

Report on Alkali-Aggregate Reactivity

Reported by ACI Committee 221

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Information that is currently available on alkali-aggregate reactivity (AAR), including alkali-silica reactivity (ASR) and alkali-carbonate reactivity (ACR) is summarized in the report. Chapters are included that provide an overview of the nature of ASR and ACR reactions, means to avoid the deleterious effects of each reaction, methods of testing for potential expansion of aggregates and cement-aggregate combinations, measures to prevent deleterious reactions, and recommendations for evaluation and repair of existing structures.

Keywords: aggregates; alkali-aggregate reactivity; alkali-carbonate reactivity; alkali-silica reactivity; concrete; concrete distress; concrete durability.

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CHAPTER 1—INTRODUCTION

In many parts of the world, precautions must be taken to avoid excessive expansion due to alkali-aggregate reactivity (AAR) in many types of concrete construction. AAR may involve siliceous aggregates (alkali-silica reactivity, ASR) or carbonate aggregates (alkali-carbonate reactivity, ACR), and failure to take precautions may result in progressive deterioration, requiring costly repair and rehabilitation of concrete structures to maintain their intended function.

Extensive knowledge is available regarding the mechanisms of the reactions, the aggregate constituents that may react deleteriously, and precautions that can be taken to avoid resulting distress. However, deficiencies still exist in our knowledge of both ASR and ACR. This is particularly true with respect to the applicability of test methods to identify the potential for reactivity, methods to repair affected concrete, and means to control the consequences of the reactions in existing structures.

Intensive research has been conducted to develop this needed information. As a result, concrete structures can now be designed and built with a high degree of assurance that excessive expansion due to AAR will not occur and cause progressive degradation of the concrete.

This report provides information for those involved with the design and construction of concrete, to make them aware of the factors involved in AAR and the means that are available to control it.

1.1—Historical perspective

1.1.1 Alkali-silica reactivity—Alkali-silica reactivity (ASR) was first recognized in concrete pavement in California by Stanton (1940, 1942) of the California State Division of Highways. Stanton's early laboratory work demonstrated that expansion and cracking resulted when certain combinations of high-alkali cement and aggregate were combined in mortar bars stored in containers at very high relative humidity. Two important conclusions were drawn from this work: First, expansions resulting from ASR in damp mortar bars were negligible when alkali levels in cement were less than 0.60 percent, expressed as equivalent sodium oxide (percent $\text{Na}_2\text{O}_e = \text{percent Na}_2\text{O} + 0.658 \times \text{percent K}_2\text{O}$). A second conclusion was that the partial replacement of high-alkali cement with a suitable pozzolanic material prevented excessive expansions. Thus, foundations for the engineering control of the reaction were developed. This work also formed the basis for ASTM C 227, the mortar-bar test procedure.

Based on Stanton's work, the U.S. Bureau of Reclamation (Meissner, 1941) conducted investigations of abnormal cracking in concrete dams. Meissner's findings generally corroborated those of Stanton, and lent further credence to the importance of cement alkali level, aggregate composition, and environmental requirements in the development of expansion due to ASR. One outcome of this work was the development of the quick chemical test, ASTM C 289 (Mielenz et al., 1948).

In the 1940s, other agencies both in the U.S. and other countries conducted further studies on ASR. These agencies included the Army Corps of Engineers, the Bureau of

Public Roads, and the Portland Cement Association in the U.S., the Australian Council for Scientific and Industrial Research (Alderman et al., 1947) and the Danish National Committee for Alkali Aggregate Research. They furthered the understanding of relationships among cement composition, aggregate types, mixture proportions of mortar and concrete, and expansion.

Other workers during this period and in the early 1950s concentrated on clarifying mechanisms expansive and non-expansive reactions. At the Portland Cement Association, Hansen (1944) proposed that osmotic pressures generated during swelling of gel reaction products were responsible for the observed expansion. Powers and Steinour (1955) proposed a variant of this hypothesis, while later researchers attempted to refine these ideas of expansion mechanisms. As with other aspects of the reaction, gaps still exist, particularly in the quantitative aspects of reactivity.

Mather (1993) reviewed the use of admixtures to prevent excessive expansion due to alkali-silica reaction. Stanton (1940, 1942) reported that 25 percent pumicite, a pozzolan, “seems to be effective” in reducing “the expansion to a negligible amount at early periods.” The proposal to use pozzolan to prevent excessive expansion due to ASR apparently was first advanced by Hanna (1947). The 1963 report of ACI Committee 212 indicated that there had been “a few instances” where a mineral admixture was used to provide protection with high-alkali cement and reactive aggregate. In spite of this statement, Mather (1993) reported that he could find no documented evidence of such use. However, Rogers (1987) had written, “At the Lower Notch Dam on the Montreal River, 20 percent fly ash replacement was used successfully to prevent cracking of concrete containing argillite and graywacke.” This appears to have been the first documented case where a pozzolan was used with cement known to have high-alkali content and with aggregate known to be potentially deleteriously reactive. A similar case was reported from Wales (Blackwell and Pettifer, 1992).

Test methods currently in use to determine potential for expansive reactivity, particularly in the United States, derive primarily from work carried out in the 1940s. However, research efforts in several countries today indicate a promise of newer, more reliable tests to identify potentially deleteriously reactive cement-aggregate combinations.

1.1.2 Alkali-carbonate reactivity—Alkali-carbonate reactivity (ACR) was identified as causing a type of progressive deterioration of concrete by Swenson (1957) of the National Research Council of Canada. He found that an alkali-sensitive reaction had developed in concrete containing argillaceous calcitic dolomite aggregate that appeared to be different than the alkali-silica reaction. Subsequent work by Swenson (1957), Swenson and Gillott (1960), and Gillott (1963) in Canada, and by various other agencies in Canada and the United States, further elucidated factors that affected the magnitude of expansion resulting from the reaction. Noteworthy among researchers in the United States were Newlon and Sherwood (1962), Newlon et al. (1972a,b), and Hadley (1961, 1964). Two hypotheses on the mechanism of ACR were developed, both of which still are cited.

Because rock susceptible to this type of reaction is relatively rare, and is often unacceptable for use as concrete aggregate for other reasons, reported occurrences of deleterious ACR in actual structures are relatively few. The only area where it appears to have developed to any great extent is in southern Ontario, Canada, in the vicinities of Kingston and Cornwall. Isolated occurrences in concrete structures have been found in the United States in Indiana, Kentucky, Tennessee, and Virginia. So-called “alkali-dolomite reactions” involving dolomitic limestones and dolostones have also been recognized in China (Tang et al., 1996).

1.2—Scope of report

This report is intended to provide information on ASR and ACR. Accordingly, chapters in this report provide an overview of the nature of both ASR and ACR reactions, the means of avoiding the deleterious effects of each reaction, methods of testing for potential expansion of cement-aggregate combinations, measures to prevent deleterious reactions, and recommendations for evaluation and repair of existing structures.

CHAPTER 2—MANIFESTATIONS OF DISTRESS DUE TO ALKALI-SILICA REACTIVITY

2.1—Introduction

The most evident manifestations of deleterious ASR in a concrete structure are concrete cracking, displacement of structural members due to internal expansion of the concrete, and popouts. However, these features should not be used as the only indicators in the diagnosis of ASR in a concrete structure. Cracking in concrete is essentially the result of the presence of excessive tensile stress within the concrete, which can be caused by external forces such as load, or by development of a differential volume change within the concrete. Early contraction, too large thermal gradients during curing of the concrete, corrosion of embedded reinforcement, freezing and thawing, and internal and external sulfate attack are some of the mechanisms that also can lead to the formation of cracks in concrete.

Diagnosing ASR-related cracking requires the additional identification of ASR reaction product in the concrete and, most importantly, requires positive indications that this product has led to the generation of tensile stresses sufficiently large that the tensile strength of the concrete was exceeded.

2.2—Cracking mechanisms

Little is usually known about the time necessary for development of cracks in ASR-affected concrete in the field. This is partly due to the heterogeneous nature of concrete as a material, and to the fact that the reaction kinetics of ASR are practically unexplored. For example:

1. Does the reaction product swell at the place it forms, or at a different place where it migrates after formation?
2. How rapidly are expansive pressures generated from the swelling reaction product?
3. How do these mechanisms produce cracks in the concrete?

However, some inferences can be made based on observing ASR-affected concrete in the field and in the laboratory. For example, in an unreinforced or minimally reinforced concrete element, such as a concrete slab or beam, the largest

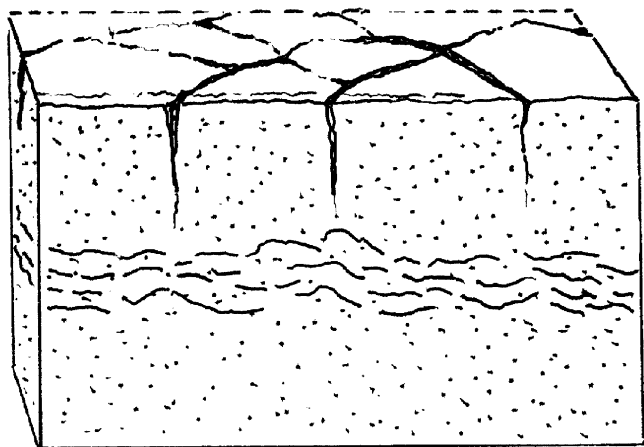


Fig. 1—Sketch showing typical features of surface map-cracking and subparallel cracks in concrete with ASR. Stresses due to ASR grades from horizontal tension near the surface to horizontal compression and vertical tension with depth.

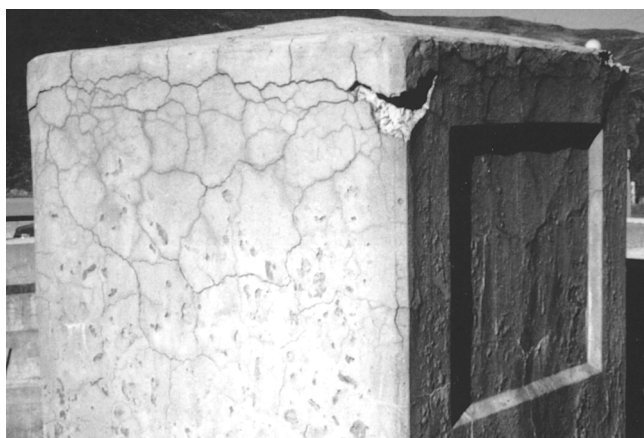


Fig. 2—Photograph of a parapet wall showing typical map-cracking at the surface.

degree of deformation of the concrete will occur in the direction of least restraint.

Fig. 1 is a sketch of the surface and a cross section of a concrete slab undergoing ASR. Swelling due to the uptake of water by alkali-silica reaction product generates tensile stresses that lead to the local formation of fine cracks in the concrete slab. Since the least restraint occurs in a direction perpendicular to the surface, the cracks tend to align themselves subparallel to the surface. The expansion occurring within the concrete causes tension to occur in the concrete near the surface of the slab, where less expansion is taking place due to a lower rate of reaction. These tensile stresses are relieved by the formation of relatively wider cracks perpendicular to the surface. Viewed from above, these cracks tend to occur in a polygonal pattern that is the basis for the term “map-cracking.” Fig. 2 shows the typical appearance of a concrete surface which has developed map-cracking due to ASR. Fig. 3 is a bridge deck core showing both the vertical and horizontal cracking due to ASR.

The relaxation of tension in the surface concrete allows further cracking subparallel to the surface to occur further

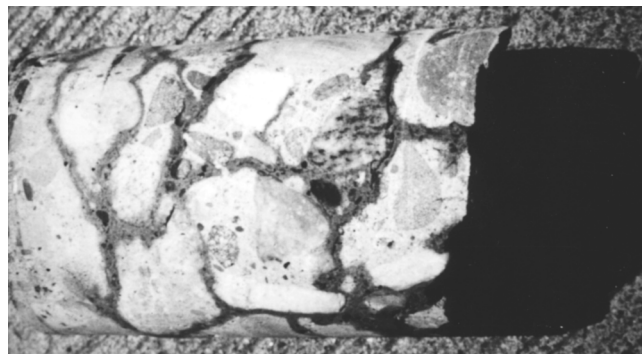


Fig. 3—Bridge deck core showing both vertical and horizontal cracking due to ASR (top of core to the right). Cracks are emphasized by retained moisture.

inward from the surface. With an excessive supply of external alkali and sufficient amounts of reactive silica in the aggregates, this subparallel cracking could theoretically continue to occur throughout the concrete. However, field experience shows that the subparallel cracking seldom goes deeper than 300 to 400 mm in unreinforced structures. In reinforced concrete, the cracking rarely progresses below the level of the reinforcement. It appears reasonable to assume that any reacting particle lying within concrete restrained by the reinforcement experiences confining pressures that exceed the expansive forces generated by the uptake of water by the reaction product. Cracking usually will not occur and the expansive pressures will most likely be accommodated by creep of the surrounding concrete. When evaluating specific structures, the type, location, and amount of reinforcement must be taken into account when considering the potential for cracking due to ASR.

The external appearance of the crack pattern in a concrete member is closely related to the stress distribution within the concrete. The distribution of strain is, among other things, controlled by the location and type of reinforcement, and the structural load imposed upon the concrete. Expansion of a concrete element will tend to occur in the direction of least restraint. Cracks caused by the expansion due to ASR tend to align parallel to the direction of maximum restraint.

Fig. 4 shows a pavement affected by ASR. In this case, stress distribution has caused the cracks to orient parallel to the slab free edges (longitudinally) over most of the slab surface, with additional cracks parallel to the transverse joints (also a free edge) in the areas near these joints.

2.3—Expansion and other indicators of alkali-silica reactivity

The development of cracks in a concrete structure due to ASR is caused by a volume increase that can be observed directly, either as a closure of expansion joints or by the misalignment of one structural element with respect to another. Also, the volume increase can be inferred from, for instance, an increasing difficulty in the operation of machinery attached to the concrete (for example, spillway gates in a dam). Fig. 5 depicts the closure of a joint and extrusion of the joint-filling material due to ASR expansion.



Fig. 4—Photograph of pavement affected by ASR. Typical longitudinal cracking is parallel to the slab free edges, with additional transverse cracks in the areas near the transverse joints.

Monitoring the amount and rate of expansion of a structure often is necessary to assess its structural integrity. Several ways of monitoring the rate of expansion exist. For example, the long-term change of length between reference points mounted on the concrete surface can be measured.

The method most suitable for monitoring the expansion must be considered in each specific case. However, it must be remembered that such observations should cover entire structural units. Measurements and summations of individual crack widths in a concrete structure are too uncertain for this purpose, because shrinkage of the concrete between the cracks will contribute to the opening of the cracks. Measurements of crack widths may thus give a false indication of the expansion in the concrete. Likewise, gathering sufficient data to be able to correct for the effects of variations in ambient temperature and humidity is important. As these variations are often seasonal or more frequent, at least several years of measurements are normally necessary before definite conclusions can be reached about the rate of ASR-induced expansion in the structure.

Popouts and exudation of gel onto the concrete surface also may indicate ASR but it does not, by itself, indicate excessive expansion of the concrete. Although the presence of alkali-silica gel on the surface of the concrete indicates the presence of ASR, it does not mean that the cracks were formed by the gel on its way to the surface. Discoloration often borders the crack in ASR-affected concrete, but discoloration may also occur for several other reasons (for example, leaching or algae growth).

“Popouts” refer to the breaking away of small conical fragments from the surface of the concrete, and can, in climates where freezing takes place, be the result of freezing of water-saturated, porous aggregate particles lying near the surface. Examining the popouts for the presence of gel is important; it can indicate whether ASR has taken place. As reactive particles are often porous and may be susceptible to



Fig. 5—Photograph showing closure of a joint and extrusion of joint-filling material due to ASR expansion.

both frost damage and ASR, unambiguously identifying the reason for the popouts is often difficult.

2.4—Alkali-silica reactivity reaction factors

The distribution of ASR in a concrete structure is often highly variable, both with regard to appearance and intensity.

ASR involves a chemical reaction, and for the reaction to occur, the following components must be present: water, reactive silica, and a high concentration of hydroxyl ions (high pH). Likewise, the concentration and distribution of these components and the ambient temperature have a significant influence on the rate and deleterious effect of the reaction. A concrete structure with ASR commonly exhibits widely differing signs of deterioration in different places. Concrete exposed to dry, interior environments without water normally does not develop cracking from ASR, even though reactive silica and alkalies are present in the concrete.

The most vulnerable parts of a concrete structure are those exposed to a warm and humid environment. Field experience and laboratory work also indicate that concrete exposed to repeated drying and wetting cycles is more likely to develop excessive expansion due to ASR than concrete stored at a uniform moisture content.

Where it is possible for water to accumulate, such as from rain or snow, a rapid progression of ASR is often observed. This applies to every free-standing concrete surface that has not been protected. Cracking in free standing walls, exposed beams, or parapets is commonly observed. Degradation of these exposed concrete elements also is enhanced where freezing and thawing occurs in conjunction with ASR.

Cracking also tends to occur in concrete embedded in moist soil, such as in bases and foundations. The largest amount of cracking tends to occur at or near the soil surface where the concrete experiences the largest fluctuations in wetting and drying.

Sodium chloride also has been reported to promote ASR due to the external supply of sodium under conditions where the chloride ion reacts to form, for example, chloroaluminates. Salt concentrations, as found in ordinary sea water, do not seem to provoke ASR, but when the sodium chloride concentration exceeds approximately 5 percent (Chatterji et

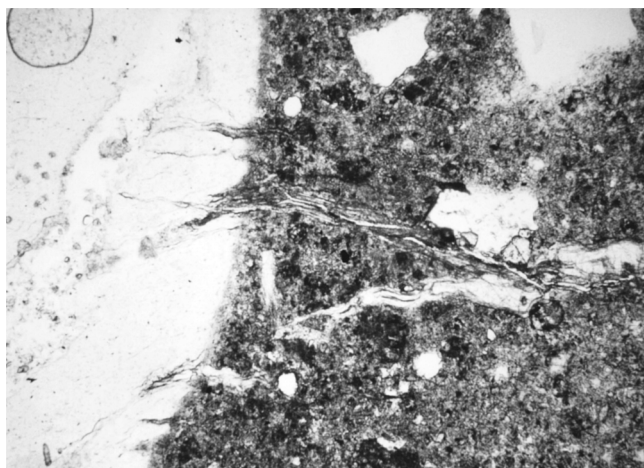


Fig. 6—Photomicrograph of gel-filled cracks extending from within a chert aggregate particle into the adjacent cement paste.

al., 1987), for instance due to evaporation, the rate of ASR may rapidly increase. The accelerating effect of sodium chloride on ASR has been reported to be a serious problem in areas where sodium chloride is used as a deicing agent on pavements, sidewalks, and in parking structures. However, recently reported research does not support this hypothesis (Duchesne and Berube, 1996).

The physical characteristics of concrete also can be decisive in determining the degree and rate of deterioration due to ASR. Air entrainment has been reported to reduce the degree of expansion due to ASR. However, air entrainment by itself should not be regarded as an effective means of preventing excessive expansion due to ASR.

The effect of water-cement ratio on ASR is more difficult to determine since a low water-cement ratio may reduce the availability of water for imbibition by the reaction product, but at the same time raising the alkali concentration of the pore fluid.

Field experience shows that initial cracking in a concrete element, such as thermal or drying shrinkage cracks, can have an accelerating effect on the development of excessive expansion due to ASR. This is probably due to both the capillary effect of the cracks promoting ingress of water into the concrete, and the reaction-product swelling that widens existing cracks instead of initiating new ones.

2.5—Microscopic evidence of alkali-silica reactivity

In most cases, absolutely diagnosing distress caused by ASR in a structure based solely on a visual examination of the concrete is difficult. In the final assessment of the causes of deterioration it is necessary to obtain samples for examination and testing. Petrographic examination should then be conducted in accordance with ASTM C 856.

In some cases, deposits of the reaction product, a transparent alkali-silica gel, are found. Fig. 6 shows a close-up of gel-filled cracks extending from within a chert aggregate particle into the adjacent cement paste. The appearance of the gel may vary depending on whether it is within an aggregate particle or in the paste. Inside an aggregate particle, the

gel may appear grainy, while it often appears more glassy within the paste.

In some cases, the amount of gel appears to be limited, while the amount of concrete cracking due to ASR can be rather high. In other cases, this behavior of the concrete is reversed, where alkali-silica gel is seen to replace practically the entire aggregate particle, apparently without causing any significant cracking.

The presence of discolored rims in reactive aggregate particles in the concrete is an indicator of ASR (Dolar-Mantuani, 1983). The presence of such reaction rims should be approached with some caution, as the formation of rims in aggregate particles can also be due to other mechanisms. Weathered outer layers of the individual particles are often seen in natural gravels, and even crushed rock can develop weathering rims if it has been stockpiled for some time. These weathering rims are often indistinguishable from reaction rims formed in concrete. Caution must also be used in identifying ASR based on deposits surrounding aggregate particles on fractured concrete surfaces. The fractured surface may have occurred along an old crack which could contain a variety of deposits (Thaulow et al., 1989). Fig. 7 shows a crushed aggregate with reaction rims (since the aggregate is crushed, it indicates the rims have formed after crushing, i.e., in the concrete) in a concrete with ASR (note cracking and ASR gel).

When observed in thin section, the disseminated calcium hydroxide in the cement paste often is depleted in the vicinity of reactive-aggregate particles. This phenomenon often occurs before other signs of ASR, such as cracking and gel formation, and is therefore helpful in detecting reacted particles in the concrete.

CHAPTER 3—ALKALI-SILICA REACTIVITY MECHANISMS

3.1—Factors influencing the reaction

Three basic conditions must exist for ASR to proceed in concrete. These conditions include high pH, moisture, and reactive silica. The rate of the reaction is influenced by temperature.

3.1.1 Cement alkali levels—Early investigators recognized that the alkali content of portland cement had a direct influence on potential expansion (Stanton, 1940, 1942). The two alkali constituents are reported from chemical analysis as sodium oxide and potassium oxide. The total equivalent alkali is calculated as percent Na_2O plus $0.658 \times$ percent K_2O , and the resulting percentage is described as equivalent $\text{Na}_2\text{O}(\text{Na}_2\text{O}_e)$. The concept has proven useful in the study of ASR. Diamond (1989) showed the relationship between the cement-alkali content and the OH-ion concentration (pH) of the concrete pore fluid. The latter is the driving factor in the chemical process of AAR.

A limit of 0.60 percent on the Na_2O equivalent alkali content of portland cement (low-alkali cement) has often been used in specifications to minimize deterioration of concrete when reactive aggregates are used. However, there have been cases where significant damage resulted despite the use of low-alkali cement (Hadley, 1968; Lerch, 1959; Stark, 1978, 1980; Tuthill, 1980, 1982; Ozol and Goudar, 1992). Based on his experience, Tuthill (1980) suggested that

a limit of 0.40 percent on the equivalent alkali content was more appropriate. An ASTM Committee C1 working group (Blanks, 1946) reported on laboratory tests of mortars containing natural aggregates, finding that excessive expansions were encountered with cements having alkali contents of 0.58 percent or greater. With alkali contents of 0.40 percent or less, excessive expansion in the mortars did not occur.

Several factors may be responsible for the problems encountered with low-alkali cements:

1. Concretes made using portland cement alone are relatively more permeable than similar concretes made with blends of portland cement and slag or pozzolan. Cyclic wetting and drying, freezing and thawing, as well as electrical currents can cause alkali migration and concentration in concrete (Xu and Hooton, 1993). Consequently, a given supply of alkali that might be tolerated if uniformly distributed throughout the concrete can become concentrated in certain areas in amounts high enough to cause distress. Lerch (1959) and Hadley (1968) reported on a pavement where damaging ASR was linked to wetting and drying; Ozol (1990) reported on the exacerbating effect of electrical currents on ASR of concrete in piers at a power substation. Moore (1978) had previously reported laboratory results indicating that passage of direct electric current through a mortar specimen containing reactive siliceous aggregate appeared to accelerate the disruption due to ASR.

2. The relative permeability of concrete also permits the migration within the concrete of alkalis from other concrete materials as well as the ingress of alkalis from external sources such as deicing salt. Studies (Grattan-Bellew, 1994, 1995; Berube et al., 1996; and Stark and Bhatt, 1986) have shown that significant amounts of alkalis can be leached from certain types of aggregates by concrete pore solutions.

3. Because the relevant issue with respect to ASR is the concentration of hydroxyl ion (pH) in the concrete, the cement factor plays an important role that is disregarded in the traditional consideration of cement-alkali content (Na_2O_e). Various limits on the mass of alkali-per-unit volume of concrete have been suggested as a more appropriate method to prevent damaging ASR. A maximum value of 3 kg/m^3 is often cited as sufficient to prevent damage in the presence of reactive aggregates (Concrete Society Working Party 1987; and Portland Cement Association 1994). The limit includes alkalis contributed from pozzolans or slag, as well as the cement. The Canadian Standards Association (CSA A23.1) places a limit of 3 kg/m^3 on the alkali contribution from the cement alone. Ozol (1990) reported on field occurrences of ASR where chemical analyses suggested concrete alkali contents of 1.8 kg/m^3 , and Ozol and Dusenberry (1992) reported ASR in concrete with an alkali content of 2.3 kg/m^3 . Based on laboratory tests, Johnston (1986) suggests that concrete alkali contents less than 0.05 percent (1.2 kg/m^3 , for concrete with a density of 2320 kg/m^3) were clearly safe, whereas alkali contents greater than 0.10 percent (2.3 kg/m^3) would clearly cause problems when used with reactive aggregate.

4. The alkali content that can be tolerated may be related to the inherent reactivity of the aggregate. Woolf (1952)

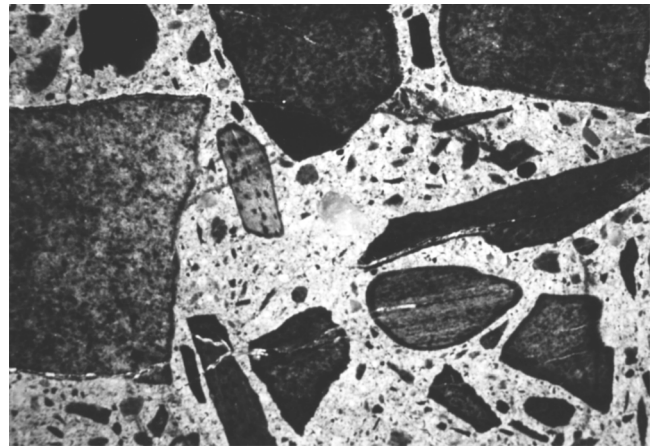


Fig. 7—Polished section showing crushed aggregate with reaction rims in concrete with ASR (note cracking and ASR gel).

reported on laboratory tests where the alkali content at which maximum expansion of mortar bars occurred varied with the percentage of highly reactive material in the aggregate. Stark et al. (1993) investigated the concept of using the accelerated mortar bar expansion test to determine a “safe alkali content” for a particular aggregate.

Although ASR problems can be minimized by limiting the alkali content of the cement or concrete, consideration must be given to the potential for alkali migration and concentration within the concrete to determine an appropriate limit. The advantages of using pozzolans or slag to produce ASR-resistant concretes with low permeability also should be considered.

3.1.2 Moisture—Moisture must be available for ASR to proceed, and below about 80 percent internal relative humidity the reaction will cease. For ordinary concretes, some portion of the original mixing water is usually available for a long period even in dry service conditions. However, for low water to cementitious ratio mixtures the water may be used up by hydration of cement. In service (such as slabs on grade) where the concrete has an external source of water, the reaction will continue until one of the reactive constituents is used up.

3.1.3 Reactive silica—Researchers first believed there was a limited group of susceptible aggregate constituents such as opal, chert containing chalcedony, and some glassy volcanic rocks. It is now recognized that ASR can occur with a wider range of siliceous aggregate constituents. Various other metastable forms of silica can be involved. Reactivity depends not only on the mineralogy but also on the mechanics of formation of the aggregate material, and the degree of deformation of quartz. Chapter 4 discusses reactive silica in detail.

3.1.4 Temperature—As temperatures increase, the rate of ASR increases. With given concrete materials and proportions, the reaction will take place more rapidly under warmer conditions. While this factor has not been quantified, it should be kept in mind when considering approaches to prevent ASR.

3.2—Basic mechanisms of reaction and expansion

The mechanisms of alkali-silica reaction and expansion have been under investigation since about 1940. The

hydroxyl ions present in the pore fluid in concrete react chemically with various forms of silica present in many aggregates. The sodium and potassium alkalis play two roles in the reaction. First, higher percentages of these alkalis in the concrete result in higher concentrations of hydroxyl ions in the concrete pore fluid (higher pH). The more alkaline (higher pH) the pore fluid, the more readily it attacks (reacts with) the reactive silica. Once in solution, the silica reacts with the alkalis forming alkali silica gel. This alkali-silica gel then imbibes water and swells so that its volume is greater than that of the individual reacted materials, and expansive stress is exerted on the concrete.

Where the reactive ingredients are present in the fresh concrete the reaction begins at the contact surface of the cement paste and the aggregate particle. Often the earliest indication is a discolored reaction rim within the surface of the aggregate particles. Increasing gel formation results in progressive cracking within the aggregate particles and in the matrix around the particles. Often a near-surface peripheral crack is evident in the aggregate.

Where the source of the alkali is external to the concrete, gel formation will advance on a front from the exposed faces. Alkalis may become available from such sources as deicing salts, seawater, and industrial solutions.

Rates of reactions are often low, and evidence of exudation of gel, pop-outs, cracking, and mass expansion may not be seen for years.

In a few cases, gel formation has been detected but has not caused disruption because of a relatively volume-stable replacement of aggregate material by gel. In most instances of ASR, however, disruptive expansive forces are generated.

CHAPTER 4—PETROGRAPHY OF ALKALI-SILICA REACTIVE AGGREGATE

4.1—Introduction

The petrography of alkali-silica reactive aggregates is discussed here, using petrographic terms which may not be familiar to engineers. These terms will be explained where first used, to the extent possible. Alkali-silica reactive aggregate constituents can be classified in two broad categories: 1) naturally occurring forms of essentially pure silica, into which minerals, mineraloids, and volcanic glasses are grouped; and 2) synthetic or artificial siliceous materials. The reactivity of an aggregate: that is whether it reacts quickly or slowly, and also the amount of sodium equivalent alkalis in the concrete necessary to cause it to react, depends on the composition, geologic origin and textural characteristics of the rock(s) from which the aggregate is derived. For further discussion of these aspects, see Stark, Morgan et al. (1993), Dolar-Mantuani (1983), and Grattan-Bellew (1983).

4.2—Potentially reactive natural silica constituents

4.2.1 Opal—Opal, either alone or as a component in a rock is probably the most alkali-silica reactive natural material (Stanton, 1940, 1942). As described in ASTM C 294, opal is “a hydrous form of silica ($\text{SiO}_2 \cdot n\text{H}_2\text{O}$) that occurs without

characteristic form or internal crystalline arrangement as determined by ordinary visible light methods.”

Optically, opal is colorless to pale gray or brown. Its index of refraction ranges from 1.40 to 1.46, and is variable based on water content (Kerr, 1959; Mather, 1945). Its form is colloform (in rounded masses) crusts, cavity fillings, or linings in seams as replacement of wood, other organic materials, or feldspars. More often it is massive without any particular structure although opals fall into several crystallographic categories. Some opals appear completely amorphous while others are composed of poorly to moderately well crystallized cristobalite, disordered cristobalite-tridymite intergrowths, or disordered tridymite (Diamond, 1976).

4.2.2 Chalcedony—ASTM C 294 describes chalcedony as a fibrous, microcrystalline form of silica. Chalcedony has been considered both as a distinct mineral and a variety of quartz. It occurs in massive form, as cavity fillings, as cementing material, and as replacement material for fossils and for opal in diatomite. It is often a major constituent of chert.

Indices of refraction range between 1.534 and 1.538; that is, lower than the lower index of refraction of quartz. Chalcedony is colorless-to-pale brown in thin section and often bluish-white in reflected light. Extinction (the optical orientation for certain minerals at which no light is transmitted when viewed through crossed polarizing lenses) is parallel to the length of the fibers (Kerr, 1959).

4.2.3 Quartz—Coarse megascopically-crystalline (visible with the unaided eye) quartz is normally not reactive. However, there have been indications that megascopic unstrained (undeformed) quartz may, with certain irregularities or inclusions present, be slowly reactive and expansive given sufficient time and exposure to alkaline conditions (Diamond, 1976; Dolar-Mantuani, 1975).

Microcrystalline to cryptocrystalline (so finely crystalline that the crystals can not be seen with a hand lens) quartz, components of some cherts, have been found extremely susceptible to reaction.

Highly fractured quartz in quartzites and gneisses, and strained quartz are also alkali reactive. Studies relating optical properties of strained quartz to mortar-bar expansion indicate an apparent correlation based on measured undulatory extinction angles (extinction, see above, occurs over a range of crystal orientation angles) of the strained quartz (Mather, 1973; Dolar-Mantuani, 1975). However, Grattan-Bellew (1992) suggests that this apparent correlation may be due to the presence of microcrystalline quartz in rocks containing strained macrocrystalline quartz grains. Characterization of reactive aggregates containing strained quartz has also been investigated by scanning electron microscope and infrared spectroscopy (Mullick et al., 1985).

4.2.4 Cristobalite—Cristobalite is found in minute square crystals or aggregates in the cavities of obsidian, rhyolite, andesite, and basalt. It also occurs as a constituent of some specimens of opal. Cristobalite has been reported as a constituent in some blast-furnace slags (McCaffery et al., 1927), and therefore the composition of slags being considered for use as aggregate should be checked. Sometimes in thin section, it is pseudoisometric in appearance, but

not the optical properties of the isometric crystal class) with principal indices of refraction of 1.484 and 1.487 (Kerr, 1959).

4.2.5 Tridymite—Tridymite occurs in minute, euhedral (well formed) crystals as cavity linings in volcanic igneous rocks such as obsidian, rhyolite, andesite, and as a porous crystalline aggregate. The crystals are six-sided, orthorhombic, thin, and tabular with characteristic wedge-shaped twins (crystal intergrowths). In the absence of twinned crystals, tridymite very closely resembles cristobalite, however the index of refraction of individual crystals is diagnostic: for tridymite, $n < 1.480$; for cristobalite, $n > 1.480$ (Kerr, 1959). The principal indices for tridymite are 1.469, 1.469, and 1.473.

4.2.6 Volcanic glasses—Volcanic glasses occur in virtually all volcanic rocks. Igneous rocks are described as acid if they contain more than 66 percent silica, intermediate when silica contents range from 52 to 66 percent, and basic when silica contents are less than 52 percent. This corresponds to index of refraction ranges of $n < 1.57$ for acidic and intermediate glasses, and $n > 1.57$ for basic glasses (Williams et al., 1954 and Mather, 1948). Acid and intermediate glasses tend to be alkali reactive, with reactivity decreasing as the amount of silica decreases. Thus, the high-silica glasses of rhyolites, dacites, and andesites (pumice and obsidian) are more reactive, while basaltic glasses are less reactive.

4.2.7 Chert—Chert is a general term applied to variously colored, fine-grained siliceous rocks composed of microcrystalline or cryptocrystalline quartz, chalcedony, opal, or mixtures of these constituents. Cherts can be dense or porous and chalky. The dense cherts are tough, with a waxy-to-greasy luster and conchoidal fracture. Chert particles may be gray, brown, white, red, green, blue, or black. ASTM C 294 and Mather (1948) delineate the chert varieties flint, jasper, agate, and novaculite primarily based on color. The porous varieties are usually chalky, lighter in color, and have a splintery fracture. In addition to potential reactivity with cement alkalies, porous cherts may cause cracking or popouts in concrete if frozen and thawed while critically saturated (Mielenz, 1956).

Chert occurs as nodules, lenses, or beds in calcareous and noncalcareous sedimentary rocks, and as discrete particles in sand and gravel. Impure cherts commonly grade into siliceous limestones (Diamond, 1976).

Most cherts are alkali-silica reactive. The degree of reactivity is dependent on several factors, including the mineralogic composition and internal structure of the chert, the amount of reactive chert relative to that of the total aggregate, and the particle size distribution.

4.2.8 Volcanic rocks—Acidic and intermediate volcanic rocks that are alkali-silica reactive include some rhyolites, dacites, latites, and andesites. The related porphyries (rocks with larger crystals in a fine grained matrix) and tuffs (rock composed of compacted volcanic fragments) of these rock types also may be alkali reactive. The reactivity of these rocks can be attributed to the texture and composition of glassy or partially glassy groundmass (matrix of the rock).

Some basic volcanic glasses and rocks are also alkali-silica reactive (Gudmundsson, 1971). Basalts containing highly siliceous interstitial glasses are slowly alkali-silica

reactive, and produce the expansion and map cracking typical of ASR in concrete.

4.2.9 Argillites, meta-graywackes, phyllites, and slates—These metamorphosed sedimentary rocks can react with cement alkalies to cause expansion and cracking. The mineralogy of these rock types is mainly quartz, feldspars, and phyllosilicates (“platey” silicates, such as mica). Associated minerals include magnetite, hematite, pyrite, graphite, and tourmaline (Gillott et al., 1973). Carbonate minerals also may be present in phyllites and slates (Regourd et al., 1981).

The reactive component in these rocks is finely divided or optically strained quartz, sometimes exhibiting inclusions (Dolar-Mantuani, 1983). Others believe the reactive component in these rocks to be finely divided quartz (microcrystalline quartz) exhibiting undulatory extinction, and sometimes fluid inclusions (Thompson et al., 1994; Langley et al., 1993; DeMerchant et al., 1995).

4.3—Potentially reactive synthetic materials

4.3.1 Silica brick—The principal constituent of silica brick is tridymite, with cristobalite also present (Kerr, 1959). Silica brick is made by using finely ground quartzites of low iron content.

4.3.2 Synthetic glasses—Many synthetic glasses are alkali-silica reactive (Mukherjee and Bickley, 1987). The aggregate used as a standard reactive aggregate in ASTM C 441 is Pyrex manufactured by Corning Glass Works. This glass contains about 80 percent SiO_2 .

The synthetic glasses generally are optically isotropic except for minor inclusions and occasional anisotropic grains (due to incomplete fusion or recrystallization). The index of refraction ranges from 1.510 to 1.555 (Meissner et al., 1942).

4.3.3 Coatings—Aggregates that are inherently innocuous may become deleterious because of surface coatings. Coatings may contain materials susceptible to reaction with cement alkalies, such as opal. The coatings may also contain salts of potassium or sodium which, if dissolved, can contribute to deleterious chemical reactions with alkali-reactive aggregate (Stanton, 1942).

CHAPTER 5—MEASURES TO PREVENT ALKALI-SILICA REACTIVITY

5.1—Overview

A distinction is made between ASR reaction and the expansion resulting from the reaction. ASR gel can form as a result of the reaction, but it is not always the direct cause of distress observed in concrete, as outlined in Section 3.1. ASR and the subsequent expansion of concrete occur only when the following conditions are present (as documented by Stark et al., 1993; Kosmatka and Fiorata, 1991; Mid-Atlantic Regional Technical Committee, 1993a, 1993b; Swamy, 1992; Helmuth, 1993; Mather, 1995):

1. Concrete is sufficiently moist in service.
2. Concrete contains aggregates with siliceous constituents that are alkali-silica reactive. These constituents may include inter-layer silicate minerals, which may cause expansion in some cases, but typically react at a slower rate. The amount of reactive aggregate required for the reaction to occur may vary widely