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THEORETICAL AND PRACTICAL RESEARCH ON THE ALKALI-SILICA REACTION

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SYNOPSIS

The results of theoretical and practical investigations on the alkali-silica reaction performed by the group at the RWTH Aachen are summarised.

The influence of different properties of the aggregate, the cement and other parameters such as temperature and relative humidity, on the ASR with opaline sandstone were investigated.

A concept has been worked out to evaluate the residual hazard in a concrete construction damaged by the ASR.

SAMEVATTING

Die resultate van teoretiese en praktiese ondersoeke oor die alkali-silikareaksie wat deur die groep by die RWTH Aachen uitgevoer is, word opgesom.

Ondersoek is ingestel na die invloed van verskillende eienskappe van die aggregaat, die sement en ander parameters soos temperatuur en relatiewe humiditeit op die ASR met opaalsandsteen.

'n Konsep is opgestel om die residuele gevaar in 'n betonkonstruksie wat deur die ASR beskadig is, te evalueer.

DISCUSSION

Mr C Semmelink, (NITRR, Pretoria) asked the author whether her explanation meant, in simple engineering terms, that if too much water were absorbed by the gel the pressure it could exert became too low to be effective in cracking the concrete.

Dr L S Dent Glasser said that this was what she felt although it was more of a theoretical than a practical appraisal of the situation. Her own feeling was that if the gel became fluid either through absorption of a great deal of water, or because there was sufficient alkali there to react it completely, then it could flow into existing pores and not exert pressure. However, she suspected that the danger lay in the situation where a particle was only partly decomposed, and was still sufficiently rigid to be able to exert pressure yet insufficiently fluid to be able to escape into the surrounding pores.

Dr A Poole, (Queen Mary College, London) agreed with Dr Dent-Glasser that the disruptive pressure exerted by a reacting particle depended partly on its size. However, he added, the reactivity of a real particle was also going to depend quite largely on the surface area available. Thus the finer the particle the more it would react. He asked Dr Dent-Glasser to enlarge on these two opposed effects.

Dr L S Dent-Glasser thought that the effects might in fact be additive in that the very fine particles could be capable of reacting rapidly and therefore reaching the fluid state quite quickly. In the intervening period before they disintegrated, they would not be capable of exerting such highly disruptive forces as would one large particle that was reacting very slowly. She thought this might well be a consideration in that one only needed one or two really badly swelling large particles to produce a crack, after which one was in another situation.

Mr H E Vivian, (Australia) added that the gel, as one normally saw it, particularly on a concrete that was somewhat old could have a variety of appearances. Sometimes it would be hard and clear, sometimes somewhat cloudy and sometimes quite white and like porcelain. He thought it was not important, as far as expansion was concerned, but undoubtedly people saw the gel and wondered how it came to appear in these different forms.

Dr L S Dent-Glasser said that she had no precise experimental knowledge of this, but suggested an explanation. They had tried reacting gel with a mixture of potassium and calcium and had found that the initial growth was quite transparent and when analysed appeared to be largely silica, with a little potassium. With increasing age the lime/silica ratio went up and finally ended at around 1,5, at which stage the gel had the appearance of CSH in the electron microscope and became increasingly cloudy in appearance when seen by the naked eye. She suspected that some of those gels which were cloudy might well have picked up calcium from the surrounding cement. She also thought that if the ratio of soda to silica were high enough, a certain amount of carbonation would take place where the exudation was protected from water and that one of the forms of sodium carbonate would probably crystallise out. She thought that this ought to be detectable by X-rays but had never actually done it. Certainly the typical appearance of the soda silica gels was very transparent and as soon as one added calcium, they begin to turn opaque.

Prof S Diamond, (Purdue University) said that they were in reality 'prisoners of our usual ways of thinking and looking at these things'. People had always thought that a gel formed and absorbed water and that the gel was then diluted and oozed out. He submitted that as a result of his experiments and some retrospective thought it was really not possible to say that a gel absorbed water. In his case the system had been sealed so the gel had to absorb pore solution. In any real case, water might enter the concrete form the surface, but all it did was to dilute the pore solution and what was actually entering the gel had to be diluted alkali hydroxide. It was a small point, but might be worth thinking about.

Dr L S Dent-Glasser said she agreed completely with Prof Diamond. He was absolutely right and she thought this explained the wet/dry cycle effect in that each time the gel dried out it sucked up some more pore fluid, i.e. alkali hydroxide and disintegrated further. She was sure that the explanation of this cycling effect lay in that if one spoke of water, one was using the term loosely.

1. INTRODUCTION

The results of the theoretical and practical investigations on the alkali silica reaction (ASR) performed by the group at the RWTH Aachen are summarised. Mineralogical and chemical analyses of the reactive minerals, flint and opaline sandstone, which occur in the north of Germany, reveal a relationship between the reactivity of the aggregates and their porosity or their calcite content.

The pressure generation due to the ASR was calculated by means of Donnan's theory of membrane equilibria. This calculation was confirmed by comparing measurements on mortar specimens. The influence of different properties, both of the aggregate and of the cement as well as of environmental factors such as temperature or relative humidity, on the ASR with opaline sandstone were investigated in different series of mortar specimens with standard composition.

The simple measurement of expansion is not sufficient to estimate the deterioration caused by the ASR. The combination of extension measurements and non-destructive resonance frequency strength tests greatly improves the estimate.

Long term tests reveal considerable differences in the determination of the influence of the kind of cement, of pozzolanic additions, of the temperature, and of the grain size of the reactive aggregate.

Furthermore a concept has been worked out to evaluate the residual hazard in a concrete construction damaged by the ASR. Recommendations are given for the prevention of further damage in a concrete construction.

2. MECHANISM OF ALKALI SILICA REACTION

The mechanism of the alkali silica reaction has already been described in former publications [1-5] as an osmotic reaction. But a complete interpretation of all the phenomena occurring during the ASR has been impossible. Together with Sideris [6,7] we were able to show that the ASR is caused by a dynamic osmotic equilibrium. For the explanation of an osmotic cell we have to take into consideration the Donnan-membrane equilibrium. With this the ion diffusion against a strong gradient of concentration is easy to explain. From the equation:

$$P = g R T 2 \Delta C$$

with ΔC = difference in concentration mol/ℓ
g = osmotic coefficient
T = absolute temperature K
R = gasconstant = 0,082 ℓ Atm/K mol
P = osmotic pressure Atm

the maximum pressure that can be expected from a reactive grain during ASR can be calculated. It was determined to be 17 to 18 N/mm^2. This corresponds well with the experimental value of 14,2 N/mm^2 [4] stated in the literature. The maximum pressure in a mortar or concrete cross section can be calculated from the equation:

$$\sigma_{eff} = P_{max} \left(\frac{a^2}{r^2 - a^2} \right)$$

where a = diameter of the reactive grain
and r = the distance factor + a.

This maximum pressure was calculated by Sideris [6] to be 1,9 N/mm^2, assuming 3 per cent m/m of reactive material in the aggregate. In later experimental work with 4 per cent m/m opaline sandstone in BRD-standard mortar the maximum pressure was determined to be 2 N/mm^2 and the maximum pressure was extrapolated to be 2,5 N/mm^2, which agrees again quite well with the theoretical value. The first crack formations which appear after surface drying are due to additional shrinkage tension.

This model also implies the limitation of the deleterious reaction by the formation of

1. coagulated Ca-alkali silicate hydrate with small amounts of Ca-ions

2. coagulated alkali silicate hydrates
   2.1 at higher alkali concentrations
   2.2 at higher temperatures
   2.3 at higher pressures.

Furthermore, all observed phenomena concerning the ASR can easily be interpreted by the mechanism of the reaction as given above.

3. EXPERIMENTAL

We did our experimental work with standard mortar samples, prepared and compacted according to DIN 1164. Most of the specimens were 1 x 4 x 16 cm^3 instead of 4 x 4 x 16 cm^3. For the expansion measurements the specimens were equipped with steel gauge points to fit into the comparator. The Portland cement used was a normal type 45 F cement with 0,90 per cent Na$_2$O equivalent.

The reactive aggregate used in the tests is opaline sandstone from Schleswig-Holstein. It is either added in varying compositions to test its influence or in a constant composition to examine other influences. In the latter case a green material with a bulk density of 1,91 g/cm^3, a porosity of 20,4 per cent by volume and a BET-surface area of 24,4 m^2/g was used in amounts of 4 per cent m/m as a replacement for the corresponding fraction of the standard sand.

After one day of curing at 20°C and high humidity, the specimens were demolded. The further storage was performed in slightly exhausted desiccators above water or above sulphuric acid solution of different concentrations to maintain the high or the chosen humidity and to prevent carbonation.

The effect of the ASR was monitored at varying intervals by measuring changes in the mass, length and natural frequency of the specimens. The determination of the expansion alone does not give a clear picture of the state of the deterioration in all cases.

These results show that the coarse highly reactive material much greater than 90 µm in the same quantities may cause greater damage after continued humid curing. This is even more pronounced if not only the expansion but also the drop in strength is considered. The theory predicts that under conditions which are otherwise the same a lower alkali content may increase the damage with less reactive aggregate and vice versa.

(c) *Influence of blended cements.* Usual blended cements are Portland-pozzolan and Portland-slag mixtures with replacement of up to 40 per cent m/m of Portland cement with a natural or artificial pozzolan or up to 70 per cent m/m with granulated blastfurnace slag [14-23].

Our work on the influence of the replacement of 20 per cent m/m of normal type 45 F Portland cement by flyash (FPZ) or the addition of 20 per cent m/m flyash (PZ + F) instead of fine inert sand reveals in both cases a minor expansion. The value of the resonance frequency of the FPZ, however, is as low as that of the ordinary PZ[9]. New unpublished test results[10], with PZ 35 F − NA of 0,4 per cent Na₂O equivalent, indicate that this cement leads to a marked expansion and resonance frequency decrease in combination with opaline sandstone of 1,9 g/cm³ bulk density\ in the fraction 0,5 to 1,0 mm after about 2 years' wet storage. Here a 20 per cent m/m replacement and, more severe, a 20 per cent m/m addition of flyash with 3,4 per cent Na₂O equivalent, result in an earlier and stronger reaction (Figure 3).

The several pozzolans which were added to or used to replace the normal PZ 45 F reduced the damage at normal and elevated temperatures (40ºC). The reduction in expansion and the drop in resonance frequency compared with the ordinary PZ is more distinct in the case of the cement replacement. In this case, the reduction amounts to 50 per cent [10, 24, 25].
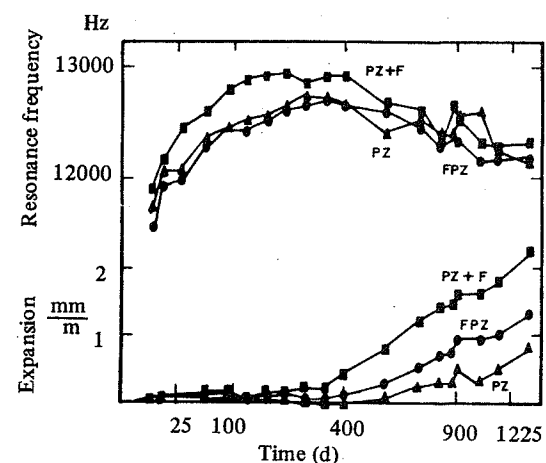
EPZ with 35 per cent m/m slag results in a 50 per cent reduction in expansion caused by ASR. No effect of the alkali content of the slag can be detected. Blastfurnace slag cement with a slag content of 65 per cent m/m showed no significant damage up to 3 years' humid curing[11, 25, 26].

The reason why the ASR is prevented by the replacement of Portland cement by pozzolans or more accurately by blastfurnace slags is only partly explained by a fixation of the alkalis. Another cause is the tighter structure of the cements containing slag or pozzolan[26, 27, 28]. The two types of cement differ in the rate of hydration of the admixtures: the slags hydrate after several hours and the pozzolans only after weeks or months.

The early influence of the slag on the mortar compaction is shown in references 26 and 28, the slower influence of a pozzolan in reference 28.

(d) *Influence of humidity.* In previous publications the influence of the relative humidity on the ASR has already been demonstrated[8, 9, 10, 24]. After several rearrangements of the mortar bars, the critical humidity required to prevent ASR damage was found to be < 85 per cent after about 3 years' curing[10, 24].

In order to examine the potential ASR of the specimens, they were transferred to a humidity > 95 per cent and in part to a higher temperature of 40ºC[10]. The results are given in Figure 4. Only the bars precured at 80 and 90 per cent RH showed a renewed expansion. At the elevated temperature, the expansion started earlier but reached higher values at normal temperature. The decrease in resonance frequency is more distinct with mortars precured at 80 per cent RH.
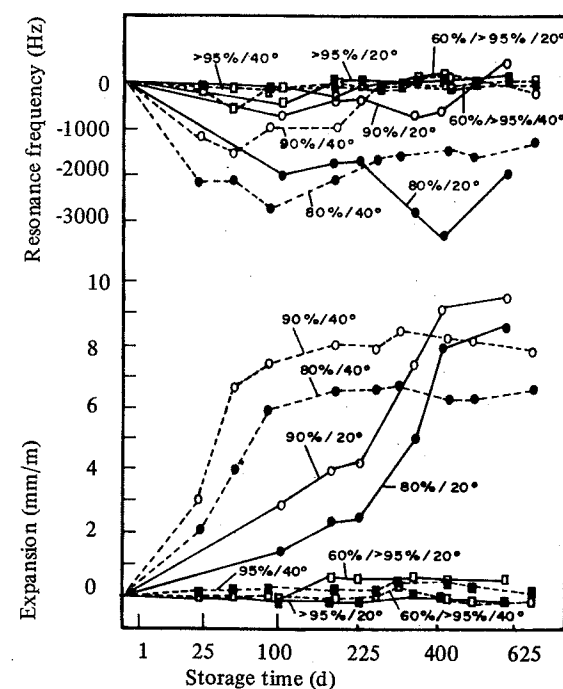

FIGURE 3: ASR with low alkali Portland cement and additional flyash or flyash as cement replacement according to Lenzner[10].

FIGURE 4: Potential ASR of mortar prisms precured for 3 years according to Lenzner[10].

4. RESULTS

(a) *Influence of the type of opaline sandstone.* First investigations [8, 9] on the nature of the reactive opaline sandstone show that it is of two main types:

1. a white-grey material and
2. a green material.

Both materials show the strong main peak of cristobalite besides smaller amounts of quartz in the X-ray diffraction pattern. The main difference in the mineralogical compositions of the two fractions lies in their calcite content. In the white material it amounts to between 9 and 35 per cent m/m and in the green one to between 2 and 6 per cent m/m. Furthermore, both materials show differences in their bulk density and therefore in their porosity. Material with a bulk density < 1,6 g/cm³ or a porosity > 40 per cent by volume showed no significant expansion or drop in natural frequency after up to one year of humid storage. Material with higher bulk density or lower porosity showed increasing expansion or a drop in resonance frequency. On the other hand, the green sandstone leads to more severe damage than the white. These results were confirmed by Lenzner[10] who found an increase in the damage with bulk density up to a figure of 2,05 g/cm³ or a porosity of 14 per cent by volume. A further increase in the bulk density was accompanied by a strong increase in the calcite content to 56 and 97 per cent m/m, respectively, for the green and white sandstones and by the disappearance of the cristobalite peak. These fractions had no deleterious effect on the mortar bars, which have so far been tested over a period of 2 years. Figure 1 shows the test results with green sandstone of various bulk densities.
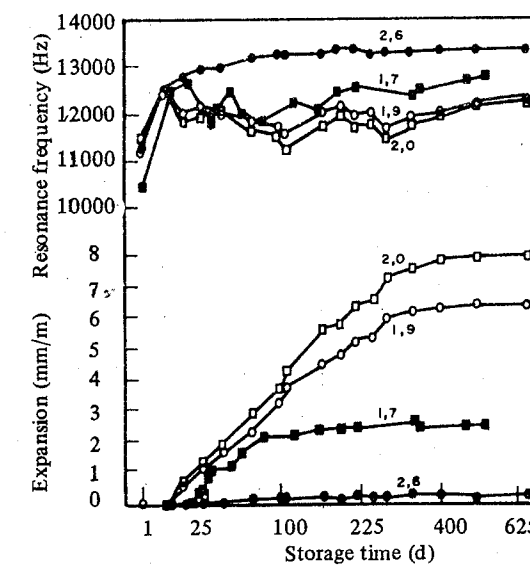
These results clearly indicate that where porosities of the sandstone are greater than 40 per cent by volume damage to the specimens is prevented. Decreasing porosity results in more expansion and a drop in the resonance frequency. Increasing calcite content reduces the ASR by simultaneously reducing the content of reactive silica. In addition there may be an interaction of the calcite with the alkali silica gel, especially at the higher curing temperature of 40ºC. The white and the green sandstone with a bulk density of 2,34 and 2,60 g/cm³, respectively, contained no reactive silica. No damage was measured.

(b) *Influence of grain size.* In the literature, the more severe cases of damage have been found mostly where particles < 90 µ m of a highly reactive aggregate have been used. With this aggregate, the pessimum amount is less than 5 per cent m/m [11, 12, 13]. Less reactive dense materials such as some flints or vitreous aggregates cause more severe damage in amounts > 5 per cent m/m and with grain diameters > 200 µm [14].

New results from Lenzner [10] indicate that highly reactive opaline sandstone causes increased damage in coarser fractions after long curing periods (Figure 2).

After 3 years' curing the greatest expansion is measured for the fraction 0,5 to 1,0 mm. The drop in resonance frequency, however, indicates that the 1,0 to 3,15 mm and 3,15 to 5,00 mm fractions have a more deleterious effect. Similar results are obtained with natural sand fractions of 2 to 4 mm and 4 to 8 mm containing reactive sandstone. After more than 3 years' humid curing the reaction is not yet terminated [10].
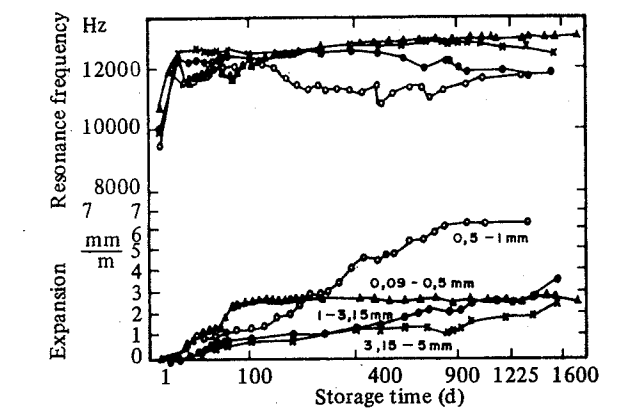

FIGURE 1: ASR with green opaline sandstone of varying bulk densities according to Lenzner[10].

FIGURE 2: Influence of grain size of opaline Sandstone on the ASR according to Lenzner[10].

(e) *Influence of the curing temperature.* The results illustrated above clearly indicate the influence of curing temperature. In the literature, the influence of the temperature on the ASR is controversial. Some results show that increased temperature results in a higher degree of expansion[12, 29-31], while others show a reduction[32-34].

Our own results clearly indicate more severe damage at room temperature. Elevated temperatures (40ºC) caused the reaction to begin earlier but led to significantly less damage[10, 24]. This effect could not be explained solely by the more plastic stage of the mortar. We should also take into account the changes in solubility, the diffusion of the calcium and alkali ions through the cement stone, and the changes in the solubility and diffusion of the ions which are incorporated as "impurities" in the reactive grains and which can act as flocculating agents. From this point of view the recent investigations[35] with pure sodium silicate solution are still incomplete, and can solve only a part of the problem.

5. EXAMINATION OF CONSTRUCTION DAMAGE AND ATTEMPTS TO PREVENT IT

The ASR may cause damage to concrete. Physico-chemical and mineralogical investigations on drilled core samples of concrete structures damaged by ASR have been carried out. Equipment has been developed to measure the expansion of the concrete cores directly after their removal from the structure so as to determine the extent of the deterioration. The residual hazard can be determined from additional curing tests.

Under similar conditions the stronger concrete will expand more severely and for longer. The long duration of the reaction is confirmed by measurement of expansion over a period of seven years. In addition to the results with mortar bars[8], it can be shown that the reacting aggregate particles can easily be made visible and can be counted so as to provide a means of evaluating the residual hazard[36].

It is well known in practice and also from the above results that damage by the ASR can be completely prevented by a suitable mix design for the concrete. Less information is available about the prevention of further damage to an affected concrete structure. In the mortar bar experiments delayed damage or none at all by the ASR was observed as a result of impregnation with about 115 g/m² alkyl alkoxy silane. The delayed damage was observed when immersing the bars three times a week for three hours in water and subsequently curing them at 80 per cent RH[8, 9]. The prevention of subsequent damage was watched under conditions which were otherwise the same with the exception that the interim curing was done at 60 per cent RH[24].

In experiments on the remedial treatment of damaged concrete, some of the alkali chlorides and silicates, described in the literature as having a favourable effect, in fact lead to further considerable expansion[13, 14]. The treatment with baryta water can claim in all cases to be beneficial[37, 39].

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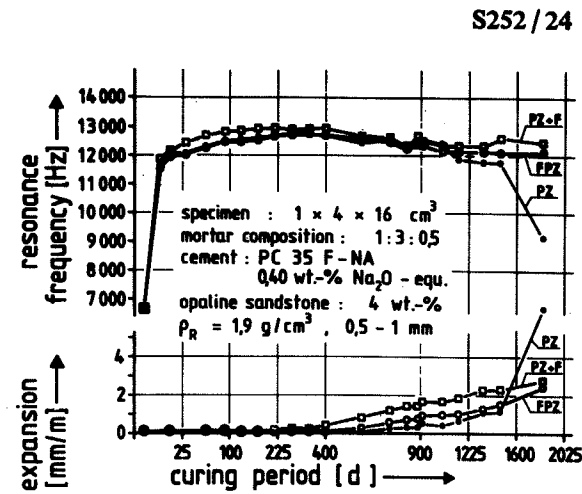1. HANSEN W C *Studies relating to the mechanism by which the alkali-aggregate reaction produces expansion in concrete.* Journ of A C I, 15 1944.

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Addendum

The following sentence should be added to the last sentence of the second paragraph under heading (c) on page 3:

At later ages, the expansion and the decrease in resonance frequency indicate the severe deteriorations with ordinary Portland cement.

The following figure was presented by the author during the conference to replace Figure 3 on page 3 of his presentation:

S252/24

specimen : 1 × 4 × 16 cm³
mortar composition : 1 : 3 : 0,5
cement : PC 35 F – NA
   0,40 wt.-% Na₂O – equ.
opaline sandstone : 4 wt.-%
ρ_R = 1,9 g/cm³ , 0,5 – 1 mm

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