

# Alkali-Silica Reaction in Several U.K. Concretes: The Effect of Temperature and Humidity on Expansion, and the Significance of Ettringite Development

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## ABSTRACT

The effects of temperature and relative humidity on alkali-silica reactive concretes from three UK structures are being investigated in a series of long-term experiments, and interim findings are presented here. Preliminary indications are that temperature has both the opposite and a far more significant effect on expansion behaviour than previously recognised. Expansion rate is initially proportional to temperature, but falls off more rapidly at higher temperatures than at lower temperatures. Maximum expansion is inversely proportional to temperature, and final expansion at lower temperatures may be more than twice that at 38°C. The cutoff humidity (defined as that below which expansion due to ASR does not occur) is higher at elevated temperatures, and expansion variability between concretes is most apparent at lower temperatures and higher humidities.

Petrological examination of test samples reveals moderate alkali contents but only small quantities of gel, and concretes from one structure contain an abundance of ettringite. In the absence of external sulphate it is concluded that the ettringite formed by recrystallization of primary sulphate minerals, and was stabilised by reaction of the limestone aggregate. This was probably facilitated by ASR, and it is proposed that the resulting pressures contributed to concrete distress.

The accepted model of alkali-silica reaction is reviewed in the light of these findings. It is proposed that temperature has a direct effect on both reactant transport and aggregate attack processes. Moisture availability is considered fundamental to expansion of the reaction product, but its effect is thought to be modified by temperature which alters the gel structure, and hence its swelling properties. It is observed that other factors may interact with ASR to cause deterioration, and that secondary processes may continue after ASR is exhausted. The implications of these findings to the management of affected structures are discussed.

## Introduction

It has long been recognised that moisture availability is an important factor governing the expansion behaviour of concretes with ASR. At present, limiting moisture access to affected structural members is the most commonly prescribed means of slowing deterioration and prolonging service life. It is widely believed that expansion will not occur if internal relative humidity is reduced below 75%. However, in the British climate this target is not readily achieved for most exterior concretes, which have humidities in the 80 to 90% RH range for much of the year (Wood 1985). The effect of temperature on expansion behaviour has not been investigated in detail, but it is generally assumed that the rate and extent of both ASR and its resulting expansion are increased at elevated temperatures. This is reflected in the widespread adoption of the 38°C, 100% RH core expansion test to quantify latent expansion and to predict future structural performance.

The effects of temperature and humidity on alkali-silica reactive concretes from three UK structures are being investigated in a series of long-term experiments, and this paper presents interim findings. An attempt is being made to delimit the environmental range outside which significant expansion due to ASR does not occur, with a view to its implications for the management of affected structures. The expansion mechanism is being investigated by petrological examination of test material.

### **Effect of temperature and relative humidity on concretes tested**

Cores of reactive material were obtained from two structures in SW England (structures H & M), and one in the English Midlands (structure S). In all cases the reactive component is chert in the fine aggregate, although aggregate sources in the two regions were different. Experiments are conducted on discs approximately 20mm thick, sawn transversely from 75 or 100mm diameter cores. In this way maximum data can be obtained from the material available, and the variability of test behaviour within individual cores can be assessed. Discs under test are stored in sealed containers under conditions of constant temperature and humidity, and expansion is monitored using a Demec 50mm demountable strain gauge.

In a preliminary series of experiments, disc behaviour in relative humidities of 75, 85 and 100% at room temperature (nominally 20°C) and 38°C was investigated. Present work has extended this range to include 65% RH and temperatures of 1, 15 and 25°C. Because it is not possible to quantify concrete expansion prior to test, all disc measurements are made relative to those at the beginning of the experiment.

Initial test behaviour follows a similar pattern in all cases, with a sharp expansion during the first 2 to 3 days followed by a gradual decrease in expansion rate. This has been demonstrated to be due to moisture uptake and thermal adjustment. Subsequent expansion is attributed to the effects of ASR, and this initially proceeds faster at elevated temperatures. However, expansion rate declines more rapidly at higher temperatures, and final expansion is inversely proportional to temperature. For example, preliminary indications are that concrete from structure H will cease to expand after about 40 days storage at 38°C regardless of humidity, whereas at 85% RH and above expansion at 20°C will continue for several months, generally significantly exceeding that attained at 38°C. In one instance, the expansion after 77 days storage in 100% RH at room temperature was more than twice that at 38°C and still increasing.

Relative humidity has a direct effect on the rate and magnitude of expansion. In concretes from structure H, expansion due to ASR is negligible at relative humidities of 75% and below regardless of temperature. At 85% RH expansion occurs at room temperature but not at 38°C, whereas at 100% RH expansion occurred at all temperatures tested. It follows that expansion variability between concretes is most evident at lower temperatures and higher humidities. In these experiments it is possible to differentiate between the reactivities of different concretes tested. Small-scale variability between discs (*i.e.* within cores) is observed, but effects are minimised by averaging the results of replicate samples in each environment. An attempt is now being made to quantify this variability and to investigate its cause.

### **Review of reaction processes**

Experimental results indicate that temperature has both the opposite and a far more significant effect on the rate and magnitude of expansion, and the range of humidities over which expansion will occur, than has hitherto been recognised. The cutoff humidity, defined here as the internal relative humidity below which expansion due to ASR does not occur, is higher at elevated temperatures, and the rate and magnitude of final expansion are decreased. These findings are in accord with those of experiments conducted by other workers on cores of reactive British concrete of several sizes (J.G.M. Wood, pers. comm.). A similar relationship between temperature and expansion was reported by Diamond *et al.* (1981) from experiments on sealed mortar samples containing Beltane Opal.

The observed effects of temperature and humidity are not readily explained by the accepted model of ASR, and suggest a need for reappraisal. Diamond *et al.* (1981) recognised two distinct stages of ASR:

**Stage I** Attack of aggregate by hydroxyl ions and production of gel

**Stage II** Sorption of fluid by reaction product, leading to concrete distress

It is considered that recognition of the separate nature of these stages is fundamental

to understanding the mechanism of ASR, and the popular misconception that expansion is synonymous with reaction is misleading. Diamond *et al.* (*op. cit.*) found that although the trend of expansion follows that of the Stage I reaction (as quantified by the proportion of alkali removed from pore solution), there is a lag effect which is greatest at higher temperatures. Contrary to kinetic theory, the Stage I reaction was also found to be inhibited by temperature. This indicates that the mechanism of Stage I is not purely chemical, and must involve a physical component. French (1976) recognised that the migration of reactants towards reactive aggregates, as shown by the high concentration of alkalis found near reactive particles, is an active process operating against the concentration gradient, and must involve the physical movement of ions through the pore solution. It is therefore suggested that Stage I of the reaction could be sub-divided:

**Stage Ia** Migration of reactants to aggregate (physical process)

**Stage Ib** Aggregate attack and gel production (chemical process)

French (*op. cit.*) proposed that the transport of ions (*i.e.* Stage Ia) occurs by solvent migration, with reactants being attracted towards the hygroscopic reactive aggregates and gel in the pore solution. It is therefore possible that Stage II processes play an important role in perpetuating the reaction; once initial chemical attack of the reactive aggregate has occurred, the gel product imbibes water and draws more alkali and hydroxyl ions to the reaction site. It is suggested that temperature may inhibit this cycle by altering the physical structure of the reaction product, rendering it less able to attract water and reactants from the surroundings.

Diamond *et al.* (1981) demonstrated that the alkali-silica reaction product is able to imbibe sufficient water from the pore solution to cause expansion, and that an external source of moisture is not required. This explains why several concrete discs on test showed significant expansion without weight gain. Drying the concrete until there is insufficient moisture for expansion provides the most obvious means of limiting deterioration, but the observed effect of temperature on cutoff humidity is not explained by classic ASR theory. It is proposed that this behaviour may be the result of two factors. Firstly, elevated temperature may affect Stage II expansion directly by altering the structure of existing reaction product so that it is either unable to swell, or has different physical properties and does not cause disruption upon swelling. The effect of this on Stage Ia reaction processes has already been discussed. Secondly, higher temperature may alter equilibrium positions in Stage Ib reactions between pore solution and reactive aggregate, so altering the composition of the reaction product and hence its swelling properties.

### **Results of petrography**

Petrological inspection of test samples is made in an attempt to gain insight into the expansion and reaction mechanisms. Selected samples are periodically removed from test and prepared for examination as polished blocks or thin sections using reflected and transmitted light microscopes, and a scanning electron microscope with energy dispersive X-ray analytical facility.

All concretes examined have normal water/cement ratios and an average entrapped air content. Microanalysis of cement paste shows that structure M concretes are slightly high in alkali, with around 0.68% Na<sub>2</sub>O equivalent, whereas those from structures S and H have more moderate alkali contents of about 0.5%. The consistency of analyses suggests that the latter low values are probably primary, and are not due to leaching during sample preparation. Reactive aggregates are widely dispersed throughout the samples, and often show interior cracking and high internal alkali concentrations. Classic reaction rims are generally absent, although cracks are often present around the aggregate margins and radiate into the surrounding cement. The paste typically shows extensive microcrack development, but alkali-silica reaction product is rarely seen infilling cracks and voids. This is in part due to sample preparation, since gel is more commonly observed in unpolished broken samples, but also reflects the characteristically small quantity of gel produced by ASR in the UK. Reaction product is most often observed exuding from cracks at the centre of reactive particles. This is commensurate with a reaction site at the centre of reactive aggregates as proposed by W.J. French (*pers. comm.*), rather than at the aggregate margins.

Concretes from structure H differ from others examined since they contain a high proportion of the mineral ettringite. In this respect they appear typical of many affected by ASR in Britain (W.J. French, *pers. comm.*). The ettringite is typically coarsely

crystalline, generally infilling microcracks and lining voids in the cement. In many instances it clearly replaces earlier alkali-silica gel, and is often associated with areas of coarsely crystalline portlandite ( $\text{Ca}(\text{OH})_2$ ) in the paste. The common occurrence of large quantities of ettringite in concretes showing evidence of ASR was recognised by Pettifer & Nixon (1980), who attributed its formation to sulphate attack - *i.e.* reaction of  $\text{C}_3\text{A}$  in the cement paste with sulphate-bearing solutions from outside the concrete. This reaction also produces portlandite, and they proposed that dissolution of this mineral in the pore water would liberate hydroxyl ions which could cause or aggravate ASR. It is considered that such a mechanism is unlikely in the concretes examined for three reasons. Firstly, there is no evidence for the presence of external sulphates, either in local groundwater or as a contaminant of the aggregate. Secondly, the presence of secondary portlandite indicates that complete dissociation did not occur, and it is unlikely that the quantity of hydroxyl ion so released would have been sufficient to cause the observed extent of ASR. Thirdly, the common replacement of alkali-silica gel by ettringite indicates that ASR must have reached an advanced stage before ettringite growth occurred.

Microanalysis indicates that concretes from structure H contain about 2% sulphate in the cement paste, whereas those from the other structures contain about 3.5%. However, in view of the local concentration of sulphate minerals in structure H concretes, it is considered that the total sulphate content of all three concretes is likely to be similar. This suggests that macroscopic ettringite development is controlled by some factor other than simply sulphate availability. It is widely believed that in the absence of free sulphate, primary ettringite (high sulphate calcium sulphaaluminate hydrate) decomposes to the monosulphate form of the mineral. However, Greening (see Hadley 1968) has shown that monosulphate becomes metastable in the presence of free  $\text{CaCO}_3$  and reverts to ettringite. It is therefore proposed that the limestone coarse aggregate in structure H concretes rendered ettringite the stable sulphate phase. Quantitative analysis by XRD and DTA (after Odler & Abdul-Maula 1984) can detect no difference in the ettringite content of samples before and after test, and it is therefore suggested that the coarsely crystalline ettringite was formed by recrystallization of the primary disperse phase. This process was probably facilitated by increased permeability resulting from the extensive microcracking caused by ASR. The principal occurrence of the mineral in cracks and voids is interpreted as resulting from the movement of pore fluids containing sulphate ions towards the hydrating alkali-silica gel. Crystal nucleation would then have occurred preferentially in the gel phase, which would offer an advantageous growth medium.

Expansion resulting from ettringite formation is generally believed to be the cause of deterioration in sulphate attack, and this mechanism is utilised to advantage in the manufacture of expansive cements. Expansion is normally attributed to the effect of colloidal ettringite (Mehta 1973, 1983), but Pettifer & Nixon (1981) observed that coarsely crystalline ettringite is almost ubiquitous when distress is severe. It therefore seems likely that pressure resulting from the growth of larger ettringite crystals may have a significant effect on expansion. It is proposed that the preferential recrystallization of ettringite in the confines of gel-filled microcracks in structure H concretes may have contributed to the observed deterioration. This process could potentially continue after ASR has ceased, until redistribution of sulphate is complete. It is noted that ettringite crystallization is inhibited by increased solubility at higher temperatures (Anon., *c.* 1985), and therefore it is expected that thermal effects would be similar to those governing ASR.

### **Implications for structural management**

The previously unrecognised relationship between temperature and expansion behaviour has important implications for the management of structures affected by ASR. The inverse temperature dependence of maximum expansion casts doubt on the wisdom of using the 38°C, 100% RH core expansion test alone as the basis for assessing latent reaction. The importance of considering expansion behaviour at other temperatures was recognised by Wood (1985). In general, it is expected that the onset of deterioration will be faster at warmer temperatures, but that damage will be less severe than in colder environments. This may help to explain why, for example, buried concrete often exhibits more severe deterioration than parts of the same pour above ground, although the moisture content of both may be similar. Where attempt is made to limit deterioration by drying the concrete, it will be necessary to lower internal RH further in colder environments to reach the cutoff humidity. This implies that control

of expansion will be easier to achieve on internal structural members than in exterior concrete, even when atmospheric humidity is the same in both environments.

Concrete is a disequilibrium assemblage of chemical constituents which reaches a state of transient stability during service life. The present poor understanding of ASR may in part be due to our taking too simplistic a view of reaction processes. Reactions do not occur uniquely in this system but interact in a complex fashion, and no concrete constituent can be regarded as truly inert. Factors other than those immediately involved in ASR may have a significant effect on deterioration, and secondary processes may continue after ASR is exhausted. This is well illustrated by the development of ettringite in structure H concretes, which indicate that sulphate content could be an important factor in later stages of the deterioration of ASR-damaged concretes containing limestone coarse aggregate.

### **Acknowledgement**

The principal author wishes to thank Dr. W.J. French and Dr. J.G.M. Wood for numerous discussions and comments. All core material was provided by Mott, Hay & Anderson Ltd. The research was conducted by T.N.J. who was funded by the Science & Engineering Research Council.

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