

A CRITICAL REVIEW OF THE RECENT DANISH LITERATURE
ON ALKALI-SILICA REACTION

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1. ABSTRACT

In Denmark researches on alkali-silica reaction have been carried out in two distinct phases. In the first phase the problem was identified as a national one. Opaline limestone, and flint of varying degree of crystallinities and porosities were identified as the main reactive aggregates. At this stage the use of a low alkali Portland cement was suggested as the effective preventive measure against alkali-silica reaction.

The second phase of research started with an investigation of the breakdown of concrete motor roads, which indicated that NaCl, a de-icing agent, accelerates alkali-silica reaction and that the presence of free Ca(OH)_2 is a pre-requisite for expansive alkali-silica reaction. At the same time the electron-probe micro-analytical technique was adapted for the analysis of the reaction products still within expanding structures. In subsequent investigations the above observations and the analytical technique were utilized to explore the reaction mechanisms, in the development of an accelerated mortar bar method for alkali-silica reactivity with its acceptance criterion, in the development of a simple chemical method for the identification of reactive aggregates. Independently of the above researches a method has been proposed to monitor continuously the dissolution of reactive silica in 10N NaOH solution as a means of evaluating alkali-silica reactivity.

In this report the literature of this second phase of research has been critically evaluated.

2. INTRODUCTION

Denmark is a small country with a substantial problem with its alkali reactive aggregates. This has resulted in extensive research programmes, in two distinct phases, on alkali-silica reaction and its prevention. The first phase identified flint and opaline limestone as the main reactive constituents. At this stage the preventive measures suggested were either use of a low

alkali cement or use of an aggregate containing less than 2% reactive component. The basic assumptions at this phase were that alkalis in a concrete are determined by the alkali content of its cement and remain uniformly distributed throughout the life span.

The second phase of research started with an investigation of breakdown of motor roads due to alkali-silica reaction. From this investigation it was inferred that de-icing agent NaCl accelerated the alkali-silica reaction; this was subsequently substantiated by a laboratory investigation (1). It was also inferred that the presence of free Ca(OH)_2 is a pre-requisite of alkali-silica expansion (2). At about this time the electron-probe micro-analytical technique was applied to determine the chemical composition of alkali-silica gel (3).

The explicit assumptions of the second phase were that the real-life structures often receive alkalis from their environments eg. ground water, de-icing agents, etc. and there is nearly always a concentration gradient of alkalis in any structure.

Most of the subsequent research in Denmark could be treated as the follow-ups of the above three papers. The object of the present paper is to review critically the development in this second phase of research.

3. THE SECOND PHASE

Recent researches could be divided into following sub-groups: i) those directed to the reaction mechanisms, ii) those directed to the development of methods of measurements of reactivity, iii) those directed to the development of preventive measures.

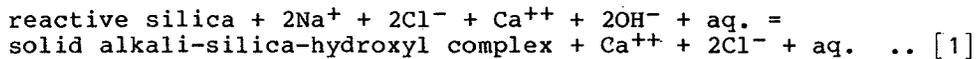
3.1 Mechanisms of alkali-silica reaction and expansion

As a preliminary to detailed studies of the reaction mechanisms the role of free Ca(OH)_2 in expansive alkali-silica reaction was explored first. Prisms made with a reactive sand and a high slag-Portland cement or a Portland cement were exposed to saturated NaCl solution at 50°C and their expansions were measured. The result showed that prisms made with a slag-Portland cement did not expand but those with Portland cement did. X-ray diffraction analyses of the prisms showed that those made with slag-Portland cement contained no free Ca(OH)_2 whereas those made with Portland cement contained crystalline Ca(OH)_2 (4). Those results confirmed the previous inference that free Ca(OH)_2 is a pre-requisite for expansive alkali-silica reaction (2).

In order to study the reaction mechanisms, prisms made from reactive sand types and Portland cement containing varying amounts of diatomites were exposed to saturated NaCl solution at 50°C. The expansion of the prisms were measured for up to about one year. At the end of this period the prisms were further examined by petrographic, X-ray diffraction and the electron-probe

micro-analytical techniques (5). The results showed that the expansion of mortar prisms, the extent of reaction, the penetration of hydrated Na, Ca and OH ions in the reacted grains decrease with the decrease in crystalline $\text{Ca}(\text{OH})_2$ in the paste. During reaction a fraction of reactive silica diffuses out of the reactive grains and the extent of silica diffusing out increases with decreasing $\text{Ca}(\text{OH})_2$ content.

The observed high Na_2O content of reacted grains, in prisms stored in NaCl solution, compared to those stored in water indicates that a reaction of the following type must have been occurring during alkali-silica reaction:



The above reaction explains how NaCl accelerates alkali-silica reaction and why $\text{Ca}(\text{OH})_2$ is a pre-requisite.

It has been postulated that in a cement environment an expansion will occur if the rate of penetration of hydrated ions of Na, Ca, OH and water molecules in reactive grains exceeds that of SiO_2 diffusing out. If the alkali content is low only a limited amount of hydrated Ca and OH ions can penetrate the grains; this is due to the large size of hydrated Ca ions. If the alkali concentration is high then smaller hydrated Na and OH ions will be able to penetrate reactive grains unhindered. This penetration of Na and OH ions will cause a breakdown of Si-O-Si bonds thereby opening the grains to further penetration of Ca, Na and OH ions and at the same time setting free a part of the reactive SiO_2 for diffusion. In the presence of excess $\text{Ca}(\text{OH})_2$ and alkali compounds only a limited amount of SiO_2 can diffuse out, but more materials are pumped in. This generates the force necessary for expansion; this also explains the role of $\text{Ca}(\text{OH})_2$. Note that according to this hypothesis the chemical reaction and expansion are not directly related.

3.2 Testing of the reaction mechanism

From the hypothesis it follows that all soluble alkali compounds will accelerate alkali-silica reaction. However, alkali hydroxides, which depress the concentration of $\text{Ca}(\text{OH})_2$ in the liquid phase, will cause less expansion than other alkali compounds eg. chlorides or nitrates. In a recent study it has been found that prisms made from a reactive sand and Portland cement expand less when stored in a 3N NaOH solution than when stored in a 3N NaCl solution; although the extent of chemical reaction was higher in the prisms stored in 3N NaOH solution than in prisms stored in 3N NaCl solution (6).

The reaction shown in [1] constitutes another test for the above hypothesis. Points to note that the reaction should occur in a system reactive sand- $\text{Ca}(\text{OH})_2$ -KCl solution and that the liquid phase gets enriched with CaCl_2 . This newly formed CaCl_2 will then depress the concentration of $\text{Ca}(\text{OH})_2$ in the liquid phase by the common-ion effect and the higher the reactivity of

an aggregate the lower will be $\text{Ca}(\text{OH})_2$ concentration in the liquid phase. This inference has been corroborated (7).

Various practical implications of the newly proposed reaction mechanisms have been discussed in a recent paper (8).

3.3 Measurement of alkali-silica reactivity of aggregates

In this phase one primary and two secondary test methods have been devised for the measurement of the alkali-silica reactivity of aggregates especially of sand fractions.

3.3.1 The primary method. The primary method is an expansion measurement method. In this method 40x40x160 mm prisms, made from 1:3::Portland cement:sand mortars having a water/cement ratio of 0.50, are exposed to a saturated NaCl solution at 50°C and their expansion measured at regular intervals up to at least 20 weeks (9). However, in most cases the expansion is over by about 10 weeks storage in NaCl solution. This testing period is much shorter than any other primary method in existence.

This accelerated test is rather severe for the following two reasons: (i) NaCl causes more expansion than NaOH, (ii) in this test the supply of alkali is unlimited. It has been observed that the method is independent of the alkali content of the cement so long the cement is free of pozzolanic additives.

The acceptance criterion is 0.1% expansion. This value was chosen on the following basis: The gravel fraction of most commonly used concrete mix compositions is about 50% by volume and the sand:cement ratio is about 2.5 to 3. If one assumes that a non-reactive gravel will be used in a good quality concrete then its expansion will be determined by its mortar and will be half of the expansion of its mortar fraction. As the test mortar has the sand/cement ratio very similar to that of the most commonly used concrete composition its expansion will be twice the expected expansion of concrete. It is however known that a structure can not tolerate more than about 0.1% expansion so that the acceptance criterion of 0.1% expansion gives a safety factor of 2. It is obvious that the primary expansion measurement method has a built-in objective basis for its acceptance criterion.

3.3.2 The secondary methods. Unlike the primary methods the secondary methods have no objective basis for their acceptance criterion; they have to be statistically correlated with expansion or service records of aggregates. Two methods which have been proposed during this phase both measure the chemical reactivity of reactive components.

The first method is a pycnometric one in which sand to be tested is exposed to 10 Normal NaOH solution at 50°C and the volume reduction due to dissolution of reactive silica is measured continuously and automatically (10). The method was expected to give information both about the reactivity and amount of reactive silica present in the sand. It has been found that the presence of CaCO_3 in sand interfere in both the above aspects.

The second method is based on the equation [1] and further detail of this method could be found in another paper presented in this volume (11).

3.4 Prevention of alkali-silica expansion

Researches carried out in this phase emphasized that alkali-silica reaction is not always accompanied by an expansion and the importance of the environment to which the concrete structure will be exposed during its use.

For an expansive alkali-silica reaction to occur a simultaneous presence of reactive aggregate, high concentration of alkali compound, $\text{Ca}(\text{OH})_2$ and water is necessary. A shortage in any one of the above four factors will either reduce or eliminate the expansion. Furthermore, to transfer the expansion of individual reactive grains to the matrix, the grains have to be enclosed by the matrix; a partial cover will reduce expansion.

The movement of ions and water molecules may be drastically slowed down by adding a very fine grained solid, eg. micro-silica or a reactive material, eg. fly-ash (12). In Denmark a Portland fly-ash cement has been introduced for this purpose which reduces expansion.

The removal of $\text{Ca}(\text{OH})_2$ may be achieved by using a slag-Portland cement or adding a pozzolan eg. fly-ash to cement in sufficient quantity (4). However, it is not very practical to add sufficient amount of a pozzolan to consume $\text{Ca}(\text{OH})_2$ completely.

The reactive grains may be partially isolated from the matrix by entraining sufficient amount of a fine grained air bubble system; some air bubbles being attached to the reactive grains. This partial isolation will reduce the overall expansion. The air-entrainment will be particularly effective if the reactive component is in the sand fraction (13).

The environment to which a concrete structure could be exposed has been classified into three classes (14):

(i) An aggressive environment in which a structure is exposed to an alkali salt solution, or to flue gases, or sea or brackish water

(ii) A moderate environment in which a structure is exposed to moist, non-aggressive out or indoor conditions or flowing or standing fresh water

(iii) A passive environment in which a structure is exposed to dry, non-aggressive conditions, particularly an indoor climate.

It has been stipulated that sand types to be used to make concrete for an aggressive or moderate environment may not contain more than 2% reactive components or may not expand more than 0.1% when tested by the NaCl bath method; in the coarse aggregate the maximum content of particles of densities less than 2400 kg/m^3 may not exceed 1 and 5% respectively.

4. ACKNOWLEDGEMENTS

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5. REFERENCES

- [1] S. Chatterji - An Accelerated Method for the Detection of Alkali-Silica Reactivities of Aggregates. Cement & Concrete Res. 8, 647-650, 1978
- [2] S. Chatterji - The Role of $\text{Ca}(\text{OH})_2$ in the Breakdown of Portland Cement Concrete due to Alkali-Silica Reaction. *ibid.* 9, 185-188, 1979.
- [3] T. Knudsen and N. Thaulow - Quantitative Micro-Analysis of Alkali-Silica Gel in Concrete. *ibid.* 5, 443-454, 1975.
- [4] S. Chatterji and N. Clauson-Kaas - Prevention of Alkali-Silica Reaction by using Slag-Portland Cement. *ibid.* 14, 816-818, 1984
- [5] S. Chatterji et al - Studies of Alkali-Silica Reaction. *ibid.* 16, 246-254, 1986
- [6] S. Chatterji et al - Studies of Alkali-Silica Reaction. *ibid.* 17, 777-783, 1987
- [7] S. Chatterji and A.D. Jensen - A Simple Chemical Method for the Detection of Alkali-Silica Reaction. *ibid.* 18, 654-656, 1988
- [8] S. Chatterji et al - Studies of Alkali-Silica Reaction. *ibid.* 18, 363-366, 1988
- [9] NORDTEST NT Build 295, 1985 "Sand-Alkali-Silica Reactivity Accelerated Test". Nordtest, Finland. 1985
- [10] T. Knudsen - A Continuous, Quick Chemical Method for the Characterization of the Alkali-Silica Reactivity of Aggregates. Institute for Mineralindustri, Technical University of Denmark, 1985. Copenhagen
- [11] S. Chatterji - A Simple Chemical Method for the Detection of Alkali-Silica Reactivity of Aggregates.
- [12] S. Chatterji et al - Studies of Alkali-Silica Reaction. *Il Cemento* 84, 47-52, 1987
- [13] A.D. Jensen et al - Studies of Alkali-Silica Reaction. Cement & Concrete Res. 14, 311-314, 1984
- [14] Danish Code of Practice for the Structural Use of Concrete. Byggestyrelsen, Copenhagen. 1985