Alkali-Silica Reactivity

One of the contracts carried out under the concrete subprogram of SHRP addressed alkali-silica reactivity (ASR) of concrete and resulted in five products and four reports. This technical brief provides excerpts from the SHRP reports on the subject. SHRP-C/UWP-92-601 provides an annotated bibliography of literature from 1939-1991 on alkali aggregate reactions in concrete, of which ASR is one specific type. Another report (SHRP-C-315) is a handbook for the identification of ASR in highway structures and relates to two products for ASR detection (SHRP products 2010 and 2013). An overview of ASR research is provided in SHRP-C-342, and investigations into ASR with an emphasis on the practical needs of the concrete engineer are reported in SHRP-C-343. The latter report relates to three SHRP products (2009, 2011, 2017) for screening reactive aggregates, mitigating ASR in existing structures, and ASR-safe concrete mix designs.

BACKGROUND

Alkali-silica reactivity in Portland cement concrete occurs when alkalis in the cement react with silicates in the aggregate or additives. The reaction results in the formation of a gel which flows into voids within the concrete or accumulates on the aggregate. When moisture permeates the affected concrete the gel expands which causes a characteristic crack pattern to develop in the structure. The cracks can weaken or degrade the condition of the structure to the extent that freeze-thaw action or traffic loading can cause premature failure.

The eventual manifestations of ASR in a particular concrete depend on hydroxyl ion concentration in the pore solution, permeability of the cement paste (water-cement ratio), composition and permeability of the reactive aggregate particle, moisture availability and restraint to expansion. Temperature, restraint and external sources of alkali are some of the factors which affect the rate and extent to which the reaction proceeds.

TECHNICAL HIGHLIGHTS

A review of research on reaction chemistry, the physical nature of swellings, mechanical effects of ASR, and environmental effects on ASR in concrete can be summarized in the following major findings:

1. The reaction chemistry of the swelling and dissolution of disordered silica in alkali hydroxide solutions in the absence of calcium hydroxide is reasonably well understood. When calcium hydroxide is present, dissolved silica reacts to form calcium silicate hydrate in the ASR gel.

2. Portland cement hydration releases sodium and potassium ions into pore solutions so that concentrations stabilize after several weeks as es-
sentially alkali hydroxide of 0.7 mol/L per percent equivalent Na₂O% in the cement, at 0.5 water/cement ratio. A simple equation was developed for hydroxyl ion concentrations that also includes w/c, and variations of the amounts of alkali retention by the cement gel. It then became possible to develop equations to estimate reductions of hydroxyl ion concentrations resulting from dilution and pozzolanic reactions when cements are replaced by pozzolanic fly ashes in order to control ASR. If low-alkali pozzolanic fly ashes are sufficiently reactive, they can reduce hydroxyl ion concentrations substantially when used with high-alkali cements.

3. It is possible to explain the variable compositions of simple calcium-alkali-silicate-hydrate gels, and those of complex ASR gels in concrete, as relatively simple two-phase composites. These composites include precipitated calcium-alkali-silicate-hydrate of compositions near 0.16 Na₂O·1.4CaO·SiO₂·XH₂O in a swellable sol/gel matrix with a molar Na₂O/SiO₂ ratio of about 0.19.

4. Consideration of the negative volume changes during dissolution of reactive silicas shows that increasing pressure does not stop the reaction, but tends to force it to completion. Hence the swelling pressure of the gel formed tends to accelerate the reaction.

5. Cracking of mortars or concretes may be initiated by swelling of solid aggregate particles before copious production of gel; large expansions of cracks caused by swelling of gel occur progressively.

6. Swelling pressures at reaction sites or in gel cracks are balanced by tensile stresses in the nearby concrete, and by any external restraint. These pressures are relieved when cracking occurs, or by gel flow and creep.

7. Expansions are reduced by external restraint which increases stress at reaction sites. This stress can increase creep or paste in the matrix, increase the rate of dissolution of the silica, reduce osmotic swelling of gel and cause gel to creep or flow through pores and/or microcracks.

8. The drying and growth of shrinkage cracks in exposed areas complicates these processes. Disparities in reaction rates caused by moisture content differences also bring further complications.

9. While generally supported by recent research, Powers and Steinour’s model for ASR has been challenged with respect to the effects of pozzolans and chloride salts. Some pozzolans (calcined kaolin, condensed silica fume) do control ASR by rapid reduction of the pH of pore solutions, however, other materials (fly ashes and slags) control ASR without much reduction or even while increasing the pH of pore solutions. These materials appear to facilitate the reaction of the aggregate so that it softens and dissolves without excessive swelling pressures.

10. Chloride salts may aggravate ASR expansion whether added to mixing water or by penetrating mortars after hardening. Both sodium chloride and calcium chloride accelerate reactions with reactive silica at elevated temperatures. The reaction with NaCl causes an increase of hydroxyl ion concentration. Pozzolans reduce these expansions but may not prevent damage to specimens exposed to large amounts of salts. Under such accelerated test conditions the formation of calcium silicate hydrate when calcium hydroxide is present may prevent the escape of dissolved silica from the reaction zone. When calcium hydroxide is leached in hot calcium chloride solutions these expansions are prevented. However, the relationship between such accelerated tests and ordinary exposures is not well understood.

Testing For ASR Expansion

SHRP report C-342 identified a number of significant gaps with respect to ASR knowledge. In particular, a rapid and reliable test method to identify potentially deleteriously reactive aggregates is most urgently needed. Evidence gathered by questionnaires found that nearly all states depend upon
ASTM C 289 (Potential Reactivity of Aggregates - chemical method) or ASTM C 227 (Potential Alkali Reactivity of Cement-Aggregate Combinations - mortar bar method) tests to carry out their ASR test procedures. While these early test procedures have been fairly successful in identifying materials that react rapidly with high alkali cements, they fail to identify slowly reactive aggregates or those which react with low alkali cements.

Moreover, these tests are often performed in conjunction with other tests, notably ASTM C 295 (Petrographic Examination of Aggregates for Concrete), to determine potential for expansive ASR in highway structures. This latter test is tedious and relies heavily on the capabilities of the petrographer. Service record is a fourth method recommended for assessing ASR potential and although it can prove to be the most accurate, it often fails since essential background information is missing. In light of the current realities of testing, there is a serious need for a single rapid and reliable test procedure to identify potential for expansive ASR of cement-aggregate combinations.

A method developed at the National Building Research Institute (NBRI) in South Africa, the ‘rapid immersion test method’, has shown promise. This test consists of calculating expansions of mortar bars, made in general accordance with C 227 but stored in 1N NaOH for 14 days after one day of storage in water, both at approximately 176°F (80°C). A major difference from C 227 is that mortar bars are made using a fixed water-cement ratio of 0.50 instead of gauging water content according to workability. This difference is necessary, because in the test, ASR is dependent on diffusion of alkali solution into the mortar bar, so permeability must be held as constant as possible. Furthermore, this method appeared to be sufficiently adaptable to resolve the important question of determining safe cement alkali levels and quantity of pozzolan required to control expansions due to ASR.

As developed by NBRI, a 1N NaOH solution was initially used for immersion of test specimens. Later, NaOH was changed to correspond to different specific cement alkali levels and water-cement ratios. The objective was to determine cement alkali levels below which excessive expansion due to ASR does not develop at different water-cement ratios. A linear regression equation relating solution normality to equivalent Na₂O of the cement at given water-cement ratio was developed.

With testing, 14-day expansions decreased progressively as concentration (normality) decreased. It was also apparent that a different test criterion would be necessary for the different solutions. Accordingly, innocuous as well as deleterious aggregates were tested in different solutions and a curve developed that related safe expansions levels to solution concentration and therefore to cement alkali level.

Furthermore, this test could evaluate the effectiveness of pozzolans in preventing excessive expansions due to ASR. This research suggested that this single rapid procedure with appropriate adjustments for alkali levels could be used to determine not only whether an aggregate is potentially deleteriously reactive, but also safe cement alkali levels and pozzolan requirements for preventing deleterious ASR.

Mitigating ASR In Existing Concrete

In order to prolong the service life of highway structures with ASR-related distress, two approaches have developed and these are 1) interference in the mechanism of the reaction, and 2) treatment of the symptoms of the reaction. Mechanistic interference can be achieved by treatment with lithium salts, by drying, and with sealants. Symptoms, on the other hand, are treated with restraint and crack filling.

Interference In The Mechanism Of The ASR Reaction

1. Treatment with lithium salts
The addition of lithium salts to fresh concrete can prevent abnormal expansion due to ASR. Furthermore, it appears that treatment of existing concrete with lithium salts, specifically LiOH, may arrest development of expansive ASR. Investigations within the framework of SHRP-C-343 were made into the chemical interactions between lithium and other components of the cement-aggregate system.
Lithium salts (lithium fluoride LiF and lithium carbonate \( \text{Li}_2\text{CO}_3 \)) added as part of the mixing water of cement quickly convert to lithium hydroxide, \( \text{LiOH} \), in the pore solution. The dosage added of \( \text{LiOH} \) was equivalent to that of 1% \( \text{Na}_2\text{O} \) in the cement rather than 1% \( \text{LiOH} \) by weight of cement. \( \text{LiOH} \) itself produces an ASR-type reaction product which appears to be non-expansive. In the presence of sodium and potassium hydroxide in pore solutions, ASR products are formed which incorporate lithium as well as other alkali cations. The higher the lithium dosage, the greater the proportion incorporated into the ASR gel formed.

Depending on the aggregate, a molar ratio of sodium to lithium of at least 1.0 to 0.5 to 1.0 to 0.60 is required to prevent expansive ASR. When 1% treatment levels of \( \text{Li}_2\text{CO}_3 \) or \( \text{LiF} \) are added to the mixing water, the added \( \text{Li}_2\text{CO}_3 \) is either directly dissolved or dissolved as the result of spontaneous precipitation of \( \text{CaCO}_3 \) when cement is added. If \( \text{LiF} \) is added, a small proportion is directly dissolved while most of the remainder is indirectly dissolved as a result of spontaneous precipitation of \( \text{CaF}_2 \). In either case, most of the \( \text{Li}^+ \) ions end up in solution partnered by \( \text{OH}^- \) ions, and result in substantial increases in \( \text{OH}^- \) concentrations. This increased \( \text{OH}^- \) ion concentration also causes a substantially higher pH, therefore increasing potential for a reaction with ASR-susceptible aggregates. The beneficial effect of this treatment is thus dependent on the specific behaviour of dissolved \( \text{LiOH} \) in solution as opposed to the behaviour of dissolved \( \text{NaOH} \) or \( \text{KOH} \) on ASR.

To assess the relative amount of ASR gel formed with \( \text{LiOH} \) compared to what would be formed with \( \text{NaOH} \) or \( \text{KOH} \), parallel experiments were conducted with reactive mortars to which \( \text{NaOH} \) or \( \text{KOH} \) were added to mixing water in the same 1% \( \text{Na}_2\text{O} \) equivalent dosage level as \( \text{LiOH} \). It was concluded that while \( \text{LiOH} \) reacts to form a lithium-bearing ASR gel, the extent of reaction and the amount of gel is considerably less than would take place with either \( \text{KOH} \) or \( \text{NaOH} \) under the same conditions. Moreover, no significant expansion was found for the lithium-bearing mortars, despite the previous evidence that ASR reaction takes place within them. The mortar bars showed no cracks or surface gel deposits, in contrast to the extensive cracking and surface gel deposits observed with the corresponding sodium- and potassium-bearing mortar bars.

The effects of \( \text{LiOH} \) on expansion due to ASR showed several meaningful relationships. Mortar bars were made with aggregate AL, containing highly reactive volcanics, and aggregate PR, consisting of slowly reactive granite gneiss. Both aggregates are highly reactive in 1N \( \text{NaOH} \) solution with no \( \text{LiOH} \) addition. However, virtually no expansion developed in 1N \( \text{LiOH} \) solution to the age of 28 days, thus demonstrating that even at high \( \text{OH}^- \) concentration, any ASR product that may form is non-expansive. Furthermore, increasing \( \text{LiOH} \) concentrations in \( \text{NaOH} \) solutions progressively decreased expansions due to ASR. It is evident that lithium hydroxide can effectively mitigate expansive ASR when used at required dosages which vary with cement alkali level, water-cement ratio and source of reactive aggregate.

Numerous highway structures exist where fly ash was incorporated into the concrete structure without regard for possible ASR. Since cement fly-ash hydration products complex sodium and potassium, it was felt they would have the same effect on lithium. In doing so, cement-fly ash would reduce lithium effectiveness while simultaneously intensifying expansive ASR due to greater alkali concentrations in pore solutions.

However, research data indicated that both fly ash and lithium ion, at the rate of 1.0%, 1.5% or 2.0% by mass of cement, were effective in reducing expansion due to ASR. The fly ash mixture developed minor expansion after four months, while the lithium-bearing structure showed no such tendency at the later ages. Immersions in \( \text{NaCl} \) solutions were conducted to simulate \( \text{NaCl} \) deicer salts applications. In these conditions, specimens with fly ash fared better than specimens with no fly ash, but expansion levels still reached 0.390% at nine months. In contrast, specimens with lithium hydroxide used as an admixture in mortars prevented abnormal expansions associated with ASR, even while immersed in \( \text{NaCl} \) and in the presence of fly ash. Thus, lithium ions in these mixtures appeared not to be complexed by cement fly-ash hydration products.
2. Drying
Drying is effective in preventing expansion due to ASR, not only by removing moisture otherwise available for absorption by ASR gels but also by initiating alkali fixation by cement hydration products. Alkali fixation appears to persist for prolonged periods of time but the alkali is slowly released, even when the concrete is rewetted. Drying may be a feasible approach to mitigating expansive ASR in some concrete members, such as bridge columns, but repeat drying likely would be necessary.

3. Sealants
It has been reported in published literature that sealants limit ingress of moisture into concrete and thereby minimize swelling of ASR gel. Field evaluations on sealants such as silane and siloxane indicate that they have little effect on the internal RH of concrete in outdoor exposures. In particular, in highway pavement they would have little beneficial effect due to availability of sub-base moisture to the pavement slab.

Treatment Of The Symptoms Of The ASR Reaction

1. Restraint
A concrete structure affected by expansive ASR may eventually develop cracking which can progress and increase in severity until the structure becomes unserviceable. A volume increase is produced in concrete as ASR develops. If the volume increase were restrained, resultant internal compressive stresses could prevent the onset of severe cracking and thus extend the useful life of a structure.

Triaxial restraint in the range of 1.73 - 2.07 MPa can prevent expansion due to ASR. At this restraint level, expansion due to ASR was balanced by creep. This approach would be feasible for bridge columns, piers, etc.

Major uniaxial restraint, such as could exist in pavement or other structures, can prevent ASR-induced expansion in the direction of restraint. However, cracking may be exacerbated parallel to this direction. Intermediate restraint levels, on the order of several MPa may extend the service life of a pavement affected by ASR although greater restraint levels tend to aggravate the problem.

2. Crack Filling
Sealing of surface cracks due to ASR with high molecular weight methacrylate appears to be beneficial in stiffening the affected pavement. Its effectiveness will depend on penetration of methacrylate into the cracks.

Pozzolans As Inhibitory Agents In ASR

Under ordinary conditions, pozzolans were considered to be effective inhibitory agents because they consumed alkalis and rapidly reduced the concentration of alkalis and hydroxyl ions in pore solutions. Reduction of alkalis was believed to slow the attack on reactive aggregates, increase calcium ion concentration, and permit more rapid diffusion of calcium ions into the reaction zone to form non-swelling product, while sufficient silica diffused out from the reacting aggregate to prevent expansion.

However, recent studies have shown that some pozzolans, such as fly ash, increase the rate of ASR rather than slow the reaction, as with calcined kaolin. Reduced pH of the pore solutions was found in mortars made with some pozzolans, but not with granulated slag, which also reduced expansions. Some researchers have argued that in order for pozzolans to be effective in the presence of unlimited alkalis from soluble salts, calcium hydroxide in the paste matrix has to be leached or reacted to insoluble products in the paste to limit Ca++ ions from diffusion into the silica. Safe reactions by this method depend completely on escape of all excess silica from the reactive particle to prevent expansion, rather than partly on the formation of non-swelling product in the particle interior.

It is now clear that Powers and Steinour's model does not account for the effectiveness of some pozzolans in controlling ASR expansions and cracking even under ordinary test conditions without salts. Some researchers have argued that calcium hydroxide must be eliminated for safe reactions to occur when reactions are accelerated by soluble salts and temperature. If this proves to be correct, then the safe reaction processes are very different under different conditions. This is a serious gap in ASR knowledge and is of great practical importance both with respect to possible effects with deicing salts and the use of
pozzolans to protect concrete from damage by ASR.

Fly ash, ground granulated blast furnace slag (GGBFS), condensed silica fume (CSF), and natural pozzolans are used to prevent abnormal expansion caused by ASR. However, existing test methods for potential reactivity of aggregates (ASTM C 289), for ASR of cement-aggregate combinations (ASTM C 227) and for the effectiveness of mineral admixtures in preventing ASR expansion (ASTM C 441) do not always provide reliable or clearly defined lines of demarcation between nonreactive and reactive combinations. This is largely because tests do not incorporate a realistic assessment of actual conditions: test mortars are made at specified fixed proportions while concrete proportions vary; tests are conducted at 100°C to accelerate ASR while concretes are exposed to varying conditions; expansions measured by C 227 are considered excessive at 0.05% at 3 months or 0.10% at 6 months while cracking occurs at about 0.03% in concretes; and reactive aggregates vary in their rates of reaction at different temperatures and pH.

Factors influencing Pozzolan testing seem to indicate that chemical tests cannot adequately assess characteristics of mineral admixtures necessary for performance. These factors are: different pozzolans function by different mechanisms; different fly ashes have different threshold pH values for reaction; reactive aggregates vary greatly in their reaction rates and other characteristics; some mineral admixtures can control both highly and slowly reactive aggregates but this is not certain if different mechanisms are involved; the chemistry of ASR involves four reactants: water, reactive aggregate, Portland cement and mineral admixture, and depends on mix proportions and other factors in concrete; and there is considerable uncertainty concerning the effects of release of alkalis from fly ash, granulated slag and superplasticizers. Consequently, mortar tests are essential.

Both the tests and specifications used to rate quality of pozzolans and the tests to determine pozzolan amounts required with different cement-aggregate combinations need improvement. A testing protocol (not necessarily as stringent) needs to be developed that will define amounts of mineral admixture required in job mixtures of cement, mineral admixture, water and reactive aggregate that are required to prevent cracking and growth of cracks. To be practical, the test must be accelerated and yield results within a reasonably short time (14-28 days), that are valid for very long term results.

**Recommendations Resulting from SHRP Research**

Based on the findings of the investigation reported in SHRP-C-343, a number of recommendations were made. These included a suggestion that personnel in transportation departments should become more familiar with manifestations of ASR-induced distress in highway structures. The rapid immersion test method should be required in the routine evaluation of aggregates and mineral admixture for use in concrete. Addition of LiOH should be seriously considered as a means of preventing development of deleterious ASR. Triaxial restraint of concrete members should be considered as a viable method of controlling expansion due to ASR. Additional research was recommended to further substantiate the rapid immersion test criteria, to monitor field installations, and to develop other projects for similar experimental means to inhibit expansions due to ASR.

**ASR TESTING IN CANADA**

In Canada, the supply and testing of concrete aggregates is governed by the Canadian Standards Association (CSA) Standard for Concrete Materials and Methods of Concrete Construction A23.1-94 and Methods of Test for Concrete A23.2-94. These standards provide specific advice on the testing of aggregates for alkali-aggregate reactivity and techniques for preventing deleterious reactions with potentially reactive aggregates. The advice given in the CSA documents may not be the same as given in the SHRP reports. Users and suppliers of concrete in Canada should ensure that aggregates meet the CSA standards.

The Concrete Prism Expansion Method, CSA Test Method A23.2-14A, is a reliable test for alkali-aggregate reactivity. Prisms are made using coarse and fine aggregates and Portland cement with a
The total alkali content of 0.9% ± 0.1%. Sodium hydroxide is added to the concrete mix water to increase the total alkali content to 1.25% Na₂O equivalent, by mass of cement. The prisms are stored for a period of one year in sealed containers at 100% relative humidity. Length is measured periodically and expansions exceeding 0.04% at one year indicate that the aggregate is potentially reactive.

The Accelerated Expansion of Mortar Bars, CSA A23.2-25A (ASTM C 1260), requires only 16 days to complete, compared to one year for the concrete prism test. Mortar bars are made of graded sand or crushed coarse aggregate and Portland cement containing 0.9% ± 0.1% alkalies expressed as Na₂O equivalent. The bars are immersed in a sodium hydroxide solution (1N) for 14 days, and periodically measured for expansions. Aggregates causing expansions of less than 0.15% after 14 days are generally considered acceptable for use. Those exceeding 0.15% may be potentially reactive, and further testing using the concrete prism test should be carried out.

In some comparisons of the accelerated mortar bar and concrete prism tests, the accelerated mortar bar test has failed to recognize the non-reactive character of some aggregates tested. In a few cases, the accelerated test has failed to identify an aggregate which is reactive in the concrete prism test. The CSA A23.2-14A Concrete Prism Method is considered the most reliable test for distinguishing between reactive and non-reactive aggregates. In the case of questionable test performance, the exposure conditions, concrete alkali levels, natural variations in the source and statistical variations in test results should be considered in applying engineering judgement on the use of these aggregates for critical applications.

The CSA Standard for Concrete Materials and Methods of Concrete Construction includes an appendix on the more general alkali-aggregate reaction (AAR) of which ASR is one type. Appendix B to CSA A23.1-94 is not a mandatory part of the standard but it provides information about methods of evaluating potential reactivity of aggregates, the distribution of such aggregates in Canada, and preventive measures to mitigate AAR. In particular, Section B5 presents reduced alkali content, supplementary cementing materials, and aggregate beneficiation as options currently available to avoid the deleterious expansion and cracking of concrete due to AAR. Readers are referred to the Standard for detailed information.
For full details of this research see:

Alkali Aggregate Reactions in Concrete:
An Annotated Bibliography 1939-1991
SHRP-C/UWP-92-601
Strategic Highway Research Program
National Research Council
Washington, DC 1992

Alkali-Silica Reactivity: An Overview of Research
SHRP-C-342
Strategic Highway Research Program
National Research Council
Washington, DC 1993

Eliminating or Minimizing Alkali-Silica Reactivity
SHRP-C-343
Strategic Highway Research Program
National Research Council
Washington, DC 1993

Handbook for the Identification of Alkali-Silica Reactivity in Highway Structures
SHRP-C-315
Strategic Highway Research Program
National Research Council
Washington, DC 1993

See also:

CSA Standard A23.1-94, Concrete Materials and Methods of Concrete Construction
CSA Standard A23.2-94 Methods of Test for Concrete
Canadian Standards Association
Toronto, Ontario 1994

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