBFS (30 or 50 percent) with cements that gave large expansions when used alone did not expand after curing at 194 $^{\circ}$ F.

Collepardi recognized the fact that an important factor in preventing DEF-induced deterioration is related to cement composition. Clinker with lower sulfate content can significantly reduce the risk of DEF-induced damage. Moreover, there is evidence that the risk of DEF-related damage significantly increases with high strength (high C₃S and C₃A) Portland cements, especially Type III cements (Collepardi 1999).

Parallel to this, Kelham analyzed hundreds of different types of cements and reached the conclusion that Type III cements have an increased risk of DEF compared with other cement types. He concluded that a vastly greater percentage of Type III cements being produced today are more susceptible to DEF at 194 °F than those produced in the 1950s, which is one explanation for the increased incidence of DEF being observed in the U.S. (McDonald 1998).

Collepardi pointed out that pozzolanic material, including silica fume at a dosage level as low as 10 percent by cement mass, can be advantageous in reducing the risk of DEF-induced damage through the pore-size refinement effect with consequent reduced diffusion rate of ions, sulfate ions in particular, through the pore solution (Collepardi 1999).

3.4 Specifications

3.4.1 Agency Test Specifications

Currently, none of the agencies studied recommend or specify any test methods to determine a cement's susceptibility to DEF. The Kelham and Fu methods are currently the most popular test methods used today, but they have not been accepted by AASHTO or ASTM and are still undergoing major testing to evaluate their effectiveness and repeatability.

3.4.2 Specified Mitigation Methods

Many international agencies have set maximum temperature limits on either the concrete or the steam used during accelerated curing to help prevent the development of DEF, as shown in Table 10. It is believed by many authors noted in this paper that keeping the concrete curing temperature below a certain threshold (between 140 °F and 160 °F) is all that is required for eliminating the possibility of DEF.

Country	Agency/Specification	Max. Temperature	Temp. applies to:	Other Comments
Canada	CSA/A23.4-94	158 °F	Concrete	
Denmark	DS482 (draft as of Jan. 1999)	158 °F	Concrete	
England	Manual of Contract Documents for Highway Works	158 °F	Concrete	Concrete shall be left for 4 hours without additional heat
Germany	Committee for Reinforced Concrete	140 °F	Concrete	Initial set required before application of heat
South Africa	SABS/0100-2:1992	140 °F	Steam	Ambient temperature limits also apply
Spain	UNE/83-301-91	158 °F	Not Specified	

Table 10 - International Accelerated Curing Specifications

Only two of the agencies studied in the U.S. specify maximum curing temperatures: the Prestressed Concrete Institute (PCI) and the American Water Works Association (AWWA), which have set temperature limits at 190 °F and 150 °F, respectively.

TxDOT has specified alternate methods of preventing DEF, in lieu of imposing a limit on the maximum concrete temperature. Special provision Item 524 gives the following guidelines for preventing DEF (TxDOT Item 524, 1995):

- Set maximum Blaine or Wagner limits on fineness values of its Type III cements.
- Limit the SO₃ content of the cements to no more than 0.5% above the optimum level.
- Demonstrate with ASTM C 265 that the CaSO₄ in the hydrated mortar does not exceed 0.5 g/liter.

The first guideline in Item 524 attempts to limit concrete curing temperatures by setting maximum cement fineness levels, while the second and third guidelines attempt to limit the sulfates available later, which are necessary in the formation of DEF.

3.5 Field Studies

DEF is a phenomenon that has not been greatly studied by field investigations. There are several reasons why this has not typically been done. One reason is that it is very difficult to distinguish a difference between DEF and ASR. Another reason is that the temperature history of the concrete is an important indicator of DEF but it is rarely known. TxDOT has elected to use the term Premature Concrete Deterioration (PCD) to describe damage caused by ASR, DEF, or combinations of the two.

3.5.1 DEF in Texas

In 1995, fifty-six of sixty-nine precast concrete box girders fabricated in San Marcos, Texas were damaged by ASR, DEF, or a combination of the two. This finding led TxDOT to survey the existing structures in Texas. They found sixteen other structures to have similar durability problems. Petrographic studies were conducted on all of the damaged structures and the damaged concrete box girders. The results show that the damage was caused by a combination of DEF and ASR. The study specifically found large amounts of ettringite in the cement paste and in the cracks in the precast concrete box girders (Lawrence et al. 1999).



Figure 13 - Premature Cracking in the End Region of a 6-year-old Box Beam due to DEF (Lawrence et al. 1999).

3.5.2 High Mast Illumination Pole Foundation on US 59

One of the field studies conducted by TxDOT found that four cast-in-place lightpole foundations were found to have extensive cracking from DEF. This cracking was so bad that the lightpoles had to be removed (Lawrence et al. 1999).



Figure 14 - High Mast Illumination Foundation with Premature Cracking from DEF (Lawrence et al. 1999)

3.5.3 Cast-In-Place Bent Caps and Columns on IH 37

Two adjacent bridge piers that were cast in place were found to have some cracking from DEF and ASR. One surprising issue with this bent cap is that it contained 3 to 5 percent air entrainment. The cracking is occurring in the areas of least restraint and highest exposure to the environment (Lawrence et al. 1999).



Figure 15 - A Cast-in-place Bent Cap with Premature Cracking from DEF (Lawrence et al. 1999)

3.5.4 Prestressed Concrete Type IV Beam on IH 45

After only 6 years of service life, more than 30 percent of the beams on this bridge were showing signs of damage from PCD. The cracks in this structure run longitudinally along the beam (in a direction perpendicular to the area of least restraint). At the ends of the beams there seemed to be more cracking; this was attributed to the fact that this area was exposed to a larger amount of moisture from the bridge joints (Lawrence et al. 1999).



Figure 16 - Premature Cracking in Prestressed I-shaped Beams from DEF. The Cracks Shown are Typical Crack Patterns from DEF (Lawrence et al. 1999)

Chapter 4 – Synergistic Effects between ASR and DEF

Numerous field investigations have indicated a possible relationship between ASR and DEF. In some of these cases, it has been concluded that ASR is the primary cause of cracking and deterioration, and that the subsequent precipitation of ettringite into the cracks is a secondary effect that may or may not cause further damage (Thomas 1998).

Other researchers have suggested that the chemical changes resulting from ASR may promote the formation of ettringite. In contrast, it has been postulated that the formation of ettringite leads to increased pore solution alkalinity, thereby enhancing the chances of ASR. Some people believe that DEF is commonly misdiagnosed as ASR because of the similar appearance of alkali-silica gel and amorphous ettringite when examined by optical microscopy. On the other hand, Shayan and Quick demonstrated that ASR was a major cause of deterioration of railway ties in Finland that had previously been determined to be suffering from DEF and freeze-thaw action (Thomas 1998).

The subordinate role of DEF was confirmed in a series of laboratory tests conducted on mortar bars and concretes with different aggregates. Expansion and cracking were not observed in heat-cured (up to 176 °F) specimens without reactive aggregate even when the gypsum content of the mix was raised. The addition of gypsum did increase the expansion of concrete containing reactive aggregate when heat cured at 176 °F but not when cured at 104 °F. The authors concluded that DEF only contributes to expansion in heat-cured concrete containing reactive aggregates (Thomas 1998).

Similar results have been reported by Diamond and Ong. Heat-cured (10 hours at 203 °F) mortars containing limestone sand did not expand significantly during subsequent storage at 73 °F and 100 percent relative humidity. However, mortars containing reactive silica (Beltane opal or cristobalite) showed considerable expansion and cracking, which, during the early stages (up to 28 days), was accompanied by the formation of alkali-silica gel. However, long-term expansion continued with no gel being produced, and the authors concluded that the later expansion may be a result of ettringite formation. The role of DEF was further confirmed by the observation that significantly increased amounts of ettringite (approximately 50 percent or more) were formed in mortars containing reactive aggregate compared with the mortar with non-reactive limestone (Thomas 1998).

The results of these experimental studies are consistent with the field observations of Oberholster et al. (1992), who determined that ASR was a prerequisite for damaging ettringite formation in concrete railway ties, and with the hypothesis of Fu and co-workers regarding the role of cracking as a precursor to DEF. However, there may also exist a chemical relationship between ASR and DEF, as suggested by Brown and Bothe. They studied the hydration of relatively pure phases of C₃S, C₃A, and gypsum in potassium hydroxide solutions of varying concentrations (0.0 to 2.0 KOH) and at various temperatures (77 °F to 176 °F). Their results show that ettringite formation is inhibited by alkali, especially in the range 0.5 to 1.0 KOH. The authors contend that the process of ASR may, by reducing the pore solution alkalinity, promote the formation of ettringite. Such an effect may be expected to occur where local concentrations of alkali are particularly low, such as at the interface between the cement paste and reactive silica. Formation of ettringite in the interfacial zone may also be promoted by the increased availability of calcium hydroxide at such locations (Thomas 1998).

It has also been proposed that ASR may be promoted by the formation of ettringite. Pettifer and Nixon observed ettringite in association with alkali-silica gel in a number of field concretes. The reaction of sulphate with calcium aluminates also consumes calcium from calcium hydroxide, thereby releasing more hydroxyl ions to the pore solution. The increased alkali hydroxide concentration increases the chances of ASR (Thomas 1998).

Hydrated calcium sulphoaluminates may not be stable in alkali-silicate solutions. In the vicinity of reacting aggregate particles, amorphous or semi-crystalline products containing calcium, silica, alkali, and some alumina may form, but the product does not incorporate sulphate. Thus, sulphate ions diffuse to areas low in silica where, if calcium and alumina are available, ettringite is precipitated. In this manner, ASR facilitates secondary ettringite formation (Thomas 1998).

Chapter 5 – Conclusions and Recommendations

With the recently discovered durability problems associated with ASR and DEF in Texas, finding a solution to preventing further problems in new structures is imperative. Much more needs to be understood about the deterioration of structures related to ASR and DEF so that design lives may be reached without early repairs and extensive costs.

Researchers must understand the chemistry and reactions associated with both ASR and DEF to provide and specify adequate mitigation methods. The basic chemical reactions and materials necessary for ASR to develop are known, but the reasons some ASR gels expand and others do not are still not understood.

Much less is known about DEF, as this method of deterioration is a relatively new problem to the concrete industry. The mechanism of DEF is still debated, but we believe that high temperature curing is a required ingredient. This has been mainly attributed to steam curing, but in a region that experiences high ambient temperatures, such as Texas, steam may not be required. Concrete elements may also experience high curing temperatures due to mixtures containing high cement contents, cements with high Blaine values, and/or the casting of large elements. Specifying maximum curing temperatures for concrete may need to be considered, as has been done in many agencies throughout the world.

Alternatively, the use of selected pozzolans and slags may be specified if imposing maximum temperature limits is not feasible. More research is needed to determine the specific type and amount of mineral admixtures needed to avoid DEF.

Several test methods have been developed for ASR, but some have been viewed as too severe and are mainly used to screen out nonreactive aggregates. ASTM C 1260 and ASTM C 1293 are two of the most common test methods to screen aggregates, but each has its drawbacks. These methods need to be adapted to improve their accuracy in determining reactive or potentially reactive aggregates.

Currently, no approved test methods exist for DEF. Extensive lab and field testing is needed to determine the adequacy of each of the methods previously discussed. These methods have shown promising results.

Field testing of lab mixtures and comparing the lab expansion results to similar mixtures in the field are necessary components of the development of adequate test methods. The adequacy of these test methods is determined by whether they accurately predict the field performance of the concrete. Exposure sites and the instrumentation of actual structures are excellent ways of determining the adequacy of any test.

ASR and DEF are significant durability problems facing the concrete industry in Texas and all over the world, but these are not the only durability issues. Corrosion, sulfate attack, and frost action, along with ASR and DEF, are all issues that can be mitigated using adequate amounts of pozzolans and/or slag and suitable chemical admixtures.

One of the drawbacks to using some of these materials is the accompanying lower early strength, which causes delays in removing forms for cast-in-place structures or releasing the strands in a prestressing bed. Mitigation methods that use these materials and that can be used to protect against any of the durability issues mentioned need to be developed in proportions or with the combination of other materials (such as silica fume in a ternary blend), which allow for adequate early strength gain. Using these materials in concrete not only prevents the need for their disposal, but also reduces the amount of cement needed, which greatly reduces CO_2 production.

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