

THE COMMITTEES ON THE "DURABILITY OF CONCRETE STRUCTURES"

An assessment of the present situation along these lines formed the background when the Academy of the Technical Sciences organized its activity on this subject. The technical work is supervised by three committees. One of them has the primary object to initiate the process of adapting know how into readily applicable, practical routines. A second technical committee shall make sure, that a sufficient and rational system is developed to communicate the adapted know how at all levels and to all categories of personal involved in concrete construction. The third technical committee deals with the planning of basic research. High priority will be given to activities, which can support the adaptation process by filling some of the know how gaps. Finally, an administration committee takes care of the coordination between the three technical committees and of the financial support of the activities.

Our chairman professor Torben Hansen has at an earlier conference a few months ago pointed out, "that it is no longer possible for any person to have the collective, theoretical and practical background, which is necessary in order to solve the problems. It is clearly a task for professional societies, who should appoint committees with construction experience to evaluate the requirement for the concrete construction process and then to develop standards to provide interface for the contributing parts to the process".

And that is in my eyes exactly what the Danish Academy of Technical Sciences has done.

You will notice that the committee primarily will focus on training of the already graduated civil engineer rather than on the classical educational system, at our universities. We will focus on the bread-and-butter type training rather than on the use of sophisticated science.

I may point out that this is the result of a short term consideration. We may - here and now - act in the real and in the political world and this outside world, expect us to repair the acute and conspicuous damages.

But it does not mean that university education and scientific research should be overlooked. A long term consideration would of course emphasize these aspects. Among the intentions of the Committee is an improvement of the technical educations on all levels as well as the creation of an officialized education for concrete craftsmen.

However, as already mentioned, we need - here and now - a strengthening of the existing practice and therefore we have given top priority to the short term consideration.

ASR-QED

AN ATTEMPT TO PROVIDE AN EXPLANATION FOR ENGINEERS OF THE EXPANSIVE REACTION BETWEEN ALKALIES AND SILICEOUS AGGREGATES IN CONCRETE

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1. ABSTRACT

1.1 Alkali silica reactions (ASR) in concrete are only partially understood and are poorly explained. In consequence "alkali" may mean "hydroxyl ion" or sometimes "alkali metal (ion)". One of the many varieties of silica may be involved, but the reacting material may be hydrated or can be a silicate. A number of three-variant (ternary) relationships have been reported to be involved in the extent of ASR in concrete, all contributing to the worst credible (pessimum) conditions for reaction, expansion and damage, and having an intriguing association with the three-branched (Manx) cracking frequently found in affected concretes (delta-star relationship).

KEYWORDS: Delta, Triangular, Manx, Star

2. INTRODUCTION

2.1 Although intended to provide an engineering image of ASR, this paper is written in "materials scientist" language to aid discussion. A suitable translation will be provided in due course.

2.2 Considerable misconception prevails concerning the reactions between alkalis and silica (ASR) in concrete and the mechanism of damage caused through this phenomenon. In part this is due to the reluctance of various parties to recognise that any problem exists, the rarity of the occurrence induces a lack of awareness and laissez-faire attitude amongst the users of concrete, and there are the usual communication difficulties between scientists and engineers. On top of all this is a veneer of media inspired scaremongering and alarmist propaganda about "concrete cancer" and "foreign disease" having connotations (as far as the British are concerned) of something nasty picked up on the Continent or imported in the much-feared German cement.

2.3 "Alkali" is often used rather loosely and can mean alkali metal, alkali metal ion i.e. the chemical elements (usually) sodium and potassium (and perhaps extended to lithium, rubidium and caesium). Or "alkali" may be used to mean hydroxyl ion or alkaline (high-pH) solution.

2.4 Similarly "silica" usually means a siliceous (high silicon content) aggregate, possibly indeed consisting of one of the varieties of silicon dioxide or hydrous silica (quartz, chalcedony, tridymite, chert, flint, opal etc.) or it may mean a siliceous glass (natural or artificial) or perhaps a rock type which contains siliceous inclusions.

2.5 This paper does not purport to explain everything about Alkali Silica Reaction - indeed there would be no need for this conference if it did - and in a developing research area such as ASR there is a danger of expounding a latter-day equivalent of the phlogiston theory. However, this contribution together with the constructive criticisms of delegates here present may act as a temporary and simplified summary which can assist in enabling interested parties to communicate more efficiently.

3. Alkalies and alkalinity

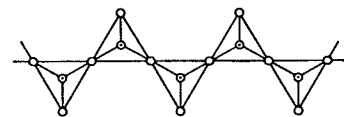
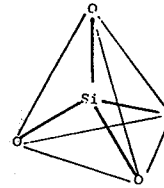
3.1 Portland cement after mixing with water is caustically alkaline and the pH of an aqueous extract of uncarbonated concrete will have a value in excess of 13. The pore fluid in concrete is, therefore, an alkaline solution with an hydroxyl ion concentration of the order of 0.75 molar (i.e. similar strength to a 3% caustic soda solution).

3.2 Analyses of the pore fluid compositions after varying lengths of time from mixing have shown that after about one month almost no calcium ions are present in the pore solution which consists essentially of hydroxyl ions and sodium and potassium ions.

3.3 Even so-called "low alkali" cements (i.e. Portland cements containing less than 0.6 per cent alkali metal expressed as sodium oxide equivalent) are strongly alkaline when hydrated and are therefore capable of initiating hydroxyl ion attack on susceptible siliceous materials.

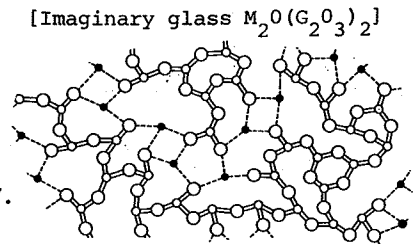
4. The structure of siliceous aggregates

4.1 Aggregates which are composed essentially of silica or which have a siliceous glassy structure are based on networks of the basic silicon-oxygen tetrahedral grouping i.e. a silicon atom at the centre of a regular tetrahedron with an oxygen atom at each corner.



4.2 The silicate structure is developed by the linking of the tetrahedra by shared oxygen atoms at the common corner.

4.3 The tetrahedra may be arranged in a regular pattern to give a crystalline structure such as quartz, or relatively small groups of random chains may be present as in silicate glasses which have short-range order but overall disorder/1/.

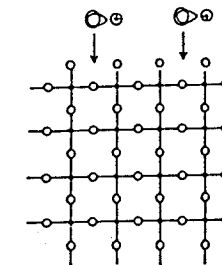


4.4 Other chemical elements may also be present and these may assist in the formation of the silicate network, may encourage the separation of the chains, or can act as stabilisers which reduce the chemical reactivity of the material.

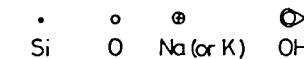
5. Alkali-silica reaction

5.1 The initial attacking reagent in ASR is the hydroxyl ion (OH^-). This reacts by either inducing fission of the Si-O-Si bond at the common tetrahedral corners of the silicate or by bonding with free Si-OH (silanol) groups at the surface.

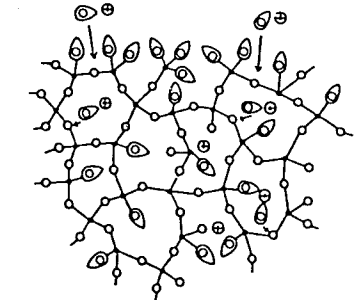
5.2 The readiness to react and the identity of the reaction products depends on the structure of the siliceous aggregate and on the conditions of reaction.



5.3 The difference between a well crystallised silica system and a poorly crystalline hydrous silica has been illustrated diagrammatically by Dent Glasser and Kataoka/2/. In the case of the well crystallised aggregate only a slow surface attack is possible and the reaction products tend to be discrete silicate ions which are able to migrate away from the reaction site.



5.4 In the case of poorly ordered, permeable, hydrous aggregates the reactants can penetrate into the interior of the aggregate to cause disintegration of the silicate network with the formation of chain fragments which are relatively immobile polyelectrolytes.



5.5 The negative charges are balanced by positive ions from the cement pore fluid. In fact in most concretes these will be potassium (K^+) or sodium (Na^+) ions, since no other positive ions are in solution and so the reaction product is an alkali metal polysilicate (gel) of indefinite composition.

5.6 The final, and damaging phase, of reaction is the attraction of water to the alkali-silicate gel by an imbibition/osmosis process to induce the gel to swell with sufficient local increase in pressure to cause expansion and possibly cracking damage to the concrete.

5.7 The actual increase in volume and eventual cracking of the concrete is due to the creation of an internal pressure by the swelling of the alkali silicate gel reaction product. The driving force for this swelling has been suggested to be inhibition^{3/} because of the presence of positive (Na⁺ and K⁺) ions and negatively charged ("silicate") groups or osmotic pressure, for which there is no need to postulate the presence of a semi-permeable membrane since the gel/pore fluid interface acts as a membrane.

5.8 Studies of laboratory-produced gels and their swelling behaviour^{4/} have shown that a wide range of compositions can act in this way and in so doing pressures up to about 11 MPa can be developed.

6. Energy considerations

6.1 All chemical reactions have minimum energy requirements before reaction can occur and a reaction which takes place spontaneously involves an overall change to a lower energy state. Initiation of reaction may also require a definite activation energy before the spontaneous process will commence.

6.2 Idorn^{5/} has drawn attention to the energy balance within concretes and in particular the fact that modern materials follow a very different energy path than concretes in the past (and incidentally very different from concrete specimens tested under standardised isothermal conditions).

6.3 Roy and Idorn^{6/} have developed this theme to consider the activation (including alkali activation) of slag cements, a reaction which shows considerable similarities to the present concept of ASR.

6.4 Whilst all siliceous aggregates are based on the silicate structure, very few such materials will actually react in a deleterious manner in the conditions prevailing in practical concretes. The energy, required for significant hydroxyl induced fission of the Si-O-Si bond depends on the disposition of the silicate tetrahedra and the overall surface area of the aggregate particles (area available for reaction)

6.5 Crystalline materials where the internal energy is raised due to mechanical strain (as with rocks subjected to metamorphic processes), porous or permeable siliceous systems (such as opaline silica or chert) or high surface area materials (such as quartzite aggregates composed of many irregular quartz grains and metamorphosed quartz with complex "sutured seam" inter-granular boundaries, or finely-divided, ultra-fine materials (such as condensed silica fume) are all more reactive towards hydroxyl ions.

6.6 Provision of external energy will also increase the reaction rate and the most usual form that this may take (at least as far as concrete is concerned) is an increase in temperature. Thus concretes exposed in high temperature (and humidity) environments or where steam or autoclave curing is employed may involve ASR with aggregates which in normal ambient conditions have been found to be innocuous. (One of the difficulties with accelerated test methods for aggregates is that elevated temperatures may provide sufficient energy for activation of materials which at ambient temperatures show no signs of reaction)

7. Diffusion movement within concrete

7.1 The reactions and processes involved in ASR require the reactants (OH⁻ and alkali metal ions) to be able to approach the siliceous aggregate and for water molecules to diffuse towards the alkali-silicate gel reaction product.

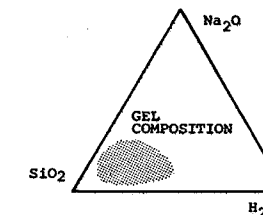
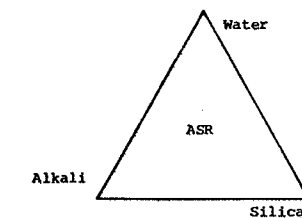
7.2 It is generally assumed that diffusion in concrete conforms with the Ficks Law model for movement in an inert porous body. However, where diffusion is accompanied by reaction an alternative mechanism may apply and certainly in the case of ASR with glassy substances where the diffusion rate is relatively slow compared with reaction rate a periodic model may be more appropriate. Thus Liesegang ring formation has been reported in silica gels^{7/} and with glasses at elevated temperatures^{8/} and cases of ASR involving glass or glass-aggregate^{9/} reveal a characteristic crack pattern sub-parallel to the aggregate surface (normal to the line of approach of hydroxyl ions). Cement-gel has previously been cited as being capable of inducing periodic deposits^{10/} and this type of reaction has been observed in cases of sulphate attack^{11/}. There is some evidence that carbonation may proceed in this manner^{12/}.

7.3 Because the rate of reaction of hydroxyl ions with silica is faster than the rate of diffusion of alkali metal ions through concrete, alkali-silicate gels tend to have an overall negative charge and hence to attract calcium ions present in adjacent cement paste. Thus, with time, the calcium content of gels tends to increase and above a certain calcium level the swelling tendency of the gel appears to be nullified. The reaction of alkali-silicate gel with the cement paste (presumably with solid calcium hydroxide, portlandite) is most readily seen where fresh gel is flowing through a crack where calcium depletion adjacent to the crack is a common phenomenon.

8. Triangular relationships

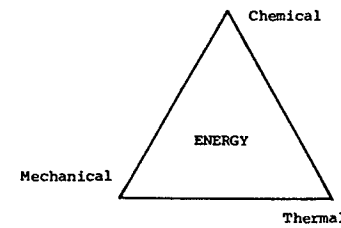
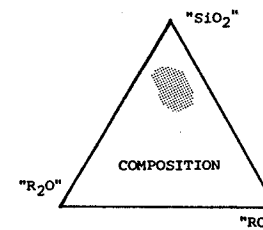
8.1 A number of three-variant systems have been identified which have been invoked to help explain some of the processes involved in ASR.

8.2 It has frequently been pointed out that before any deleterious ASR processes can occur it is necessary to have a reactive aggregate, a source of alkali (here meaning alkali metal ions) and the availability of water^{13/}.



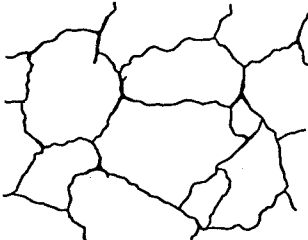
8.3 There appears to be a range of gel compositions which will swell when in contact with water and these are conveniently shown on a triangular (ternary relationship) diagram^{14/}.

8.4 The reactivity of siliceous glasses, in part, can be explained by compositional relationships and this has proved a useful concept for understanding the weathering behaviour of glasses/15/.



8.5 An energy balance ternary diagram can also be drawn/16/ once again illustrating a three-variant relationship which affects ASR.

8.6 The combination of all such three-sided factors governs whether or not a deleterious ASR will occur and the extent to which it will proceed. The worst-credible case (pessimum combination) will, of course, create the greatest damage.

8.7  The characteristic formation of three branched (Manx, Isle of Man or Triskele) cracks in concretes affected by ASR/17/ was first suggested to the second alkali conference in 1975. This observation has subsequently been confirmed and elegantly illustrated by Fookes, Comberbach and Cann/18/ who have sketched a number of types of cracking in concrete.

8.8 The 3-crack pattern is an external expression of the internal pressures and tensile stresses developed in the ASR. Model experiments in Denmark/19/ have shown that pressures of the order of about 12 MPa are required to produce such damage in structural concretes i.e. comparable with the known range of gel swelling pressures.

9. IN CONCLUSION

9.1 ASR is a complicated process involving a number of different factors some of which may be conveniently described via triangular (delta) diagrams. The resultant damage is due to internal volume change and pressure-induced stresses which characteristically result in three-branched (Manx) cracking.

9.2 An analogy from electrical engineering (although curiously converse) may be made with three-phase motors which after starting with the windings connected in a three-branched (star) formation are run in a triangular (delta) configuration.

9.3 It is important to distinguish between alkali metal (ions) and alkalinity (hydroxyl ion concentration) to avoid ambiguity when considering ASR.

9.4 Portland cement was so called by its inventor, Joseph Aspdin, because of a fancied resemblance of the hardened material to the high class building stone quarried on the Isle of Portland. In London, as elsewhere, the name Portland retains connotations of excellence and quality, the Royal Institute of British Architects is at Portland Place and in the fashionable district of Holland Park can be found the only "Portland Arms" public house. There, prophetically displayed on the inn sign in the second and third quarters of the heraldic shield, is revealed the three-legged Triskele device, the symbol of ASR

—QED

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EDUCATION FOR EFFECTIVE UTILIZATION OF ALKALIS IN CONCRETE

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ABSTRACT

Contemporary concrete deserves to be considered a continuously reacting system which must be monitored all the way through its processing from the mixer to load application. Alkalis have gained noticeable influence throughout the chemical processes. It is proposed to recognize this development by appertaining changes in engineering education and in research.

The availability of blast-furnace slag and fly ash improves the opportunities for higher social and industrial return on investments with concrete works if educations are updated.

KEY WORDS: Alkalis, Education, Chemistry, Engineering

INTRODUCTION

Recent research, Wu and Roy /1/, Regourd /2/, suggests that the alkali content of concrete made with blast-furnace slag (or fly ash) may significantly influence the workability of the fresh cement paste.

Numerous workers have during the last twenty years shown that alkalis in concrete act as activators of the hydration of blast-furnace slag and fly ash during the curing of concrete.

And several workers, referred to elsewhere in the conference papers, have shown that blast-furnace slag and fly ash may contribute higher denseness and longer term strength development to concrete than portland cement alone can supply.

These impacts on the characteristics of concrete: both in the fresh state and during the curing and performance are inseparably interconnected and time dependent in such ways that the concrete production engineer must count with the changes continuously during the entire duration of the processing: transport, placement, compaction, curing and load application.

The technology must in other words throughout become based upon the dynamic character of concrete as a reacting system. This is not different from the ways in which a cement plant engineer must operate, or for that sake engineers in paper, plastic, margarine and other industries. But it is a change which will not come easy for civil engineers engaged in concrete production.

In actual practice the fresh concrete is still largely controlled by the slump test specified as one figure though frequently to be repeatedly checked for ensuring that the slump stays as specified.

The curing of concrete is still predominantly checked by compressive strength test specimens cured at room temperature; sometimes at intervals, when early strength is desirable, and to ensure that the figures attained per duration of curing periods comply with the specifications.