ASPECTS OF THE PREVENTION AND REPAIR OF CHLORIDE-INDUCED CORROSION OF STEEL IN CONCRETE

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SUMMARY

Sodium formate, potassium acetate and a mixture of calcium and magnesium acetate (CMA) have all been identified as effective deicing agents. In this project an attempt has been made to elucidate potentially deleterious effects of these substances on the durability of reinforced concrete.

Aspects involving the corrosion behaviour of embedded steel along with the chemical and physical degradation of the cementitious matrix were studied. Ionic diffusion characteristics of deicer/pore solution systems in hardened cement paste were also studied since rates of ingress of deleterious agents into cement paste are commonly diffusion-controlled.

It was found that all the compounds tested were generally non-corrosive to embedded steel, however, in a small number of cases potassium acetate did cause corrosion. Potassium acetate was also found to cause cracking in concrete and cement paste samples. CMA appeared to degrade hydrated cement paste although this was apparently less of a problem when commercial grade CMA was used in place of the reagent grade chemical. This was thought to be due to the insoluble material present in the commercial formulation forming a physical barrier between the concrete and the deicing solution. With the test regimes used sodium formate was not seen to have any deleterious effect on the integrity of reinforced concrete.

As a means of restoring the corrosion protective character of chloride-contaminated concrete the process of electrochemical chloride removal has been previously developed. Potential side-effects of this method and the effect of external electrolyte composition on chloride removal efficiency were investigated.

It was seen that the composition of the external electrolyte has a significant effect on the amount of chloride removed. It was also found that, due to alterations to the composition of the C_3A hydration reaction products, it was possible to remove bound chloride as well as that in the pore solution. The use of an external electrolyte containing lithium ions was also tried as a means of preventing cathodically-induced alkali-silica reaction in concretes containing potentially reactive aggregates. The results obtained were inconclusive and further practical development of this approach is needed.

Keywords: reinforced concrete, deicing chemicals, electrochemical chloride removal

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GLOSSARY OF ABBREVIATIONS

AAS	Atomic Absorption Spectroscopy
Ac	Acetate ion
AR	Analytical grade
ASR	Alkali Silica Reaction
ASTM	American Society of Testing and Materials
BAA	British Airports Authority
BFSC	Blast Furnace Slag Cement
C_3A	Tricalcium Aluminate $3CaO.Al_2O_3$
C_4AF	Tetracalcium Aluminoferrite $4CaO.Al_2O_3.Fe_2O_3$
CMA	Calcium Magnesium Acetate
CP	Cathodic Protection
C_2S	Dicalcium Silicate $2CaO.SiO_2$
C_3S	Tricalcium Silicate $3CaO.SiO_2$
CSE	Copper Sulphate Electrode
C-S-H	Calcium Silicate Hydrate
DTA	Differential Thermal Analysis
DTG	Differential Thermogravimetric Analysis
ECM	Environmental Corrosion Monitors
EDXA	Energy Dispersive X-Ray Analysis
FHWA	Federal Highway Research Administration
Fo	Formate ion
MIP	Mercury Intrusion Porosimetry
M-S-H	Magnesium Silicate Hydrate
OPC	Ordinary Portland Cement
SCE	Standard Calomel Electrode
SEM	Scanning Electron Microscope
SHRP	Strategic Highway Research Project
SLR	Standard Laboratory Reagent
SSD	Saturated Surface Dry
TGA	Thermogravimetric Analysis
w:c	Water:Cement ratio
XRD	X-Ray Diffraction

CHAPTER 1 - INTRODUCTION

Reinforced concrete has been used as a construction material since the middle of the 19th century. It was considered for a great number of years to be maintenance-free. Although the great majority of structures are sound, the idea of them being maintenance-free is now known to be untrue. There are a number of mechanisms that can adversely affect the durability, the most serious being chloride-induced corrosion of the steel reinforcement.

Chloride ions can be introduced at the time of mixing by using contaminated water, aggregates or chloride-based admixtures. Penetration can also occur into hardened concrete if the structure is one exposed to a marine environment or to the application of chloride-based deicing agents.

When corrosion occurs the cross-section of the load bearing steel is reduced and corrosion products are formed. The corrosion products have no mechanical strength and occupy a larger volume than the original material. This induces cracks in the concrete which then become filled with rust-coloured corrosion products which can stain the exterior of the concrete member. At the very best the structure will merely become unsightly. More commonly, the cracking will force sections of concrete to spall off. Although the reduction in the cross-sectional area of the steel will reduce the overall load-bearing capacity of the structure, it is unlikely that chloride-induced corrosion will cause the unexpected collapse of a reinforced concrete structure. The inherent overdesign incorporated into reinforced concrete structures means that cracking and spalling will occur long before the structural integrity of the member is put in doubt.

However, with prestressed concrete structures where the load is carried by highly stressed steel strands of relatively small cross-section, any corrosion of the steel can cause a significant reduction in the load-carrying capacity of the member. This can cause the sudden collapse of the structure concerned before any visible signs of corrosion are detected [Hatchwell, 1989].

Methods have been developed to prevent or delay the onset of corrosion and these are discussed later, but first it is necessary to understand the corrosion behaviour of steel embedded in good quality concrete and how it is affected by the ingress of chloride ions.

1.1 The Composition and Structure of Ordinary Portland Cement (OPC)

Unhydrated OPC clinker is made up of four major constituents

Name of Compound	Oxide composition	Abbreviation [1.1]
Tricalcium silicate	$3CaO.SiO_2$	C_3S
Dicalcium silicate	$2CaO.SiO_2$	C_2S
Tricalcium aluminate	$3CaO.Al_2O_3$	C_3A
Tetracalcium aluminoferrite	$4CaO.Al_2O_3.Fe_2O_3$	C_4AF

In reality, the chemistry is far more complex. These four major compounds are not pure. The silicates contain other minor oxides (e.g. Mg, Ti, Mn etc.) in solid solution. The C_4AF is actually a solid solution of compounds ranging from C_2F to C_6A_2F. Gypsum ($CaSO_4.2H_2O$, $C\overline{S}H_2$ in shorthand notation) is also added during the clinker production stage to prevent the flash setting of the C_3A phase

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[1.1] The standard abbreviated notation of cement chemistry is as follows: C = CaO, S = SiO_2, A = Al_2O_3, F = Fe_2O_3 ,$\overline{S}$ = SO_3, H = H_2O.

[Neville, 1981]. Sodium sulphate (Na_2SO_4) and potassium sulphate (K_2SO_4) are also present in the clinker as a solid solution [Lea, 1970].

When Portland cement is hydrated, the following reactions occur (in shorthand notation) [Young, 1981]

$$\begin{aligned} 2C_3S + 7H &\longrightarrow C_3S_2H_4 + 3CH \\ 2C_2S + 5H &\longrightarrow C_3S_2H_4 + CH \\ C_3A + 3C\overline{S}H_2 + 26H &\longrightarrow C_6A\overline{S}_3H_{32} \\ C_4AF + 13H &\longrightarrow C_4(A,F)H_{13} \end{aligned}$$

As with the composition of the unhydrated compounds, the above reactions have been considerably simplified. The C:S:H ratio in the calcium silicate hydrates ($C_3S_2H_4$) varies, with different methods of analysis yielding different results. For simplicity it is referred to as C-S-H gel. The C-S-H gel also contains some of the metallic ions from the minor oxides mentioned earlier. The CH (calcium hydroxide) forms into hexagonal plates which then merge into large deposits. These deposits are called portlandite. $C_6A\overline{S}_3H_{32}$ (calcium sulphoaluminate), also called ettringite, is formed from the reaction between the C_3A and the gypsum, but this can eventually change through a number of reactions to form tricalcium aluminate hydrate (C_3AH_6). As the hydration process develops the alkali sulphates held in solid solution are released. These are highly soluble and take part in a series of reactions with the hydrating tricalcium aluminate (C_3A) and calcium hydroxide (CH) [Neville,1981]. This results in the precipitation of more ettringite, leaving an aqueous pore solution primarily of sodium, potassium and hydroxide ions.

Only a very small amount of water is required for the hydration reactions to take place, but to ensure adequate workability of the concrete while being placed and compacted it is necessary to add more water. This large amount of 'excess' water gives rise to a hardened cement paste with a continuous, open pore structure. The pores vary in size from ultra-fine gel pores (<10nm) through coarser capillary pores to discrete macroscopic air voids (>10μm) [Powers & Brownyard, 1948]. From the durability aspect, it is the capillary pores that are the most important as they provide the majority of the interconnecting pathways that allow aggressive ions such as chloride to enter the concrete.

Due to the presence of the 'excess' water and the fact that hardened cement paste is hygroscopic, the voids will, to some extent, contain water. The amount is dependent on the relative humidity of the surrounding area, but even at very low relative humidities the drying out process is very slow and water adsorbed in the gel pores will remain there indefinitely. As the majority of structures are periodically wetted the larger pores may contain water as well. The combination of moisture-containing pores and the sodium, potassium and hydroxide ions liberated during hydration produces an alkaline solution within the pores. The concentration of this solution is dependent on the water content and the composition of the unhydrated cement, but, in the absence of any interaction with external species, it is generally in the order of a few hundreds of millimoles per litre. This results in a pore solution with a pH in the range 13 - 14 [Longuet *et al.*, 1973].

1.2 Mechanisms of the Protection and Corrosion of Steel in Concrete

When corrosion occurs, the metal is anodically oxidised to form a soluble species (e.g. $Fe \longrightarrow Fe^{2+} + 2e^-$). The electrons released in this process flow through the metal to cathodic sites where they are consumed by a reduction reaction (e.g. $O_2 + 2H_2O + 4e^- \longrightarrow 4OH^-$). In order to maintain electro-neutrality, the process is then completed by the electro-migration of ions through the aqueous phase (the electrolyte) [Page, 1988].

However, these reactions can also lead to the formation of an insoluble protective film on the surface of the metal that reduces the corrosion rate to insignificant levels and this is generally the case when steel is embedded in good quality concrete. This condition is known as passivity and the layer is known as the passive film. For simplicity it is can be assumed that the film is made of Fe_2O_3 although in reality it is more complex. A number of different compositions and structures have been suggested [Cohen, 1978; Glasser & Sagoe-Crentsil, 1989], but the majority of them include the Fe_2O_3 species at the exterior surface and the Fe_3O_4 species next to the metal substrate. The passive layer is not perfect and breaks are continually occurring. However, they are normally quickly repaired restoring the integrity of the film which ensures that loss of iron is insufficient to cause any significant reduction in the cross-sectional area of the steel.

However, if the dissolved oxygen level in the pore solution becomes depleted such as in some waterlogged or buried concretes, then the passive film can break down and uniform dissolution of the steel occur. Under these situations the soluble $FeO.OH^-$ species is formed. However, the dissolution process is cathodically restrained by the same lack of dissolved oxygen and therefore it occurs at a very slow rate [Arup, 1983].

The theoretical stability domains of these species can be seen on a simplified Equilibrium Potential - pH diagram for the Fe/H_2O system at 25°C (Figure 1.1)

Figure 1.1 - Simplified Equilibrium Potential - pH Diagram for Iron in Water [Pourbaix, 1966]

1.2.1 The Role of Chloride ions in the Corrosion of Steel in Concrete

If the pore solution in the concrete is contaminated with chloride, then the passivity can be broken down by a condition known as pitting. Pitting is characterised by an intense anodic dissolution of metal occurring over a very small area.

The role of chloride ions in inducing pitting is not fully understood and several theories have been developed. For this work it is not necessary to be aware of the discussion on the relative advantages and disadvantages of each individual proposed mechanism. A full review was given by Galvele [1978], but it does appear from later work that he and his co-workers favoured the theory of localised acidification [Galvele, 1981; Alvarez & Galvele,1984]. When a breakdown occurs in the passive film, instead of re-forming the passive film, the presence of the chloride ions causes the metal to dissolve and form Fe^{2+} ions. These are then rapidly hydrated to form $Fe(OH)_2$ and hydrogen ions. Therefore the immediate area near to a site of breakdown is acidified. This acidification then further promotes the oxidation of the metal to form Fe^{2+} ions and thus the corrosion process is locally accelerated.

The effect of chloride addition to the iron-water system at 25°C is particularly well demonstrated by the changes to the potential - pH diagram (Figure 1.2). Where initially passivity occurred there are now three zones; perfect passivity, imperfect passivity and pitting. In the zone of perfect passivity the passive layer is stable and any breakdowns in the film are quickly repaired. In the pitting zone localised anodic dissolution occurs by the mechanism described previously. In the zone of imperfect passivity, the conditions are such that new pits will not form, but any existing pits will continue to grow.

Figure 1.2 - Experimentally Derived Potential - pH Diagram for Iron in 0.01M Aqueous Chloride Solution [Pourbaix, 1974]

The chloride to hydroxide concentration ratio of the pore solution is of primary importance in governing whether or not the passive film is repaired. A regularly quoted figure for the critical chloride to hydroxide ratio of an electrolyte surrounding mild steel is 0.6 [Hausmann, 1967]. However, this figure was determined for steel in solutions of saturated calcium hydroxide to which varying amounts of sodium chloride had been added. For steel embedded in good quality concrete, corrosion has been seen to occur once the ratio has exceeded approximately 3 [Lambert *et al.*, 1991]. This difference is primarily due to portlandite and other alkaline products being preferentially formed at the cement/steel interface during hydration forming a physical barrier [Page,1975]. It can also act to buffer any decrease in the solution alkalinity.

The extraction of pore solution, which would allow determination of the chloride to hydroxide ratio, is not a technique that can be readily applied to the routine testing of concrete structures. It is more usual to analyse for the acid soluble chloride content in the concrete as a whole. However, the alkali content of cement can vary quite considerably from concrete to concrete and chloride ions in solution are able to react with the C_3A reaction products to form the insoluble complex Friedel's salt ($3CaO.Al_2O_3.CaCl_2.10H_2O$) [Heller & Ben-Yair,1961] removing them from the pore solution. It is, therefore, impossible to predict a precise maximum safe acid soluble chloride content.

Despite these difficulties it was suggested, following certain surveys, that if the acid soluble concrete chloride content is less than 0.4% by weight of cement the risk of corrosion-induced cracking is low, but it is great if it exceeds 1% [Building Research Establishment, 1982].

1.3 Preventative and Remedial Measures to Combat Chloride-Induced Corrosion

A number of options are available to reduce the risk of chloride-induced corrosion and they can either be preventative or remedial.

1.3.1 Mix Contaminants

Potential sources of contamination from the mix constituents are well documented and therefore, in theory, no more cases should appear. In the UK the use of calcium chloride as a hydration accelerating agent has been effectively banned since 1977 and it should be possible to ensure the mix water and the aggregates are sufficiently free of chloride. However, in reality, especially in less well developed countries, this view may be over-optimistic.

1.3.2 Cement Replacements

In new construction, it is possible to replace a percentage of the OPC in the concrete mix with materials such as slags or pozzolanas. These form their own reaction products which act to decrease the capillary porosity and thus slow down the ingress of aggressive ions such as chloride ions [Page *et al.*, 1981]. As the cement replacements react more slowly than portland cement it is important that the concrete is well cured. If not, the capillary porosity may be greater than if they were not added.

1.3.2.1 Slags

Slag is a waste product from the manufacture of pig iron. It can be incorporated into the mix in two ways. The first is as Blast-furnace slag cement (BFSC) which is made by intergrinding dry granulated slag with portland cement clinker. The product is then used in the same way as OPC. The percentage replacement varies from country to country, but can be as high as 85%. The second is where ground granulated slag is added to the other constituents at the mixer as a partial replacement for the OPC. The hydration process is not completely understood, but it is believed that the calcium hydroxide produced during OPC hydration acts as the necessary catalyst for the slag to react and form its own reaction products which fill the void spaces [Neville, 1981]. Once the reaction has started the production of further calcium hydroxide is not required for slag hydration to continue.

1.3.2.2 Pozzolanas

Unlike slags, pozzolanas have no cementitious properties of their own, but react with the calcium hydroxide liberated in the OPC hydration process to form C-S-H gel [Neville, 1981]. Pozzolanas can be either naturally occurring or artificially produced. The most common one is pulverised fuel ash (PFA) which is produced as a waste material at coal fired power stations. As with slags, pozzolanas can be used either in Portland-pozzolana cements or as a partial replacement for OPC incorporated at the mixing stage.

1.3.3 Corrosion Inhibitors

It has also been suggested that various chemicals can be added to the concrete mix so that the pore solution becomes dosed with a corrosion inhibitor. In the early trials most attention was focused on sodium nitrite, potassium chromate and sodium benzoate [Craig & Wood, 1970]. Unfortunately, with the addition of these chemicals, a marked decrease was found in the compressive strength of the mortar test samples. Calcium nitrite has been found not to cause a decrease in compressive strength and is therefore being commercially marketed. Care has to be taken when using inhibitors such as nitrites as they can be potentially dangerous. They can cause serious pitting of steel in solutions containing chloride and/or sulphate ions if their concentration falls below a certain level [Shreir, 1982].

1.3.4 Coated or Corrosion Resistant Reinforcement

When coated or corrosion resistant reinforcement is used no attempt is made to prevent or retard the ingress of chloride ions into the concrete. Instead the reinforcement is modified so that it is stable in the aggressive environment. The coatings used on reinforcement are usually either zinc or epoxy which have both been employed for a number of years.

1.3.4.1 Galvanised Zinc Coatings

In atmospheric conditions the steel is sacrificially protected by the more anodic zinc coating. Fortunately, the rate of anodic dissolution of the coating is restrained by the precipitation of insoluble corrosion products. However, at high pH values the corrosion rate of zinc increases significantly. On research carried out in simulated pore solutions it has been shown that this occurs at pH values greater than 13.35 [Macias & Andrade, 1983]. Chloride ions have also been found to be detrimental to the coating [Sergi *et al.*, 1985]. It seems that all theoretical considerations indicate that zinc coatings will not be of much value in providing long-term protection to steel in concrete, yet this is contradicted by the apparently successful usage in the USA. [Porter, 1976].

1.3.4.2 Epoxy Coated Reinforcement

Epoxy coated reinforcement can provide a good level of protection by forming a layer impermeable to chloride ions. However, if the coating is damaged either prior to or during the construction process, breaks in the film can act as sites for underfilm corrosion [Treadaway *et al.*, 1988]. This problem has been seen most noticeably in the marine environment of the Florida Keys, USA. Although the specific mechanism of deterioration was unclear, Sagues *et al.* [1990] tentatively speculated that the corrosion was due to the formation of large macrocells between uncoated areas of steel in both chloride and non-chloride contaminated areas.

1.3.4.3 Stainless Steels

Stainless steels have been used in the past, but due to the high costs they will probably only be used for special applications. In addition to iron and carbon, they also include a number of other elements, primarily chromium and nickel. The improved corrosion resistance is provided by the formation of a complex protective film of mainly chromium oxide (Cr_2O_3). Austenitic grades are usually used as they are more resistant to pitting than other stainless steel grades. It is currently recommended that Type 316 steel (16-18% Cr, 10-14% Ni and 2-3% Mo) is used in concrete which is liable to become highly contaminated with chloride [Treadaway *et al.*, 1988].

1.3.5 Non-Chloride Deicing Chemicals

As stated previously, one of the major causes of chloride contamination of concrete is the use of chloride-based deicing chemicals (rock salt). Any significant reduction in the quantity of rock salt used on highway structures will reduce the degree of chloride present in the concrete and therefore delay or possibly prevent the onset of corrosion. Both urea and ethylene glycol have been used as deicers on airport runways for a number of years, but for a variety of reasons they have not been used on a wide scale on highway structures. Recently, a number of other compounds have been developed based on the alkali or alkali earth metal salts of either acetic or formic acid. Although a limited amount of research has already been carried out regarding their effects on the durability of reinforced concrete, there still remains a great many aspects that have not been investigated.

1.3.6 Surface Coatings

In order to retard or completely prevent chloride ingress into concrete from external sources it is possible to use a coating on the outer surface. The various coatings used can be categorised as follows into three main types.

1.3.6.1 Impermeable Surface Membranes

These are more commonly known as waterproofing membranes. An example of these are bitumen based paints or preformed sheets. In laboratory tests they have been found to reduce chloride ingress, but these improvements may not be obtained on real structures as the success of their application is dependent on the quality of workmanship and the degree of substrate preparation [American Concrete Institute, 1985]. To ensure adherence to the concrete substrate it must be relatively dry and free from curing membranes, laitance and other contaminants associated with construction practices. Waterproofing membranes are also susceptible to blistering. This is where entrapped gases, solvents and moisture in the concrete form at the interface between the film and the concrete.

1.3.6.2 Surface Penetrants

Surface penetrants are used to block the pores in the surface layer of the concrete. A monomer, such as methyl methacrylate, is impregnated into the concrete, which is then polymerised, filling the pores. This type of system also requires a degree of preparation to the concrete, but as with the surface films it may not be as easy or successful on site as in the laboratory. Water in the surface pores will reduce the degree of impregnation. The water can be displaced by a number of methods such as heating or soaking with impregnant. The effectiveness of the soaking process can be further improved by evacuation prior to impregnation or applying pressure to the system during impregnation [Swamy, 1979].

1.3.6.3 Pore Liners

The walls of the pores can be lined by an hydrophobic film which prevents capillary suction of liquids into the body of the concrete. The majority of the commercially available penetrants are based on silane, siloxane or silicone resins. However, in the U.K., only materials containing a minimum of 95% silane are permitted [Department of Transport, 1990]. They are sprayed on to the surface of the concrete and then penetrate into the concrete. Moisture is required for the silane to react with pore walls, but if too much is present the material will not enter the concrete. Silane also tends to evaporate and therefore to ensure a successful application, the reaction with the pore walls must occur quite rapidly. The rate of reaction increases in alkaline environments and is therefore more successful on new construction where carbonation has not yet occurred than on older structures [McGill & Humpage, 1990].

As all the waterproofing agents are applied to hardened concrete, they can be applied to previously contaminated concrete in an attempt to prevent further chloride ingress and, depending on the specific conditions, to reduce the corrosion rate of the actively corroding steel by reducing the moisture content. However, to maximise the service life of the structure, it would seem sensible to use them on new construction before significant amounts of chloride can accumulate. This, in particular, applies when silane is used since the rate of reaction is aided by the alkaline conditions at the exterior surface of new construction.

To ensure continued benefits it may be necessary to replace the coatings during the service life of the structure. It is thought that silane-based impregnants will last approximately 15 years before re-application is required [Kay,1992].

1.3.7 Cementitious Overlays

On North American bridge decks, surface film waterproofing agents tend not to be used. Cementitious overlays are more popular. They are placed on top of the structural concrete and may be made of either dense, latex modified or microsilica concretes [Broomfield, 1992]. These materials are less porous than the substrate and therefore retard the rate of contamination. Dense concrete is produced by using a low water:cement ratio (≈0.32). The workability is increased by using plasticising and water reducing admixtures. Latex-modified concretes are created by the addition of a polymeric latex emulsion to normal OPC concrete during mixing. As the OPC hydrates the polymer particles flocculate and fill the larger capillary pores. Microsilica is a highly reactive pozzolana which, as with PFA, will form reaction products that decrease the capillary porosity.

Cementitious overlays have been applied on both new and old construction, but as with surface coatings it would seem more sensible to use them before any significant contamination can occur. Problems occurring with these materials seem to be restricted to cracking and debonding. These problems have been seen to be more severe when applied on old construction [American Concrete Institute, 1985].

1.3.8 Patch Repairs

The traditional approach to repairing chloride-contaminated structures is to make patch repairs. This involves removing the concrete surrounding the reinforcement. The bars are cleaned and, if required, extra steel added. The steel is then coated with a primer and the cover material replaced. The new surface can then be coated to prevent further contamination by chloride ions [John, 1992]. However, it has been seen that unless all the significantly contaminated material is removed and not just that surrounding the areas of active corrosion it is likely that corrosion will be initiated in the areas around the repair [Thompson, 1989]. This phenomenon, termed 'incipient anode formation', occurs because the initial anodic zones sacrificially protect the surrounding areas which contain smaller, but still significant amounts of chloride. Once the highly contaminated zones are removed and replaced with fresh non-contaminated material this protection is removed and the surrounding areas become the new anodes.

Delamination can also be encountered between the new and old material, but the use of bonding agents and ensuring the repair material has a low shrinkage should ensure a satisfactory repair [John, 1992]. If the area requiring treatment is extensive or the damage is so great that temporary supports are required the costs involved can be very great.

1.3.9 Cathodic Protection (CP)

The technique of cathodic protection was originally developed in the early 19th. century to prevent the corrosion of copper sheathing of the wooden hulls of British naval ships. Approximately 100 years later the method was adapted to protect underground pipelines. The object of the technique is to lower the potential of the structure so that it becomes so cathodic that the condition of the steel shifts from the domain of corrosion to that of immunity (stable species changes from Fe^{2+} to Fe - Figure 1.1). In order to achieve this it is necessary to apply a current between the structure and an external anode. It can be achieved by one of two means. A direct current from an external power supply can be applied using an auxiliary anode. Alternatively, a sacrificial anode can be used, in which case the anode material is chosen so that it corrodes in its environment with a potential more negative than that of the metal being protected. The electrons released in the corrosion process of the external anode or from the external power source flow via an electrical conductor to the structure and make it cathodic.

Ideally, the potential should be reduced to give a corrosion rate of zero, but in practice it may not be possible. A potential of -0.85V when measured against a saturated copper/copper sulphate electrode (CSE) is usually specified for ferrous structures in either soil or sea-water [Shreir, 1976] to produce a negligible corrosion rate. The application of cathodic protection to reinforced concrete structures does not require such a high degree of potential reduction as in alkaline conditions it is only necessary to prevent pitting by shifting the potential of the steel from the pitting zone into that of perfect passivity (see figure 1.2). It is usually sufficient to suppress the potential of the steel by between 150mV to 300mV [McAnoy, 1992]. Due to the high resistivity of concrete, it is not usually possible to provide enough protection using a sacrificial electrode system. With an impressed current system, the necessary potential shift is usually achieved by applying current densities of up to 20mA/m^2 of concrete surface area [John, 1992].

Variations in the concrete resistivity can also make it difficult to ensure an even distribution of current to all the steel [John, 1992] which would allow adequate and uniform protection, but not over-protection. For satisfactory operation, the anode system has to be carefully designed and checks have to be carried out to ensure that all the steel reinforcement is electrically connected. The installation is required for the whole service-life of the structure so the anode system needs to be robust. At the present time the two most popular anode systems are a conductive paint overlay or a noble metal oxide coated titanium mesh covered in a cementitious overlay.

This method is primarily intended as a repair technique, but some work is being carried out on new construction as it is claimed that it is easier to prevent corrosion from occurring than to stop it once it has started [Pedeferri, 1992].

1.3.10 Electrochemical Chloride Removal

The technique of electrochemical chloride removal or, as it is sometimes known, desalination is similar to CP in that the reinforcement is cathodically polarised by an anode system attached to the surface of the concrete. Far larger currents are applied than with CP which forces the aggressive chloride ions away from the steel by electromigration [Slater *et al.*, 1976]. Current densities used for desalination are usually in the range 0.5 to 1A/m^2 of concrete surface area. The advantage over CP is that the process is temporary taking only a matter of months to complete after which the anode system and power source can be removed.

1.4 Plan of Presentation

It can now be seen that the problem of chloride-induced corrosion of steel reinforcement is of major practical concern and that a number of methods have been developed either to delay or completely prevent its occurrence. However, some of these methods are quite new and are not fully understood. This prevents the optimum strategy being chosen in the design or repair phase of a structure's lifetime to ensure the maximum possible usage before replacement is necessary.

The complete elimination of chloride ions from the surrounding environment has obvious advantages in that the cause of the problem is removed at source. Therefore, the use of non-chloride deicing chemicals could potentially have great benefits in prolonging the lifetime of certain highway structures. However, rock salt was used as a deicing chemical for a great number of years before any consideration was given to its harmful side effects. It is therefore imperative that all new deicing chemicals are thoroughly investigated prior to their widespread usage so that no deleterious mechanisms come to light after they have been in use for a number of years.

The process of electrochemical chloride removal is also potentially very important as a means of increasing the service lifetime of structures already contaminated with chloride ions. It has advantages in that, unlike cathodic protection, the treatment time is relatively short, but unlike patch repairs, it attempts to remove large percentages of the chloride ions from all over the structure and not just from the actively corroding zones. There are a number of questions regarding both the amount of chloride it is possible to remove and also the potential side-effects of applying a relatively large current to structures. These will require answers before the process can be used safely and to its maximum effect.

Both these topics (viz. chloride-free deicing agents and electrochemical chloride removal) will be investigated in the following chapters. They will be presented in two separate sections, each made up of three chapters; a review of the relevant literature, a description of the experimental methods used and then a discussion on the results. Part 1 of the thesis, incorporating chapters 2, 3 and 4 deals with the subject of non-chloride-based deicing chemicals. Part 2 (chapters 5, 6 and 7) deals with the technique of electrochemical chloride removal.

PART 1

NON-CHLORIDE BASED DEICING CHEMICALS

CHAPTER 2 - LITERATURE REVIEW: NON-CHLORIDE DEICING CHEMICALS

Since the 1950s it has been common practice to apply rock salt to trafficked surfaces to keep road networks free from ice and snow during the winter months. Rock salt is a naturally occurring impure form of sodium chloride (NaCl) and is usually added in small proportions to sand or other abrasives prior to application.

In addition to the corrosive effects of sodium chloride on many metals, and on steel in particular, a number of other potential problems have come to light. It is known to have a detrimental effect on ground water, surface water, soil structure, vegetation and animal/human health [Hamilton *et al.*, 1989].

Primarily due to the corrosive aspects there has been increased interest in finding alternative deicing chemicals. Urea ($NH_2.CO.NH_2$) and ethylene glycol ($OH.CH_2.CH_2.OH$), either individually or as a mixture, have been used on airport runways for a number of years. Urea has also been used on highway structures. For a variety of reasons that will be explained later neither urea or ethylene glycol have been used on a wide scale. Both solid calcium chloride ($CaCl_2$) and 'pre-wetted' salt[2.1] have also been used. They are more effective than sodium chloride alone and therefore less is required, but are still corrosive.

In the 1970s the American Federal Highway Administration (FHWA) started to look for an effective, but non-corrosive deicer. Their initial literature review concluded that calcium magnesium acetate (CMA) was the most promising of the compounds tested [Dunn & Schrenk, 1980]. It is formed by reacting acetic

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[2.1] Pre-wetted salt is a mixture of solid sodium chloride to which either water, an aqueous solution of calcium chloride or an aqueous solution of sodium chloride have been added acid with dolomitic limestone. The nominal molar ratio of calcium to magnesium in the commercial formulation is 3:7, but in practice it can vary between 3:7 and 4:6. It is supplied in the form of small off-white free flowing pellets. An attempt to improve on the deicing chemicals used at airports (urea and/or ethylene glycol) has led to the commercial development of a liquid acetate based deicer. It is primarily a 50% by weight alkaline solution of potassium acetate ($CH_3.COO.K$) to which corrosion inhibitors have been added [Man *et al.*, 1990; Gustafson, 1993].

Formate salts have also been suggested as potential deicers. They were first mentioned in 1965 [Boies & Bortz], but for some unknown reason were not included in the FHWA research programme. Of the formates, the sodium salt (HCOO.Na) has been commercially promoted, but with very limited success [2.2]. It is supplied in the form of hard, irregularly shaped particles similar in appearance and density to rock salt. If it is intended for use as an airport deicer a proprietary corrosion inhibitor is also added [Celanese Canada Inc., 1992].

Although the primary concern of this part of the thesis is the compatibility of acetate and formate salt deicing chemicals with reinforced concrete, there are, of course, a large number of other points that require clarification before a potential deicer can be put into general use. These will also be briefly discussed in the literature review. Data regarding the other deicing agents will be included where available.

[2.2] Since the beginning of the project the Hoechst Celanese Corporation, the company responsible for commercially producing and marketing sodium formate as a deicer, have ceased its product development. The reason for the cancellation of the project was said to be entirely a business decision and did not reflect any technical problems with the use of sodium formate as a deicer [Slinkard, 1993].

2.1 Deicing Performance

2.1.1 Chemical Properties and Deicing Mechanisms

Figure 2.1 shows a phase diagram representative of that for water [Glasstone & Lewis, 1963]. Line OA shows the variation in vapour pressure of pure water with temperature. Line OB shows the variation in vapour pressure of ice with temperature (ie. the temperature at which sublimation of ice to water vapour occurs at a given pressure or vice versa). Where the two curves meet (point O) all three phases are able to co-exist. This point is known as the triple point. Since both the solid and liquid phases are in equilibrium at the triple point it can also be characterised as a melting point and line OC denotes the change in melting point between ice and water with change in pressure.

Aston University

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Figure 2.1 - The Effect of the Addition of a Soluble Non-Volatile Chemical on the Freezing Point of Water [Glasstone & Lewis, 1963]

The addition of a small quantity of a soluble non-volatile chemical to the water reduces the water's vapour pressure (line O'A') and therefore shifts the position of the triple point. It can be seen that the melting point curve also has to shift its position (line O'C') and therefore at a given pressure, the melting point, or perhaps better described in this context, the freezing point of water is reduced. This is the mechanism by which deicing chemicals work.

For dilute solutions, the degree by which the vapour pressure is lowered is given by Raoult's law. This states that the lowering of the vapour pressure is proportional to the mole fraction of the solute in the solution. From this it can be concluded that for a given concentration of solution (in moles/litre) the degree by which the freezing point of water is suppressed is independent of the actual chemical added. Therefore an efficient deicing chemical is one with a high solubility (in moles/litre) at low temperatures.

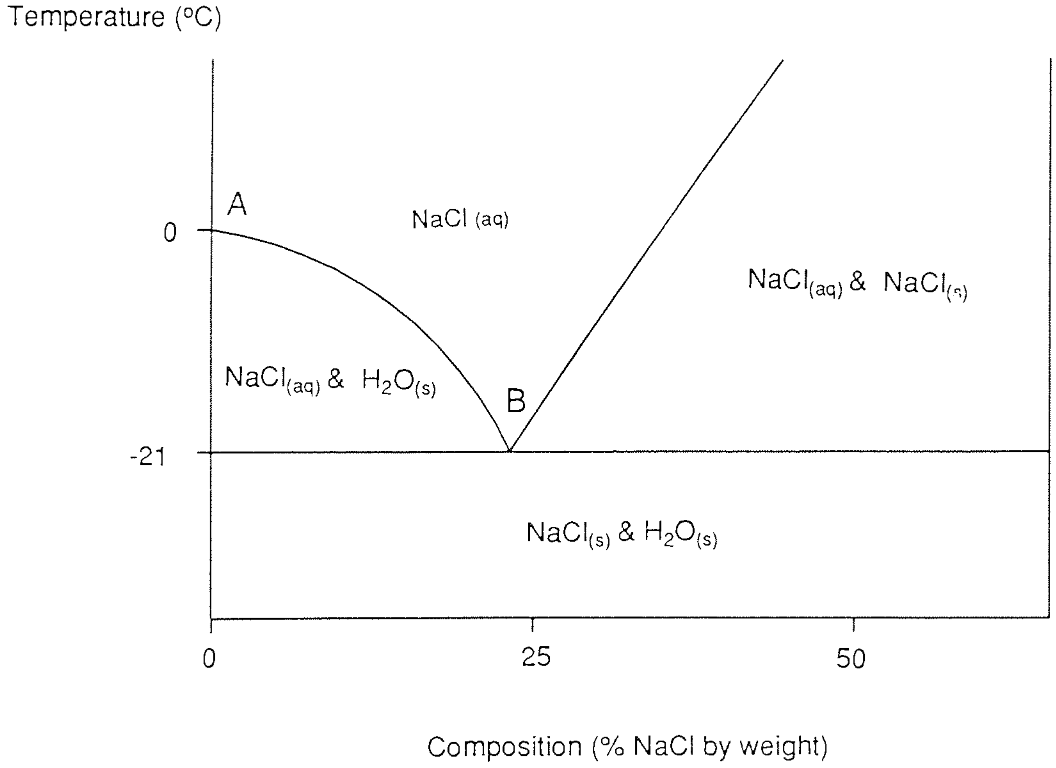

Figure 2.2 - Freezing Point Diagram for Sodium Chloride and Water

Further additions of the deicing chemical will further lower the freezing point until the limit of the solubility of the chemical in water at that particular temperature is reached. This can be seen on a freezing point diagram (Figure 2.2). Line AB shows the amount by which the freezing point of water is depressed by the addition of sodium chloride. The depression continues until point B where no more sodium chloride will dissolve. This point is known as the eutectic. The addition of any more sodium chloride would be wasteful as it will not dissolve or lower the freezing point of water any further.

The mechanism of snow and ice removal for a solid deicer is considered to be as follows. As the deicer is spread over the road surface, each individual particle dissolves in moisture to form a small pond of solution. Under gravity, the solution and the remaining particle melt a narrow hole through to the pavement surface. At the pavement surface the solution spreads along the interface and undercuts the main body of the ice. It can then be broken up and removed by the combined action of traffic and snow ploughs [Trost *et al.*, 1987].

Liquid deicers work similarly, but as there is no solid deicing particle to help maintain the concentration of the solution and the solution is sprayed more uniformly over the whole treated area, they tend to act more on the main body of the ice and less by the mechanism of undercutting.

Therefore in practice the actual deicing ability is not only dependent on the chemical's solubility at low temperatures. In the case of solid deicers, it can be seen that the ease with which they absorb moisture to form a solution will affect the melting rate. The heat of dilution and, in the case of solid deicers, the heat of solution will also affect the rate of melting. If they are exothermic, heat is given out as they dissolve or are diluted and therefore the melting process will be carried out more rapidly than those which are endothermic where energy has to be absorbed from the external environment.

Calcium chloride has the highest theoretical deicing ability of the commonly used deicers. If added in sufficient quantities it is capable of preventing ice formation at temperatures down to -55°C where a eutectic is formed. The speed of ice melting is relatively rapid as it absorbs moisture readily and its heat of solution is exothermic.

Sodium chloride is less effective as it forms a eutectic at -21°C. Sodium formate and urea can prevent the formation of ice at temperatures down to -18°C and -11°C respectively. An exact figure for the maximum level of freezing point depression for ethylene glycol could not be found in any literature, but it is believed to be below -50°C [Boies & Bortz, 1965]. The potassium acetate based deicer is claimed to have a freezing point of -50°C [BP Chemicals Ltd., 1989] and the eutectics of the primary constituents of CMA, calcium acetate and magnesium acetate are -15°C and -30°C respectively [Boren, 1986]. The addition of a calcium and magnesium acetate mixture can lower the freezing point of water to between -10°C and -28°C depending on the calcium to magnesium ratio; the optimum is obtained with a molar ratio of between 3:7 and 2:8 [Öberg *et al.*, 1991].

The results of basic ice penetration and melting laboratory tests carried out by McElroy *et al.* [1988a] for sodium chloride, calcium chloride and urea seem to agree with the expected theoretical results. It was seen that calcium chloride was quicker acting than sodium chloride, but at temperatures above -10°C there was no significant difference in the final amount of ice removed. Calcium chloride was also found to be more effective than sodium chloride at very low temperatures (below -15°C). At temperatures below approximately -10°C urea was found to be almost completely ineffective and at higher temperatures it was still found to be far less efficient than sodium chloride. CMA was also included in the tests, but despite its theoretical deicing potential, it was found to be ineffective at temperatures below -5°C, and at higher temperatures it was less effective than sodium chloride [McElroy *et al.*, 1988b]. Unfortunately potassium acetate and sodium formate based deicers were not included in the tests.

2.1.2 Physical Parameters

The properties and laboratory tests mentioned above only give an indication of the potential effectiveness of a deicing chemical. In order to assess the deicer fully it is necessary to consider other aspects.

The particle shape and size distribution of solid deicers affects the deicing efficiency. Solid deicing chemicals presently used vary in shape from irregular flakes (flake calcium chloride), irregular shaped grains and platelets (rock salt) to regular shaped pellets (pellet calcium chloride, urea and CMA). A large percentage of fines amongst the particles increases the amount that can be blown off the carriageway before they can act on the snow and ice. Too great a percentage of large particles may cause small areas to be overtreated at the expense of the remainder.

In the case of CMA it has been seen that the finer particles tend to float as opposed to sinking to the pavement surface. The larger particles have also been seen not to dissolve fully on the pavement surface [McElroy *et al.*, 1988b]. Both these factors were claimed to be partially responsible for reducing its ability to undercut the main body of the ice from the pavement.

To some degree all deicers are sensitive to moisture. High moisture contents can cause the solid particles to agglomerate. When this occurs it reduces the degree of uniformity and therefore the effectiveness of the deicing treatment. Rock salt absorbs up to about 0.1% of moisture from the environment at relative humidities of less than 70%. Due to their hygroscopic nature and their higher costs, calcium chloride, sodium formate and urea have to be stored in sealed containers. Potassium acetate is particularly hygroscopic and it is therefore necessary to store it as a liquid.

2.1.3 Site Trials

Rock salt has been banned from use on a number of important structures in the UK [Hatchwell, 1989]. Urea has been used to replace rock salt on the elevated sections of the Midlands Link motorways [Keron, 1992]. It was found to be capable of keeping the road surfaces free from snow and ice, but the task had been harder than when rock salt had been used. It was thought that if the conditions had been more severe, the authorities would have had to revert to using rock salt. In practical circumstances, urea is thought only to be capable of working effectively at temperatures above -3°C compared to -12°C for rock salt [Wyatt and Fritzsche, 1989].

A trial was carried out in Ottawa, Canada [Sypher:Mueller Int., 1988] to compare rock salt, CMA and sodium formate. The conclusions made were that, under those particular conditions, CMA was capable of clearing pavement surfaces of snow and ice, but it was somewhat slower to react and it required an application rate of 1.6 times that of rock salt. Sodium formate was found to act similarly to rock salt in terms of speed of action and application rate. A minor field test carried out in Sweden also found sodium formate to be comparable to sodium chloride [Gustafson, 1993].

In other trials, CMA has been found to be more effective. In contradiction to the results of McElroy *et al.* [1988b], it was found to be capable of working at temperatures as low as -13°C [Noyce, 1989]. The application rates relative to rock salt varied from storm to storm. In some cases more and in others less CMA was required. Also, in contradiction to the conclusions of McElroy *et al.* [1988b], site trials have shown that CMA acted less on the main body and more on undercutting the snow and ice from the pavement surface.

The potassium acetate based deicing chemical has been used at airports owned by the British Airports Authority (BAA) and also some in Sweden [Hatchwell, 1989; Gustafson, 1993]. It has also been used at the Dartford crossing of the river Thames in London (Queen Elizabeth bridge and the tunnel approaches) [King, 1992]. In tests carried out for BP Chemicals by the Transport Research Laboratory (TRL), formerly the Transport and Road Research Laboratory (TRRL), using the SCRIM device[2.3] it was found to be more effective than urea and/or glycol at returning the skid resistance of the road surface to its original value [BP Chemicals Ltd., 1989]. Tests in Sweden found it had a more rapid and better melting effect than urea or ethylene glycol, but doubts were cast as to its long term effectiveness [Gustafson, 1993]. It was thought that its hygroscopic nature could prevent the pavement from drying out and cause the deicer solution to be diluted perhaps allowing the reformation of ice.

[2.3] The SCRIM device (Sideway Force Coefficient Routine Investigation Machine) is a method by which the skid resistance of wet roads can be continually assessed. A test wheel is mounted on a lorry of set weight at an angle of 20°C to the direction of travel. This generates a sideways force which is measured. The ratio of this force to the vertical force supplied by the weight of the lorry gives a measure of the skidding resistance.

2.2 Effect on the Environment and Aspects of Health and Safety

Sodium chloride can have a number of adverse effects on the environment. It can damage the structure of the soil and kill the roadside vegetation [Hanes *et al.*, 1976; Dunn & Schenk, 1980 both cited by Hamilton *et al.*, 1989]. It has been found, in general, to have only minor harmful effects to animal and aquatic life at the levels caused by deicing operations. However, it can pass into the water supply system and high sodium concentrations have been linked to hypertension in humans. Animals exposed to very high concentrations can also experience moderate skin and eye irritation [Hiatt *et al.*, 1988].

At room temperature aqueous solutions of urea decompose readily to form ammonia and carbonic acid [Sadegzadeh & Page, 1986]. Ammonia is highly toxic and further reactions also occur which have a high oxygen demand affecting both animal and plant life [Hamilton *et al.*, 1989]. Therefore urea can have a significant deleterious effect on the environment.

Sodium formate solutions are thought to have a similar effect to sodium chloride on soil structure, roadside vegetation and on both aquatic and animal life [Hamilton *et al.*, 1989].

Damage to the soil associated with the application of sodium chloride based deicing chemicals is thought to be caused by the displacement of calcium and magnesium ions in the soil by monovalent sodium ions [Dunn & Schenk, 1980 as cited by Sypher:Mueller, 1988]. It is thought that the application of CMA may be able to reverse the damage caused by previous applications of sodium chloride [Hamilton *et al.*, 1989]. It has been seen to be harmless to both aquatic and animal life [Winters *et al.*, 1985]. However, when it degrades it consumes dissolved oxygen [Sypher:Mueller, 1988].

Very little published information is available about the potassium acetate based deicer, but promotional literature claims it does not affect aquatic life and has a lower oxygen consumption than urea [BP Chemicals Ltd., 1989].

Both urea and ethylene glycol reduce the skid resistance of the ice free pavement surfaces. Ethylene glycol is also highly flammable and therefore, under some circumstances, can constitute a safety risk. Although one of the most effective deicers available, calcium chloride is hardly ever used on its own (ie. without rock salt or sand) as at low temperatures it can cause the formation of 'black ice'[2.4] [Wyatt & Fritzsche, 1989].

2.3 Compatibility with Structural and Automotive Related Materials

A part of the FHWA research programme was to investigate the effect of CMA on a number of highway related materials, comparing the results to the effect of sodium chloride. The materials tested included asphalt, plastics, rubbers, paints, sealants and various plain and coated metals. The testing regimes used were as set down by various ASTM standards (American Society of Testing and Materials). The general conclusions were that in the vast majority of cases CMA either caused the same or less damage than sodium chloride [Slick, 1987].

[2.4] 'Black ice' is the name given to a thin hard transparent layer of ice. It is particularly dangerous as is difficult to spot and therefore vehicle drivers are unlikely to be able to avoid it.

Provided there is a certain level of dissolved oxygen in the solution acetate salts are known to be non-oxidising anodic inhibitors for mild steel and should therefore not cause corrosion. Anodic inhibitors prevent corrosion by either forming or maintaining a passive film. Acetate salts are able to repair breakdowns in the passive film over a certain range of pH and dissolved oxygen concentrations in the electrolyte by the formation of insoluble basic ferric salts [Mayne & Page, 1974].

In agreement with the above information, in certain cases, the corrosion rate of steel in solutions of CMA have generally been seen to be only a fraction of that seen in chloride-containing solutions [McCrum *et al.*, 1985; Machowski & Lyle, 1988; McKenzie & Morgan, 1988]. However, when Locke and Kennelley [1986] immersed samples in static solutions of CMA the air-formed passive film became unstable causing large negative potential shifts and significant corrosion rates. Later work suggested, however, that the potential shift was due to the precipitation of magnesium hydroxide (and possibly calcium carbonate) on the cathodic areas of the steel acting as a cathodic inhibitor [Kennelley & Locke 1990].

Therefore it appears that although initially steel immersed in static solutions of CMA are passive, the production of hydroxide ions at the cathode ($O_2 + 2H_2O + 4e^- \longrightarrow 4OH^-$) locally increases the pH and forms insoluble magnesium hydroxide on the cathodic sites. Kennelley [1986] has shown that in solutions of CMA steel has an active/passive transition. Subsequently, therefore, the production of magnesium hydroxide suppresses the potential of the steel into the actively corroding zone (Figure 2.3). Kennelley [1986] also found that it was possible to re-initiate passivity by bubbling oxygen through the test solution. Therefore it can be surmised that any stirring or agitation of the solution returns the pH of the solution around the cathodic areas to that in the bulk of the solution which removes the hydroxide layer and restores passive conditions and potentials. Inspection of the experimental procedures used by McCrum *et al.* [1985], Machowski and Lyle [1988] and McKenzie and Morgan [1988] shows that they all involved some agitation of the solution (either aeration, addition of deionised water to counter the effects of evaporation or cyclic immersion) and presumably this was responsible for no significant corrosion being seen on their samples.

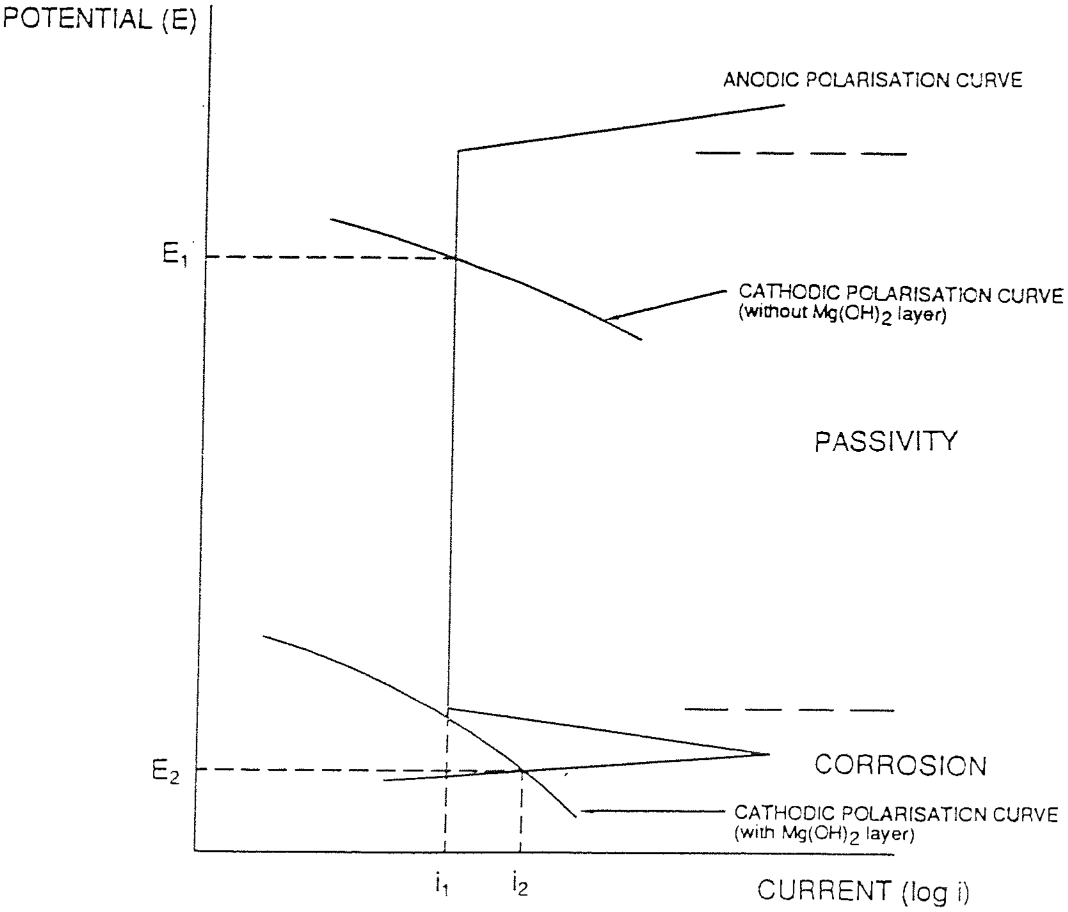

Figure 2.3 - Anodic and Hypothetical Cathodic Polarisation Curves for Steel in a Solution of CMA

The condition of steel in CMA solutions therefore partially depends on the amount of movement of the solution, but it was thought by Locke and Kennelley [1986] that, under the conditions which metals would be exposed to CMA in a deicing context, structural steel would be actively corroding albeit at a rate between two and four times smaller than would be seen for steel in a sodium chloride solution.

The potassium acetate based deicer has not been tested on such a wide scale, but in addition to passing various ASTM standards it has passed the relevant approval procedures for use at airports indicating that it is significantly less corrosive than sodium chloride [Noyce, 1989].

Less work has been carried out investigating the corrosive or inhibitive effects of formate salts. For mild steel, formate ions are generally considered to be corrosive [Hancock & Mayne, 1959]. This was also seen by Brasher [1969] in aerated solutions of sodium formate up to 5 molar in concentration. However, at concentrations above this the percentage of the steel sample which was corroding decreased with increasing concentration. More recent testing has shown that sodium formate is capable of passing the ASTM standards regarding corrosion. With the addition of a proprietary inhibitor package it has also received approval for use as a runway deicer in both the USA. and Canada [Celanese Canada Inc., 1992; Slinkard, 1993]. Whereas this does not say that solutions of sodium formate are non-corrosive, it does imply that under practical conditions they will not be sufficiently corrosive to reduce the service life of the object concerned to any great extent.

2.4 Compatibility with Reinforced Concrete

There are three main areas to be taken into account when evaluating a new deicing chemical's compatibility with reinforced concrete.

2.4.1 Freeze/Thaw Damage

It has long been established that, under the action of cycles of alternate freezing and thawing, concrete degrades. When deicing chemicals are present the damage is almost always seen to be exacerbated. Verbeck and Klieger [1957] found that the most severe damage occurred at relatively low concentrations of deicer (3-4% by weight). From this it was concluded that the mechanism responsible for the exacerbation of freeze/thaw damage by the presence of deicing chemicals was primarily of a physical nature.

2.4.1.1 Laboratory and Site Experience

Under site conditions it can take a number of years to assess how a particular deicer will affect the degree of freeze/thaw damage. It is therefore necessary, as with most durability problems, to use accelerated testing regimes when evaluating new products. However, there are a number of different regimes that have been used by researchers. This prevents direct comparisons being made between the various reports.

Parmenter [1989] used the RILEM recommendations (International Union of Testing and Research Laboratories for Material and Structures) for the test regime[2.5] and the concrete mix was made to the specifications set down by

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[2.5] The Rilem recommendations involve ponding the 'floated' surface of a concrete sample with a small volume of test solution and then carrying out freeze/thaw cycles of 16-17 hours at -20°C & 7-8 hours at room temperature.

the body responsible for the maintenance of the majority of U.K. civilian airport runways (BAA). Water as a control and 3% solutions of sodium chloride, urea, glycol, CMA and the potassium acetate based deicer were assessed. A number of methods, including weight loss, visual assessment and area and depth of surface scaling were used to quantify the extent of the damage. After 50 freeze/thaw cycles the results showed that sodium chloride caused the most damage, closely followed by urea. Glycol and the potassium acetate based deicer caused less damage. CMA was found to cause no more damage than was found on the control specimens. In the conclusion, however, it was stated that even the most severe damage was still considered to be at an acceptable level.

Numerous other reports have been published that also indicate that CMA causes only very little, if any, freeze/thaw damage in excess of that seen with no deicing chemical and far less than sodium chloride [Slick, 1987; Pianca *et al.*,1987].

Work carried out by Nadezhdin *et al.* [1988] showed that sodium formate caused less scaling than urea, but more than CMA. Litvan [1989] found that, using a number of mortar mixes, sodium formate did not cause any more damage than sodium chloride.

2.4.1.2 Proposed Mechanisms

As with ordinary freeze/thaw damage (ie. in the absence of a deicing chemical), the mechanism by which damage of concrete is exacerbated by deicing salts is, at present, unclear but a number of possibilities have been suggested.

One of the suggested mechanisms for normal freeze/thaw damage is that osmotic pressures are developed within the concrete [Powers, T.C., 1975 & 1976]. When freezing occurs, ice formation first occurs in the largest water-filled pores and the concentration of the remaining pore solution is increased. Therefore it is possible that a situation will exist where two interconnecting pores of different sizes will contain pore solution of differing concentration. In order to counteract the concentration gradient the water would tend to diffuse out of the smaller pore into the larger one and the ions would tend to diffuse from the larger pore into the smaller one. It was suggested that, if the zone in which the two pores were connected was able to act as a semi-permeable membrane retarding the diffusion of the ions, osmotic pressure would be developed which could damage the pore structure. Therefore if deicing chemicals were present in the pore solution it is possible that the osmotic pressure would be increased.

It has also been thought that the ingress of deicing chemicals into the pore solution can raise the degree of saturation. As stated earlier, aqueous solutions have a lower vapour pressure than pure water and usually have a greater surface tension. Lumley [1987] states that both these factors cause the liquid to be more securely retained in the pore structure and thus have a higher degree of saturation. Therefore as the concrete is cooled there is potentially more water available to form ice and therefore cause more scaling damage.

Another mechanism has been suggested where the deicing chemicals induce the formation of a number of discrete ice layers in the concrete which sandwich layers of pore solution [Snyder, 1965 as cited by Lumley, 1987]. If it is assumed that a concrete member saturated with water is ponded with a deicing chemical, then the deicer begins to diffuse into the concrete. If the surface of the concrete is then cooled sufficiently for ice to form, the deicer solution just within the surface of the concrete is concentrated with a subsequent lowering of its freezing point. However, further into the concrete the pore solution is less concentrated with a higher freezing point and as the concrete cools it is possible that ice may form in a layer some distance from the exposed surface sandwiching the layer of concentrated pore solution. With further cooling the ice layers can expand compressing the layer of solution thus damaging the concrete.

Another theory suggests that the damage caused by chloride-based deicing chemicals is due to the formation of Friedel's salt within the matrix. The damage would occur in a manner somewhat analogous to secondary ettringite formation. As enhanced damage is seen with non-chloride based deicers, even if it does occur, it is not thought to be the main mechanism [Lumley, 1987]. It could only be a major factor in the enhancement of freeze/thaw damage if the other deicing chemicals also form similar C_3A based reaction products.

It has also been claimed that damage is caused by the crystallisation of the deicing chemical in the pores. However, as damage has been seen to be greatest with moderately small concentrations and has been seen at temperatures well above the eutectic, this theory does not seem to be accurate. This also seems to make the theory of damage caused by the production of C_3A based reaction products less likely.

The problem of freeze/thaw damage, although significant, is not as serious as reinforcement corrosion and its onset can be delayed by a number of methods. One is to keep the material below the critical degree of saturation and this can be obtained by sealing the surface. The capillary porosity can be limited by using a suitably low w:c ratio and frost resistant aggregate in the mix [Neville, 1981]. The final method is to use an air-entraining agent (AEA). This involves the addition of an anionic surfactant to the fresh mix. It stabilises fine air voids (20µm to 1mm dia.) within the matrix and these provide free surfaces for water to expand into as it flows away from the sites of freezing [Page, 1981].

2.4.2 The Corrosion of Steel Reinforcement

There is a wealth of literature on the effects of chloride ions on steel in a cementitious environment and the mechanism was discussed in chapter 1. Urea is not considered to produce significant amounts of corrosion of steel in a cementitious environment [Sadegzadeh *et al.*, 1993; Ushirode *et al.*, 1992].

Acetate salts are normally only used as inhibitors in near neutral solutions. For air-saturated acetate solutions of 0.05M, inhibition occurs at pH 8 and above [Mayne & Page, 1974]. At higher values of pH (pH 12 and above) the uptake of acetate ions into the passive film becomes negligible and although no corrosion occurs they again cease to be effective as inhibitors. Instead the breakdowns in the passive film are repaired by the usual mechanism of Fe_2O_3 formation [Mayne & Page, 1974]. Therefore, from the theoretical point of view, the inhibitive effect of acetate ions on mild steel in new concrete construction will be negligible, but on the other hand is not required. Experimentally this has been seen in work by Ushirode *et al.* [1992].

However, the results of longer term testing programmes have shown contradictory results as to the effect of CMA on steel in concrete. Chollar and Virmani [1988] ponded externally stored reinforced concrete slabs with 3% and 5% solutions of CMA twice weekly during the winter season for a total of four years. It was reported that at no time during the test period was corrosion seen to occur. In addition Callahan [1989], using an accelerated laboratory ponding regime on steel embedded in concrete, found that CMA did not initiate corrosion. Potential measurements and visual inspections at the end of the tests were used to assess the degree of corrosion. However, Boren [1986] found that in simulated pore solutions, mortars and concrete blocks, it was possible, if sufficient CMA was present, to cause large negative potential shifts which were thought to indicate active corrosion. The fact that no visual inspection was made of the samples embedded in concrete/mortar at the end of the tests has led doubt to be cast on the results in some quarters [Chollar & Virmani, 1988]. However, in some samples corrosion rates were measured using the technique of linear polarisation. The results indicated corrosion was occurring. The large potential changes were attributed to the reduction of the pH by the removal of hydroxide ions from the pore solution in the form of precipitated calcium and magnesium hydroxide.

The potential shifts seen in the work on simulated pore solutions can be explained by the precipitation of magnesium and calcium hydroxide. From measurements taken by Boren as to the pH value of the simulated pore solutions it is clear that low additions of CMA were unable to cause reaction with all the hydroxide present. Therefore the samples were essentially immersed in a highly alkaline environment containing no soluble calcium or magnesium ions. At high CMA additions there were not sufficient amounts of hydroxide ions to remove all the soluble calcium and magnesium ions from solution and therefore, in a similar way to that seen by Kennelley [1986] (see section 2.3.1), the further production of hydroxide ions at the cathodic sites on the steel allowed an insoluble layer to form which then suppressed the potential into the active zone.

However, the ponding of cementitious samples containing embedded steel with CMA would result in the precipitation of calcium and magnesium hydroxide on the surface of the slabs and not on the surface of the steel. It is therefore not clear how it was possible to obtain the large potential shifts in these cases.

Very little published work has been carried out to evaluate the effects of the potassium acetate based deicer on steel in a cementitious environment, but Man *et al.* [1990] found that it showed no evidence of corrosion initiation. Care should be taken when relying entirely on the results of Man *et al.* as the experimental method used adapted Cormon Environmental Corrosion Monitors[2.6] (ECMs) to assess the corrosion. The adapted ECMs cannot be considered to give a realistic simulation of steel embedded in concrete.

Initial tests found that sodium formate is non corrosive to mild steel embedded in concrete [Sypher:Mueller, 1988]. However, the report from which the results were quoted was an internal document prepared by the Hoescht Celanese Chemical Company which is not freely available. However, the general conclusions were confirmed by another report, carried out for Hoescht Celanese and Perstorp Polyols [Davis, 1990]. Reinforced concrete blocks were prepared and then ponded with water or a 10% solution of either sodium chloride or sodium formate for 24 weeks. Both potential measurements during the test period and visual examinations at the end of the test period showed that no corrosion was evident in the samples exposed to either water or sodium formate. Corrosion was seen in the specimens exposed to sodium chloride.

[2.6] An adapted Cormon Environmental Corrosion Monitor consists of 50 mild steel washers sandwiched between 1mm thin discs of OPC mortar all loosely mounted on a central PTFE coated support rod. If corrosion occurs in the particular environment the stack arrangement expands due to the formation of corrosion products which is then measured by a linear displacement transducer.

The effect of a combination of acetate/formate and chloride ions on the condition of steel embedded in concrete is also very important as the majority of the structures that could potentially be treated with the new deicers would already contain chloride ions from previous deicing treatments with rock salt. It has also been suggested that due to the high costs of CMA it may be possible to mix it together with sodium chloride to produce a non corrosive and less expensive mixture [McCrum, 1989].

Sagoe-Crentsil *et al.* [1993] have suggested that the carboxyl group (COO^-) present in both deicers are corrosion inhibitors in chloride contaminated concrete. It was thought that they competed with the chloride ions in the production of Fe^{2+} based complexes. The carboxylate complex was claimed to be electrochemically neutral and thus remained around the anode, breaking the cycle of corrosion. However, their theory regarding anodic inhibition by non-oxidising ions does not agree with that generally recognised of plugging the breakdowns in the passive film with insoluble basic ferric salts [Mayne & Page, 1974]. Sagoe-Crentsil *et al.* [1993] claimed that all the ions tested were, to varying degrees, able to inhibit chloride-induced corrosion. However, inspection of the data indicates that only the addition of malonate ions could be classed as being able to reduce corrosion levels to anywhere near acceptable levels.

Man *et al.* [1990], using the adapted ECM method, found that both CMA and the potassium acetate based deicer were capable of significantly retarding pre-initiated chloride induced corrosion. CMA was also seen to have a similar effect in tests carried out by the Danish Corrosion Centre [Noyce, 1990], but as no report was available, the results cannot be evaluated.

In contradiction to the aforementioned studies, other work has shown that acetate ions are not capable of reducing the corrosion rate of steel in chloride contaminated steel [Ushirode *et al.*, 1992; Locke and Boren, 1986]. Locke and Boren claimed that CMA has the potential to enhance the corrosion rate by reducing the alkalinity of the pore solution and thus increasing the chloride to hydroxide ratio.

2.4.3 Interaction with and/or Degradation of the Cementitious Matrix

The majority of work studying degradation of the cementitious matrix in relation to deicing chemicals has looked at freeze/thaw damage which can obscure other physical and chemical processes. In freeze/thaw experiments Verbeck & Klieger [1957] and Gustafson [1993] found that in addition to the damage seen at low concentrations (≈4%), certain chemicals (calcium chloride & magnesium chloride) were also capable of causing even more damage when present in higher amounts. From this it is possible to infer that the damage seen at higher concentrations may be due to either the crystallisation of the deicer in the matrix or some form of chemical reaction.

Figure 2.4 - Relationship between Concrete Scaling and Deicer Concentration [Gustafson, 1993 after Verbeck & Klieger, 1957]

It is well known that chloride ions can become bound up in the cementitious matrix. In chapter 1, the binding mechanism was attributed to a reaction with the C_3A phase. Although this is by far the most predominant and widely accepted mechanism, a number of others have also been proposed. The ferrite phase, C_4AF, is also able to take part in a similar set of reactions leading to the formation of calcium chloroaluminate and chloroferrite [Roberts, 1962]. However, the practical significance is reportedly small [Mehta, 1977]. It is also claimed that chloride ions are chemically adsorbed into the C-S-H gel [Ramachandran, 1971 & 1976], but this is disputed by others [Lambert *et al.*, 1985].

Urea decomposes to form carbonic acid and ammonia. Carbonic acid can react with the alkaline pore solution (ie. carbonation) to remove the protective environment surrounding the reinforcement. Under the harsh experimental conditions used by a number of investigators the degree of carbonation of concrete blocks was seen to increase if exposed to solutions of urea [Blunk & Brodersen, 1980 cited by Sadegzadeh & Page, 1986]. Sadegzadeh *et al.* [1993] have shown that the bulk mechanical properties of concrete are not significantly affected by urea. It was seen, however, that a concentrated crystal growth on the sides of specimens was capable of destroying the integrity of concrete.

Work on the effect of CMA on concrete has also been carried out in Sweden for the State Road and Traffic Institute (VTI). In agreement with other freeze/thaw damage investigations it was shown that CMA caused very little damage at the low concentrations usually associated with scaling damage, but the amount of damage was seen to increase as the deicer concentration increased [Öberg *et al.*, 1991].

Work carried out for VTI by Lund Institute of Technology found that CMA 'dissolved' cement paste. It was attributed to the magnesium content of the deicer which was thought to act in a similar way to magnesium chloride [Peterson, 1991] where decalcification of the C-S-H gel occurs to form a non-binding hydrated magnesium silicate hydrate. The project was originally carried out with CMA which had a high free acetic acid content and therefore the results may not have been totally reliable. The tests were then repeated with the commercial product, but to date the results have not been published.

Research undertaken in the USA and Denmark also apparently found deterioration in cement pastes after being exposed to CMA solutions, but it was not possible to obtain a copy of either report to evaluate the results [Noyce, 1990].

The effect of sodium formate was investigated by Stratfull *et al.* [1974]. Concrete cylinders were either continuously partially immersed or subjected to cycles of alternate complete immersion in solution and then oven drying at 60°C. After only three cycles, the samples exposed to the latter regime were seriously degraded. Samples were also immersed in sodium chloride to give a comparison and 80 cycles were required to exhibit similar levels of damage. No damage was seen on the partially immersed samples which had been placed in either solution.

2.5 Conclusions

One of the primary reasons why the search for a new deicing chemical was initiated was to find a way of reducing reinforcement corrosion. The effect of acetate and formate salts on this aspect is by no means certain. The effect of acetate/formate ions on the condition of the steel reinforcement in chloride-contaminated concrete also remains unclear.

From the small amount of literature already available, it appears that all the new potential deicing chemicals may, under certain circumstances, have deleterious side-effects on the integrity of concrete. Acetate and formate based deicers have all been seen capable of exacerbating freeze/thaw damage in concrete. However, in all cases the amount was less than that seen when sodium chloride was used and therefore their usage would provide some improvement. It is also possible that components of the deicers may chemically interact with the concrete in some way or crystallise within the pore structure inducing cracking.

All the above aspects, perhaps with the exception of exacerbation of freeze/thaw damage, require urgent investigation if the new deicing chemicals are to be introduced on a wider scale. Of the possible options available, the areas considered in the experimental section are that of the effect of acetate and formate salts on the corrosion behaviour of steel in concrete (in the absence of chloride ions) and potential chemical and physical interactions with the cementitious matrix.

CHAPTER 3 - EXPERIMENTAL DETAILS: NON-CHLORIDE DEICING CHEMICALS

In response to the conclusions of chapter 2, an experimental programme was developed to investigate

- the corrosive effects of the deicing chemicals on steel embedded in concrete in terms of pore solution composition
- the diffusion characteristics into the pore solution of the various constituents of the deicing chemical and any associated interactions with the phases of hardened concrete
- the effect of crystallisation of the deicing chemicals within the pore structure of concrete

The experimental and analytical details of the work are described below. The results and discussion are contained in chapter 4.

3.1 Diffusion and Chemical Interaction of Formate and Acetate Salts with Hardened Cement Paste

3.1.1 Sample Preparation

Cement paste samples with a water to cement ratio (w:c) of 0.4 were cast in 75 x 49mm diameter PVC cylindrical moulds. They were vibrated to remove excess air and then carefully sealed. They were rotated end over end at 5rpm. for 24 hours to prevent segregation after which they were demoulded and stored above water in sealed containers for 56 days at 20±2°C. The composition of the OPC cement used for the samples is shown in table 3.1.

During the curing period the samples were temporarily removed from the containers and prepared for immersion in the deicing chemical. A fresh end face was cut on each sample using a diamond tipped rotary cutting blade lubricated with deionised water. The new end face was then ground smooth on grade 600 silicon carbide grit paper. The remaining cast surfaces were coated with two layers of paraffin wax before being placed back in the curing containers.

Elemental Oxide (%)		Bogue Compounds (%)[3.1]	
CaO	63.53	C_2S	24.52
SiO_2	21.20	C_3S	48.18
Al_2O_3	5.34	C_3A	9.72
Fe_2O_3	2.62	C_4AF	7.96
SO_3	3.38		
MgO	1.30		
Na_2O	0.09		
K_2O	0.75		
L.O.I.	1.53		

Table 3.1 - OPC Cement Analysis

3.1.2 Solution Preparation

The solutions used were sodium chloride, sodium formate, potassium acetate and a 3:7 molar ratio calcium and magnesium acetate mixture. Each solution contained 1 mole/litre of the relevant anion. They were made up from standard laboratory grade reagents (SLR) and deionised water.

[3.1] Calculated using the method as demonstrated in Neville [1981]

3.1.3 Experimental and Analytical Procedure

For each test solution 2 batches of 10 samples were laid horizontally in polythene containers and immersed in 4.5 litres of solution. The containers were then sealed and stored at 20±2°C for 112 days. The solution was changed every 28 days.

3.1.3.1 Diffusion

After the immersion period had elapsed all the samples were removed for analysis. 16 of the samples were dry cut into overlapping 7mm discs (see figure 3.1) using a mechanical hacksaw with a silicon carbide blade. The paraffin wax was removed from the circumference and the disc immediately placed in a sealable polythene bag to prevent moisture loss. The 8 discs from each depth were placed together and the pore solution extracted using a pore press similar to that developed by Longuet *et al.* [1973] and modified by Barneyback and Diamond [1981]. The load was applied at 0.3kN/s up to a maximum value of 600kN. The solution was collected in a sterile polythene vial which was immediately sealed when the maximum load was reached.

The pore solution was analysed for hydroxide, sodium, potassium, calcium and, where determined by the test solution, magnesium, chloride, formate and acetate. They were determined by the following methods

- Sodium and potassium - Atomic absorption spectroscopy in flame emission mode (FEM) [Perkin Elmer, 1976]
- Calcium and magnesium - Atomic absorption spectroscopy in absorption mode (AAS) using a lanthanum buffer solution [Perkin Elmer, 1976]

- Hydroxide - Titration against 10mM nitric acid using phenolpthalein as indicator
- Chloride - Spectrophotometrically at 460nm in combination with ferric ammonium sulphate and mercury thiocyanate reagents [Vogel, 1961]
- Acetate and formate - Ion chromatography using a 5mM sodium tetraborate eluant [Dionex, 1987]

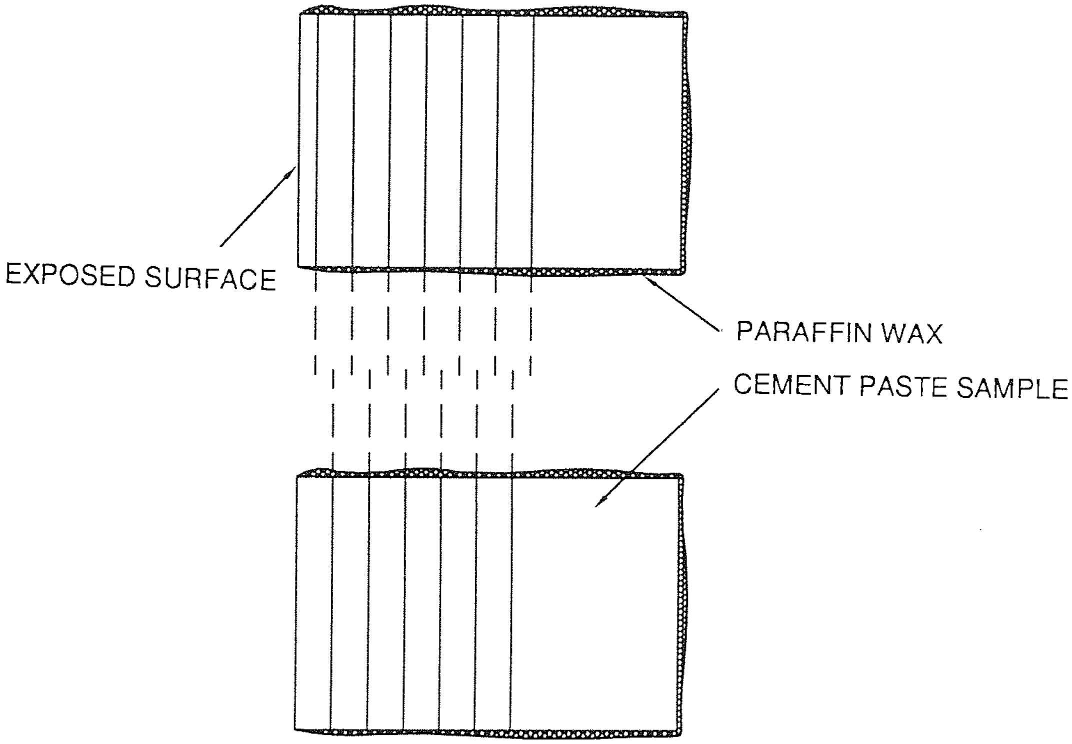

Figure 3.1 - Diffusion Specimen Disc Arrangement

The results obtained from each particular chemical solution were combined to form ionic concentration profiles along the diffusion path. The depth along the diffusion path represented the distance of the middle of the disc from the exposed surface.

3.1.3.2 Chemical Interaction

One of the remaining samples from each solution was made into a petrographic thin section for microscopic analysis. The remaining samples were then wet cut up into 5mm discs using a diamond tipped rotary cutting blade and placed in a desiccator containing silica gel until analysed. Primarily the analysis was carried out using the well established techniques of thermogravimetric analysis (TGA), differential thermal analysis (DTA) and X-ray diffraction (XRD) to determine any chemical changes. Mercury intrusion porosimetry (MIP) was used to determine changes in the pore structure. Scanning electron microscopy (SEM) linked to an energy dispersive x-ray analysis spectrometer (EDXA) for semi-quantitative elemental analysis was also used when considered necessary.

The thermal analysis, consisting of TGA and DTA, was carried out simultaneously on the same test sample using a Stanton and Redcroft 1500 Thermal analysis system. All the tests were carried out at 20°C/min up to a maximum temperature of 950°C against an inert calcined alumina reference material. The XRD was carried out using a Philips X-ray diffractometer with Cu $K\alpha$ radiation. In the cases of both the TGA/DTA and XRD the cement samples were prepared in the same way. The central area of each disc was ground up in a pestle and mortar and then sieved to collect material less than 150μm in diameter. The fine material was stored in a desiccator over silica gel for 24 hours and then analysed.

As with the TGA/DTA and XRD, only the central portion of each disc was used in the MIP analysis. The central portion was broken up in to small pieces and then dried using the solvent replacement and vacuum drying method. Each sample ($\approx$10g) was placed in a clean glass beaker and covered in 50ml of propan-2-ol. The beaker was placed in an ultrasonic bath for 30 minutes at which point the solution was decanted. This process was carried out a total of five times at which point the sample was placed in a vacuum desiccator and dried. The measurements were made on a computer controlled Micromeritics 9310 Porosimeter which was capable of analysing approximately 3g of sample. The contact angle of mercury required for the pore size calculations was taken as 130°.

3.1.4 Discussion of the Experimental Details and Analytical Techniques

3.1.4.1 Experimental Techniques

The experimental techniques used in this section were adapted from those originally developed and used by Sergi [1986] to study ionic diffusion. Of all the test solutions, sodium chloride is the only one that has been used before under these test conditions. However, it is usually added to a solution of saturated calcium hydroxide, or of sodium or potassium hydroxide of an equivalent pH. This is done to simplify the model by reducing the amount of hydroxide ions leaching from the sample and preventing alterations to the pore structure in the surface zone. The hydroxide ions were omitted from the test solution in the present investigation to try and simulate more closely the conditions experienced in real situations.

3.1.4.2 Analytical Techniques

The methods of pore solution analysis were ones commonly used in chemical analysis. The only variation from the norm is the use of AAS for the determination of calcium and magnesium. Although these two elements are regularly and routinely determined by this method, there are various species, which if present in the test solution, reduce the intensity of the signal measured by the instrument. Aluminium, silicon and sulphate are three such species and are all present in cement. It is claimed that the use of a buffer solution containing lanthanum reduces the interferences [Perkin Elmer, 1976], but it has been seen that the results are still not as accurate as they would be if determined by other methods such as titration with EDTA[3.2] [Figg & Bowden, 1971]. If total acid soluble calcium and magnesium contents of the cement paste were being determined AAS would not have been used. In pore solutions the interfering species are only present in very small quantities, if at all. For this reason it was felt to be adequate to use AAS provided a lanthanum buffer was used.

When carrying out the TGA/DTA, XRD and MIP, only the central portions of each disc were used in case the paraffin wax coating influenced the results. Both TGA/DTA and XRD were used as neither technique is capable of detecting all the phases present in hydrated cement paste. DTA is only capable of detecting cement minerals which exhibit appreciable endo or exothermic heat changes when they react or change phase. TGA only detects minerals which show noticeable changes in weight when reacting. XRD can be used to identify minerals that are crystalline in nature.

MIP cannot be used accurately to determine absolute values for the volume and diameter of the pores. However, the method is capable of allowing comparisons to be made between different samples made from the same cement paste. The equation used to calculate the pore sizes assumes that the pores are cylindrical and this is not an accurate representation. The pressure exerted during the test may damage the pore structure making it seem more porous than it actually is. In order to intrude mercury into the sample it is also

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[3.2] Diamino-ethane-tetra-acetate solution necessary to dry the sample and this moisture movement can damage the pore structure. A number of methods have been proposed to lessen the amount of drying damage and the one used in the experimental work has been shown to cause the least amount of damage [Feldman & Beaudoin, 1991]. To calculate the pore diameters it is also necessary to know the contact angle of mercury. A number of values have been used by various workers, but it has been shown that there is not a set value that can be used in all circumstances. The value of 130° used in this work is known to be a good approximation [Shi & Winslow, 1985].

3.2 Damage associated with the Crystallisation of Formate and Acetate Salts within the Cementitious Matrix

3.2.1 Sample Preparation

The cement paste samples were made and cured in the same way as those in section 3.1.1. They were made with the same batch of OPC cement (Table 3.1) and with the same w:c ratio of 0.4. During the curing period fresh end faces were cut on both ends leaving a cylindrical specimen 65mm in length and 49mm in diameter. The end faces were cut using a diamond tipped rotary cutting wheel lubricated with deionised water and were ground smooth on grade 600 silicon carbide grit paper.

3.2.2 Solution Preparation

The solutions tested were sodium formate, potassium acetate and a 3:7 molar ratio of a mixture of calcium and magnesium acetate. All the solutions contained 1mole/litre of the relevant anion. They were made up from standard laboratory grade reagents (SLR) and deionised water.

3.2.3 Experimental and Analytical Procedure

Each sample was placed in a sealed polythene container (Figure 3.2) and filled with solution so that it was half immersed (±5mm). It was then placed in a fixed temperature environment (20°C and 30°C). As the solution level fell it was replaced with fresh solution.

After one year the samples were removed and inspected. Visual assessments were made and one sample from each regime was made into a thin section for microscopic analysis. Other samples were cut up into various pieces and then ground up into a powder (<150µm). The powder samples were analysed using TGA/DTA and XRD as described in section 3.1.3.2.

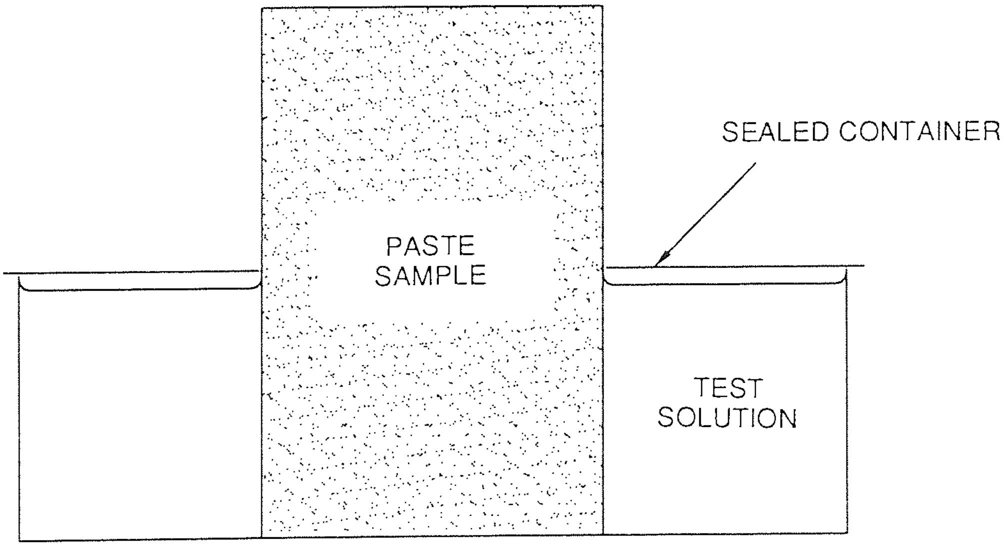

Figure 3.2 - Partial Immersion Experimental Arrangement

3.2.4 Discussion of the Experimental Procedure

The test regime was developed to try and simulate the effect of a concrete structure or pavement becoming contaminated with deicing chemical which is then left to concentrate and possibly precipitate in the pores. As with the majority of the experiments, the regime had to be made far more severe than would be seen in real situations.

3.3 Long Term Ponding Tests of Formate and Acetate Salts on Reinforced Concrete Slabs

3.3.1 Sample Preparation

Reinforced concrete blocks were prepared to the dimensions as shown in figure 3.3. They were made upside down so that the bottom of the pond had an 'as cast' surface. Grooves were formed into the opposite face of each block so that it could more easily be broken up into cubes as was required for the subsequent chemical analysis.

The composition of the steel is shown in table 3.2.

Fe	C	Si	Mn	S	Cr	Mo	Ni	Al	Cu	Sn
97.94	0.14	0.31	0.95	0.03	0.12	0.03	0.10	0.01	0.17	0.20

Table 3.2 - Composition of the Mild Steel Bar(%)

Each length was abraded with grade 600 silicon carbide grit paper and then degreased in acetone. A known area of steel was then masked off with a duplex coating of cement/styrene-butadiene rubber and epoxy resin [Lambert, 1983]. A diagram of a completed piece of steel cast into a concrete block can be seen in figure 3.4. Three bars were placed at each of three depths (15, 30 and 45mm) from the cast top surface as can be seen in figure 3.3. In addition to the reinforced blocks a similar number of unreinforced blocks were also made to provide samples for chemical analysis.

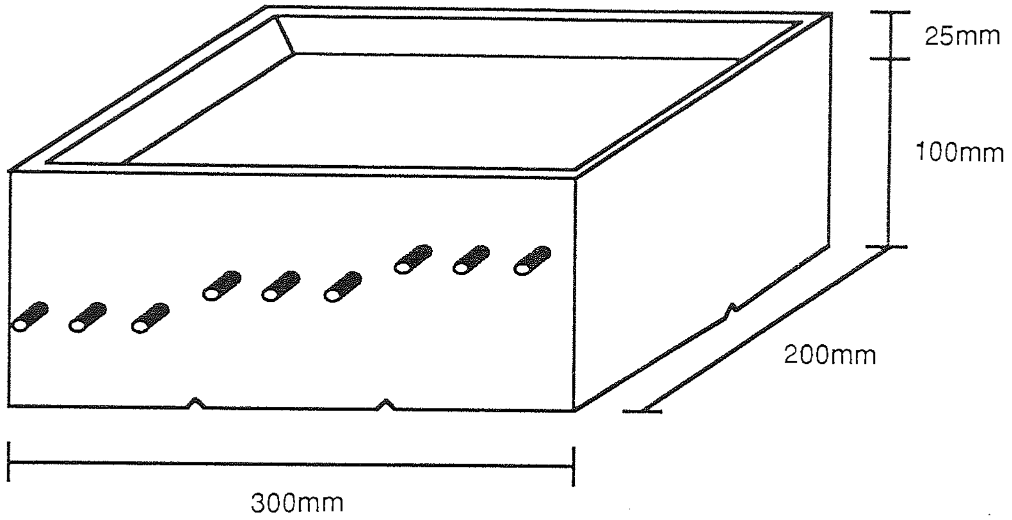

Figure 3.3 - Concrete Block Specimens

The concrete mix details are shown in table 3.3 and the cement used was from the same batch used in the previous two sections (Table 3.1).

Cement	405.00kg/m^3
Deionised Water	182.25kg/m^3
Fine Agg.	770.00kg/m^3
10mm Agg.	940.00kg/m^3

Table 3.3 - OPC Concrete Mix Details

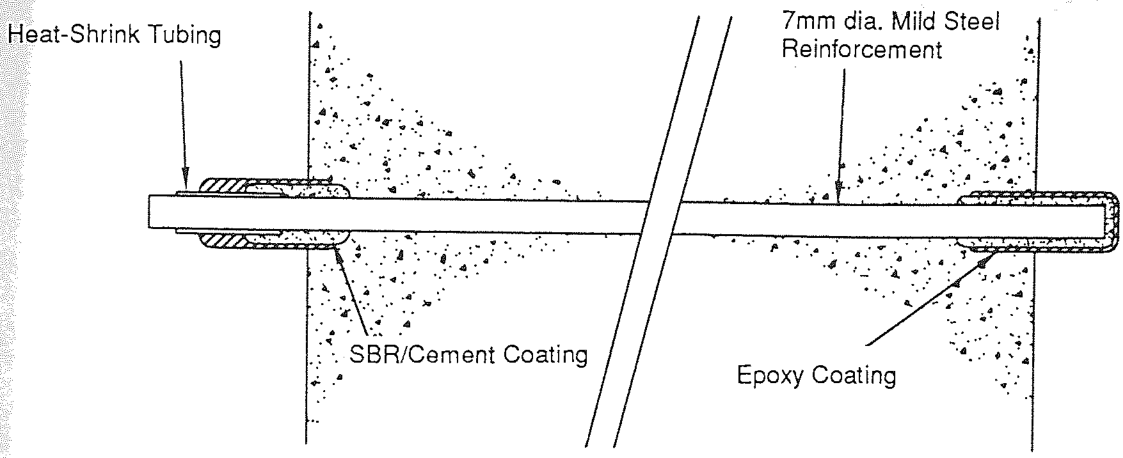

Figure 3.4 - Embedded Steel Arrangement

All the blocks were cured above water for 28 days at 20±2°C. Before any of the samples were ponded with solution, the top ponding surface was abraded with grit paper to remove any loose deposits and any remaining traces of demoulding oil. All the other surfaces were covered with two coats of bituminous paint to prevent chemical ingress from any surface other than the ponded face.

3.3.2 Solution Preparation

Solutions of sodium chloride, sodium formate, potassium acetate and a nominal 3:7 molar ratio of calcium and magnesium acetate were used. All the solutions, with the exception of the calcium and magnesium acetate, were prepared from deionised water and SLR grade reagents. The calcium and magnesium acetate mixture was prepared from commercial grade CMA deicer. They were all made up to contain 1 mole/litre of the relevant anion.

3.3.3. Experimental Procedure

Three reinforced and three unreinforced blocks were used for each chemical solution. Each block was ponded on a 28 day cycle. The cycle consisted of storage in an environmental room at 38°C for 7 days. Upon removal the blocks were ponded with one litre of the relevant solution and left in the laboratory for 21 days. At the end of the cycle any remaining solution and/or crystals were removed before the blocks were put back into the 38°C environment.

The specimens were subjected to a total of 24 cycles. At the end of the final cycle, they were stored in the laboratory and the remaining solution and/or crystals left on the ponded surface. 250ml of deionised water was added weekly to the ponds for 7 weeks. At this point the pore solution of two of the unreinforced blocks was extracted and analysed using the techniques described in section 3.3.4.3. The third unreinforced block was used to produce a thin section for microscopic analysis. For a number of weeks after this, the remaining (reinforced) blocks were kept moist by periodically applying small amounts of deionised water to the top surfaces. Throughout the whole time period the condition of the steel was monitored by measuring both the rest potential and corrosion rate (see sections 3.3.4.1 and 2). After this the blocks were broken up and the condition of the steel noted.

3.3.4 Analytical Techniques

3.3.4.1 Potential Measurements

In general, the potential of each piece of steel was measured once every 28 day cycle, 7 days after the concrete block had been ponded with solution. The potential compared to a SCE electrode was measured with a high impedance voltmeter. The electrode was placed on the ponded surface in the solution. At the beginning and the end of the testing period the measurements were taken more regularly.

3.3.4.2 Corrosion Rate Measurements

As with the potential measurements, the corrosion rate was assessed 7 days after the block had been ponded with solution. In general, it was only measured every three cycles, but at the beginning and end of the testing regime it was determined more frequently.

The corrosion rate was determined by the technique of linear polarisation carried out on a computer controlled PARC model 273 potentiostat. For each measurement the SCE reference electrode was placed on the ponded concrete surface directly above the bar in question (the working electrode). The potential of the working electrode was scanned from -10mV to +10mV with respect to the value of rest potential using the preceding bar in the block as the counter electrode. The potential was scanned at a rate of 0.1mV/s. The ohmic drop between the working and the reference electrode was compensated for using a current interrupt module in the potentiostat. The Tafel coefficients used in the calculation of the corrosion rate were assumed to be 120mV/decade.

3.3.4.3 Pore Solution Analysis

The sampling and extraction process was carried out as follows. Each unreinforced block was broken into six 100mm cubes which were immediately wrapped in cling film to prevent moisture loss. Each cube was then wrapped in strong PVC tape. One of the cubes was then placed in a compression testing rig and crushed well beyond its failure point. Using a scalpel, the PVC tape and cling film were carefully cut away at various depths and the crushed material sampled. The material from each layer was then sieved and the material smaller than 2.34mm in diameter was collected in a sealable glass container. The percentage of 'evaporable' pore water present at the various depths was determined by weighing both before and after being stored at 105°C until constant weight had been reached.

While the samples were being dried, the remaining cubes from the same block were crushed in a similar manner. The material from each cube at the same depth was stored together in a sealable polythene bag and crushed further. It was then sieved and the fine material (<2.34mm) placed in a sealable polythene jar.

Deionised water was added to each sample and mixed thoroughly until it was brought to a saturated surface dry (SSD) condition. The state was deemed to have been reached when the material just started to adhere to a clean gas stirring rod. Generally, the amount of water added was between 2% and 7%. After 24 hours a small sample was taken and the percentage of 'evaporable' water determined using the same method described above. The remaining sample was placed in the pore press and loaded at 0.3kN/s to 600kN. The solution was collected and analysed for hydroxide and either chloride, formate or acetate. Hydroxide concentrations were determined by acid base titration using a Radiometer automatic titrator. Chloride, acetate and formate were analysed using the same methods described earlier in the chapter.

The concentrations measured were then corrected to account for the added water. However, no attempt was made to compensate for the increase in calcium hydroxide solubility. The method and a worked example are shown in appendix A. As with the diffusion work in section 3.1, it was assumed that the concentrations determined were those present at the centre of that section.

3.3.5 Discussion of the Experimental and Analytical Techniques

3.3.5.1 Experimental Techniques

The techniques used in this section were modified from those used by Page and Lambert [1986]. Although the ponding and drying cycle used does not represent the process of diffusion, it has been found to be the most efficient at promoting the ingress of chemical solutions into a concrete block which is necessary if meaningful results are to be obtained in the time span allowed. The limitation of the regime is that the forced drying phase prevents a free water profile developing as would have been present if diffusion alone had caused the ingress. For this reason, after the cyclic ponding phase had been completed, the blocks were constantly ponded with deionised water for a number of weeks. During this time the potential and corrosion rate were monitored in case the change in procedure affected the condition of the steel bars .

For electrochemical corrosion rate measurements it is necessary to know the surface area of the steel sample. However, covering parts of the steel with a non conductive coating can induce crevice corrosion at the interface between the masked and unmasked areas. The duplex method of coating the steel has been shown to minimise this problem [Lambert, 1983].

It would have been preferable to use the same grade of chemical for all the test solutions. This is particularly relevant in the case of commercial grade CMA as it contains an amount of insoluble material (unreacted dolomitic limestone). However, due to the costs of the SLR grade calcium acetate and magnesium acetate this was not practical. In order to ensure the solution of CMA contained the same amount of the major anion as the other solutions it was compared to a 1mole/litre solution of acetate ions (SLR grade) using ion chromatography.

3.3.5.2 Analytical Techniques

ASTM standard C 876 states that when the potential of steel is more negative than -350 mV when measured relative to a copper/copper sulphate reference electrode (CSE) then the probability of active corrosion is high [ASTM, 1987]. When measurements are taken using a saturated calomel electrode (SCE) the reading corresponding to -350 mV would be approximately -290 mV. However, the accuracy of this method is only thought to be good in cases where the member concerned is adequately prewetted and is also exposed to air [American Concrete Institute, 1985]. Due to the ponding regime where the blocks were continually immersed in static solutions for up to three weeks, this simple criterion was not used. Instead judgements were made from a combination of the corrosion rate measurements and the potential differences recorded from one cycle to the next. A piece of steel was assumed to be corroding when the measured rate exceeded $0.1\mu A/cm^2$.

Linear polarisation scans of -10mV to +10mV (w.r.t the rest potential) at a rate of 0.1mV/s have been seen to give corrosion rates comparable with the data obtained from gravimetric weight loss experiments [González *et al.*, 1985]. To convert the value of polarisation resistance to that of a corrosion rate it is necessary to assume a value for the Tafel coefficients. Values of 120mV/decade that were used in the experiments are known to give a good approximation [Andrade & González, 1978].

From preliminary tests, it was clear that it would be impossible to extract analysable quantities of pore solution using the technique of 'crush sectioning' developed by Page and Lambert [1986]. For this reason it was necessary to adapt the method to that described in section 3.3.4.3. Although it meant that the results obtained from the analysis were not the actual ones present in the cement pores, it was thought that after the mathematical manipulation to allow for the added water the accuracy would be acceptable. It was necessary to crush and sieve the concrete prior to pore expression to remove any large pieces of inert aggregate. This would increase the percentage of 'pressable' material and reduce the amount of damage to the pore press.

CHAPTER 4 - RESULTS AND DISCUSSION: NON-CHLORIDE DEICING CHEMICALS

4.1 The Effect of Sodium Chloride on Reinforced Concrete

4.1.1 Electrochemical Behaviour of the Embedded Steel and Associated Pore Solution Data

The first layer of steel in the concrete blocks started to corrode after approximately 20 weeks (5 cycles)(Figure 4.1). As the ponding regime continued, the average corrosion rate in this top layer increased up to a value of approximately 0.4μA/cm^2 (Figure 4.2). The pore solution analysis (Table 4.1) gives a Cl:OH ratio at this depth in excess of 4.6. This result agrees with the work of Lambert *et al.* [1991] which showed corrosion occurred with ratios in excess of 3.

Block No.	Depth (mm)	Evap. Water (%)	Chloride (mM)	Hydroxide (mM)
1	3.75	8.26	1864	105
	15	7.60	1395	300
	30	7.05	1109	355
	45	7.12	862	378
	60	7.37	---	---
2	3.75	7.89	1999	160
	15	7.15	1368	281
	30	7.59	1407	228
	45	7.31	1022	342
	60	7.12	1613	310

Table 4.1 - Pore Solution Data from Ponded Slabs (Sodium Chloride)

Both the second and third layers started to corrode approximately 50 weeks after the first. It was expected that the third layer would have started to corrode

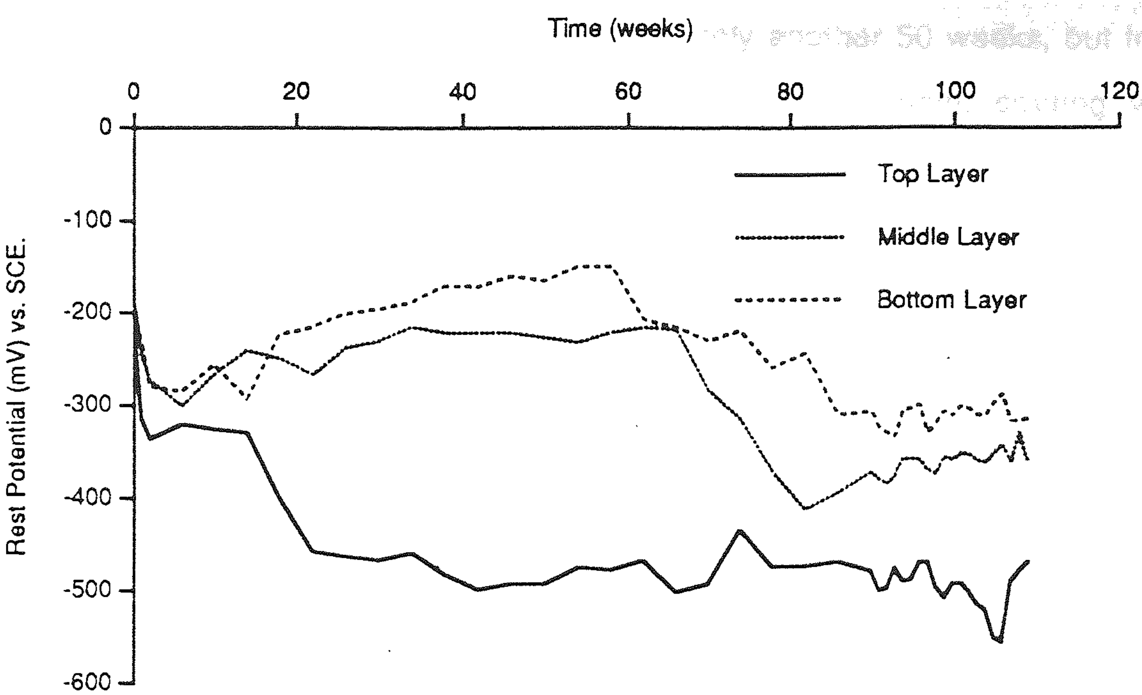

Figure 4.1 - Rest Potential against Time (Sodium Chloride)

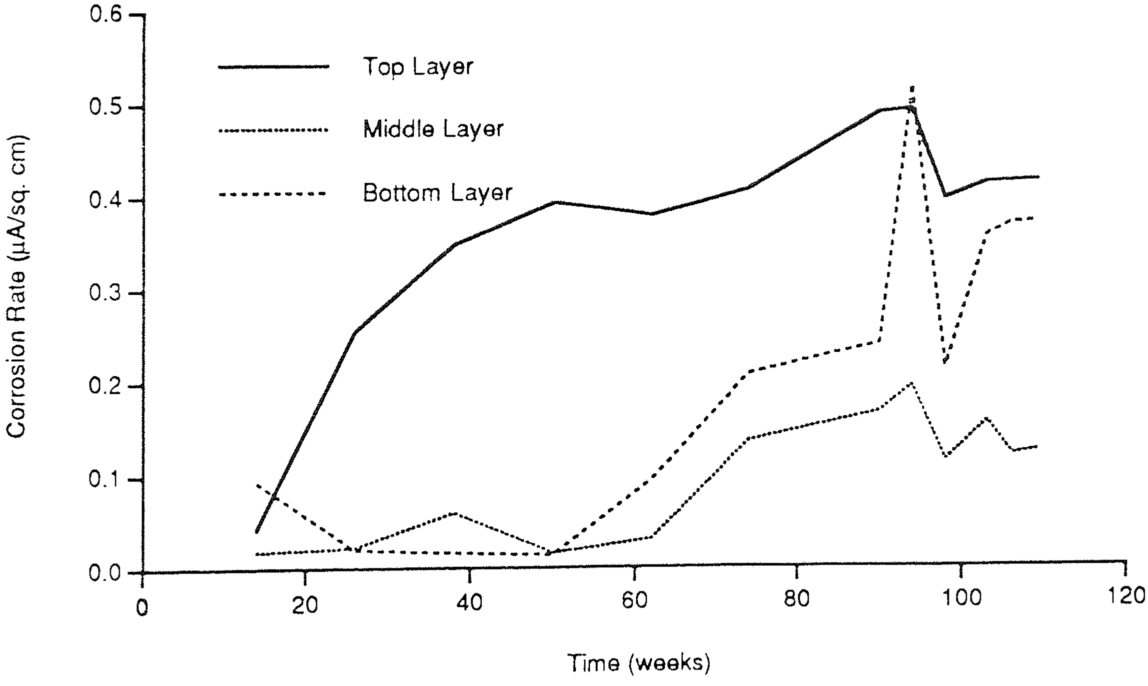

Figure 4.2 - Corrosion Rate against Time (Sodium Chloride)

sometime later still; perhaps after approximately another 50 weeks, but from the pore solution data it appears that the bitumen paint coating was insufficient to completely prevent the ingress of test solution that had accumulated under the blocks from spillages. This could explain the premature initiation of corrosion in the bottom layer. In general, although the pore solution data indicates that the Cl:OH ratio was less than 3, when the degree of experimental scatter was taken into account it was not significantly so and therefore corrosion was likely.

After the reinforced blocks were broken up the condition of the steel bars was seen to confirm the electrochemical data. On the majority of samples small areas of corrosion were evident (Plate 4.1).

4.1.2 Chemical and Physical Interaction with the Cementitious Matrix

Both visual and microscopic analysis showed negligible damage to the integrity of the concrete. On the majority of the concrete blocks there was only a very small amount, if any, of surface scaling (Plate 4.2). Inspection of the thin section showed a very small amount of cracking close to the ponded face, but none in the main bulk of the specimen.

Although not included in the partial immersion phase of the experimental work, sodium chloride had been previously tested on mortar cylinders using a similar, but more aggressive regime (50°C) [Walker, 1990]. At no time during the testing period was any damage evident.

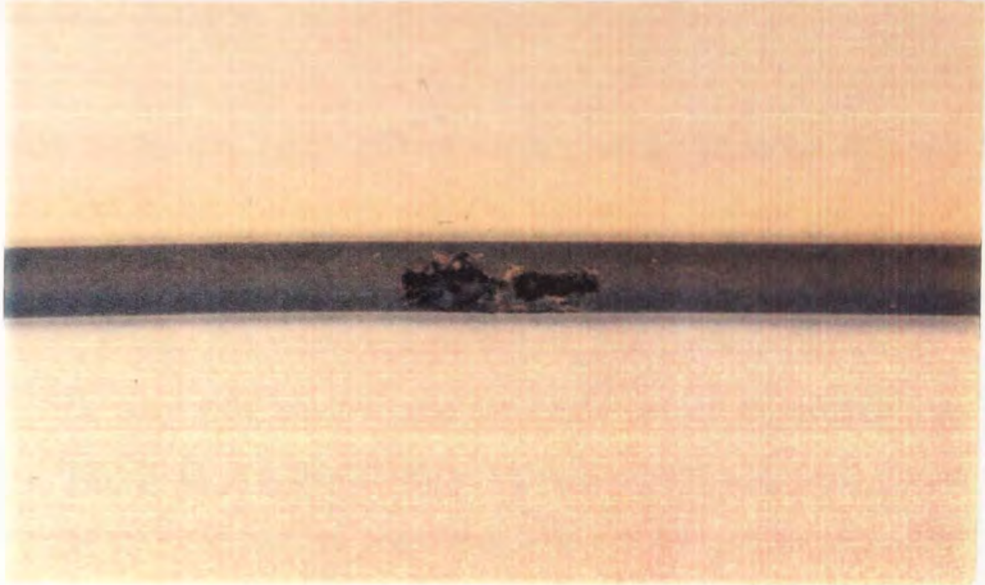

Plate 4.1 - Chloride-Induced Corrosion, x 1.3 Mag.

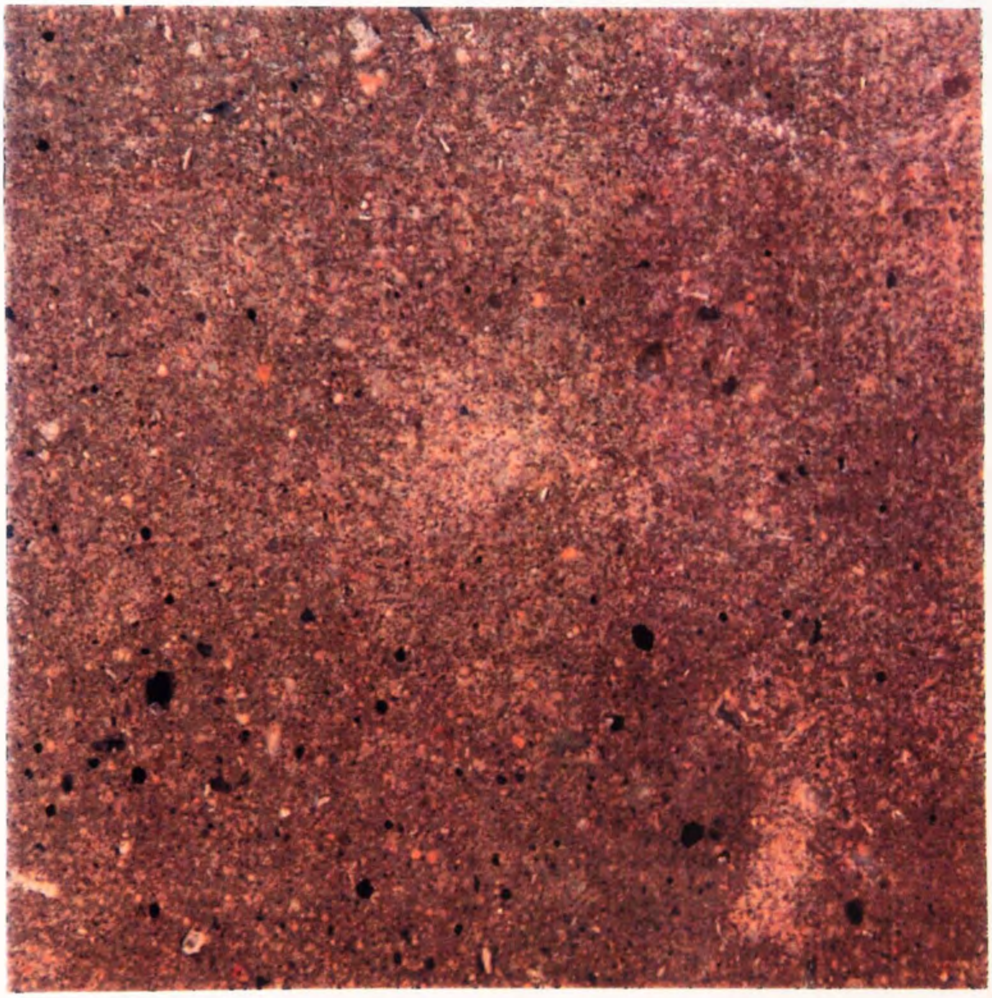

Plate 4.2 - Surface Scaling (Sodium Chloride) x 3 Mag.

4.1.2.1 Ionic Diffusion

Although hardly any visible difference was noted after the different samples had been exposed, the constituents of hardened cement paste, both in liquid and solid phase, are known to interact in various ways with solutions of sodium chloride. The chloride ions diffuse into cement [Sorensen & Maahn, 1982]. The total acid soluble chloride profile which developed was seen to follow Fick's 2nd. law of diffusion. Later Sergi *et al.* [1992] noted that the majority of the ionic species present in both the cement pores and the external solution, such as sodium, potassium and chloride could also be modelled using Fick's 2nd. law. Hydroxide, however, was seen to deviate from the law near the specimen surface. It was observed that if the calcium and sulphate ions in the pore solution were neglected the hydroxide profile could be constructed from charge balance considerations after all the other ions had been modelled. Both calcium and sulphate ion concentrations could be neglected as they are present in only very small amounts in normal OPC pore solutions.

A number of the observations made by Sergi *et al.* were seen in this present work. Sodium, potassium and chloride were all able to be interpolated using Fick's 2nd. law. The experimental values are given in table 4.2. Although Sergi *et al.* used an external test solution incorporating both sodium chloride and calcium hydroxide, the hydroxide profile was still seen to follow a similar trend. Of course, the concentrations at the surface were far lower due to the absence of saturated calcium hydroxide in the external solution. This reduction in pH near the surface increased the solubility of calcium ions in the pore solution and were seen to reach significant values which could not be neglected. This was also shown by both the DTA and microscopic analysis. The intensity of the DTA peak corresponding to the dehydration of calcium hydroxide (Peak A - Figure 4.3) was relatively less intense near the surface than in the bulk of the sample. Inspection of the thin section showed a layer approximately 1mm thick at the surface of the specimen where the visible portlandite deposits were depleted.

Depth	OH^-	Cl^-	Na^+	K^+	Ca^{2+}
1.8	41	1079	1089	80	64
3.5	47	961	725	199	45
7.0	122	534	261	425	0
10.5	215	331	119	448	2
14.0	382	105	82	359	1
17.5	478	29	84	404	2
21.0	540	4	84	400	1
24.5	540	10	87	426	1
28.0	576	4	79	435	1
31.5	583	9	97	467	1
35.0	587	10	90	472	1
38.5	601	11	116	486	1
42.0	584	10	77	462	1
45.5	592	4	86	525	1
49.0	617	10	79	481	1

Depth in mm and concentrations in mM

Table 4.2 - Experimental Diffusion Data (Sodium Chloride)

The apparent diffusion coefficients for the chloride, sodium and potassium ions were 3.5 x 10^{-12} m^2/s, 1.0 x 10^{-12} m^2/s and 1.3 x 10^{-12} m^2/s respectively. The theoretical interpolated concentrations and the apparent chloride diffusion coefficients were calculated using the FINDCOEF computer program [Yu *et al.*, 1993a]. The experimental pore solution values and their theoretical interpolated profiles are shown graphically in figure 4.4. Where it was not possible to calculate profiles using the computer package, as in the case of the hydroxide ion profile which did not follow Fick's 2nd. law, a curve was drawn by eye to produce a smooth line through the experimental values.

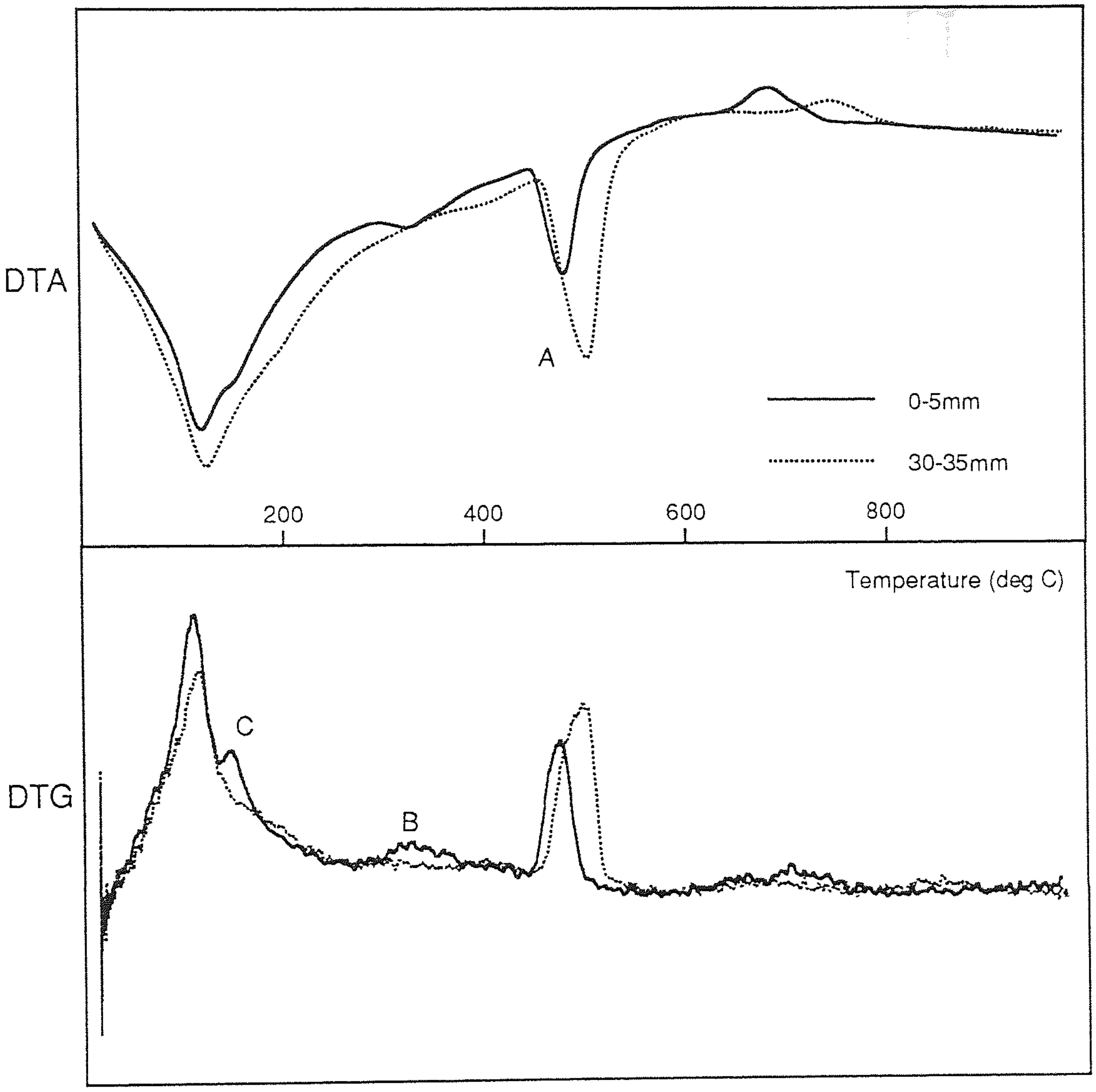

Figure 4.3 - DTA and DTG Analysis (Sodium Chloride)

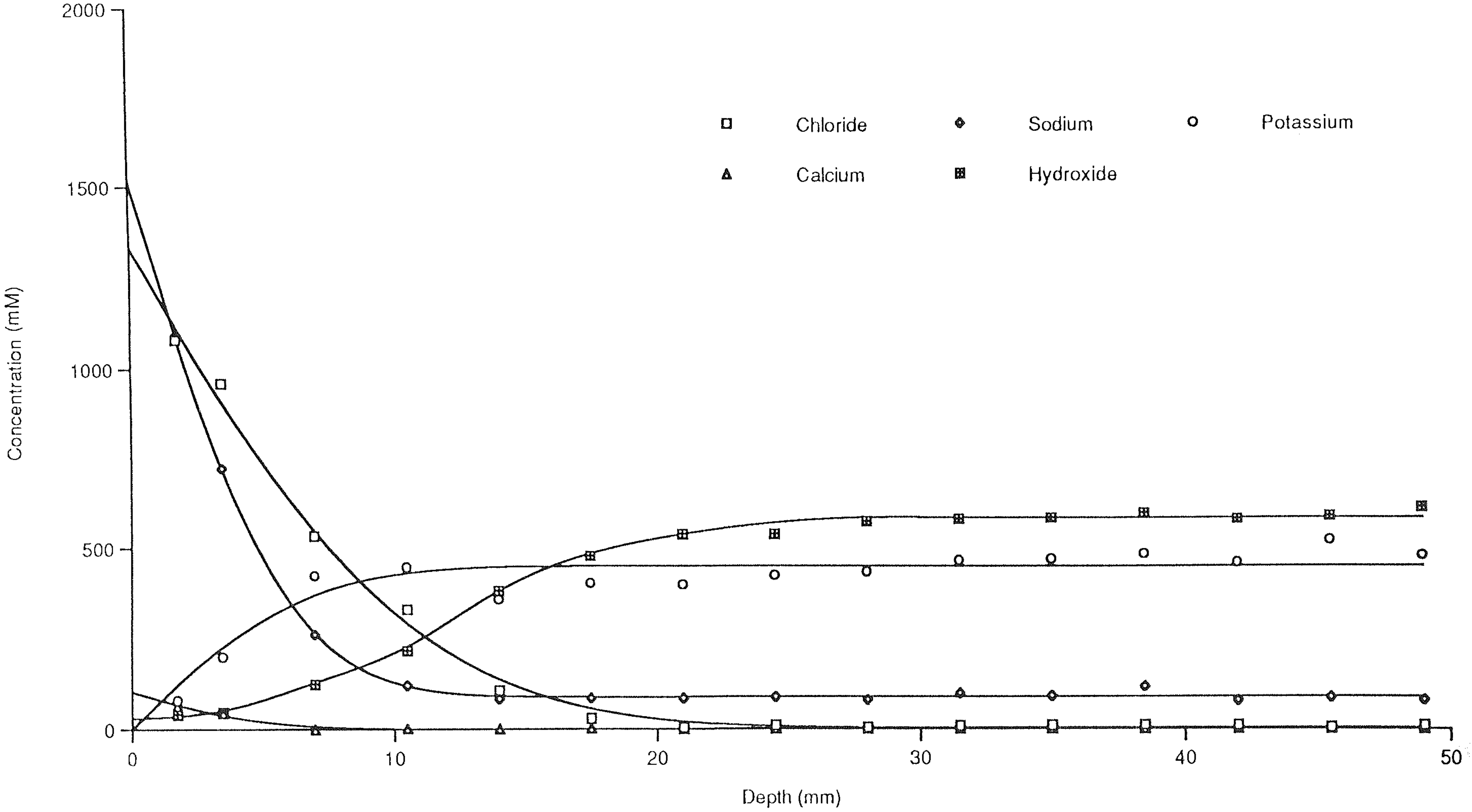

Figure 4.4 - Actual and Theoretical Pore Solution Profiles (Sodium Chloride)

4.1.2.2 Effects on Porosity

The MIP data showed an increase in the total porosity in the first 5mm zone when compared to the other samples taken from further into the specimen. It was 0.1084 cubic centimetres of mercury per gram of dried paste (cc/g) at the surface and 0.0893cc/g between 5mm and 10mm from it (Figure 4.5). The increase in porosity was due to the increase in the number of pores in the 0.05μm to 0.9μm diameter range. It was thought that such increases in porosity are due to the release of portlandite and C_3A reaction products (such as ettringite and, in this case, Friedel's salt) into solution [Sergi, 1986]. It was claimed that C_3A reaction products are unstable in low pH solutions and may be released increasing the porosity in the surface zone, but no experimental evidence of this was found in the present tests. However, Sergi was studying the diffusion of admixed chloride out of cement paste which had a C_3A content over 50% greater than that used in the present work. For this reason it was thought that, although they may be unstable at low pH values, in this case the change was primarily due to the release of portlandite into solution as was seen in the analysis of both the pore solution and solid phases.

4.1.2.3 Chloride Binding

The binding effect of the C_3A phase on chloride ions in solution was also seen. The DTA trace from the diffusion samples clearly showed an endothermic peak starting at approximately 295°C (peak temperature 325°C) indicating the presence of Friedel's salt in the surface layer (Peak B - Figure 4.3). The intensity, as also seen by Sergi [1986], decreased with increasing depth from the exposed surface. Inspection of the DTG[4.1] trace from the exposed surface also showed a peak at 150°C with a characteristic

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[4.1] DTG is a trace of the first derivative of the TGA curve against temperature

temperature of 135°C (Peak C - Figure 4.3). The intensity of the peak decreased with increasing depth from the exposed surface. There was no similar peak on the trace obtained from SLR grade sodium chloride and therefore it can be concluded that it was due to alterations in the composition of the cement paste. At these sort of temperatures, the peaks in OPC cements are usually representative of calcium sulphoaluminate hydrates such as ettringite or calcium monosulphoaluminate hydrate. However, results from the XRD analysis indicated that there was no monosulphoaluminate phase present and no appreciable increase in the amount of ettringite. In addition to the chloroaluminate peak around 300°C, Heller and Ben-Yair [1966 as cited by Ramachandran, 1969] found that the DTA analysis of chloride contaminated hardened cement paste exhibited another peak at approximately 190°C which they also attributed to the chloroaluminate phase. Although this peak occurred at a higher temperature than the small peak seen in this work it is thought to be the most likely cause.

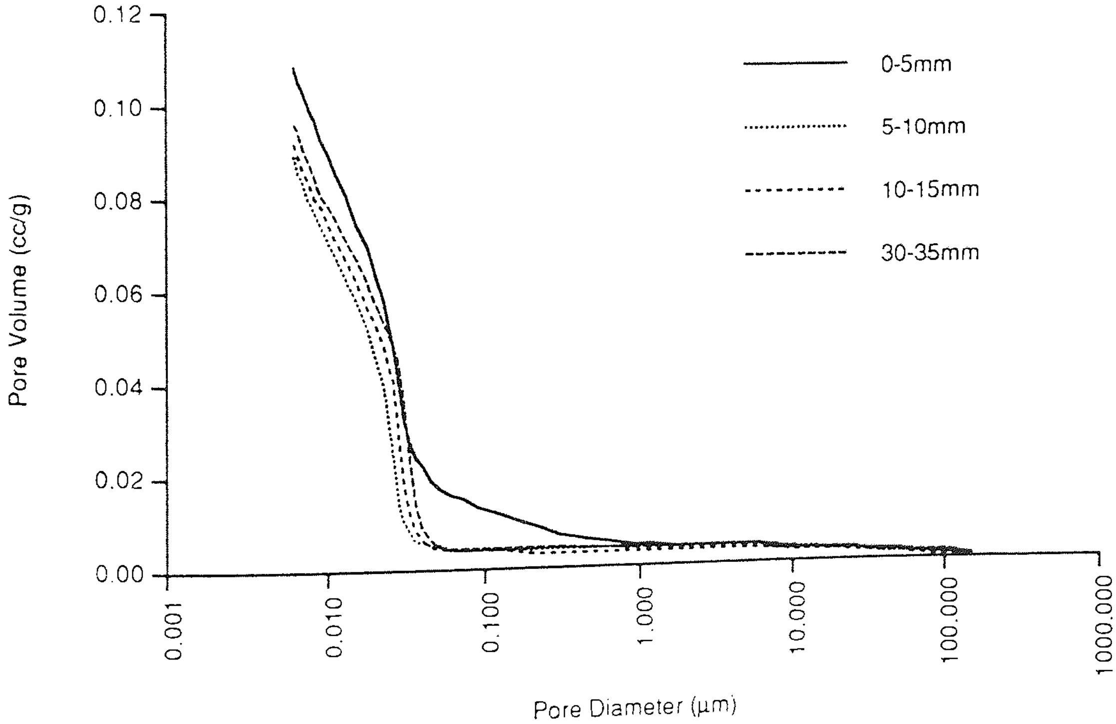

Figure 4.5 - Cumulative Pore Size Distribution (Sodium Chloride)

4.2 The Effect of Sodium Formate on Reinforced Concrete

4.2.1 Electrochemical Behaviour of the Embedded Steel and Associated Pore Solution Data

During the first 40 weeks of the ponding regime, the rest potentials of the steel samples embedded at all depths became less negative and stabilised with values of approximately -100mV vs SCE (Figure 4.6). Similarly corrosion rates were seen to drop finally reaching values between 10nA/cm^2 and 20nA/cm^2 (Figure 4.7) which is well below the threshold level.

When towards the end of the cyclic ponding regime, potential readings were taken more frequently at different times during each cycle, it was noted that they were less stable varying between -100mV and -200mV vs SCE, presumably dependent on the moisture content of the concrete at the time of measurement. After 90 weeks, the continuous ponding with deionised water began. During this stage the same instability was seen. However, even with this instability, the corrosion rate of the steel bars stayed relatively constant and at no time could be assessed as being actively corroding. Visual inspection of the steel at the end of the test period confirmed this view as no areas of corrosion were evident on any bar.

The associated pore solution data is shown in table 4.3. As with the data obtained for a solution of sodium chloride there is evidence that the external bitumen coating was insufficient to prevent ingress from the bottom face.

If a similar criterion to that usually used for chloride ingress (ie Cl:OH ratio) is employed, the formate to hydroxide ratios in the zones containing steel varied

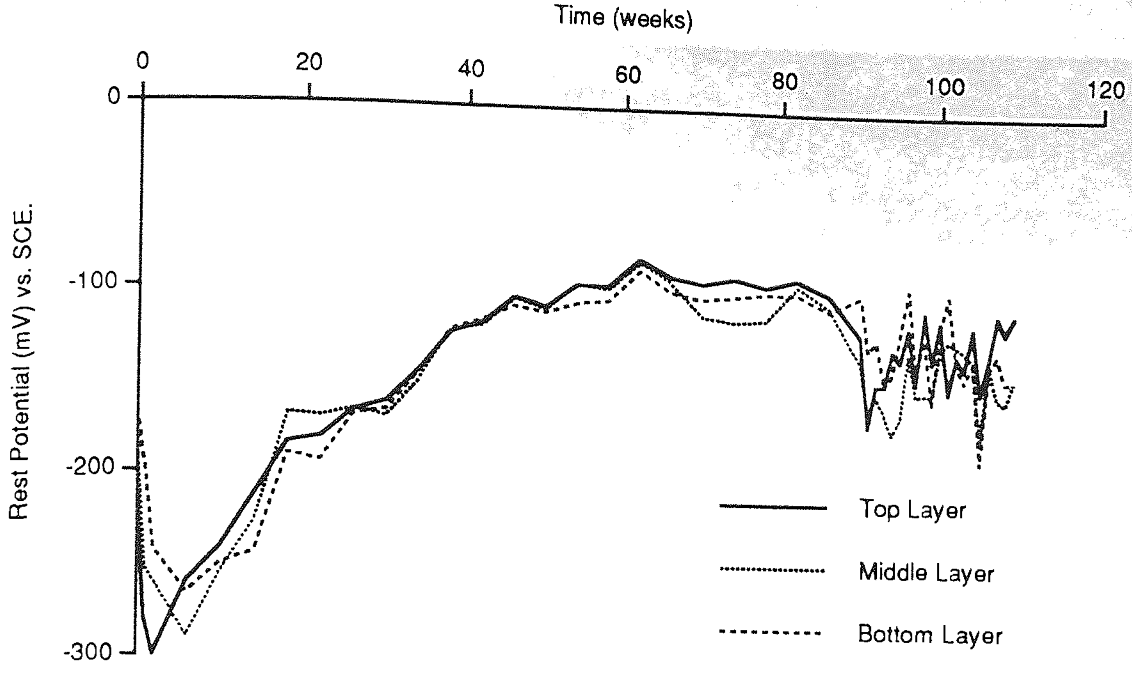

Figure 4.6 - Rest Potential against Time (Sodium Formate)

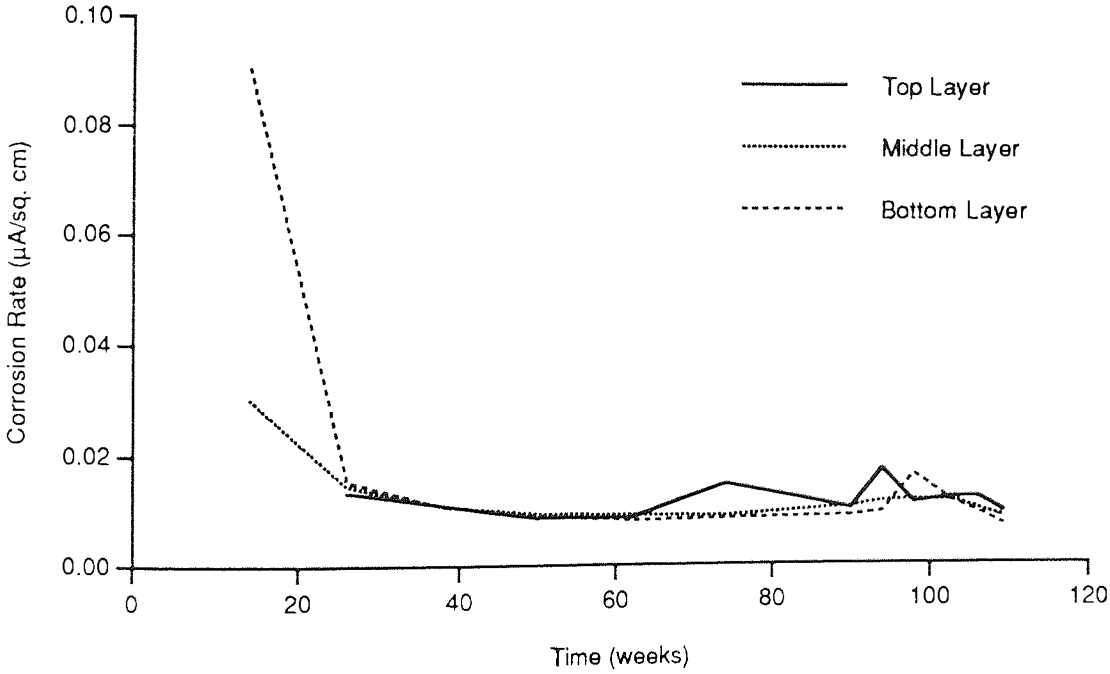

Figure 4.7 - Corrosion Rate against Time (Sodium Formate)

Plate 4.3 - Cracking of Ponding Surface (Sodium Formate) x 1.5 Mag.

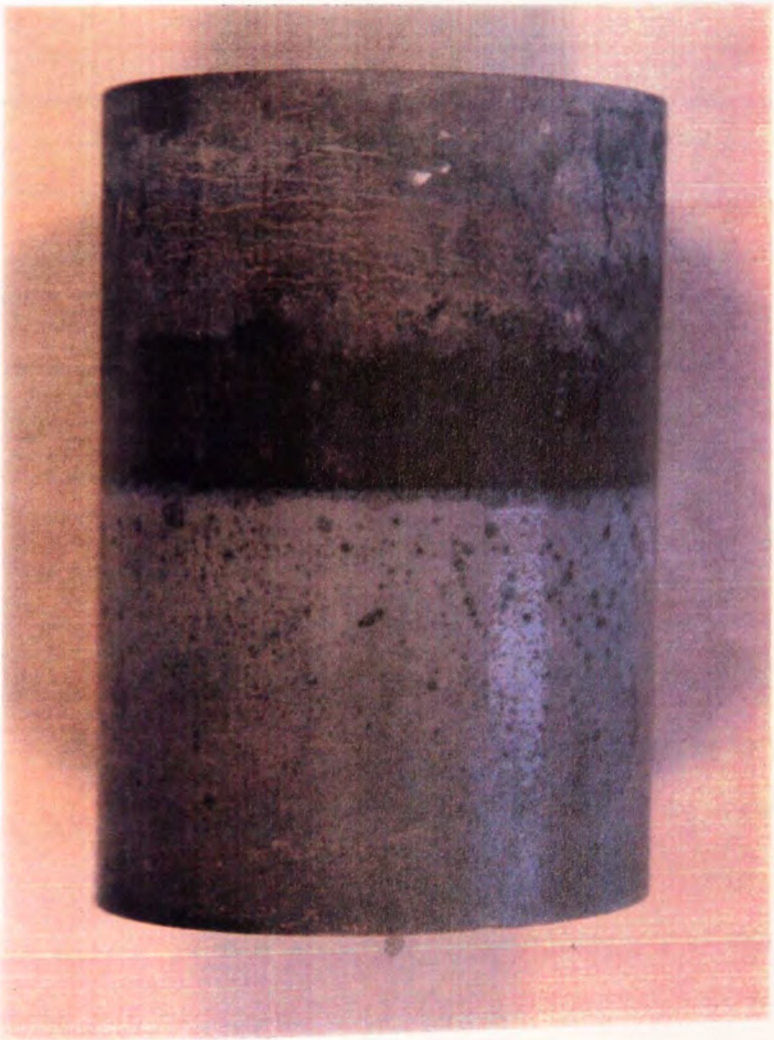

Plate 4.4 - Partially Immersed Sample (Sodium Formate) x 1.5 Mag.

between 19.90 and 1.77. On average this is well in excess of the threshold value of 3 for chloride-induced corrosion. As it is known that in non-alkaline solutions formate ions can cause corrosion [Hancock & Mayne, 1959; Brasher, 1969], it is quite possible that if the ratio exceeds a certain threshold level corrosion will occur. However, it can be concluded that formate ions are far less corrosive than chloride ions in concrete and that, in good quality concrete, they are unlikely to promote significant corrosion .

Block No.	Depth (mm)	Evap. Water (%)	Formate (mM)	Hydroxide (mM)
1	3.75	6.26	1999	301
	15	6.24	1431	373
	30	6.67	956	457
	45	6.08	804	453
	60	6.53	875	368
2	3.75	9.69	2976	111
	15	9.73	3503	176
	30	10.18	2145	222
	45	9.59	2549	251
	60	10.07	1527	257

Table 4.3 - Pore Solution Data from Ponded Slabs (Sodium Formate)

4.2.2 Chemical and Physical Interaction with the Cementitious Matrix

Visual inspection of the concrete blocks showed no damage or scaling to the main ponded surface indicating that sodium formate causes less damage than sodium chloride. However, small hairline cracks were seen in the zone between the base and half way up the reservoir sides (Plate 4.3). Under the microscope the thin section revealed a small degree of cracking near the ponded surface, but there was little evidence of any damage anywhere else in the sample.

The samples which were partially immersed in solution also showed no visible evidence of paste degradation (Plate 4.4). The only evidence of any alteration to the cement structure or composition was the reduction in the amount of portlandite in the surface zone of the submerged section as was seen from the thin section.

4.2.2.1 Ionic Diffusion

As with sodium chloride, sodium formate was seen to diffuse into the paste specimen and the profiles followed similar trends. The diffusion of sodium, potassium and formate ions could be modelled using Fick's 2nd. law. The apparent diffusion coefficients of the formate, sodium and potassium ions were calculated at $1.91 \times 10^{-12} m^2/s$, $8.4 \times 10^{-13} m^2/s$ and $2.92 \times 10^{-12} m^2/s$ respectively. The hydroxide concentration deviated from Fick's law near the exposed surface and the calcium concentration increased near the surface due to the change in solubility of calcium ions with change in pH. The experimental data is shown in table 4.4 and can be seen graphically along with the theoretical interpolated values in figure 4.8.

4.2.2.2 Effects on Porosity

The MIP data for sodium formate (Figure 4.9) showed similar trends to those seen with sodium chloride. At the specimen surface the total porosity was 0.0943cc/g which shows a significant increase over that at between 5 and 10mm from surface (0.0848cc/g). The increase was due to an increase in the volume of the voids in the diameter range 0.03µm to 0.3µm. It was primarily attributed to the release of portlandite into solution.

Depth	OH^-	Fo^-	Na^+	K^+	Ca^{2+}
1.8	46	1094	791	106	72
3.5	75	778	568	224	36
7.0	221	311	133	349	0
10.5	406	67	83	367	1
14.0	466	18	81	387	0
17.5	521	16	90	441	0
21.0	536	5	81	468	0
24.5	558	8	83	469	0
28.0	542	7	76	487	0
31.5	560	9	78	473	0
35.0	572	3	76	492	0
38.5	575	6	93	512	0
42.0	559	9	78	507	0
45.5	577	7	78	502	0
49.0	578	6	83	558	0
Depth in mm and concentrations in mM					

Table 4.4 - Experimental Diffusion Data (Sodium Formate)

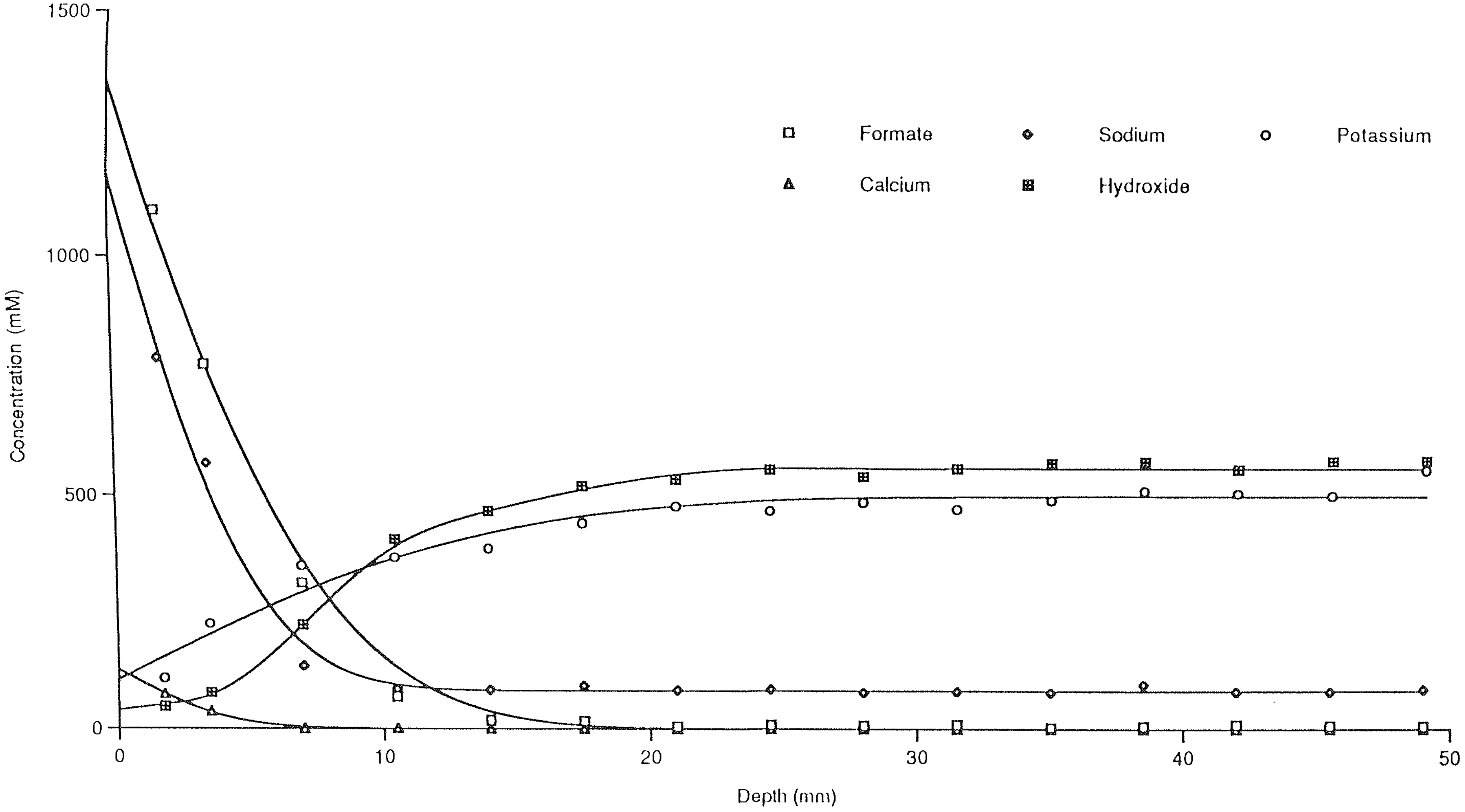

Figure 4.8 - Actual and Theoretical Pore Solution Profiles (Sodium Formate)

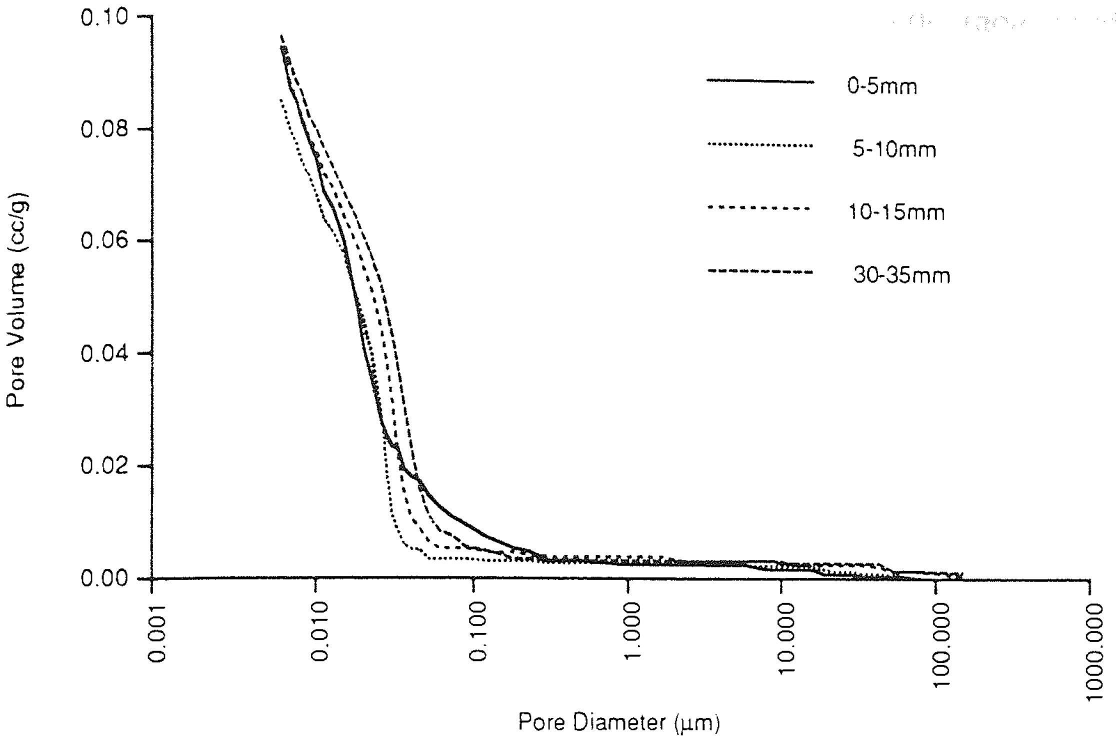

Figure 4.9 - Cumulative Pore Size Distribution (Sodium Formate)

4.2.2.3 Chemical Interaction

With the exception of the reduction in portlandite, there were no other easily identifiable changes in the DTA traces obtained from the diffusion specimen samples. However, upon closer inspection, there were two extra reactions evident from the TGA results (more evident on the DTG curve) which coincided with slight changes on the DTA trace which otherwise would have been overlooked (Peaks D and E - Figure 4.10). The intensity of the peaks decreased with increase in depth from the exterior surface. The reactions started to occur at 645°C and 830°C respectively. However, at these two temperatures the trace obtained from pure sodium formate shows chemical reactions both involving weight losses taking place. Hence it is thought that the two reactions detected on the trace from the cement pastes are due to the chemical present in the pores and not the degradation of a formate based cement reaction product. It is interesting to note, however, that the cement paste traces did not pick up a reaction indicating the partial degradation of the pure sodium formate which involved quite a substantial weight loss. This reaction was observed on the trace from the pure chemical to begin at approximately 420°C and therefore could have been masked by the large portlandite reaction which begins at only a slightly higher temperature.

XRD data from both the submerged area of the partial immersion sample and, to a lesser extent, the surface of the diffusion sample did show peaks that were not apparent on the control OPC paste sample. The d-spacings of these peaks were 2.336Å and 2.021Å (Appendix B - Trace 2). They do not coincide with the published data for sodium formate.

It is therefore hard to assess the effect of sodium formate on the cementitious matrix. Sagoe-Crentsil *et al.* [1993] think that there is no chemical interaction, but the XRD results may indicate otherwise. What can be concluded, however, is that even if some form of interaction does occur it does not seem to have any apparent significant deleterious effect.

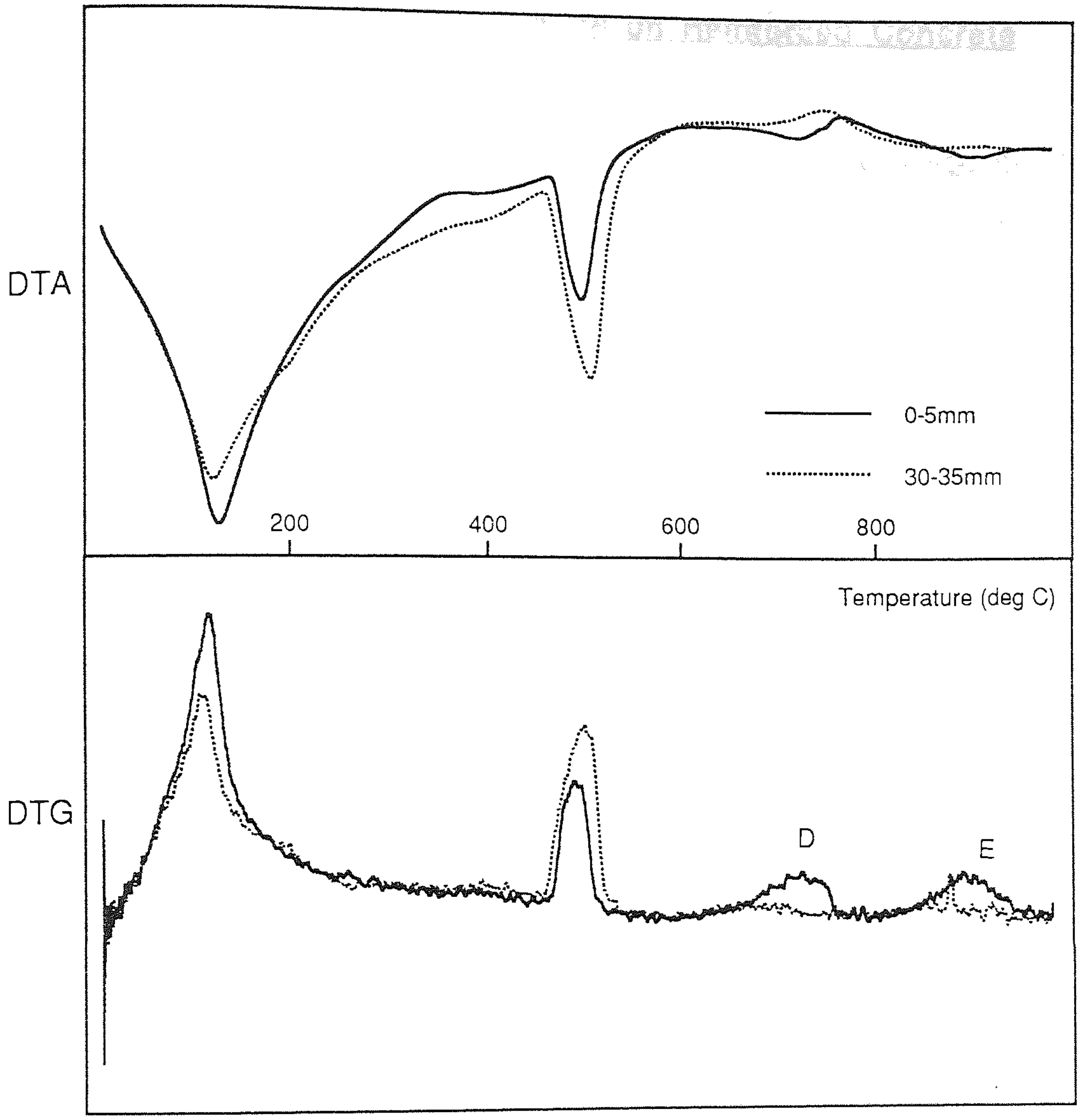

Figure 4.10 - DTA and DTG Analysis (Sodium Formate)

4.3 The Effect of Potassium Acetate on Reinforced Concrete

4.3.1 Electrochemical Behaviour of the Embedded Steel and Associated Pore Solution Data

During the first 90 weeks all the rest potentials became less negative eventually coming to rest in a band between -100mV and -200 mV vs SCE. The associated corrosion rates were also small and could not be associated with active corrosion. The potential measurements for the first layer of steel seemed to stabilise in the band more quickly than layers two and three. It is possible that this may be due to the ingress of acetate ions providing extra protection, but it may also be just normal experimental scatter in the results. From the literature reviewed in section 2.2.2 it is thought that the latter reason is the more feasible. Once the readings started to be taken more frequently, similar instability to that seen with sodium formate was noted.

During the last ponding cycle and throughout the time when the blocks were ponded with deionised water, the potentials of the majority of the steel bars became even less stable. In the majority of cases, the corrosion rates increased slightly, but not to a point where they could be classed as being active. However, the potentials of two pieces of adjacent steel in the top layer dropped significantly (<-600mV vs SCE) (Figure 4.11) and the corrosion rates increased to approximately 0.3μA/cm^2 (Figure 4.12). They remained at these values until the continuous ponding was stopped and the blocks started to dry out. The potentials then became less negative and settled around the -300 mV vs SCE range. At these potentials the corrosion rates were higher than the initial passive ones, but were less than the corrosion threshold. When the blocks were broken up and the steel inspected, no signs of corrosion were

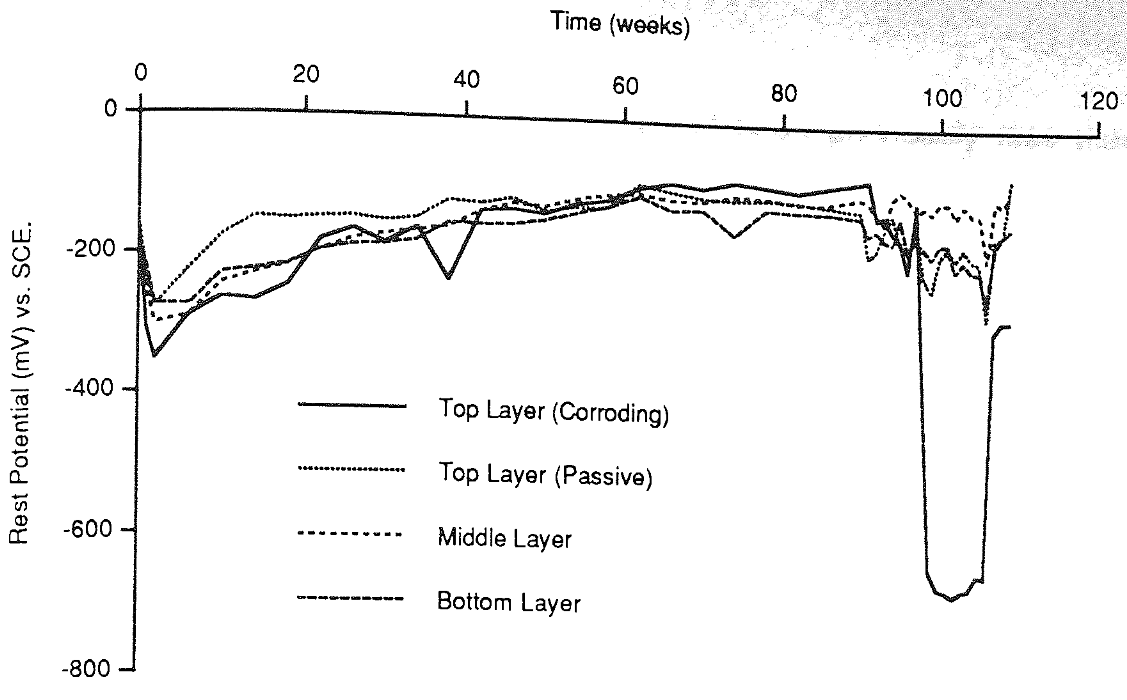

Figure 4.11 - Rest Potential against Time (Potassium Acetate)

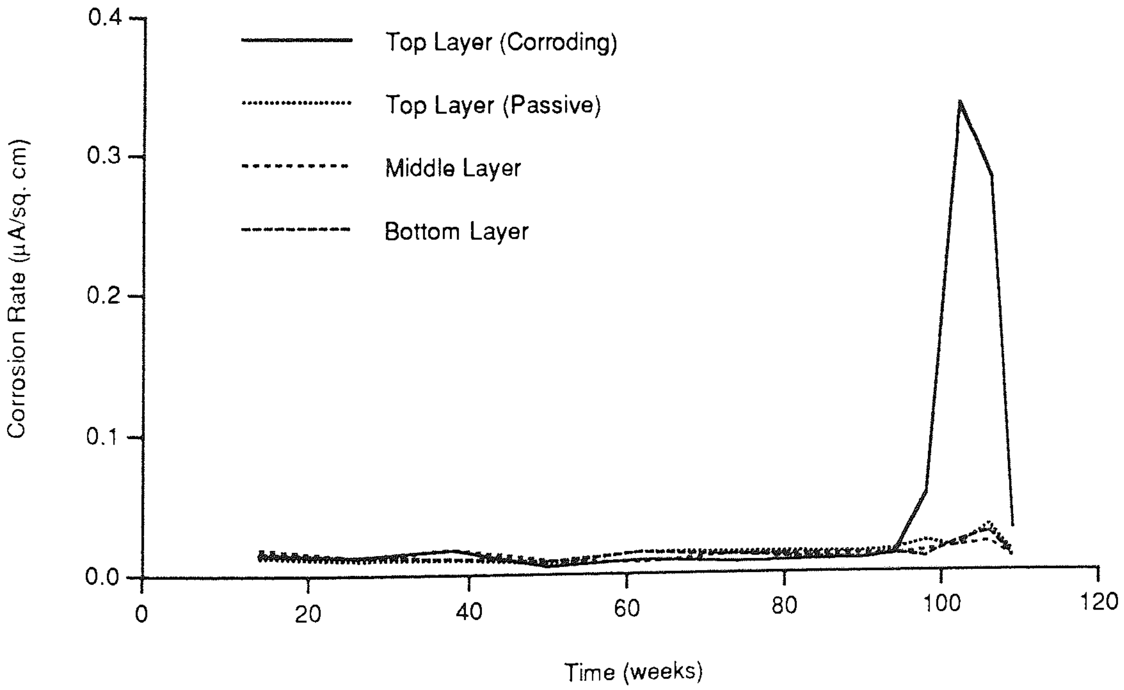

Figure 4.12 - Corrosion Rate against Time (Potassium Acetate)

evident, even on those whose potentials had been previously less than -600mV vs SCE.

In conclusion, it was seen that potassium acetate generally did not induce corrosion in the embedded steel bars. However, the question still remains as to why the potential of two of the bars in the top layer suddenly dropped to such a level with large increases in the electrochemically assessed corrosion rate even if no visible corrosion products were seen.

It has been seen that, in static conditions, both solutions of commercial and SLR grade calcium and magnesium acetate can cause similar potential changes with bare steel samples (not embedded in concrete). The reason for this was thought to be the precipitation of insoluble compounds suppressing the reduction of oxygen at the cathodic sites [Kennelley & Locke, 1990]. Presumably as a result of the hygroscopic nature of potassium acetate, the amount of evaporable water in the concrete blocks was significantly greater than that seen in either the sodium chloride or sodium formate ponded blocks (Table 4.5). The average percentage when compared to the weight of 'as sieved' concrete was 10.66% when compared to 8.12% and 7.45% for sodium formate and sodium chloride respectively. If the pores became saturated then it is possible that the level of dissolved oxygen surrounding the samples could, in time, drop sufficiently to induce depassivation. A solution of potassium acetate also appears to be a good medium for bacteria to grow. Bacterial growths were visible on the surface of the concrete only two weeks after the potential drops were noted. The bacteria will reduce the amount of dissolved oxygen in the external solution and this would presumably have an effect on levels in the body of the concrete.

Block No.	Depth (mm)	Evap. Water (%)	Acetate (mM)	Hydroxide (mM)
1	3.75	13.03	2131	44
	15	11.20	2872	61
	30	11.31	3017	75
	45	10.60	2825	97
	60	10.65	2544	105
2	3.75	10.62	2537	60
	15	10.03	3023	69
	30	9.84	2950	81
	45	9.67	2645	107
	60	9.66	2590	119

Table 4.5 - Pore Solution Data from Ponded Slabs (Potassium Acetate)

However, in situations like these, corrosion rates are typically very small as they are cathodically restrained and their associated potentials are in the range -850mV to -1000mV vs SCE [Page, 1988]. The measured corrosion rates were relatively large and the potentials were not in the usual accepted range which seems to exclude this explanation.

It was thought that work on the inhibitive effects of azelate salts solutions may cast some light on the effect. It has been seen that when an iron sample with a pre-formed oxide film is immersed in a deaerated solution, the film breaks down after a number of hours. In aerated solutions, the formation of ferric azelate, which plug the breakdowns in the passive oxide film, is balanced by the cathodic reaction involving the reduction of the dissolved oxygen. In the absence of sufficient dissolved oxygen the balancing cathodic reaction was thought to be reduction of the oxide film to form soluble ferrous ions (Fe^{2+}) [Mayne, 1968 cited by Evans, 1976]. Similar effects have been seen for acetate solutions [Hancock & Mayne, 1959] and this could explain the phenomenon.

However, the question still arises as to why the oxygen level dropped at that particular point in the testing period. There seems to be no reason why the dissolved oxygen level surrounding the steel should be different from that during the previous cycles.

4.3.2 Chemical and Physical Interaction with the Cementitious Matrix

From plate 4.5 it is evident that the surfaces of the concrete blocks were affected by the potassium acetate. Even halfway through the cycling period the blocks were showing signs of severe distress. Initially the cement rich surface layer separated from the main body (delaminated), then cracked and finally broke up leaving relatively large areas of each slab with an 'exposed aggregate' finish. Similar delamination and cracking was seen on the sides of each reservoir.

Microscopic analysis of the thin section showed extensive cracking throughout the full depth of the sample. Cracks were present in the bulk of the cement paste and also at the interface between paste and aggregate (Plate 4.6). Crystal growth was evident in both cracks and a number of air voids (Plate 4.7).

Similar damage was also noted on the partial immersion samples. Flakes of cement paste broke off in a band just above the solution level. With the exception of portlandite depletion in the surface zone of the submerged sections and slight carbonation of the surface zone of the top section, the thin section showed no evidence of alteration to the paste composition. Further

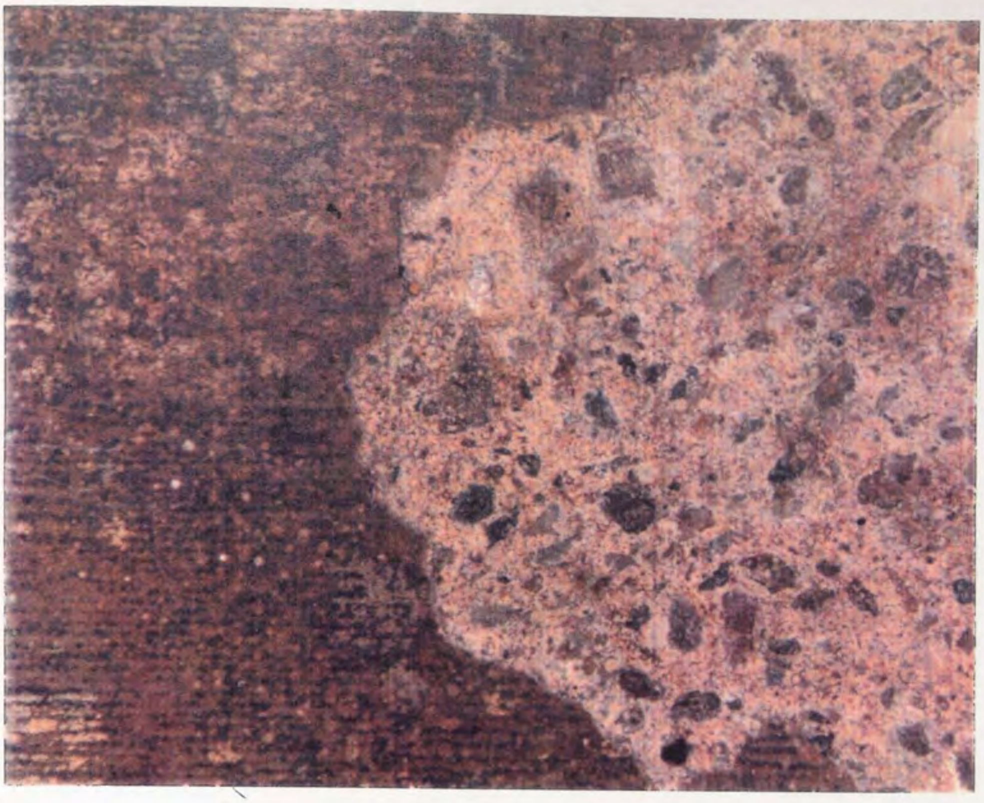

Plate 4.5 - Cracking and Scaling of Ponded Surface (Potassium Acetate) x 1 Mag.

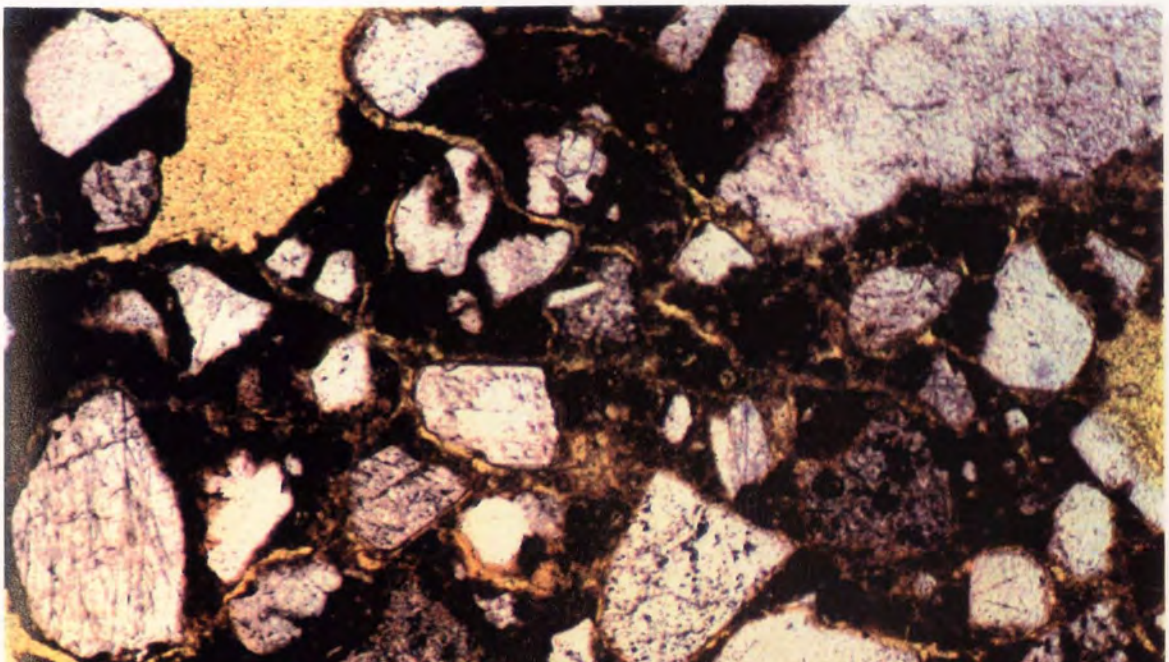

Plate 4.6 - Petrographic Image of Cracking in the Interior of Ponded Slabs (Potassium Acetate) x 100 Mag.

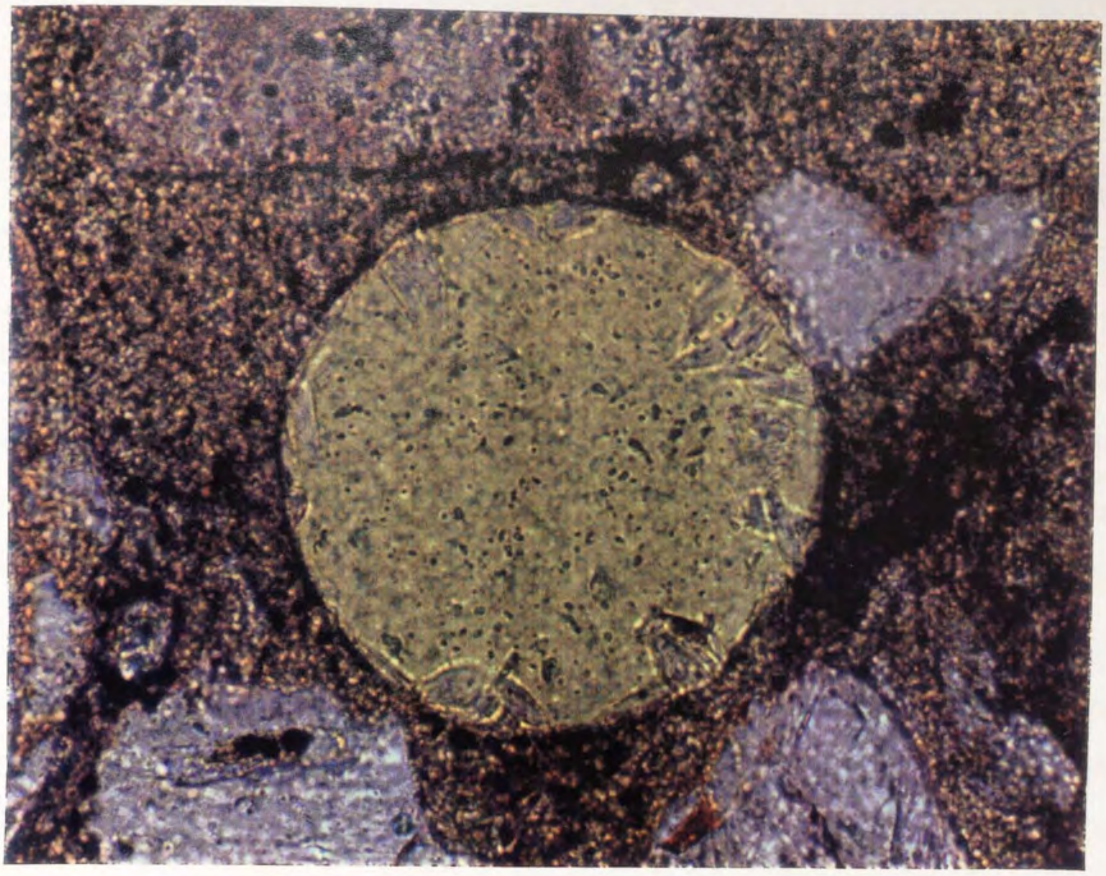

Plate 4.7 - Petrographic Image of Crystal Growths within Pores (Potassium Acetate) x 400 Mag.

Plate 4.8 - Scaling Damage to Bottom Surface of Partial Immersion Sample (Potassium Acetate) x 1.6 Mag.

damage was also noted on the bottom face of the samples. Flakes of discoloured cement paste became loose and separated from the main body of the sample (Plate 4.8).

TGA/DTA analysis of the loose material from both above and below the solution level was inconclusive as the trace obtained showed no identifiable characteristics of a cement paste. It was assumed that the test sample contained so much potassium acetate that the OPC peaks were obscured. XRD analysis of the material only showed that the portlandite levels had been reduced and that calcite ($CaCO_3$) was present. The calcite was most likely due to the natural carbonation process acting on the material above the solution level. Due to the problems incurred with the thermal analysis, the sample had been gently rinsed in deionised water prior to analysis and therefore it was understandable that no potassium acetate was evident in the sample.

However, the XRD analysis of other sections of the partially immersed samples did show a number of peaks of which not all could be explained. The sample taken from the surface of the immersed section gave peaks with d-spacings of 7.020Å, 2.331Å and 2.021Å (Appendix B - Trace 3). The sample taken from the interior of the immersed section also gave peaks with d-spacings of 2.331Å and 2.021Å. None of these d-spacings coincide with the published data for potassium acetate. An extra peak was also observed from the sample taken from the surface of the top section, but this appeared to be due to calcite (carbonation).

XRD analysis from the surface area of the diffusion sample showed no differences when compared to the control OPC sample. However, the DTG trace obtained showed two changes from that obtained from the bulk of the specimen (Peaks F and G - Figure 4.13). A peak was present prior to that representing the dehydration of the C-S-H gel at between 50°C and 60°C. It was thought that this would most likely be due to the release of water. Normally the moisture present in samples is removed in the desiccator by the silica gel. However, potassium acetate attracts moisture very strongly and it is therefore likely to remain in the sample. A sample containing potassium acetate is also likely to pick up moisture very rapidly from the laboratory atmosphere when being packed into the sample holder and placed into the apparatus.

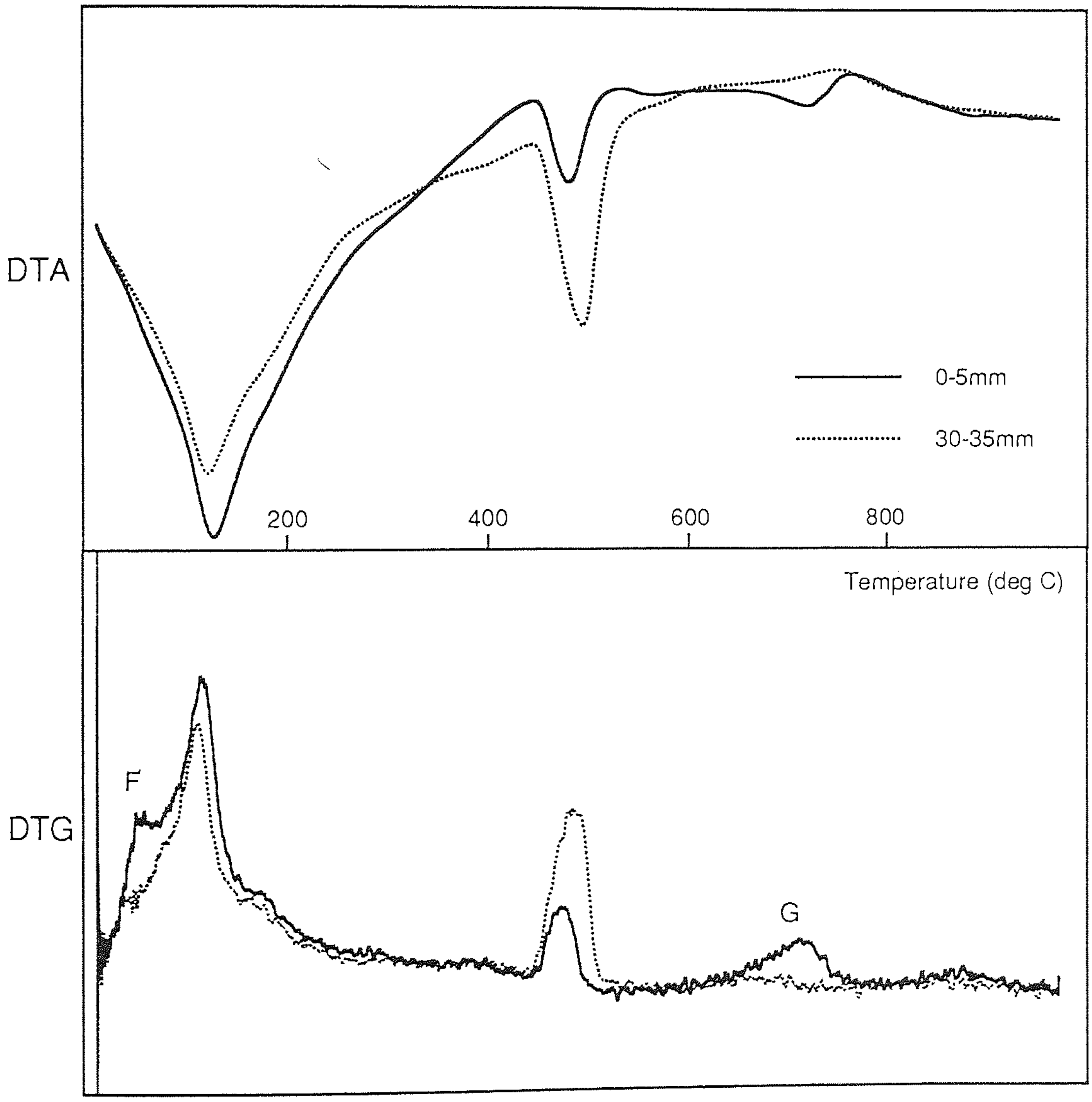

Figure 4.13 - DTA and DTG Analysis (Potassium Acetate)

The characteristic temperature of the second extra peak is hard to identify, but the peak temperature occurs at approximately 710°C. As with the sodium formate samples, this peak coincides with a peak present in the trace obtained from the pure chemical (≈725°C) and it is most likely the source.

The unidentified XRD peaks indicate that some form of chemical interaction may have occurred, but as it appears that degradation was only visible when a forced drying regime was employed, the primary mechanism of damage was of a physical nature due to crystallisation of the chemical within the pores and not of a chemical one.

4.3.2.1 Ionic Diffusion

Depth	OH^-	Ac^-	Na^+	K^+	Ca^{2+}
1.8	47	1199	38	921	100
3.5	60	972	58	812	67
7.0	233	351	79	432	2
10.5	334	191	77	419	1
14.0	448	69	69	419	2
17.5	477	63	77	441	2
21.0	449	61	72	432	1
24.5	502	49	77	478	1
28.0	464	36	72	436	1
31.5	500	49	77	468	1
35.0	477	71	72	436	1
38.5	514	64	77	507	2
42.0	486	91	84	468	2
45.5	535	65	104	497	1
49.0	513	88	79	459	1
Depth in mm and concentrations in mM					

Table 4.6 - Experimental Diffusion Data (Potassium Acetate)

As with the other test solutions, the constituents of the solution diffused into the paste samples and the ionic profiles followed the trends as described previously. The apparent diffusion coefficients for the acetate, sodium and potassium ions were $1.91 \times 10^{-12} m^2/s$, $4.0 \times 10^{-13} m^2/s$ and $7.5 \times 10^{-13} m^2/s$ respectively. The experimental results are shown in table 4.6 and graphically in figure 4.14.

4.3.2.2 Effects on Porosity

The MIP results also showed similar trends to those seen previously for the other test solutions. There was an increase in the volume of pores in the 0.03μm to 0.2 μm diameter range in the surface sample. This resulted in an increase in total porosity from 0.0914cc/g between 5mm to 10mm from the surface to 0.1052cc/g at the surface (Figure 4.15). As with the other test solutions this change was primarily attributed to the release of calcium hydroxide deposits into solution.

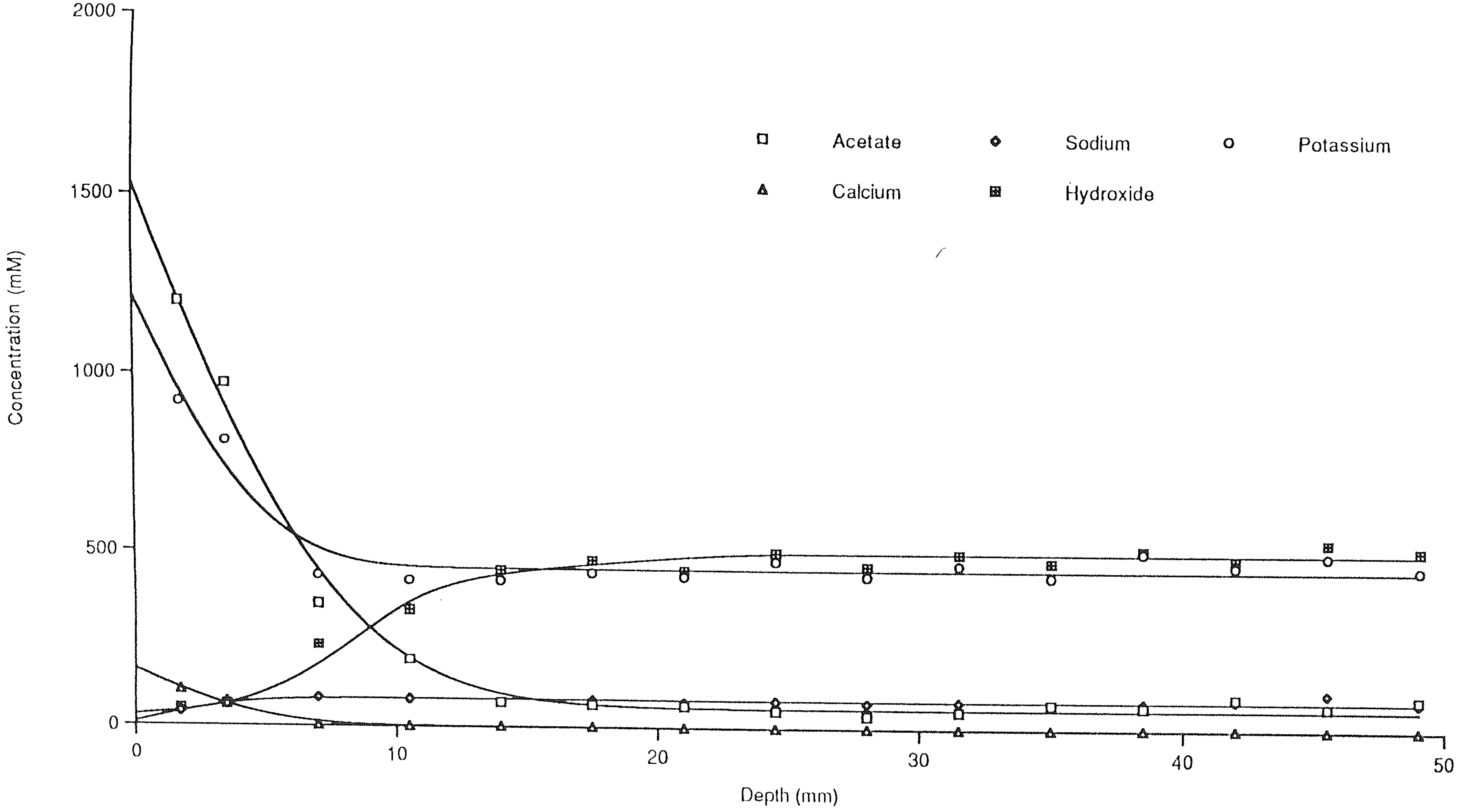

Figure 4.14 - Actual and Theoretical Pore Solution Profiles (Potassium Acetate)

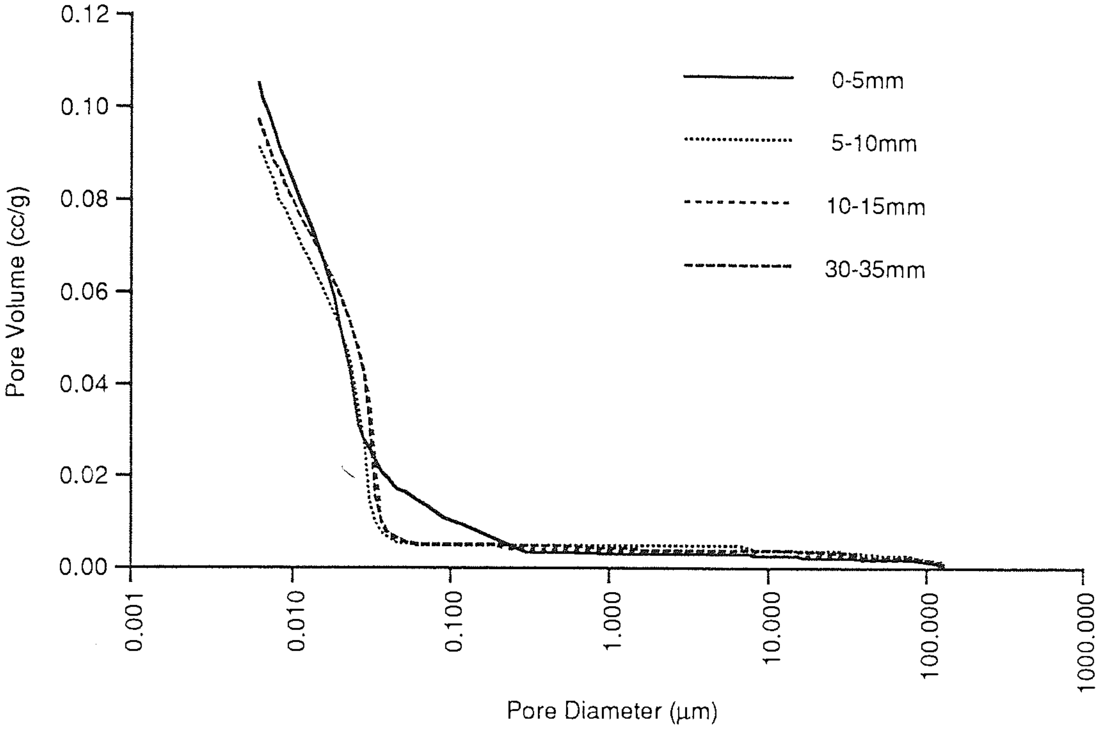

Figure 4.15 - Cumulative Pore Size Distribution (Potassium Acetate)

4.4 The Effect of Calcium Magnesium Acetate on Reinforced Concrete

4.4.1 The Electrochemical Behaviour of the Embedded Steel

Figures 4.16 and 4.17 show the results obtained from monitoring the potential and corrosion rates of the steel bars. As the cycling regime progressed the recorded potentials at all three depths became less negative until they reached a steady value of approximately -50mV vs SCE. When the readings were taken more frequently, the potentials became a little less stable, but never reached levels below -100mV vs SCE. During the constant ponding stage, the instability was reduced presumably due to the standardisation in moisture content and when the slabs were allowed to dry out, the potentials became more positive with values between 0mV and +50mV vs SCE. Throughout the whole test period the corrosion rates were very low and never exceeded the threshold value. When the reinforced samples were broken up the steel samples showed no evidence of corrosion.

As the potentials of the steel bars were quite high and all three layers of steel were seen to follow the same trends with very similar values, it was thought that the readings may not be giving an accurate indication as to the actual potential of the steel. It was thought that the surface deposits which formed on the surface of the blocks, which will be discussed later, may have been responsible by increasing the resistance of the circuit. At the end of the main testing period, the top 5mm of two of the reinforced concrete blocks was removed with an orbital grinding wheel lubricated with water. Potential readings were then immediately taken. For a number of weeks afterwards the blocks were continuously ponded with deionised water and the potential of the steel bars recorded. Although initially the potentials did drop from the

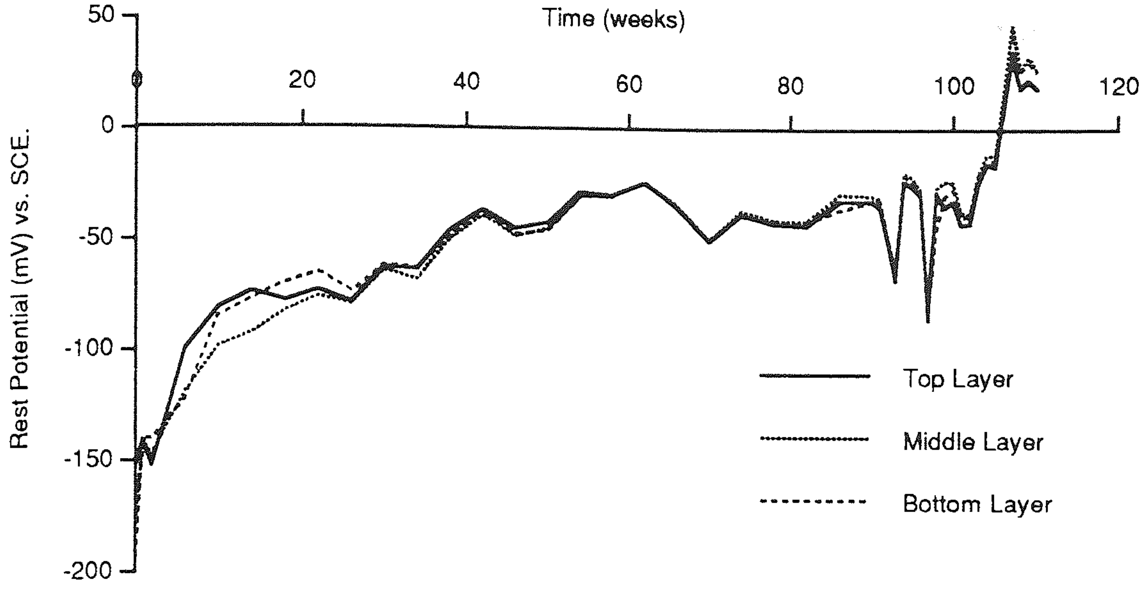

Figure 4.16 - Rest Potential against Time (Commercial grade CMA)

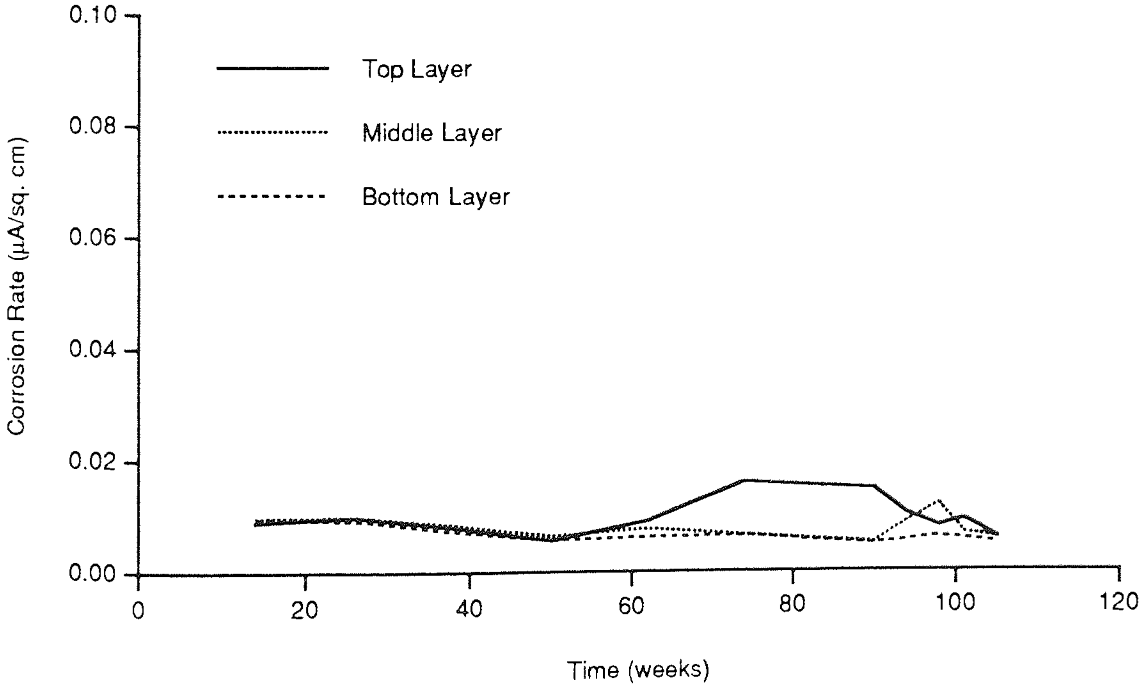

Figure 4.17 - Corrosion Rate against Time (Commercial grade CMA)

previous values (+50mV vs SCE) to around -100mV vs SCE, the potentials then rose back to those recorded prior to removing the top of the concrete blocks. It was thought that with the removal of the top surface the potentials would have changed to values in the range -100mV to -200mV vs SCE as was seen with the samples ponded with sodium formate and potassium acetate. As this was not the case it can only be assumed that those recorded throughout the test period were correct readings of the potential of the steel.

4.4.2 Chemical and Physical Interaction with the Cementitious Matrix

4.4.2.1 Surface Deposits

Although no damage was visible on the top surfaces of the blocks, their appearances had changed. A powdery off-white deposit was present which was thought to be insoluble calcium and magnesium carbonate which is a constituent of the commercial grade chemical. Underneath the loose material there was another layer of white material which appeared to be attached to the surface (Plate 4.9).

Similar deposits were seen on both the paste diffusion and partial immersion samples. Both visual and microscopic inspection showed this layer on the paste samples to be comprised of two parts. The outer layer consisted of loose white crystalline deposits which can be seen on plate 4.10. TGA/DTA analysis of this material indicated that it was entirely made up of magnesium hydroxide. The inner layer was almost transparent and could only be seen clearly under a microscope. The layer was made up of what appeared to be fibres aligned perpendicular to the exterior surface of the specimen (Plate 4.11). EDXA analysis of this layer showed that the composition varied considerably depending where on the layer the reading was taken, but magnesium was

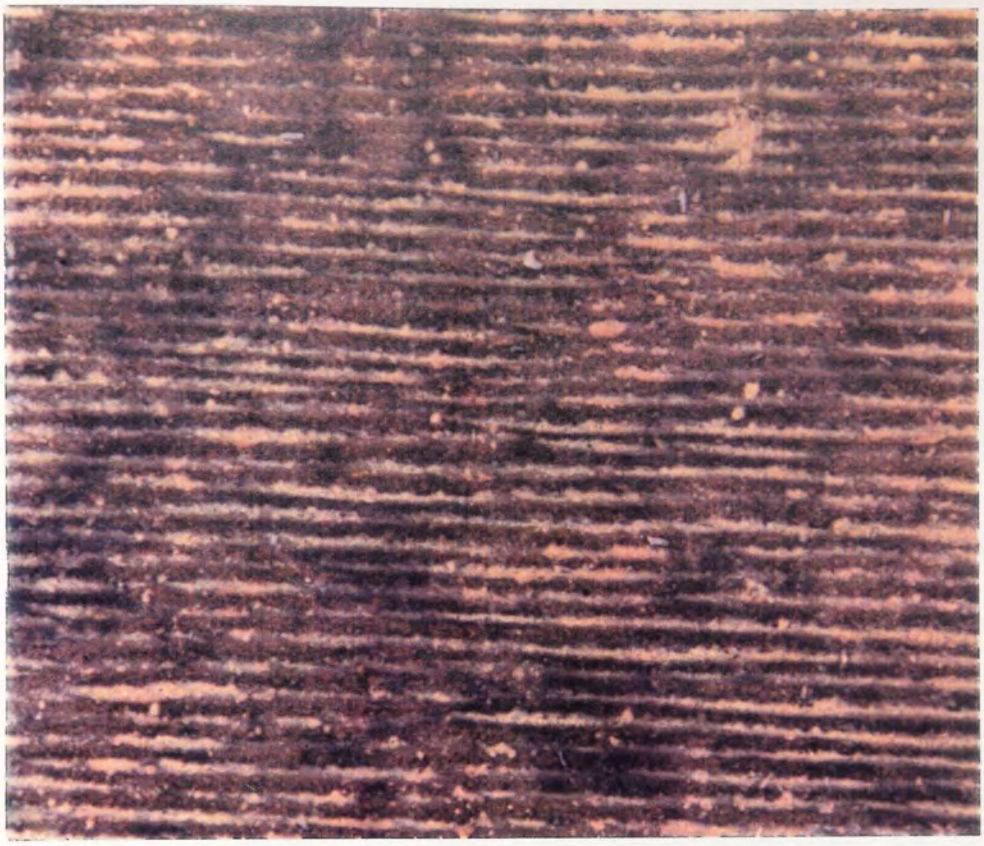

Plate 4.9 - White Deposits Precipitated in Grooves on Ponded Surface (Commercial grade CMA) x 3 Mag.

Plate 4.10 - Deposits Precipitated on Diffusion Specimens (Calcium and Magnesium Acetate) x 1.8 Mag.

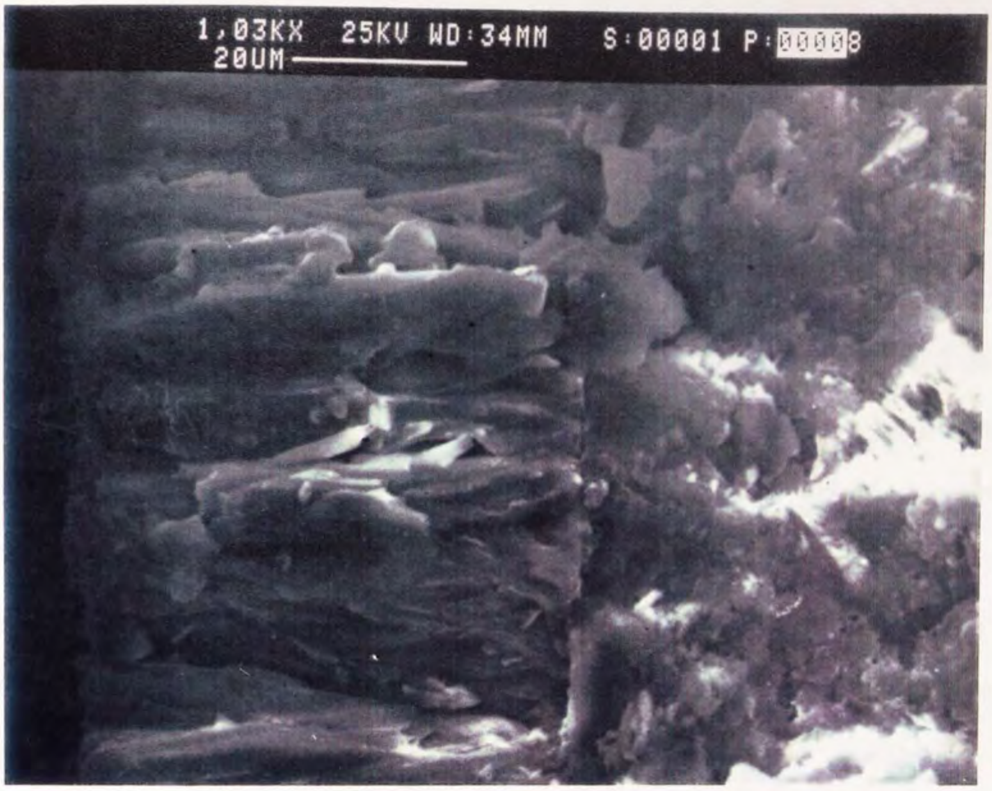

Plate 4.11 - SEM Image of Surface Zone of Diffusion Specimen (Calcium and Magnesium Acetate) x 1030 Mag.

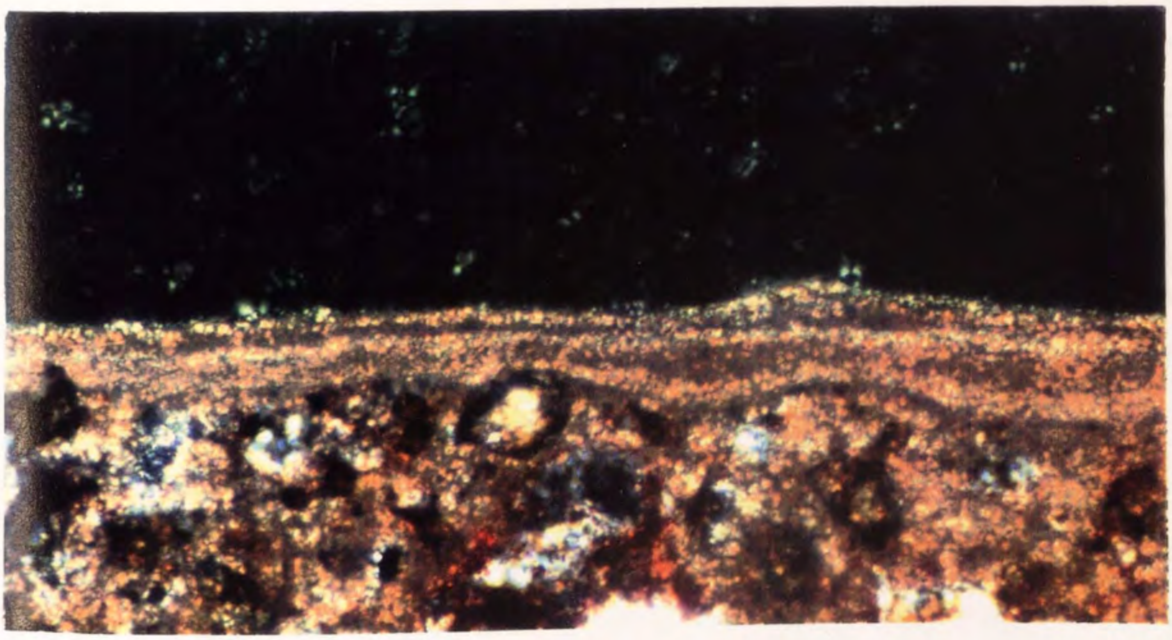

Plate 4.12 - Petrographic Image of Surface Deposit on Concrete Block (Commercial grade CMA) x 400 Mag in Plane Polarised Light

found to be most abundant. Of the elements capable of being determined by the method, between 41% and 83% was magnesium. The next most abundant element detected was calcium with between 10% and 47%. From this it was concluded that the surface deposits on the paste surface were of mixed composition; mainly consisting of calcium and magnesium hydroxide.

The build-up of the deposits on the paste samples was thought to be based on the following model. As the hydroxide ions diffuse out from the paste into the external solution, in the absence of external stirring, the pH of the external solution is increased. At these pH values the solubility of calcium and magnesium decrease. When the solubility for that pH is reached they react with the hydroxide ions and precipitate out as magnesium and calcium hydroxide. Magnesium hydroxide has a lower solubility (0.009g/l at 18°C) than calcium hydroxide (1.85g/l at 0°C) and therefore magnesium hydroxide will predominate in the deposits. The remaining soluble hydroxides diffuse away into the bulk of the external solution and an hydroxide profile will develop close to the sample's exterior surface. When the pH has dropped below 12.6, the pH of saturated calcium hydroxide, only magnesium hydroxide will be precipitated and therefore as the distance from the concrete surface increases the predominance of magnesium hydroxide in the surface deposits will increase as was seen in the experimental results.

However, no insoluble hydroxide layer was visible in the thin section produced from the concrete block. What was evident was a thin deposit of material on the surface which appeared to have been laid down in a number of very thin layers (Plate 4.12). It was not possible to determine the composition of the layer, but it appeared to resemble the general appearance of carbonated cement paste [Sibbick, 1994]. It is thought that a thin layer on the surface was composed of the calcium and magnesium carbonate present in the commercial deicer.

4.4.2.2 Ionic Diffusion

As both calcium and magnesium ions have very low solubilities in alkaline solutions, it implies that neither ion is able to diffuse into the cement paste until the pH of the pore solution has been significantly reduced. This was seen experimentally in the results of the diffusion experiments which can be seen in table 4.7. Magnesium was only evident in very small quantities in the pore solution taken from the area closest to the exposed surface.

Depth	OH^-	Ac^-	Na^+	K^+	Ca^{2+}	Mg^{2+}
1.8	31	1315	11	37	666	1
3.5	44	912	46	180	422	0
7.0	52	650	88	386	111	0
10.5	246	223	76	397	5	0
14.0	326	156	70	384	5	0
17.5	457	60	72	408	5	0
21.0	500	35	69	420	5	0
24.5	514	38	70	429	3	0
28.0	542	16	71	434	3	0
31.5	544	27	69	441	3	0
35.0	562	14	71	448	3	0
38.5	549	22	70	450	3	0
42.0	565	12	74	455	3	0
45.5	557	21	69	443	3	0
49.0	567	21	78	474	3	0

Depth in mm and concentrations in mM

Table 4.7 - Experimental Diffusion Data (Calcium and Magnesium Acetate)

Calcium was only present in significant amounts close to the surface. It is noticeable that where high calcium concentrations were found, the associated hydroxide level was low.

Whereas the deposited layer seen on the partial immersion specimen appeared to be made up in one growth, the layer on the diffusion sample appeared to be constructed in four separate stages. The four stages were thought to coincide with the four changes in solution. Each crystal growth was thinner than the previous one. It is possible therefore that the hydroxide layer acted to impede the diffusion of hydroxide out of the paste sample and as the thickness increased so the amount of hydroxide available to form the next layer decreased. It is also possible that the diffusion of hydroxide ions from the interior of the sample was insufficiently rapid to maintain the concentration at the surface which subsequently reduced the amount of insoluble material produced. The effect of the precipitation of calcium and magnesium hydroxide on the sample surface means that the pH of the external solution is kept at a lower level than would have been present with the other test solutions. The increased concentration gradient would aid the diffusion of hydroxide out of the paste sample which may have implications for the long term protection of any embedded steel.

As with the other test solutions, the sodium, potassium and acetate ion profiles could be modelled using Fick's 2nd. law. The apparent diffusion coefficients of the acetate, sodium and potassium ions were $2.91 \times 10^{-12} m^2/s$, $6.86 \times 10^{-13} m^2/s$ and $1.91 \times 10^{-12} m^2/s$ respectively. Both the actual and theoretical profiles are shown in figure 4.18.

As the pH of the pore solution near to the exposed face was reduced more than with the other test solutions, it was only to be expected that the degree of

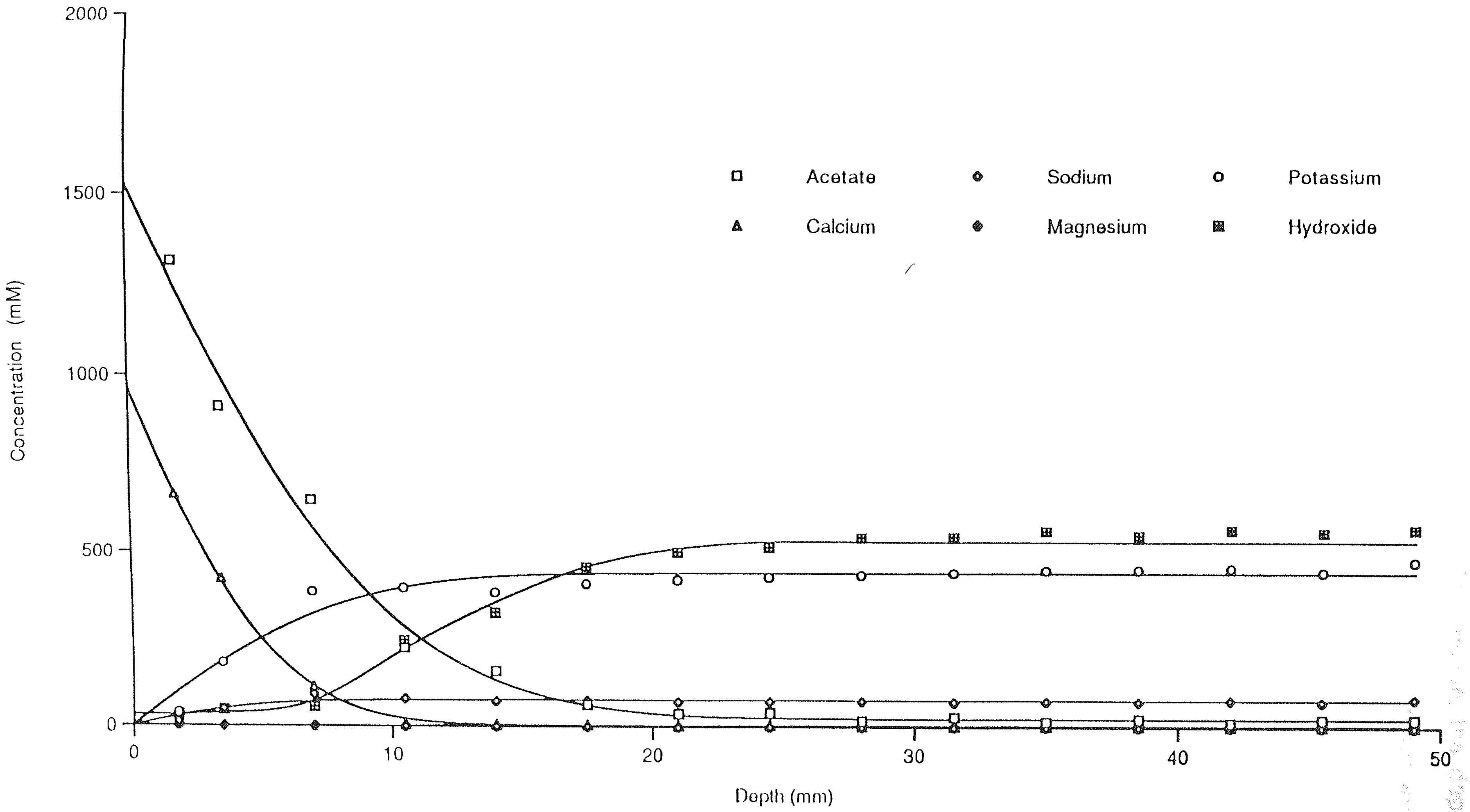

Figure 4.18 - Actual and Theoretical Pore Solution Profiles (Calcium and Magnesium Acetate)

portlandite depletion would be greater. In the thin section, the depth of the depletion zone was just under twice that seen with the other test solutions. A far greater reduction in the intensity of the portlandite DTA peak was also seen.

4.4.2.3 Effects on Porosity

The results of the MIP analysis showed very similar trends to that seen with the other test solutions (Figure 4.19). The total porosity of the 5mm layer closest to the exposed surface (including the insoluble hydroxide layer) had the highest value (0.1210cc/g). The porosity between 5mm and 10mm from the surface was 0.0853cc/g. The difference between the two values was accounted for by an increase in the volume of pores in the 0.03µm to 0.2µm diameter range which was thought to be due primarily to the release of portlandite into solution.

4.4.2.4 Pore Solution Data from the Concrete Blocks

Block No.	Depth (mm)	Evap. Water (%)	Acetate (mM)	Hydroxide (mM)
1	3.75	4.88	397	132
	15	5.01	182	253
	30	4.40	190	303
	45	4.47	129	321
	60	5.14	201	229
2	3.75	4.61	537	125
	15	4.63	139	347
	30	4.98	109	312
	45	4.44	---	---
	60	4.74	271	193

Table 4.8 - Pore Solution Data from Ponded Slabs (Commercial grade CMA)

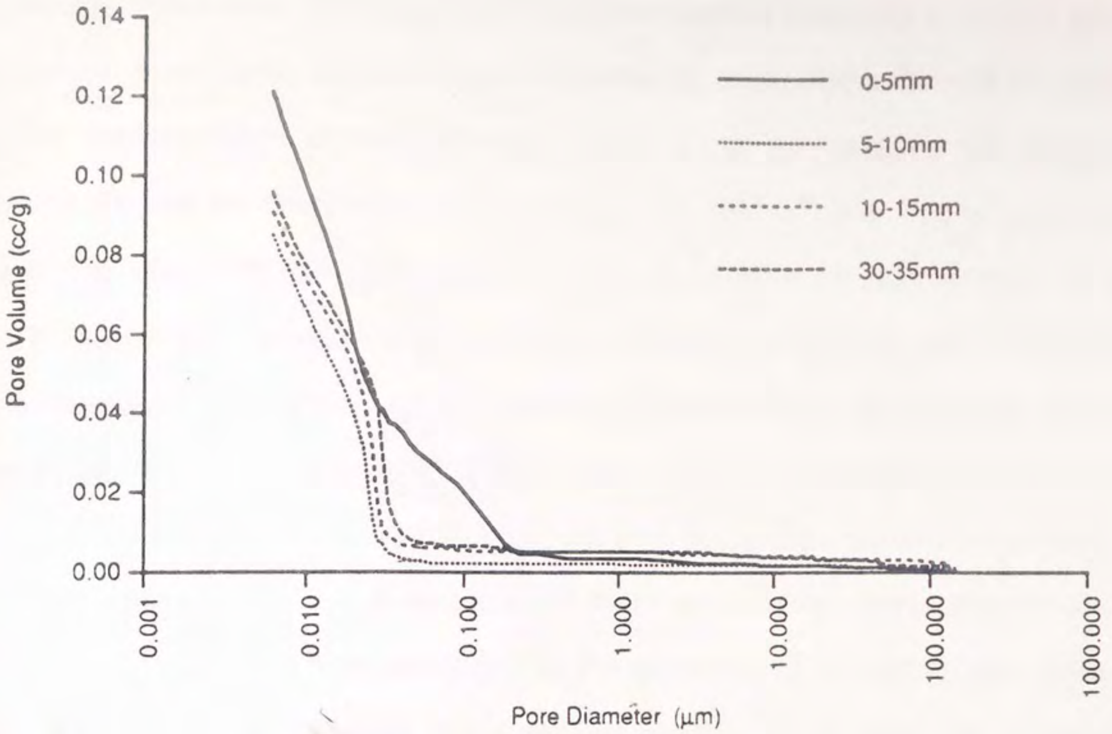

Figure 4.19 - Cumulative Pore Size Distribution
(Calcium and Magnesium Acetate)

Plate 4.13 - Damage on Side Wall of Ponded Slab Reservoir
(Commercial grade CMA) x 1.5 Mag.

Although there were differences in the ionic profiles obtained from the paste specimens for each of the four test solutions, the general levels of deicer anion ingress were similar. However, this was not the case for the concrete blocks as can be seen when the pore solution data (Table 4.8) is compared with that seen with the other test solutions. In addition to the reduction in the level of acetate ingress, the amount of evaporable water was also lower than the others. It was thought that these differences were due to the surface deposits. From the pore solution data it was clear that hydroxide did leach out of the blocks into the external solution and therefore insoluble hydroxides must have been formed. It was thought that the carbonate layer prevented the insoluble hydroxides from attaching to the concrete block. When the remains of the deicer were removed at the end of each cycle so were the hydroxide deposits.

4.4.2.5 Chemical Degradation

Although the main surface of the test slabs seemed to be unaffected (with the exception of the surface layer), there was slight damage seen in small isolated areas on the sides of the reservoirs (Plate 4.13). The hardened cement matrix seemed to be reduced to a fine non binding paste. Damage of this sort was also seen on the partial immersion specimens. The damage was more serious on and above the level of the solution where a trough in the cement formed around the circumference of the sample. Below the level of the solution under the hydroxide layer a slower but still noticeable uniform level of disintegration was seen to be occurring all over the submerged area. The damage seemed to be in the form of discoloration and softening of the paste. Inspection of the thin section from the partial immersion sample showed a zone of portlandite depletion on the submerged section extending between 2mm and 5mm into the body of the specimen. The calcium and magnesium hydroxide layer was evident on the external surface of the submerged sections and also in some air voids close to the surface. No other differences could be seen. As with the thermal analysis of the damaged section of the potassium acetate sample, the trace obtained with calcium magnesium acetate was far removed from the normal OPC trace which made analysis difficult, but a number of differences were noted. The portlandite deposit was severely depleted and magnesium hydroxide deposits were visible. A peak which was thought to represent the breakdown of calcium carbonate was also seen to be present in the test sample. However, this may have been due to the natural carbonation process after the damaged material had broken away from the remainder of the specimen.

As the diffusion paste samples were not as contaminated with calcium and magnesium acetate as the partial immersion samples, it was possible to draw more conclusions as to the chemical's effect on cement from these. As with the other test solutions, the DTG trace proved to be the most useful in establishing the differences in the samples (Figure 4.20). A number of differences were seen when the traces were compared, but the majority could be explained by combining those from the OPC control specimen and the deicing chemical. Of those which could not be attributed to the normal OPC or deicing chemical peaks, the first difference was that in the surface layer there was a peak with characteristic and peak temperatures of 330^{o}C and 385^{o}C respectively (Peak H). This coincided with the dehydration of magnesium hydroxide. The peak was not seen in the sample between 5mm and 10mm from the surface, thus confirming the view that under normal circumstances magnesium ions are not able to diffuse into cement paste. The relative intensity of the portlandite peak in the surface layer was reduced when compared to that in the other three samples taken from further into the interior of the specimen. At approximately 900^{o}C (peak temperature 930^{o}C) a reaction was recorded (Peak I), but it was not possible to explain its appearance. The peak superimposed on to that of the dehydration of C-S-H gel with a peak temperature of 95°C was thought to be due to magnesium acetate (Peak J). The one with a peak temperature of 730°C (Peak K) coincided with one seen on the pure calcium acetate trace.

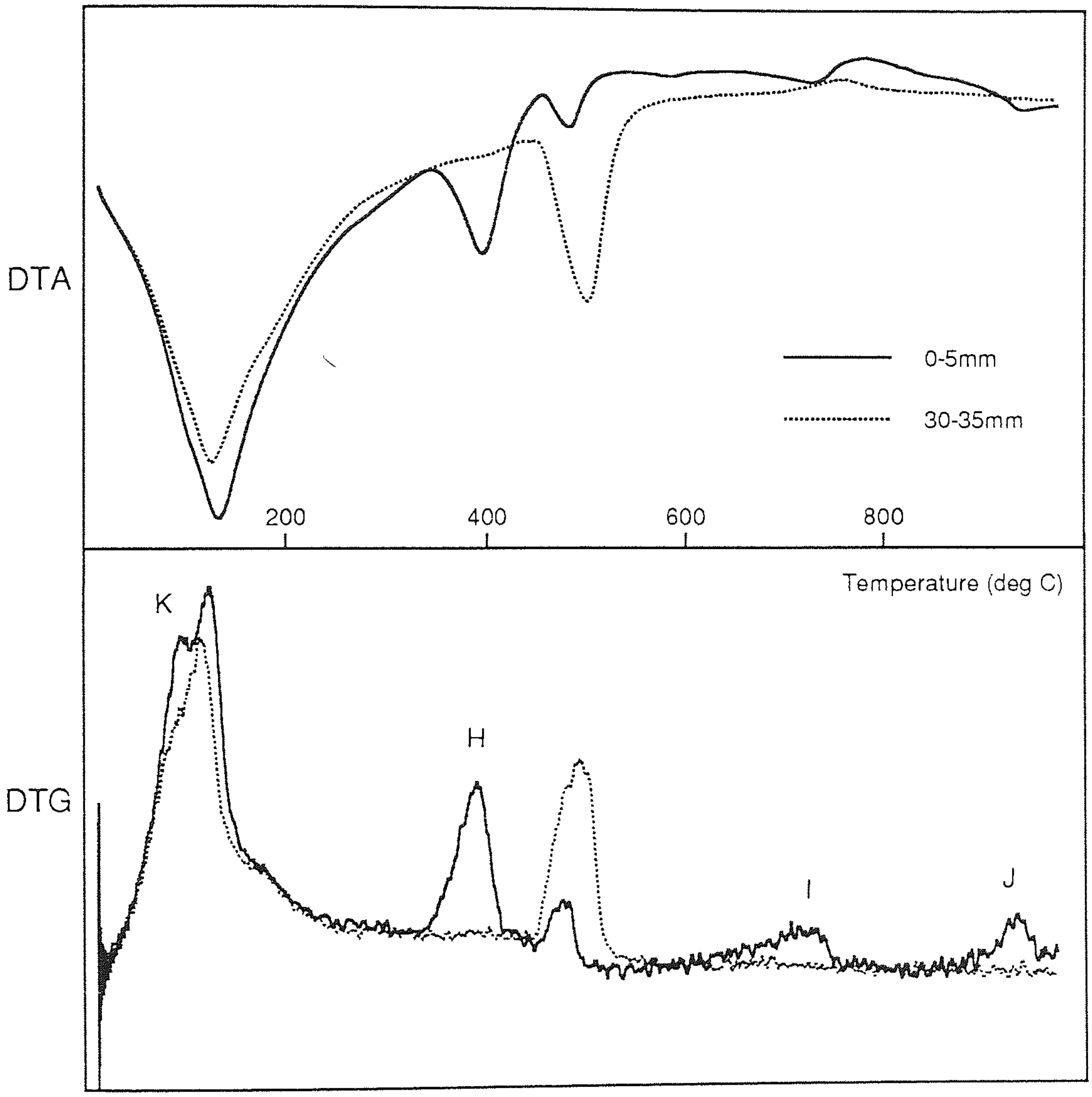

Figure 4.20 - DTA and DTG Analysis (Calcium and Magnesium Acetate)

In chapter 2 it was stated that CMA induced damage was thought to be similar to that induced by magnesium chloride. Biczok [1964] has claimed that this type of damage is completely due to the magnesium ion and not chloride. It has already been shown that magnesium hydroxide is formed on the surface of cement paste samples when in contact with magnesium acetate in the absence of insoluble carbonates. The pH of a saturated solution of magnesium hydroxide is approximately 10.6. At these pH values hydrated calcium silicate is unstable and it releases calcium hydroxide into solution to re-establish its equilibrium pH [Lea, 1970]. Immediately the calcium hydroxide reacts with more magnesium acetate again lowering the pH to 10.6. Assuming the layer of magnesium hydroxide remains on the surface of the concrete or cement the magnesium hydroxide layer acts as a semi-impermeable barrier to slow down the ingress of magnesium acetate and therefore the rate at which the decalcification of the C-S-H gel occurs. However, the layer is not completely impermeable and the process still occurs. The silica gel formed then reacts very slowly with the magnesium hydroxide forming what is sometimes called M-S-H gel. It is thought that this hydrated magnesium silicate has no binding power and therefore the cement matrix begins to deteriorate [Steopoe, 1936 as cited by Lea, 1970].

Cole [1953] analysed a sample of M-S-H gel by both XRD and thermal methods. It was found that the composition could be expressed ideally as $4MgO.SiO_2.8.5H_2O$, but suggested that the structural formula was $3Mg(OH)_2.MgSiO_3.5.5H_2O$. The XRD trace of the damaged material did show a number of extra peaks to those present on the control sample and also a number which were missing. However, all but one could be attributed to the removal of portlandite and deposition of magnesium hydroxide. The exception was a very sharp peak with a d-spacing of 2.047Å (Appendix B - Trace 4). Unfortunately Cole did not publish d-spacings for the M-S-H compound and therefore it is not possible to say categorically that it was present in the sample, but there is a small amount of evidence that the quantity of C-S-H gel was depleted. Hydrated C-S-H gel is not very easy to identify by XRD as its peaks tend to be far less intense and therefore overwhelmed by the more crystalline deposits such as portlandite. One of the larger C-S-H gel peaks has a d-spacing of 3.07Å and it was seen both in the trace from the surface of the diffusion specimen and the damaged material that the intensity of this peak may have been reduced when compared to that of the control sample (Appendix B - Traces 4 and 5).

In addition to the differences stated above, a number of others were noted. The surface of the diffusion sample exhibited a single peak with a d-spacing of 3.373Å. A peak with a d-spacing of 2.325Å and a smaller one with a value of 9.205Å were noted on the sample taken from the surface of the submerged section of the partially immersed sample.

Although there was no direct evidence to suggest the mechanism responsible, It was clear that a mixture of calcium and magnesium acetate is capable of degrading cement paste. It seems acceptable to suggest that the degradation occurred by a similar mechanism to that seen with magnesium chloride. However, as the majority of the top surface of the concrete slab was unaffected, it is thought that the insoluble surface carbonate layer, formed when using commercial grade CMA, was responsible for slowing down and possibly entirely preventing the process of attack.

4.5 General Discussion

4.5.1 Ionic Diffusion

In the situation of constant immersion using SLR grade chemicals similar ionic profiles were evident for all four solutions. From the apparent diffusion coefficients (Table 4.9) it was seen that chloride ions from the sodium chloride solution diffused at a faster rate than the other deicing anions.

Anion	Apparent Diffusion Coefficient (m^2/s)
Chloride	3.50×10^{-12}
Formate	1.91×10^{-12}
Acetate (K)	1.91×10^{-12}
Acetate (Ca & Mg)	2.91×10^{-12}

Table 4.9 - Comparison of Apparent Anion Diffusion Coefficients

One of the better ways of demonstrating the effect of different apparent diffusion coefficients is to calculate the time taken for a threshold concentration to be reached at a specified cover depth. BS5400 [British Standards Institute, 1990] states that for concrete directly exposed to deicing chemicals (ie. bridge parapets) the minimum accepted cover depth between the reinforcing steel and the external surface is 50mm. For structures treated with rock salt it has been suggested that a realistic external chloride concentration would be 2 molar [Sibbick, 1994]. If the apparent diffusion coefficients calculated previously and the assumptions above are used then it is possible to calculate the time for a set concentration to be reached. For example, for a threshold concentration of 500mM then it would take 104 months for it to be reached when sodium chloride was used. With calcium and magnesium acetate the time span would be 125 months and 191 months for either sodium formate or potassium acetate[4.2] .

The reason for the difference in apparent diffusion coefficients can be related to the size of the hydrated ion. In the absence of chemical interaction with the pore walls of cement and other species, the smaller the size of the hydrated ion, the greater its diffusion rate. However, the diffusion rate is greatly affected by the diffusing counter ion [Kondo *et al.*,1974]. For example, in their work on chloride salts, it was seen that chloride ions diffused more rapidly when introduced as potassium chloride rather than sodium chloride, potassium ions being smaller than sodium ions.

Therefore, as hydrated chloride ions are smaller than hydrated formate ions, the apparent diffusion coefficient of chloride ions (when introduced as sodium chloride) is greater than that for formate ions (when introduced as sodium formate), as can be seen from the experimental data in table 4.9. The apparent anion diffusion coefficients for sodium formate and potassium acetate can also be seen to be the same. This demonstrates the effect of differing cation on the apparent diffusion coefficient of the anion. Although hydrated formate ions are smaller than hydrated acetate ions, the difference in diffusion rates is cancelled out by the size of their respective cations.

Kondo *et al.* also found when magnesium chloride was used as the external solution, the diffusion rate for chloride ions was greater by approximately 2.8 to 3.3 times that when the cation was sodium or potassium. When calcium chloride was used, it was between 1.3 and 1.6 times greater. The increase in anion diffusion rate when in combination with calcium and magnesium based

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[4.2] Times to reach the threshold concentration were calculated using the VARYCOND computer program [Yu *et al.*, 1993b] compounds was also seen in the experimental work. The apparent acetate diffusion coefficient was 1.5 times that when potassium acetate was used.

As stated earlier, for all the four test solutions, the diffusion profiles for the major deicing anion could be modelled by an interpolation of Fick's 2nd. law. For this to be strictly correct it requires that at the surface of the sample the concentration of the anion in the pore solution is equal to that in the external solution. However, this was not seen from the experimental data.

Anion	Theoretical Conc. at Surface (mM)	Av. Actual Conc. between 0 & 3.5mm from Surface (mM)
Chloride	1334	1079
Formate	1362	1094
Acetate (K)	1534	1199
Acetate (Ca & Mg)	1531	1315

Table 4.10 - Comparison of Actual and Theoretical Surface Concentrations

In all cases both the interpolated theoretical surface concentrations and those present in the surface slice were significantly in excess of that of the external test solution (Table 4.10). Whereas the estimation process used in determining the theoretical surface concentration could give erroneous readings, there is no such reason for the same to be true for the actual pore concentrations determined for the surface slice.

The data from all four test solutions also appears to disagree with the published values of the calcium hydroxide solubility product. Values of 4.68×10^{-6} [Chang, 1992] and 8.9×10^{-6} [Damidot & Glasser, 1993] have been quoted, but those calculated from the pore solution data give values between one and two orders of magnitude greater. The values calculated from the work of Sergi [1986] also give values similar to those calculated in this present work. In calculating the solubility products the following equation was used.

$$K_{Ca(OH)_2} = [Ca^{2+}][OH^-]^2$$

However, this equation is not strictly correct as it assumes that the ionic activity coefficients are equal to unity. A more accurate form of the previous equation is

$$K_{Ca(OH)_2} = a_{Ca} \cdot a_{OH}^2$$

where a is the activity of the particular ion and is the product of the concentration of the ion multiplied by its activity coefficient.

The use of concentrations as opposed to activities is usually acceptable if the solid is sparingly soluble as the ionic strength of the solution is low and therefore the activity coefficients are close to unity. However, as has been seen, the pore solution of cement is not simply a saturated solution of calcium hydroxide. Firstly, the high hydroxide concentration will cause its activity coefficient to change and secondly, as stated by Glasstone and Lewis [1963], if other non-common ions are present in the saturated solution, its solubility increases due to the decrease in the activity coefficients. Therefore, in the context of a pore solution contaminated with a deicing salt, it is highly probable that the solubility products calculated from consideration of only the ionic concentrations will not be accurate.

Although the pore solution study of the diffusion characteristics of the four deicing solutions into hardened cement paste have demonstrated a number of features, they have also posed two questions. An attempt was made to explain the apparent deviation of the 'as calculated' calcium hydroxide solubility product from the values published in the literature, but it is still unclear why the deicing anion should appear to be present in the outer zones of the hardened cement paste at concentrations greater than that in the external solution. However, before too many conclusions are drawn from this apparent phenomenon it is felt that it would be prudent to repeat the experiments for at least one of the deicing solutions to verify the accuracy of the experimental methods.

4.5.2 Changes in Porosity

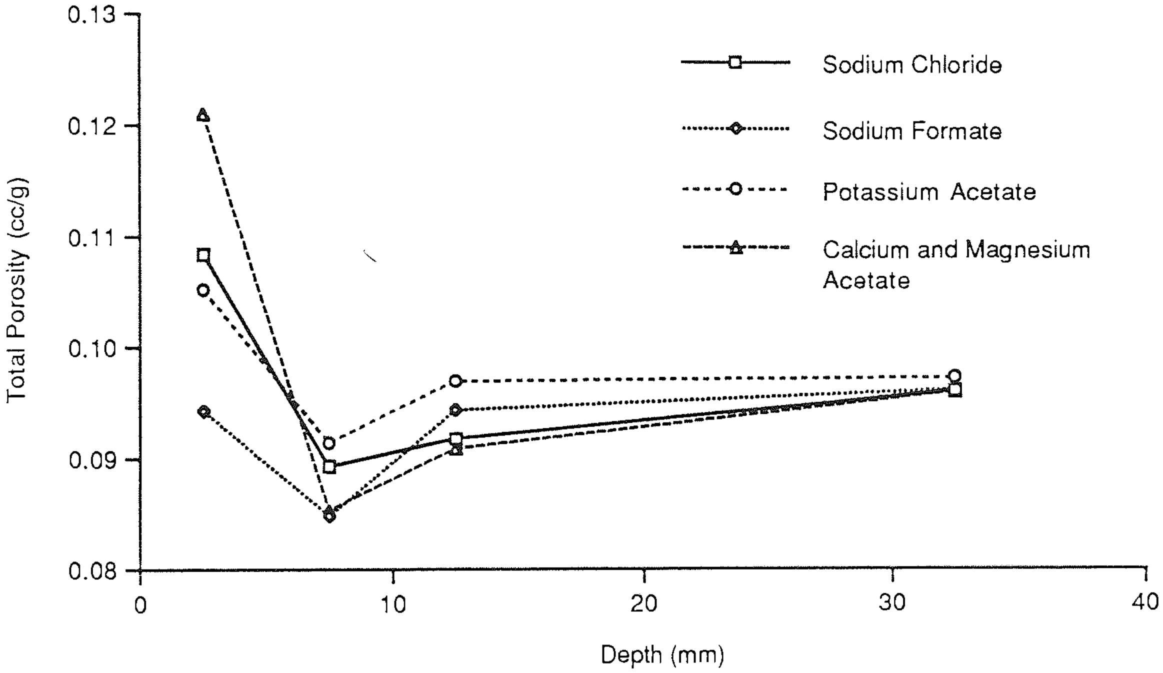

Figure 4.21 - Total Porosity against Depth

It has already been stated that at the exposed surface of all the diffusion specimens, irrespective of test solution, there was an increase in total porosity when compared to material taken from the next sample depth (5-10mm). This increase was attributed primarily to the dissolution of the portlandite deposits into solution, but also possibly from the dissolution of the C_3A reaction products as well. However, the results also appear to show that at greater distances from the exposed surfaces there then appeared to be an increase in total porosity, when compared to the 5-10mm samples, to a value of approximately 0.0965cc/g between 30 and 35mm from the exposed surface (Figure 4.21).

It seems reasonable to suggest that this value of 0.0965cc/g was the value of the total porosity of the paste samples prior to any interaction with the external test solutions and therefore it can be seen that, with the exception of the very surface layer, the external test solutions had the effect of apparently decreasing the total porosity. However, it is unwise to suggest that this apparent decrease in porosity would prove to be beneficial in reducing the degree of ingress of potentially aggressive ions.

It is possible that the cement hydration process had not finished by the end of the curing period and continued while the samples were immersed in the test solutions. Sergi [1986] has shown that, under similar immersion conditions, the evaporable water content was higher in the first 10mm from the exposed surface and this may have encouraged more rapid curing up to this depth. This theory agrees with the MIP data in that the larger decreases in porosity were only apparent in the zone between 5mm and 10mm from the exterior surface. However, in real situations with possibly older concrete samples, subjected to both intermittent wetting and drying cycles, it is unclear, if this is the mechanism responsible, whether the effect would be seen. It is also unclear whether the same effect would be seen when the paste samples were immersed in water without any deicing chemical. Sergi [1986] saw no such effect, but paste samples used in that work had been cured for a full year.

It is also possible that there was no reduction in the porosity of the cement paste, but the effect was merely due to the drying procedure which was carried out prior to the mercury intrusion. During the drying process, the ions crystallise out and partially reduce the pore space. The total ionic strength did not vary considerably between the 5-10mm and the 30-35mm sections of the samples immersed in any of the solutions, but the proportions of the actual species did. The size of each crystal formed depends upon its density and this may result in an increase in the volume of crystals formed.

4.6 Conclusions

It was seen that all the non-chloride deicing agents tested in this research programme were less corrosive than sodium chloride to steel embedded in concrete. However, the results appertaining to potassium acetate did give some cause for concern in that a small number of the steel samples near the exposed surface did show corrosion activity for a period of time. Potassium acetate also appeared to be unsuitable for use due to its deleterious effect on the cementitious matrix which was thought to be primarily a physical effect.

The calcium and magnesium acetate mixture also appeared to have potentially deleterious side effects in that the magnesium ion seemed to react with the C-S-H gel to form a non binding M-S-H gel. However, this effect may be reduced if insoluble material is combined in the commercial formulation allowing the formation of an impermeable barrier.

From the parameters studied, it appeared that sodium formate was the most promising replacement for sodium chloride as it had no significant deleterious effect on the integrity of reinforced concrete.

4.6.1 Recommendations for Further Work

In chapter 2 it was shown that although the new formate and acetate deicing chemicals show a great deal of promise in preventing the deleterious side-effects incurred with the use of rock salt there still remain a great number of aspects requiring further work and clarification. The test programme was devised to try and elucidate a small number of these and although it has gone some way to answering these questions the results also raise a number of new ones.

Of all the areas still requiring clarification it is felt that the following two are of most importance. Sodium formate's relatively benign effect on reinforced concrete makes it a potential replacement for sodium chloride. However, it would be beneficial to determine the maximum level of contamination that can be tolerated before corrosion of embedded steel is initiated. This could be carried out by embedding mild steel samples in cement paste or mortar samples to which varying amounts of sodium formate had been included in the mix water. By monitoring the condition of the steel over a length of time and also extracting the pore solution from parallel samples it would be possible to determine how much formate could be tolerated.

Since this programme was initiated it has come to the author's attention that the use of the commercial formulation of potassium acetate is being tried at airports, not only as deicer, but also as a means of reducing the amount of wear on the aircraft tyres during landing [Subramanian, 1994]. It is therefore likely to be used in much greater frequency than was formerly the case. It is thus very important that the deleterious effects experienced in this test programme are researched further to determine whether they will occur under the conditions experienced during normal usage.

PART 2

ELECTROCHEMICAL CHLORIDE REMOVAL

CHAPTER 5 - LITERATURE REVIEW: ELECTROCHEMICAL CHLORIDE REMOVAL

The process of the electrochemical removal of chloride ions from a reinforced concrete structure, as briefly stated in chapter 1, involves cathodically polarising the steel reinforcement with respect to a temporary anode attached to the exterior surface of the concrete. Under the action of the electric field, the negatively charged chloride ions (and hydroxide ions) migrate away from the reinforcement towards the concrete surface [Slater *et al.*, 1976]. The positively charge ions (sodium and potassium) are attracted to the steel reinforcement and this combined with the production of hydroxide ions at the steel locally increases the alkalinity. This decreases the chloride to hydroxide ratio and thus after the current is switched off the environment is less aggressive than before.

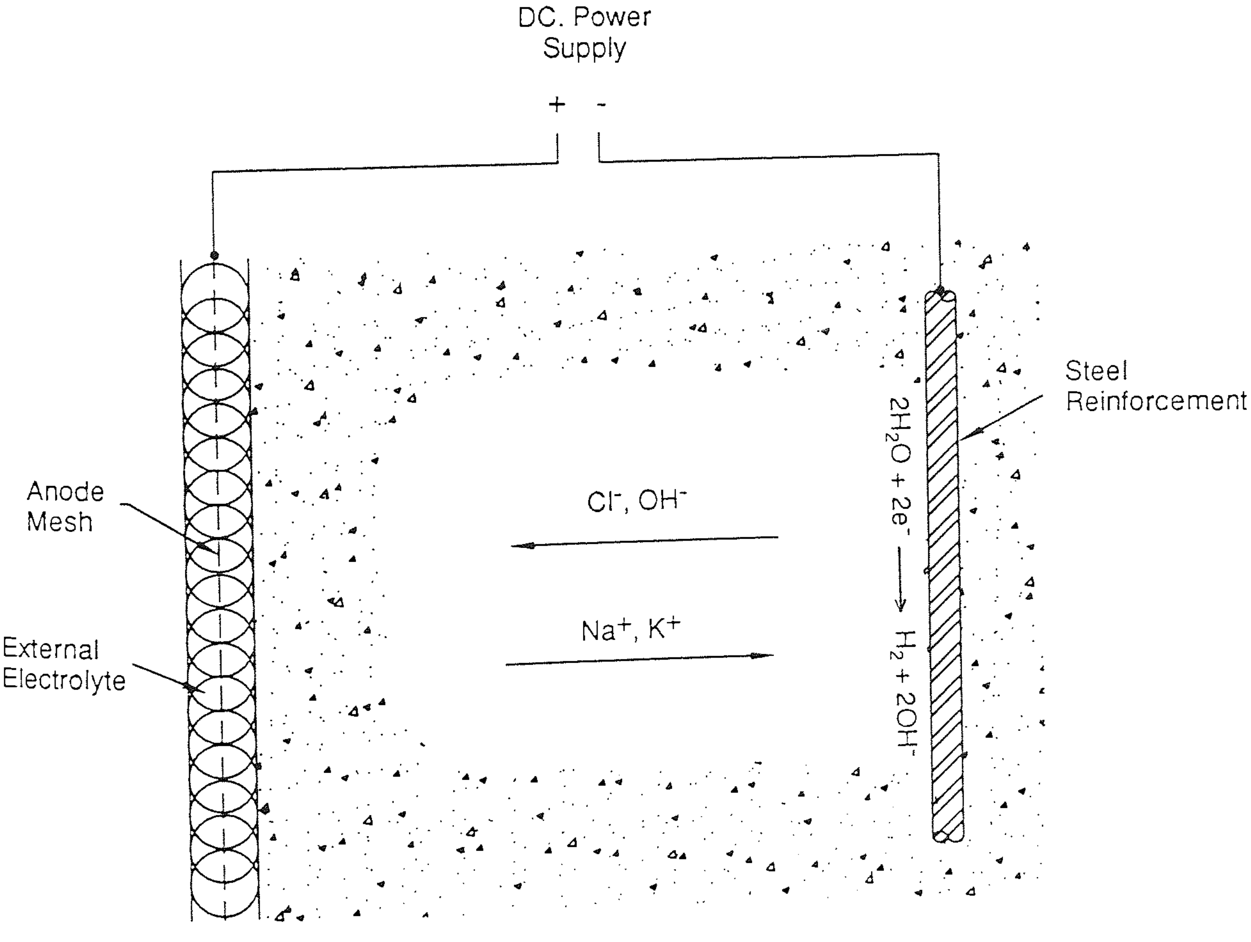

Figure 5.1 - Treatment Processes

5.1 Treatment Procedure

The first stage in the process is to ensure that all the reinforcement in the area requiring treatment is electrically connected. Insulated wires are then attached to the steel to provide the electrical connection to the power source. An anode system, comprising an electrode surrounded by an aqueous electrolyte, is fixed on to the surface of the concrete. The electrolyte ensures a uniform current distribution over the whole of the concrete surface. Connections from the anode and the reinforcement are then made to a suitable direct current electrical power source and current applied for the desired length of time. The current is then switched off and the anode system removed. It is also usual at this point to clean the treated surface and then, if considered necessary, to apply a surface coating to prevent further chloride ingress.

To ensure a relatively equal level of chloride removal from all areas of the concrete, it is necessary that the electrical resistance between the surface of the concrete and the reinforcement is uniform as current will flow preferentially through the areas of lowest resistance. The resistivity and, if a uniform cover depth is assumed, the total resistance between the concrete surface and the reinforcement is lower in corroding zones when compared to those which are not corroding [Polder & Ketelaars, 1991]. In cases where corrosion is exacerbated by low concrete cover depths the resistance in those areas will be even lower. Therefore, it is likely that the zones requiring the most treatment (the anodic areas) will receive a greater percentage of the current. However, the application of large amounts of current to relatively small areas may both locally damage the integrity of reinforced concrete and may also leave adjoining areas with significant amounts of chloride still present. (Both these potential side effects are considered in greater detail in section 5.4.) Attempts to improve the uniformity of the concrete resistivity can involve the patch repairing of areas of bad cracking and/or spalling. Whereas this will prevent the occurrence of short circuits between the anode and the reinforcement (which prevent the removal process being carried out), it is unclear how successful they are in ensuring uniform chloride removal. It is also possible to reduce the total treatment area into a number of smaller zones which can then be treated separately [Polder & Hondel, 1992], a technique frequently used in CP projects [Wyatt, 1992]. This gives an increase in the degree of control, but also increases the complexity of the treatment process.

5.2 Treatment Processes

5.2.1 Electrochemical Theory

A metal placed into an aqueous solution of its own ions has an equilibrium such as

$$M^{n+} + ne^- \rightleftharpoons M$$

For many systems this equilibrium is established rapidly and these are known as 'reversible' reactions. In other cases it can be established extremely slowly and these types of reactions are known as 'irreversible' [Crow, 1988]. Once equilibrium has been reached where the number of ions passing into and out of solution are equal, the potential of the electrode is known as the equilibrium potential (E_{eq}). The value of the equilibrium potential is governed by the difference in the electrochemical free energy between the electrode and that of a reversible reference electrode [West, 1970]

$$E_{eq} = \frac{-\Delta G_{eq}}{nF}$$

where

E_{eq} is the equilibrium potential

ΔG_{eq} is the change in electrochemical free energy between the electrode at equilibrium and the reversible reference electrode

n is the number of electrons transferred in the reaction

F is the Faraday constant

The value can also be calculated using Nearnst's equation

$$E_{eq} = E_o + \frac{RT}{nF} \ln \frac{a_{oxid}}{a_{red}}$$

where

E_{eq} is the equilibrium potential

E_o is the standard equilibrium potential

R is the gas constant

T is the absolute temperature

n is the number of electrons transferred in the reaction

F is the Faraday constant

a_{oxid}, a_{red} are the activities of the oxidised and reduced species

The application of an external current across an electrode/electrolyte interface which was previously at equilibrium changes the potential of the electrode by an amount known as the overpotential (η). The total overpotential can be thought to be made up of three major components; the activation overpotential, the concentration overpotential and the resistance overpotential [Crow, 1988].

5.2.1.1 Activation Overpotential

Figure 5.2 shows the electrochemical free energy changes at a metal/electrolyte interface at equilibrium. For the continual and equal movement of ions into and out of solution energy is required so that they can pass over the activation energy barrier and this is supplied by the thermal energy of the ions [West, 1970].

Aston University

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Figure 5.2 - Electrochemical Free Energy Profile across an Electrode/Electrolyte Interface [West, 1970]

If the potential of an electrode is changed by a small amount in the anodic direction from its equilibrium value by the application of an external emf. then the electrochemical free energy profile is changed as demonstrated in figure 5.2. The effect of this overpotential is twofold in that the activation energy barrier in the direction

$$M \longrightarrow M^{n+} + ne^-$$

is reduced and in the reverse direction it is increased. This results in a increase in the rate of the dissolution process, a decrease in the deposition process and therefore a net anodic flow of current [Crow, 1988]. As the electrode process is rate-determined by the activation energy barrier then the overpotential is known as the activation overpotential.

The relationship between activation overpotential (η_A) and current (I) for a particular system is given by the empirical 'Tafel' equation [Shrier, 1982].

$$\eta_A = a \pm b \log I$$

where a and b are constants and are determined experimentally.

5.2.1.2 Concentration Overpotential

Concentration overpotentials (η_c) occur when the rate at which the reaction is taking place becomes limited by the mass transport of the reactant species either to or from the electrode surface [Page, 1988]. In the case of the dissolution of a metal anode, if the reaction is proceeding at a sufficient rate so that the metal ions are unable to move away into the bulk of the solution at the same rate at which they are being produced then they will become concentrated at the surface of the electrode. By considering Nernst's equation it becomes clear that the equilibrium potential for the reaction will increase [Shreir, 1982] and therefore the potential required at the electrode for the reaction to proceed at the specified rate when compared to the original equilibrium potential (ie. the overpotential) increases.

When plotted on an η - log I curve (a 'Tafel' plot), the effect of the concentration overpotential on the previously linear activation overpotential - log I relationship as dictated by the 'Tafel' equation can be seen in figure 5.3.

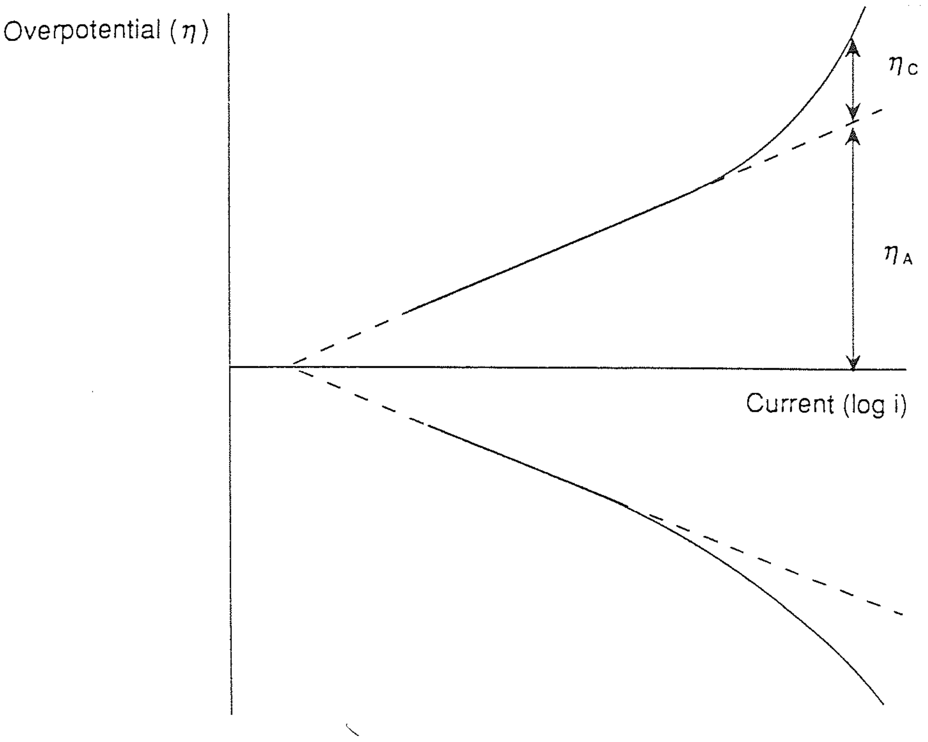


Figure 5.3 - Hypothetical 'Tafel' plot

5.2.1.3 Resistance Overpotential

The electrolyte around the electrode does not have an infinite conductivity and there is resistance against the flow of current between the anode and cathode. In order for the required current to flow, the potential has to increase to overcome the resistance.

Resistance overpotentials may also be caused where the surface of the electrode is covered by a relatively poor conducting layer. Such layers include oxide films and may result in quite large overpotentials.

5.2.2 Electrochemical Reactions Occurring During the Chloride Removal Process

So far when considering the effect of a given current flow on the potential of an electrode, it has been assumed that only one reaction is possible. In systems where the electrodes are inert, the composition of the electrolyte is relatively simple (ie. a molten salt) and the current flow is small, then it may be possible that only one reaction occurs at either electrode.

However under desalination treatment conditions a number of reactions are possible which will depend on the composition of the external electrolyte, the anode/cathode material and the applied current density. The order in which the possible reactions occur during polarisation is dependent on their equilibrium potentials and the rate at which they occur is determined by the magnitude of the overpotential.

Figure 5.4 shows a galvanostatic polarisation curve for a hypothetical case of an anode in an electrolyte solution where more than one reaction is possible.

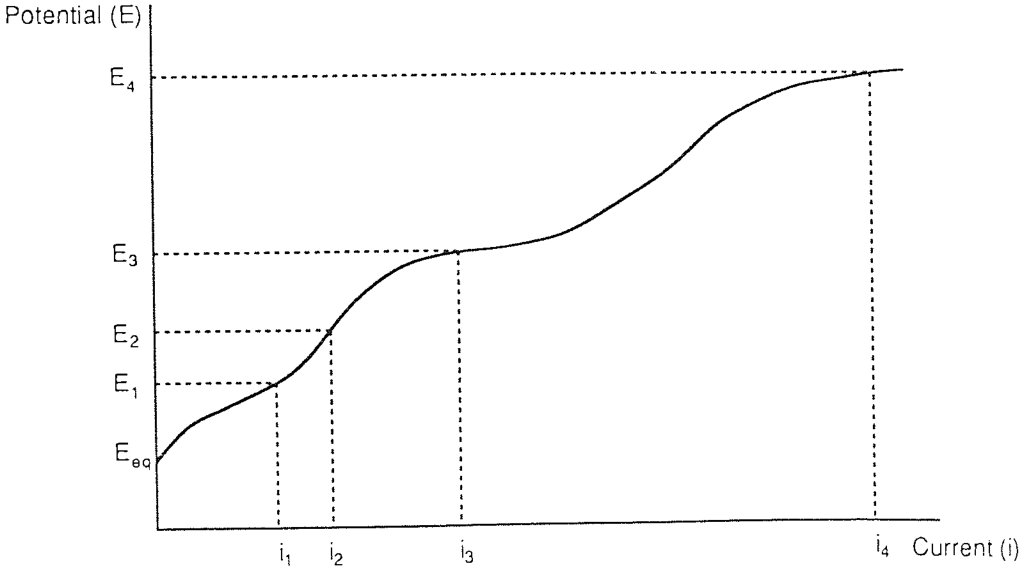


Figure 5.4 - Hypothetical Potential - Current Curve

If no current is applied, then providing the particular reaction is reversible, the electrode reaches its equilibrium potential (E_{eq}) where, if the electrode is comprised of a metal M,

$$M^{n+} + ne^- \rightleftharpoons M$$

If a small anodic current (i_1) is applied then the potential increases to a value E_1 and dissolution of the electrode material starts to occur. If the applied current had been larger (i_2) then the dissolution reaction would have to occur more rapidly and subsequently the potential (E_2) would have to increase to allow for the resistance of the external electrolyte and to remove the dissolved ions away from the electrode/electrolyte interface. If the applied current (i_3) was so large that the dissolution of the anode was not able to occur at the required rate then the potential would rise to a level where another reaction, such as oxidation of one of the components of the electrolyte, could occur (E_3). Similarly if the applied current was even larger (i_4) and both reactions were not able to occur rapidly enough to satisfy the demand then the potential would rise to a new value (E_4) where another reaction could occur at a rapid enough rate to allow the applied current to flow.

Even if the applied current is such that the anode initially reaches a potential E_5 (Figure 5.5), it is possible for the potential to rise after a length of time to a new value (E_6). This is observed when the concentration of the particular oxidant responsible for the anode attaining potential E_5 is depleted in the bulk of the electrolyte and therefore as electrolysis continues the degree to which it is able to contribute to the current flow decreases with time. At some point the concentration of the species will be so depleted that the potential will rise sufficiently so that another new reaction can occur.

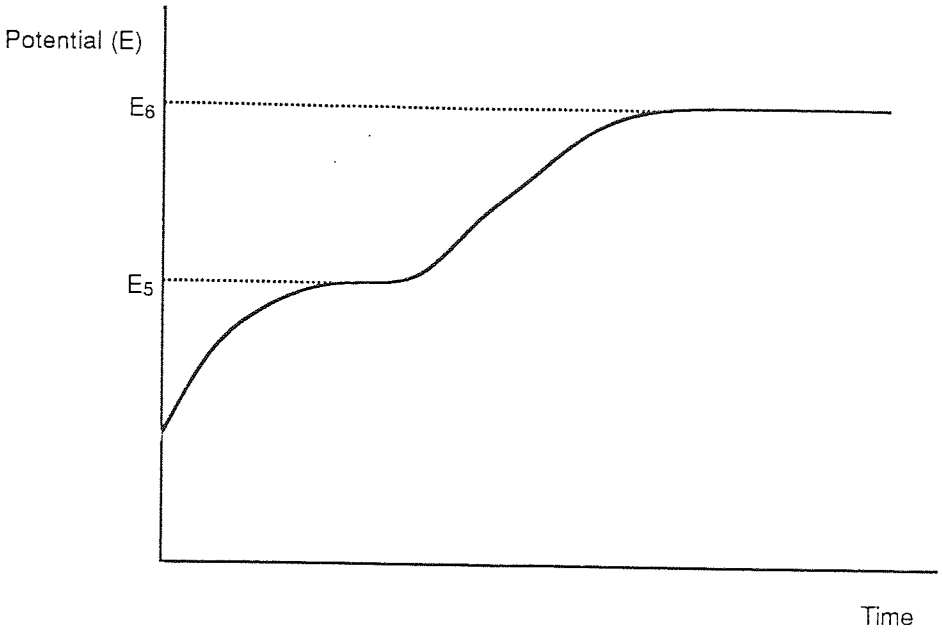


Figure 5.5 - Galvanostatic Anodic Polarisation Curve

5.2.2.1 Cathodic Reactions

The steel reinforcement acts as the cathode and the pore solution as the electrolyte. Under desalination conditions the following reactions take place. Dissolved oxygen in the electrolyte is reduced to hydroxide ions [Isecke, 1992].

$$O_2 + 2H_2O + 4e^- \longrightarrow 4OH^-$$

Due to the high current densities used and the limited diffusivity of oxygen through hardened cement paste, this reaction is very quickly stifled by the lack of oxygen and by far the majority of the current is passed by a second reaction; the evolution of hydrogen by the reduction of the water [Bennett & Schue, 1990].

$$2H_2O + 2e^- \longrightarrow H_2 + 2OH^-$$

It can be seen from the Pourbaix diagram for Fe at 25°C [Pourbaix, 1966] that at the potentials reached during hydrogen evolution, the Fe_2O_3 oxide film and any corrosion products on the steel reinforcement are reduced to most probably either Fe or Fe_3O_4. It has also been suggested that, as the pH of the pore solution increases due to the hydroxide production during treatment, the soluble $FeO.OH^-$ species may be formed instead [Buenfeld, 1993].

Nustad [1992] discovered black deposits on the surface of cathodically polarised steel samples embedded in concrete. This tends to imply that magnetite was formed, but it is not clear whether it was formed during the polarisation process itself or after the current had been switched off as the potential of the steel was in the process of returning to its equilibrium value.

5.2.2.2 Anodic Reactions

The anodic reactions depend very much on the anode material and the composition of the external electrolyte. Materials that have been used as anodes are steel, graphite, copper and noble metal coated titanium [Miller, 1989; Collins, 1983; Morrison *et al.*, 1976; Slater *et al.*, 1976]. Noble metal coated titanium (in the form of an expanded mesh) and sacrificial steel anodes (usually reinforcing mesh) are the only ones that have been used in commercial applications. The noble metal coated expanded titanium mesh is a relatively new electrode material. The composition of the oxide coating can vary, but it is generally considered to be mainly ruthenium oxide [Caldwell, 1981]. It is relatively expensive, but has the advantage of being reusable. The advantage of using steel reinforcing mesh is that, although it is consumed during treatment, it is relatively cheap and readily available. Tap water, solutions of calcium hydroxide or solutions of sodium carbonate have all been used as external electrolytes [Morrison *et al.*, 1976; Slater *et al.*, 1976; Collins & Kirby, 1992].

When a coated titanium mesh is used as the anode and the external electrolyte is water, water is oxidised to oxygen [Isecke, 1992].

$$2H_2O \longrightarrow O_2 + 4H^+ + 4e^-$$

and chloride ions, when they reach the anode in sufficient quantities, are oxidised to chlorine gas [Slater *et al.*, 1976].

$$2Cl^- \longrightarrow Cl_2 + 2e^-$$

For environmental reasons it is preferable not to evolve significant quantities of chlorine gas [Bennett & Schue, 1990]. A number of methods have been used to try and suppress chlorine evolution.

Initially it was thought that noble metal oxide coated titanium meshes would be able to prevent chlorine evolution as they are claimed to be highly oxygen selective (ie. a relatively low overpotential for the evolution of oxygen when compared to that for the evolution of chlorine)[Slater *et al.*,1976]. However, tests have shown that coated titanium meshes do evolve significant amounts of chlorine when used in desalination applications [Bennett & Schue, 1990].

The use of sacrificial anodes can also limit chlorine evolution [Bennett & Schue, 1990]. In the presence of chloride ions, dissolution can occur at a rate rapid enough to prevent the anode reaching a potential where chlorine might be given off.

The addition of a small amount of manganese sulphate ($MnSO_4$) to the electrolyte, has been shown to be effective at minimising chlorine evolution [Bennett & Schue,1990]. It is oxidised at the anode to form manganese oxide (MnO_2) in sufficient quantities to prevent the potential at which chlorine is evolved from being reached. In the initial trials an ion exchange resin was added to the electrolyte, but was found to be ineffective and inconvenient in that it did not exchange efficiently at the high pH of the external electrolyte (>pH 12) and the process of recovering and regenerating the resin between applications was troublesome and time consuming [Bennett & Schue,1990].

The most widely used method of preventing chlorine evolution is to use an external electrolyte with a high pH. Both solutions of calcium hydroxide and sodium carbonate have been used. Bennett and Schue [1990] reported that, under the normal process conditions, chlorine gas evolution was effectively eliminated if the pH was maintained above a value of 12. It was attributed to the reduction in the required oxygen evolution electrode potential (which is pH dependent) when compared to the chlorine evolution electrode potential (which is dependent on the concentration of chloride ions in the electrolyte). However, there are a number of other possibilities why chlorine was not evolved. In alkaline conditions, in addition to the oxidation of water, the hydroxide ions can also be oxidised to form water and oxygen [Tritthart *et al.*, 1993].

$$4OH^- \longrightarrow 2H_2O + O_2 + 4e^-$$

If this reaction is capable of occurring at a sufficient rate at potentials lower than that of chlorine evolution, it will lower the potential of the anode and prevent the chlorine evolution potential from being reached. Should the applied current be so large as to exhaust the charge carrying potential of the two oxygen evolving reactions then it is thought that chlorine will still not be evolved. It is thought that various other chlorine based soluble species will be formed such as hypochlorite, chlorate and perchlorate ions [Pourbaix,1966]. Maintaining a high pH value for the external electrolyte also has the benefit of preventing acidic attack of the cementitious material.

5.3 Treatment History and Case Studies

The process was first carried out for the Battelle Colombus corporation on a bridge deck in the state of Ohio in the USA [Slater *et al.*, 1976]. Large amounts of current (up to 1000A/m^2) were applied to try and remove all the chloride in one day. The test was successful in that up to 90% of the acid soluble chloride was removed from around the steel and post-treatment potential measurements (up to three months after treatment) showed that all the steel was passive whereas before treatment 55% had been corroding. A pond of external electrolyte was used on the bridge deck to ensure electrical contact between the external anode and the reinforcement. The large applied current caused large temperature rises in the concrete (up to 113^{0}C) and the use of a liquid external electrolyte prevented the use on any other than horizontal surfaces.

In Norway in the mid-late 1980's the technique was adapted so that it could be applied to vertical and overhead surfaces as well. It was at this point that the technique became commercially viable as a method of treating chloride-contaminated reinforced concrete structures. The adaptation involved spraying a moist fibrous cellulose material on to the anode mesh which had been attached to the concrete [Vennesland & Miller, 1987]. It became known as the NORCURE process.

Later, the Strategic Highway Research project (SHRP) in the USA. instigated a research program to investigate the effect of current on reinforced concrete. It concluded that currents should be limited to less than $2A/m^2$ of steel or concrete surface area (A/m^2_{steel} or A/m^2_{conc}) as higher values could cause damage due to thermally induced cracking [Bennett & Schue, 1990]. To avoid the problems of thermal cracking, the process is now usually carried out over a longer length of time (3 weeks to 3 months) using current densities in the range 0.5 to $1A/m^2_{conc}$.

The NORCURE method has been evaluated on a number of structures. A pier on the Burlington Bay Skyway in Canada was treated for 60 days at a current density of less than $1A/m^2_{conc}$. It was found that similar percentages of acid soluble chloride were removed (87 - 42%) when compared to the Ohio field test [Manning, 1990].

Significant amounts of chloride were also removed from a bridge pier in Sydney harbour, Australia. However, 16 months later when further concrete samples were taken and analysed, whereas the chloride concentration in the areas of the pier in the atmospheric zone remained as low as those recorded immediately after treatment, the areas in the tidal and splash zones showed chloride levels similar to those before treatment [Collins & Kirby,1992].

A subway under a Swiss highway showed an approximate 40 to 50% reduction in the acid soluble chloride content after being treated for 8 weeks at an applied current of between 0.3 to $0.75A/m^2_{conc}$. After five months the treated area was potential mapped. From the results is was seen that corrosion was still occurring in a small number of areas which were then treated again. After treatment, the chloride content in these small areas was seen to have been reduced by a further 50% [Elsener *et al.*, 1992]. From these results, it was inferred that the free chloride in the pore solution and the bound chloride in the matrix are connected by a chemical equilibrium. If the free chlorides are removed, after a sufficient length of time, the bound chlorides come into solution until a new equilibrium is reached.

A recent commercial development has been to revert to using a reservoir of liquid electrolyte which can be held in place on non horizontal surfaces by a sealed fibre-glass tank [Hammond, 1993].

5.4 Aspects Requiring Clarification

Despite the number of apparently successful full scale trials there still remain a number of points that require elucidation before the treatment process can be applied to contaminated structures with the necessary degree of confidence. They are

- The factors affecting the efficiency of the removal process and possible re-initiation of corrosion.
- The effect of current on the bond between concrete and steel.
- Electrochemically induced alkali-silica reaction.

5.4.1 Removal Efficiency and Corrosion Re-initiation

In the case of many chloride-contaminated structures it is preferable to minimise the amount of disruption and the total cost by carrying out the process as quickly as possible. The speed of removal can be improved by increasing the current density, but as there is a limit that can be applied, it is necessary to see how other factors may affect the removal efficiency. (Since the original SHRP report limiting current densities to less than $2A/m^2$, it has been reported that samples have been subjected to current densities of up to $5A/m^2$ without any signs of damage [Polder & Hondel, 1992].)

As explained previously, the chloride ions are removed because, along with hydroxide ions, they are attracted to the anode and the positively charged sodium and potassium ions are attracted to the cathode. It can therefore be seen that the fraction of the total current carried by the chloride ions in the cover zone of the concrete is an indication as to the efficiency of the removal process.

The fraction of the total current carried by a specific ion is defined as its transport number (t). Therefore, the chloride transport number (t_{Cl^-}) is defined as

$$t_{Cl^-} = \frac{I_{Cl^-}}{I_{Tot}}$$

where I_{Cl^-} = current carried by the chloride ions and

I_{Tot} = total current

The current carried by a specific ion is given by

$$I = c.u.z$$

where c is the concentration of the ion

u is the ionic mobility

z is the valency of the ion

Polder and Hondel [1992] have used this method to calculate the theoretical chloride transport number for hypothetical cases of chloride removal using data taken from investigations into the pore solution composition of chloride-contaminated mortars and concretes [Polder, 1986; Page *et al.*, 1991]. The theoretical method takes no account of either the electrostatic interactions that occur in real solutions or any interaction between the ions and the solid phases of the cement paste. Therefore it is unlikely to be able to predict accurately values of actual removal efficiency.

However, the theoretical approach does help demonstrate the effects of using various external electrolytes. If an electrolyte containing highly mobile ions is introduced into the system then the proportion of current carried by the chloride ions in the cover zone, and therefore the rate at which they are removed from the concrete is reduced. At present it is not known how much effect the use of different electrolytes will have in practice [Polder & Hondel, 1992].

The success of the treatment process will also be governed by the effect of remigration after the current has been switched off. If, during the process, the mobile chloride ions are only moved away from the steel or unequal levels of chloride removal leave areas of concrete still containing significant amounts of chloride, then once the electric field has been removed the concentration profile will cause chloride to diffuse towards the areas of low chloride concentration. This is of particular relevance if chloride ions are present behind the steel. It is thought to be highly unlikely that significant quantities of chloride ions would be removed from such places [Collins & Kirby, 1992].

At present it is not known, especially in light of the large amounts of hydroxide ions produced at the steel, whether this proposed mechanism will induce corrosion in treated structures, but it does show that a number of aspects still need further investigation and that relatively long-term monitoring of the structure after treatment would be a prudent measure.

The possible existence of a free to bound chloride equilibrium could also have serious implications for the long term durability of the structure. In addition to the observations of Elsener *et al.* [1992], Tritthart *et al.* [1993] have also found that the electrochemical treatment process is not only capable of removing the chloride in the pore solution, but also from the matrix. Tritthart attributed this to the desorption of the chloride adsorbed into the C-S-H gel (see section 2.2.3). These results have prompted interest in developing a multiple treatment regime to remove far larger percentages of chloride [Pocock, 1992]. It was suggested that after an initial period of treatment, the current could be turned off to allow bound chloride to be released into solution which would then subsequently be removed by repeating the treatment process.

5.4.2 The Effect of Current on the Concrete/Steel Bond

There has been a great deal of discussion regarding the effect of current on the bond strength of steel in concrete. Both Locke *et al.* [1983] and Vrable [1977] have found that a reduction in bond strength can occur due to the application of cathodic current. Locke *et al.* found that there was an approximate 20% reduction after reinforced concrete samples had been subjected to a total charge of approximately 1200 Amp hours per square metre of steel surface (Ah/m^2_{steel}). This was applied by treating samples for around four years at $33mA/m^2_{steel}$. Vrable used considerably higher current densities (0.5 to $10A/m^2_{steel}$) and treatment times of up to 60 days. An approximate 10% reduction was noted for every $38400Ah/m^2_{steel}$ of charge passed.

More significant reductions in bond strength were seen in an earlier study by Rosa *et al.* [1913] which was cited by Locke *et al.* [1983]. It found an approximate 80% reduction in bond strength after a current of $4.4A/m^2_{steel}$ had been applied for one year ($38900Ah/m^2_{steel}$). In addition, Casad [1951] also cited by Locke *et al.* [1983] noticed quite a significant decrease in the bond strength after treating samples for 60 days at currents greater than $1.5A/m^2_{steel}$.

Nustad [1992] compiled the results of a number of test programmes. Three of the research programmes reviewed showed first a decrease in bond strength, but then, as the amount of charge increased, a subsequent increase. In one of the programmes the bond strength had returned to the untreated value after approximately $8000Ah/m^2_{steel}$ and then rose to a value approximately 200% of the original.

A relationship between the measured bond strength and the time lapse between the end of treatment and testing has also been observed [Buenfeld, 1993] in that as the time lapse increased so did the bond strength.

It has been noted that the majority of research carried out on samples containing ribbed steel have shown no significant reduction in bond strength [Nustad, 1992]. In such cases, the interlock between the ribs and the concrete provide the majority of the strength. It can therefore be inferred that the phenomenon affects only the interface between the concrete and the steel and not the bulk properties of the concrete.

In common with all bond strength measurements, there is an inherent degree of scatter present in all the sets of results. This, in combination with the quite small reductions seen when small current densities were applied, has led to the conclusion that moderate levels of cathodic protection are unlikely to cause any significant degradation of bond strength [Page, 1992]. However, it looks likely that the use of higher current densities (as used in the chloride removal process) can, under some circumstances, significantly reduce bond strength.

A number of mechanisms have been proposed to explain the electrochemically induced reduction of bond strength and they are

- Hydrogen Gas Evolution
- Thermal Cracking
- Iron and Corrosion Product Dissolution
- Paste Softening
- Reduction of Frictional Forces

5.4.2.1 Hydrogen Gas Evolution

In section 5.2.2.1 it was seen that hydrogen gas is formed at the cathode. It will try to diffuse through the pores to the surface of the concrete. Assuming the rate of evolution is greater than the rate at which it can disperse then bursting forces will be induced in concrete surrounding the steel. If the bursting pressures exceed the tensile strength of the concrete cracking will start to occur which will reduce the bond strength. It is not clear, at present, how much of a role the evolution of hydrogen plays in the reduction of bond strength. Hydrogen was not evolved in the samples tested by Locke *et al.* [1983], but small reductions in bond strength were still evident. It therefore appears that even if this mechanism is responsible for bond strength loss at high current densities it is not the only mechanism occurring.

5.4.2.2 Thermal Cracking

Concrete has a high resistivity and therefore when a current is applied, a percentage of the electrical energy is converted to heat energy. The rise in temperature causes expansion which in turn induces tensile stresses and may subsequently cause cracking.

5.4.2.3 Iron and Corrosion Product Dissolution

The basis for the proposed mechanism of iron dissolution is that at high pH values the $FeO.OH^-$ species can be formed from the steel and its oxides [Pourbaix, 1966]. This species is soluble and therefore, it is claimed that, a space is formed between the steel and the hardened concrete. The cathodic reactions produce large amounts of hydroxide ions and it has been seen that the pH of the concrete in the vicinity of the steel can exceed 14 [Bertolini, 1993]. By considering the equilibrium potential - pH diagram for iron (Figure 1.1) [Pourbaix, 1966] it can be seen that at the potential of hydrogen evolution and at these high pH values $FeO.OH^-$ production is very likely. This theory is also supported by experimental evidence that increased levels of iron have been found in the cement paste surrounding treated pieces of steel [Buenfeld, 1993].

5.4.2.4 Paste Softening

The softening of the matrix has been attributed to the gradual accumulation of sodium and potassium in the zone around the steel. The hydroxides of these ions are believed to be detrimentally incorporated into the C-S-H gel which cause soluble silicates to be formed [Locke *et al.*, 1983]. This reduction in the percentage of C-S-H gel would locally reduce the strength of the matrix surrounding the steel. It has been proposed [Page, 1992] that the mechanism is somewhat similar to that accounting for the degradation by admixed NaOH on the bulk mechanical properties of cement paste [Shayan & Ivanusec, 1989].

5.4.2.5 Reduction of Frictional Forces

Loss of friction has been associated with the production of hydroxide ions at the cathode. It has been claimed that if enough hydroxide is produced, sodium and potassium hydroxide, which have no cementitious properties, will be precipitated around the steel. It was also suggested that their precipitation may locally disrupt the interfacial bond [Ali & Rasheeduzzafar, 1991].

Another theory that has been proposed is that, as sodium and potassium hydroxides are hydrophilic, they form as a wet 'soapy' film on the surface of the steel and thus reduce frictional forces [Nustad, 1992]. The 'soapy' film was seen when a number of laboratory specimens were broken up after treatment. This theory seems unlikely as solutions of sodium and potassium hydroxide have no 'soapy' properties of their own, but only when they react with fatty acids to form stearate salts.

Nustad [1992] also used the 'soapy' film theory to account for the apparent decrease and then subsequent increase in bond strength. It was suggested that at low total charges the reaction reducing the dissolved oxygen predominated, but as the total charge passed increased, the hydrogen evolution reaction predominated which consumed larger amounts of water. This was thought to dry out the concrete, increasing the friction. It was also thought that sodium and potassium hydroxides would be precipitated in the area around the steel filling any pores.

5.4.3 Electrochemically Induced Alkali-Silica Reaction (ASR)

It has been seen that electrochemical repair techniques can induce ASR in concretes containing susceptible aggregates [Sergi *et al.*, 1991]. As stated earlier the pore solution in hydrated cement paste is highly alkaline. Certain siliceous aggregates are unstable in alkaline conditions. The unstable aggregates exhibit slightly acidic characteristics. They react with the hydroxide ions, attacking some of silicon-oxygen bonds and form a hydrous silicate gel [Hobbs, 1988]. Alkali metal ions are attracted to the reaction site to maintain the charge balance and to counteract the ionic concentration water flows into the gel. The gel expands and cracks form in the aggregate. They can also propagate into the cement matrix. In reinforced concrete these cracks form along the line of the reinforcement and allow the easier ingress of aggressive ions such as chlorides.

From the above it can be seen that there are three conditions required for ASR to occur

- Moisture
- Reactive silica
- Reactive alkali

If any of these three are not present then ASR will not occur.

5.4.3.1 Moisture

A sufficiently low moisture content can be achieved if the concrete (after curing) is exposed to an environment with a relative humidity of less than 75% [Concrete Society, 1987]. Such an environment can be found in dry, well-ventilated areas of buildings, but is unlikely to be occur anywhere else. During the treatment process the external electrolyte will increase the moisture level in the concrete.

5.4.3.2 Reactive Silica

The first cases of ASR in the UK were discovered in concretes containing sea-dredged flint-bearing sands or chert-rich gravels. Since this time a number of other aggregates have been found to be reactive; siltstones, silicified limestones and greywackes. In the majority of cases, micro and cryptocrystalline silica or chalcedony was found to be the reactive constituent. It is also thought that strained quartz found in some quartzites can be reactive. On the island of Jersey opaline silica found as a minor constituent in a crushed igneous rock aggregate has been seen to cause ASR, but to date it has not been found in any rocks on the mainland [Concrete Society, 1987]. The alkali level required to cause expansion can vary quite markedly from aggregate to aggregate [Sibbick & Page, 1992].

The amount of expansion seen in a concrete sample is not simply proportional to the amount of reactive aggregate in the mix. For each ASR susceptible aggregate, there is a ratio of reactive to non reactive material which, if all other factors are equal, will cause the greatest expansion. This is called pessimum behaviour [Hobbs, 1988].

5.4.3.3 Reactive Alkali

In concretes, the alkali level is conventionally expressed as the sodium oxide equivalent (Na_2O_e).

$$Na_2O_e = Na_2O + 0.658K_2O$$

Present guidelines recommend that the available reactive alkali content in concrete should not exceed 3.0kg/m^3 of equivalent sodium oxide for concretes containing potentially reactive aggregate [Concrete Society, 1987].

The alkali content of the cement can be limited by careful selection of the raw materials used in the cement production process. The actual production process can also have a small effect on the alkali content. To prevent ASR from developing the alkali level of the cement should not exceed 0.6%. In the UK the average alkali content of normal OPC varies between 0.5 and 0.83% and on average is greater than the recommended level with a weighted mean of 0.62% [Corish, 1994].

The use of slags or pozzolanas as cement replacements can reduce the effective reactive alkali level in concretes. As stated in chapter 1, they react with the alkalis produced during the OPC hydration and therefore reduce the pH of the pore solution. Both slags and pozzolanas can contain comparatively high levels of alkali themselves, but they are mainly bound up in their glassy structure. It has been found that these alkalis are released only slowly during the hydration process and do not seem to be able to take part in promoting the ASR reaction [Concrete Society, 1987]. However, it has still not been seen if the alkalis will start to have an effect over a longer period of time and this is a matter of on-going research.

Alkalis can also be introduced from sources other than from the cementitious materials. When sodium chloride is introduced into concrete it can react with the C_3A mineral and calcium hydroxide to form chloroaluminates and sodium hydroxide [Nixon *et al.*, 1988]. As shown in section 5.2.2.1 the cathodic reactions at the steel reinforcement during electrochemical treatment also produce hydroxide ions which will be available to initiate ASR.

5.4.3.4 Prevention of ASR

Lithium ions have been found to be capable of suppressing ASR if admixed into concrete [McCoy & Caldwell, 1951]. Diamond and Ong [1992] have suggested that, in the absence of sodium and potassium hydroxide, admixed lithium hydroxide reacts with the reactive silica to form an ASR gel, but this gel appears to be non expansive. In mixed alkali systems (sodium, potassium and lithium hydroxides) it was seen that a mixed alkali ASR gel was formed, but with lithium present in smaller amounts than the sodium and potassium when compared to the amounts incorporated at the time of mixing. It was suggested that a large percentage of the lithium was rapidly absorbed into the hydrating cement minerals (≈40% after 1 day in the absence of sodium and potassium hydroxide) and would not be available to form non expansive ASR gel.

Another aspect of the addition of mixed alkalis to reactive mortar samples was that as the percentage of lithium increased the uptake of the alkalis into the gel decreased. It was concluded from this that as the lithium content increased the total amount of ASR gel decreased.

From Diamond and Ong's results it was seen that lithium is capable of reducing the effects of ASR, but for the reasons stated above, would be required in large dosages. It has been proposed that lithium could be introduced into hardened concrete under the application of an electric field in a similar way to the removal of chloride [Page, 1991]. The process would involve dosing the external electrolyte with lithium ions. The positively charged lithium ions would then electromigrate towards the reinforcement. As hydration had already taken place, less would be absorbed into the cement matrix and more would be available to combat the production of expansive ASR gel.

5.5 Conclusions

It has been seen in the preceding sections that the technique of electrochemical chloride removal is potentially a very useful method of repairing chloride contaminated structures. However, there are a number of aspects that require further investigation. In view of the possible link between the amount of charge passed and reductions in bond strength and the induction of ASR in susceptible concrete mixes, it is important to determine the factors responsible for altering the chloride removal efficiency which in turn govern the amount of charge required. One such factor is the composition of the external electrolyte and that is the aspect under investigation in the remaining two chapters.

CHAPTER 6 - EXPERIMENTAL DETAILS: ELECTROCHEMICAL CHLORIDE REMOVAL

The effect of electrolyte composition on chloride removal process was investigated in two separate sections. Each one compared two different electrolytes and as well as their effect on removal efficiency, their effect on the integrity of the cementitious matrix was also investigated.

6.1 The Effect of Calcium Hydroxide and Sodium Carbonate External Electrolytes on Chloride Removal Efficiency

The work as described in this section (6.1) was carried out as part of a more comprehensive project entitled 'Chloride Removal from an Existing Quay Wall - Laboratory Tests' which was in turn included in the COST 509 European collaboration programme 'Corrosion of Metals in Contact with Concrete' under code NL-2. The investigation was financed jointly by TNO Bouw and Bouwdienst Rijkswaterstaat. TNO Bouw is the building and construction department of the Netherlands organisation for applied scientific research. The Bouwdienst Rijkswaterstaat is the body responsible for the building and maintenance of all Dutch coastal protection works. The experimental samples were prepared and electrochemically treated by the staff of TNO Bouw. The sampling and pore expression processes were all carried out primarily by the author at the laboratories of TNO Bouw in the Netherlands. The chemical analysis of the pore solution took place both in the Netherlands and at the laboratories at Aston University.

The intention of the project was to supply useful information which would facilitate the application of the chloride extraction process to a full scale structure. Such a study was required as the majority of concrete construction in the Netherlands is made from blast furnace slag cement (BFSC) and it was not known how successful the technique would be with this type of concrete. Calcium hydroxide and sodium carbonate were chosen as the two external electrolytes to be evaluated.

6.1.1 Sample Preparation

The cores were wet cut from a quay wall situated on the North Sea coast near to the Eastern Scheldt Storm Surge Barrier in the south of the Netherlands. It was built in 1983/84 and, at the time of coring, had been exposed to a marine environment for 8 years. The quay was constructed of blast furnace slag reinforced concrete slabs and beams, supported on concrete piles. The cores were cut from the side surface of the slabs, approximately 1 metre above the high water mark.

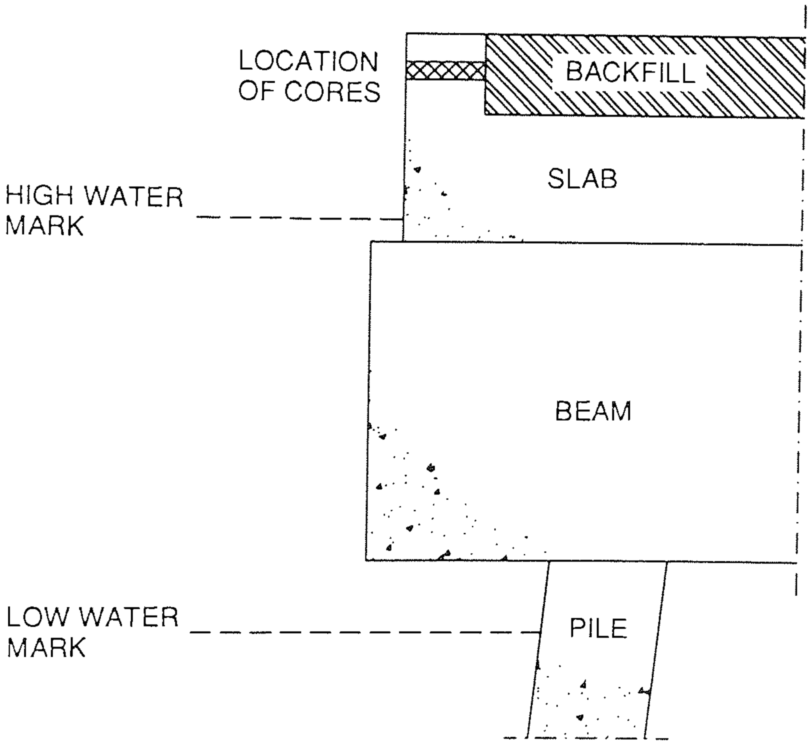


Figure 6.1 - Cross Section of BFSC Quay Wall and Core Location

After coring, the samples were immediately placed in polythene bags to avoid moisture loss. They were taken to the laboratory and stored outside until required. 4 No. 150mm dia. cores (labelled. A, B, C and D) and 4 No. 100mm dia. cores were used [6.1] . The 150mm dia cores were cut so as to include 2 pieces of intersecting 16mm dia. steel reinforcement. The minimum cover to the steel was 30mm. The 100mm dia. cores were cut so as to avoid any reinforcement.

The concrete mix used for the slab construction is shown in table 6.1

Blast Furnace Slag Cement (70% Slag replacement)	300kg/m^3
Water / Binder ratio	0.54
Plasticiser	0.55% by wt. cement
Sand	870kg/m^3
Coarse Aggregate	1085kg/m^3

Table 6.1 - BFSC Concrete Mix Details

Electrical connections were made to the steel in the 150mm dia. cores and the cut cylindrical surfaces coated with an epoxy sealant.

6.1.2 Electrolyte Solution

Two external electrolytes were used namely saturated calcium hydroxide (sat. $Ca(OH)_2$) and 1 molar sodium carbonate (Na_2CO_3). They were all prepared from deionised water and SLR grade chemicals.

[6.1] In the final project report [Polder, 1993] a different nomenclature was used. Core A = no. 16, B = no. 19, C = no. 31, D = no. 34 and the 4 No. 100mm dia. cores were nos. 26, 29, 32 & 35.

6.1.3 Experimental Procedure

The exposed face of each 150mm dia core was placed upside down in a 1litre pond of electrolyte which contained an piece of noble-metal-coated titanium mesh (Figure 6.2).

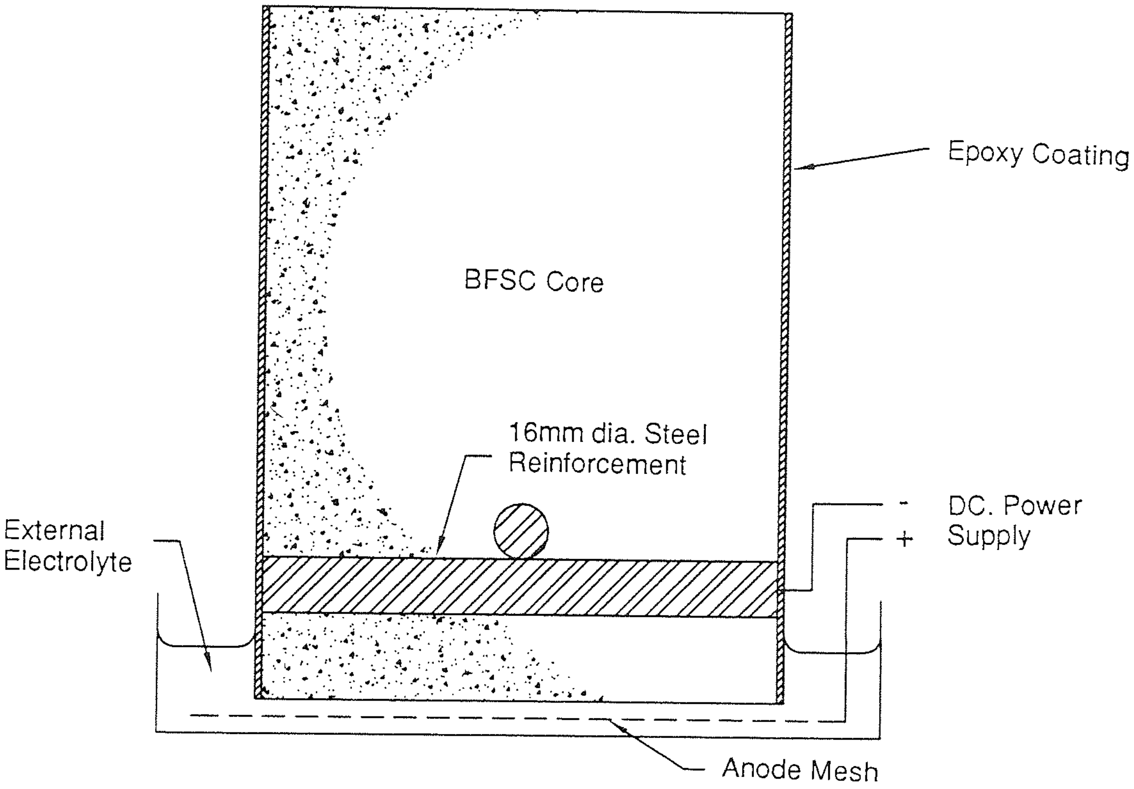


Figure 6.2 - Desalination Experimental Arrangement for BFSC Cores

For each electrolyte, two design current densities were used; 1A/m^2 and 4A/m^2 of steel surface. The specimens were polarised for 6 weeks and the electrolyte was changed every week. During the treatment they were stored in the laboratory at 20°C and 80% RH.

Core No.	Electrolyte	Current Density
A	1M Na_2CO_3	1A/m$^2_{steel}$
B	1M Na_2CO_3	4A/m$^2_{steel}$
C	sat. $Ca(OH)_2$	1A/m$^2_{steel}$
D	sat. $Ca(OH)_2$	4A/m$^2_{steel}$

Table 6.2 - Theoretical Treatment Regimes

Due to the resistance of the dense BFSC concrete mix, it was found to be impossible to achieve the design current density when calcium hydroxide was used as electrolyte. The maximum current density passed in these cases was approximately $0.7A/m^2_{steel}$. To allow valid comparisons to be made, the current passed through each sample was continually monitored and recorded on data-loggers.

6.1.4 Analysis

The untreated cores were wet cut into overlapping 20mm discs using a diamond impregnated saw in a similar way to the hardened cement paste discs in section 3.2.3.1. The treated samples were cut into 3 slices; one slice comprising the first 20mm of the cover zone, one 44mm slice containing the reinforcement and 5mm of cover at either side and another 20mm slice comprising the material behind the steel.

Each slice was crushed and then passed through a 2.34mm sieve to remove any large pieces of aggregate for the reasons stated in section 3.4.5. The fine material was then brought to a saturated surface dry (SSD) condition by carefully adding deionised water and mixing thoroughly to ensure a uniform moisture content. The state was deemed to have been achieved when the material just started to adhere to a clean dry glass stirring rod.

The pore solution was then extracted using a press similar to that described in chapter 3. The load was applied at a rate of 0.3 kN/s to a value of 830kN. As before, the solution was collected in a sterile polythene vial and immediately sealed until ready for analysis.

Sodium and potassium were determined using atomic absorption spectroscopy in absorption mode [Perkin Elmer, 1976]. Ion chromatography using a sodium carbonate/bicarbonate eluant was used to quantify the amount of sulphate present [Dionex, 1987]. Chloride concentrations were determined using the same spectrophotometric method used in chapter 3. Solutions obtained from the untreated cores and cores C and D were analysed for hydroxide by acid-base titration with nitric acid using phenolpthalein as indicator. The solution obtained from cores A and B were analysed for carbonate and hydroxide. This was done by carrying out two acid-base titrations with nitric acid using phenolpthalein and bromcresolgreen as indicators. A full explanation of the method and a worked example is given in appendix C.

6.1.5 Discussion of the Experimental Details and Analytical Techniques

As with chapter 3, the process of resaturation means that the concentrations determined were not those originally present in the pores. The decision to resaturate was taken for two reasons. From past experience it was known that, without resaturating, insufficient pore solution would be obtained for the necessary analysis. This was particularly important as only one core was available from each treatment regime.

Secondly, prior to analysis, the untreated and treated cores had been stored in completely different environments. The untreated cores had been wrapped in polythene bags and stored outside from the time they had been removed from the structure to when they were cut into slices. During the desalination process the treated cores had been kept in the laboratory (20°C and 80% RH) and their external end face ponded in the electrolyte. If the actual structure had been treated, after allowing a suitable time for conditions to stabilise, the moisture content of the concrete both before and after the process would have been the same. It was felt that to allow valid comparisons to be made it was necessary to standardise the moisture content.

It is not claimed that the moisture content of samples immediately prior to pore water expression was the original level and it is recognised that there was some uncertainty about the method of achieving a SSD condition, but from the results obtained it is felt to be reasonably successful. The work was carried out prior to that in part 1 and before the method had been fully developed.

Again as only one core was available for each regime, wet cutting was used as opposed to the method of 'crush sectioning' as developed by Page and Lambert [1986] and as described in section 3.3.4.3. This ensured a more accurate depth profile. Leaching was not judged to be a major problem as the concrete had already been seen by microscopic methods to be very dense with very low porosity.

6.2 The Effect of Lithium Based External Electrolytes on Chloride Removal Efficiency and Electrochemically Induced Alkali Silica Reaction

As lithium ions have been seen to be capable of preventing ASR-induced expansion, their use as a component of the external electrolyte may be useful in combating electrochemically induced ASR. However, it is not known how successful the lithium ions will be under these circumstances and how they will affect the chloride removal efficiency. To investigate this aspect lithium hydroxide and deionised water were chosen as the external electrolytes to be evaluated.

6.2.1 Sample Preparation

Concrete samples were prepared as shown in figure 6.3. They consisted of a 100 x 100 x 95mm concrete block with a mild steel cathode cast into the centre.

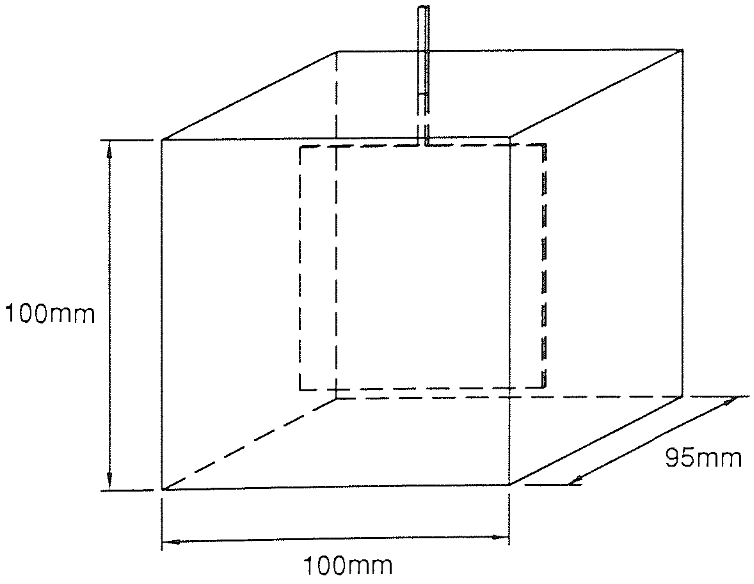


Figure 6.3 - OPC Concrete Sample

The cathode was made from a 70 x 70mm mild steel plate to which a small length of 4mm diameter mild steel bar had been spot welded. The assembly was then grit blasted and degreased. A length of insulated wire was attached to the connecting bar. The bar was then covered in shrink fit tubing and stopping-off lacquer. The elemental composition of the mild steel cathode is shown in table 6.3.

Fe	C	Si	Mn	S	Cr	Mo	Ni	Al	Cu	Sn
99.51	0.04	0.01	0.28	0.03	0.04	0.01	0.03	0.01	0.02	0.01

Table 6.3 - Composition of the Mild Steel Plate(%)

The basic concrete mix is shown in table 6.4.

White Ordinary Portland Cement	400kg/m^3
Deionised Water	200kg/m^3
Grade 14's Leighton Buzzard Sand	310kg/m^3
Grade 16/30 Leighton Buzzard Sand	100kg/m^3
Grade 8/16 Leighton Buzzard Sand	300kg/m^3
10 - 6 mm Cheddar Limestone Agg.	990kg/m^3

Table 6.4 - OPC Concrete Mix Details

The analysis of the cement is seen in table 6.5. The alkali level was artificially increased to 2.5kg/m^3 Na_2O equiv. by the addition of sodium hydroxide (SLR grade) to the mix water.

Either 0%, 0.5% or 2% Cl^- (by weight of cement) was added to the specimens in phase 1 by the addition of sodium chloride (SLR grade) to the mix water. In phase 2 no chloride was added, but 170kg/m^3 of the grade 8/16 Leighton Buzzard sand was replaced with the same amount of calcined flint (a synthetically produced reactive aggregate) which was known to exhibit significant expansion in concrete with alkali levels in excess of 2.5 kg/m^3 .

All the samples were cured for 28 days at 20±2°C over water. During the curing period the samples were periodically removed and prepared for treatment. Perspex cells were attached to the two 100 x 100mm faces of all the specimens with silicone rubber sealant. Prior to starting treatment, the insides of the cells were rinsed with deionised water to remove the traces of acetic acid liberated from the sealant. For phase two specimens, Demec expansion points were attached to the two 100 x 95mm side faces. The remaining exterior faces were then wrapped in towelling. The specimen arrangement is shown in figure 6.4. The towelling was kept moist throughout the whole treatment process. For each treatment regime at least two samples were prepared.

Elemental Oxide (%)		Bogue Compounds (%)[6.1]	
CaO	67.60	C_2S	4.58
SiO_2	21.20	C_3S	74.62
Al_2O_3	4.70	C_3A	11.98
Fe_2O_3	0.28	C_4AF	0.85
SO_3	2.60		
MgO	0.30		
Na_2O	0.12		
K_2O	0.18		
L.O.I.	2.60		

Table 6.5 - OPC Cement Analysis

6.2.2 Electrolyte Solutions

The two electrolytes used were deionised water and a 1mole/litre lithium hydroxide solution. The lithium hydroxide (LiOH) used was AR grade reagent and made up with deionised water.

[6.1] Calculated using the method as demonstrated in Neville [1981]

6.2.3 Experimental Procedure

The cells were filled with 250ml of electrolyte solution and sections of noble metal coated expanded titanium mesh inserted to act as the anode. The completed specimens (Figure 6.4) were then stored at 25±2°C throughout the whole test period.

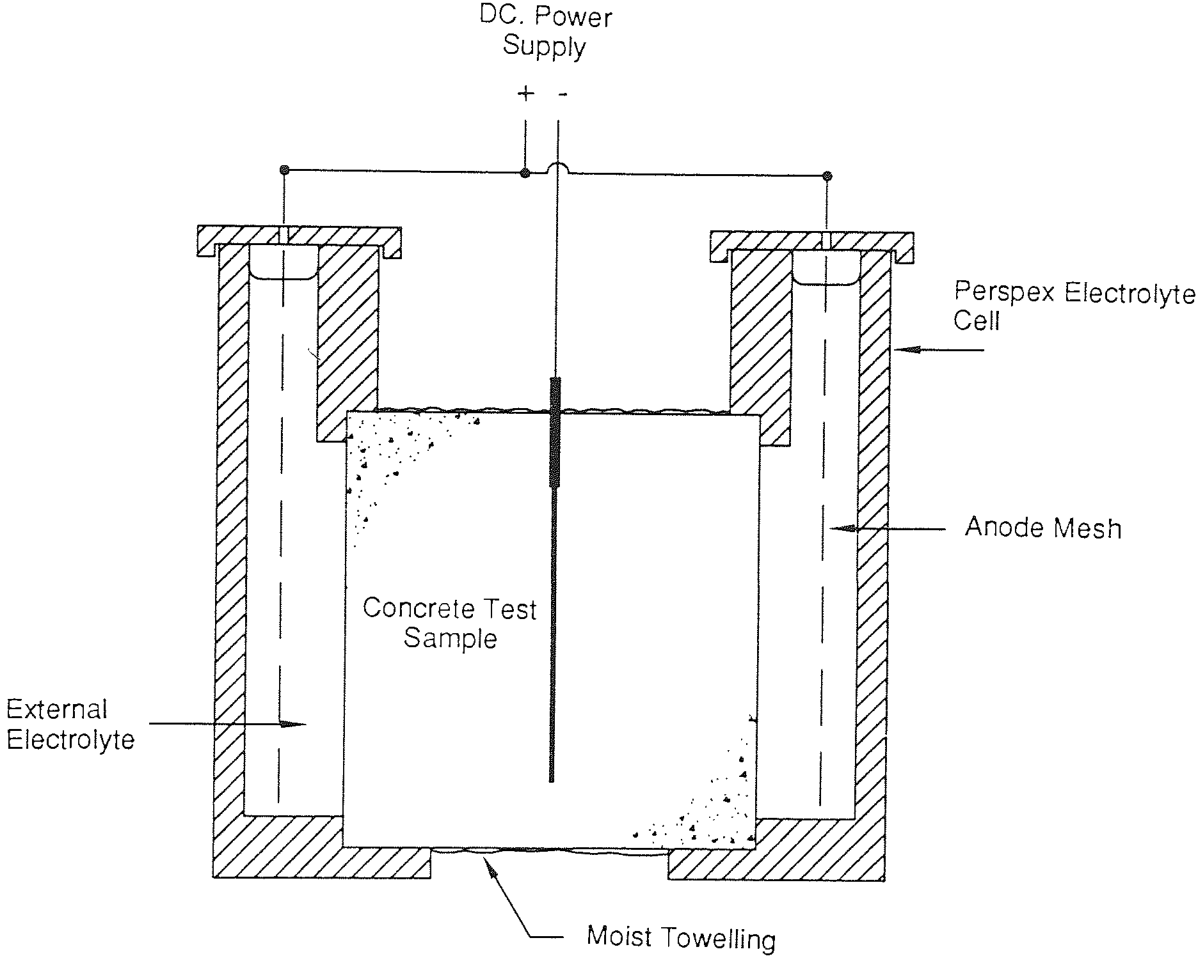


Figure 6.4 - Desalination Experimental Arrangement for OPC Samples

6.2.3.1 Phase 1

The treatment was carried out as per table 6.6 and the current was applied at $2A/m^2_{steel}$.

% Cl (wt cement)	Electrolyte	Treatment Time
0.0	LiOH	28 days
0.5	H_2O	28 days
0.5	LiOH	28 days
2.0	H_2O	28 days
2.0	LiOH	28 days
2.0	H_2O LiOH	28 days and then 28 days

Table 6.6 - Phase 1 Treatment Regimes

6.2.3.2 Phase 2

The treatment was carried out as in table 6.7

Electrolyte	Current Density	Treatment Time
H_2O	$0A/m^2_{steel}$	70 days
H_2O	$2A/m^2_{steel}$	70 days
LiOH	$2A/m^2_{steel}$	70 days

Table 6.7 - Phase 2 Treatment Regimes

After the current was switched off all the electrolyte solutions were replaced with fresh deionised water and kept at 25±2°C for a further 133 days.

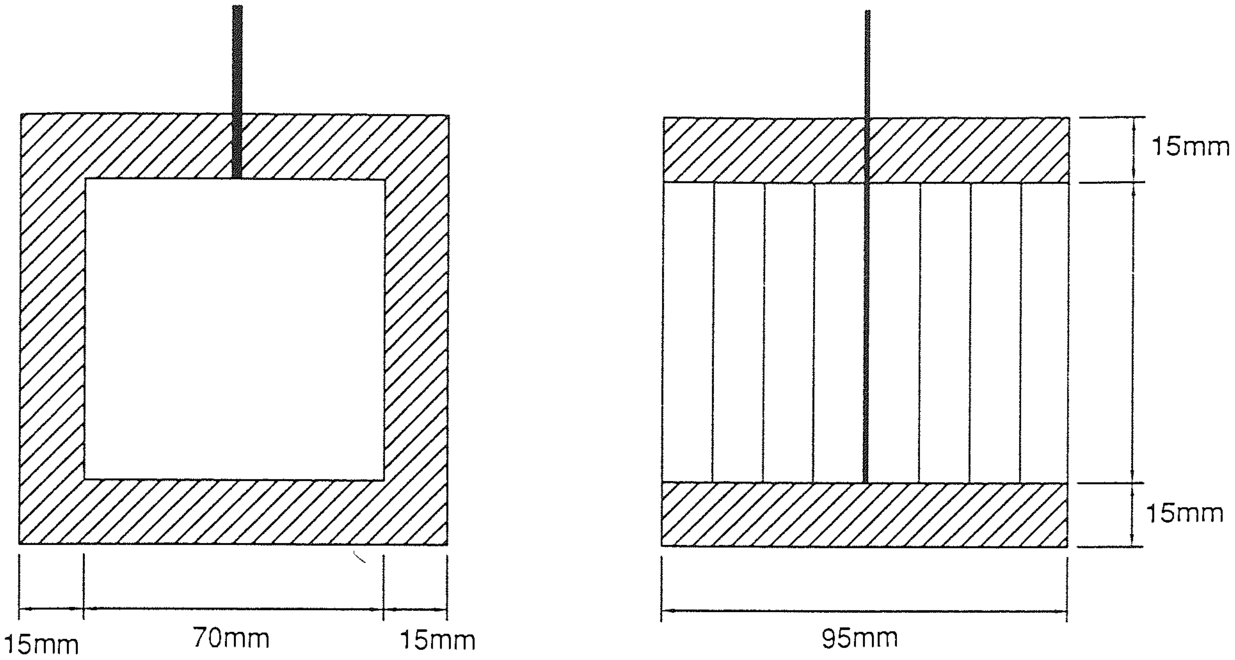
6.2.4 Analysis

6.2.4.1 Phase 1

During the treatment process the external electrolyte was periodically sampled and analysed. 100µl aliquots were removed and analysed for either chloride and/or lithium depending on the treatment regime. Lithium was determined using atomic absorption spectroscopy in absorption mode [Perkin Elmer, 1976] and chloride using the spectrophotometric method used in chapter 3.

At the end of the treatment, each cube was dry cut into a 70 x 70 x 95mm block by removing the 15mm of cover from all the non treated surfaces (Figure 6.5). The block was then cut parallel to the steel electrode into 8 slices of approximately the same thickness. The dimensions of each slice were measured and then the material was placed in an oven at 105°C until constant weight was reached. From this the bulk density of each slice was determined. Every slice was then broken up and powdered in a ball mill. The powder was sieved to collect all the material less than 600µm in diameter. A representative sample (≈25g) was collected and again dried to constant weight at 105°C. After weighing the sample was dissolved in nitric acid (AR grade), filtered and made up to a standard volume. The solution was then analysed for either chloride and/or lithium using the same methods as described above.

In response to the results from section 6.1, one of the cubes containing 2% Cl^- which had been treated with both H_2O and then LiOH was subjected to further examination. Samples from the main body and the area surrounding the cathode were taken and analysed by TGA/DTA. The sample preparation procedure was the same as in section 3.2.3.2. A thin section was also made.



Hatched areas disgarded

Figure 6.5 - Cutting Up Arrangement for OPC Samples

6.2.4.2 Phase 2

Throughout the treatment and storage period the expansion between the demec points was measured.

At the end of the time period one half of each specimen treated with LiOH was cut up and analysed for lithium ingress as in section 6.2.4.1. The remaining halves were made into thin sections for microscopic analysis and compared to a thin section made from a specimen treated using H_2O electrolyte.

6.2.5 Discussion of the Experimental Details and Analytical Techniques

The samples used were quite different from those that would be treated in real circumstances in that a steel plate was used as opposed to reinforcing bar and anode systems were attached to two opposite faces. The reason for this was to ensure symmetrical treatment of the cube and a more uniform current distribution through the specimen.

The percentage of calcined flint added to the phase 2 specimens was chosen to produce the maximum amount of expansion should ASR occur. The initial alkali level was set at the threshold level where ASR would just not occur in the untreated specimens in the time span allowed for the experiments.

During the treatment procedure, it was apparent that, although the silicone rubber was known to be resistant to saturated calcium hydroxide solutions, it was attacked by very alkaline solutions (ie. 1M LiOH). After approximately 3-4 weeks of treatment some of the electrolyte cells were seen to be leaking. In these cases the treatment was stopped, the seals replaced, fresh solution added and then the treatment continued. It was noted when and on which samples this happened for the subsequent discussion of the results.

CHAPTER 7 - RESULTS AND DISCUSSION: ELECTROCHEMICAL CHLORIDE REMOVAL

Although the experimental work, as described in chapter 6, was carried out in two completely separate phases, the discussion and conclusions frequently required the results to be combined. For this reason the results are presented first (sections 7.1 and 7.2) along with any necessary comments. Points were only discussed in these sections if they had no bearing on the results of the other experimental work. The full discussion is given after the results in section 7.3.

7.1 The Desalination of Reinforced BFSC Concrete Cores with Calcium Hydroxide and Sodium Carbonate External Electrolytes

In addition to the pore solution study, various other aspects of the desalination process were investigated in the project 'Chloride Removal from an Existing Quay Wall - Laboratory Tests'. These results were collected by the technical staff at TNO Bouw and compiled by Dr. R.B. Polder. Where it is deemed helpful to the discussion the results are included, but are referenced to the final project report [Polder, 1993].

7.1.1 Untreated Cores

As with the diffusion experiments in part 1, it was assumed that the ionic concentrations determined for each slice were those present at the centre of that slice. Where more than one slice was available for any one depth the results were averaged. The original data from the untreated cores can be seen in appendix D. The averaged results prior to treatment are shown in table 7.1.

Depth	Na^+	K^+	OH^-	Cl^-	SO_4^{2-}
5	315	30	0.5	380	---
10	235	32	14	292	4
20	110	47	44	85	4
30	99	47	102	14	3
40	90	44	97	5	1
50	93	49	109	5	3
60	82	36	88	3	2
80	91	38	86	7	---

Depth in mm and concentrations in mM, --- not analysed

Table 7.1 - Average Pore Solution Results from the Untreated Cores

From the values, the chloride to hydroxide ratio at the concrete/steel interface (26mm from the exterior surface) was estimated to be approximately 0.8. From the results of Page and Lambert [1986] it can be predicted that the likelihood of chloride induced corrosion of the main reinforcing steel was low. If the process had been carried out on the actual structure it would have been a preventative rather than a remedial measure.

7.1.2 Treated Cores

A summary of the data collected regarding the amount of charge passed through the samples is shown in table 7.2.

	Core			
	A	B	C	D
Av. Current Density (A/m^2_{steel})	1	4	0.65	0.70
Total Charge Passed (Ah)	14	55	8.2	9.1

Table 7.2 - Summary of Current Supply Data [Polder, 1992]

The pore solution results from the treated cores are shown in table 7.3.

Core	Depth	Na^+	K^+	OH^-	CO_3^{2-}	Cl^-	SO_4^{2-}
A	0-20	978	38	201	119	394	69
	20-64	280	92	278	43	12	7
	64-84	96	47	89	21	4	2
B	0-20	1957	30	743	283	307	160
	20-64	1060	157	706	165	22	39
	64-84	111	59	116	25	2	1
C	0-20	140	17	68	---	57	2
	20-64	140	78	179	---	7	3
	64-84	98	52	125	---	4	2
D	0-20	147	13	62	---	62	2
	20-64	148	71	176	---	7	3
	64-84	85	39	99	---	3	1

Depth in mm and concentrations in mM, --- not analysed

Table 7.3 - Pore Solution Results from Treated Cores

The differences in the pore solution composition before and after treatment are shown in table 7.4.

Core	Depth	Na^+	K^+	OH^-	CO_3^{2-}	Cl^-	SO_4^{2-}
A	0-20	+743	+6	+187	+119	+102	+65
	20-64	+190	+48	+181	+43	+7	+6
	64-84	+9	+10	+2	+21	-1	0
B	0-20	+1722	-2	+729	+283	+15	+156
	20-64	+970	+113	+609	+165	+17	+38
	64-84	+24	+22	+29	+25	-3	-1
C	0-20	-95	-15	+54	---	-235	-2
	20-64	+50	+34	+82	---	+2	+2
	64-84	+11	+15	+38	---	-1	0
D	0-20	-88	-19	+48	---	-230	-2
	20-64	+58	+27	+79	---	+2	+2
	64-84	-2	+2	+12	---	-2	-1
Depth in mm and concentrations in mM, --- not analysed							

Table 7.4 - Differences in Pore Solution Composition due to Treatment

When calcium hydroxide was used as the external electrolyte a large percentage of the chloride in the pore solution was removed from the cover zone of the cores (C and D). The amount of chloride in the external electrolyte was found to be 975 mg and 1087 mg for cores C and D respectively [Polder, 1992]. At no time during the experiments was the odour of chlorine gas detected indicating that the alkaline electrolyte was capable of suppressing chlorine evolution and that the amount of chloride present in the external electrolyte was representative of that removed from the core. The total acid soluble chloride content in the cover zone (0-20mm) was reduced from approximately 1.15% to 0.5 % (by weight of cement)[Polder, 1993].

The changes in the other species present were all in line with the recognised principles of electrolysis as described in chapter 5. The hydroxide concentration increased in all areas. It is thought that the majority was supplied from the reaction at the steel cathode, but it is possible that some may have diffused or been absorbed into the concrete from the electrolyte although the amount would be small as its flow is opposed by the electrical field. Sodium and potassium ions migrated from the cover zone towards the steel. Small quantities may also have been lost from the cover zone into the external electrolyte.

No such decrease in the pore solution chloride concentration was apparent in cores A and B when sodium carbonate was used as the external electrolyte. It appears that treatment with it may actually have increased the amount. Compared to the average untreated values, the results show a noticeable increase in the amount present in the cover zone of core A and a small one in core B. Although the results were only based on two individual concrete slices, even after allowing for the experimental scatter in the original untreated results, the increases do appear to be significant. Sampling of the electrolyte indicated that 456mg of chloride was removed from core A and 780mg from core B. Again, no chlorine gas evolution was evident. The total acid soluble chloride content in the cover zone was reduced to 0.9% (by weight of cement) for core A and 0.6% for core B.

As expected, potassium levels increased around the steel. The hydroxide levels increased which seem to be approximately in line with the amount of charge passed. Both sodium and carbonate ions entered the concrete in significant quantities. Whereas sodium can be expected to migrate towards the negatively charged reinforcement, the movement of carbonate into such samples is less well accepted and understood.

In addition to the technique of electrochemical chloride removal, a similar process has been developed to treat concrete structures where the protective alkalinity of the concrete has been destroyed (ie. carbonation) [Vennesland & Miller, 1987]. Realkalisation, as it is known, is a very similar technique to electrochemical chloride removal in that the reinforcement is cathodically polarised with respect to an external anode system. Sodium carbonate is used as the external electrolyte and usually the current is applied at densities less than 1A/m^2 for only a matter of days.

The alkalinity of the concrete is restored by the production of hydroxide ions at the steel and also, it is claimed, by the ingress of carbonate ions by electro-osmosis [Odden,1990] . Electro-osmosis, in this particular case, is where the positively charged outer section of the electric double layer between the pore solution and the pore wall is attracted to the steel cathode. The movement of the ions 'drags' along the rest of the solution, including the dissolved components. The technique has been used, apparently with successful results, on a number of structures in a commercial context. However, no evidence of either electro-osmosis or carbonate ingress was seen in tests carried out by Polder and Hondel [1992]. After treatment for up to 8 days, the carbonate ingress was only seen to have entered up to a maximum depth of 5mm. It was concluded that the realkalisation process was almost entirely due to the production of the hydroxide ions around the steel. More recent work [Mietz & Isecke, 1994] has shown that carbonate ions do enter concrete, but, it was thought, not by electro-osmosis. Tests carried out on carbonated mortar samples showed the level of realkalisation from the exposed surface was not dependent on the applied current density. It was concluded that the penetration of the alkaline external electrolyte was primarily controlled by diffusion and adsorption. If electro-osmosis did occur it was thought to have only a minor effect.

The results of this present work do agree with that of Mietz and Isecke [1994] in that carbonate ingress is possible, but it does appear that the depth of penetration from the exterior concrete surface seen here was greater than that seen by Mietz and Isecke and that the amounts in the cores increased with increase in current density. However, the time the samples were immersed in the electrolyte was greater than that used by Mietz and Isecke and the experimental arrangement may have led to the sodium carbonate solution being wicked up into the core. It is also possible that the wicking effect may have been accelerated at higher current densities by the removal of water from around the cathode by both evaporation and electrochemical means.

There were also quite large increases in the sulphate concentrations from practically zero in the untreated cores (and cores C and D) to a maximum of 160 mM in the cover zone of core B. Although not quantified, the analysis by ion chromatography detected small, but still noticeable, thiosulphate concentrations in the samples which had high sulphate concentrations. Blast furnace slag cements usually have only very small concentrations of both of these species [Tyrer, 1992]. It was suggested by Polder that this increase of sulphate based species was due to the dissolution of sulphoaluminates in the cement matrix due to the high pH [Polder *et al.*, 1993]. Subsequent work by Bertolini [1993] has seen a similar effect in polarised OPC paste samples. It was seen that significant concentrations of sulphate ions were released from the cement paste when the pH value exceeded 14.

When comparing both the pore solution and total acid soluble chloride contents of the treated cores (A and B) it can be seen that although the total chloride level had decreased the chloride concentration in the pore solution had not. It can therefore be inferred that the extra chloride in the pore solution must have been released from the matrix perhaps in a similar way to the sulphate ions. These apparent changes in the cement matrix are discussed further in section 7.3.2.

Core	% Cl (wt. cement)	Charge (Ah)
A	0.9	14
B	0.6	55
C	0.5	8.2
D	0.5	9.1
Untreated	1.15	0

Table 7.5 - Total Chloride in Surface 20mm Slice

The release of chloride from the matrix prevents the actual removal efficiency from being discussed in terms of changes in the pore solution composition. However, from the total chloride analysis (Table 7.5), it appears that, especially when the total charge passed was considered, the total amount of chloride removed was reduced when sodium carbonate was used when compared to calcium hydroxide.

As part of the full project [Polder, 1993], a further four cores were treated under similar conditions (but the pore solution was not extracted). The amount of chloride collected in the external electrolyte for all eight cores was compared to the amount of charge passed. The result can be seen in figure 7.1. The relationship also shows a distinct drop in removal efficiency when sodium carbonate is used as the external electrolyte when compared to calcium hydroxide.

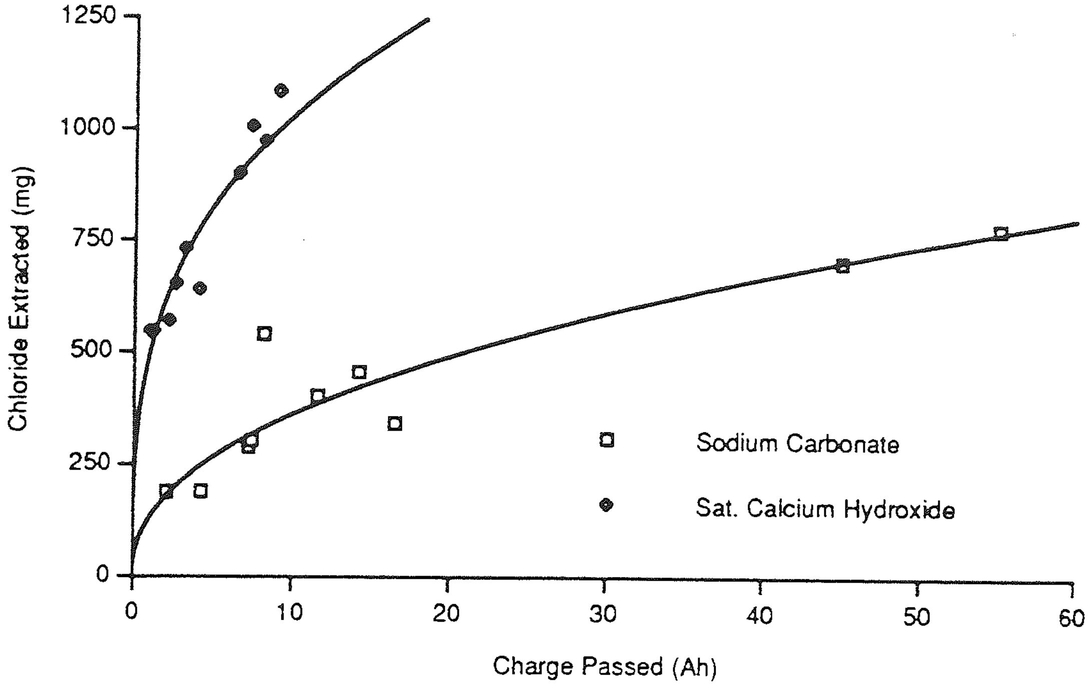


Figure 7.1 - Comparison of Chloride Removal for Calcium Hydroxide and Sodium Carbonate External Electrolytes [Polder *et al.*, 1993]

7.2. The Desalination of Laboratory Produced Concrete Specimens with Deionised Water and Lithium Hydroxide

7.2.1 The Chloride Removal Effect

7.2.1.1 2% Admixed Chloride

Figure 7.2 shows the total chloride profile for the control samples (Deionised water and LiOH as external electrolytes) with 2% admixed chloride where no current was applied. In the surface zone there was a reduction in the amount of chloride present from an average of 3.44mg/g to 2.47 mg/g. The reduction was attributed to the leaching of free chloride out into the external electrolyte. The chloride content in the external solutions rose to values around 100mg/l.

After treatment there were reductions in chloride levels at all depths; the greatest being around the steel electrode (Figure 7.3). When only a single stage treatment was employed the average chloride level at the cathode was around 0.82mg/g. This is equivalent to a level of 0.48% by weight of cement which suggests that, in the absence of any remigration after treatment, the risk of subsequent corrosion induced cracking of the concrete was low. During the treatment process the odour of chlorine gas was evident. Analysis of the external electrolyte showed that, although the chloride levels in the alkaline lithium hydroxide solution rose steadily throughout the treatment time, the chloride levels in the water electrolyte initially rose, but then decreased. A representative example can be seen in figure 7.4. The exposed surfaces of these samples were also stained and degraded whereas those in lithium hydroxide were not (Plate 7.1). From this it can be assumed that, in line with the recognised principles of electrolysis at the anodes, the deionised water external electrolyte was acidified and chlorine was evolved. It was therefore not possible to use the external electrolyte analysis to evaluate the effect of the two different solutions on removal efficiency.

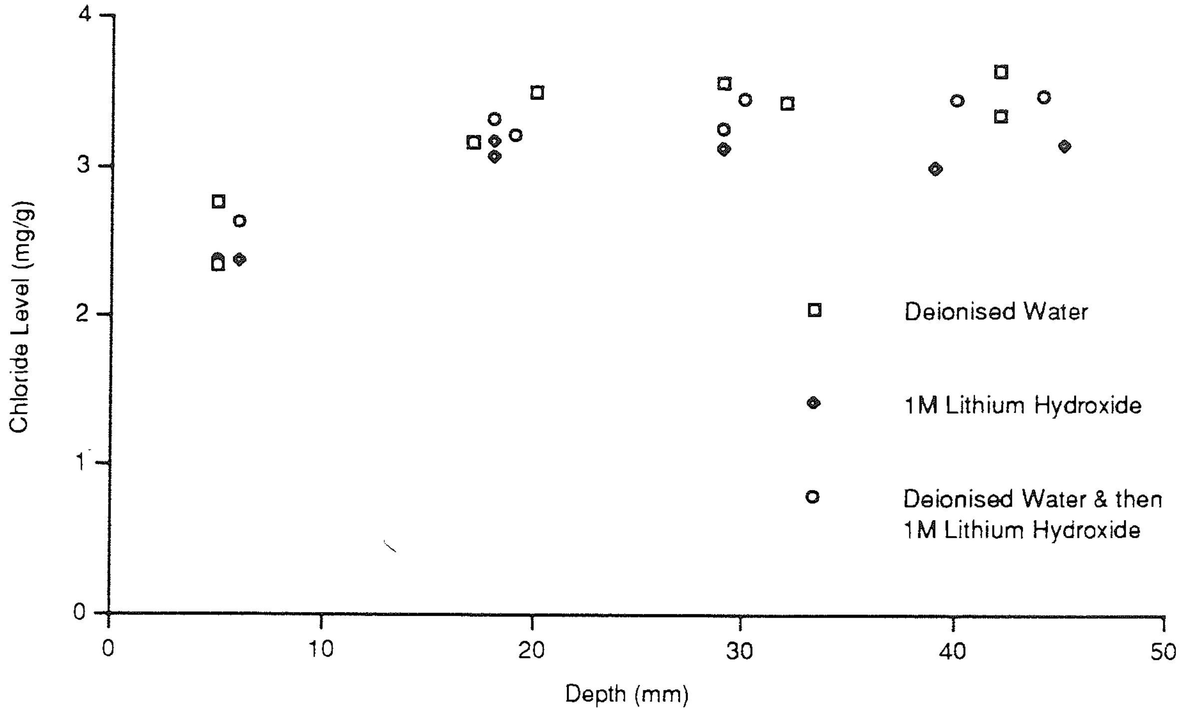


Figure 7.2 - Chloride Profiles (2% Cl) before Treatment

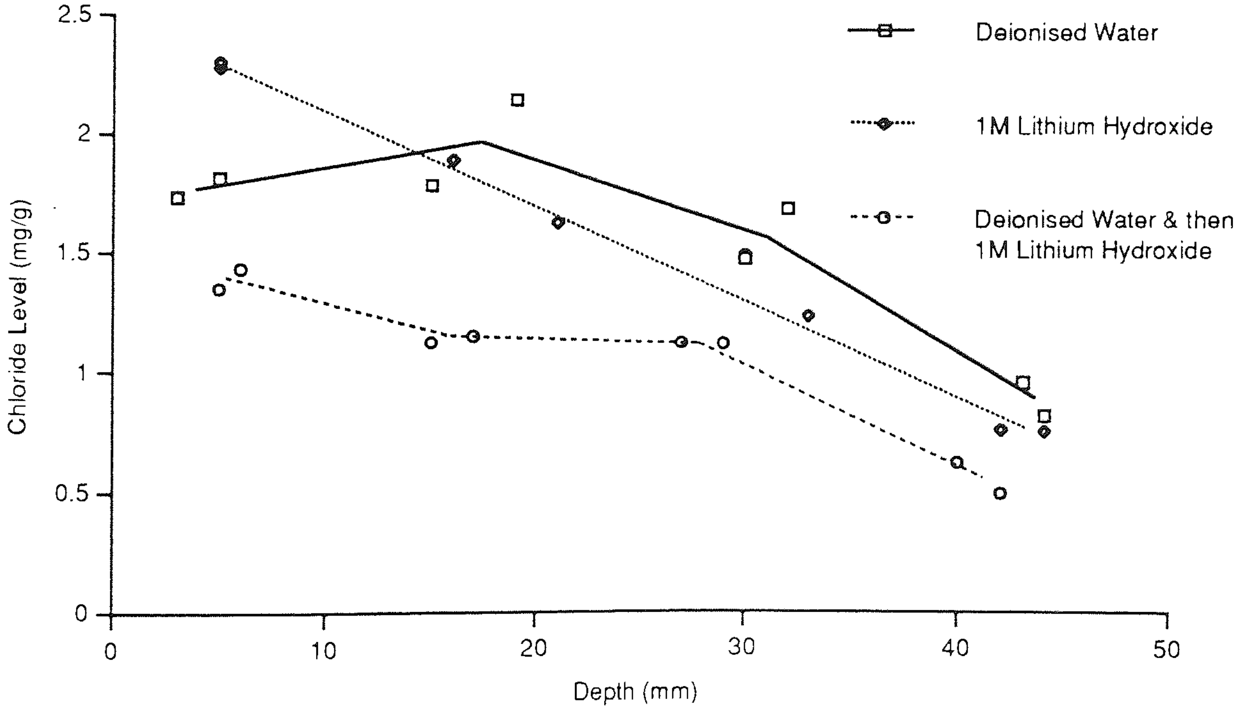


Figure 7.3 - Chloride Profiles (2% Cl) after Treatment

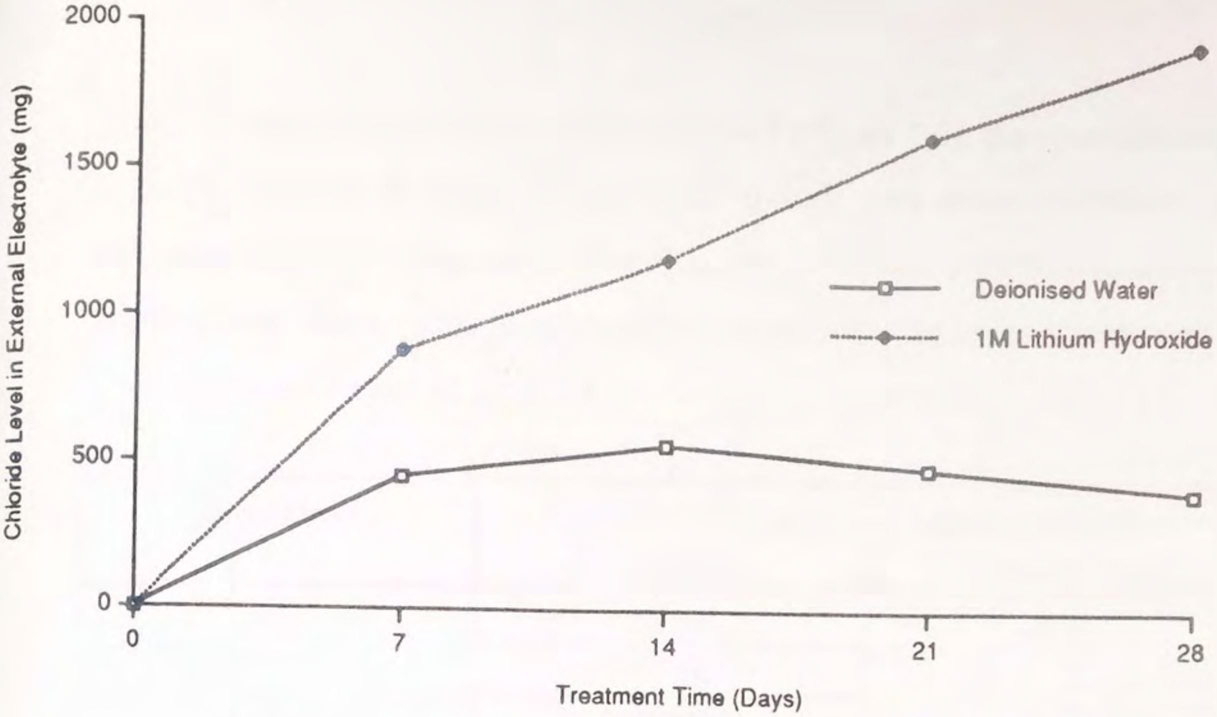
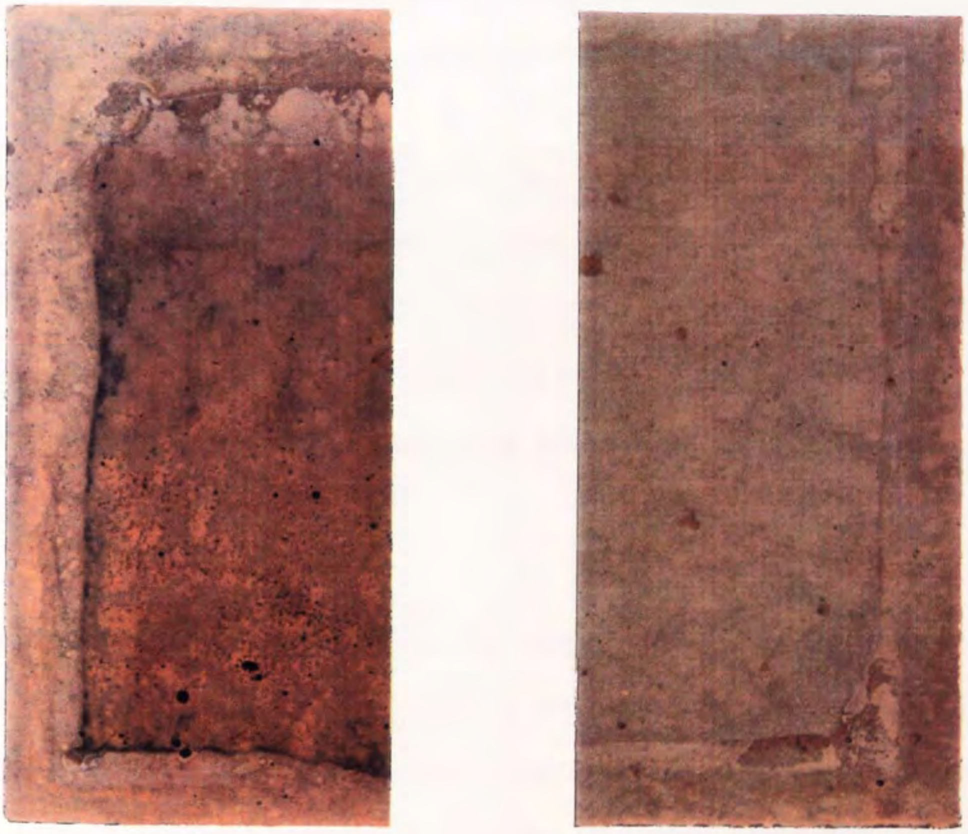


Figure 7.4 - Comparison of Chloride Levels in External Electrolyte with Increase in Treatment Time



Deionised Water 1M Lithium Hydroxide

Plate 7.1 - Exposed Surface of OPC Sample after Treatment (4wks at 2A/ sq m) x 1 Mag.

Using the total chloride profiles after treatment (Figure 7.3), the total quantity of chloride present in each sample both before and after treatment was calculated. In calculating the amount of chloride present prior to treatment, no account was taken of the leaching effect of chloride ions into the reservoirs. The results are shown in table 7.6

Electrolyte	Treated Chloride Content (mg)	Untreated Chloride Content (mg)
H_2O	1798	3192
	1577	
LiOH	1598	
	1726	
H_2O and LiOH	1077	
	1104	

Table 7.6 - Total Chloride Content between Exposed Surface and Electrode

There was very little difference in the final chloride levels when either deionised water or lithium hydroxide was used as the external electrolyte. In both cases approximately 48% of the total chloride was removed by the desalination process. However, near the surface there was a significant dip in the chloride content when deionised water was used when compared to lithium hydroxide (Figure 7.3).

In the two stage process 66% of the total chloride was removed. Assuming that the amount of chloride remaining after the first stage of treatment was 1688mg (The average of the results shown in table 7.6 for the samples treated with deionised water) and hence 1504mg had been removed. Therefore only a further 597mg were removed during the second stage of treatment.

7.2.1.2 0.5% Admixed Chloride

There was no significant surface dip in the chloride profile from the control samples when only 0.5% chloride was admixed into the samples (Figure 7.5). The chloride level in the side reservoirs reached a maximum of 15mg/l. From this it can be concluded that at this level of chloride addition, the great majority was bound into the matrix. However, after current was applied there were quite significant reductions in the chloride level nearest to the electrode (Figure 7.6). It is therefore reasonable to assume that the bound chloride was released into solution and then removed. The chloride levels nearest to the electrode indicate that more chloride was removed when lithium hydroxide was used. However, the inherent heterogeneity of concrete can show quite large amounts of experimental scatter in the results of total chloride analyses and there were not enough sets of data to see if the results with the two electrolytes were statistically different. It is thought that, in reality, there was very little difference in the levels present in the cement around the cathode.

7.2.2 Lithium Migration and its Effect on Electrochemically Induced ASR

Figure 7.7 shows the average expansion of each of the specimens made with calcined flint reactive aggregate. The expansion of the control specimens to which no current was applied was virtually zero. When current was applied and deionised water was used as external electrolyte, expansion started to occur between 4 and 7 weeks after the current had been switched off (14 to 17 weeks after the start of treatment). At the end of the test period the final expansion was approaching 0.025% and the rate of expansion was showing no sign of decreasing. In the majority of cases cracks were visible on the outside of the samples following the line of the electrode. Microscopic analysis of the concrete near to the electrode showed small cracks which had formed

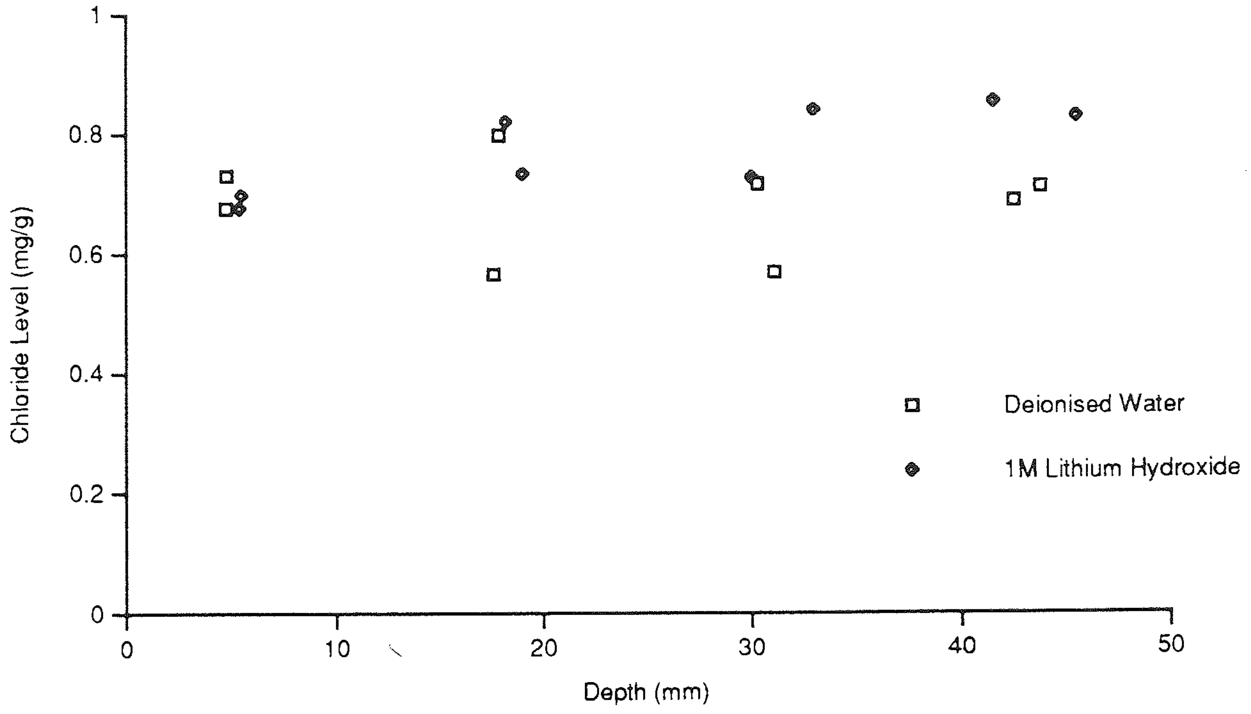


Figure 7.5 - Chloride Profiles (0.5% Cl) before Treatment

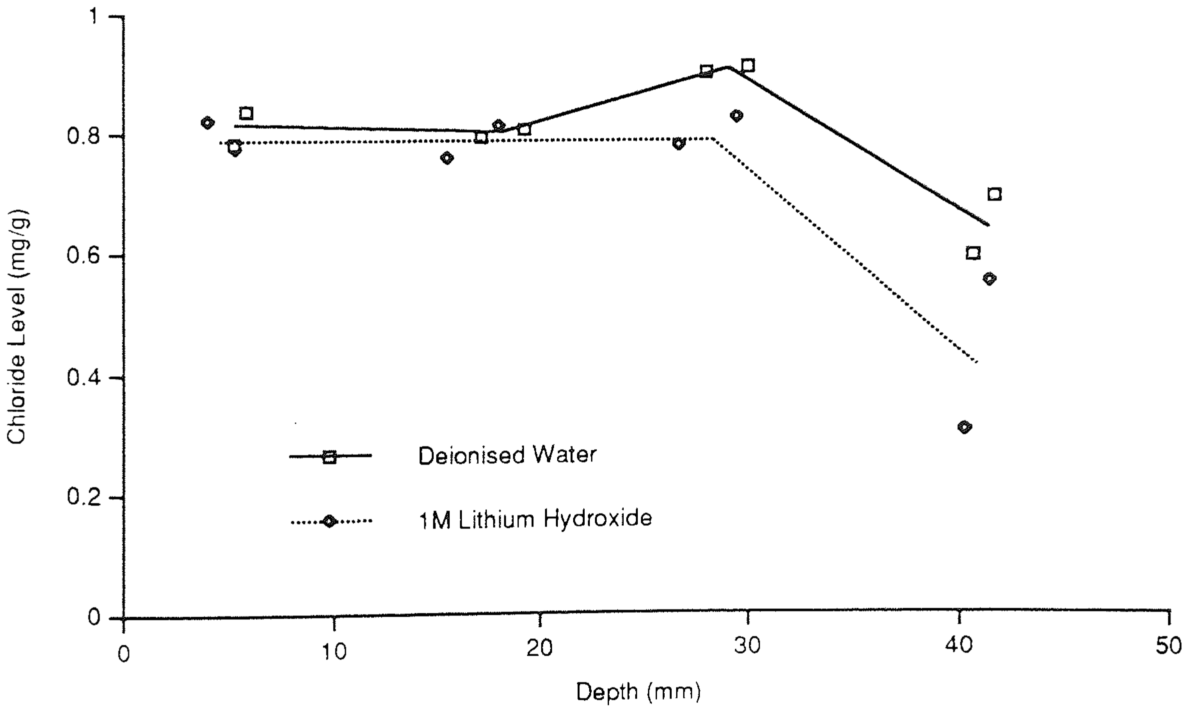


Figure 7.6 - Chloride Profiles (0.5% Cl) after Treatment

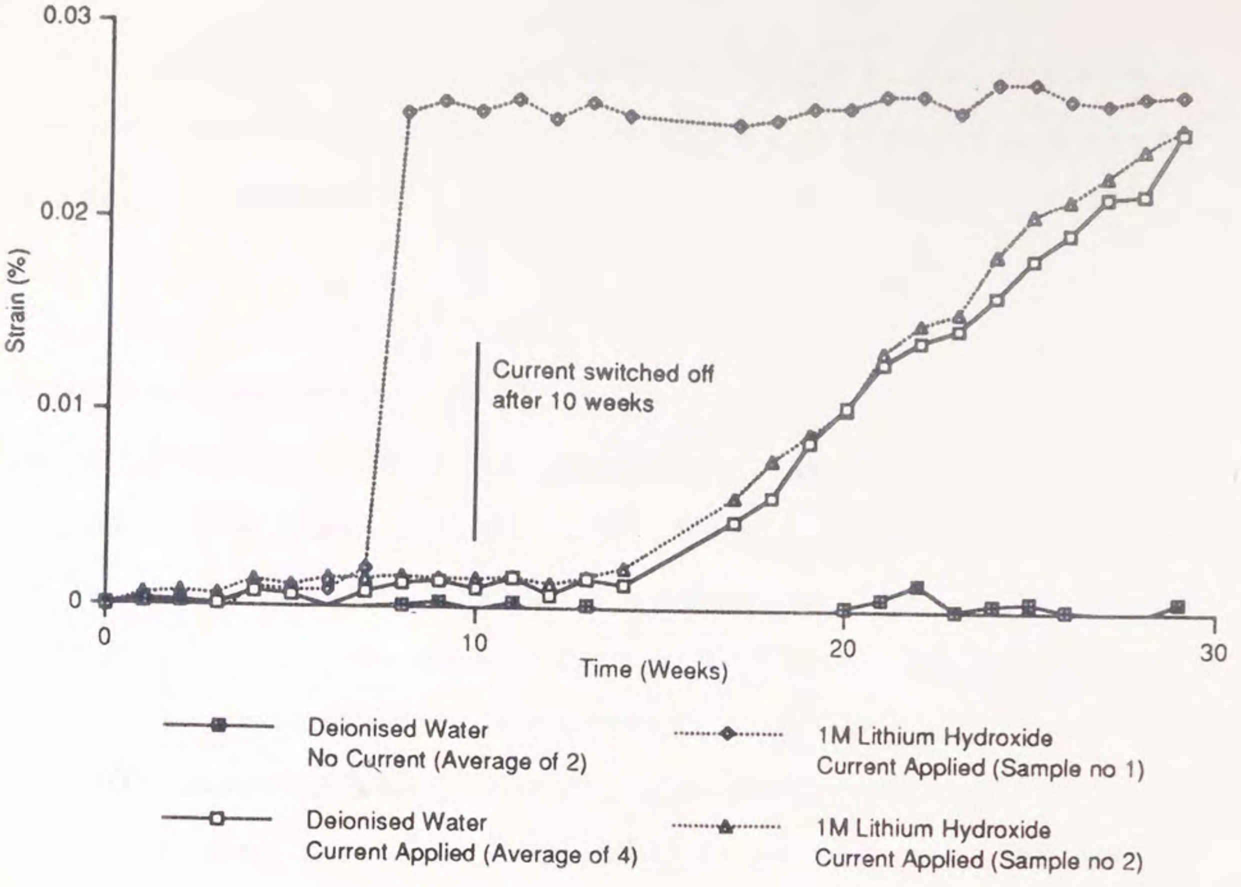


Figure 7.7 - Expansion against Time

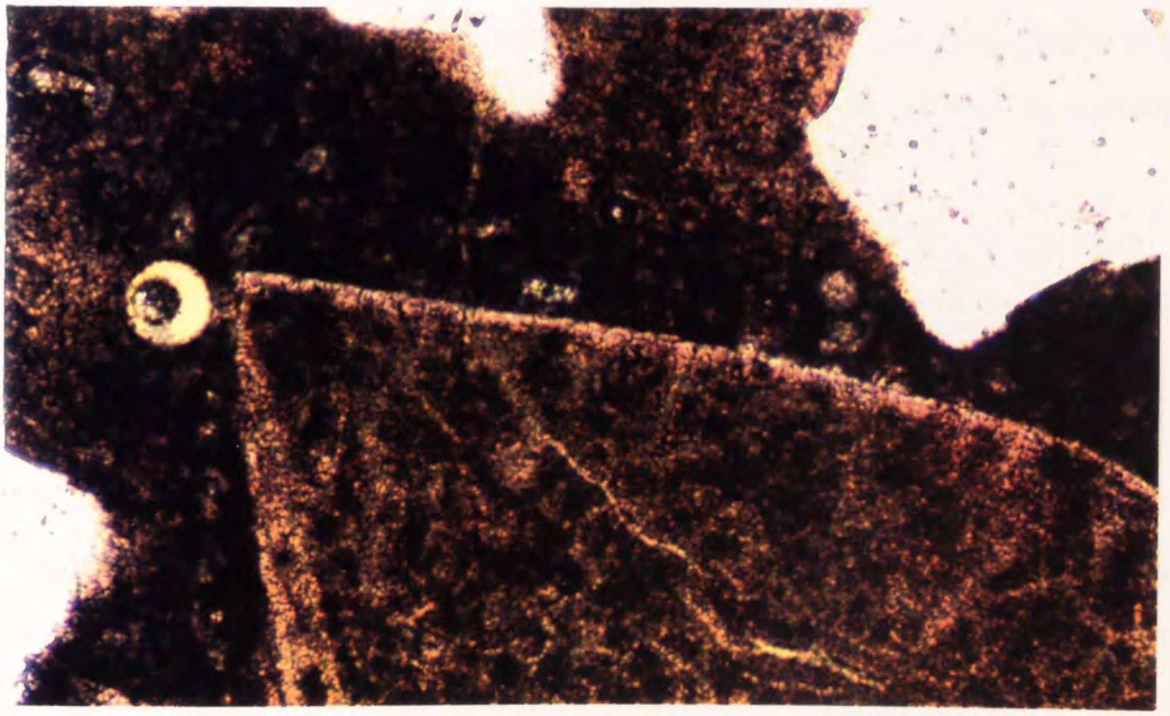


Plate 7.2 - Petrographic Image of ASR-Induced Cracking near Electrode (Deionised Water) x 100 Mag.

in the aggregate of which a limited number extended into the matrix (Plate 7.2). Away from the electrode surface the appearance of the concrete was no different to that of the control samples.

The two samples that were treated with lithium hydroxide as the external electrolyte gave differing results. One of the samples showed expansion characteristics very similar to those seen with the samples treated with deionised water (Labelled sample no. 2 - Figure 7.7). The remaining sample (no. 1) started to expand earlier and at a greater rate. Only 8 weeks into the treatment period, a crack similar to that seen on the other specimens formed. In the week prior to the crack developing, the expansion had increased from practically zero to 0.025%, but was then apparently exhausted with no further expansion being seen. Microscopic analysis showed that ASR induced cracking had occurred, but it appeared to be no more severe than in the samples where deionised water was used as the external electrolyte. However, the thin section prepared from the sample which expanded more gradually (No. 2) showed more severe ASR induced cracking (Plate 7.3). Whereas the actual number of cracks was similar, a greater percentage continued into the matrix. They also appeared to be wider.

The total lithium profiles indicated that lithium ions were able to electromigrate through hardened cement paste (Figure 7.8). However, with the exception of the surface layer, the levels of lithium ingress were quite small. After the current had been applied for 10 weeks the amount of lithium which had reached the electrode in the samples containing reactive aggregates was approximately 25µg/g of dry concrete. As would be expected, when samples (not containing reactive aggregate) were treated for a shorter length of time (4 weeks), the lithium content at the electrode was lower (Figure 7.8). In the absence of admixed chloride, the amount present at the cathode surface was

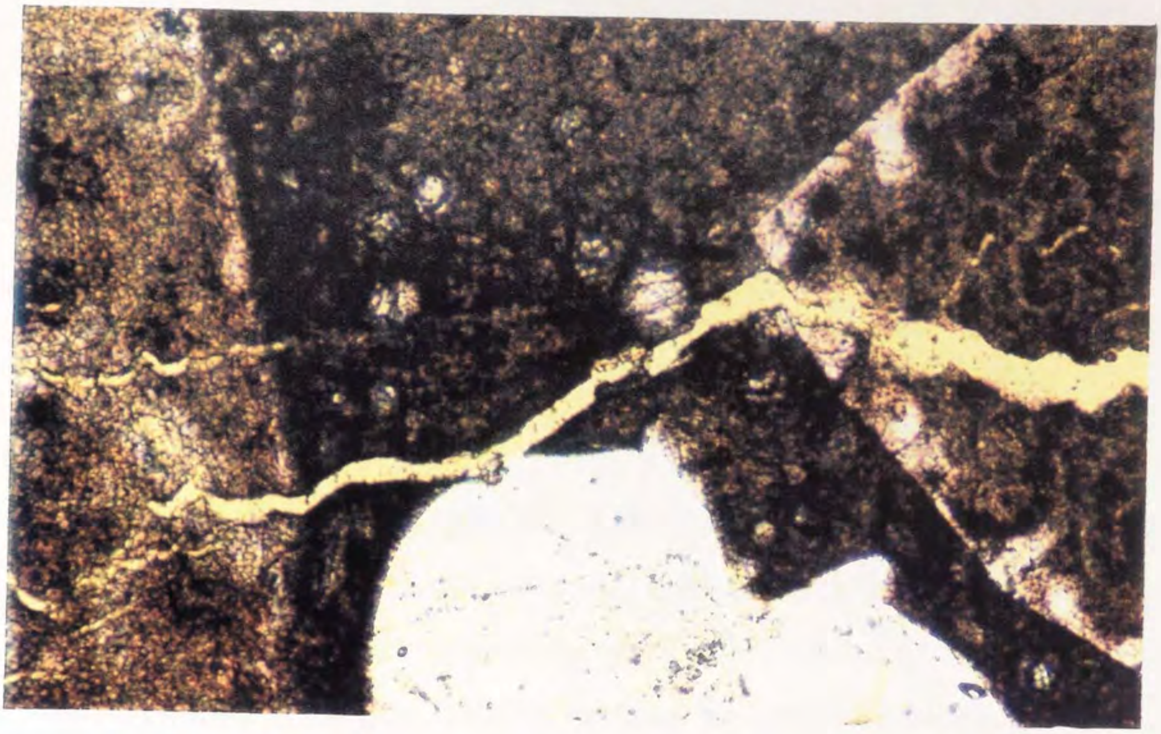


Plate 7.3 - Petrographic Image of ASR-Induced Cracking near Electrode (1M Lithium Hydroxide) x 100 Mag.

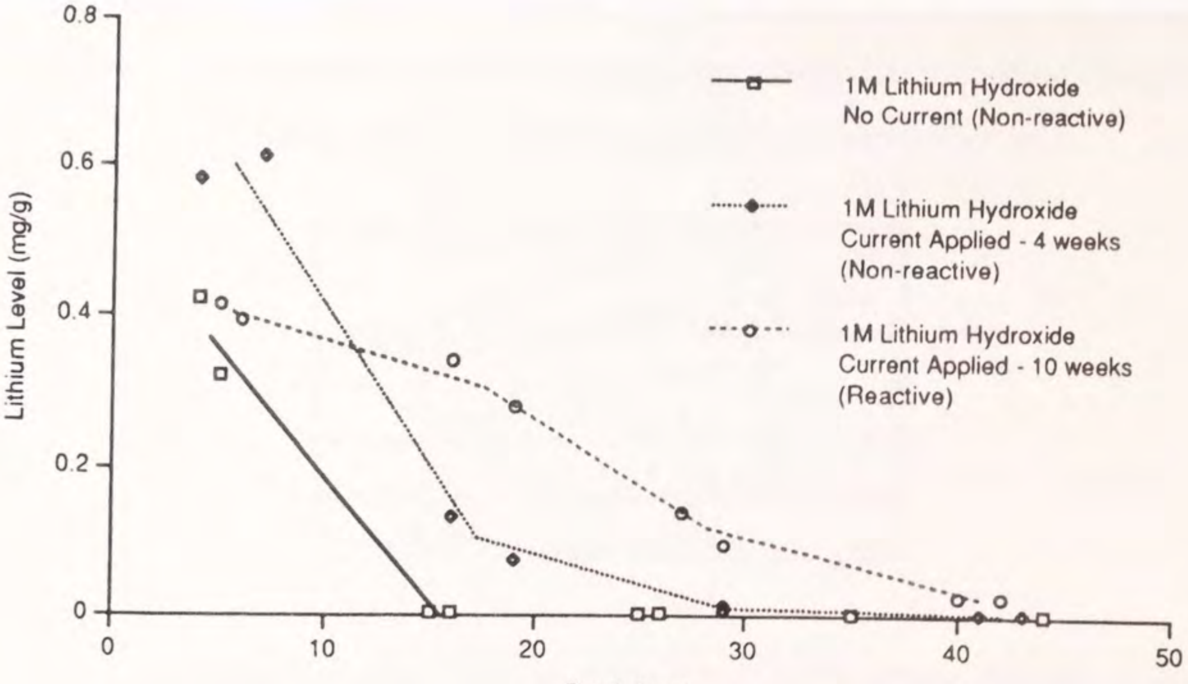


Figure 7.8 - Lithium Profiles (0% Cl) after Treatment

on average 2.7µg/g of dry concrete. Where chloride was present in the samples the value was of the same order, but generally slightly smaller at on average 2.3µg/g. It was also noted that the lithium content of the concrete at the exposed surface was less after 10 weeks treatment when compared to that after 4 weeks. It is, at present, unclear why this was so as it appears to contradict the trends seen further into the samples.

Although Diamond and Ong [1992] attempted to explain the way by which lithium ions were capable of reducing ASR induced expansion, the exact nature of the relationship between the lithium ions and the sodium and potassium ions in the pore solution required to reduce expansion is not clear. It may be speculated that for a given set of conditions, there will be a critical ratio of lithium to sodium and potassium ions which will have to be exceeded for ASR induced expansion to be reduced. If this is correct then the success of the technique of dosing the external electrolyte with lithium ions to reduce expansion will depend on the lithium ions being able to be concentrated at the cathode at a greater relative rate than the sodium and potassium ions.

Ion	Limiting Ionic Mobility at 25°C ($m^2s^{-1}V^{-1}$)
Li^+	4.0×10^{-8}
Na^+	5.2×10^{-8}
K^+	7.6×10^{-8}

Table 7.7 - Limiting Ionic Mobilities [Crow, 1988]

Table 7.7 shows the ionic mobilities of the lithium, sodium and potassium ions at infinite dilution. As stated in chapter 5, they cannot be used to show directly the actual velocity at which the ions migrate towards the cathode, but they do show that lithium ions will tend to migrate slower than either sodium or potassium ions. It is therefore likely that sodium and especially potassium ions will accumulate preferentially around the cathode when compared to lithium ions. This is especially so as the sodium and potassium ions are already present in the pore solution around the steel and do not have to electromigrate from the surface of the concrete.

It is clear that the use of a lithium based electrolyte did not entirely prevent electrochemically induced ASR from occurring. Diamond and Ong [1992] had to add quite large quantities of lithium to achieve similar amounts of expansion to that seen in specimens made from a non-reactive aggregate and it was also claimed that lithium, if added in insufficient amounts, could marginally increase the amount of expansion seen with a reactive cristobalite aggregate [Diamond & Ong,1992] (Calcined flint aggregate primarily consists of cristobalite [Sibbick, 1993]). Although direct comparisons cannot be drawn between the results of Diamond and Ong and those here it does seem unlikely that the small amounts of lithium ions present at the cathodes would be capable of entirely suppressing ASR induced expansion and, of course, this is what was seen in both the expansion results and the microscopic analysis.

However, what the expansion results do not make clear is whether the method of introducing lithium ions into concrete by applying an electric field was capable of either reducing or increasing long-term ASR induced expansion. Further expansion monitoring of the samples containing the reactive aggregate may have elucidated the effect, but unfortunately, this was not allowed by the time span of the project.

Recent work in the USA. has claimed that lithium electro-migration into hardened concrete successfully inhibits ASR [Bennett *et al.*, 1993]. From the information that can be obtained from the report, it appears that only one sample was made and treated (no duplicate and no direct control specimens). 0.1M LiOH was used as the external electrolyte and current was applied at $6A/m^2$ although it was not made clear whether this was of steel or concrete surface area. The total charge applied was $3000Ah/m^2$. Petrographic analysis showed no indication of ASR activity. However, in the absence of duplicate and control specimens and as no chemical analysis was carried out on the specimen, it is difficult to draw firm conclusions.

A possible explanation for the difference in the present results and that of Bennett *et al.* [1993] is that microscopic analysis of the samples in this present piece of work showed that there was a higher percentage of unhydrated cement powder in the concrete than might normally be expected [Sibbick, 1994], perhaps indicating insufficient curing of the sample prior to treatment. As stated in chapter 5, lithium appears to be removed from solution and incorporated into the cement reaction products [Diamond & Ong, 1992]. Therefore it is quite possible that a large proportion of the lithium in the concrete may have become bound up in the hydration products and had not been available to reduce ASR induced expansion. Clearly, further work is needed to both resolve the inconsistencies in the data and to clarify the results of Bennett *et al.* [1993].

7.3 General Discussion

7.3.1 Effects of Electrolyte Composition on Removal Efficiency

Analysis of both the total acid soluble chloride contents and the external electrolyte composition from the BFSC concrete cores showed that there was a significant reduction in the removal efficiency when sodium carbonate was used when compared to calcium hydroxide. Figure 7.1 showed that when a total charge of 5Ah was passed the approximate amount of chloride removed into the sodium carbonate external electrolyte was 0.27g, but when calcium hydroxide was used it was 0.90g. In addition to the general reduction in removal efficiency with sodium carbonate when compared to calcium hydroxide, the rate at which the removal efficiency decreased with the increase in charge was also higher with sodium carbonate (Figure 7.1). It appeared that no amount of charge would be able to remove more than 0.8g of chloride

With cores C and D, although not analysed, it is reasonably safe to assume that there was very little calcium in the pore solution due to its low solubility in alkaline solutions. The flow of hydroxide ions from the external electrolyte into the concrete sample was also likely to be small as the hydroxide concentration in saturated calcium hydroxide is comparatively small and its flow is retarded by the electrical flow. Therefore the ionic strength of the pore solution, which subsequently affects the chloride removal efficiency, was only significantly increased by the reactions occurring at the cathode and in the concrete.

Consideration of the pore solution data for core numbers A and B showed that the total ionic strength was greatly increased due to the sodium and carbonate ions in both the cover zone and that surrounding the steel. Clearly, this reduced the transport number of the chloride ions in the surface zone of the concrete and therefore the amount of chloride removed from the concrete.

When compared to deionised water, the use of lithium hydroxide as external electrolyte showed no overall reduction in amount of chloride removed. However, it was apparent that there was a localised reduction in the amount removed from the zone nearest to the exposed surface in the samples with 2% chloride addition. In this area the lithium concentration was significant and could therefore have reduced the chloride transport number in the surface zone and subsequently the amount of chloride removed from that area.

A localised reduction in removal efficiency associated with the use of lithium hydroxide may not be the only reason for the lower chloride content at the surface of the samples treated with deionised water. It was noted that a small degree of degradation of the cementitious material occurred on the exposed surface which, it was assumed, was due to the deionised water becoming acidic as the anodic reaction proceeded. The dissolution of the cementitious matrix would release bound chloride into the external electrolyte solution. However, the depth of attack was very small (<1mm) and when compared with the total thickness of the slices used for the analysis (≈10mm) the effect on the chloride level would be small.

A significant drop in removal efficiency was also seen during the two stage process. During the first four weeks treatment 1688mg of chloride was removed which compared to only 597mg for the second four weeks. As it has already been shown that the use of lithium hydroxide had only a limited effect on the overall amount of chloride removed from the concrete samples, the results demonstrate the reduction in removal efficiency with increase in treatment time. This effect is predicted by considering the effect of treatment on the chloride transport number in the cover zone. As treatment proceeds the relative ratio of free chloride to hydroxide decreases due to both the chloride removal and hydroxide production. The amount of charge carried by the chloride ions is therefore reduced and less chloride is removed.

The results indicate that the choice of external electrolyte can have a significant effect on the amount of chloride removed. As dictated by the concept of transport numbers, for the external electrolyte to have a minimal effect the amount of chloride removed from the concrete the degree to which it is able to enter the surface zone of the concrete must be small. Assuming, as thought by Polder and Hondel [1992] and Mietz and Isecke [1994], that either electro-osmosis does not occur in concrete or has only a very minor effect, the ingress of the components of the external electrolyte into the concrete will by governed by the mechanisms of electromigration, diffusion [Crow, 1988] and absorption [Mietz & Isecke, 1994].

Absorption will occur because the pores in the concrete, especially at the surface, will not be saturated and therefore the external electrolyte will flow into concrete to counteract the moisture gradient. Diffusion of all the ions in the external electrolyte and the concrete pore solution will also occur depending on their concentrations profiles. The application of a current between the two electrodes will cause electromigration to occur due to the potential gradient. Although electromigration induces ions to move in both directions, in this context of external electrolyte ingress into the cover zone of the concrete, it is the movement of the cations which is of interest. Presumably, in chloride removal treatment, it is thought that the process of electromigration is the most significant mechanism of ionic transport, but, from the degree of carbonate ingress seen in cores A and B, it can be seen that the mechanisms of absorption and diffusion cannot always be ignored.

In terms of chloride removal efficiency solutions of calcium hydroxide appeared to give relatively good results. It is thought that the reasons for this is that calcium hydroxide is fairly insoluble (when compared to lithium hydroxide or sodium carbonate) producing a relatively dilute external electrolyte. Furthermore, in alkaline conditions such as those generally experienced in the pore solution of OPC concrete, it becomes even more insoluble and is therefore unable to any great extent to electromigrate, diffuse or be absorbed into the concrete.

Sodium carbonate is far more soluble in water and is therefore able to be made into more concentrated electrolyte solutions (as required to maintain a high pH and prevent chlorine evolution). It has been shown that it is also able to move through hardened cement paste. Therefore, once in the cover zone of the concrete, the chloride transport number and therefore the amount of chloride removed was reduced.

As with sodium carbonate, lithium hydroxide is quite soluble and therefore is able to be made into concentrated solutions (required to maintain a high pH during treatment and to aid lithium ingress). However, although a localised reduction in the amount of chloride removed was noted, the overall effect when compared to that of deionised water was not a major one. Lithium ions have a fairly low ionic mobility (Limiting Ionic Mobility at 25°C is 4.1×10^{-8} $m^2s^{-1}V^{-1}$ [Crow, 1988]) and may also have been incorporated into the C-S-H gel reaction products [Diamond & Ong, 1992]. It is thought that this tended to reduce the effect on the amount of chloride removed. The limited effect on the amount of chloride removed also implied that the hydroxide ions were not able to significantly diffuse or be absorbed into the concrete either before or during treatment using that particular experimental arrangement. It would have tended to reduce the amount of absorption by continually wetting the non-treated faces with water, but this may not be the case in all circumstances.

When deionised water was used as the external electrolyte, prior to the application of current, the absorption mechanism would not have increased the ionic strength of the pore solution and the diffusion mechanism would have tended to marginally reduce it. During treatment the external electrolyte was acidified by the production of hydrogen ions at the anode. Hydrogen ions have an ionic mobility far in excess of any other ion (Limiting ionic mobility at 25°C is 36.3×10^{-8} $m^2s^{-1}V^{-1}$ [Crow, 1988]) and therefore, if not passing through a cementitious environment, would have greatly reduced the amount of chloride removed. However, the hydrogen ions reacted with the hydroxide ions in the pore solution and when sufficient acidity was produced also caused the dissolution of the hardened cement paste. This removed the hydrogen ions from the pore solution and thus reduced the degree by which the chloride removal efficiency was reduced. It is, of course, not possible to say what effect the ionic species released by the dissolution of the hardened cement paste had on the chloride removal efficiency.

It is not possible directly to compare the chloride removal results of the two sets of electrolyte solutions to determine the most efficient external electrolyte solution of those tested in terms of chloride removal efficiency as the experimental conditions and samples were so different. However, the general conclusions that can be made from the results appear to indicate that there are two main methods by which the ingress of the ionic species from the external electrolyte into the cover zone can be reduced, thus limiting the effect on chloride removal efficiency. If the electrolyte has a low concentration then there will be a smaller number of cations to electromigrate into the cover zone. A low concentration will also tend to reduce the degree of ionic diffusion into the concrete and, if significant absorption of the electrolyte into the concrete occurs, then the effect would be less than if an electrolyte with a high ionic concentration was used. Secondly, the species of cation in the external electrolyte can be chosen so that it is not able to migrate easily into the matrix. This can be by choosing one with a low ionic mobility, one with a low concentration in alkaline environments or one which reacts with the cementitious matrix and is thus removed from the pore solution.

It therefore appears that if the anode comprises of activated titanium mesh and both chlorine gas evolution and staining and dissolution of the concrete are to be avoided, the most promising external electrolyte solution would be saturated calcium hydroxide. This conclusion is in conflict with the recommendations of the recently published SHRP electrochemical chloride removal implementation guide [Bennett & Schue, 1993]. Here it was suggested that 0.2 M sodium borate should be used where non-ASR susceptible concretes are being treated. The choice of sodium borate appeared to made entirely upon the criterion of preventing of chlorine gas evolution [Bennett *et al.*, 1993], but from the conclusions made above it would seem that its use would reduce the chloride removal efficiency.

7.3.2 Effects of Treatment on the Hardened Cement Phases

From the experimental results described previously, it is clear that the electrochemical treatment process has an effect on the composition of cement paste. It was seen that treatment of BFSC concrete cores with Na_2CO_3 caused both chloride and sulphate ions to be released into solution. Total chloride analysis of all of the treated OPC samples containing 0.5% chloride also seemed to imply that amounts of bound chloride were removed from around the cathode. DTA and DTG analysis of one of the OPC concrete blocks containing 2% chloride also showed alterations to the composition of the cement paste (Figure 7.9). In the bulk of the specimen there is a small peak at 180°C (Peak A) which is missing from the trace obtained from the electrode surface. It is not clear whether the peak is due to ettringite or Friedel's salt, but it does indicate that changes took place. The peaks (B) which started at 675°C on both of the traces were due to the thermal decomposition of calcium carbonate to form calcium oxide. The peak intensity was greater in the sample taken from the main body of the sample because it had a greater aggregate fraction than the cement rich layer taken next to the electrode.

Holden *et al.* [1983] added both chloride and sulphate ions to the mix water when preparing cement paste samples. It was noted that for a cement with a set C_3A content the addition of chloride to the mix water increased the hydroxide concentration in the pore solution. When the same amount of chloride was added as well as a quantity of sulphate ions the proportion of the total chloride in the pore solution increased and the hydroxide concentration increased even further. Struble [1987] also found that the sulphate level present in the pore solution (expressed from chloride free mortar samples made with limestone fine aggregate) increased as the alkali level of the cement increased. Between pore solutions with a pH of 13.4 and 14 the concentration increased by approximately a factor of 10 to over 100mM/l.

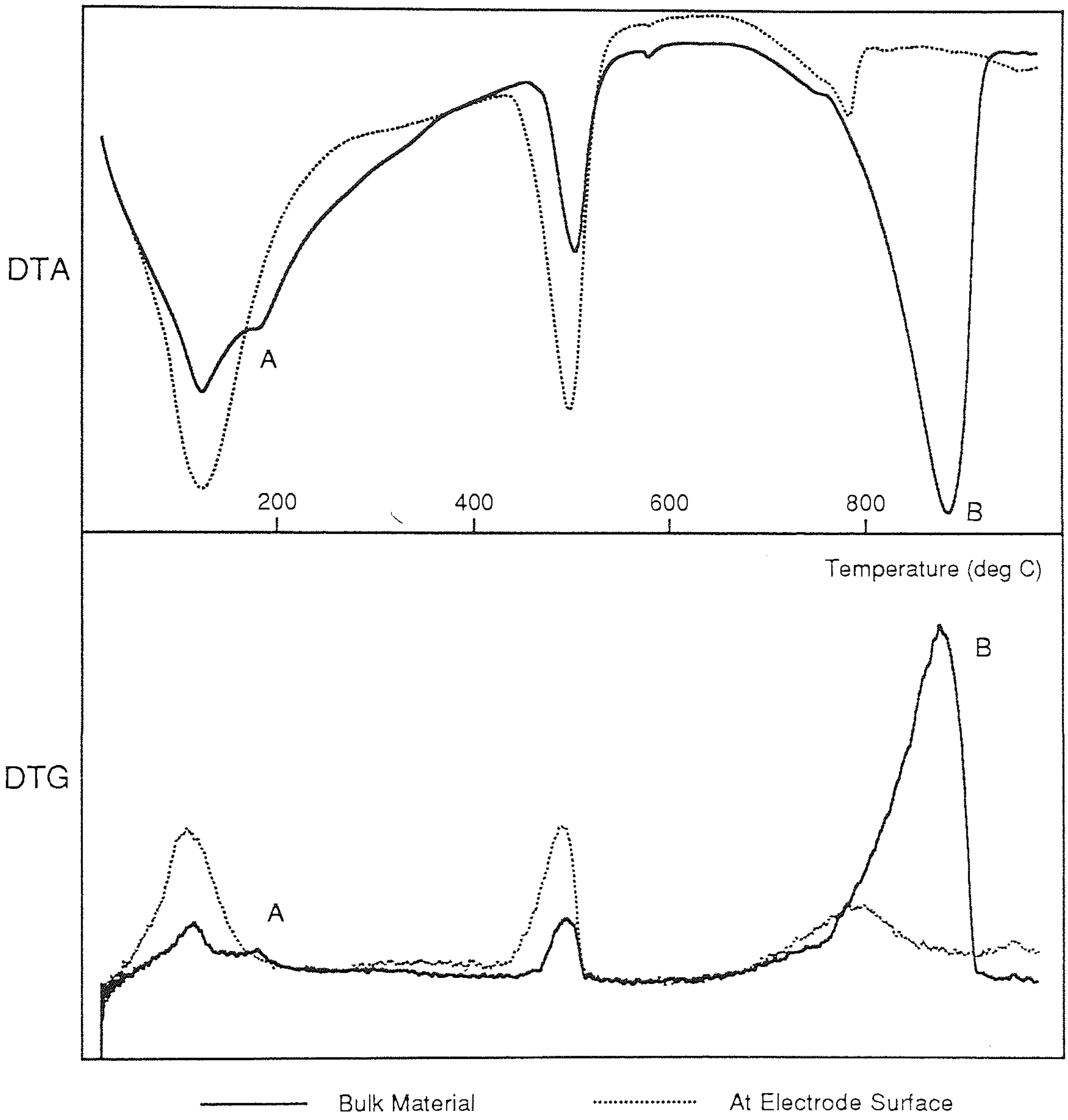


Figure 7.9 - DTA and DTG Analysis of Treated OPC Sample

Therefore it appears that if pure unhydrated C_3A is added to an aqueous solution containing hydroxide, chloride and sulphate ions, then a set percentage of each of the ions are removed from solution and bound up in the solid phase. The relative amounts of the three species removed from the solution would depend on their affinities to react with the C_3A and their relative concentrations. If the concentration of one of three species is increased with respect to the other two then the relative amount of that species bound up will also be increased, leaving greater amounts of the other two in solution.

The relationships between the various ions described above were seen for cements where the ions were present at the time of mixing. However, there appears to be no reason why the equilibrium would not still exist in hardened pastes where the position of the equilibrium is shifted by the increase in one of the species from an external source. Practically this has been seen in cases where ASR has been exacerbated in concrete due to an increase in the alkali content. This was in turn attributed to the ingress of road deicing salt (NaCl) [Sibbick & West, 1992]. Therefore as the cathodic electrode reactions occur the hydroxide ions are substituted for the chloride and sulphate ions in the C_3A reaction products.

It has also been seen that the equilibrium is affected by changes in temperature. Roberts [1962] has shown that as the temperature is increased the chloride content of the pore solution is increased and hydroxide content is decreased, indicating the temperature rises induced by the treatment process will help the release of bound chloride into solution.

7.3.2.1 Implications of Alterations to the Composition of the Hardened Cement

The most important implication is that in addition to the removal of free chloride in the pore solution, it is also possible to remove the bound chloride. Theoretically, therefore, if enough hydroxide is produced at the cathode, all the bound chloride in very close proximity to the steel could be released into solution and subsequently removed from the structure. In fact, this may actually have occurred in treated structures, but the usual site method of collecting samples for analysis would be too inexact to detect this.

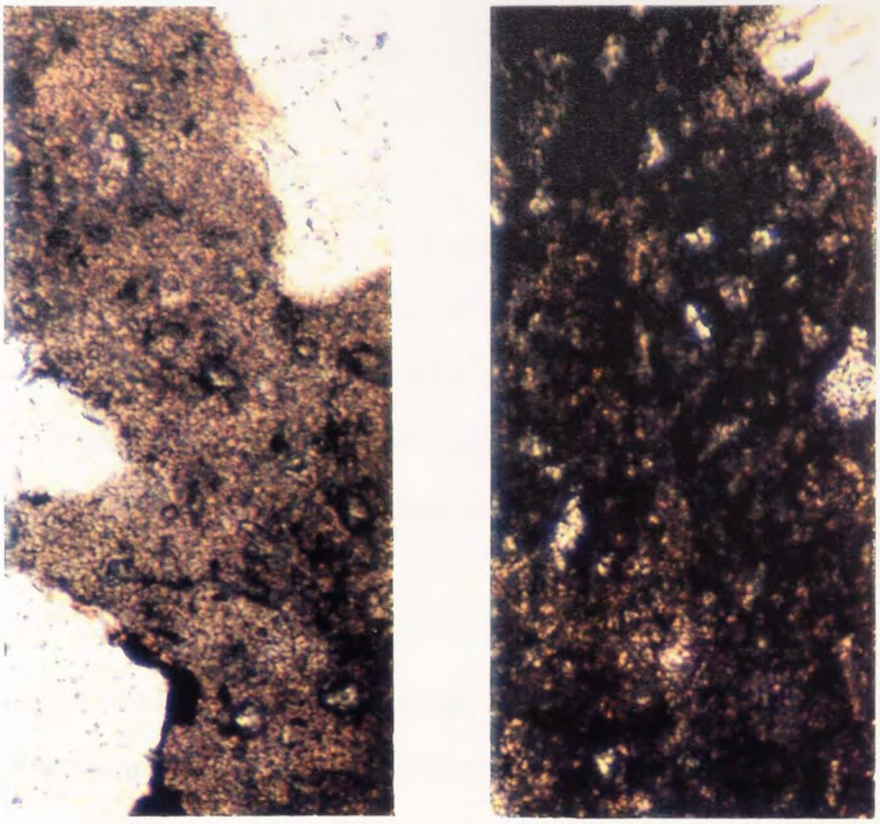
Of course, the release of chloride and sulphate ions into solution near to the steel reinforcement could have implications regarding the corrosion resistance of the steel reinforcement once the treatment has been concluded. While the aggressive ions are present in the matrix they are not able to initiate corrosion of the steel reinforcement, but once they have been released into solution this is no longer the case. It has already been shown that the choice of an unsuitable electrolyte (such as sodium carbonate) may prevent the removal of the ions from the concrete. The situation here becomes complex, but it can be predicted that, if chloride and sulphate ions, are left in the body of the concrete then they will remigrate towards the steel and the hydroxide ions will diffuse away from the steel increasing the ratio of aggressive to inhibitive ions. It is not clear whether the ratio will increase sufficiently to initiate corrosion, especially as the proposed equilibrium relationship between these three species and their C_3A based reaction products will tend to release hydroxide ions into solution and remove the aggressive ions.

At present site experience tends to suggest that there will not prove to be a problem as studies on treated structures have shown that the potential of the steel, after sufficient time had been allowed for them to reach a steady state, became less negative after treatment indicating that the environment was less corrosive [Manning, 1990; Elsener *et al.*, 1992]. However, until the long-term effectiveness of the process has been proven, it would be prudent to undertake long-term monitoring any treated structure for signs of reinforcement corrosion.

Another aspect that has to be considered is the effect on the mechanical properties of the structural member, in particular bond strength. One of the more widely advanced theories on bond strength reduction is that the C-S-H gel is softened by the high alkali levels [Locke *et al*, 1983] associated with the treatment process. Way and Shayan [1988] found changes occurred to both the C_3S and C_3A phases when the alkali level of cement paste was increased. When sodium hydroxide solutions of 2.5M and 4M were reacted with ground cement clinker, a sodium substituted monosulphate phase ('U' phase) with a structure of $4CaO.0.9Al_2O_3.1.1SO_3.0.5Na_2O.xH_2O$ was formed from the C_3A instead of either ettringite or the monosulphate phase. A crystalline form of C-S-H was also detected in addition to the usual gel form. During curing the samples were seen to crack demonstrating the adverse effects of the new phases on the strength of the cement. However, Shayan and Ivanusec [1989] found that the greatest degree of strength loss was seen before any of the new phases were formed (or were present in quantities that were too small to analyse) at relatively low levels of alkali addition. They thought that sodium substitution into the C-S-H gel probably occurred and was responsible for the majority of the strength loss.

Inspection of the petrographic thin section prepared from one of the samples not containing reactive aggregate (treated for 28 days with H_2O and then 28 days with 1M LiOH) indicated that there was a change in the appearance of the hardened cement paste around the steel cathode when compared to that in the bulk of the specimen. It was not possible to determine the nature of the changes, but the colour of the paste was lighter in the area around the cathode (Plate 7.4). There was also a small degree of evidence that the porosity around the steel was greater than in the bulk of the sample. In the production of a thin section it is usual to vacuum impregnate the sample with an epoxy resin to prevent it from breaking up while being ground to the correct thickness. In this case a fluorescent dye was added to the resin. Inspection of a fresh face cut from the impregnated concrete block under ultra-violet light showed that the resin had reached a far greater depth in from the electrode surface than from the other faces (Plate 7.5). Inspection of a control sample indicated that, although a percentage of the increase in porosity may have been due to a lesser level of compaction being achieved around the steel cathode during the sample production, the remainder may have been due to the treatment process. Similar increases in porosity around steel cathodes embedded in concrete have also been seen using the technique of MIP [Bennett *et al.*, 1993].

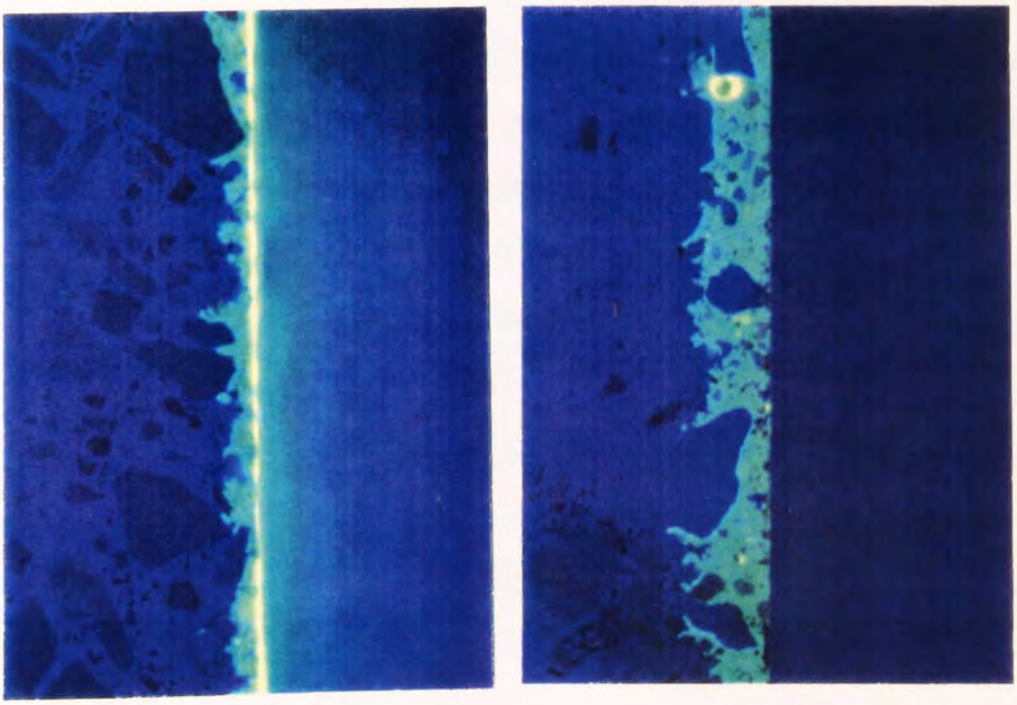
It remains unclear whether the apparent decreases in bond strength as seen by various researchers can be attributed to a small increase in porosity around the cathode. Further work is also required before the mechanism responsible for the increase in porosity can be identified, but in addition to the changes seen to the C-S-H gel it is possible that those seen here to have occurred to the C_3A hydration products may also play a role.



Near Electrode

Bulk Material

Plate 7.4 - Colour Change to Cement Matrix. x 100 Mag.



Prior to Treatment

After Treatment

Plate 7.5 - Depth of Resin Impregnation at Electrode Surface. x 2 Mag.

7.4 Conclusions

The present work has shown that the composition of the external electrolyte can significantly affect the amount of chloride removed. For maximum removal efficiency the ionic species in the electrolyte should not be able to migrate into the concrete. This can be achieved by either using an electrolyte whose ionic constituents have a low ionic mobility and/or are only able to be present in low concentrations in the pores of hardened cement.

The electromigration of lithium ions as a means of suppressing electrochemical induced ASR was not successfully achieved in the samples used in the present work. Primarily this was thought to be due to the low ionic mobility of lithium ions preventing sufficient quantities reaching the cathode, but it may also have been due to inadequately cured concrete. It was thought that the lithium ions may have been absorbed into the cementitious matrix which retarded their flow into the bulk of the concrete.

It has been shown that the hydroxide production at the steel reinforcement associated with any of the electrochemical treatment processes can alter the composition of the C_3A hydration products. It involves the release of both chloride and sulphate ions. By these means not only the free chloride in the pore solution, but also that bound into the matrix can be removed from around the cathode.

7.4.1 Recommendations for Further Work

The alterations to the C_3A hydration products may also play a role in the reduction in bond strength as seen by a number of researchers, but further work is required before it can confidently be accepted or rejected. As bond strength measurements tend to show a large amount of scatter and will, to some degree, be reliant on the surface preparation of the steel, a useful starting point in this work would be to study the effect of alkali additions to the mix water on cementitious samples made from cements containing varying C_3A contents containing no steel. Initially, compressive strength measurements would indicate whether the additions were having any deleterious effect and then this could be investigated further by analysing for changes to the chemical composition and the microstructure of the cement.

Another area that needs further consideration is the situation regarding the use of lithium based external electrolyte solutions to prevent or reduce electrochemically-induced ASR in concrete samples containing potentially reactive aggregates. The most urgent need is to resolve the inconsistencies between this present study and that of Bennett *et al.* [1993] by carrying out a more comprehensive test programme on similar lines to that described in section 6.2, involving samples in at least triplicate, longer term expansion measurements, petrographic analysis and determination of lithium levels at the cathode after treatment. If the results indicate that, as shown in this present study, the use of lithium based external electrolytes were not able to prevent or even reduce electrochemically-induced ASR then an area of further work could be to investigate ways to increasing the amount of lithium around the steel. One such way would be to place the lithium based electrolyte on the surface of the concrete some time before the application of the current to allow lithium ions to be absorbed and/or diffuse towards the steel. This process could possibly be made more efficient by drying the concrete prior to application of the electrolyte.

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Appendix A : Calculation of the Original Pore Solution Composition from the Expressed Solution

For example, Sample taken from block 2 (Sodium Chloride) at depth 3.75mm.

Weight of 'insitu' sample = 21.3122g
Weight of 'insitu'sample dried to constant weight at 105°C = 19.7530g

Therefore evaporable water content $= \frac{21.3122 - 19.7530}{21.3122}$

$= 0.0789$

Weight of resaturated 'insitu' sample = 15.8010g
Weight of resaturated 'insitu'sample dried to constant weight at 105°C = 14.0458g

Therefore evaporable water content $= \frac{15.8010 - 14.0458}{14.0458}$

$= 0.1250$

Dilution factor $= \frac{0.1250}{0.0789} = 1.58$

'Insitu' Conc. = 'as analysed' Conc. x Dilution factor

Chloride concentration in analysed pore solution = 1265 mM
Therefore chloride concentration in the 'insitu' pore solution = 1.58 x 1265
= 1999mM

Appendix B : XRD Traces

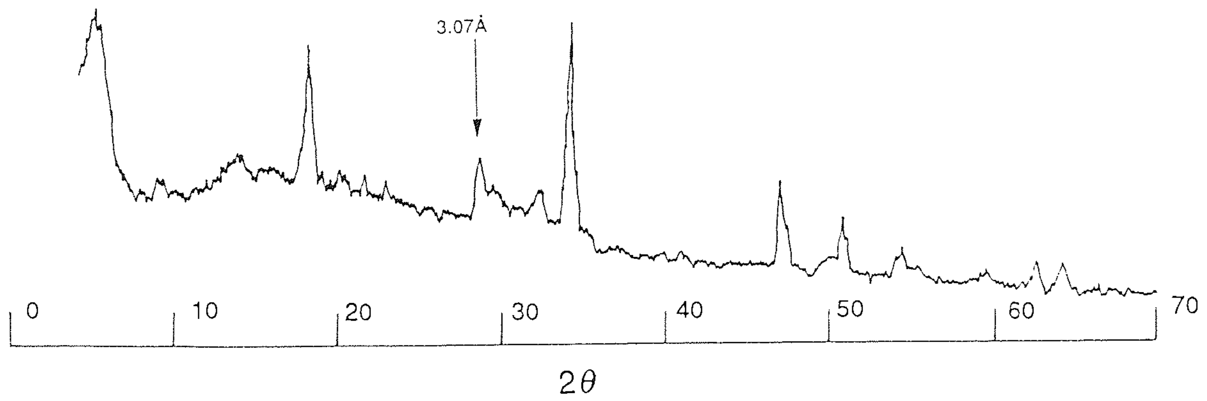
The following XRD powder diffraction patterns are shown in terms of 2θ where θ is the angle of incidence or reflection of the X-ray beam from the test sample in the diffractometer. D-spacings are calculated by Bragg's law

$$d = \frac{n\lambda}{2\sin\theta}$$

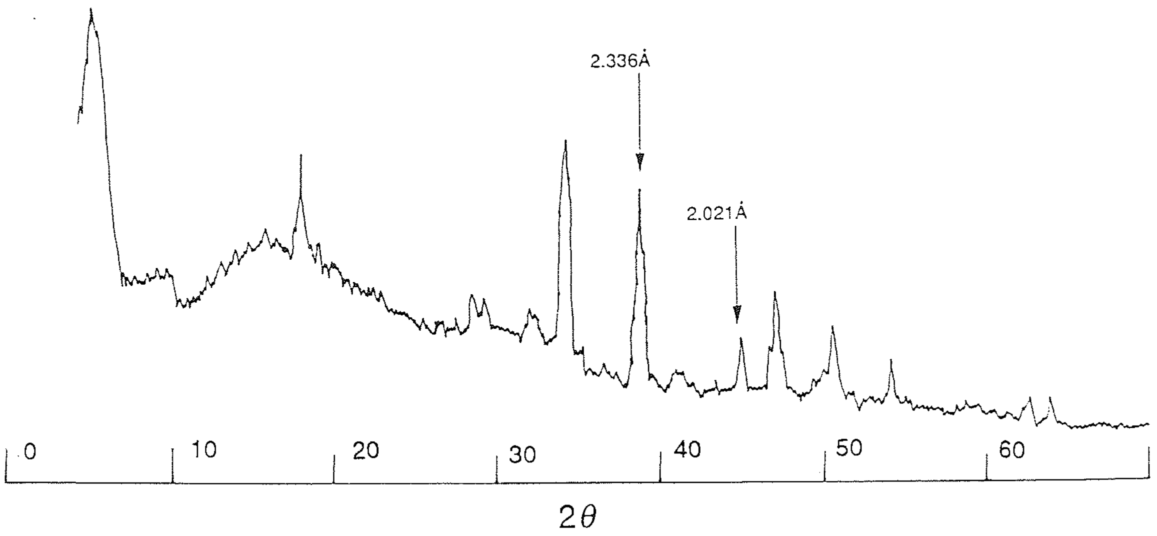
where d is the spacing of the crystal planes
n is the order of reflection (1,2 etc)
λ is the wavelength of the X-rays (for Cu Kα $\lambda = 1.542$Å)
θ is the angle of incidence or reflection

For convienience the d-spacings of the peaks indicated in the main body of the thesis are shown on the traces.

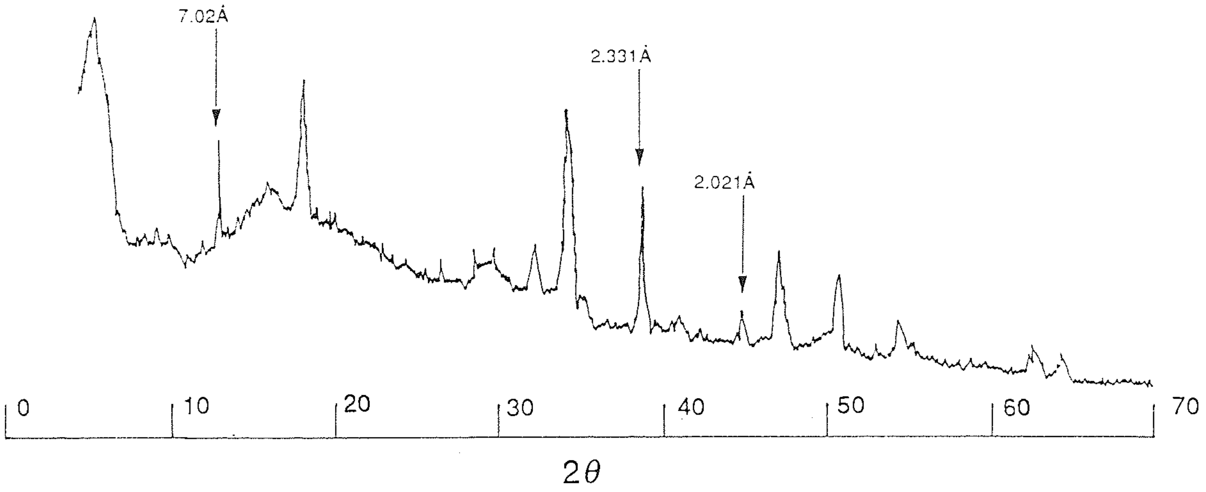
Trace1 - Hydrated OPC Paste



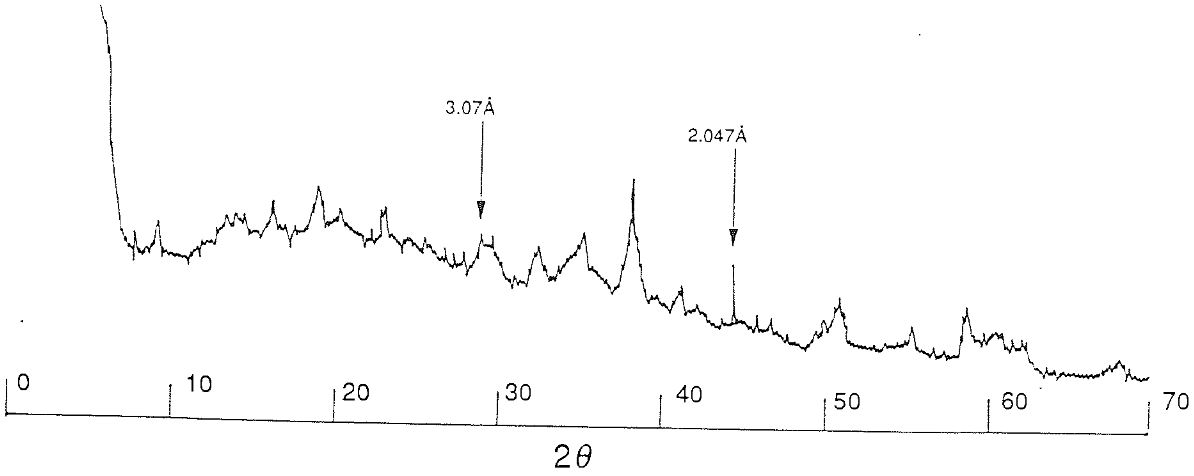
Trace 2 - Surface of Submerged Section of Partially Immersed OPC Paste Sample (Sodium formate)



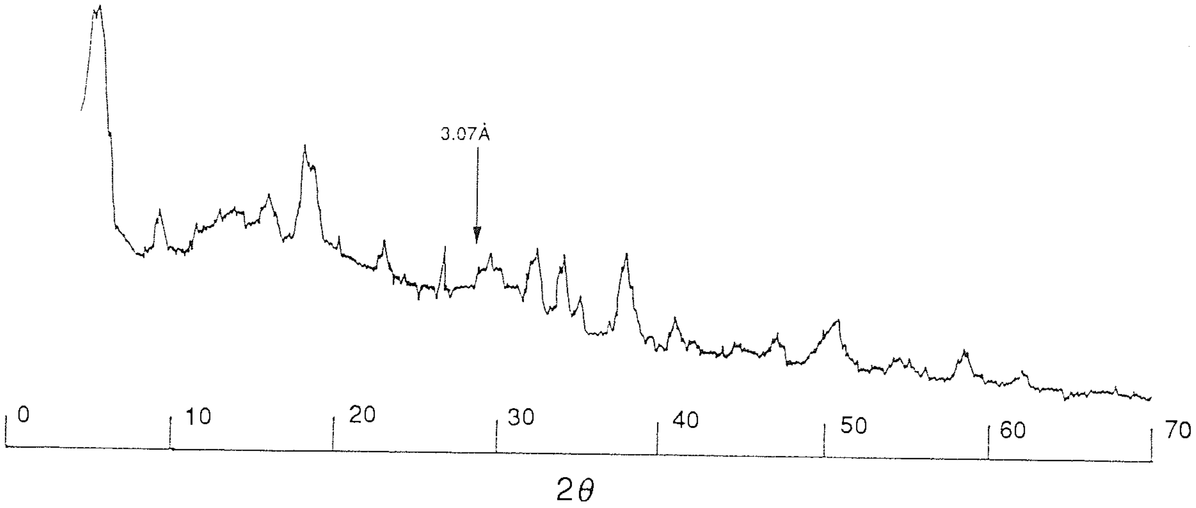
Trace 3 - Surface of Submerged Section of Partially Immersed OPC Paste Sample (Potassium Acetate)



Trace 4 - Loose Material Removed from the Waterline of Partially Immersed OPC Paste Sample (Calcium and Magnesium Acetate)



Trace 5 - Surface Section of Diffusion OPC Paste Sample (Calcium and Magnesium Acetate)



Appendix C : Calculation of the Hydroxide and Carbonate Concentrations in Expressed Pore Solution

Using a pH electrode it was seen that, in an acid-base titration, the colour change of

1. Phenolphalein indicator occurred at pH 8.31
2. Bromocresolgreen indicator occurred at pH 3.95

Using equilibrium equations [Pourbaix, 1966],

$$\frac{[CO_3^{2-}]}{[HCO_3^-]} = -10.34 + pH \quad \text{and}$$

$$\frac{[HCO_3^-]}{[H_2CO_3]} = -6.38 + pH$$

Let:

Total Carbonate = $[CO_3^{2-}] + [HCO_3^-] + [H_2CO_3]$ = a moles
Addition of acid (H^+) to take pH from 8.31 to 3.95 = b moles

At pH 8.31, $[H_2CO_3] \approx 0; \frac{[CO_3^{2-}]}{[HCO_3^-]} = 10^{-2.03} \approx 0.009$

Therefore $1.009\,[HCO_3^-] = a$

and this gives $[HCO_3^-] = 0.991a$; $[CO_3^{2-}] = 0.009a$

At pH 3.95, $[CO_3^{2-}] \approx 0; \frac{[HCO_3^-]}{[H_2CO_3]} = 10^{-2.43} \approx 0.004$

Therefore $1.004\,[HCO_3^-] = a$

and this gives $[H_2CO_3] = 0.996a$; $[HCO_3^-] = 0.004a$

Hence:

Titration from pH 8.31 to pH 3.95 causes:

0.991a moles HCO_3^- + 0.009a moles CO_3^{2-} + b moles H^+

to be converted to

0.996a moles H_2CO_3 + 0.004a moles HCO_3^-

NB. At pH 8.31 the hydroxide concentration in the pore solution is negligible and can be neglected.

Therefore

$b = (0.991-0.004)a + 2(0.009a) = 1.005a$

<u>Thus a = 0.995b</u>

<u>Example</u>

For the case of 0-20mm slice of core A it takes

1. 439 mM H^+ to reach the bromocresolgreen colour change
2. 319.5 mM H^+ to reach the phenolpthalein colour change

$b = 439-319.5 = 119.5$ mM

$a = 0.995 \times 119.5$
$= 119$ mM

Therefore

$[CO_3^{2-}] = 119$ mM

Also $[OH^-] = 439 - 2(119) = 201$ mM

Appendix D : Original Pore Solution Data from Untreated BFSC Concrete Cores

Core	Depth	Na^+	K^+	OH^-	Cl^-	SO_4^{2-}
26	0-20	240	34	9	337	4
	20-40	103	48	96	18	3
29	0-20	228	30	19	247	3
	20-40	95	46	108	10	2
	40-60	93	49	109	5	3
32	0-10	315	30	0	366	---
	10-30	109	47	63	78	4
35	0-10	---	---	1	391	---
	10-30	---	---	24	89	---
	30-50	90	44	97	5	1
	50-70	82	88	88	3	2
	70-90	91	86	86	7	---

Depth in mm & concentrations in mM, --- not analysed due to insufficient pore solution

Appendix E : Published Work from the Study

ELECTROCHEMICAL CHLORIDE REMOVAL TESTS OF CONCRETE CORES FROM A COASTAL STRUCTURE

Rob B. Polder[1], Robert Walker[2], Christopher L. Page[2]