

Appendix D Alkali-Silica Aggregate Reactions

D-1. Alkali-Silica Aggregate Reactions

a. General. The use of certain aggregates in concrete may result in a chemical process in which particular constituents of the aggregates react with alkali hydroxides dissolved in concrete pore solutions. These alkali hydroxides are derived mostly from the sodium and potassium in portland cement and other cementitious materials, but occasionally alkalis may be introduced into concrete from external sources or may be released slowly from certain alkali-bearing rock components within the aggregate. While many aggregates may react in concrete, distress in structures is observed only when significant amounts of expansive reaction products are formed, and they take up water and expand. The reaction products concerned are hydrous gels whose chemical composition always includes silica, alkalis, and at least a little calcium. The silica component is always derived from the reactive aggregate, which is usually an amorphous or metastable crystalline form of silica; sometimes it is a more complex assemblage of fine-grained silicate components. Some authorities distinguish between "alkali-silica" and "alkali-silicate" reactions, but the distinction is not clear cut. By itself, the formation of alkali-silica reaction product creates little distress; the damage in concrete is associated with subsequent expansion and cracking that occurs when the reaction product gel absorbs water and swells. Keeping affected concrete dry often prevents or at least mitigates the deleterious response. Alkali-aggregate reactions were first observed in California in the 1940's but have subsequently been recognized in many countries. In the United States, alkali-silica reactive aggregates are more common in western and southwestern states; in certain parts of the Southeast, including especially Alabama, South Carolina, and Georgia; and in some of the Great Plains states.

b. Nature of the reaction. Field evidence for the occurrence of alkali-silica reaction in a given concrete includes expansion and development of polygonal or map cracking as a characteristic feature, especially when accompanied by gel deposits exuding from the cracks. However, a number of other causes of distress may show superficially similar features, and a petrographic examination of the affected concrete is generally necessary to confirm that alkali-silica reaction is actually taking place. Generally speaking, the higher the alkali content of the cement used, the higher the resulting alkali-hydroxide concentration and pH and the greater the potential for alkali-silica attack. The specific reacting agent is the hydroxide

ion itself. The hydroxide ions break Si-O-Si bonds in the reactive silica or siliceous aggregate components, thus breaking up their cross-linked structure and isolating and dissolving individual silica tetrahedral units. In the absence of calcium, such reaction merely produces dissolved silica. However, in the presence of the solid calcium hydroxide always found in hydrated cement, an alkali-silica gel containing some calcium is formed. In the past, it has been suggested that only gels of minimum calcium content were expansive and gels of higher calcium content were limited swelling gels not capable of causing distress, but some workers now suggest that this seems not to be the case. One of the common petrographic features of alkali-silica reaction is the occurrence of a zone immediately surrounding the reacting aggregate particle in which the cement paste is partially or wholly depleted of calcium hydroxide, the latter having been incorporated into the gel. The actual distress in concrete is associated not with formation of the gel product but with subsequent expansion taking place when gel absorbs water (or solution) and swells. The swelling pressure generated may be of the order of 7 MPa (1,000 psi), sufficient to crack the surrounding paste. If many aggregate grains have reacted to form gel and if sufficient water is available, the combined effect results in macroscopic swelling and eventually a visible crack pattern develops. In some concrete structures that are geometrically sensitive, the irregular expansion itself may be highly damaging to proper functioning, even if visible cracks or other evidences of concrete deterioration are hardly developed. Reactions with strained quartz and with reactive silicate aggregates generally are slower than other alkali-silica reactions, but slow expansion may continue for many years. Such reactions may produce comparatively little reaction gel and are particularly difficult to identify without petrographic examination. Among the unusual features of the alkali-silica reaction is the existence of a so-called "pessimum effect." If mortars or concretes are made using varying proportions of reactive and inert aggregate, the expansion may be greatest for a mixture with a comparatively small proportion of the reactive component. The proportion giving rise to the greatest expansion is the pessimum proportion. This proportion is particularly low with opal. With most other common types of reactive aggregate, the pessimum proportion is usually higher, and in some cases, it is 100 percent, i.e., the pessimum effect does not occur.

D-2. Criteria for Recognition of Potentially Deleterious Constituents in Aggregate

A number of siliceous components of aggregates may be potentially reactive. Reactive aggregate components may be found in igneous, sedimentary, or metamorphic rocks of

various textures and ages. Among the more commonly encountered reactive aggregate components are:

a. Reactive substances.

(1) Opal. Opal is a variety of amorphous silica with a porous internal structure which contains water. Opal may occur in cherts, volcanic rocks, shales, sandstones, and carbonate rocks; frequently, it may occur in segregated forms in cavity fillings, crack linings, or as cementing material in concretions. Opal is the most reactive of the various reactive aggregate components ordinarily encountered and may cause damage in concrete when as little as a fraction of a percent is present in the aggregate.

(2) Chalcedony. Chalcedony is a siliceous component of some cherts; microscopically it is distinguished by radiating sheaf-like or fibrous structures embedded in a groundmass from which they cannot be separated. Chalcedonic material is largely very fine quartz, but amorphous silica may be present as well.

(3) Volcanic glass. Particles of volcanic glass or sometimes devitrified volcanic glass in aggregates may be reactive, depending on composition. Acid glasses (those of silica content above 65 percent) and intermediate glasses (of silica contents between 55 and 65 percent) are commonly reactive; more basic glasses (silica content below 55 percent) are less so. Reactive glasses may be identified by refractive indices below 1.57. The presence of water in volcanic glasses seems to be associated with reactivity.

(4) Tridymite and cristobalite. These are crystalline forms of silica that are metastable at ordinary temperatures but that may be found in various igneous rocks, especially andesites and rhyolites.

b. Other potentially reactive substances. In addition to these substances just listed, the following may also be reactive:

(1) Quartz. Well crystallized quartz may be reactive and may give rise to problems in concrete if the crystals are strained and finely crushed material produced as in fault zones (mylonite) by virtue of previous geological activity. Strained quartz can be detected petrographically by measurement of the undulatory extinction angle. Rocks such as granites and sandstones may thus be suspect if the formations from which they are derived have a history of extensive metamorphic activity.

(2) Silicates. Various sedimentary or metamorphic rock types containing clays or micas have been observed to

be reactive. Such rock types include graywackes, argillites, phyllites, siltstones, etc. There is considerable dispute as to whether the reactive component is finely divided quartz or amorphous silica within the rock or whether the reaction involves the clay mineral or mica components. Alkali reactions with such rock types tend to be unusually slow and may escape detection by the normal screening tests for reactive aggregate. If aggregate to be used contains significant contents of such rock types, low-alkali cement should be used where available. If not available or if it is available only at greatly increased cost, additional studies may be required and HQUSACE should be notified (Attention: CECW-EG).

(3) Sandgravel. "Sandgravel" aggregates in parts of Kansas, Nebraska, and Wyoming, especially those from the Platte, Republican, and Laramie Rivers, have been involved in the deterioration of concrete. Aggregates from these areas should be viewed with suspicion unless an acceptable service record has been compiled or no reactive constituents are found on petrographic examination.

(4) Disseminated silica in limestones. A number of instances of alkali silica reactivity leading to serious distress have been observed with limestone aggregate that contains small amounts of dispersed silica, often skeletal remains of small organisms. The fact that limestone aggregates may not be of the characteristic dolomite composition and impurity content that results in alkali-carbonate reaction does not preclude the possibility of alkali-silica reaction if disseminated reactive silica exists in the material.

D-3. Methods of Determining the Potential for Reactivity

a. Standard methods.

(1) American Society for Testing and Materials (ASTM) C 227 (CRD-C 123) - "Potential Alkali Reactivity of Cement-Aggregate Combinations (Mortar-Bar Method)."* In this method the length change of mortar bars prepared with the aggregate in question (prepared to a specified particle size distribution) and either high-alkali or the specified job cement is measured over a 1-year period.

* Test methods cited in this manner are from the *Annual Book of ASTM Standards* (ASTM 1992) and from the *Handbook of Concrete and Cement* (U.S. Army Engineer Waterways Experiment Station (USAEWES) 1949), respectively. References cited in this appendix are given in Appendix A of this EM.

(2) ASTM C 289 (CRD-C 128) - "Potential Reactivity of Aggregates (Chemical Method)." In this so-called "quick chemical test," finely crushed aggregate is immersed in concentrated sodium hydroxide and heated under pressure for 24 hours. The reaction is monitored by subsequent determination of the amount of dissolved silica and the degree of reduction in the alkalinity of the solution. This test gives an indication of possible reactivity but is not sufficiently definitive to be used alone without additional testing.

(3) ASTM C 295 (CRD-C 127) - "Petrographic Examination of Aggregates for Concrete." This is the procedure for petrographic examination of aggregates, including the determination of whether potentially deleterious components are present. The services of a qualified petrographer are required.

(4) A test method involving measurement of length change of concrete prisms rather than mortar bars has recently been adopted by the Canadian Standards Association (CSA) (CSA A23.2-14A 1986). It is intended to overcome criticism of other tests that they do not involve concrete specimens.

b. Nonstandard methods of determining the potential for alkali reactivity.

(1) General. A number of nonstandard methods have been developed to determine potential reactivity of aggregates. Noteworthy among these is the osmotic method described by Stark, high-temperature accelerated test described by Oberholster and Davies (1986), and two very recent rapid tests: a staining procedure developed by Poole, McLachlan, and Ellis (1988) and a fluorescent method reported by Natesaiyer and Hover. While none of these procedures has yet replaced any of the standard methods of test for reactive aggregates, they may constitute useful supplementary tests that can be carried out relatively quickly. Most of them require some special apparatus.

(2) Osmotic method. In the osmotic method, powdered aggregate is immersed in sodium hydroxide and separated by a cement paste membrane from a reservoir of sodium hydroxide of the same concentration. The osmotically induced flow of the fluid from the reservoir to the solution containing the aggregate is monitored, and if it exceeds a specified amount in several weeks, the aggregate is considered reactive.

(3) Accelerated test. In the high-temperature accelerated test, mortar prisms made according to the procedure of ASTM C 227 (CRD-C 123) are immersed in

a one-normal sodium hydroxide solution at 80 °C (176 °F) for 12 days with measurements of expansion made daily. An expansion of 0.11 percent or greater over this period is taken as indicating that the aggregate is deleteriously reactive.

(4) Staining test. In the staining procedure, the potentially reactive rock is reacted with a special alkali solution so that the gel formed gives rise to a blue-colored complex; the intensity of the color is measured and related to the reactivity of the rock.

(5) Fluorescence test. In the fluorescence method, uranyl acetate solution is applied to the concrete; if gel has formed, uranyl ions are quickly exchanged for alkali ions. The presence of such uranyl-bearing gel is easily observed by examination under ultraviolet light.

D-4. Reliability of Available Test Methods

a. General. Despite continuing research and improvements, none of the standard methods can be relied on independently or collectively to provide an unquestionably definitive answer, especially to the question of whether seriously deleterious reaction should be expected if small amounts of moderately reactive components are discovered.

b. Petrographic examination. The results of petrographic examination by an experienced petrographer should provide an indication of the presence of any potentially reactive components in the aggregate. The mortar-bar test should provide an indication of whether any reactions taking place will be extensive enough to induce unacceptable levels of expansion. Thus, combining the results of petrographic examination with mortar-bar expansion test results is considered to be the most reliable way to predict possible excessive expansion using the standard test procedures. However, contradictory indications will sometimes be provided by the results of the two methods, and both methods entail certain uncertainties. Petrographic examination requires interpretation, and small amounts of certain important components, especially opal, can readily be missed. Mortar-bar tests require at least 6 months and may not even then detect certain slow forms of reactivity. Furthermore, the reproducibility of the mortar-bar test is not high.

c. Quick chemical test. The quick chemical test is generally considered to be of limited reliability; its major advantage is that it can be accomplished in little more than a day. Spurious results may be obtained in the presence of carbonate rock components.

d. Test samples. All of these methods require that the small volume of aggregate sample examined be truly representative of the very large and often inhomogeneous deposit being sampled. This often poses an impossible condition, even when standard methods of aggregate sampling (e.g. those specified in ASTM D 75 (CRD-C 155) and ASTM D 3665) are employed.

e. CSA concrete test. The CSA concrete test was designed to provide a rapid indication of reactivity particularly with a fine-grained silicate rock. Unfortunately, since no minimum expansion limit is prescribed, interpretation of the results are difficult.

f. Osmotic test. The osmotic test has been used for a number of years by the Portland Cement Association and its Construction Technology Laboratories Division and appears to give promising results. Similarly, the accelerated high temperature test has been used for a few years by the National Building Research Institute in South Africa, and it too appears promising for future adoption. The staining and fluorescent analysis procedures are so new that their reliability has not been assessed.

D-5. Criteria for Evaluating Potential Reactivity

a. General. The fine and coarse aggregates suggested for use in a given concrete mixture should be evaluated separately for potential reactivity, regardless of whether or not they come from the same source.

b. Petrographic analysis results. A fine or coarse aggregate will be classified as "potentially deleteriously reactive," i.e. capable of causing damage to concrete made with high-alkali cement, if the petrographic examination reveals any of the following:

- (1) Presence of any opal.
- (2) More than 5 percent of particles of chert in which any chalcedony is detected.
- (3) More than 3 percent of particles of glassy igneous rocks in which any acid or intermediate glass is detected.
- (4) More than 1 percent of particles in which any tridymite or cristobalite is detected.
- (5) More than 20 percent of particles containing strained quartz in an aggregate in which the measured average extinction angle is at least 15 degrees.

(6) More than 15 percent of particles consisting of graywacke, argillite, phyllite, or siltstone containing any very finely divided quartz or chalcedony.

c. Mortar-bar results. A fine or coarse aggregate will be classified as "potentially deleteriously reactive" if the expansion measured in tests with cement containing not less than 1.0 percent alkalis calculated as Na_2O is more than 0.05 percent at 6 months or 0.10 percent at 1 year. Additionally, the following interpretations should be made:

(1) Measured expansions greater than 0.10 percent at any age are indications that the aggregate should be regarded as potentially deleteriously reactive.

(2) Measured expansions greater than 0.05 percent at 6 months but less than 0.10 percent at 1 year usually indicate that the aggregate is not deleteriously reactive, but in borderline cases, the slope and trend of the length change versus time curve should be examined for assistance in interpretation.

(3) If the aggregate contains strained and very finely divided quartz, but either the content of such particles or the degree of strain is such that the criteria mentioned previously for strained quartz aggregate are not exceeded, additional special mortar-bar tests should be carried out. In these tests the mortar bars are made using a nonreactive fine aggregate, but five particles of a size between 12.5 and 19.0 mm (1/2 to 3/4 in.), consisting entirely or mostly of the strained quartz, are inserted into each bar. The bars are stored under conditions of 100 percent RH and a temperature of $60 \pm 5 \text{ }^\circ\text{C}$ ($140 \pm 10 \text{ }^\circ\text{F}$). The aggregate so tested will be considered potentially deleteriously reactive if expansion at 6 months exceeds 0.025 percent or expansion at 1 year exceeds 0.04 percent. These special criteria are invoked because of the observed slow rate of expansion of concrete containing reactive strained and very finely divided quartz.

d. Quick-chemical test criteria. A fine or coarse aggregate will be classified potentially deleteriously reactive or deleteriously reactive if the data point plotted for it falls to the right of the line on the standard graph accompanying the description of the test method.

e. Service record. A fine or coarse aggregate will be classified as potentially deleteriously reactive when service records establish that excessive expansion due to alkali-silica reaction has occurred in a structure in which the aggregate has been used. Where service records indicate deleterious

reactivity, the aggregate should be so classed, regardless of laboratory test results. As previously indicated, the laboratory test methods cannot be absolutely relied on, individually or collectively, to provide an unquestionably positive indication of potentially excessive expansion. Every effort should be made to obtain prior performance records, especially where cements of high-alkali contents have been used, and especially if exposure conditions have been similar to those predicted for the proposed work. It should be noted that some reactions occur slowly and take years to become evident. Care should be taken on younger structures.

f. Blended aggregates. If either the coarse or fine aggregates for a project will be blended from aggregate derived from two or more sources, the combined coarse or fine aggregate, in the proportion intended for use, will be evaluated for potential reactivity. In the petrographic examination, the estimated amounts of potentially deleterious constituents present will be calculated by the method of weighted averages, using the proposed grading of the blended coarse or fine aggregate. For the mortar-bar test, where fine aggregate is to be blended from two or more sources, each sieve fraction used in the test shall be in proportion to that sieve fraction in the proposed blended fine aggregate. For blended coarse aggregates, the crushed material from which the test mortars are prepared shall include all of the rock types occurring in the combined coarse aggregate, in the percentages of each size group anticipated for the combined grading of the project aggregate. Similar procedures should be used to select aggregate to be powdered for sample material for use in the quick-chemical test.

g. Application of standard test criteria. It is preferred that each fine or coarse aggregate be evaluated based on a combination of service record, petrographic examination, mortar-bar, and quick-chemical test results. If the indications disagree, aggregates are to be considered potentially deleteriously reactive if so indicated by the following combinations of tests:

- (1) Service records and mortar-bar test results.
- (2) Service records and petrographic examination.
- (3) Mortar-bar test results and quick-chemical test results.
- (4) Petrographic examination and quick-chemical test results.
- (5) If in the absence of mortar-bar test results,

petrographic examination indicates that the aggregate is potentially deleteriously reactive, but this is not confirmed by either service record or results of the quick-chemical test, the aggregate should not be used until the results of mortar-bar testing can be obtained.

D-6. Control of Alkali-Silica Aggregate Reactions

Aggregates considered potentially deleteriously reactive should not be used in concrete that will be exposed to moisture in service. If such use is unavoidable, suitable precautions must be taken to minimize the probability of harmful internal expansion and cracking. Such precautions include the following:

a. Use of low-alkali cements. If it appears likely that low-alkali cement, i.e., cement meeting the optional requirement for low-alkali content of ASTM C 150 (CRD-C 201) will be available at little or no increase in cost, this optional requirement should be invoked and such cement used. However, experience has indicated that such use does not provide a complete guarantee that no distress will be experienced, especially if (a) the structure is a slab on grade exposed to relatively high temperature and low relative humidity conditions so that the alkalis become concentrated in the region near the surface, (b) alkali from external sources can be expected to penetrate the concrete, or (c) alkalis are released internally from certain aggregate components as a result of reaction with cement hydration products.

b. Use of slag or pozzolans. If low-alkali cement is not available or available only at excessive cost, the use of a GGBF slag or a mineral admixture such as a pozzolan (fly ash, silica fume, or natural pozzolan) (or a blended cement containing such a component) is indicated. These components effectively absorb hydroxide ions and alkali ions from the concrete pore solutions, thus reducing the driving force for the deleterious alkali-silica chemical reaction with aggregate. While blended portland blast-furnace slag cements are not widely available, separately batched GGBF slag may be used to provide a GGBF slag-portland-cement concrete highly resistant to alkali-silica attack. Silica fume added in much smaller percentages than slag has also been highly effective, although the cost involved may be high. Some slags, fly ashes, and other pozzolans provide effective protection against the alkali-silica reaction, some do not. Fly ashes and natural pozzolans must meet the requirements of ASTM C 618, Table 2A, Supplementary Optional Physical Requirements, Reactivity with Cement Alkalies, to be considered effective. Slag must meet the requirements of ASTM C 989, Appendix X3, to be considered effective. These

specifications give criteria for determining the effectiveness of the material. Silica fume should be considered a pozzolan for this discussion and should be evaluated per ASTM C 618.

c. Determination of the minimum amount of pozzolan or slag to use to control alkali-silica reaction.

(1) The proposed material should be given a preliminary characterization by a combination of physical, chemical, and petrographic methods to assure that it is a reasonable candidate material and that it meets the applicable specifications.

(2) Prepare four mortar mixtures according to ASTM C 441 (CRD-C 257). Use the proposed cement or high-alkali cement and Pyrex glass as the aggregate on the assumption that if the candidate pozzolan (fly ash, silica fume, or natural pozzolan) or slag will control this combination, it will control the actual job materials. Pyrex glass is preferred since its pessimum amount is 100 percent. This avoids the need to conduct tests to determine the pessimum amount of reactive material in the actual aggregate and possible fluctuations in test results due to nonuniformity of the aggregate. A control mixture without pozzolan or slag should be made.

(3) Test the bars from these mixtures by ASTM C 441 (CRD-C 257) for a minimum of 14 days, longer if possible.

(4) Evaluate the expansion data to determine the amount of slag or pozzolan needed to keep expansion from exceeding the criteria given in the appropriate specifications.

(5) This is the amount to use in the concrete. If may be necessary to make slight modifications to the intended concrete mixture to assure desired workability or strength gain or other needed properties.

(6) Once a material and its amount to use has been selected, the continued suitability of this material during the duration of construction should be periodically monitored by selected physical or chemical or petrographic methods or a combination of these. For example, one might use fineness, silica content, or relative amount of glass. Similar monitoring should be used for the cement. The frequency

of testing and parameters to be used must be determined and documented in the concrete materials design memorandum.

(7) It is desirable to approximate the actual environmental conditions during the laboratory testing. If there is a significant source of alkali from the environment, it may affect the control provided by the pozzolan or slag and could necessitate the use of nonreactive aggregate.

d. Decreasing the availability of water. Concretes batched at low w/c have only a limited supply of internal water needed to cause the alkali-silica reaction product gel to swell, and the permeability of such concretes to outside water is also reduced. Thus, the deleterious consequences of the alkali-silica reaction may be slowed down significantly. Experience has also indicated that when concrete dries sufficiently that the relative humidity in the pores of the concrete falls below and remains below 80 percent, no adverse expansion occurs. However, the chemical reaction is not necessarily precluded, and subsequent rewetting may produce rapid and serious expansions.

e. The sandgravel problem. So-called sandgravel aggregates derived from river-transported deposits along the Platte, Republican, Laramie, and several other rivers in the Great Plains states (notably Kansas, Nebraska, Colorado, Wyoming, and to a lesser extent Iowa and Missouri) cause characteristic problems in concrete. In part, these difficulties are due to the poor grading of these materials, but alkali-aggregate reactivity is associated with glassy volcanic components in the western part of the region and opal combined with lesser amounts of volcanic glass to the east. Neither the use of low-alkali cements nor the use of pozzolans have completely succeeded in controlling the problem. Accordingly, aggregates from these sources should be avoided if economically feasible to do so. If this is not feasible, replacement of at least 45 percent of the aggregate with crushed limestone appears to be an effective remedy when combined with the use of low-alkali cement.

f. Decreasing the amount of reactive aggregate. It may be economical to use some proportion of local reactive aggregate with the rest being more expensive imported nonreactive aggregate, rather than use all imported aggregates. The proportion of reactive aggregates that can safely be used must be carefully investigated.