EFFECT OF APPLIED CURRENT ON MOISTURE DISTRIBUTION IN CEMENTITIOUS MATERIALS

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Abstract.

This report deals with the influence of applied polarisation, as encountered in the use of cathodic protection, upon the moisture distribution present within cementitious materials. The elucidation of the mechanisms involved in this situation is an important goal in the analysis of the behaviour of reinforced concrete structures because changes in internal moisture profiles can affect the corrosion performance, dimensional stability and cracking behaviour of concrete. This topic is of particular relevance to the application of cathodic protection because it has been postulated that such an effect may be related to the occasional failure of the overlays placed around or above retrofitted activated titanium mesh anode systems.

A brief review of the mechanisms believed to be the controlling factors behind moisture movement in cathodically protected concrete is presented, along with a summary of two simple experiments designed to assess the magnitude of such movement at various applied current densities. The findings of these experiments are that polarisation significantly influences moisture movement within the hydrated cement paste samples under consideration, but that the surface strain induced by such changes are negligible when compared to those due to thermal expansion and contraction.

Keywords: Cathodic protection; Impressed current: Moisture movement; Reinforced concrete.

1. Introduction.

A common approach often used for the cathodic protection (CP) of concrete reinforcement involves the application of an anode that consists of a mesh of mixed metal oxide coated over a valve metal. Titanium is often used as this underlying material, but as valve metals such as titanium passivate when connected as an anode a mixed metal oxide coating is used to activate the titanium substrate. The coating is typically formed from one or more metal oxides of the platinum group, such as iridium, ruthenium, or palladium. Due to the robust and enduring nature of this system it is often used where long anode lifetimes are required and where high current densities need to be supplied. The disadvantage of this approach is that for retrofitted systems, which comprise of the vast majority of the structures protected at present, a covering layer of concrete or sprayed gunite is required above the mesh in order to provide an ionically conductive path to the substrate.

The failure of overlays above mesh anodes has been found to present an occasional problem. An example of such a failure, that of the base of a bridge column in North Carolina U.S.A., has been attributed to poor adhesion between the parent concrete and the sprayed concrete layer [1]. In general the information relating to failures of this type is largely anecdotal and is ascribed to poor surface preparation, lack of substrate pre-wetting, inferior application and applicator technique and insufficient curing. It has also been stated that such failures are occasionally due to shrinkage of the overlay material [2].

There may also be an additional contributory factor that has previously been overlooked in these circumstances. A hypothesis exists that suggests that the subsequent disbonding of the overlay is the result of drying shrinkage following anodic polarisation. Certainly both observational and anecdotal evidence suggests that increases in water content occur at the cathode [3], whilst anodic reactions at the mesh serve to dry the adjacent concrete under the influence of applied current [4]. Limited experimental results have previously suggested that the adhesion of the sprayed layer to the substrate is affected by the applied current density from the mesh and the chloride concentration present in the substrate. Pull off tests conducted to determine the tensile bond strength between a concrete substrate and anode encapsulating sprayed concrete overlays found that an increase of applied current density from 20 to 50 mA/m^2 resulted in a decrease in the measured bond strength. Those specimens containing chlorides were found to be particularly susceptible to this phenomenon [5].

It is the purpose of this paper to present a brief overview of the mechanisms of moisture movement within concrete under such conditions and to provide a review of a number of experiments conducted as part of an EPSRC funded project to follow up the findings noted in the work described above.

2. Overview of Moisture Movement Mechanisms in Cementitious Materials.

2.1. Ionic Migration and Diffusion.

The pore structure within concrete or other cementitious materials typically contains an encapsulated liquid known as the pore water solution, which acts as the supporting electrolyte that enables the corrosion of reinforcement in concrete to occur. This solution is of a highly alkaline nature due to the alkali metal ions of potassium and sodium that are dissolved in it during hydration. The pH value of the pore solution can vary widely depending upon the type of cement used in manufacture and the environment to which the material has subsequently been exposed, but typical values lie in the range pH 13 to 14.

The anodic and cathodic reactions that result from the application of CP engender a change in the ionic composition of the surrounding pore water electrolyte. Migration and diffusion subsequently cause a redistribution of the ionic species throughout the material in question. This is of importance when considering the moisture distribution in the cementitious matrix because water will be moved by an osmotic mechanism as a result of changes in ionic concentration at various locations.

The microstructure of a concrete is paramount in controlling the rates of species movement within, and into, a structure. At lower water to cement ratios of below 0.5 the large capillary pores become blocked due to the deposition of CSH (calcium silicate hydrate) gel. This deposit has similar activation energies for ionic diffusion as that found for OPC (Ordinary Portland Cement) pastes and, as such, presents a major barrier to diffusion [6].

The prevailing view amongst contemporary workers in this field is that ionic movement is strongly influenced by the dielectric properties of the cement paste on a colloidal scale. Comparative diffusion experiments between chloride and the similarly sized, yet neutrally charged, oxygen molecule have highlighted the possibility that chloride and other similarly charged species are retarded by the surface charge of hydrated cement gel [7].

Studies of sodium and potassium transport have also been conducted. Alkali diffusion rate coefficients have been found to range from 5.1×10^{-9} cm^2 s^{-1} to 9.8×10^{-8} cm^2 s^{-1}, depending upon the experimental conditions studied [8][9]. Other experimental results have identified the fact that significant alkali migration occurs under the influence of humidity gradients and applied potentials. Samples analysed using neutron activation analysis show that sodium and potassium move from the wet to dry parts and from the anodic to the cathodic areas of specimens respectively [10]. Further investigations have confirmed the migration of sodium, potassium and calcium ions towards the cathode under an applied potential and have found potassium to be the most mobile of the three species [11]. Potassium was also found to migrate faster in chloride-bearing concrete than in similar concrete without chloride.

2.2 Bulk Moisture Movement.

In addition to the production and redistribution of ionic species as a result of cathodic protection, water flow in concrete is also thought to occur due to the presence of pressure differentials, adsorption, wick action and electro-osmosis [12]. The first three mechanisms occur as a result of the capillary structure found in cementitious materials and are a function of mix proportions and admixture types used to form a particular mortar or concrete and also occur in the absence of any applied polarisation.

The last of these processes, that of electro-osmosis, is often cited as the mechanism by which moisture movement occurs in concrete under the action of an applied electric field. The theory involves the formation of an electrochemical double layer at the interface between the cementitious matrix and the pore solution due to a tendency for charged particles to be attracted or repelled from the surface. It is widely believed that when current is applied to concrete the mobile outer region of the double layer is attracted towards the cathode, whilst that molecular layer closest to the pore wall remains tightly bound. This process results in pore water moving en masse and drawing further liquid along behind it by a suction effect. In a very dilute electrolyte, the double layer can be over 1000 water molecules thick, whereas in a strong salt solution the layer will only extend to the thickness of a few molecules.

It is this latter fact that poses the biggest doubt as regards the applicability of the electro-osmotic theory to moisture movement in concrete. Within the micropores of a concrete the pore solution found for typical mixes is of a highly concentrated nature. As such the double layer thickness will be small, of the order of 10 Å in 0.1 M solution and 4 Å in 0.7 M solution [13], where it would be expected that such a tightly bound and compact double layer would not allow significant moisture movement through the pore structure by electro-osmosis.

Investigations to elucidate whether moisture movement is caused by electro-osmotic or by purely osmotic mechanisms are very sparse, primarily due to the difficulty of separating one action from the other. However, some information has been published that claims to prove the effect of electro-osmosis [14]. This investigation found that mortar bars containing embedded electrodes at the top and bottom experienced deflection for applied currents of 80 mA at applied potentials of 20 to 40 Volts, following previous work conducted using 200 Volts. Whilst these conclusions purport to prove the existence of electro-osmosis, at no point is the process confirmed in any determinable or mechanistic way. The significant levels of ionic transport recorded in polarised samples and discussed in section 2.1, above, would seem more than sufficient to cause osmotic effects to predominate beyond any electro-osmotic transport mechanism when related to moisture movement under conditions in the presence of a concentrated electrolyte.

As already mentioned, the moisture content of cementitious materials does not stay constant over time, even in the absence of applied potentials. Adsorption, desorption and, hence, water content are dominated by pore size and external relative humidity. Increasing water content in the relative humidity range 0 to 80 % is believed to be primarily due to increased molecular adsorption, whilst capillary condensation becomes increasingly influential at relative humidities above 60 % [15]. Changes in the external humidity, therefore, obviously affect the internal moisture distribution of cementitious materials.

The humidity gradients present in cementitious materials due to a variation between the internal and external humidities can persist for extended periods before a state of equilibrium is achieved. Cylinders of 40 mm height and diameter exposed to various humidities for 256 days have been found to only achieve constant weight in 98.5 % and 90 % relative humidity conditions [15]. At external relative humidities of 80, 70, and 60 % the specimens continue to record a decrease in mass.

The water content of concrete can also vary over time following changes in the capillary system. Cement hydration products occupy more than twice the volume of the original cement particles, so as hydration proceeds the volume of the capillary system is reduced [16]. This effect has been quantified and it has been found that the total porosity of a hydrated cement paste kept at 98.5 % relative humidity falls from 29 % at 40 days to 25.8 % at 296 days [15]. This causes a change in moisture content regardless of the environmental relative humidity. This mechanism is found to be most marked immediately following casting and falls with increasing specimen age. It has also been confirmed by investigations into the drying behaviour of concrete specimens [16], where rates of drying are found to be dependent upon the moist curing exposure time used. Specimens cured for three days show greater rates of drying than do comparable specimens cured for 28 days. This is partly attributed to lesser hydration in the three day samples, but it is also believed that the greater openness of the pore network at earlier stages of hydration also allows higher rates of moisture diffusion during this period.

A change of moisture content can also lead to dimensional changes in a specimen. Cement paste can shrink or swell because of the colloidal dimensions of its hydrated reaction products, where hydrated cement forms poorly crystalline colloidal reaction products along with some non-colloidal products such as calcium hydroxide [17]. Most work conducted on this subject concerns the mechanism of drying shrinkage of either hardened concrete or hydrated cement paste samples.

In cementitious materials exposed to ambient air two main drying processes occur. The first of these is moisture diffusion due to surface drying, whilst the second is self-desiccation. The latter is particularly prevalent in high cement mixes where hydration binds water into the cement matrix [16]. Drying shrinkage stops when equilibrium is reached between ambient humidity and the humidity in the concrete capillaries or, alternatively, when the hydrostatic tensions that retain water in fine capillaries are equal to the forces that will cause such water to evaporate [17]. Values of 28 day strain following drying shrinkage have been measured for 0.45 water to cement ratio concrete and are found to vary from $+13 \times 10^{-6}$ to -410×10^{-6} depending on the curing regime used [18].

Hysteresis is observed in the behaviour between moisture adsorption and moisture desorption. For concrete that is initially dried, and then subsequently wetted, not all of the drying shrinkage is recovered. For a typical concrete this irreversible amount typically accounts for 30 % of the drying shrinkage. This is attributed to the formation of extra bonds within the gel matrix during drying when closer contact between the gel particles is established.

3. Experimental Work to Assess Magnitude of Moisture Movement Under an Applied Potential.

3.1 Introduction.

That moisture movement will occur in cathodically protected structures is not in doubt. In fact, a technique utilizing this mechanism has recently reached the marketplace and has been utilised on a number of structures, including the Widnes Bridge approach viaducts in the North East of England. What has yet to be established is the mechanism controlling this behaviour. The prevailing view that electro-osmosis is responsible is difficult to reconcile with the predicted double layer thicknesses involved in the concentrated electrolytes found in concrete.

In an attempt to provide some groundwork upon which further studies can be based, a series of experiments was conducted to assess the comparative magnitudes of moisture movement in a number of polarised cementitious samples. A summary of the fundamentals of the experiments, the procedures followed and the results obtained from them are described in the following sections.

At this point it must be stressed that it is not within the scope of the project to identify the mechanisms responsible for moisture movement. This is a task that must await a more comprehensive and detailed investigative programme, although it is envisaged that the results of the present study may aid in the elucidation of such behaviour in the future.

3.2 Overview of Experimental Arrangements.

Temperature Effects.

Whilst only two basic types of experiment were undertaken as part of this work, it was necessary to conduct some preliminary testing to determine the limits under which these would be conducted. The most important determination was the effect that electrical resistance-induced heating would have on the samples as a result of passing current between the embedded anode and cathode elements. Heating of the samples as a result of polarisation would have greatly affected the measurements of moisture movement and so it was deemed prudent to limit the applied current to a range within which excessive heat build-up was not apparent.

The specimens used for this study consisted of a number of embedded thermocouples set in hydrated cement paste cubes containing a cast in anode and cathode (see Figure 1). Current was passed through these cubes and the temperatures of the thermocouples monitored and compared to those measuring the ambient conditions around the specimens.

The samples were cast from hydrated cement paste of 0.5 water to cement ratio, manufactured with OPC of the composition given in Table 1. A hydrated cement paste mix was used for two reasons. Firstly, it provided a material of greater homogeneity than would either mortar or concrete, where the addition of aggregate could have acted to unpredictably influence heat conduction and the formation of temperature profiles within the cubes. The second reason was that a mix without aggregate was much easier to cast around the embedded components without causing disruption to their position. Three cubes were cast in order to obtain triplicate results for each thermocouple position. Following curing and demoulding the cubes were transferred to an exposure cabinet maintained at an approximate relative humidity (RH) of 97 %.
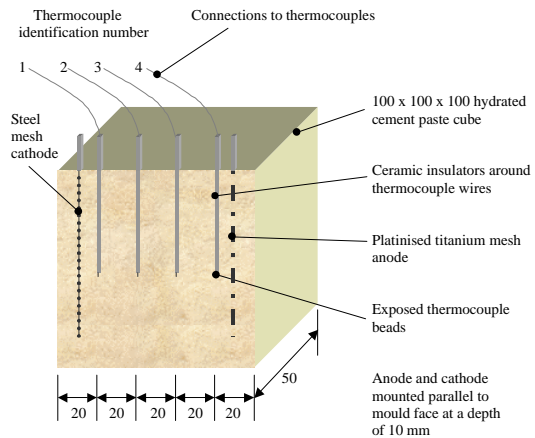

Figure 1 - Cut away view of thermocouple specimens.

Compound	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3	K_2O	Na_2O	Cl_2	LOI
% b.w.c.	21.2	5.34	2.62	63.53	1.3	3.38	0.09	0.75	0.015	1.53

b.w.c. and LOI denote by weight of cement and loss on ignition respectively.

Table 1 - Composition of the standard OPC used in this work.

Weight Change of Sandwich Specimens.

The purpose of this experiment was to assess the rates of any moisture movement following the generation of an applied potential between an anode and cathode embedded in hydrated cement paste. A number of separate elements were held between the anode and cathode in a sandwich arrangement. The weights of these four intermediate elements, along with the weight of the elements containing the anode and

cathode, were measured at weekly intervals throughout the period of current application. The experimental variables within the study were the chloride content of the paste samples and the applied current passed between the anodic and cathodic elements.

Other methods of measurement were deemed inappropriate to assess moisture movement within the samples. For instance, electrical impedance spectroscopy has been used to assess the moisture profile of drying concrete [19]. This does not, however, take into account species migration due to drying of the surface of the sample. Methods such as the placing of a humidity probe into holes drilled into the sample [16] were also discounted due to the local changes to the cross-sectional area of the specimens that this would cause.

The elements that comprised the sandwich specimens used in this work were manufactured from hydrated cement paste of 0.5 water to cement ratio, using the OPC described in Table 1. Hydrated cement paste was used because the specimens needed to be as homogeneous as possible to provide consistent results. In addition, the grinding of the elements, as discussed later in this section, necessitated the use of a mix without any aggregate. As for the temperature specimens, the embedded cathode was formed from a mild steel mesh and the anode was cut from activated titanium mesh.

Surface grinding of the specimens was required to produce smooth, flat mating faces between the elements of the sandwich samples. The grinding was carried out using a vertical grinding machine with the samples held in a specially constructed jig. The anode and cathode containing elements, and the associated control samples, were ground on their inner face only and grinding was continued until the depth to the anode or cathode was approximately 7 mm. The remaining samples were ground on both faces until the overall thickness of each element was approximately 7 mm.

The grinding process could only be accomplished successfully under wet conditions. As this may have upset the balance of the pore solution contained within the material it was decided that the specimens should be equilibrated to a known condition prior to experimental exposure. This was accomplished by immersing the samples into artificial pore solutions manufactured from KOH, NaOH, NaCl and distilled water. The concentration of KOH and NaOH was chosen based upon previous work requiring the use of artificial pore water solution [20]. The solution was designed to have a composition of 0.4M KOH, 0.2M NaOH and a level of chloride of equal concentration to that added to the mix water during casting of the specimens. To introduce this solution to the samples they were part immersed in a batch of the liquid and placed inside a chamber that was partially evacuated using a vacuum pump in order to draw the artificial pore water into the cement paste.

Figure 2 - Cut away view of weight change sandwich experiments.

The tests were conducted in a humidity cabinet containing a saturated salt solution of potassium sulphate, used to give a nominal RH of 97 % at a temperature of 20°C. Testing was commenced once weight change measurements indicated that the samples had reached an approximately steady state condition and equilibrated to the conditions.

The samples were arranged in the form shown in Figure 2 and held together in specially constructed cradles (as shown in Figure 3). The sandwich elements were formed from samples cast and preconditioned so that they contained three levels of chloride. The levels of added chloride were set at 0 %, 0.2 % and 1 % by weight of cement (b.w.c.).

Four values of current density were applied to the samples using a galvanostat. The levels chosen were 0 mA/m^2, 10 mA/m^2, 100 mA/m^2 and 250 mA/m^2 of sample cross-sectional area. These values were chosen to give control values with no applied current, typical current levels applied during cathodic protection and two elevated levels of current so as to
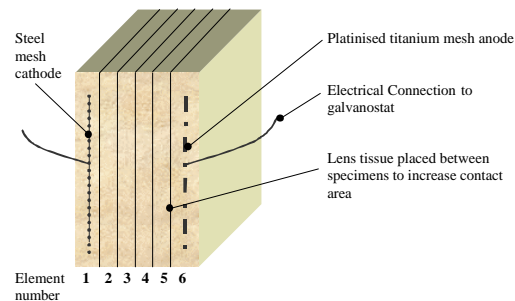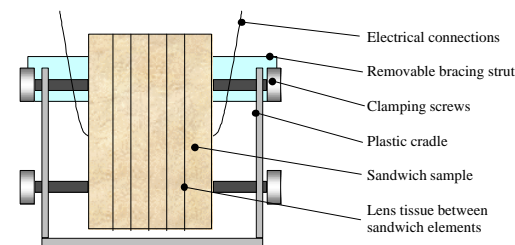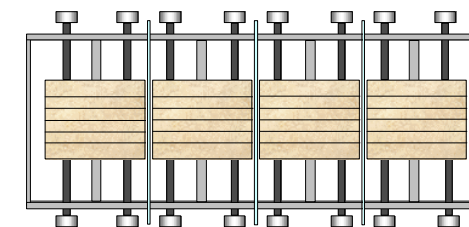

1. Side view of cradle

2. Top-down view of cradle

Figure 3 - Diagram showing cradle for holding sandwich specimens.

provide accelerated test results. The maximum level of applied current was limited to 250 mA/m^2 following the preliminary testing with the thermocouple-containing specimens.

Dimensional Changes of Monolithic Specimens.

An alternative method of ascertaining the magnitude of moisture movement occurring in a cementitious specimen under polarisation is to measure the dimensional changes taking place within the material. Such data is then more readily transferable to considerations of anode overlay failure in reinforced concrete structures undergoing cathodic protection.

The dimensional changes occurring in galvanostatically polarised hydrated cement paste cubes were measured using an array of Demec points fixed to one face of the sample. As for the weight change tests described above, specimens were cast with chloride contents of 0 %, 0.2 % and 1 % by weight of cement and exposed to current densities of 0 mA/m^2, 10 mA/m^2, 100 mA/m^2 and 250 mA/m^2 of cube cross-sectional area.

The specimens were manufactured from hydrated cement paste, both to provide an approximately homogeneous medium and to allow comparison with the weight change results. The large size of the specimens meant that it was unlikely that they would fully equilibrate to the humidity conditions of the experiment in a suitable period. Even though it was envisaged that steady state weight conditions would not be achieved, a prolonged period of exposure following curing and prior to polarisation was scheduled to allow moisture uptake to proceed as far as possible. In this interval the possibility existed that mild steel cathodes would undergo deleterious levels of corrosion in the presence of elevated levels of chloride. For this reason, both the anodic and cathodic elements cast into the cubes were formed from activated titanium diamond mesh.

A number of Demec markers were applied to one of the side faces of the cubes, as shown in Figure 4 (dimensions in mm). Five pairs of markers were placed so as to measure any dimensional changes in the region between the anode and cathode. Following the fixing of the Demec markers to their surfaces, the cubes were transferred to a humidity cabinet where they were exposed above a saturated salt solution of potassium sulphate at a nominal RH of 97 % at 20°C.

The cubes were weighed at weekly intervals throughout the duration of the experiment to an accuracy of 0.1 g. At the same time, a Demec gauge was used to measure the relative strain between the Demec points. The samples were subjected to polarisation for a period of 120 days, after which the supply of current was terminated. Weight change and Demec measurements continued through this period and for a further 50 days following depolarisation.
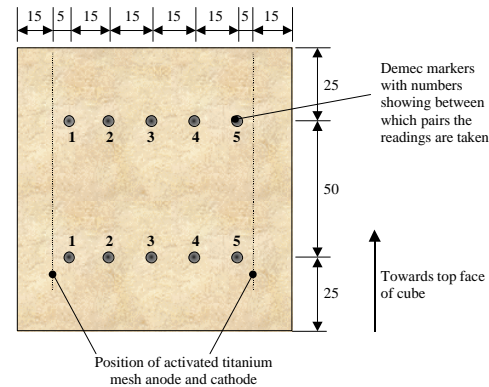

Figure 4 - Side view of dimension change experiments.

3.3 Results.

Temperature Effects.

As remarked in the preceding section, the primary purpose of these tests was to determine a cut-off point in the level of current applied in the moisture movement experiments to follow. By its very nature, this is a highly subjective value as it is reasonable to assume that any degree of current flow will change the temperature profile of a sample and subsequently affect the rate and extent of internal moisture movement.

The measurements from the thermocouples showed that there was no effect on the results originating from the position of the thermocouple in the cubes and their respective distance from the anode and cathode. A significant amount of data scatter was detected in the results, although it is unclear whether this was due to the design of the experiment, or additional effects such as reactions between the cement paste pore solution and the
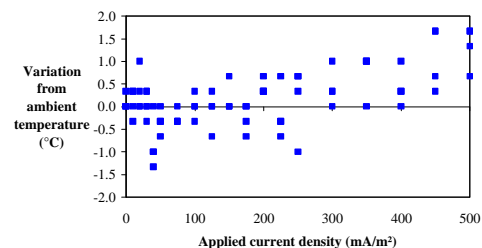

Figure 5 - Variation of measured temperature from ambient for thermocouple 4.

exposed thermocouple components.

The results shown in Figure 5 are from thermocouple position 4, that closest to the anode. The data clearly identify a rising trend in internal cube temperature, above that measured in the ambient environment, with increases in applied current density. The influence of this seems to be greater at current densities of 300 mA/m^2 and above, with a further significant increase at 450 mA/m^2 and above.

As a result of these findings it was decided to limit the applied current densities in the ensuing experiments to a maximum of 250 mA/m^2.

Weight Change of Sandwich Specimens.

Weight change measurements of the sandwich specimens detailed in section 3.2 were carried out for hydrated cement paste samples with chloride contents of 0 %, 0.2 % and 1 % by weight of cement. These were subjected to applied current levels of 0, 10, 100 and 250 mA/m^2 of cross-sectional area for a period of 120 days. At the end of this period current supply was terminated and weight change measurements then continued for a further 50 days.

A representative sample of the weight change results, for specimens containing 0 % admixed chloride treated at 0, 10 and 100 mA/m^2, is provided in Figures 6 to 8. The first conclusion that can be drawn from these figures is that whilst the results impart a visually rough look to the graphs during the period of applied polarisation, the traces generally maintain a much smoother profile following the cessation of current flow at 120 days. Why this should occur is not immediately clear, as the same experimental procedure was followed throughout. Study of the RH measurements taken from the cabinet show that these values also experienced less weekly variation following the cessation of current flow. This suggests that it is these variations in the cabinet humidity that have acted to influence the weight change results.

The cause of the humidity changes is also unclear. An explanation can however be offered, although it cannot be positively proven. The weight change results show that in certain cases the moisture profiles of the specimens have been dramatically altered as a result of current flow. This would be expected to create moisture profiles at the external faces of the sandwich elements, as the internal humidity of the pastes varies from that contained in the cabinet, resulting in the surface of the elements either imbibing or releasing water. This in turn would

Figure 6 - Weight change measurements. 0 % chloride b.w.c. with an applied current density of 0 mA/m^2.

Figure 7 - Weight change measurements. 0 % chloride b.w.c. with an applied current density of 10 mA/m^2.

Figure 8 - Weight change measurements. 0 % chloride b.w.c. with an applied current density of 100 mA/m^2.

have altered the internal humidity of the cabinet, which would have needed time to be balanced by the saturated sodium sulphate solution held in the base of the cabinet.

Figures 9 to 12 compare the final weight change results of the specimens. This is taken as being the final reading measured under applied current conditions following 120 days of polarisation. Figure 9 shows the weight change of the samples containing the three different chloride concentrations under conditions where no current was passed through the specimens. These can be considered as being the control samples for this experiment and illustrate that the moisture distribution in the chloride-free sample is very different from that in either of the samples containing chloride. The end pieces, corresponding to the anode and cathode in the polarised samples, show a significant uptake of water whilst the internal elements have experienced considerably lower weight gain. By comparison, the chloride-containing samples display a much flatter moisture distribution. It is possible that the hygroscopic nature of chloride salts has resulted in a greater uptake of water through the smaller surface area of elements 2, 3, 4 and 5 than has occurred in the chloride-free elements.
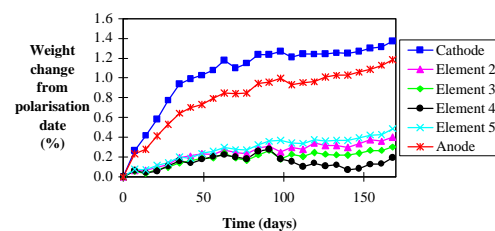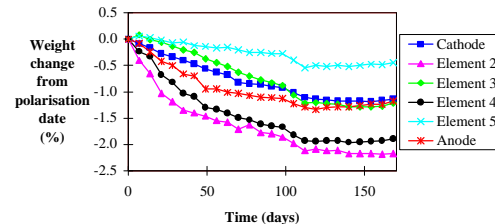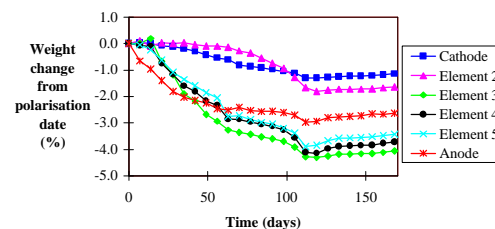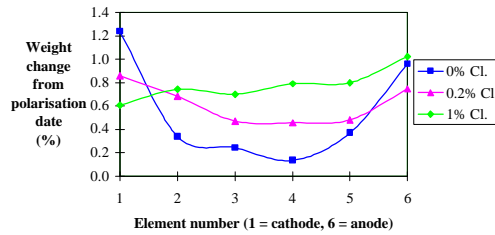
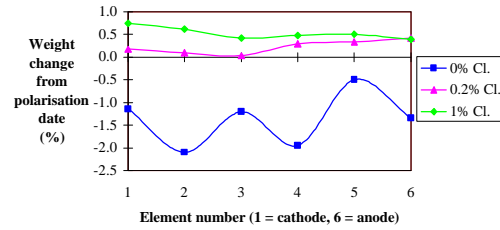Figure 9 - Final weight change. Applied current density of 0 mA/m^2.

Figure 10 - Final weight change. Applied current density of 10 mA/m^2.
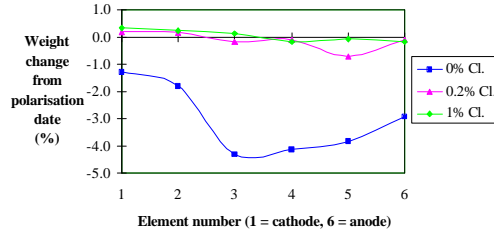
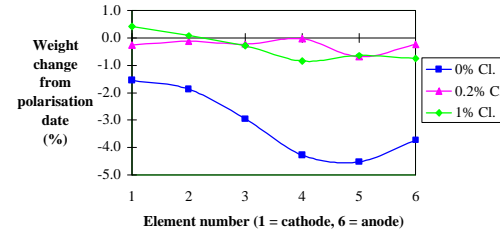Figure 11 - Final weight change. Applied current density of 100 mA/m^2.

Figure 12 - Final weight change. Applied current density of 250 mA/m^2.

Figure 10 details the effect on the 120 day measurements of applying a current density of 10 mA/m^2 across the samples. Such a current can be considered typical of that applied to many cathodically protected concrete structures. The results from the chloride-free samples again showed a significant variation from those containing chloride. The mixes cast with 0.2 and 1 % chloride by weight of cement generally show weight gain and a relatively flat weight change profile between the six elements. By contrast, the chloride-free samples experience a significant decrease in weight and a variation between adjacent elements of up to 1 % of their initial weight. This again may be a result of the increased difficulty of moisture movement in the chloride-free conditions.

The behaviour of the samples at increased applied current densities of 100 and 250 mA/m^2 are very similar and are shown in Figures 11 and 12, respectively. The samples with 0.2 and 1 % chloride by weight of cement record little weight change from the initial values at polarisation. There is, however, generally a slight decrease in the weight of the anodic element when compared to the cathodic one. Again, the chloride-free specimens demonstrate a significant variation from this behaviour. The cathodic side of the samples show decreases in weight from those at polarisation of between 1 and 2 %. The weight loss of those elements towards the anodic side of the specimens display a much greater weight loss, in the region of 4 to 5 % over the same period. For both levels of applied current the weight loss of the anodic element is less than those adjacent to it, this possibly being a result of the increased surface area of the end element acting to permit greater rates of water adsorption from the atmosphere within the cabinet.

At the end of the 120 day polarisation period the supply of current to the specimens was halted, although weight change measurements were continued for a further 50 days. These measurements were conducted to assess the level from which the moisture profile of the specimens subsequently recovered towards their equilibrium profiles following the cessation of current flow.

For those specimens to which no current was applied, the profiles of the weight change measurements after 50 days remain similar to those recorded during the preceding 120 days. The only significant difference is that the weight gain of the end elements for the chloride-free samples is less for the 120 to 170 day data. This is because of the fact that, as the elements have had longer to imbibe water, they will be closer to their equilibrium internal humidity and so will progressively take on water at a lesser rate.

At an applied current of 10 mA/m^2 the profiles are modified slightly from those obtained at zero current. The profiles of the chloride-bearing samples are similar to the zero current specimens, with the exception that the anode and cathode containing elements of the sample with 1 % chloride by weight of cement show increased weight gain (see Figure 13). By contrast, there is a significant variation in behaviour from the cathodic to the anodic side of the specimen for the chloride-free sample. Whilst the results at 120 days were inconclusive, the 170 day
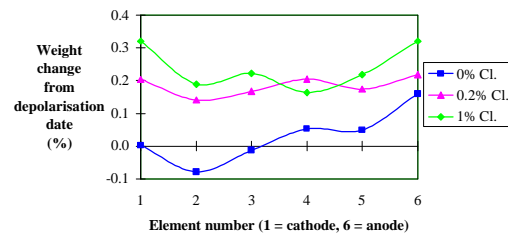
Figure 13 - Weight change 50 days after depolarisation. Applied current density of 10 mA/m^2.

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results suggest that increased drying occurred around the anode during the polarisation period and that this has subsequently caused an uptake of water following the cessation of current flow.

The weight change following depolarisation of those samples subjected to a current of 100 mA/m^2 indicates that the chloride-containing samples again generally demonstrate a consistent level of weight gain across the whole of the specimen. The significant weight loss experienced by the 0 % chloride samples during the polarisation period is partially recovered, providing further evidence that those elements that show the greatest rates of drying under polarisation are generally those showing the greatest amount of weight gain following depolarisation. The results for the 250 mA/m^2 samples are very similar and can be seen as reflecting the similarity of the results obtained from these two current densities under polarised conditions.

Weight change measurements of the four levels of applied current for the chloride-free samples are shown in Figure 14 for the 50 day period following the cessation of current. This figure shows that two distinct forms of behaviour are apparent. Those samples previously exposed to the two highest current densities show significantly greater weight gain, particularly for those elements towards the anodic side of the specimen.
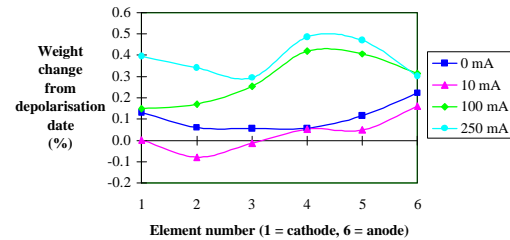

Figure 14 - Weight change 50 days after depolarisation. 0 % chloride b.w.c.

Taken as a whole, these results suggest that the application of current to a cementitious material can dramatically influence the water content within the sample. This proves to be particularly apparent in chloride-free samples where greatly increased levels of weight loss are recorded following the application of a galvanostatically applied current. Such an effect would be expected to be exacerbated when a chloride-free overlay is added to a chloride-containing structure, a situation that is often the case in cathodic protection applications. If it is assumed that the overlay has broadly similar transport characteristics to the hydrated cement pastes tested, a possibility for a poor quality material, then the results of these tests imply that the overlay would experience significant drying, whilst the concrete substrate would dry to a much lesser degree. If such changes are reflected in the dimensional characteristics of the overlay then such drying could induce significant stress generation at the overlay to substrate interface.

Dimensional Changes of Monolithic Specimens.

Following the results of the weight change specimens described above, it was decided that the tests would be repeated with 100 mm hydrated cement paste cubes with Demec gauges mounted on the side. These gauge lengths were designed to measure any changes in the dimensions of the cubes induced by internal water transport under the influence of an applied electric current. This is considered an important step in the investigation as it provides a means to relate the findings of the weight change results to the potential mechanism of overlay disbondment.

The weight of the cubes used to conduct the dimension change experiment was measured at weekly intervals throughout the 120 day period of polarisation and for a 50 day period following the cessation of current flow. The results of these measurements show that the cubes experienced an approximately linear degree of weight increase over time, with the specimens containing 1 % chloride by weight of cement taking on more water than the 0 % and 0.2 % chloride-containing cubes. Table 2 shows the weight change of the cubes from their initial value following 120 days of polarisation and during the subsequent 50 days with the current supply

Chloride content of sample (% b.w.c.)	Applied current density (mA/m^2)	Change in mass from date of polarisation at 120 days (%)	Change in mass from date of polarisation at 170 days (%)	Change in mass during 50 day depolarised period (%)
0	0	0.895	1.115	0.245
0	10	0.788	0.991	0.258
0	100	0.830	1.060	0.277
0	250	0.882	1.162	0.318
0.2	0	0.976	1.236	0.266
0.2	10	0.985	1.226	0.244
0.2	100	0.975	1.234	0.267
0.2	250	0.845	1.114	0.317
1	0	1.387	1.818	0.311
1	10	1.242	1.63	0.313
1	100	1.239	1.657	0.337
1	250	1.433	1.927	0.345

Table 2 - Mass change of monolithic specimens at end of 120 day polarisation period and following 50 days of depolarisation.

disconnected. The 120 day and 170 day results show no obvious trends between the chloride content, applied current and weight change of the specimens. If these two weights are compared, however, then it can be seen that the difference between the weights increases for those specimens that were exposed to higher levels of current density.

The results obtained from the demec gauges were found to be dominated by thermal effects, rather than any influence of moisture movement. A typical example is shown in Figures 15 and 16, where the temperature readings within the exposure cabinet are compared to the strain rates measured for the 0.2 % chloride by weight of cement sample exposed to an applied current density of 250 mA/m^2.
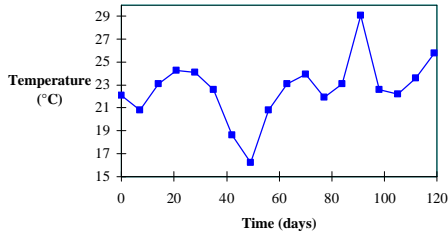
9

Figure 15 - Temperature measurements of humidity cabinet for dimension change specimens.
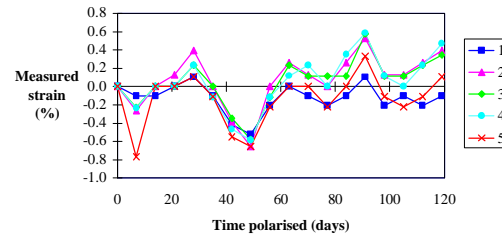

Figure 16 - Strain measurements for dimension change specimens. 0.2 % chloride b.w.c. with an applied current density of 250 mA/m².

It is unclear why the results from the dimension change experiments should vary to such a large degree from the weight change results discussed previously. The greatest difference between the two sets of samples was the fact that the weight change specimens were preconditioned by vacuum saturation in an artificial pore water solution. This technique was considered unnecessary for the cubes because they were not subjected to wet surface grinding and so would not have had their pore solution chemistry affected in the same way. The size of the samples was also a consideration because the time to achieve full saturation and constant weight conditions would have been prohibitive.

The fact that the cubes continued to increase in weight throughout the duration of exposure, under conditions in which the weight change specimens did not, indicates that the cubes had a lower internal moisture content or were still undergoing substantial hydration. It could be that under such conditions the humidity gradients present within the cubes were able to either mask or stifle water movement due to polarisation.

3.4 Experimental Conclusions.

The results from the study of temperature changes caused by galvanostatic polarisation showed that, for the experimental arrangement used, current densities in excess of 300 mA/m² of sample cross-sectional area resulted in the generation of heating by electrical resistance to a level that was considered likely to affect the moisture movement measurements. As such, a limiting value of 250 mA/m² was adopted for this work.

The weight change measurements of sandwich specimens conducted under various levels of galvanostatic polarisation indicated that preferential drying of the hydrated cement paste samples occurred in the region adjacent to the anode.

Under the control conditions, where no current was passed through the weight change specimens, the chloride-free samples showed weight gain. At modest levels of applied current of 10 mA/m² this behaviour was transformed into significant levels of weight loss. As the current was increased further, the levels of weight loss in those elements positioned towards the anode increased to levels of approximately 4 % over 120 days of polarisation.

Evidence of preferential drying in the region around the anode was also found in the weight change tests for hydrated cement pastes of 0.2 % and 1 % chloride by weight of cement, although the changes were not as extreme as for the chloride-free samples. Again increases in the level of applied current caused an increase in the magnitude of weight loss towards the anode. The levels of weight loss of these specimens were generally mirrored in the level of weight gain they experienced in the 50 days following the cessation of current supply.

Results from the monolithic specimens, however, strongly suggest that at the levels detected in this study moisture movement through capillary pores has very little, if any, influence on dimensional stability. No changes in the external dimensions of the samples could be attributed to internal moisture movement because the results were influenced to a large degree by thermal expansions.

The progressive drying of the material around the anode may, however, have another effect on the operation of CP systems in reinforced concrete. Many mature CP systems experience a time dependent increase in their operating resistance. Whilst this is commonly attributed to the degradation of the anode material over time, it is also possible that the loss of pore water electrolyte from around the anode location may also contribute to this behaviour.

4. Conclusions.

In conclusion, the results of the weight and dimension change experiments suggest that the reported failures of cementitious overlays covering embedded cathodic protection mesh elements are unlikely to be a result of drying and shrinkage of the overlay following the influence of an applied electric field on moisture movement. From these findings it is likely that the faults more typically ascribed to such failures of poor surface preparation, inferior application and applicator technique and poor curing are of much greater importance.

The mechanism of the weight change seen in this study as a result of an applied polarisation has not been fully clarified, although it would seem to involve interactions between the level of charge passed, the ionic concentrations within the pore solution, ionic movement, heating and the moisture content of the material. Review of available literature would also suggest that the mechanism of electro-osmosis, frequently cited as the primary driver for pore water movement under polarised conditions, will not be a factor in typical concrete or mortar compositions due to the high ionic concentrations evident in the pore water solution. This is due to the influence such concentrations have in decreasing the double layer thickness to a level at which electro-osmotic movement would be severely constrained or stifled completely.

5. Acknowledgements.

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