

reactivity. Alkali-silica reaction (ASR) is the most widespread, extensively known and studied.

Mechanism of Alkali-Silica Reaction

Concrete is composed of aggregates and paste. The paste is composed of the products of the hydration between the cementitious materials and water. Although appearing as a solid (discounting the entrained and entrapped air voids) the cementitious paste actually consists of a matrix of solid material with an internal network of interconnected pores. The volume of these pores and their interconnectedness depends on factors such as water-cement ratio, curing regime, and the cementitious materials used.

Water can enter and move through this network of pores, dissolving soluble salts of calcium and alkali metals (sodium and potassium). The dissolution of these salts increases the hydroxide ion (OH) concentration or pH of the resulting solution. In the portland cement paste, the hydration reaction produces sufficient calcium hydroxide to saturate the pore solutions with respect to this compound. In solutions saturated with calcium hydroxide, the maximum pH is about 12.5; however, increasing amounts of alkali will increase the pH. Consequently, the soluble alkali content of a concrete's cementitious paste affects the upper limit of pH or alkalinity of the pore solution.

The ASR process begins with the reaction of hydroxide ions from a highly alkaline pore solution with silica in the aggregate. This reaction produces a gel which may cause the aggregate and the concrete to crack. The cracking is also believed to be associated with the expansion of the gel due to water absorption. Depending on the aggregate mineralogy and reaction conditions, even very small amounts may cause cracking; under different conditions alkali-silica gel may not be deleterious.

Factors Affecting the Potential for ASR Related Distress

In order for ASR related distress to occur in concrete, three factors are required:

- 1) The presence of reactive forms of silica in the aggregate;
- 2) A sufficiently high alkali content in concrete pore solution;
- 3) Sufficient moisture.

Other factors may affect the development of ASR related distress. Among them are admixtures, deicing chemicals, concrete permeability, and conditions placement and curing.

Reactive silica SiO_2 , occurring in a variety of forms, is a common constituent of many aggregates. In neutral and acidic environments, the various forms of silica are chemically very stable. As a consequence of this stability, silica forms the bulk of the natural sands and gravels. However, in highly alkaline environments, such as occur in concrete, the solubility of silica increases dramatically.

The reactivity of silica, in addition to being affected by the alkalinity or pH, is also affected by the form, grain size, or crystalline structure of the silica. Descriptions of the various forms can be found in ASTM C 294 [11]. Amorphous, or non-crystalline and poorly crystalline silica, such as volcanic glasses and opal, are the most reactive forms. The high temperature materials, tridymite and cristobalite, and chalcedony, a fibrous form occurring in some chert, are also fairly reactive. The above forms can all be classed roughly as rapidly-reactive and typically will be classified as potentially deleterious by traditional tests such as ASTM C 227 and C 289 [11]. These rapidly-reactive forms often exhibit the pessimum effect, where the maximum expansion occurs when the aggregates contain a certain proportion of the reactive element. At proportions greater or less than the pessimum, the expansion is less. For example, an opal content in aggregate about 5 percent (the pessimum amount) yields the maximum expansion. Greater or lesser amounts of opal yield lower expansions, whereas, for some other mineral maximum expansion is achieved when aggregate consists of 100 percent of that mineral.

More slowly reacting forms of silica include metamorphically strained quartz, and micro crystalline quartz. These forms have been found to cause deleterious reactivity in concrete, although it may take longer to develop than with rapidly-reactive aggregates. These forms of silica are a primary constituent of quartzite, sandstone and sand and gravel. Chert, composed of microcrystalline quartz and sometimes chalcedony, is found in sand and gravel and some carbonate rocks. Unstrained quartz, may be found in granite and granitic gneiss appear to be the least reactive form of silica but has been associated with deterioration due to ASR [24]. The greater the porosity of the aggregate due to either its natural internal structure or fractures induced during crushing, the greater the extent of the reaction is due increased surface area of silica available for reaction.

Alkalies

The potential for ASR increases with the alkali content of the concrete. This is because the hydroxide ion concentration (alkalinity, pH) increases as the alkali content increases. Portland cement is usually the primary source of alkalies in concrete. Although these alkalies are reported as Na_2O and K_2O the readily soluble portions in the cement generally occur as alkali sulfates. Other internal sources include mineral and chemical admixtures; some aggregates (typically glassy volcanic rocks) and mix water. Deicing chemicals and seawater are external sources which supply alkalies to the pore solution.

Moisture

Water as a constituent of the pore solution in concrete is necessary for ASR to proceed. Concrete which is allowed to dry after proper curing and will remain dry in service is unlikely to be affected by ASR. However, concrete members with large cross-sections may retain enough residual moisture to cause reactivity even though they are in a dry environment.

Concrete which is in contact with ground or water or is periodically wetted will most likely contain sufficient moisture to cause reactivity. Moisture in excess of 80 percent relative humidity in concrete is necessary to cause the gel to swell [23]. A certain level of protection can be provided to concrete by decreasing the permeability, and thus the availability of external moisture to the system.

Fly Ash, Ground Granulated Blast-Furnace Slag, and Silica Fume

Fly ash, ground granulated blast-furnace slag (GGBF), and silica fume can be effective in preventing deleterious expansions resulting from ASR. The primary constituent in each of these materials is amorphous or glassy silica. Because they are fine grained they react very rapidly with the hydroxide ions in the pore solution forming a compound similar to that formed by the hydration of portland cement. This compound fills in spaces between the hydrated cement grains reducing the permeability of the concrete. It effectively ties up the alkalis thus reducing the potential for ASR.

Identification of ASR Distress in Concrete

There are three commonly used ways to identify the occurrence of ASR in a concrete structure. Visual signs include expansion and exudation of gel. Signs of expansion include cracks, closing of joints, and displacement of pavement in severe cases. The cracks will be either longitudinal or map-type. SHRP Handbook [25] is a very good photographic guide for showing ASR cracking in pavement.

The examination of hardened concrete by procedures in ASTM C 856 [11] petrographic practice can identify ASR. A gel fluorescence test was developed under SHRP to identify ASR gel in hardened concrete [25].

Evaluation of Materials and Environment

There are several methods for evaluating aggregates. They include:

Guide for Petrographic Examination of Aggregates for Concrete ASTM C 295 [11].

Test Method for Potential Reactivity of Aggregates (Chemical Method) ASTM C 289 [11],

Test method for Potential Alkali Reactivity of Cement-Aggregate Combinations (Mortar-bar Method) ASTM C 227 [11], and

Proposed Test Method for Accelerated Detection of Potentially Deleterious Expansion of Mortar Bars Due to Alkali-Silica Reaction (ASTM Proposed Method).

Wherever possible the results of the above tests should be used in conjunction with information obtained from the service record of the aggregates over a period of years in similar concrete exposed to comparable service conditions.

Alkalies are present in varying amounts in all portland cements primarily in readily soluble sulfate compounds. The alkali content is calculated on an oxide basis and reported as Na_2O equivalent. A limit of 0.06 percent Na_2O equivalent is listed in the optional chemical requirements of the portland cement specification ASTM C 150 [11]. This limit should be specified when portland cements may be used with aggregates which could be potentially deleteriously reactive. However, the 0.60 percent limitation on the alkali content does not always provide protection from ASR. Several factors play a role in such cases:

Alkalies are concentrated in the concrete due to cyclic wetting and drying,

Alkalies are contributed from other ingredients,

Alkalies are contributed from external sources, and high cement contents.

Blended hydraulic cements specified in ASTM C 595 [11] includes an optional mortar expansion requirement using test method ASTM C 441 [11] to evaluate effectiveness in preventing expansions due to ASR. The procedure discussed in the following paragraph on testing and evaluation is suggested. Fly ash specified in ASTM C 618 [11] should also be evaluated as discussed in the paragraph on testing and evaluation. Class F fly ashes generally have a lesser amount of available alkalies and contain larger amounts of silica and alumina which make them more effective than Class C fly ashes in minimizing the alkali-silica reaction. Silica fume is effective in reducing expansions caused by ASR in concrete provided the silica fume is completely distributed throughout the mixture during the concrete mixing. GGBF slag specified in ASTM C 989 [11] should also be evaluated as discussed in the paragraph on testing and evaluation.

Chemical admixtures have not been identified as being a significant contributor to ASR. However, chloride ions may increase the potential for expansion of ASR gel. Research has found the introduction of lithium salts prevent deleterious ASR. This was first revealed by McCoy and Caldwell [26] and extensive confirming research was recently done by SHRP [23].

Testing and Evaluation

Each material considered for use should be tested and evaluated in accordance with the appropriate ASTM procedure by a laboratory qualified to do the work.

ASTM C 441 [11] is the test method for evaluating the effectiveness of fly ash, GGBF slag, and silica fume in reducing expansions caused by ASR. The procedure is similar to ASTM C 227 [11] but uses pyrex glass as a standard reactive aggregate. A criteria of a maximum of 0.02 percent expansion at 14 days is the recommended limit. This test method and criteria should not be used because of difficulties in reducing expansions below this limit.

An alternative is to determine the expansion of a control and test mixtures. Each mixture uses 900 grams of pyrex glass aggregate as specified in ASTM C 441 [11]. The amount of mixing shall be that needed to produce a flow of 110 to 115 as determined by ASTM C 109 [11]. The control mixture shall be made with 400 grams of portland cement with an equivalent alkalis of 0.50 to 0.60 percent. The test mixture shall be made with a portland cement with a total alkali content exceeding 0.08 percent and blended with fly ash, GGBF slag or silica fume or with a blended hydraulic cement. The total weight of the cement plus fly ash, GGBF slag, or silica fume or blended hydraulic cement shall be 400 grams. Except for proportioning of the mortar, prepare, store, and measure the specimens as required by the applicable sections of ASTM C 227 [11]. The 14 day expansions of the test mixture shall be no greater than the control mixture.

It has been proposed by others that the proposed ASTM test method be used to test the effectiveness of fly ash, GGBF slag, or silica fume or blended hydraulic cements [23].

Mechanism of Alkali-Carbonate Reaction

Alkali-carbonate reaction (ACR) occurs between the hydroxide ions in the alkaline pore solution in concrete and carbonate aggregates which are characterized by the presence of discrete crystals of dolomite. The reaction is believed to involve dedolomitization producing calcium carbonate and alkali carbonate, while releasing magnesium ions which combine with hydroxide ions to form brucite. In a subsequent process, the alkali carbonate reacts with calcium hydroxide to form calcium carbonate and alkali hydroxide. Thus the alkalies which originally involved in attacking the dolomite are released back into the pore solution for further assault. The expansion which accompanies this reaction is not completely understood, is believed to be related to the swelling of the interstitial clay caused by association with alkaline pore solution [27].

Factors Contributing to Alkali-Carbonate Reactivity

Aggregates which are susceptible to ACR seem to exhibit a characteristic lithology. They consist roughly equivalent amounts of calcite and dolomite with an insoluble residue

of 10 to 30 percent consisting primarily of clay minerals. They are usually dark colored, fine grained, and exhibit conchoidal fracture. The distinctive microtexture identifiable in thin sections is a rhombs of dolomite, roughly 25 microns across, floating in a fine grained matrix of calcite and clay.

The amount of ACR expansion is directly related to maximum size of the aggregate particle and the amount of reactive constituent in the rock. As either increases, the amount of concrete expansion increases. Factors that cause ASR, i.e., source of alkalies and moisture are also the same factors that cause ACR.

Identification of Alkali-Carbonate Reactivity Distress In Concrete

ACR causes expansions of concrete and, as such, the outward manifestations of distress are similar to ASR or any other process which causes differential volume change in a mass. Most evident will be map and pattern cracking. If the pavement is restrained in a particular direction, the cracking will align itself in that direction. Signs of expansion include closing of joints, offsets or misalignments, crushing of concrete, and pavement blowups. Petrographic examination by ASTM C 856 [11] has to be used to confirm expansion distress is caused by ACR.

Evaluation of Materials

ASTM C 289, C 227, and proposed ASTM test method [11] are appropriate for determining ACR. Petrographic examination of the aggregate by ASTM C 295 [11] and the Handbook of Concrete Aggregates [28] should be used. Rocks suspected of being reactive on the basis of compositional and textural characteristics should be subjected to further testing by the rock cylinder test ASTM C 586 [11]. The concrete prism test, ASTM C 1105 [11] is a method to determine the potential of ACR in concrete. However, this test method is time consuming requiring 6 to 12 months for results. Service record may also be evaluated.

Minimizing Potential for Alkali-Carbonate Reactivity Distress

When the concrete's service environment is conducive to ACR and the aggregate to be used is potentially reactive, several factors should be considered to reduce the risk of deleterious expansion.

1. The amount of expansion is directly related to the amount of reactive rock in the aggregate.
 - a. Carbonate rocks are stratified. If layers containing the reactive lithology can be identified, they can be avoided in the quarrying process.
 - b. Reactive rocks can be blended with non-expansive aggregates.