AN INVESTIGATION OF ALKALI-SILICA REACTION IN SEVEN-YEAR OLD AND MODEL CONCRETES USING S.E.M. AND E.D.S.

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The microstructure of a seven-year old concrete containing a reactive aggregate has been investigated using scanning electron microscopy (S.E.M.) and energy dispersive x-ray spectrometry (E.D.S.). Analysis of the reaction gel product shows a phase separation in composition. A model concrete system has also been devised in order to investigate the interface region between a reactive aggregate and cement paste. Some preliminary results from this system are shown.

SEVEN-YEAR OLD CONCRETES

Introduction

Various compositions of the gel formed by alkali silica reaction (A.S.R.) have been reported. The role of gel composition, in particular the role of calcium, in determining the overall expansion is unclear. Knudsen and Thaulow (1) noted the change in calcium content of the gel as it moved through the concrete, being high in alkalis in the aggregate and higher in calcium in the cement paste. As early as 1955 Verbeck and Gramlich (2) suggested that if calcium hydroxide was present the gel had a higher calcium content and its fluidity was reduced. Work on synthetic gels by Diamond et al (3) also showed higher calcium gels had reduced fluidity but could find no clear correlation between gel composition and swelling. Buck and Mather (4) reported the tendency of the calcium to move into the initially high alkaline gel and noted the depletion of calcium hydroxide in the surrounding cement paste. More recently Chatterji et al (5) have suggested that calcium hydroxide is a requirement for A.S.R., a view endorsed by results from Diamond (6) and Davies and Oberholster (7).

Experimental

An ordinary Portland cement (O.P.C.) concrete containing Thames Valley sand reactive aggregate was investigated. Thames Valley is a flint aggregate and the size fraction used was 1.18 mm to 5 mm. The O.P.C. used had an alkali content of 1.07% Na_2O_e (1.3% K_2O and 0.21% Na_2O). Sections from the sample were resin-impregnated with an Araldite resin, cut using a diamond saw, lapped flat using 9 μm alumina grit and then polished to ¼ μm diamond grit. The sections were sputtered with a coat of carbon for use in the S.E.M. The sections were analysed using a Jeol JSM 35-CF scanning electron microscope coupled with a Link AN10000 E.D.S. system.

Results

A backscattered electron (b.s.e.) image of a region of the concrete is shown in Figure 1. A crack about 100 μm wide is seen extending through the Thames Valley sand grain (left), into the cement paste, through a limestone grain and into a large pore (right). The crack is filled with the reaction product gel from A.S.R. Areas in the sand grain where A.S.R. has occurred appeared dark and on closer examination were found to be more porous. These areas were also found to have a higher potassium content than the surrounding, 'unaffected' areas. The composition of the gel at different sites was analysed using E.D.S. and the results are shown in Figure 2. It can be seen that the composition falls into two distinct categories. Composition A is a low calcium, high sodium and potassium state and composition B is a high calcium, low sodium and potassium state. The gels in the sand grain, the limestone aggregate and the large pore were found to be of composition A and the gel in the cement paste of composition B. The gel in the sand grain appeared granular in some areas and clear and featureless in others, although the composition of both types was similar.

Discussion

The composition of the gel in the limestone was similar to the gel found in the sand grain and is low in calcium and high in alkali. This would suggest that this was the composition of the gel when the gel moved through the crack. There is also no evidence of crack widening after it fills with gel suggesting that the gel has not swelled further. This observation of variable gel composition depending on location and the fluidity of the gel depending on composition is supported by results from Thaulow et al (8).

The composition of the gel is obviously dependent on its position in the concrete. In the cement paste the gel takes up calcium from the paste and the gel composition moves towards that of the C-S-H gel formed in cement hydration. The distribution of the analyses between two distinct compositions and with relatively few points inbetween would suggest that there is a phase separation between the gel compositions. There does not appear to be complete solid solubility between the K-C-S-H and the C-S-H gels. Once a critical level of calcium is exceeded a phase change appears to occur. The existence of a phase boundary in alkali-C-S-H gels is supported by Macphee et al (9) who suggested an immiscibility gap (an incomplete range of solid solubilities) between a high Si, low Ca gel (similar to A.S.R. gel) and the higher Ca, C-S-H gel found in cement paste.

MODEL CONCRETES

Introduction

A.S.R. is a complicated chemical reaction between the aggregate and the pore solution in the cement. It is logical, then, to focus on the region where these components meet, the aggregate-cement paste interface. Analysis of this region using a model system can yield information on the chemical state of both components of the concrete during the reaction and their changes over time.

Experimental

Discs of Beltane opal, 5 mm thick and 30 mm diameter, were cut from a bulk sample and one surface polished flat on SiC paper. The discs were placed in containers and O.P.C. (with water/cement ratio = 0.5 and alkali content = 1.2% Na_2O_e) was poured on to the polished surface. The containers were continually agitated to eliminate large air bubbles from the interface region. The containers were kept sealed at 20°C, being topped up with water at regular intervals. At the required age the samples were cut along their length using a slow speed saw and then freeze-dried to stop the cement hydration reaction. The samples were then impregnated with an Araldite resin and polished using the same method as used for the seven year old concretes above. The sample surface was sputtered with carbon and analysed using the S.E.M. and E.D.S. systems.

Results and discussion

Figure 3 shows a b.s.e. image of the interface region between the opal and cement paste at one day. The opal is still intact but porous areas are evident. The shape of the interface suggests that the gap at the interface has formed during preparation but a band of gel product is seen to have formed at the interface. This gel band is 15 μm wide. At one month (Figure 4) the amount of porosity in the opal has increased and the width of the gel band increased to 120 μm. Gaps in the gel have appeared, sometimes close to the interface with the opal. The width of the reacted region within the opal is still not definite but a more porous region is evident extending 80 μm from the gel band, which has also widened. The six month sample (Figure 5) shows a definite reaction zone, 800 μm wide. The opal appears to have dissolved away during the reaction and is highly porous and contains many large gaps. There is a large band containing gel which is 300 μm wide. Large drying cracks are seen in the gel band, indicative of the high water content in the gel. The gel at all ages is of the clear, featureless type and its composition is high sodium and potassium, very low calcium, as shown in Figure 6. A few areas of gel close to the cement paste were noted as having a higher calcium content. None of the samples showed evidence of large cracks or gel in the cement paste, even near to the interface. In the six month sample map-cracking was noted far from the interface, the cracks being empty of gel.

These results suggest that in the early stages of A.S.R. the reaction is mainly the dissolution of the silica in the aggregate to form an alkali-silica gel structure. It is this gel which swells and causes large gaps to occur at the interface. The few points analysed close to the paste which show higher calcium counts suggest that the with time calcium from the paste is incorporated within the gel.

These preliminary findings illustrate how this model can follow the development and extent of A.S.R. with time. The gradients of the ions that are significant in A.S.R. can be mapped across the aggregate interface. The formation of gel and its composition with time and the depletion of calcium from the cement paste and silica from the aggregate can also be monitored.

CONCLUSIONS

1. Analysis of polished concrete sections using S.E.M. and E.D.S. can provide useful information about the microstructure and composition of A.S.R. affected samples.

2. A.S.R. gel exhibits a composition dependent on location in the microstructure. The gel shows a phase separation between high potassium, low calcium composition and low alkali, high calcium composition.

3. The model concrete system is useful in illustrating the changes in the microstructure and composition at the aggregate-cement interface due to A.S.R. with time. This model system shows the increasing dissolution of silica from the aggregate and formation of a high sodium and potassium, low calcium gel with increasing age.

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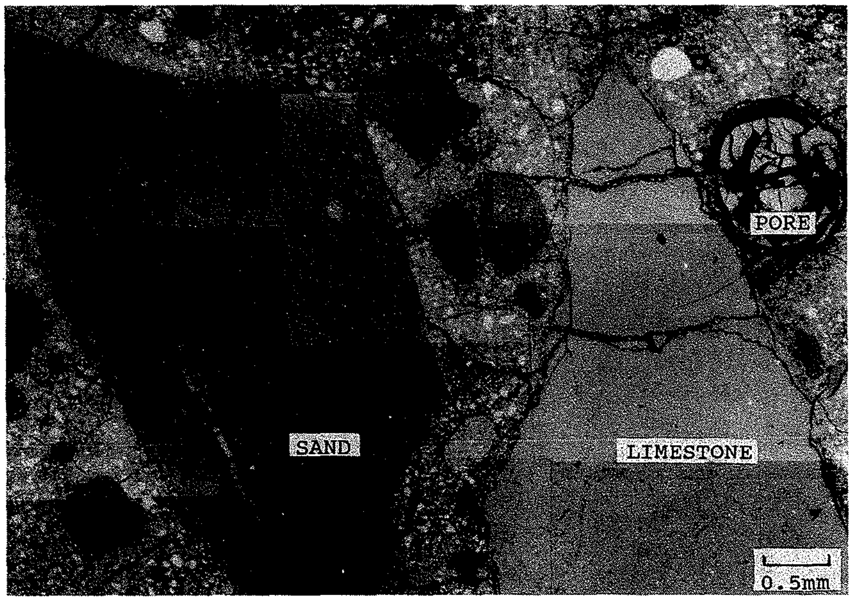

Figure 1 B.s.e. image of 7-year old concrete affected by A.S.R.

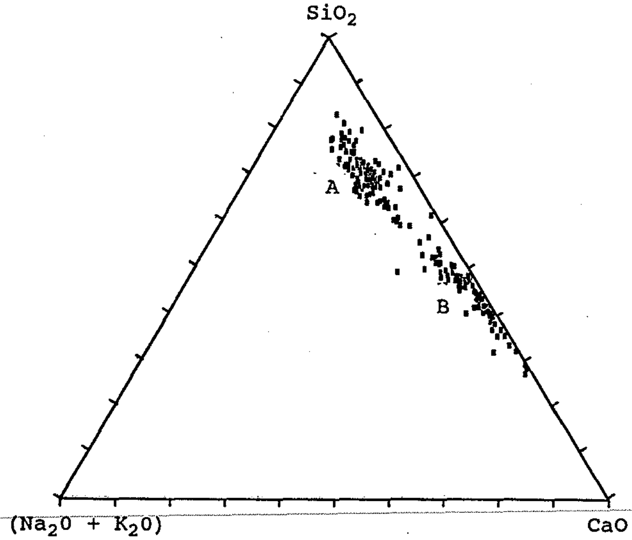

Figure 2 Ternary phase diagram showing composition of gel in 7-year old concrete

Figure 3 B.s.e. image of opal-cement interface after 1 day

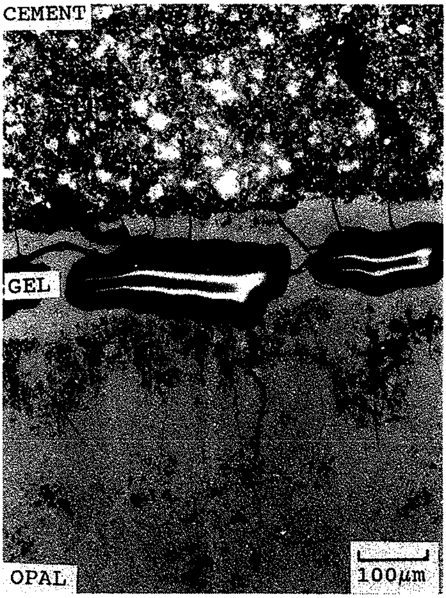

Figure 4 B.s.e. image of opal-cement interface after 1 month

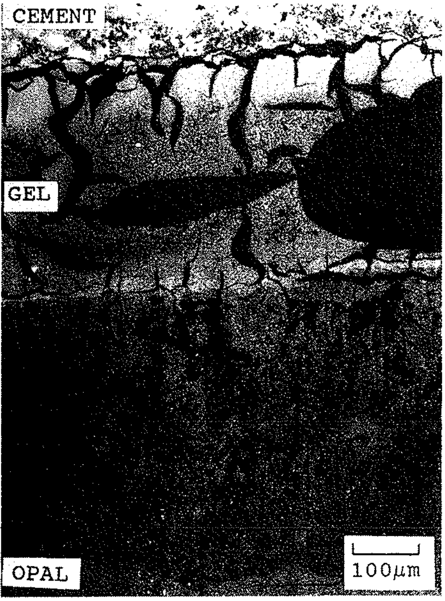

Figure 5 B.s.e. image of opal-cement interface after 6 months

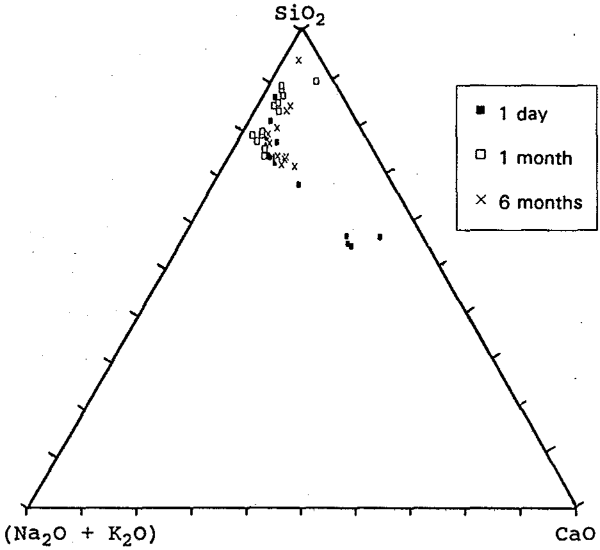

Figure 6 Ternary diagram showing composition of gel in opal-cement system at different ages