Microstructure

in

Alkali-Aggregate Reaction

ALKALI SILICA AND ETTRINGITE EXPANSIONS IN 'STEAM CURED' CONCRETES

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ABSTRACT

As part of a programme of investigations into the cement paste microstructure of precast concrete cured at elevated temperatures a laboratory study of the relationship between alkali–silica reaction and development of delayed ettringite has been undertaken. Evidence from laboratory prisms stored at 40°C and 80°C in humid conditions and then on an exposure site for 375 days is presented. Results indicate that gel reaction products of ASR provide a mechanism where sulphate solutions are drawn towards the gel which absorbs the OH ions thus concentrating the sulphate solution which in turn leads to the formation of ettringite in the cement paste close to the gel and along the adjacent microcrack network developed as a consequence of ASR induced expansion.

Keywords: Alkali–silica reaction, delayed ettringite expansion, electron microscopy, steam cured concrete.

INTRODUCTION

In the precast concrete industry elevated temperature curing (steam curing) at atmospheric pressure is a widely used technique to obtain high early strengths and as a consequence an increase in the rate of production. In recent years cases of 'steam' cured concrete units exhibiting premature deterioration due to expansion and cracking have been reported for example, (Tepponen & Kriksson. 1987), (Oberholster et al. 1992) and (Shayan & Quick. 1992). Recent work indicates a growing concern that concrete cured at elevated temperatures may show abnormal expansions after long term exposure in moist conditions and a number of research studies have been undertaken to determine the mechanisms operating.

In most of these studies either alkali–silica reaction or delayed ettringite formation have been identified as the probable mechanism, (Johansen et al. 1993) and (Heinz & Ludwig. 1987). In many case study examples both mechanisms are present and in some cases there are divergent views as to which mechanism is the primary cause of the deterioration.

THE MECHANISMS

The mechanism of alkali–silica reaction is now clearly established as the reaction between alkali and hydroxyl ions usually from the cement and amorphous or poorly crystalline silica components of the aggregate. The reaction may be regarded as proceeding in two stages firstly the formation of an alkali silica–gel reaction product which then absorbs water expanding in the process producing pressure which can exceed 4 MPa (Diamond. 1989) and may lead to cracking and failure of the concrete.

The role of sulphate in regulating the set of Portland cement principally through its reaction with C_3A is complex but well documented, for example in section 7.3 of (Taylor. 1990). The details of the mechanisms involved in the attack on hardened concrete by external sulphate solutions remain controversial, (Odler & Gasser. 1988), Cohen & Mather. 1991) and (Metha. 1993) in spite of over 60 years of research investigations. Nevertheless, the severity of the attack depends on the concentrations of sulphate in solution, the ease with which the sulphate ions can migrate through the concrete, the amounts of remnant C_3A, and of calcium aluminate hydrate present in the cement paste. The physical mechanisms of deterioration include the expansive formation of ettringite and/or gypsum in the fabric of the cement paste and the reaction with, and removal of the calcium silicate hydrates and the calcium hydroxide.

The expansion of some of the reported cases of 'steam cured' concrete has been ascribed to the formation of new ettringite within the concrete after a period of years of in–service use. The development of this delayed ettringite from the pre-existing monosulphate type hydrates in the concrete can lead to expansive mechanisms within the cement matrix very similar to the effects of the sulphate attack resulting from external sulphate solutions. Thus the mobility of sulphate ions within the concrete and their localised concentration within the cement paste will be important factors controlling the formation of the ettringite and the consequent expansion of the concrete.

The majority of these case study examples of premature deterioration of 'steam' cured concretes have been concerned with railway sleepers and in these examples alkali silica reactivity has been shown to be present. The principal cause of the expansion and cracking whether delayed ettringite or alkali silica reactivity is unclear.

The experimental programme summarised below has the primary objective of determining the relationship between alkali–silica reactivity and delayed ettringite formation. It forms part of a larger programme concerned with the effects of elevated temperature curing on the microstructure of concrete.

EXPERIMENTAL PROCEDURES

Previous studies, (Patel, Bland & Poole. 1995), have shown that as curing temperature rises monosulphate hydrates become increasingly important while ettringite becomes less important in the cement pastes of 28 day old concretes. It is also observed that sulphoaluminate hydrates infill some of the hollow CSH shell hydrate grains and that coarsely crystalline calcium hydroxide plates form in localised areas of the cement paste giving these areas an open porous texture.

As a consequence of the possible later breakdown of the monosulphates to form ettringite which may lead to expansion and cracking precast manufacturers usually limit the maximum temperature of curing to below 60°C. Previous studies in the main research programme have demonstrated that reducing the size of laboratory specimens down to a minimum cross–section of 70 mm had a negligible effect on the microstructural feature of the concrete and was comparable with sections from full size units.

The specimens

A duplicate series of concrete prisms were made in 75 x 75 x 250 mm steel moulds and subjected to a 60° maximum curing cycle as illustrated in figure 1 using a Weiss Technique SB11/80/40 climatic test cabinet. The curing cycle and maximum temperature were selected to simulate typical manufacturing conditions at the maximum 'National' guideline's temperature of curing.

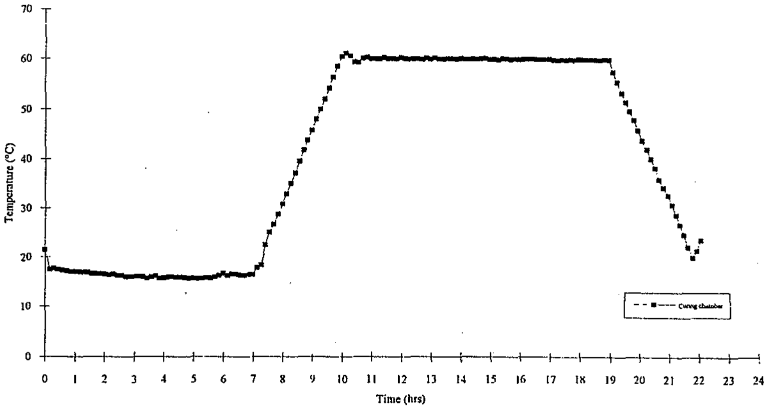


Fig. 1 . The steam curing cycle for the test prisms

The three basic mix designs selected are shown in table 1 below, water/cement ratio was 0.39 for all mixes. The three mixes were made using two cement types, an OPC with alkalis 0.31% Na_2O and 1.08% K_2O (sodium oxide equivalent: 1.02%) and a RHPC with 0.65% Na_2O and 0.13% K_2O (sodium oxide equivalent 0.56%).

Table 1. Mixes used for the prisms used in this study

Mixes		Cement	Sharp Sand	Fused Silica	Chard Sand	20 mm Granite	10 mm Granite	Water	Liquid Plasticiser
OPC	RHPC								
5	3	1224	2221	117	—	2267	1162	477	31.4
6	4	1224	—	—	2338	2267	1162	477	31.4
8	2	1224	2338	—	—	2267	1162	477	31.4

The aggregates used for the prisms were Mont Sorrel 'granite' coarse aggregate, a sharp sand from Bedfordshire, 3 mm fused silica which is known to be highly alkali–silica reactive and Chard sand from Somerset also known to contain reactive cherts.

After completing the curing cycle all the prisms were demoulded and microcracking was induced in the control prisms (mixes 2 and 8) by gentle hammer chiselling along lines transverse to the length. This was done to provide pathways for moisture movement through the specimens.

Storage

All prisms were then wrapped in cotton cloth saturated with distilled deionised water and sealed into individual polythene bags containing an additional 5 ml of deionised water. The sealed bags were then placed in individual containers containing 20 mm depth of water sealed and stored in 40°C and 80°C environments.

Steel studs cast into the end of each prism allowed expansion measurements to be made at weekly intervals during storage. Prior to taking expansion measurements the prisms were removed from storage and allowed to cool to 20 ± 2°C for 24 hours.

After a period of 70 days one set of the duplicate specimens was removed to an outdoor exposure site at Queen Mary and Westfield College, the second set were subjected to detailed petrographic study. After a period of 375 days exposure the second set of samples were measured for length change after rehumidifying them for

90 hours. They were then sliced and specimens from the central portion of each prism was subjected to detailed petrographic examination.

RESULTS

Length changes

After small initial expansions the control prisms exhibited no significant length change over the period of 70 days or when remeasured at 375 days. Similarly the prisms containing the chard sand specimens showed a small initial expansion in the first seven days but no further expansion up to 375 days.

The prisms containing reactive fused silica showed the expected rapid expansions, with the prisms in 80°C storage conditions showing greatest expansion in the first 21 days while prisms sorted at 40°C showed a more gradual and sustained expansion which reached 0.29% in the case of mix 3 and 0.35% for mix 5 after a further 375 days exposed to external environmental conditions. The expansion obtained for the first 70 days are illustrated in figure 2.

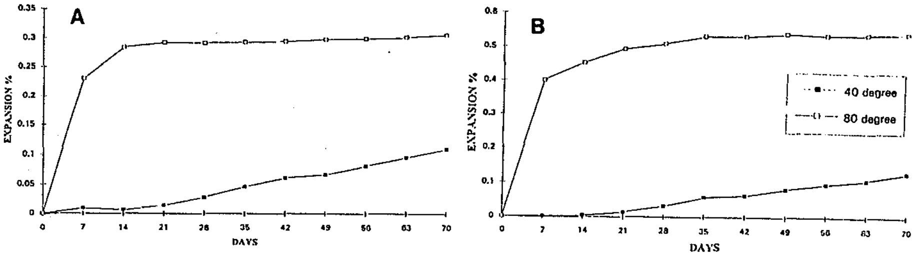
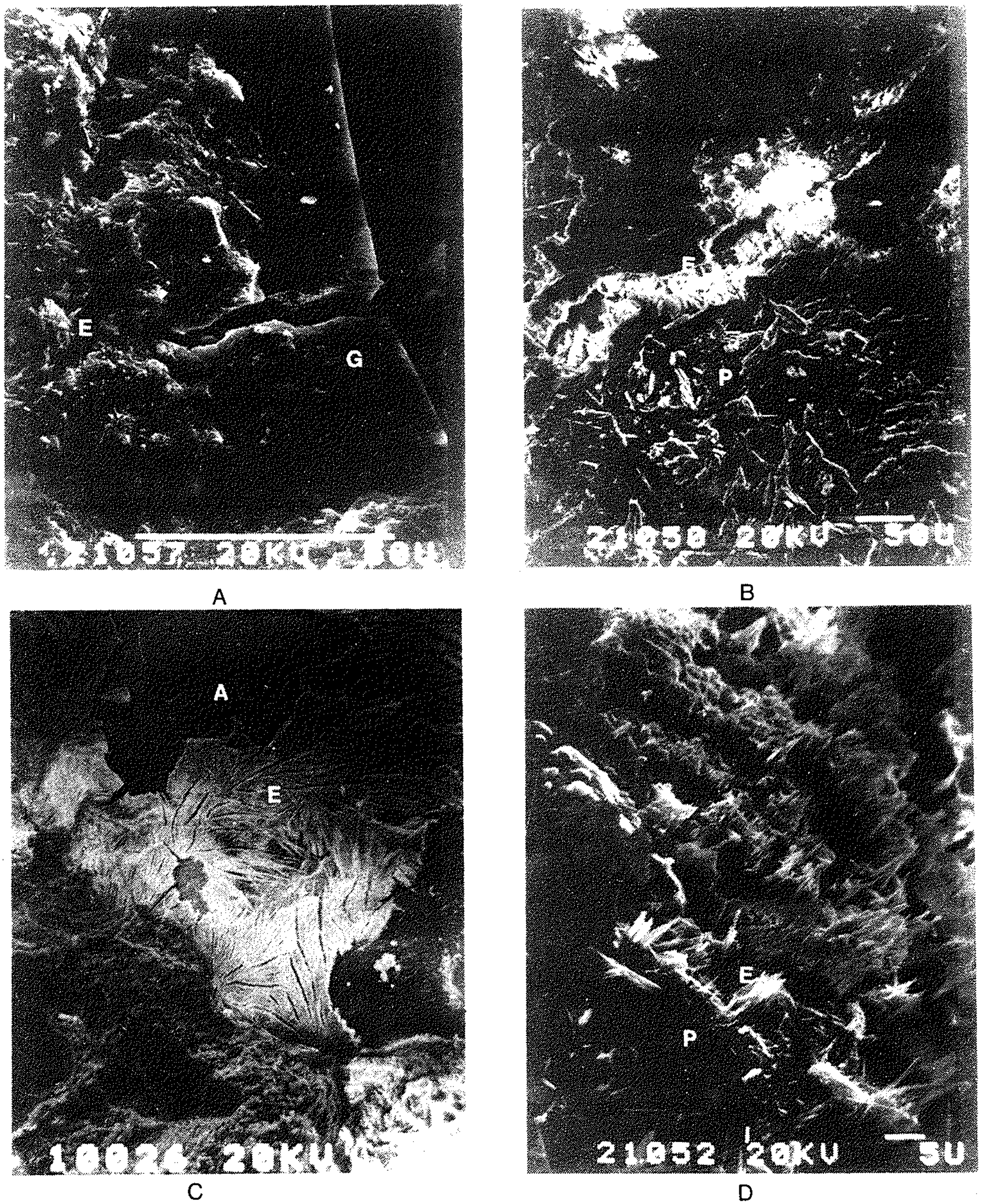


Figure 2. Expansion for the first 70 days (A): OPC specimens (B) RHPC specimens

Petrographic investigations

The petrographic investigations were undertaken using a modern Zeiss petrographic microscope and with a Hitachi 5450 scanning electron microscope with an Oxford AN100 microanalytical system. At 70 days the specimens containing chard sand and the control specimens showed no significant development of ettringite under examination by either optical or scanning electron microscopy. Minor cracking through the cement paste in the precracked control specimen was observed. both the OPC and RHPC specimens containing fused silica showed extensive evidence of ASR with extensive cracking and gel development associated with the particles of fused silica. Analyses of the gels showed them to be potassium rich. Detailed study failed to identify development of ettringite in these specimens.

The second set of prism specimens were examined at the end of the period of exposure using electron microscopy on rough and polished specimens. Small amounts of ettringite were identified in both the control specimen and the prism containing he chard sand. Minor microcracking of the paste was observed in both specimens but no evidence of any alkali–silica reactivity was detected. The two specimens containing fused silica contained extensive cracking and gel development associated with the fused silica particles. Excessive development of ettringite was also observed in the cement paste close to the areas of alkali-silica gel, in the cracks developed due to the expansion of the reaction product, as crack infilling peripheral to aggregate particles and on the surfaces of coarsely crystalline calcium hydroxide crystals which develop in small relatively porous areas of cement paste adjacent to aggregate particles as a consequence of elevated temperature curing (Patel, Bland & Poole. 1995). Illustrations of these ettringite developments are given in the electron micrographs figure 3.



A B

C D

Fig. 3. A: Gel (G) coating a void with ettringite (E) developed in the adjacent cement paste. B: Ettringite infilling a crack, note the coarse grained calcium hydroxide (P). C: Ettringite infilling a crack at the surface of an aggregate particle (A). D: Development of ettringite on the surface of coarse grained calcium hydroxide crystals

DISCUSSION AND CONCLUSIONS

Expansion measurements

The expansion of prisms containing fused silica are interesting in that the expansions are more rapid at 80°C storage as expected the expansion slows down after a period of between 14 and 35 days storage. The expansion for prisms made with RHPC are nearly twice that of the (high alkali) OPC prisms. It is suggested that the initial expansion due to reaction is absorbed during the longer setting and hardening times of the OPC prisms under these conditions and accounts for the difference. It is also probable that the slowing of the rate of expansion is due to the reaction nearing completion after a short period at these high storage temperatures.

Ettringite development

With these laboratory scale prisms ettringite was not present in significant amount after 70 days storage at either 40 or 80°C though ASR was well advanced in prisms containing fused silica. After one year exposure to climatic conditions extensive ettringite development was present only in the prisms suffering ASR. The distribution of the ettringite with respect to the ASR gels is thought to be significant in that it suggests a mechanism for its formation.

The hydrophilic properties of the alkali–silica gel causes the gel to absorb water expand and exert expansive pressures on the adjacent concrete which is sufficient to cause cracks to propagate. This water absorption provides the necessary gradient for moisture movement towards the gel to develop and allows sulphate concentration in the solution to rise to levels where ettringite crystallises in cracks and pore spaces close to the gel. The development of ettringite n the cement matrix may cause additional expansion within the cement paste and lead to extension and widening of the existing crack network.

As noted in the abstract and elsewhere in the text this presentation outlines results from a small part of a much larger research study concerned with the relationships between elevated temperature curing regimes and concrete microstructure. The full study is concerned with both laboratory specimens and case study material. The part of the study which investigated 'scaling effects' on concrete microstructure using laboratory specimens cast in a range of sizes from full scale downwards is complete and being written up. Another on going part of the same study is concerned with crack development and propagation due to a variety of causes including those of delayed ettringite expansions and ASR.

ACKNOWLEDGEMENTS

The authors wish to thank Mr C. Mole for his skill with the SEM and Mrs R. Chew for typing the manuscript. The main research project is funded by the EPSRC.

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