ALKALI-AGGREGATE REACTION

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Summary - The various aspects of alkali-aggregate reaction in
concrete are described and discussed in some detail. The highly
significant materials factors and the modifying influence of
environmental factors are pointed out and their effects on the
mechanisms of reaction and expansion are discussed. The most
widely used test procedures are indicated briefly and comments
on the interpretation of test results obtained by them are
given. Comments are also included on the signs and symptoms
used for recognizing alkali-aggregate reaction in existing
structures and on ways of preventing reaction in new construction.

Introduction

In 1940 T.E. Stanton[1] indicated that concrete could be deteriorated
by a reaction between cement and aggregate. His subsequent experimental
work, which supported these original observations, showed that cracking an
expansion of concrete were caused by combinations of high alkali cement an
opaline aggregates. Shortly afterwards Blanks (1941)[2] and Meissner (194
described the cracking and deterioration observed in Parker dam. It was
indicated that an alkali-silicate reaction product was being produced in
the concrete and that the deleterious component of the aggregate consisted
of altered andesite and rhyolite fragments, which constituted approximatel
2% of the total aggregate. These initial disclosures showed that detailed
studies of a wide range of factors and a general understanding of the

mechanism of expansion were needed. Studies progressed rapidly in a number of different directions such as:

1.   Examination of aggregate materials that could react with cement and their possibility of occurring in commercially used aggregates.

2.   The effects induced by cements of different alkali contents and means of producing low-alkali cement.

3.   A wide variety of effects caused by subjecting concrete and mortar to different environmental conditions.

4.   A general understanding of the mechanism of the chemical reaction and its ensuing physical effects on the mortar or concrete.

5.   Test procedures and the interpretation of test data.

6.   Diagnosis of alkali-aggregate reaction and assessments of the type and extent of damage to the structure.

7.   Possible means of preventing damage in future construction.

In the following sections of this paper, the chemical reaction and the subsequent disruptive swelling of the reaction product will be discussed and related to a variety of more practical endeavours concerned with recognition of this problem, material test procedures, interpretation of test data and available means of preventing damage in future construction.

Materials

Very extensive studies for potential reactivity were made on commonly occurring aggregates and their mineral components. In addition a number of less common and artificial materials was examined. Significant reactivity was shown by opal and cryptocrystalline silica and by acid and intermediate glasses occurring in volcanic rocks such as obsidian, rhyolite, trachyte and andesite. All of these materials are very widely distributed and may occur in aggregates. Cristobalite and tridymite, which are rare, and manufactured materials such as fused silica glass and the more usual commercial siliceous glasses are reactive but, except for the latter, are

unlikely to be of concern in practice.

Quartz and quartz-containing rocks, glassy basic rocks, such as basa
and devitrified glasses in acid and intermediate volcanic rocks are not
reactive. Crystalline igneous and metamorphic rocks and sedimentary rock
consisting of re-cemented crystalline fragments are also non-reactive.
At various times some rocks and minerals have been thought to be reactive
but subsequent studies have shown them to be non-reactive. Phyllite,
muscovite, chlorite and basaltic scoria have been quite erroneously regan
as being potentially reactive.

The quantity of reactive component in an aggregate which significant
affects the magnitude of expansion of mortar or concrete generally lies
between 0.5 and 40% by weight of the aggregate. A wide variety of factor
affects expansion and very small amounts of reactive material may cause
occasional and localized "pop-outs" rather than an overall expansion.

The component of portland cement that is pertinent to the reactive
system is its alkali content. Sodium and potassium oxides are generall)
introduced into clinker in the clay or shale fraction of the raw meal.
A proportion of these oxides will be retained in the clinker either in s
solutions, in combination with the aluminate and silicate phases, or as a
soluble salt (e.g. potassium sulphate). The amount of alkali retained i
the clinker will depend largely on the clinker manufacturing practice,
notably on whether precipitator dust is returned to the kiln. Various
attempts have been made to remove alkalis during burning by their volati
lization as chlorides. Generally these processes have caused additional
operating problems or have not been effective or economic. The use of l
alkali raw materials is the most effective and cheapest method of produc
a low alkali clinker.

A portion of the alkalis in cement becomes water-soluble during mi>
and the alkalis will continue to dissolve as the clinker hydrates. The
alkalis form hydroxides in solution. As other anions (e.g. sulphate io)

are removed from solution by reacting with the aluminate component of clinker they are replaced by hydroxyl ions, which can react with silica. Alkalis derived from other sources (e.g. water or from sources outside concrete) have the same reactive effect as those derived from cement.

The total alkali contents of portland cements range from <0.1 up to >1.0% expressed as %Na_2O. Although cements containing <0.6% total alkalis (%Na_2O + 0.658%K_2O) are generally accepted as having an innocuous, low alkali content, it is considered that this limit may be too high for certain concretes which contain sufficient reactive aggregate and which are subjected to ideal exposure conditions for very long periods of time.

The reacting and expanding system

When cement containing alkalis and aggregate containing a reactive siliceous component such as opal or volcanic glass are combined in concrete, the essential reactants are brought together. The alkalis react rather slowly with the siliceous material to form an alkali-silica complex of variable composition which may be set down as 1(alkalis): 2-4(silica) by weight. This complex is rather deficient in alkalis compared with the typical meta- and ortho-silicates. It should be noted here that no other components of cement or aggregate are necessary for the reaction to proceed (Vivian[4]). The clear alkali-silica complex may react if it comes in contact with calcium ions derived from calcium hydroxide or from the various hydrated cement compounds and will form a white, opaque calcium-silica or an alkali-calcium-silica complex. These latter reaction products have vastly different water absorbing properties from those of the first formed alkali-silica complex.

Free water is of course present in the concrete and is necessary in the first instance for reaction to occur since hydroxyl and alkali metal ions have to diffuse to the silica surface. The long delay that occurs before significant amounts of reaction are observed is due to the slow rate of ion diffusion. The alkali-silica reaction product is capable of

absorbing water and increasing in volume. During this process of absorbing water and swelling the alkali-silica reaction product changes from a hard solid to a softer gel and finally to a sol. Initially the alkali-silica reaction product is completely enveloped in hardened cement paste which is permeable to water. As water is absorbed the swelling reaction product exerts a disruptive force on the surrounding cement paste and cracks it. As more water is absorbed the crack is propagated into the mortar and becomes wider. The forces produced by many swelling particles may interact and accentuate the propagation and widening of a crack. Changes in the overall measurement of a specimen indicate changes that are occurring in the swelling reaction product and in the concomitant widening of cracks in the mortar or concrete. In addition, as the reaction product absorbs more water it becomes increasingly more fluid and more deformable. Consequently the swelling force that can be exerted to widen a crack in the mortar or concrete diminishes, and the overall expansion of a specimen tends to approach a maximum. The deformable or fluid reaction product is forced into or flows into the open crack in the specimen and may form a clear exudation or a wet spot on the surface of the specimen or in an internal void. These clear fluid products react readily with lime and form opaque, white, non-swelling alkali-lime-silica products. Sodium and potassium hydroxides released by this secondary reaction could react again with any residual un-reacted silica. Since hardened cement paste is permeable to water but is relatively impermeable to the swelling gel, it is not necessary to postulate the formation of a semi-permeable membrane around the reacting particle. As the gel becomes more fluid it can penetrate the hardened cement paste more readily and react with lime. These later formed secondary reaction products have sometimes been assumed to be confining semi-permeable membranes. It will be noted that basically only alkalis, reactive silica and water are necessary for reaction and expansion to occur. Concrete expansion becomes apparent as a result of the semi-

permeable characteristics of hardened cement paste and the operation of
some essential environmental factors.

Other factors that influence reaction and expansion

Environmental conditions affect aggregate reaction, gel swelling and
concrete expansion and these changes are further modified by the type of
concrete construction. Exposure to a dry atmosphere removes free water from
concrete and consequently inhibits reaction and prevents expansion. Thin
section concrete is completely affected by evaporative drying while
evaporation can affect only the surface of mass concrete. Concrete, such
as a pavement in contact with the ground, is affected to a lesser extent
by evaporation than is suspended concrete, such as a bridge deck.

The alkali content of concrete which is continuously immersed in water
is reduced by diffusion and leaching. This reduction can decrease the
extent of aggregate reaction while the presence of excess water in the
concrete minimizes expansion by promoting the rapid transformation of gel
to sol. Under this exposure condition thin section concrete will undergo
less deterioration than mass concrete.

The environmental temperature significantly influences the rate of
silica reaction, which increases as the temperature increases. Thus at
very low temperatures the rates of reaction and expansion will be very small
while at elevated temperatures (60-71°C) reaction
and expansion proceed rapidly. At these elevated temperatures some silica
reactions, which proceed very slowly at moderate atmospheric temperatures
(13-24°C), may be accelerated to such an extent that they contribute
significantly to mortar or concrete expansion. Some of the microcrystalline
and chalcedonic silicas may react and cause expansion only at these elevated
temperatures. Consequently care must be exercised in interpreting test
results obtained under accelerating, high temperature conditions.

Although intermittent wet-dry and freeze-thaw conditions modify the
rate of reaction and the measured expansion especially during the adverse

portion of the cycle, neither reaction nor expansion is permanently inhibited and both will continue under favourable conditions. These cycles generally induce additional changes in concrete which may be damaging and tend to confuse the more usual alkali-aggregate reaction symptoms.

The expansion of concrete is significantly changed by the application of restraint to its movement (McGowan and Vivian[5]). In large mass structures, or under applied directional loading or significant restraint, expansion in the direction of restraint is resticted while it proceeds in the other unrestrained directions. The usual random crack pattern has superimposed on it another series of large cracks, open at the surface and parallel to the direction of load application.

Any modification that augments the number of large voids in concrete or aggregate will reduce and,if sufficiently great (>7% by volume),will inhibit expansion by creating sufficient unoccupied space which can accommodate the swelling reaction product. Entrained air bubbles are not sufficiently large to inhibit expansion. Lean mixes, low water/cement ratios, incomplete compaction and porous, light-weight aggregates effectivel inhibit expansion. These effects can confuse or even invalidate the conclusions drawn from the expansion tests.

Test procedures and interpretation of test data

Although various test procedures have been proposed, two have become widely used. These are:

1. The mortar bar expansion test, (A.S.T.M. C.227).

2. The rapid chemical test first proposed by Mielenz et al[6] (1947). (A.S.T.M. C.289).

Two additional techniques are fairly widely used and yield useful information. These involve (a) petrological examination of the aggregate and examination of any light fraction extracted from the aggregate and (b) a low-power stereo-scopic examination of mortar at various intervals of time after it has cured.

The mortar bar test, which usually extends over a period of 6-12 months, defines the potential reactivity of an aggregate more clearly than does the rapid chemical test because the cement and aggregate are reacted together under atmospheric moisture and temperature storage conditions which accord reasonably closely with those that are encountered in a large mass of concrete. Moreover the reaction sites in the specimen can be examined.

The ASTM expansion test (C.227) requires specimens to be stored in moisture saturated air at $100^{\circ} \pm 3^{\circ}F$. It is considered that cement-aggregate combinations which expand more than 0.10% in 6 months, or 0.05% in 3 months, are capable of deleterious reactivity.

In Australia specimens have been stored in moisture saturated air usually at $70^{\circ}F$ but in some instances at $110^{\circ}F$. Although elevated temperatures accelerate the rate of reaction, the mortar expansions at different temperatures are comparable. An expansion exceeding 0.05% within 12 months is considered deleterious. The expansions of a large number of different cement-aggregate combinations have confirmed the significance of these criteria. In addition deleterious expansions are always accompanied by typical and readily demonstrable reaction symptoms in the specimens.

The rapid chemical test which can be completed in 3 days requires the aggregate to be reacted with N solution of sodium hydroxide at $80^{\circ}C$ for 24 hours. These reaction conditions are relatively severe and determinations of reduction in alkalinity and silica dissolved and present in solution are made. The authors of this test indicated that precise correlation between the results achieved with it and those obtained by the mortar bar test is not possible because there are many extraneous factors which modify the chemical test. Some judgement is therefore necessary to interpret the chemical test results correctly. First it should be remembered that concrete or mortar damage is caused only by a relatively large amount of deleterious material. Consequently the estimated dissolved silica should exceed a threshold quantity which represents a known and proven amount of

potentially reactive silica in the aggregate before the aggregate is considered to be deleterious. On the basis of mortar bar expansions, examination of the extent of reaction in mortar and concrete and on field behaviour of concrete, it is considered that less than 100 millimoles/litre dissolved silica indicates that the aggregate will not cause a deleterious expansion in concrete. The alkalinity reduction determination is much less significant than the dissolved silica determination for various reasons. Alkalis can be absorbed or exchanged with other ions on the surfaces of clays and zeolites and they can react with iron and magnesium-containing compounds and with some organic compounds. In these latter cases hydroxyl i removed from solution while alkalis associated with dissolved silica are estimated as being present in solution.

Consequently judgement of potential reactivity of an aggregate must be based on test data, such as mortar bar expansion or amount of dissolved silica being in excess of a permissible threshold quantity and on its projected use which involves the type of structure, the cement alkali conter the environmental conditions to which the structure will be subjected and other items such as aggregate porosity. Assessments of this type, which have estimated the potential reactivity performance in concrete, have been made successfully for very many years.

A brief comment on sampling and testing is appropriate here. A report on the potential reactivity of an aggregate deposit depends on the con- clusions drawn from tests made on samples obtained from it. The validity of these conclusions further depends on whether the samples faithfully represent the material in the deposit. Each aggregate deposit has its own intrinsic defects and variations. Stone quarries, although difficult to sample effectively, are generally fairly uniform with some clearly defined and apparent variable features. The bulk of the stone usually has a uniform reactivity characteristic. Although sand and gravel deposits on the other hand are more readily sampled than stone deposits, their variati

are neither apparent nor clearly delineated. Some deposits may be quite variable, exhibiting very wide changes in reactivity within very small distances because their constituent particles were derived from different parent rocks. Consequently the potential reactivity of sand and gravel deposits can only be evaluated properly by continued systematic sampling and testing.

Diagnosis of alkali-aggregate reaction in structure

The qualitative diagnosis of alkali-aggregate reaction in a concrete structure is relatively easy provided evidences of other changes are not permitted to confuse the symptoms. The most apparent symptom on exposed surfaces is a random crack pattern that, in certain very large structures, may be modified by applied restraints. The random surface crack pattern however will be apparent in areas between the large open cracks induced by restraint. Construction joints will close up and surface pop-outs will be apparent especially in instances where the reactive constituent occurs as large particles. Wet surface spots and gel exudations are generally not observed on exposed surfaces due to surface washing and erosion or to severe drying; these symptoms may be observed however on protected concrete surfaces. It should be noted that alkali-aggregate reaction develops slowly and that the surface random crack pattern does not begin to appear until at least a year, and possibly very much longer, after the concrete has been placed.

When affected concrete is spalled and the broken surfaces are examined microscopically, wet, swelling reacted particles, which may have white secondary reaction products associated with them will be observed. These reacted particles will be associated with cracks some of which will contain gel or sol. Reacted particles and cracks will be observed in every field examined at 25-30X magnification. Examination of cores will reveal the same reaction symptoms and will indicate the degree of damage and the depth of concrete affected by reaction. Deterioration in very massive

structures, such as concrete dams, may be arrested internally due to
(a) the inertia of the external mass of concrete and (b) a general desic-
cation of the heart concrete. The structure could therefore appear to
be sound and unaltered internally although cracked and deteriorated
externally. Removal of cores to moist storage, laboratory conditions will
allow the reaction process to proceed and expansion and deterioration will
then increase. Such a performance of cores does not indicate the true
condition within the structure but does indicate that a potentially
serious expansive condition exists.

Concrete that has been cracked and deteriorated by reacting aggre-
gate can deteriorate at an increasingly rapid rate through environmental
changes. The cracks produced by the reactive aggregate particles expose
the interior of the concrete mass to environmental influences such as
frost action, excessive movements due to wet-dry cycling coupled with
severe expansions due to the acceleration of the long-delayed expansions
that some cements undergo, or the action of aggressive salt solutions.
Moreover, as expansion exposes reinforcement, its accelerated corrosion
will contribute to the disruption of the structure.

Although minor repairs can sometimes be effected, they are merely
temporary palliatives and not permanent cures. Grouting a deteriorated
structure with various solutions may produce limited benefits but they
will not restore the structure to its original effectiveness. Scrapping
the affected work and re-constructing it is generally the most effective
method of correcting a defective structure. In many instances scrapping
does not entail significant economic losses, since the useful economic
life of the structure has been attained when deterioration becomes seriou

Prevention of damage in new construction

The choice of suitable, non-reactive aggregate is easily the most
effective method of avoiding damage caused by reactive aggregate expansio

Aggregates should therefore be tested for reactivity before use to ensure that they are non-reactive. Further, periodic checks are desirable, especially for sand and gravel deposits, to ensure that their expected reactivity characteristic does not vary significantly. Alternative sources of known non-reactive aggregates are generally available and should be substituted for reactive materials.

In a few areas all the available aggregates are known to be reactive and economics dictate that they must be used for local construction. Under these circumstances a low alkali cement containing less than 0.6% total alkalis expressed as Na_2O must be used to ensure reasonably trouble-free behaviour during the life of the structure. If the structure is large and is expected to have a very long effective life, the total alkali content of the cement should be as low as possible, preferably less than 0.4% total alkalis expressed as Na_2O.

The incorporation of fine, reactive pozzolanic material in the concrete as a replacement for a proportion of the portland cement offers a further safeguard against aggregate expansion under certain circumstances. Since many pozzolans reduce the rate of strength development and increase the magnitude of shrinkage, their use is usually restricted to mass concrete construction. The amount of cement replaced by a pozzolan in mass concrete is a variable and depends, along with a number of design factors, on the reactivities of the aggregate and the pozzolan and the amounts of reactive material in the aggregate and alkalis in the cement. The action of the pozzolan is twofold in reducing aggregate reaction. In the first instance a low-alkali-containing pozzolan effectively reduces the alkali content of the cement-pozzolan mixture, while in the second the major portion of the available hydroxyl ion reacts preferentially with the pozzolan on account of its large surface area compared with that of the reactive aggregate. Most of the alkali is therefore prevented from reacting with the reactive aggregate. Some care must however be exercised in the choice of

pozzolan because in at least one known instance the pozzolan contained much more water-soluble alkali than the portland cement. Its use as a cement replacement would have caused disastrously greater expansion than was expected for a normal portland cement concrete.

The effects on expansion of various interactions between concrete and environmental conditions have been discussed earlier. These effects should always be considered in assessing the possible use of an aggregate because certain conditions, notably complete protection and dryness, complete immersion and saturation and a high degree of porosity in the aggregate or concrete, will allow some potentially reactive aggregates to be used without causing serious damage to concrete.

Concluding remarks

In concluding it should be noted that alkali-aggregate reaction and expansion in concrete depend on a series of interdependent factors such as:

(1) The aggregate must contain sufficient but not too much reactive material. Although maximum expansion is usually caused by 3-5% of reactive material in the aggregate, the presence of greater or lesser amounts can cause significant mortar and concrete expansions.

(2) The cement must contain sufficient but not too much alkali. Portland cements contain up to approximately 1% total alkalis expressed as Na_2O with the majority within the range 0.4 - 0.8%. A total alkali content <0.6% has been widely adopted as the permissible maximum in cements which are to be used in concrete containing potentially reactive aggregate.

(3) The concrete must contain sufficient free water but not an excessive amount. Most concretes of relatively large dimensions contain adequate amounts of uncombined mix water to permit aggregate reaction and expansion to proceed.

(4) Cement paste in concrete is sufficiently permeable to allow water or water vapour to move to the reacting aggregate but is sufficiently impermeable to envelop the reacting particle and prevent its rapid dispersal into unoccupied void spaces.

Some concretes inadvertently possess all of these requirements and consequently aggregate reaction and expansion proceed and the concrete expands, cracks and deteriorates. Removal of any one of the above factors will either inhibit reaction or prevent expansion.

Each affected structure must be studied for its own intrinsic merits and a specific alleviating treatment be accorded to it. Prevention of concrete expansion by prior testing and exclusion of reactive aggregate remain the most effective ways of overcoming this problem.

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