DEVELOPMENT OF ALKALI-SILICA REACTION IN REINFORCED CONCRETE
SUBJECTED TO CATHODIC PROTECTION

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Concrete specimens containing steel electrodes were made from a mix
that contained a reactive aggregate but insufficient alkali concentration
to cause expansion due to alkali-silica reaction (ASR). Cathodic
protection was applied to the steel at various levels of potentiostatic or
galvanostatic polarisation and the strains in the concrete were
monitored over gauge lengths close to and remote from the steel.
Expansions in the vicinity of the steel were found to be dependent on
the level of applied polarisation and were associated with local
development of ASR in a zone of enhanced alkalinity formed
around the cathode. Practical implications with regard to cathodic
protection of reinforced concrete are considered.

INTRODUCTION

Cathodic protection has been used on an increasing scale over the last few years as a remedy for
corrosion of reinforcing steel in highway bridges and other sorts of concrete structure where
chloride salts are present (Concrete Society (1)). A potential side-effect which has caused some
concern is the possibility that ASR may be promoted by the generation of alkaline reaction
products at the surface of the cathodically polarised metal (Natesaiyer and Hover (2), Sergi et al
(3)).

The research to be described is an extension of work published elsewhere (3) and its aims
were as follows:

(i)   to determine whether the enhanced alkalinity produced in the vicinity of steel electrodes,
subjected to various controlled levels of cathodic polarisation, would induce significant local
expansion in concrete containing a potentially reactive aggregate in a cement matrix of low bulk
alkali content;

(ii)   to assess whether cathodic polarisation of embedded steel would cause intensified strains to
develop in concrete containing a reactive aggregate in a cement matrix of sufficient bulk alkali
content to cause significant expansion even in the absence of applied polarisation.

EXPERIMENTAL

Expansion of Concrete in the Absence of Cathodic Protection

Before the effects of cathodic protection could be examined it was necessary to characterise
the expansion behaviour of plain concrete specimens, which were cast in the form of prisms, 500
X 100 X 100 mm, from mixes with the following proportions by weight:

Water 0.5 : Cement 1.0 : Fine Aggregate 2.25 : Coarse Aggregate 2.0.

The cement was of the composition shown in Table 1 and its alkalinity was supplemented by the addition of KOH to the mix water to give an alkali content in the concrete of 2.5 kg m^{-3} Na_2O equivalent. The coarse aggregate was an unreactive limestone (10-5 mm), whilst the fine aggregate was made up of mixtures, in various proportions, of unreactive quartz sand and reactive calcined flint. The latter material, which consisted largely of cristobalite (Lumley (4)), was included in proportions ranging from 0-15 % of the total aggregate. Additions of NaCl to the mix water were made at levels corresponding to 0, 0.2, 0.5, 1.0 and 2.0 % Cl$^-$ by weight of the cement. It has been shown elsewhere that, at low dosage levels, such additions effectively increase the Na_2O equivalent content of the concrete in proportion to the quantity of NaCl (Nixon et al (5)).

TABLE 1 - Chemical Analysis of Cement (% by weight)

CaO	SiO$_2$	Al$_2$O$_3$	Fe$_2$O$_3$	SO$_3$	MgO	P$_2$O$_5$	Na$_2$O	K$_2$O	Ignition Loss
67.6	21.1	4.7	0.28	2.6	0.3	0.11	0.12	0.18	2.6

Expansion measurements were taken over gauge lengths of 200 mm for 800 days, during which time the specimens were stored at approximately 20 $^{\circ}$C in contact with moist tissue paper. The results are summarised in Figure 1, in which the expansion data are all mean values for duplicate specimens recorded at 800 days.

Whilst concretes of baseline alkali content, 2.5 kg m^{-3} Na_2O equivalent, showed no appreciable expansion, those with added NaCl expanded significantly when the mix contained 10 or 15% of calcined flint, even at the lowest level of chloride addition (0.2% Cl$^-$). Thus concrete with 10% calcined flint and 2.5 kg m^{-3} Na_2O equivalent represented a 'near-threshold' mix which might be expected to expand if the alkalinity of the material were to be increased by a relatively small amount.

Effects of Cathodic Protection on Expansion

To examine whether ASR-induced expansion could in fact be stimulated by applying cathodic protection to steel in concrete of 'near-threshold' mix composition, specimens of the form described previously (3) and illustrated in Figure 2 were made. They were composed of 8 concrete prisms, each 500 X 100 X 100 mm, which were grouted together to form a slab. Mild steel plates, each 70 X 70 mm, were sand-blasted and degreased before being cast into the mid-sections of the prisms and connected together to form a continuous cathode. Anodes, consisting of a titanium mesh coated with electrocatalytic noble metal oxides and a conductive paint overlay were fixed at the ends of the slabs, parallel to the embedded steel plates. This ensured a uniform current distribution when polarisation was applied.

Three identical slabs with an alkali content of 2.5 kg m^{-3} Na_2O equivalent were made, each of them containing 6 prisms of 'near-threshold' composition (10% calcined flint) and 2 non-reactive control prisms (0% calcined flint). After 28 days of curing in moist air, the slabs were connected to a potentiostat/galvanostat and cathodic protection was applied to the steel under the following conditions, as described in further detail elsewhere (Sergi and Page (6)):

Slab X: potentiostatic polarisation, steel potential (-850 mV,SCE scale)
Slab Y: potentiostatic polarisation, steel potential (-700 mV,SCE scale)
Slab Z: galvanostatic polarisation, steel current density (20 mA m^{-2}).

The slabs were stored under these conditions with moist tissue paper in contact with the surfaces of the concrete at approximately 20 °C. For slabs X and Y, the cathodic current densities were recorded (Figure 3) whilst for slab Z, the potential of the cathode was monitored relative to a saturated calomel electrode (Figure 4).

Strains developed around the steel cathodes during an exposure period of some 800 days (gauge length A in Figure 2) are plotted in Figure 5. The data points shown in this figure were average values determined for the 6 prisms containing 10% calcined flint in each of the slabs. No significant expansions were recorded remote from the steel cathodes (gauge length B in Figure 2) in any of the prisms, or over gauge lengths A of the control prisms which contained no calcined flint. The expansions recorded in Figure 5 were therefore attributable to the presence of reactive aggregate particles and their magnitudes were apparently related to the intensity and extent of the cathodic process leading to the formation of OH^- ions:

$$O_2 + H_2O + 4e^- = 4OH^- \qquad (1)$$

The levels of potentiostatic polarisation applied to slabs X and Y were such that the cathodic current densities recorded in the initial stages of exposure were substantially higher than those recommended for practical applications of cathodic protection to reinforced concrete structures (1). It should be borne in mind, however, that whilst overall average values are normally limited to about 20 mA m^{-2}, local current densities within real structures to which cathodic protection is applied may vary substantially, as shown for example by Hunkeler (7), owing to variations in bar spacing, cover thickness, concrete resistivity and corrosion rate from place to place. In a related context, it is interesting to note that electrochemical techniques for removing Cl^- ions from salt-contaminated reinforced concrete structures, which are presently being evaluated as alternatives to cathodic protection (Bennett and Schue (8)), employ overall average cathodic current densities well in excess of even the highest values recorded in Figure 3.

To elucidate the possibility that cathodic polarisation of embedded steel might exacerbate the expansion of concrete, in which conditions necessary for expansive ASR were already present, a further slab specimen, designated X*, was made. This was of similar form and composition to those described previously, but an addition of NaCl was made to the mix water, corresponding to 1% Cl^- by weight of the cement. This implies an effective increase in Na_2O equivalent from 2.5 kg m^{-3} to 6.0 kg m^{-3}.

After 28 days of curing in moist air, slab X* was connected to a potentiostat and the embedded steel was subjected to polarisation at -850 mV (SCE scale), as in the case of slab X. The current density/time relationship is shown in Figure 6 and the average expansions recorded over gauge lengths A and B of the prisms containing 10% calcined flint are represented in Figure 7; again no significant expansions were observed in the control prisms.

The results in Figure 7 indicate that ASR-induced expansion was enhanced in the cathodic regions of the specimens (gauge length A) and also suggest that some increased expansion may have occurred elsewhere in the material. This may be seen by comparing the expansion of gauge length B for slab X* with that shown in Figure 1 for the concrete containing 1% Cl^-. A possible explanation for this effect may be that the extent of OH^- formation by the predominant cathodic reaction (equation (1)) exceeds that of OH^- consumption at the anode (reverse reaction, equation (1)) owing to the fact that a substantial fraction of the anodic current density is involved in the oxidation of chloride ions.

Microscopy and Chemical Analysis

After 800 days, the expansions of reactive prisms in slabs X and X* were apparently complete (see Figures 5 and 7). The concrete exhibited extensive cracking around the steel

electrodes, with some more widespread cracks also appearing in slab X*. At this stage, polarisation was terminated and the concrete was sampled for microscopy and chemical analysis.

Petrographic examination of thin sections from cracked regions of the slabs confirmed that the calcined flint particles had suffered ASR, as illustrated in micrographs published elsewhere (6). Analyses for Na^+, K^+ and Cl^- concentrations of slices of material, 2 mm in thickness, taken parallel to the steel plates at various distances from them, were performed by standard wet chemical methods. Similar analyses were also made of samples from the corresponding specimens used to assess expansion in the absence of cathodic protection. These specimens served as controls.

The concentration profiles recorded, with comparative data for the control specimens, are shown in Figures 8 and 9 for slabs X and X* respectively. From these, it is clear that electromigration of Na^+ and K^+ had produced a zone of enhanced concentration of these ions extending some tens of millimeters from the cathode. This was so both for prisms containing calcined flint and for ones with no reactive aggregate. The magnitude of the effect in a zone extending 2 mm from the steel was very substantial, representing a local increase of alkalinity to about 7 kg m^{-3} Na_2O equivalent in slab X, for which the bulk alkali content was only 2.5 kg m^{-3} Na_2O equivalent. For slab X*, the Cl^- concentration was found to have decreased in the vicinity of both the cathode (due to electromigration) and the anodes (due to anodic oxidation of Cl^-). The latter observation supports the earlier suggestion that the application of cathodic protection to chloride-contaminated concrete leads to an increase in the bulk OH^- concentration.

Whilst the results for slabs X and X* are now complete, cathodic polarisation of the steel in slabs Y and Z is presently being continued. It is, however, intended that the reactive prisms in these specimens will also be subjected to petrographic and chemical analysis when their expansion has ceased.

CONCLUSIONS

The research described has yielded the following conclusions:

1.   Sustained potentiostatic cathodic polarisation of steel in concrete at -850 mV or -700 mV (SCE scale) caused expansion and extensive cracking due to ASR in specimens which contained calcined flint aggregate but just insufficient alkalinity in the mix materials to induce expansion in the absence of the applied current. To achieve the above levels of polarisation, however, the current densities initially required were significantly higher than those that would normally be recommended for practical applications of cathodic protection to reinforced concrete structures.

2.   Sustained galvanostatic cathodic polarisation of steel in concrete at 20 mA m^{-2} caused slight expansion due to ASR in specimens which contained calcined flint aggregate but just insufficient alkalinity in the mix materials to induce expansion in the absence of the applied current. No significant cracking of the specimens has been observed within the timescale of the experiments to date but monitoring is being continued.

3.   Sustained potentiostatic cathodic polarisation of steel in concrete at -850 mV (SCE scale) exacerbated the expansion of specimens with sufficient alkalinty in the mix materials to exhibit expansive ASR even in the absence of polarisation.

4.   Whilst practical implications of the research cannot be fully assessed at this stage, the results obtained to date suggest that the potential risk of inducing or exacerbating ASR should be considered when contemplating the application of cathodic protection to reinforced concrete structures. If cathodic protection were to be applied to a structure containing potentially reactive aggregates then it would be prudent to undertake careful monitoring and to ensure that the applied cathodic current density is maintained at a reasonably low level, taking account of heterogeneities that may influence the current distribution.

5.   The research described has further possible implications regarding the use of electrochemical techniques for removal of chloride ions from reinforced concrete. These are now being studied in a separate programme of research at Aston University.

ACKNOWLEDGEMENT

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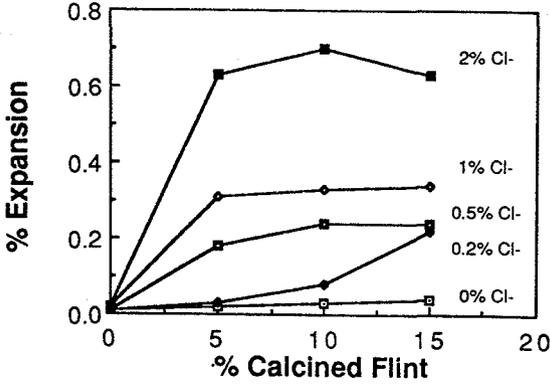
Figure 1   Expansion of concrete prisms containing varied amounts of chloride and calcined flint
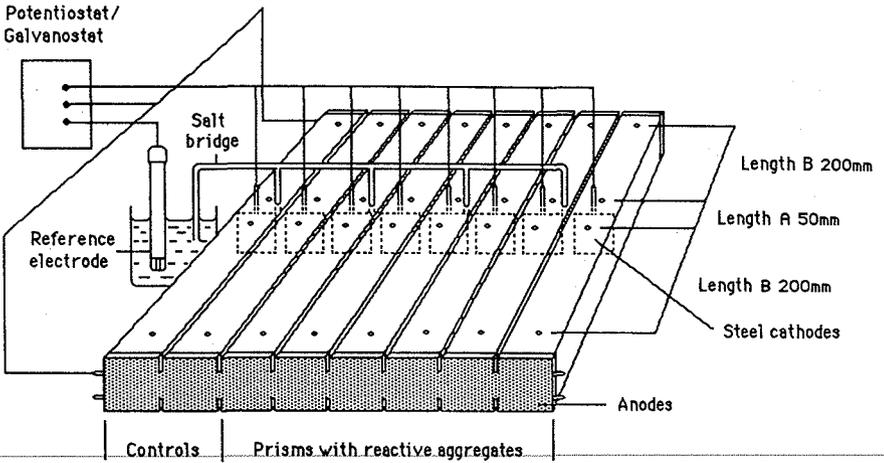

Figure 2   Schematic arrangement of specimens containing cathodically protected steel
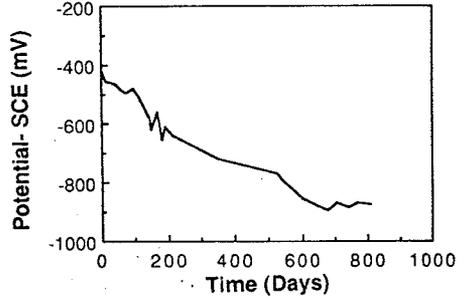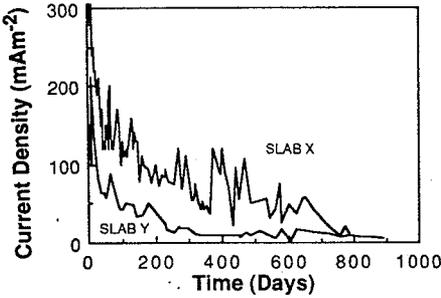
Figure 3   Variation of cathodic current density with time of potentiostatic polarisation for slab X (-850 mV, SCE) and slab Y (-700 mV, SCE)

Figure 4   Variation of potential with time of galvanostatic polarisation for slab Z (20 mA m^{-2})
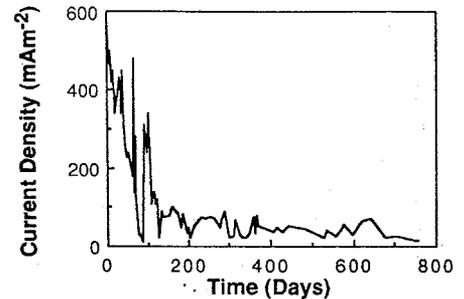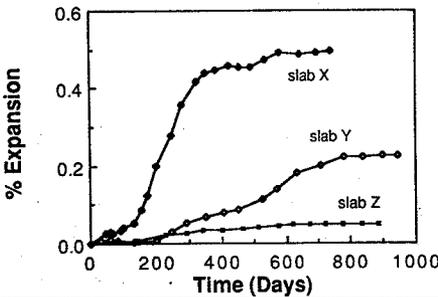

Figure 5   Average expansions recorded over gauge length A for the six prisms containing reactive aggregate in slabs X, Y and Z

Figure 6   Variation of cathodic current density with time of potentiostatic polarisation for slab X* (-850 mV, SCE)
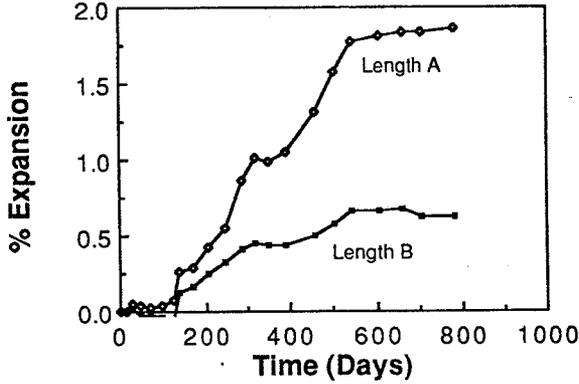
Figure 7   Average expansion recorded over gauge length A for the six prisms containing reactive aggregate in slab X*
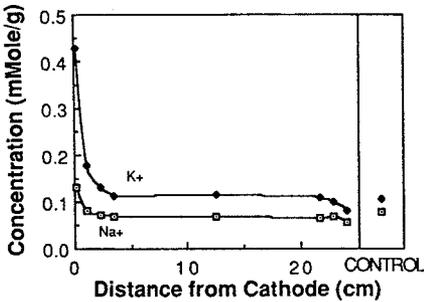

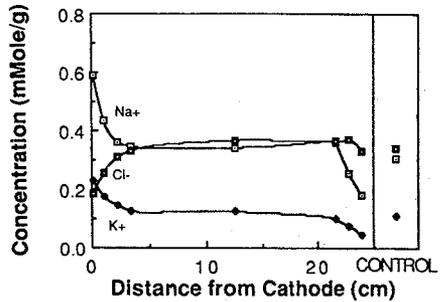Figure 8   Sodium and potassium concentration profiles of slab X after 800 days

Figure 9   Sodium, potassium and chloride concentration profiles of slab X* after 800 days