

PRACTICAL IMPLICATIONS OF THE MECHANISMS
OF ALKALI-AGGREGATE REACTIONS

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The alkali-silica reaction was investigated in detail during the period from about 1940 to 1960 and because of the volume of work the term alkali-silica reaction became almost synonymous with alkali-aggregate reaction. It is now increasingly recognized that aggregates can react expansively with alkalis by more than one mechanism.

Cement alkalis react with the microforms of silica to form an alkali-silica gel which causes deleterious expansion of concrete by taking up water. The mechanism is related to osmosis but a semi-permeable membrane is probably unnecessary. Some rocks, in which expansive forms of silica are absent or present in only very small amounts, expand by different mechanisms. Alkali induced expansion appears in certain argillaceous dolomitic limestones, in some phyllites, greywackes and argillites and possibly in some granitic rocks and quartzites. Expansion of the argillaceous dolomitic limestones is attributed to water uptake by dry clay and other fine constituents which are exposed by the dedolomitization reaction (Gillott, 1964; Gillott and Swenson, 1969). Exfoliation and water uptake by certain phyllosilicates is held to play a large part in the alkali-expansion of the phyllites and greywackes found in Nova Scotia (Gillott, et al, 1973).

It is suggested that the alkali-aggregate reaction be subdivided into three main types termed the alkali-silica reaction, alkali-silicate reactions and the alkali-carbonate rock reaction. It cannot be too strongly emphasized that there is a difference

between these reactions and it should be clearly understood that this is not only of theoretical interest. The distinction is also of practical concern since it strongly influences the criteria used for identification of potentially expansive rocks and minerals, it affects the evidence used for recognition of alkali-aggregate reaction, and may affect measures designed to prevent expansion of concrete when use has to be made of such aggregates.

RECOGNITION OF POTENTIALLY EXPANSIVE AGGREGATES

(a) Petrography

A petrographer familiar with alkali-aggregate reaction is able to identify the common alkali-expansive minerals and rocks by their appearance on the petrographic microscope. The materials can be characterized in greater detail by X-ray diffraction, electron microscopy, differential thermal analysis and other methods.

The rocks and minerals involved in the alkali-silica reaction include opal, chert, chalcedony, cryptocrystalline quartz, silicified limestone and glassy and cryptocrystalline volcanic rocks. They are products of igneous, metamorphic and sedimentary processes and originate in high and low temperature environments. On the petrographic microscope the silica appears isotropic or cryptocrystalline and commonly the refractive index is lower than that of quartz (1.544 to 1.553). Many of the expansive materials show weight loss when heated due to evaporation of non-essential water or hydroxyl. On the electron microscope alkali-expansive minerals vary in appearance. Some opals are essentially featureless, some contain biological remains and some reveal internal porosity. Some cherts are mainly composed of anhedral quartz while in others grains are interlocking

sometimes showing euhedral forms; gradations of size and extent of recrystallization are common over small areas.

The alkali-expansive argillaceous dolomitic limestones also have a characteristic appearance though exceptions are known (Highway Res. Record, 1964). The rocks are commonly grey in hand sample and in thin section under the microscope dolomite euhedra of 50 μm or less can be seen in a matrix of dusky calcite, clay and other detrital constituents; the fabric is generally tight (Gillott, 1963). The electron microscope has confirmed that clay minerals are sometimes included in the dolomite crystals and clay has a preferential distribution close to the dolomites. X-ray diffraction showed that the dolomite is of the metastable variety which contains an excess of calcium above the ideal 50 mole per cent; the calcite contains magnesium ions in the dolomitic limestones from Kingston, Ontario.

The clearest evidence for expansion due to an alkali-silicate reaction has been obtained in studies of greywackes, phyllites and argillites from Nova Scotia (Duncan, et al, 1973, a, b, c). Greywackes are sandstones in which there is a significant proportion of interstitial matrix of an original muddy composition. The sand-size constituents are generally quartz, feldspar and accessory rock fragments. The less than 20 μm matrix consists of quartz, feldspar, layer structure silicates, iron minerals and graphitic material. In the Nova Scotia rocks porphyroblasts of a brown pleochroic mineral which looks like biotite are common. Shear has induced strain effects in many of the minerals. Phyllosilicates constitute a larger proportion of the mineral constituents in phyllites and argillites and quartz, feldspar, rock fragments and other detrital

components are of silt-size range or smaller. Detailed studies using X-ray diffraction and scanning electron microscopy showed that some of the phyllosilicates exfoliate on treatment with alkali. This was regarded as of major importance in the expansive mechanism of these rocks (Gillott, 1970; Gillott, et al, 1973).

Other cases are known where alkali-aggregate reaction has involved different minerals from those associated with alkali-silica reaction. Quartz and plagioclase feldspar were identified as reactive in granitic gneiss coarse aggregate in Georgia (Mather, 1973). Corrosion by alkali of minerals in greywackes from the Northwest Territories, Canada was shown by scanning electron microscopy (Gillott and Swenson, 1973).

(b) Dimensional Change Tests

Mortar bars, concrete prisms and rock cylinders are commonly used to obtain dimensional change data though powders have also been employed (Gillott, 1963). Test specimens are held at high humidity and constant temperature and length change is recorded over several months (ASTM, 1971 a, b). Aggregates are classed as deleterious or innocuous on the basis of per cent expansion after some pre-determined time. The limits and conditions of test are arrived at on the basis of experience; as knowledge increases so these variables may require modification. Disagreement between field performance of concrete and evidence from laboratory tests has in several instances been the first indication that different rocks, minerals and expansive mechanisms may be involved in alkali-aggregate reactions. The alkali-carbonate rock reaction was in this category (Swenson, 1957). Concrete performance in the field and large rapid expansions of concrete test prisms showed that some of the dolomitic limestones

from Kingston, Ontario were highly alkali-expansive. In the mortar bar test however this rock registered expansions which did not exceed the limits considered indicative of a deleteriously expansive material. The difference in behaviour in the two tests was related to decrease in expansion with decrease in particle size (Swenson and Gillott, 1960). In the alkali-silica reaction also, particle size affects expansion (Diamond and Thaulow, 1974). Proportion of reactive component sometimes has a marked effect. When opal is the reactive constituent large expansions are registered at the "pessimum". This is less well defined or non-existent when rocks and minerals other than opal are involved.

Aggregates which expand very slowly but continuously for a long period (Duncan, et al, 1973 a, b, c) and so-called "late expanders" (Dolar-Mantuani, 1964) are difficult to detect by tests of short duration. From both the practical and theoretical viewpoints it is important to be able to identify expansive aggregates in the shortest possible time so factors which accelerate dimensional change tests require consideration. Methods of acceleration include artificial increase in the alkali concentration, elevation of conditioning temperature and concentration of rock types. Effect of particle size and the "pessimum" proportion on rate and degree of expansion should also be considered. Control specimens are needed when accelerating procedures are used. For such cases consideration also has to be given to the chosen limits of expansion as a function of time at which deleterious expansion is separated from innocuous behaviour.

(c) Chemical Methods

With the object of developing a more rapid means of recognition

of potentially expansive aggregates various chemical procedures have been investigated (ASTM, 1971 c). One approach was to determine the weight loss, or extent of etching, of aggregate placed in alkaline or other solutions. Another was to estimate changes in the composition or concentration of solutions held in contact with the suspect aggregate. Interest in this approach faded because anomalous results are common (Mielenz, 1958).

EVIDENCE OF ALKALI-AGGREGATE REACTION IN CONCRETE

Concrete affected by all varieties of alkali-aggregate reactions has certain common features and knowledge of these symptoms is important in the correct diagnosis of the cause of durability failure. Conversely absence of certain features associated with alkali-silica reaction does not imply that alkali-aggregate reaction can be ruled out since such absences may be characteristic of a difference in expansive mechanism rather than indicative of a completely different cause of durability failure.

Map cracking or pattern cracking is one of the most universal symptoms of alkali-aggregate reaction in field concrete. It results from differences in rate and degree of expansion in different parts of a concrete element. Other causes of differential stress due to other destructive agents may however produce a crack pattern of similar appearance. When such concrete is examined microscopically internal cracks are found in cement paste and aggregate. Only infrequently do cracks have a radial relationship to aggregate particles. Field concrete shows other manifestations of expansion. In side-walk slabs joint-filler may be extruded and buckling is sometimes present in severe cases. Machines set in concrete develop

progressive misalignment of working parts. Observation of survey points over a sufficient time interval will reveal expansion.

Pop-outs above expansive aggregate particles are sometimes to be seen but this is not an exclusive feature of alkali-aggregate reaction. Nor are pop-outs invariably present even when concrete is affected by severe expansion due to this cause.

Emphasis has been placed upon the importance of discoloured rims surrounding aggregate as an indication of alkali-aggregate reaction. It has been shown that rims may be more resistant (positive) or less resistant (negative) to etching than the surrounding concrete. Where aggregate is made from crushed-rock, and in other cases where rim-formation by earlier weathering can be excluded, rims indicate reaction between aggregate and cement. Such reaction however is not necessarily of the kind accompanied by deleterious expansion and rims surrounding aggregate can often be seen in perfectly sound concrete. Evidently reaction rims form by a variety of mechanisms.

Concrete affected by the alkali-silica reaction often displays exudations of gel or the white deposits which form when this material dries. This should not be confused with deposits caused by leaching, efflorescence and carbonation and which are not uncommon on concrete in moist environments. In thin section gel fills void spaces and cracks and appears isotropic or partly anisotropic if strained, devitrified or if it contains crystalline inclusions. Hence gel formation is often an indication of alkali-silica reaction but the absence of gel should not be taken to indicate that alkali-aggregate reaction may be dismissed as a cause of poor concrete durability. Severe concrete distress is known to result from alkali-carbonate rock reaction and some varieties of alkali-silicate reaction where

because the expansive mechanisms are distinct gel and dehydrated gel are virtually absent or present in only small amounts.

METHODS OF CONTROLLING ALKALI-AGGREGATE REACTIONS

Rate and degree of expansion in all alkali-aggregate reactions are affected by concentration of alkali in concrete pore solutions. The importance of hydroxyl has long been recognized (Vivian, 1951; Powers and Steinour, 1955, p.501) and its role has recently been re-emphasized by Diamond (in press). Similarly the nature and concentration of the alkali cation is important. A widely used method of control when expansive aggregate is known to be present has been to reduce alkali concentration. The upper limit commonly adopted in North America for low-alkali cement is 0.6 per cent equivalent Na_2O based on total alkali (ASTM, 1971 d).

The cations affect the course of the reaction. An addition of about 1 per cent of various lithium salts inhibits expansion in the alkali-silica reaction (McCoy and Caldwell, 1951) an effect attributed to the low solubility of lithium silicate gel. Lithium does not retard expansion due to the alkali-carbonate rock reaction (Swenson and Gillott, 1960). This is to be expected if expansion results from water uptake by the clay and other fine constituents. The extent of the hydrous double-layer which forms is unlikely to be much affected by lithium in solution so there should be no marked effect on expansion.

Moisture is essential to expansion in all alkali-aggregate reactions and design to reduce wetting is one method by which the possibility of durability failure from this cause can be reduced.

Water-cement ratio is also a factor and a low water-cement

ratio has been found to reduce expansion of mortar bars containing reactive silica. Conversely in the alkali-carbonate rock reaction low water-cement ratios actually led to slightly higher expansions (Swenson and Gillott, 1960).

Pozzolans have been used as a means of controlling expansion due to alkali-silica reaction and have been effective even when waste glass is used as coarse aggregate (Johnston, 1974). Suitable pozzolans also significantly reduced expansion associated with the greywackes, phyllites and argillites found in Nova Scotia (Duncan, et al, 1973). In the alkali-carbonate rock reaction however, pozzolans had either no effect on expansion, or only a small influence at early ages (Swenson and Gillott, 1960).

Entrained air may also be considered as a method of control of some reactions. This has been shown to reduce or prevent expansion due to alkali-silica reaction (Vivian, 1947; McCoy and Caldwell, 1951). However no similar effect was found in concretes containing alkali-expansive carbonate rock as aggregate (Swenson and Gillott, 1960). Differences in expansive mechanism are clearly responsible.

When alkali-expansive rocks or minerals are identified prior to use of an aggregate it is sometimes possible to upgrade the quality of the deposit. In gravels beneficiation by methods such as flotation should be considered and where ledge rock is exploited selective quarrying can be effective (Smith, 1964).

DISCUSSION

Opaline silica when present in the "pessimum" proportion and appropriate size range is a common cause of concrete deterioration due to alkali-silica reaction. It is readily identified by modern

methods. Cherts and other disordered siliceous minerals and rocks too are readily recognized. While progress is being made in understanding the behaviour of this type of material (Idorn, 1974) its potential for producing expansion due to alkali-silica reaction is unpredictable at the present time. The pessimum proportion is also much less clearly defined than for opal in the case of other forms of alkali-expansive silica. Experimental work has shown that microcrystalline quartz can cause marked expansion in the mortar bar test (Mielenz, et al, 1947) while other aggregates of similar appearance on the electron microscope produce only low expansions. Attempts to correlate expansivity with degree of recrystallization, structural disorder, internal porosity and surface area, water loss and refractive index (Kneller, 1968) have been only partially successful. The nature of the cation has an important effect on the expansivity of siliceous glasses (Pike, et al, 1960). Until recently it was considered that only those volcanic glasses of acid or intermediate composition were alkali-expansive but basaltic rocks are now known to be involved (Gudmundsson, 1971). Probably the nature of the cations in poorly crystallized volcanic rocks plays a major role in determining the expansivity of this class of reactive aggregates. Other factors known or considered to be significant include the local radius of curvature of the silica surface, the nature and amount of adsorbed ion (Iler, 1973) and internal stress. It is evident that while the nature of the alkali-silica reaction is understood in general terms a great deal more has to be learned about factors which have a significant effect on rate and degree of expansion before accurate predictions of behaviour in concrete can be made.

In the case of the alkali-carbonate rock reaction it is rather straightforward for a petrographer to recognize the "typical" argillaceous dolomitic limestones which have been associated with expansion. Anomalies exist in that different varieties of carbonate rock have sometimes been found to be expansive and in that rocks which have the petrographic characteristics of expansive rocks sometimes cause little or no expansion in alkali. Reasons can be advanced for some of these anomalies. If the dolomite crystals are sufficiently coarse ($> 100 \mu\text{m}$ approximately) dedolomitization takes place only very slowly and so expansion will be correspondingly retarded. Even if the dolomites are observed to be in the right size range for rapid dedolomitization, expansion may not take place since this also depends on the extent to which the clay and other fine-grained constituents have been pre-wetted. This information is not readily obtained by present-day methods though a petrographer may make an "educated guess" if the rock fabric is tight. Conversely it is equally clear that moisture uptake by dry clay-grade material may also cause expansion of rocks in which the fabric is opened up by physical and chemical processes different from dedolomitization (Swenson and Gillott, 1967). This may account for the seemingly anomalous expansion of some "non-typical" rocks.

Phyllites were implicated at an early date with durability problems in concrete (Kammer and Carlson, 1941) but rocks of this sort did not receive detailed study until fairly recently (Duncan, et al, 1973 a, b, c). In Nova Scotia phyllites and related rocks were investigated in detail because poor performance of concrete was known to be occurring on a wide scale. In the Maritime region of Canada at least, the reaction, classed here as alkali-silicate in

type, differs from the other categories in important respects. Some of the negative evidence which suggests that the reaction is of a different type involved lack of correlation between expansion of test specimens or deterioration of field concrete and amount of gel; another difference is the very slow rate of the expansion but its continuation over a very long time interval; again the absence or presence in only very small amounts of minerals known to be alkali-expansive is significant. Strained quartz was present and may have contributed to expansion but the extent of this effect, if it occurred, is not known. Positive evidence that the expansive mechanism is different was provided by peak shifts on X-ray diffractograms and exfoliation of phyllosilicates observed on scanning electron micrographs after alkali treatment. Direct comparison of the same areas of rock before and after alkali treatment make the exfoliation particularly clear. As identification of expandable phyllosilicates is readily accomplished the distinction of this type of reaction is important in the petrographic evaluation of potential aggregate sources.

CONCLUSION

Depletion of good quality aggregate supplies in some urban areas and the trend towards production of portland cements containing higher contents of alkali make durability failure of concrete from alkali-aggregate reaction of increased concern. A better understanding of the different mechanisms by which alkali causes rocks to expand is of practical as well as theoretical importance. This follows since it makes the identification of potentially deleterious aggregates more certain, makes it easier to recognise alkali-aggregate reaction as a cause of distress in concrete and places methods of control on a firmer foundation.

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