

THE EFFECT OF ELECTROCHEMICAL RE-ALKALISATION ON ALKALI-SILICA EXPANSION IN CONCRETE

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ABSTRACT

Electrochemical re-alkalisation re-establishes the alkalinity of carbonated concrete allowing the protective passive film of oxide to form again on the reinforcing steel. Inward migration of sodium carbonate solution during this process may be expected to increase the risk of alkali-silica reaction in susceptible concretes. Laboratory specimens of carbonated concrete containing reactive aggregate were re-alkalised under standard industrial conditions and the resulting ASR expansion monitored. Compared to the uncarbonated control specimens expansion is significantly less in carbonated concrete and less again in re-alkalised concrete. The absence of calcium hydroxide and the relatively low pH in the treated concrete outweighs its increased sodium content.

Keywords: Concrete, Alkali-silica expansion, Electrochemical treatment, Tests.

INTRODUCTION

Electrochemical re-alkalisation is a commercial process which has been used to rehabilitate tens of thousands of square metres of concrete which is suffering from carbonation to such an extent that the steel is at risk of corrosion. A low voltage direct current is applied between the reinforcing steel (cathode) and an external temporary anode, which in turn is immersed in an electrolyte solution held against the external face of the concrete. During treatment the alkaline electrolyte solution (commonly sodium carbonate) migrates into the carbonated concrete, raising its pH, while simultaneous production of hydroxyl ions by oxidation of water at the cathodic steel re-establishes the passive layer.

Faced with buildings and structures in which the concrete is showing signs of reinforcement corrosion consulting engineers advising building owners have traditionally had a single option - hack out and patch repair. In such a case unrepaired concrete remains at risk and it is not uncommon for further patch repairs to be needed. The advent of electrochemical methods presents the possibility of lasting rehabilitation for concrete through tackling the causes instead of symptoms. Re-alkalisation sits alongside chloride removal and cathodic protection in the engineer's armoury of electrochemical methods. Being longest established, standards and codes of practice exist for the latter but re-alkalisation and its sister technique, chloride removal, have been introduced relatively recently to the UK and despite a record of success, engineers are understandably wary of potential side effects.

The main and desirable effect of re-alkalisation is to re-establish passivity of the reinforcing steel but would-be users are concerned about the effect the treatment has on other properties of the concrete. Miller (1994) reviewed evidence on the structural effects of both re-alkalisation and chloride removal, dealing with such matters as cracking, effects on concrete-steel bond strength, and durability. The main concern of this paper is that because alkali metal ions migrate into the concrete during the treatment and the pH of the concrete rises, this may promote conditions conducive to the alkali-

silica reaction (ASR). Recognising that ASR requires the simultaneous presence of suitable quantities of alkali reactive aggregates, moisture and alkali metal ions at temperatures above freezing and at pH above about 12 (Hobbs, 1988), it seems likely that ASR will be a potential problem more in chloride contaminated concrete than in the lower pH of carbonated or re-alkalised concrete. Page and Yu (1995) confirmed the expansion due to ASR in chloride free concrete specimens, which had been electrochemically treated at the current densities typical of chloride removal, and found 'pessimism' effects of the total charge passed. However, Miller argued that because the equilibrium pH of the sodium carbonate solution introduced into the concrete is about 10.7 the pH will not be high enough to activate ASR, but no experimental work on the effect of re-alkalisation on the alkali-silica reaction has been reported to date.

The aim of this work was to investigate the effect of electrochemical re-alkalisation on alkali-silica reaction in treated concrete. It was part of a wide ranging study of the effect of treatment on the various properties of a standard concrete.

PRACTICAL ASPECTS OF ASR IN ELECTROCHEMICALLY TREATED CONCRETE

Recognising that the occurrence of ASR depends in a complex way on the concentrations of sodium, potassium, calcium and hydroxyl ions and calcium hydroxide in the concrete, together with the presence of reactive aggregate and free moisture, the following situations bearing a different risk of ASR under electrochemical treatment could arise in real structures.

1. Concrete carbonated near the surface but uncarbonated around the reinforcement.
2. Concrete carbonated from the surface to the reinforcement.
3. Concrete chloride contaminated near surface but uncontaminated around the reinforcement.
4. Concrete chloride contaminated from the surface to the reinforcement.
5. Concrete both carbonated and chloride contaminated near the surface but uncarbonated and uncontaminated around the reinforcement.
6. Concrete carbonated from the surface to the reinforcement and chloride contaminated near the surface but uncontaminated around the reinforcement.
7. Concrete carbonated near the surface but uncarbonated around the reinforcement and chloride contaminated from the surface to the reinforcement.
8. Concrete carbonated and chloride contaminated from the surface to the reinforcement.

In principle, consideration needs to be given to all of these situations, but Page and Yu's work was directed towards the effect of electrochemical treatment on case 4. The present investigation considered case 2, using sodium carbonate as the electrolyte, and as far as is known the other cases have not yet been studied by any workers and will be the basis for future work.

EXPERIMENTAL PROGRAMME

All tests were carried out on a standard concrete consisting of 300 kg/m³ cement, 1800 kg/m³ siliceous aggregate (20 mm max size, 40% sand), 0.62 water/cement ratio giving a slump of about 85 mm, density 2370-2390 kg/m³ and a target 28 day cube strength of 35 N/mm². The cement was a grade 42.5 portland cement containing 0.6% equivalent Na₂O. This concrete is a typical structural concrete and was chosen to represent normal practice in preference to using a mortar bar or other artificially sensitive system. In this concrete the total alkali content derived from the cement is 1.8 kg/m³. The alkali reactivity was provided by additions of calcined flint cristobalite (CFC, 1-2mm particle size, Blue Circle Industries, Greenhithe, Kent), which Lumley (1993) reported to expand significantly above a threshold of 10% reactive aggregate content and 2.6 kg/m³

total equivalent Na_2O content in the concrete. This, and our preliminary work, suggested that to give the best sensitivity it would be necessary to choose mixes at and just below this threshold level of reactivity and alkali content. Therefore three mixes were selected to have the best chance of demonstrating whether the re-alkalisation process would induce ASR and expansion. These were:

Mix A: 4% CFC, 1.8 kg/m^3 equivalent Na_2O

Mix B: 10% CFC, 1.8 kg/m^3 equivalent Na_2O

Mix C: 10% CFC, 2.6 kg/m^3 with the additional alkali provided by adding potassium sulphate.

PROCEDURE

Carbonated concrete was produced in two stages. First, in a preconditioning period of typically 6-8 weeks the concrete specimens were demoulded after 24 hours and dried in air at 25°C until their internal relative humidity had dropped to 70%. This was measured using an electronic humidity probe (Concretemaster II) inserted in a 10 mm diameter hole drilled 40 mm deep into a dummy concrete specimen. Second, the specimens were exposed to pure carbon dioxide in an enclosed cylindrical chamber at 15 bar pressure for two weeks. By this means it was possible to produce fully carbonated concrete with a minimum dimension of 100 mm in as little as 10 weeks from casting. Petrographic and microstructural examination of thin sections of the carbonated concrete so produced confirmed that it showed all the features of naturally carbonated concrete (Al-Kadhimi et al 1996). By contrast, it should be noted that methods operating at atmospheric pressure but increased carbon dioxide concentration would have taken at least a year to achieve the same result.

After carbonation the specimens were fully saturated by placing in a vacuum chamber which was evacuated to a pressure of 50 mbar prior to filling with water. Specimens were left immersed for 24 hours before they were connected to the rectifier for re-alkalisation. In re-alkalisation the current flows and, hence, the electrolyte penetrates towards the cathodic steel through the minimum path length of concrete and in an incorrectly designed specimen this could bypass some parts of the material. It was therefore necessary to design specimens to ensure that the whole volume was subjected to the treatment current. $270 \times 75 \times 75$ mm prisms were cast with one long face against sheet steel plates, which were perforated to add some degree of mechanical adhesion to the specific adhesion developed by interfacial contact. During electrochemical treatment the steel plate became the cathode, with an electrical connection to a self tapping screw, and the specimens were immersed in a tank of electrolyte solution (1 M sodium carbonate solution) and surrounded by the inert metal mesh anode (platinised titanium). Care was taken to ensure that sodium carbonate solution could only penetrate in one direction towards the cathode (rectilinear from the face opposite the cathode) by coating the other faces of the specimens with an impermeable silicone based sealant. Fig. 1 shows the apparatus schematically. The metal plates were removed from the prisms after treatment and before testing.

A multichannel dc rectifier allowed 10 specimens to be re-alkalised simultaneously. Each channel was individually controlled by a manually variable resistor to ensure that the treatment current passing through each specimen was maintained at 1 A/m^2 of concrete surface. To keep the current constant the treatment voltage was reduced in line with the drop in electrical resistance as electrolyte solution penetrated the concrete through the unsealed face and measurement of the electrical resistance gave a simple guide to the progress of the treatment. Re-alkalisation was continued until the resistance had reached a constant value typically 20-30% of the starting value and the time to complete penetration was about 3-4 weeks. This is somewhat longer than is used in industrial practice, where the carbonation zone is normally thinner. The total charge passed was $500 \pm 50 \text{ Ah/m}^2$.

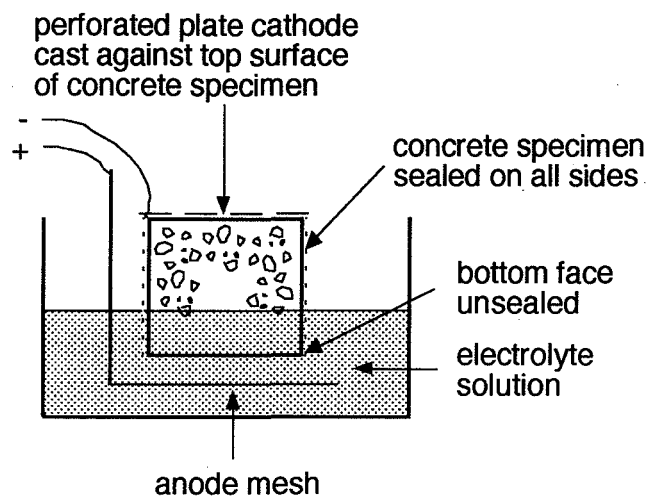


Fig. 1 Electrochemical re-alkalisation apparatus (schematic).

After re-alkalisation all coating materials were stripped from the specimens and measurement points were affixed on the four long faces of the prisms to permit expansion to be measured with a demec gauge (200 mm gauge length). The uncarbonated and carbonated specimens were also saturated and kept wet at the same time to ensure that the results are directly comparable.

Expansion was measured at intervals over 9 months storage in the moist conditions prescribed by British Cement Association (1992) at 38°C, preliminary measurements having shown that no expansion took place at 20°C even with higher reactive aggregate contents.

RESULTS AND DISCUSSION

Figures 2-4 show the expansion with time of uncarbonated (control), carbonated and carbonated/re-alkalised specimens respectively. Each reading is the mean of four measurements carried out on each of three specimens. The experimental error is such that differences of >+10% in strain are significant.

The most striking feature of these results is that the general level of expansion, even at 38°C, is low compared to the levels reported to give problems in practice. In the ASTM mortar bar test (1986) 0.5 mm/m expansion in 3 months or 1 mm/m in 6 months is considered to represent potentially reactive materials, but in this work the aim was to see if re-alkalisation adversely affected ASR expansion. Therefore the potential for expansion is more important than the actual levels achieved. There is also a general trend of decreasing expansion from uncarbonated to carbonated to carbonated/re-alkalised concrete. This is especially notable for mix C. This is an important finding because it shows that electrochemical treatment is not necessarily aggravating the alkali-silica reactivity. It clearly confirms that the condition of the concrete and the electrolyte used play a major role in determining the extent of ASR. However, other more detailed interpretation of the trends can be made, as follows.

In the uncarbonated (control) samples the amount of expansion increases considerably as the alkali content increases, indicating that the system is below the pessimum alkali/silica ratio. This confirms that any additional alkalis incorporated by the treatment would be expected to show a positive effect on expansion. Thus at the alkali/silica ratio in the range 0.01-0.05 in these experiments there is enough reactive aggregate present to respond to any increased alkalinity from the treatment.

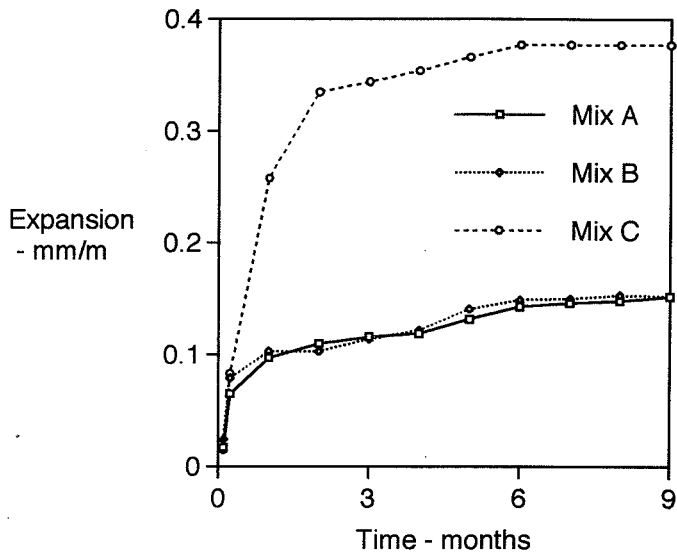


Fig. 2 Alkali-silica expansion of uncarbonated specimens.

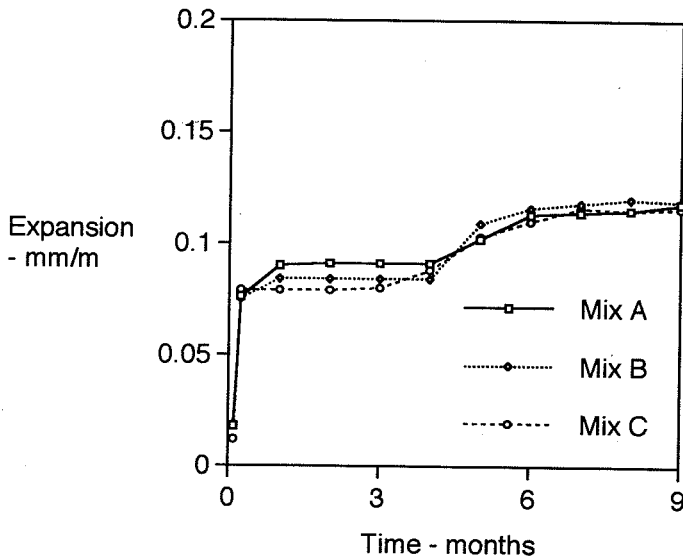


Fig. 3 Alkali-silica expansion of carbonated specimens.

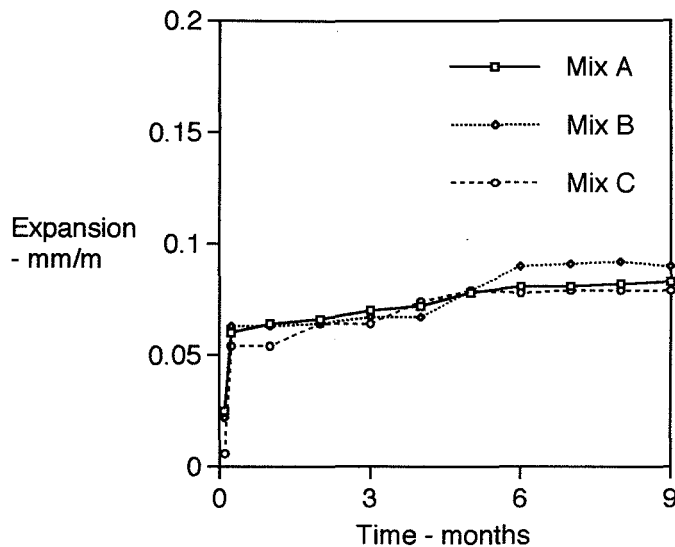


Fig. 4 Alkali-silica expansion of carbonated and re-alkalised specimens.

In the carbonated samples there is a clear reduction in expansion compared to the controls. The trend and rate of expansion with time are similar for both high and low alkali or silica contents, but significantly lower than for the uncarbonated samples. This is because the enhancing effect produced by the high alkali content on alkali-silica reactivity in the uncarbonated samples is lost.

In the carbonated and re-alkalised samples there is a further slight reduction in expansion and a similar trend and rate of expansion with time as compared to the carbonated samples.

The differences between this work, which shows that electrochemical re-alkalisation of the mixes tested reduces ASR in the conditions used, and that of Page and others, which shows that electrochemical chloride removal increases ASR, can be understood by reference to the conditions prevailing in concrete during electrolysis.

In amorphous or glassy silica the Si-OH groups react with hydroxyl ion at low concentrations while in more stable silica the Si-O-Si bridging groups react at higher concentrations. In both cases the product of reaction is alkali-silica gel, a poorly defined colloidal isotropic coagulate with exceptional swelling capacity which may cause expansion and cracking in moist conditions. Formation of the gel is only possible if sodium and hydroxyl ions are present and the hydroxyl ion concentration must exceed a threshold of 250-500 mM/l. Calcium hydroxide acts as a reserve of hydroxyl ions, feeding the reaction. The extent of reaction and consequent expansion depends on the alkali/silica ratio with a pessimum value in the range 0.01-0.05. Once formed, the alkali-silica gel imbibes water and swells because of the osmotic potential developed by the sodium ion concentration gradient between the gel and the matrix. Finally, if the rate of reaction is high silica will diffuse out and react with calcium hydroxide to form calcium silicate hydrate near the reactive grain which means that calcium hydroxide increases the rate of expansion. All this shows that calcium hydroxide is very important (Wang & Gillott, 1991) but it is not present in carbonated concrete and therefore electrochemical re-alkalisation reduces ASR compared to the uncarbonated controls.

When concrete is carbonated the pH is reduced and the hydroxyl concentration falls below the threshold value. Calcium and alkali hydroxide are converted to calcium and alkali carbonate and the lime/silica ratio in the calcium silicate hydrate is reduced below

1.4 thus increasing the sorption capacity for alkali (Durand et al, 1990). The cement matrix is densified, reducing the mobility of water and ions. All this reduces alkali-silica reactivity, but when the concrete is re-alkalised the ingress of sodium ions and the production of hydroxyl ions by electrolysis at the reinforcement increases reactivity again and this may offset the lack of calcium hydroxide. Apparently in our experimental system the lack of calcium hydroxide is the dominant feature.

Although not studied in this work it should be noted that the role of chloride in ASR in contaminated concrete depends on its type and origin. External contamination by sodium chloride increases the sodium concentration in the gel and the matrix, increases ionic strength and compresses the double layer around calcium silicate hydrate releasing hydroxyl ion into solution and this increases alkali-silica reactivity (Chatterji et al, 1986). External contamination by calcium chloride causes calcium hydroxide to dissolve and leach out of the concrete decreasing alkali-silica reactivity (Chatterji, 1979). Internal contamination by cast in sodium or calcium chloride accelerates hydration leading to more calcium hydroxide and a denser more rigid microstructure, less able to accommodate swelling which is therefore more destructive. Some of the chloride is bound as Friedel's salt which also releases calcium hydroxide. Thus greater alkali-silica reactivity results. In addition, the pH of contaminated concrete is high and rises further around the reinforcement as a result of electrolysis so that the threshold hydroxyl concentration is exceeded and ASR can result.

Thus it seems that in electrochemical re-alkalisation the absence of calcium hydroxide and the low resulting pH reduce the risk of ASR, whereas in electrochemical chloride removal the high pH increases the risk of ASR. However, as was noted in the introductory discussion, there are a possibly infinite number of combinations of carbonation and chloride contamination in real concrete and much further work is needed to form a comprehensive database of the risks of ASR expansion in the various situations.

CONCLUSIONS

Electrochemical re-alkalisation, under the conditions used in this investigation, which were representative of industrial practice, of a potentially ASR susceptible structural concrete reduces alkali-silica expansion relative to untreated concrete. This could be due to the inherently low ASR reactivity of carbonated concrete resulting from the absence of calcium hydroxide and a hydroxyl concentration below the threshold for expansion.

Thus engineers considering the use of electrochemical methods for rehabilitating structures should be aware that the risks posed by the treatments depend on the conditions prevailing in the concrete.

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