# Use of Admixtures to Prevent Excessive Expansion of Concrete Due to Alkali-Silica Reaction

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In the reports of the American Concrete Institute Committee 212 on Admixtures, beginning in 1954, reference was made to the use of admixtures, both chemical and mineral, to prevent excessive expansion of concrete caused by the alkali-silica reaction. Work on this topic began at least as far back as 1947. Few data on the use of admixtures for this purpose in field concrete are known to have been published. Laboratory test results suggest that mineral admixtures are effective in smaller and smaller amounts as the silica content, silica solubility, and fineness increase. Ground granulated iron blast-furnace slag, a hydraulic cement (often incorrectly called a mineral admixture), is highly effective when used to make up 60 percent or more of the cementitious medium. Its effectiveness probably derives from its ability to reduce the permeability of concrete to $\frac{1}{10}$ to $\frac{1}{100}$ that of concrete of equal strength made using portland cement alone. Similar effects may occur when mineral admixtures are used. The use of chemical admixtures based on soluble salts of lithium has been referred to in the literature for many years and was reexamined in detail by Stark in 1992 in the recent Strategic Highway Research Program project on alkali-silica reaction. It may be technically feasible, but it may not be cost-effective.

To discuss the role of admixtures in preventing excessive expansion of concrete due to alkali-silica reaction, it is first necessary to define some terms and review some of the mechanisms involved in alkali-silica reactions. American Concrete Institute (ACI) 116R-90 defines an admixture as "a material other than water, aggregates, hydraulic cement, and fiber reinforcement, used as an ingredient of concrete or mortar, and added to the batch immediately before or during its mixing." Ground granulated iron blast-furnace slab (ggbfs) is a hydraulic cement, so it is not, by definition, an admixture.

ACI 116R-90 defines alkali-silica reaction as "the reaction between the alkalies (sodium and potassium) in portland cement and certain siliceous rocks or minerals, such as opaline chert, strained quartz, and acidic volcanic glass, present in some aggregates; the products of the reaction may cause abnormal expansion and cracking of concrete in service."

It is not the alkalies that cause the thermodynamically metastable silica to gelatinize, but the high pH of the aqueous phase of the concrete that is created by the association of hydroxide ions with sodium and potassium ions in the solution. This association comes about after the chloride or sulfate or other ions with which the sodium and potassium were associated (before going into solution) have precipitated out in relatively insoluble hydration products such as calcium sulfoaluminate or calcium chloroaluminate.

## BACKGROUND

The occurrence of alkali-silica reaction was first reported by Stanton (*1*). However, when ACI Committee 212 on Admixtures published its first report (*2*), the only paper by Stanton that was cited was his 1938 paper on attack by sea water and "alkali" soils (*3*). Although the word "alkali" is used, it is clear that he means sulfate attack. He does report that "durability of a cement can be increased . . . by intergrinding a siliceous admixture [sic] with the cement clinker; even a clinker relatively high in $C_3A$" (*3*,p.443). This conclusion was based on experiments using portland-pozzolan cements as well as portland cements of differing calculated $C_3A$ content. Some of his cements contained the pozzolan, ground calcined Monterey shale. His fifth conclusion is as follows: "A non-durable standard cement can be made more durable by the use of a good siliceous admixture." The same conclusion could be restated with no change at the end of this paper.

It is worth noting that the paper immediately following the 1944 report of ACI Committee 212 is Tremper's paper "The Effect of Alkalies in Portland Cement on the Durability of Concrete" (*4*).

By 1954, when Committee 212 released its second report (*5*), there were two relevant categories—pozzolans, and . . . alkali-aggregate expansion inhibitors"—and one stated objective of the use of admixtures was "control of alkali-aggregate expansion." In the latter section, it is stated: "certain . . . pozzolans are capable of reducing the expansion caused by high-alkali cements . . . used . . . with reactive siliceous aggregates." The report says that effective pozzolans are those containing "amorphous" siliceous or siliceous and aluminous substances such as opal, certain volcanic glasses, diatomaceous earths, calcined clays, and fly ash. It is also noted that McCoy and Caldwell found lithium salts to be effective (*6*).

## RECENT STATUS

The third report was published in 1963 (*7*). Section 8 included a section on the use of finely divided mineral admixtures for reducing expansion caused by alkali-aggregate reaction, and Section 11 discussed chemical admixtures to reduce alkali-

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aggregate reaction. In the former it noted that Hanna was the first to recommend using pozzolan to prevent expansion due to alkali-aggregate reaction (*8*). The committee then noted that "there have been only a few instances in which an admixture has been used in concrete containing known reactive aggregates and a known high-alkali cement and the pozzolan relied on to prevent the expected excessive expansion. Performance data on these projects are not available to the committee." I wrote these words. Originally, instead of "only a few" I wrote "no," but I was told that there were "a few." I still have no citations of performance data on them or any others. At the Ninth International Conference on Alkali-Aggregate Reaction in Concrete in 1992, I listened with some care for reports of such cases. There may have been one, as I will discuss later (*9*). There was a report (*10*) that an aggregate now known to be reactive and a cement now known to be high alkali had been used together in more than one construction, at least one of which also contained a pozzolan—the use of which was in no way intended to control expansion by alkali-aggregate reaction, but it had nevertheless done so, not surprisingly. So long as low-alkali cement is not much more expensive per unit quantity than cement not required to be low alkali, there is little or no incentive to establish that there is a more cost-effective method of dealing with alkali-aggregate reaction expansion involving the use of pozzolan or ggbfs.

## DANGER OF USING TOO LITTLE POZZOLAN

In the 1963 report a caution was sounded:

> Certain materials when finely divided and of high opal content (e.g., certain diatomaceous earths and opaline cherts) will prevent expansions when used in amounts of less than 15 percent by weight of the cement. In proportions of 10 percent or less by weight of the cement, certain pozzolans may increase expansion of concrete containing reactive aggregate and high-alkali cement, presumably because interaction of a portion of the cement alkalies with the pozzolan produces a ratio of reactive silica to the available alkalies which more closely approaches the pessimum for formation of expansive alkali-silica gel.

No reference was given. This problem has received little reported attention since 1963, but it has remained to worry people.

Helmuth said,

> If the quantity of reactive aggregate is very large or if the specific surface is very high, the available alkalies are distributed in low concentration over the reactive surfaces and the expansion rate is very low. If there is very little reactive aggregate or aggregate surface for reaction of alkali, the rate of expansion is also reduced. At a certain proportion, dependent on aggregate type and fineness, the expansion will be at a maximum; this is referred to as the "pessimum" proportion. Maximum expansion may occur with small proportions of highly reactive material. This is the reason for the 15% lower limit of pozzolan content of ASTM Type P and IP cements and for the six tests for alkali reactivity of pozzolans in Type I (PM) [pozzolan-modified] cements in ASTM C595 (See Table 1.3) (*11*).

ASTM C595-89 provides in Section 10.1.13 ["Mortar Expansion of Pozzolan for Use in Pozzolan-Modified Portland Cement Types I (PM) and I (PM)–A"] that

> using the pozzolan and the clinker or cement that are to be used together in the production of the blended cement, prepare pozzolan-modified portland cements containing 2.5, 5, 7.5, 10, 12.5, and 15 weight [sic] % of the pozzolan. These blends shall be tested in accordance with Test Method C 227 using a sand judged to be a nonreactive by the mortar bar test in Test Method C 227. The expansion of the mortar bars shall be measured at 91 days and all the six blends shall meet the expansion requirement of Table 3.

The requirement of Table 3 is "mortar bar expansion at 91 days, max, % 0.05."

Popovics says that expansion can be prevent by replacing "a portion of the cement with certain fine powdered materials containing reactive silica, such as pozzolan, in the quantity of 20 g of reactive silica for each gram of alkali in excess of 0.5% of the weight of cement (Powers & Steinour, 1955 [*12*]; Mehta & Polivka, 1976 [*13*])," but "note that inadequate amounts of reactive silica would increase, rather than reduce, the expansion" (*14*,p.217). Vivian reported that the maximum expansion of mortar bars with amounts of opaline rock ranging from 0.02 to 40.0 percent took place when the amount was 5 percent, that is, about 60,000 particles per bar (versus 240 at 0.02 percent or 480,000 at 40.0 percent (*15*).

ACI 226.3R-87 makes no mention of possible harm resulting from use of too little fly ash but emphasizes throughout the discussion of effects of fly ash on alkali-silica reaction (Section 2.2.13) the need for "suitable quality and quantity," possibly implying a performance basis for selection of amount to use.

Diamond discusses the use of pozzolans to mitigate the effects of alkali-aggregate reactions but does not address the issue that a little could make it worse (*16*). Tuthill wrote

> The amount of pozzolan needed in concrete to control reactive expansion will vary with the individual pozzolan, aggregates, and with the alkali content of the cement. . . . As a safety precaution against the possibility of increased alkali-silica expansion in concretes containing small (pessimum) amounts of certain pozzolans less than 10 percent by weight (sic) of the cement, ACI Committee 212 (Mather, 1971 [*17*]) advises that pozzolans should not be used in amounts less than about 15 percent by weight of total cementitious material (*18*).

The ACI 212 report said, "The use of too small a proportion of pozzolan may actually increase detrimental effects of alkali-silica reaction" (*17*). Its reference is to Stanton, who reported results of tests in which he used finely divided reactive aggregates as pozzolans (*19*). He found that 1½ to 5 percent of ground opaline chert accelerated and magnified the expansion.

In summary, I believe that what this means is never to use fly ash or a natural pozzolan in an amount less than 15 percent by mass of the cementitious material. ASTM Committee C01 should probably revise C595 to delete Type I (PM). Research should be conducted to see whether there are conditions under which small amounts of silica fume (i.e., less than 15 percent by mass of the cementitious materials in concrete) can increase expansion when high-alkali cement is used with reactive aggregate. I am not aware that any research has been reported that shows that this has happened.

## 1981 STATUS

The 1981 report of ACI 212 (212R-81) discusses the effects of mineral admixtures on expansion caused by alkali-aggregate reaction in 6.10 and chemical admixtures to reduce alkali-aggregate expansion in 7.11. In 6.10 the report says that "almost any pozzolan when used in sufficient quantity is capable of preventing excessive expansion" and cites References 58 and 120: Reference 58 does not deal in any way with alkali-aggregate reaction, and Reference 120 is to Pepper and Mather, who reported results of work using cements of different alkali content and a variety of mineral admixtures, ggbfs, natural cement, and ground quartz (*20*). On the basis of expansion tests of mortar bars with high-alkali cement and Pyrex glass, they found that to reduce expansion by 75 percent at 14 days, the amount of the portland cement that needed to be replaced ranged from 10 to 45 percent by mass. It was shown that the amount of replacement decreased as the silica content, the solubility of the silica in NaOH, and the fineness of the replacement material increased. The Type F fly ashes used required 40 to 44 percent, a very fine synthetic silica glass of 98.6 percent $SiO_2$ required only 10 percent, and ggbfs needed to be used at 45 percent of the cementitious medium. In 7.11 the committee indicates little change in the state of the art since its 1963 report.

## 1989 STATUS

In 1989 ACI 212.3R was published, mineral admixtures having been assigned to ACI Committee 232 on Fly Ash and Natural Pozzolans. 212.3R-89 in Section 6.11 speaking of chemical admixtures to reduce alkali-aggregate expansion indicated no change since Committee 212's 1963 report (*7*). ACI 226.3R-87 notes that "some fly ashes . . . may reduce the severity of alkali-silica reactions by reacting with alkali hydroxides that would otherwise be available to attack reactive aggregate constituents." In 2.2.13 the report states: "The use of adequate amounts of some fly ashes can reduce the amount of aggregate reaction and reduce or eliminate harmful expansion" (*21,22*). The effectiveness of a given fly ash can be investigated by using ASTM C441 and C227 or CAN 3-A 23.5-M82. The report notes that some aggregates not regarded as deleteriously reactive by current criteria may be reactive and suggests that "a suitable quality and quantity of fly ash may be used as a general preventive measure." This is one of those rare cases in which taking a "general preventive measure" will almost always reduce rather than increase the cost of the concrete.

## CURRENT STATUS

Of the papers in the *Proceedings of the 9th International Conference on Alkali-Aggregate Reaction in Concrete*, the organizing committee classified 22 as dealing with cement replacements and additives. There was one each from China, Egypt, Italy, and the United States (*23*); there were two from France; five each from Canada and Japan; and six from the United Kingdom. The admixtures dealt with included

- Zeolite: 30 percent clinoptilolite blended in the cement is effective (*24*).
- Metakaolin: 10 percent metakaolin replacement of cement is effective (*25*).
- Silica fume: how permanent is the effectiveness? (*26*); combining air entrainment with silica fume decreased expansion more than silica fume alone (*27*).
- Fly ash and silica fume (and ggbfs): a test method involving autoclaving (*28*).
- Fly ash and natural pozzolan (and ggbfs): method for selection of amount used based on expansion at elevated temperature (*29*).
- Fly ash (and ggbfs): cement with 28 percent fly ash was effective (*30*).
- Fly ash: 25 percent or more fly ash was effective (*9*); "fly ash was used (20% replacement) to minimize the risk of [alkali-aggregate reaction] in the Lower Notch Dam built with aggregate proven to be reactive." Rogers was cited: "20% fly ash replacement was used successfully to prevent cracking of concrete containing argillite and greywacke" (*31*). It may be that this is the long-sought-for example of use of a mineral admixture BRYANT intentionally with known high-alkali cement and known reactive aggregate, but I could not find a reported value for the alkali content of the cement used in the Lower Notch Dam.
- Fly ash: all fly ashes studied were effective at 35 percent (*32*).
- Fly ash: two dams were built with reactive aggregate and a cement likely to have been considered low alkali in the United Kingdom: one contained fly ash, not for preventing alkali-silica reaction expansion, although it did; the other did not have fly ash and is showing damage (*10*).
- Silanes: expansion is decreased, most effectively with hexyl trimethoxy silane, which gives the mortar water repellency (*33*).
- Chelation: reaction can be inhibited by chelating the cations adsorbed by the gels (*34*).
- Catalyzed alkali discharge: use of a "crystal breeding type waterproof agent"—sodium silicate, lime, and catalyst—was effective (*35*).
- Nonchloride acclerators: calcium formate, calcium nitrate, sodium benzoate, and sodium nitrite effects were questionable, but future work is indicated (*36*).
- Various chemical admixtures: air-entraining, water-reducing, and high-range water reducing admixtures were tried; there was less expansion due to air entrainment and reduction of cement content (*37*).
- Various chemical admixtures: $CaCl_2$ increased expansion, sucrose decreased expansion but also decreased strength; oxalic acid had little effect (*38*).
- Lithium salts: certain lithium salts are very effective at dosages of about 1 percent (*23*).

I do not comment on the discussions of coatings or the use of ggbfs. As indicated, more attention was given to fly ash than other mineral admixtures. Materials locally available—metakaolin in the United Kingdom and zeolite in China—were reported on favorably, and the chemical admixtures, except for lithium salts, appear to be unlikely candidates.

## CONCLUSION

The use of pozzolanic admixtures, especially fly ash, appears to be well established as a means of mitigating or preventing excessive expansion of concrete due to alkali-silica reaction. However, there are few, if any, adequately documented case histories of an owner or engineer deciding to use a known high-alkali cement with a known alkali-silica reactive aggregate plus a pozzolan, relying solely on the pozzolan to prevent damage that would otherwise be expected. The economics and regulatory and environmental benefits of using fly ash are usually such that concrete should contain fly ash in an amount of 25 or more percent of its cementitious medium for reasons unrelated to alkali-silica reaction. Lithium salts are now better understood because of Stark's Strategic Highway Research Program work (*23*) and may well constitute an alternative. The question about silica fume raised by Berubé and Duchesne (*26*) needs to be answered.

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