CORROSION AND PASSIVATION OF STEEL IN CONCRETE

by

PAUL LAMBERT

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SUMMARY

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A study of several chemical and electrochemical factors which affect the behaviour of embedded steel in cement pastes and concrete has been made.

The effects of internal and external sources of chloride ions on the pore solution chemistry of Portland cement pastes, with and without additions of anodic corrosion inhibitors, have been studied using a pore solution expression device which has enabled samples of pore solution to be expressed from hardened cement pastes and analysed for various ionic species.

Samples of pure alite and tricalcium aluminate have been prepared and characterised with respect to morphology, free lime content and fineness. Kinetics of diffusion of chloride ions in hardened pastes of alite and alite blended with tricalcium aluminate have been investigated and an activation energy obtained for the diffusion process in alite. The pore structures of the hardened pastes and the chloride ion binding capacity of alite have also been determined.

Concrete cylinders containing embedded steel with four different surface conditions were exposed to various environments. The electrochemical behaviour of the steel was monitored during the period of exposure by means of rest potential measurements and the steel corrosion products analysed before and after being embedded. An examination was made of the nature of the interfacial zones produced between the embedded steel and cement.

Rest potential measurements were monitored for steel embedded in alite paste in the presence of chloride ions and cement paste containing various levels of inhibitors in combination with chloride ions. In the latter case the results were supported by polarisation resistance determinations.

KEY WORDS cement, steel, chlorides, corrosion, inhibitors

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CHAPTER 1

INTRODUCTION

1.1 BACKGROUND

Concrete is a compound material made from sand, gravel and cement. The cement is a mixture of various minerals which when mixed with water hydrate and rapidly become hard. The oldest known surviving concrete is to be found in Yugoslavia and was thought to have been laid in 5,600 B.C. using red lime as the cement. The first major concrete users were the Egyptians in around 2,500 B.C. and the Romans from 300 B.C. The Romans found that by mixing a pink sand-like material which they obtained from Pozzuoli with their normal lime-based concretes they obtained a far stronger material. The pink sand turned out to be fine volcanic ash and they had inadvertently produced the first 'pozzolanic' cement. Pozzolana is any siliceous or siliceous and aluminous material which possesses little or no cementitious value in itself but which will, if finely divided and mixed with water, chemically react with calcium hydroxide to form compounds with cementitious properties. (1)

The Romans made many developments in concrete technology including the use of light weight aggregates as in the roof of the Pantheon, and embedded reinforcement in the form of bronze bars, although the difference in thermal expansion between the two materials produced problems of spalling. It is from the Roman words 'caementum' meaning a rough stone or chipping and 'concretus' meaning grown together or compounded, that we have obtained the names for these two now common materials. (2)

Lime and Pozzolana concretes continued to be used intermittently for nearly two millenea before the next major development occurred in 1824 when Joseph Aspdin of Leeds took out a patent for the manufacture of Portland cement, so named because of its close resemblance to Portland stone. Aspdin's cement, made from a mixture of clay and limestone which had been crushed and fired in a kiln, was an immediate success. (3) Although many developments have since been made, the basic ingredients and processes of manufacture are the same today.

In 1830, a publication entitled, "The Encyclopedia of Cottage, Farm and Village Architecture" suggested that a lattice of iron rods could be embedded in concrete to form a roof. Eighteen years later, a French lawyer created a sensation by building a boat from a frame of iron rods covered by a fine concrete which he exhibited at the Paris Exhibition of 1855. Steel reinforced concrete was now born. The man normally credited with its introduction as a building material is William Wilkinson of Newcastle who applied for a patent in 1854 for "improvement in the construction of fireproof dwellings, warehouses, other buildings and parts of the same." (4)

It is not only fire resistance that is improved by the inclusion of steel in the concrete matrix. Concrete, although excellent in compression, performs poorly when in tension or flexure. By introducing a network of connected steel bars, the strength under tension is dramatically increased allowing long, unsupported runs of concrete to be produced. (5) Steel and concrete complement each other in many ways. For example, they have similar coefficients of thermal expansion so preventing the problems the Romans had with bronze. Concrete also protects the steel, both physically and chemically, an aspect that will be discussed later.

When water is mixed with Portland cement a complicated set of reactions is initiated. Although the starting point for the cement is little more than clay and limestone it is a complex mixture of minerals. (6) The main strength giving compounds are the calcium silicates which react with water to produce a calcium silicate hydrate gel (C-S-H gel) which provides the strength, and calcium hydroxide which contributes to the alkalinity of the cement. Tricalcium silicate reacts quickly to provide high, early strengths while the reaction of dicalcium silicate is far slower, continuing, in some cases, for many years. The other cement compound of particular relevance to steel reinforced concrete is tricalcium aluminate. It reacts rapidly with water to produce calcium aluminate hydrates. (7) The amount of tricalcium aluminate present may well be limited as in the case of sulphate resisting Portland cement, so as to prevent adverse reactions between the hydrate and sulphates from the environment which can result in swelling and cracking of the cement matrix. (8) The great advantage tricalcium aluminate does have is its ability to combine with chlorides, so removing them from the liquid phase of the cement. (9) Chloride ions, as will be seen, are one of the major causes of corrosion of embedded steel.

Exposed steel will corrode in moist atmospheres due to differences in the electrical potential on the steel surface forming anodic and cathodic sites. The metal oxidises at the anode where corrosion occurs according to

$$\mathrm{Fe\ (metal)} \rightleftharpoons \mathrm{Fe^{2+}\ (aq.)} + 2e^-$$

Simultaneously, reduction occurs at cathodic sites, typical cathodic processes being

$$\tfrac{1}{2}O_2 + H_2O + 2e^-\ \mathrm{(metal)} \rightleftharpoons 2OH^-\ \mathrm{(aq.)}$$

$$2H^+\ \mathrm{(aq.)} + 2e^-\ \mathrm{(metal)} \rightleftharpoons H_2\ \mathrm{(gas)}$$

The electrons produced during this process are conducted through the metal whilst the ions formed are transported via the electrolyte. (10)

The environment provided by good quality concrete to steel reinforcement is one of high alkalinity due to the presence of the hydroxides of sodium, potassium and calcium produced during the hydration reactions. (11) The bulk of surrounding concrete acts as a physical barrier to many of the steel's aggressors. In such an environment steel is passive and any small breaks in its protective oxide film are soon repaired. If, however, the alkalinity of its surroundings are reduced, such as by neutralisation with atmospheric carbon dioxide and sulphur dioxide, or depassivating anions such as chloride are able to reach the steel then severe corrosion of the reinforcement can occur leading to staining of the concrete by rust and spalling of the cover due to the increase in volume associated with the conversion of iron to iron oxide. (10) The factors which determine the corrosion rate of steel in concrete are the presence of an ionically conducting aqueous phase in contact with the steel, the existence of anodic and cathodic sites on the metal in contact with this electrolyte and the availability of oxygen to enable the reactions to proceed.

The permeability of the concrete is important in determining the extent to which aggressive external substances can attack the steel. A thick concrete cover of low permeability is more likely to prevent chloride ions from an external source from reaching the steel and causing depassivation. (12)

Where an adequate depth of cover is difficult to achieve due to design considerations or where aggressive environments are expected such as in marine structures or bridge decks, additional protection may be required for the embedded steel. This may take many and varied forms and commercial interest in this field is strong. The steel reinforcement itself may be made more able to resist corrosion by providing it with a protective coating such as zinc, epoxy resin or stainless steel cladding. (13) In extreme circumstances, solid stainless steel reinforcements may be used, although the price would be prohibitive in all but the most specialised applications.

Cathodic protection systems involving the use of an applied potential to maintain the steel in its passive condition are aptly suited to the protection of embedded steel but require careful planning and constant monitoring during use. (14)

Anodic corrosion inhibitors such as nitrites and benzoates have been used successfully for many years for the protection of steel in aggressive aqueous environments such as boiler tubes and car radiators. In the right amounts they will maintain a protective oxide film on the surface of the steel, thus protecting it from corrosion. (15) Their use in steel reinforced concrete has, to a certain extent, been limited. Although they are easy to use, there are difficulties in calculating the concentration required to maintain passivity. Too much inhibitor is both expensive and liable to cause a weakening of the concrete; too little can produce severe localised corrosion, so worsening the situation. To evaluate their true potential in reinforced concrete, it is therefore necessary to understand more fully the extent to which inhibitors are complexed by cement hydration products and leached out by external solutions as would be the case in a marine environment.

There can be little doubt that the most effective way of protecting steel which is embedded in concrete is to provide it with an adequate depth of cover by high strength, low permeability concrete free from depassivating ions such as chlorides. However, in the real world, concrete is laid by the tonne in all weathers and environments, exposed to industrial atmospheres, de-icing salts and sea water. Contaminated materials and poor workmanship are hard to avoid completely but by understanding the often complex chemical and electro-chemical conditions that can exist, it should be possible to develop ways of producing structures which will last long into the next century.

1.2 PURPOSE OF INVESTIGATION

The general aims of this work have been to study certain chemical and electro-chemical factors relating to steel embedded in cement and concrete. These are more specifically defined as follows :

1. To determine the effects of internal and external sources of chloride ions on the concentration of bound and free chloride ions and hydroxyl ions in Portland cement pastes.

2. To synthesize pure cement minerals and characterise them in terms of crystal structure, level of impurity and particle size.

3. To measure the diffusivity of chloride ions through hydrated cement minerals and to determine an activation energy for the diffusion of chloride through alite (substituted tricalcium silicate).

4. To observe the effects of surface condition and environment on the passivity of mild steel embedded in concrete.

5. To determine the effects of internal and external sources of chloride ions on the concentration of anodic corrosion inhibitors in ordinary Portland cement paste.

The majority of work in this investigation has been carried out with cement pastes rather than mortars or concretes, so as to obtain accurate information regarding the behaviour of the hardened cement, while avoiding possible interference due to the presence of aggregates. Where a concrete has been used (Chapter 6) great care has been taken to ensure consistency within the mix.

1.3 PLAN OF PRESENTATION

The introduction given in Chapter 1 covers background information relating to the history of steel reinforced concrete, its properties and the problems attendant in its use which result in the corrosion of embedded steel. This is followed by a description of the scope of this research. In Chapter 2 the materials and experimental procedures used in this work have been described. The effect of chloride ions from internal and external sources on the pore solution chemistry of ordinary and sulphate resisting Portland cements has been studied in Chapter 3. The laboratory preparation and characterisation of the cement minerals, alite (substituted tricalcium silicate) and celite (tricalcium aluminate) is covered in Chapter 4 while the determination of chloride ion diffusion data through discs of these minerals occupies Chapter 5. Chapter 6 describes the setting-up and subsequent monitoring of a number of steel electrodes with various surface conditions, embedded in concrete, and exposed to different environments. The effect of anodic corrosion inhibitors on the pore solution chemistry of cement paste exposed to chloride ions from internal and external sources and on the electro-chemistry of steel embedded in cement pastes containing various levels of inhibitors and chloride ion has been studied in Chapter 7. The general conclusions and recommendations for further work can be found in Chapter 8. Each of the experimental chapters (3 to 7) is in the form of an introduction followed by a review of previous work, a discussion of the results obtained and the conclusions made from them.

CHAPTER 2

MATERIALS AND EXPERIMENTAL TECHNIQUES

2.1 INTRODUCTION

This chapter outlines the major experimental procedures employed in the subsequent chapters. Some of the techniques such as specific surface determination and compressive strength measurements have been used to characterise physical aspects of the specimens while others such as total chloride analysis and polarisation resistance measurement provide chemical or electro-chemical data. Details of the materials used in the manufacture of specimens and the methods adopted for their preparation are also given.

2.2 MATERIALS

CEMENTS

The majority of specimens used in this research have been prepared from a single batch of research grade ordinary Portland cement supplied by the Blue Circle cement company. Where a sulphate resisting Portland cement was required, 'Ketton' low alkalinity S.R.P.C. has been used. Both cements have been stored in airtight drums until required and passed through a 150 micrometre sieve before use. Chemical analyses of the two cements are given in table 2.1.

AGGREGATES

Most of the specimens used in this work are made from cement pastes containing no aggregates. Concrete has only been employed in Chapter 6 where 1:2:4 mix has been used ie. one part cement to two parts fine aggregate to four parts coarse aggregate. The fine aggregate used was a 'zone 2' concreting sand and the coarse aggregate in irregular gravel of between 5 and 10 mm in size. Both aggregates were washed and dried before use.

CEMENT MINERALS

In this work where alite and tricalcium aluminate have been used the minerals were prepared in the laboratory. Chapter 4 deals exclusively with their manufacture.

STEEL

Where steel specimens have been embedded into the cement or concrete a mild steel has been used. An analysis of the steel used in Chapters 5 and 6 is shown in table 2.2.

2.3 METHODS OF PREPARING SPECIMENS

CEMENT PASTE

Neat cement paste specimens for use in Chapters 3 and 7 have all been made in the same manner. The sieved cement was mixed with de-ionised water in a ratio of 2 to 1, more commonly referred to as a water-cement ratio of 0.5. Any admixtures such as chlorides or inhibitors were dissolved in the water prior to mixing which was carried out by hand for three minutes. The paste was then poured into moulds and vibrated for two minutes to remove trapped air. The layer of bubble-laden cement on the surface of the specimen was removed and the mould topped up with fresh paste. This procedure of vibrating and topping up was then repeated. The surface of the paste was carefully levelled and the mould sealed taking care not to trap any air. To prevent segregation or bleeding in the cement paste where a water layer forms on the surface, the sealed moulds were slowly rotated end over end for several hours as shown in figure 2.1. The specimens were then cured as required for their use.

CEMENT MINERALS

Discs of alite and alite containing tricalcium aluminate have been produced in a similar manner to that described above. The mixing was carried out in the mould so as not to waste the material and a water-solid ratio of 0.6 has been used to improve the workability of the paste. Where the discs contain tricalcium aluminate, 33% gypsum (calcium sulphate dihydrate) by weight of the tricalcium aluminate content has been added to the mixing water. The gypsum prevents rapid setting of the tricalcium aluminate which produces heat and can cause the disc to crack. Rather than rotating, the discs were remixed and vibrated several times until no more bleeding was apparent.

CONCRETE

The concrete used in Chapter 6 has been made in a conventional manner. The cement and aggregate were dry mixed in a mechanical mixer (figure 2.2) for two minutes. The water was then added and the mixing continued for a further five minutes. The mixture was then hand mixed with a trowel to ensure that no areas of segregation were present. The moulds were filled in several layers while being vibrated and once filled were vibrated for a further three minutes (figure 2.3). The filled moulds were then kept at 20°C and high humidity until demoulding at six hours. They were ready to be placed in their test environment after forty eight hours.

STEEL

All steel specimens have been abraided with emery cloth or grit blasting, degreased with acetone and left in a desiccator over silica gel to form an even oxide film. Other surface conditions have been produced by holding the cleaned steel in de-ionised water vapour and water containing sulphate and chloride ions. In such a manner three kinds of 'rust' have been produced.

The specific forms of steel specimen are described fully in the relevant chapters.

2.4 COMPRESSIVE STRENGTH MEASUREMENT

In order to ensure the quality and consistency of the concrete used in the large scale rest potential experiment the compressive strength test described in British Standards has been followed. (16) For each batch of five specimens, one 100 mm standard test cube was cast. The cubes were then demoulded at forty eight hours and stored under water until twenty eight days old. At this age the cubes were removed from the water and weighed prior to testing. The testing was carried out on a compression testing machine which complied with the requirements of British Standards. (17) (See figure 2.4).

The cubes were loaded at a rate of 15 megaNewtons per square metre (MN/m^2) per minute until no greater load could be sustained. Figure 2.5 shows the most common mode of failure of the cubes. The compressive strength of each cube was calculated by dividing the maximum load sustained by the cross sectional area of loading and expressed in MN/m^2.

A worked sample of the calculation and statistical analysis of all the compressive strength measurements is given in Appendix 1.

2.5 EXPRESSION OF PORE SOLUTIONS

The development by Longuet et al (18) of a method of removing capillary pore solutions by pressure has allowed greater study of the chemistry of hydrated cements. Using a suitable press it has been possible to study the levels of several ionic constituents in many cement paste specimens. Figures 2.6 and 2.7 show the press used and its manner of construction. Pressure was applied to the cement pastes by means of the piston and the expressed solutions drawn up into a plastic syringe via the collection channel and fluid drain . The solutions were stored in sealed plastic vials to prevent exposure to the air prior to analysis. The press was thoroughly cleaned with water and acetone between specimens and the piston, bore and platten were protected and lubricated by P.T.F.E. applied by an aerosol. A pressure of around 375 megaPascals is capable of expressing two to three millilitres of pore solution from a cement paste specimen of 0.5 water-cement ratio and fifty to one hundred days of age.

2.6 PORE SOLUTION ANALYSIS

The expressed pore solutions have been analysed for several ionic species using titrimetric and spectrophotometric methods requiring only 0.1 millilitre portions (taken by micropipette) per test. In each case triplicate tests were performed and an average taken.

HYDROXYL ION (pH)

The level of hydroxyl ion in the solutions was determined by standard acid/base titration with 10 millimolar nitric acid using phenolphthalein indicator. The acid was dispensed from a microburette graduated in 0.01 millilitre steps. The 'pH' of the solution was then calculated from the hydroxyl ion concentration as follows. (19)

$$pH = -\log_{10}(H^+)$$
$$pOH = -\log_{10}(OH^-)$$
$$pH + pOH = 14$$
$$\therefore\ pH = 14 + \log_{10}(OH^-)$$

(After Sörensen)

CHLORIDE ION

The level of chloride ion was determined by a spectrophotometric method. Each 0.1 millilitre aliquot of pore solution was made-up to 10 millilitres with distilled water in a volumetric flask. To these were added 2 millilitres of 0.25 molar ferric ammonium sulphate ($Fe(NH_4)(SO_4)_2,12H_2O$) in 9 molar nitric acid and 2 millilitres of saturated mercuric thiocyanate in ethanol. Chloride causes the thiocyanate ion to be displaced which then forms a highly coloured complex with the ferric ion.

$$2Cl^- + Hg(SCN)_2 + Fe^{3+} \longrightarrow HgCl_2 + 2(Fe(SCN))^{2+} \qquad (20)$$

The intensity of the colour is proportional to the chloride ion concentration and may be determined on a spectrophotometer which measures the absorption of light at specific wavelengths. A glass cell filled with the coloured solution is placed alongside a similar cell containing water and a beam of light is passed through the cells onto a photoelectric device. A prism is used to select the wavelength of light to be measured which for this analysis is 460 nanometres. The difference in absorption between the blank and test solutions is proportional to the amount of chloride ion present and may be found in terms of molarity by constructing a calibration curve of standard chloride solutions against absorption.

The theoretical background of spectrophotometry is provided by the Beer-Lambert law which states that

$$It = Io.10^{-\epsilon ct}$$

where

It = intensity of transmitted light

Io = intensity of incident light

ϵ = molecular extinction coefficient

c = concentration of solution

t = thickness of solution

Hence, for a constant path length, the intensity of a beam of monochromatic light is inversely proportional to the concentration of the absorbing substance it passes through.(21) Figures 2.8 and 2.9 show the spectrophotometer used and its method of operation.

NITRITE IONS

Levels of nitrite ion were also determined using a spectrophotometric method calibrated by standard solutions. The reagents used were sulphanilic acid (in hydrochloric acid) and α-napthylamine solution which in the presence of nitrite ions form α-napthylamine-p-azobenzene-p-sulphonic acid, a red azo dye.(22) Sodium acetate was used as a buffer to maintain the solution at pH 2.0 to 2.5. The optical density of the test solutions was then measured at 520 nanometers with the spectrophotometer and the molarity of nitrite ion present obtained from a calibration curve.

BENZOATE ION

Those specimens containing benzoate ions were analysed by means of a two-step microtitration technique. The first step involved the neutralisation of hydroxyl ions by titration with sulphuric acid. As this involves the titration of a strong base with a strong acid the end point was determined with phenolphthalein indicator (apparent indicator constant, $pK'_{in} = 9.60$). (23) Once the solution had been neutralised it was titrated with 10 micromolar sulphuric acid in the presence of ether. The acid reacts with the benzoate ions to produce benzoic acid which although only slightly soluble in water is very soluble in ether. As the dissociation constant of benzoic acid is 4.21 bromophenol blue ($pK'_{in} = 4.10$) was used to indicate the end point. The concentration of benzoate ion present in the solution was then calculated on the basis of the reaction

$$H^+(aq.) + C_6H_5CO_2^-(aq.) \longrightarrow C_6H_5COOH(ether)$$

Examples of the calculations involved in all four analyses and calibration curves for chloride and nitrite ions are given in Appendix 2.

2.7 EVAPORABLE AND NON-EVAPORABLE WATER

In order to make full use of the data obtained from the pore solutions concerning the levels of ionic species it is necessary to determine the amounts of bound and free water in the cement. As there is no clear distinction between the free and bound water the method of determination must be somewhat arbitary. The method adopted involves measuring the loss of water of a small portion of the hydrated cement at 105 and 950 degrees Centigrade. This gives reasonably accurate results although some water of hydration is invariably lost at the lower temperature.$^{(24)}$ At 950 degrees Centigrade, the cement also loses mass by ignition and this must be measured before the evaporable and non-evaporable water contents may be determined. The loss-on-ignition for each type of cement and cement mineral was found by the method given in British Standards.$^{(25)}$ A small portion of unhydrated cement is weighed before and after heating in a platinum crucible to 950 degrees Centigrade for thirty minutes and the weight loss converted into a percentage 'loss-on-ignition.' The amounts of evaporable and non-evaporable water may then be determined in terms of grammes of water per gramme of 'unhydrated' cement having first corrected for ignition loss and any admixtures present such as chlorides which contribute to the specimen's mass.

The mass of the test specimen before and after heating to 105 and 950 degrees Centigrade may be defined as follows

$$Wo = Wc + We + Wn + Wa \qquad \text{-(A)}$$

$$W_{105} = Wc + Wn + Wa \qquad \text{-(B)}$$

$$W_{950} = Wc\left(\frac{100-i}{100}\right) + Wa \qquad \text{-(C)}$$

where

Wo = original mass of specimen (grammes)

W_{105} = mass of specimen at 105°C (grammes)

W_{950} = mass of specimen at 950°C (grammes)

Wc = mass of unhydrated cement (grammes)

We = mass of evaporable water (grammes)

Wn = mass of non-evaporable water (grammes)

Wa = mass of admixtures (grammes)

and i = loss-on-ignition (% grammes per gramme of unhydrated cement)

From these three equations may be developed expressions for evaporable and non-evaporable water content

(A)minus(B) :

$$We = Wo - W_{105} \qquad -(D)$$

If $$Wa = \frac{Wc.a}{100} \qquad -(E)$$

where a = admixture content (% grammes per gramme of unhydrated cement)

From (C) :

$$W_{950} = \frac{Wc(100-i)+Wc.a}{100} = \frac{Wc(100-i+a)}{100} \qquad -(F)$$

$$\therefore Wc = \frac{100.W_{950}}{(100-i+a)} \qquad -(G)$$

EVAPORABLE WATER (%grammes per gramme unhydrated cement) = $\frac{We}{Wc} \times 100\%$

Substitute We from (D) :

$$E.W.(\%) = \frac{Wo-W_{105}}{Wc} \times 100$$

Substitute Wc from (G) :

$$= \frac{Wo-W_{105}(100-i+a)}{100.W_{950}} \times 100$$

Therefore

$$E.W.(\%) = \frac{Wo-W_{105}}{W_{950}} \times (100-i+a)$$

NON-EVAPORABLE WATER (%grammes per gramme unhydrated cement) $= \frac{Wn}{Wc} \times 100\%$

From (B) :

$$Wn = W_{105} - Wc - Wa$$

Substitute Wa from (E) :

$$= W_{105} - Wc - \frac{Wc.a}{100}$$

$$= W_{105} - Wc\ (1 + \frac{a}{100})$$

Substitute Wc from (G) :

$$= W_{105} - \frac{100.W_{950}}{(100-i+a)}\ (1 + \frac{a}{100})$$

$$= \frac{W_{105}(100-i+a)-(100+a)W_{950}}{(100-i+a)}$$

Divide by Wc from (G) and multiply by 100 to give non-evaporable water (%) :

$$N.E.W.(\%) = \frac{\{W_{105}(100-i+a)-(100+a)W_{950}\}(100-i+a)}{(100-i+a) \quad x \quad 100.W_{950}} \ x\ 100$$

$$= (W_{105}(100-i+a)-W_{950}(100+a))\ \frac{1}{W_{950}}$$

Worked examples of the calculations for evaporable and non-evaporable water are given in Appendix 3.

2.8 TOTAL CHLORIDE CONTENT DETERMINATION

Where cement paste specimens have been cured in solutions containing chloride prior to pore water expression it has been necessary to determine the total chloride content of the cement. Using a development of Berman's technique (26), a small sample of cement was dried to constant weight at 105°C and ground to a powder in a pestle and mortar. A weighed sample of 1 to 3 grammes was then placed in a glass vessel with 7 millilitres of deionised water and 3 millilitres of concentrated nitric acid. This mixture was boiled for one minute to allow the nitric acid to dissolve the chloride. A condenser was used to prevent loss of water by evaporation (see figure 2.10). Once the solution had cooled it was filtered to remove the remaining solids and analysed for chloride content by the same method as that used for the pore solutions. The total chloride content was then calculated as follows

$$\text{TOTAL CHLORIDE (moles Cl}^- \text{ per gramme cement)} = \frac{\text{MOLARITY OF Cl}^- \text{ IN SOLUTION}}{\text{WEIGHT OF SAMPLE}(950^{\circ}\text{C}).100}$$

The weight of the cement sample needed to be corrected to that at 950°C by means of the data obtained in the non-evaporable water content determination.

An example of the calculation is given in Appendix 4.

2.9 PARTICLE SIZE DETERMINATION

The fineness or surface area of a cement powder is important in determining the rate at which it hydrates when mixed with water. The rate of hydration of a cement may be increased by making it more finely ground and hence have a greater surface area exposed in proportion to its mass. British Standards recommend that an ordinary Portland cement should have a specific surface of around 2250 square centimetres per gramme (cm^2/g). A rapid hardening Portland cement should have a minimum specific surface of 3250 cm^2/g. (27)

For the work involving manufactured cement minerals it was therefore necessary to find their specific surfaces and ensure that they were similar to those of normal cements. As the cement minerals are reactive to water the most suitable way of determining their specific surface was by means of a gas permeability method. Such methods observe the flow of a gas through a powder bed of known porosity. Carman applied this method to cements using liquids but achieved only limited success. (28) Lea and Nurse developed the Carman technique for measuring the flow of air. (29) Both sets of workers used the equation developed by Kozeny relating the surface area to the permeability and porosity of the powder bed and the viscosity of the air. (30)

The method used with the cement minerals is given in the British Standards and involves the use of the Lea and Nurse technique. (31) The apparatus used was slightly different in that a direct reading flow-meter was used rather than a capillary flow-meter. (See figures 2.11 and 2.12). A consequence of this was that the Carman equation needed to be used rather than that given by Lea and Nurse which involves calibrating the equipment. As nitrogen was used as the permeating fluid, a slightly different value for the kinematic viscosity has been taken to that given for air at the operating temperature.

The specific surface may be found from the following equation

$$S = \frac{14}{\sigma(1-\epsilon)}\sqrt{\frac{\epsilon^3.A.i}{v.Q}} \times 100$$

(After Carman)

where

S = the specific surface (cm^2/g)

σ = the powder density (g/cm^3)

ϵ = the porosity of the powder bed = 0.475

A = the cross sectional area (cm^2)

i = the hydraulic gradient

v = the kinematic viscosity of the permeating fluid (Ns/m^2)

Q = the rate of flow (cm^3/s)

Before the fineness was measured it was necessary to determine the densities of the powders. A suitable method is given in the British Standards using a density bottle. (32)(33) (See figure 2.13). To prevent the cement minerals reacting, paraffin oil was used as the displacement liquid. The density of the displacement liquid at the selected operating temperature was found using the following equation

$$\rho L = \frac{W_2}{W_1} \times \rho W$$

where

ρL = the density of the displacement liquid (g/cm^3)

ρW = the density of pure water (g/cm^3)

W_1 = the mass of water to fill the bottle (grammes)

W_2 = the mass of displacement liquid to fill the bottle (grammes)

A small sample of powder was then taken and placed in the bottle which was then filled with displacement liquid. Trapped air was removed by placing the bottle in a vacuum desiccator. The density of the powder was then found as follows

$$\rho = \frac{W_4 \times \rho L}{W_3 + W_4 - W_5} \times 1000$$

where

ρ = the density of the powder (Kg/m^3)

ρL = the density of the displacement liquid (g/cm^3)

W_3 = the mass of the bottle, stopper and displacement liquid to fill the bottle (grammes)

W_4 = the mass of the powder sample (grammes)

W_5 = the mass of the bottle, stopper, powder sample and displacement liquid to fill the bottle (grammes)

Worked examples of the calculations for both density and fineness are given in Appendix 5.

2.10 POROSITY MEASUREMENT

Measurements of pore size distribution have been carried out on the hydrated cement mineral discs used for chloride diffusion measurements. (See Chapter 5). The pore size distributions for hydrated cement minerals may be found most effectively by means of mercury intrusion porosimetry where the quantity of a non-wetting liquid (mercury) forced into the pores of a specimen is measured at various pressures which may be carried out as follows. (34)(35) A small sample of the material to be tested is dried to constant weight at 105 degrees Centigrade and placed into a glass cell. (See figure 2.14). The cell is fixed into the porosimeter and the system evacuated to remove any adsorbed vapours and gasses. Mercury is introduced into the cell and pressure applied. The pressure at which mercury enters pores of a given size may be calculated from the Washburn equation (36)

$$P = \frac{-4\gamma \cos\theta}{d}$$

where

P = the applied pressure (Pascals)

d = the pore diameter (microns)

γ = the surface tension of the mercury (N/mm)

θ = the contact angle between mercury and the material (degrees)

For each pressure and therefore pore size, the volume of the pores may be determined from the amount of mercury which has intruded into the specimen.

The measurements have been carried out on a 'Micromeritics Instrument Corporation' porosimeter (model 900/910) as shown in figure 2.15.

An example calculation of pore size distribution is given in Appendix 6.

2.11 FREE LIME DETERMINATION

The main impurity likely to be found in laboratory produced alite and tricalcium aluminate is free lime (calcium oxide plus calcium hydroxide). A method of determining the amount of free lime present is given in the British Standards (37) and involves titrating glycol (1:2 ethane-diol) into which the lime has been dissolved. A 1 gramme sample of the mineral to be tested was placed in a flask with 1 to 2 grammes of dry glass beads. 40 millilitres of glycol which contained 0.5% of a special mixed indicator was added to the sample and the flask stoppered. The indicator was made by dissolving 0.05 grammes of methyl red and 0.05 grammes of bromocrescol green into 100 millilitres of absolute ethyl alcohol. The mixture of dissolved lime and indicator was heated to 70 degrees Centigrade and magnetically stirred for 30 minutes after which it was filtered and the flask rinsed out with three 10 millilitre portions of hot glycol. This solution was then titrated against 0.1 molar hydrochloric acid until the colour changed through brown to orange. It was necessary to standardise the procedure by titrating a sample of calcium oxide produced by igniting a small amount of calcium carbonate in a platinum crucible at 1000 degrees Centigrade. The percentage of free lime was then determined as follows

$$\text{FREE LIME \%} = \frac{t \times 100W}{t_s}$$

where

W = weight of standard calcium oxide (grammes)

t_s = volume of acid used in standardisation (millilitres)

t = volume of acid used in determination of the sample (millilitres)

The value obtained gives a good indication of the purity of the sample.

An example of the calculation is given in Appendix 7.

2.12 X-RAY ANALYSIS

In order to ensure that samples of alite and tricalcium aluminate have been produced correctly the technique of x-ray diffraction has been employed. This is only possible because both are crystalline materials. Crystals diffract x-rays in a similar way to which light may be diffracted by wire gratings. In the case of visible light, gratings with line separations of between 10 000 and 20 000 Ångstroms are used to diffract wavelengths in the range 4 000 to 8 000 Ångstroms. In crystals the separation between parallel rows of equally spaced atoms is in the order of a few Ångstrom units and fortunately, low voltage x-rays have suitable wavelengths of less than one Ångstrom so allowing them to be diffracted. The conditions that must be satisfied for the reflection of rays of a specific wavelength are given by Bragg's law (38) which states that

$$n\lambda = 2d \, \mathrm{Sin}\theta$$

where

n = the order of reflection (1, 2, 3 etc)

λ = the wavelength of the x-rays

d = the spacing of the crystal planes

θ = the angle of incidence or reflection of x-ray beam

Hence for a given wavelength and angle of incidence where reflection occurs the atom spacing may be calculated.

The analysis of powder specimens has been carried out on a 'Philips' x-ray spectrometer (see figures 2.16 and 2.17) which uses an electronic counter tube to measure the intensity of the x-ray reflections. The specimen and counter are both rotated in the x-ray beam. The counter tube is moved at twice the speed of the specimen so as to maintain the correct angle for each Bragg reflection. The output from the spectrometer is a trace of intensity against Bragg angle from which the 'd'-values may be determined and compared with standard data. (39) The full analysis of a cement mineral specimen is given in Appendix 8.

2.13 DIFFERENTIAL THERMAL ANALYSIS

Differential thermal analysis, (D.T.A.), provides a convenient method of observing the effects of admixtures such as chlorides and nitrites on the hydration products of cements and cement compounds. (40) The technique measures the absorbtion and release of energy due to thermal changes such as the loss of water of crystallisation.

Prior to testing, the samples were powdered, sieved and surface dried in a desiccator. A small portion of the sample to be tested was then packed into a platinum/rhodium crucible and placed in the furnace of the analyser next to a similar crucible packed with a thermally inert substance (alumina). The furnace raises the temperatures of the crucibles from ambient to 950 degrees Centigrade at a rate of 20 degrees per minute. Thermocouples measure the difference in temperature between the two crucibles which is then plotted against furnace temperature on a pen recorder. The peak positions are characteristic of the compounds present and the peak heights proportional to the amount of a specific compound. The effects of time and environment on certain compounds may therefore be compared between specimens and the traces produced checked against standard data. (41) Figures 2.18 and 2.19 show the analyser used and a schematic diagram of its layout.

2.14 MÖSSBAUER SPECTROSCOPY

It has been found that firmly bound atoms in solids can emit or adsorb low-energy γ-rays from their nuclei without recoil. This is known as the Mössbauer effect and is most commonly observed with Fe^{57} nuclei which account for around 2% of natural iron. A consequence of this is that steel corrosion products which are difficult to analyse by x-rays due to their small crystal sizes may be successfully characterised by Mössbauer spectroscopy. (42) This technique has been used to characterise the corrosion products present on the steel specimens used in Chapter 6 before, and where possible, after being embedded in concrete. Specimens of corrosion products were scraped from the steel and sandwiched between mylar tape before being placed into the spectrometer between an oscillating γ-source and a detector. In order to obtain a sufficient number of counts it was necessary to leave the specimens for up to twenty four hours. The γ-ray detector is connected to a single channel analyser which counts the γ-rays in terms of their velocities. Figures 2.20 and 2.21 show the spectrometer used and a schematic diagram of the system. The spectra produced have been compared with those of known corrosion products. (43)

2.15 ELECTRON MICROSCOPY

The scanning electron microscope (S.E.M.) has proven to be a useful tool in the study of cement/steel interfaces. (44) Easy specimen preparation, high resolution and excellent field depth allow steel/cement specimens to be examined in detail. Prior to observation the specimens must be dried, mounted on aluminium stubs and coated with a thin conducting film of carbon to carry the incident electrons away to earth. The carbon layer is produced by a carbon arc in a vacuum and is only around 250 Ångstroms thick. A 'Cambridge Stereoscan 150' scanning electron microscope fitted with a 'LINK' energy dispersive x-ray analysis spectrometer (E.D.X.A.) was used in this work. (See figure 2.22). The E.D.X.A. unit allows rapid elemental analysis of areas of the specimen by detecting characteristic x-rays. (45) The x-rays are produced when the atoms of the specimen are excited by the electron beam and are analysed in terms of their energies. They interact with a silicon detector held at liquid nitrogen temperature and the signals produced are fed to a micro-computer from which an elemental analysis is displayed.

2.16 REST POTENTIAL MEASUREMENT

Whenever a steel specimen is in contact with an electrolyte it assumes a potential which can be measured relative to a reference electrode, as shown in figure 2.23. In this state the steel has both anodic and cathodic currents present on its surface but as these currents are of equal magnitude no net current can be measured.

By measuring this 'rest potential' and relating it to the chemical nature of the environment it is possible to determine the electro-chemical state of the steel. (46) The most common factors which affect the passivity of the steel in cement and concrete are the lowering of the alkalinity by carbonation and the presence of depassivating ions such as chloride. It is the effect of chlorides which was of greatest interest in this work as the effect of carbonation on any of the specimens was likely to be negligible. The presence of chlorides has the added disadvantage of causing severe localised corrosion or pitting as well as more general corrosion. Figure 2.24 shows a diagram of potential against pH for iron in a chloride solution. (47)

2.17 POLARISATION RESISTANCE MEASUREMENT

Polarisation resistance or linear polarisation is an electro-chemical method for the determination of corrosion rates. It is especially suitable for studying steel in cement or concrete where anodic inhibitors such as nitrites are present which may alter the rest potential and give unrepresentative results. The technique is carried out by applying a potential scan over a small range, typically 20 millivolts either side of the rest potential. The current produced is plotted against the potential and the polarisation resistance obtained from the slope. By relating the polarisation resistance to constants it is possible to determine a value for the corrosion current, I_{corr}. The theoretical background for the technique has been provided by Stern and Geary (48) and developed by Stern for determining a corrosion rate from polarisation data. (49) The value of the corrosion current may be obtained from the Stern-Geary equation

$$\frac{\Delta E}{\Delta I} = \frac{\beta a . \beta c}{(2.3)\ (I_{corr})\ (Ba+Bc)}$$

where

$\frac{\Delta E}{\Delta I}$ = the polarisation resistance

I_{corr} = the corrosion current

$\beta a, \beta c$ = the anodic and cathodic Tafel constants

This only applies when ΔE is small. The Tafel constants are the gradients of the anodic and cathodic polarisation curves. Ideally they should be determined experimentally for each specimen which involves a scan of several hundred millivolts either side of the rest potential. (See figure 2.25). As such a large shift in potential is liable to alter the electro-chemical state of the steel it is common to assume Tafel constant values in the range 20 to 120 millivolts. For this work I_{corr} has been calculated using Tafel constant values of 0.052 V/decade for passive conditions and 0.026 V/decade where the steel was.active. (50) I_{corr} has also been determined using an overall value of 0.1 V/decade. The experimentally determined polarisation resistance has also been used to indicate the corrosion rate of the steel.

The polarisation resistance measurements have been carried out on an 'E.G.&G./P.A.R. model 350' microprocessor controlled corrosion measurement console which was programmed to carry out the scan and output the results by means of an integral 'x-y' plotter. (See figures 2.26 and 2.27). (51) This equipment was not fitted with I.R. compensation whereby the resistance between the working and reference electrodes is allowed for. It has been necessary therefore to check the results with those obtained from a more conventional set-up which has an I.R. compensation capability. This was carried out with an 'AMEL model 551' potentiostat with positive feed-back that compensates for the I.R. drop. (52) Positive feed-back involves introducing an 'in-phase' signal from the output, back into the input. This results in a regenerative effect which increases the voltage across the cell and nullifies the voltage drop between the working and reference electrodes. When used on the specimens it was found that no I.R. compensation was required and the values of the polarisation resistance obtained compared well with those carried out on the microprocessor controlled module. The arrangement of the potentiostat is shown in figures 2.28 and 2.29. The measurement of polarisation resistance was carried out by polarising the working electrode anodically by 10 millivolts with respect to the rest potential and measuring the produced current on a digital voltmeter across a voltage/current converter. The current was measured thirty seconds after polarisation to allow the specimen to achieve a steady state. The polarisation resistance was then found by dividing the degree of polarisation (10 millivolts) by the current per area of the working electrode. (53)

An example of the calculation and comparison of values obtained is given in Appendix 9.

	ORDINARY PORTLAND CEMENT	SULPHATE-RESISTING PORTLAND CEMENT
CaO	63.4	64.0
SiO_2	20.2	20.2
Al_2O_3	7.3	4.1
Fe_2O_3	2.3	5.3
SO_3	3.1	2.6
MgO	1.2	1.4
Na_2O	0.43	0.28
K_2O	0.54	0.39
Ignition loss	0.9	1.1

Table 2.1
CHEMICAL ANALYSES OF CEMENTS (%)

Carbon	0.200
Sulphur	0.040
Silicon	0.270
Phosphorous	0.023
Manganese	0.860
Nickel	0.060
Chromium	0.150
Molybdenum	0.010
Copper	0.160
Tin	0.035
Iron	BALANCE

Table 2.2
CHEMICAL ANALYSIS OF MILD STEEL (%)

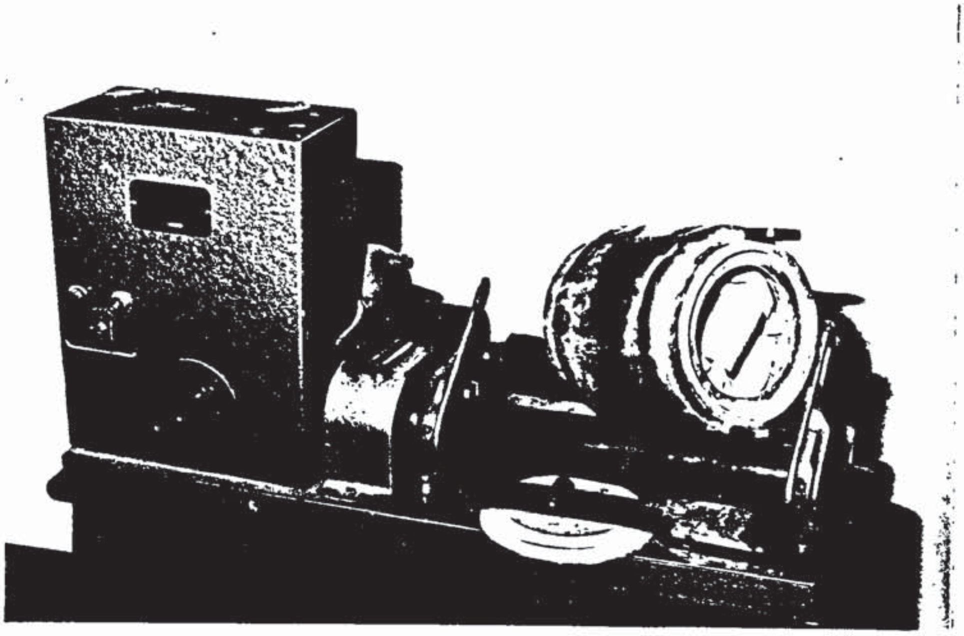


Figure 2.1
ROTATION OF MOULDS TO PREVENT SEGREGATION

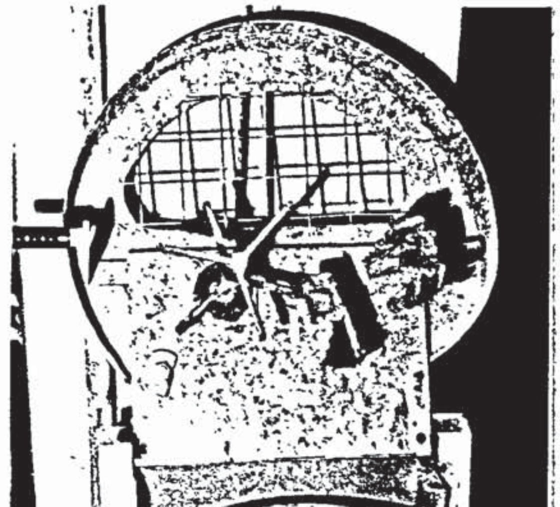


Figure 2.2
MECHANICAL MIXER FOR CONCRETE

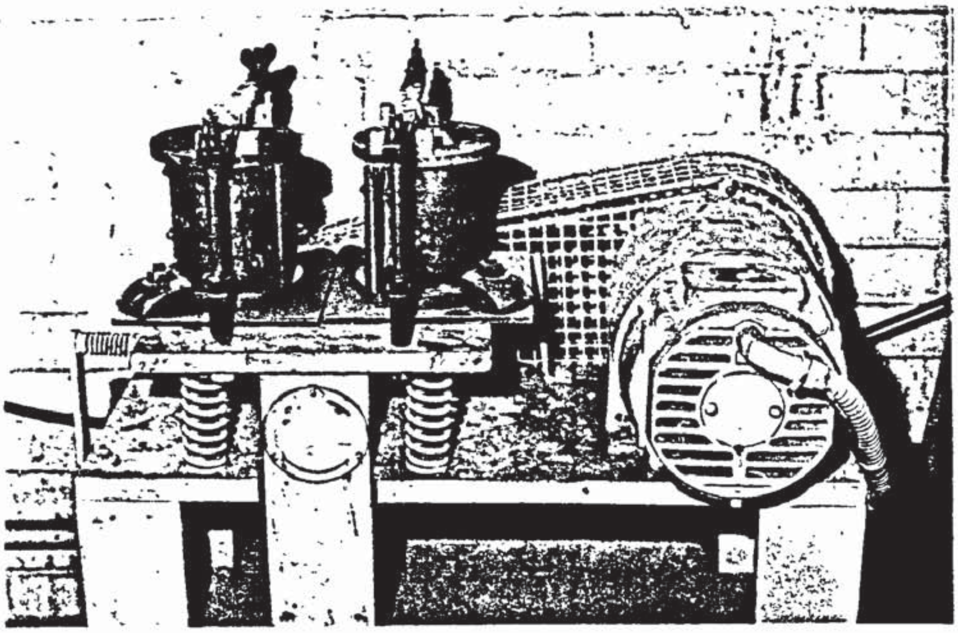


Figure 2.3
MOULDS ON VIBRATING TABLE

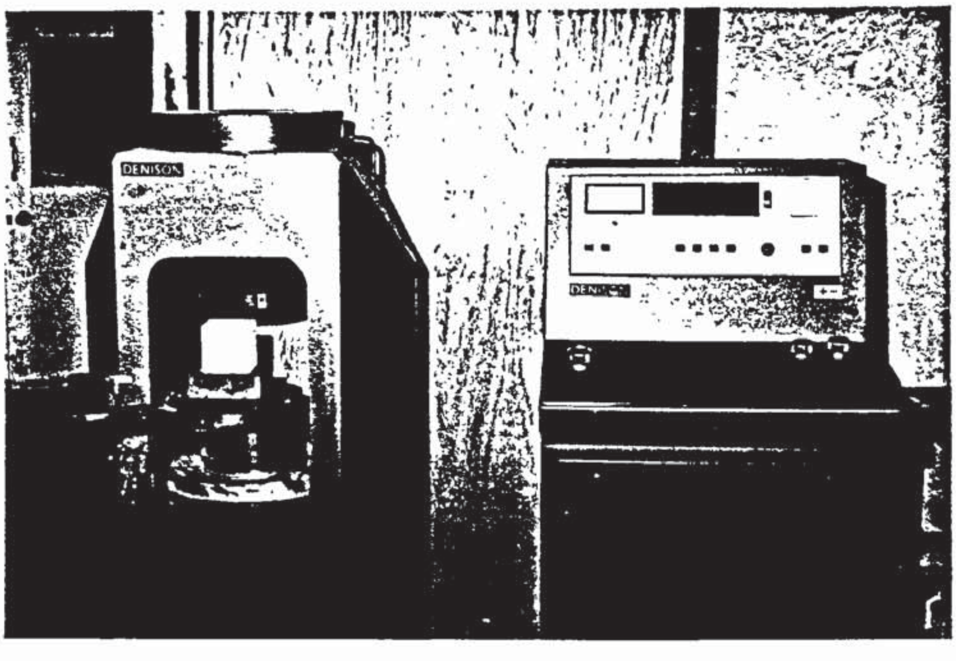


Figure 2.4
CUBE COMPRESSION TESTING MACHINE

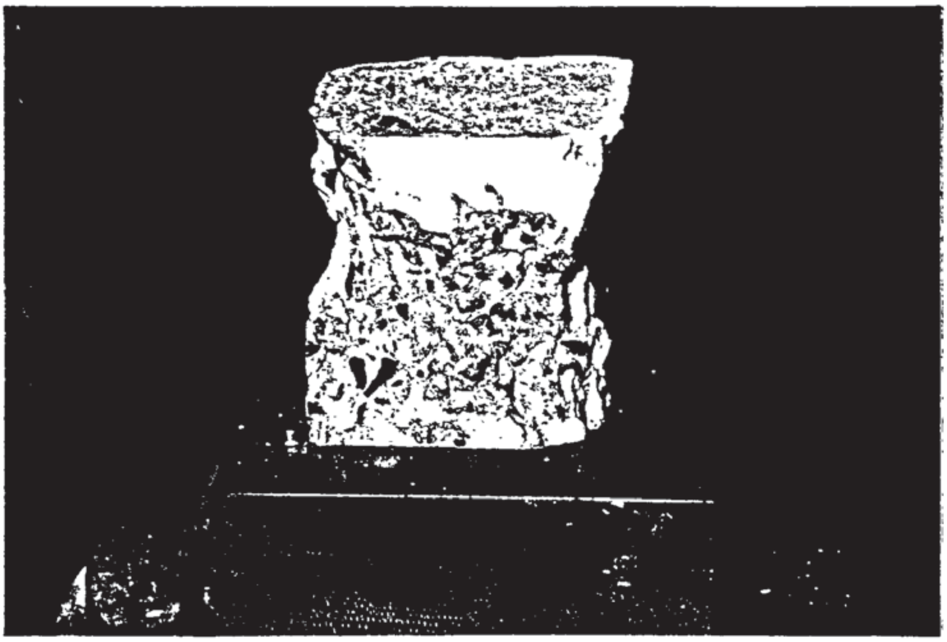


Figure 2.5
COMMON MODE OF FAILURE OF CONCRETE CUBE

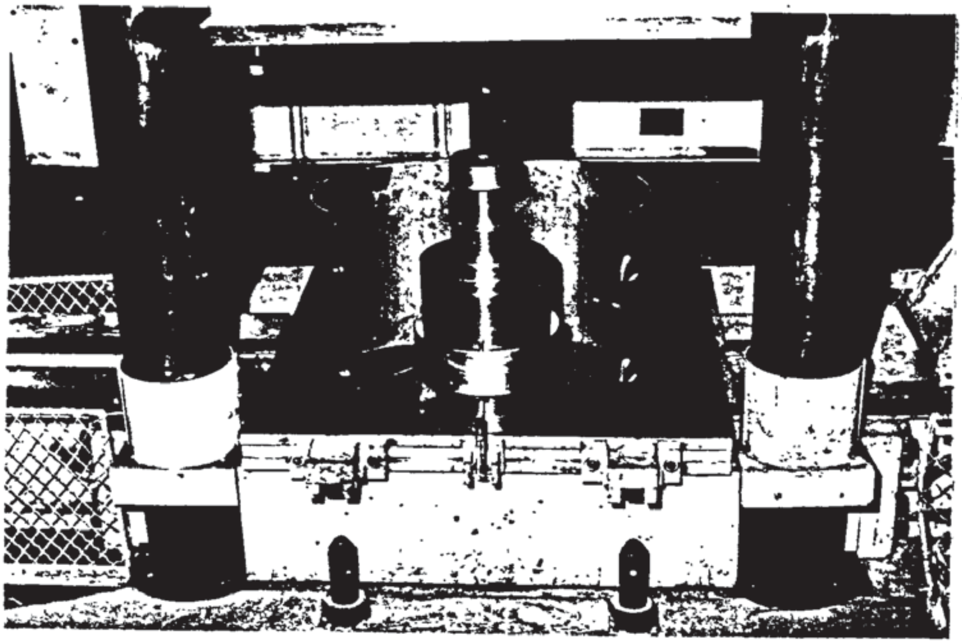


Figure 2.6
PORE SOLUTION EXPRESSION DEVICE

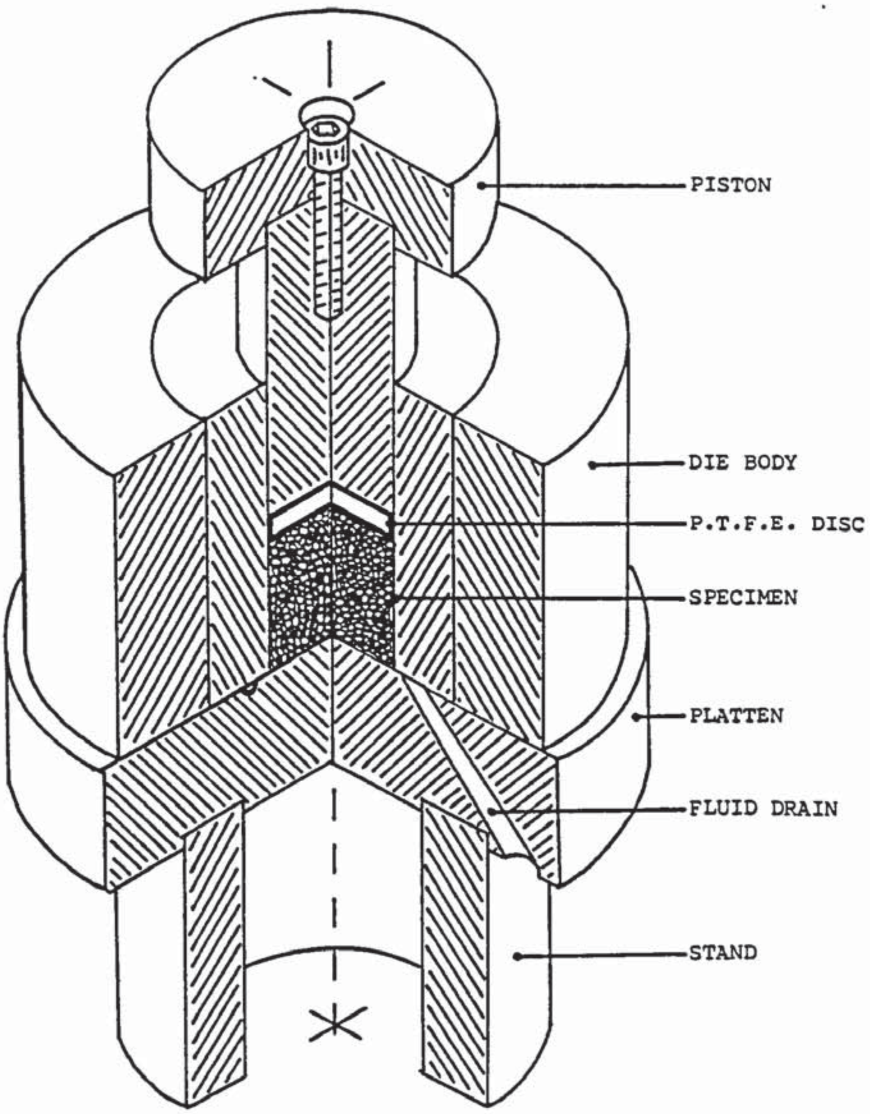


Figure 2.7
SECTIONAL DIAGRAM OF PORE SOLUTION EXPRESSION DEVICE

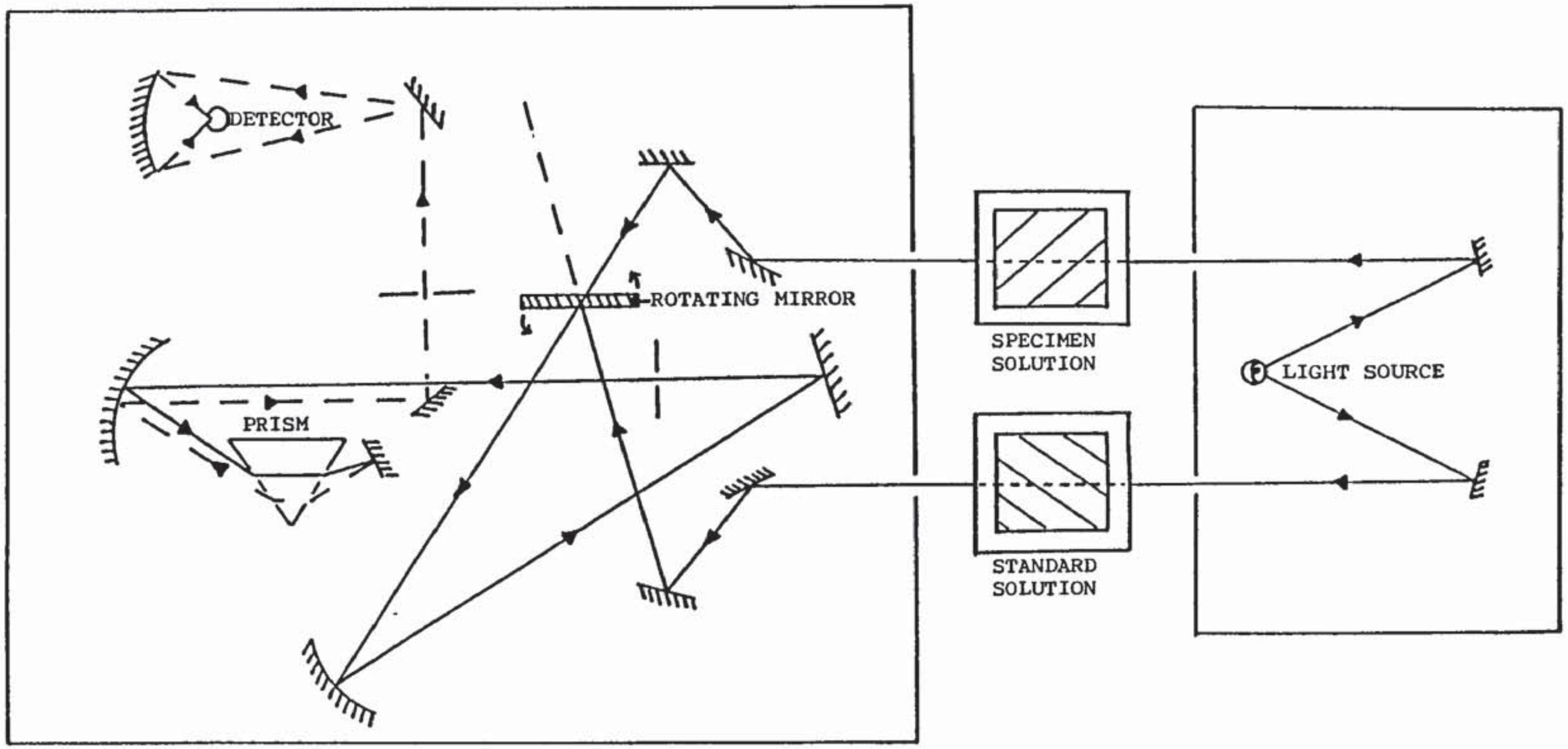


Figure 2.8
SCHEMATIC DIAGRAM OF A TWIN BEAM SPECTROPHOTOMETER

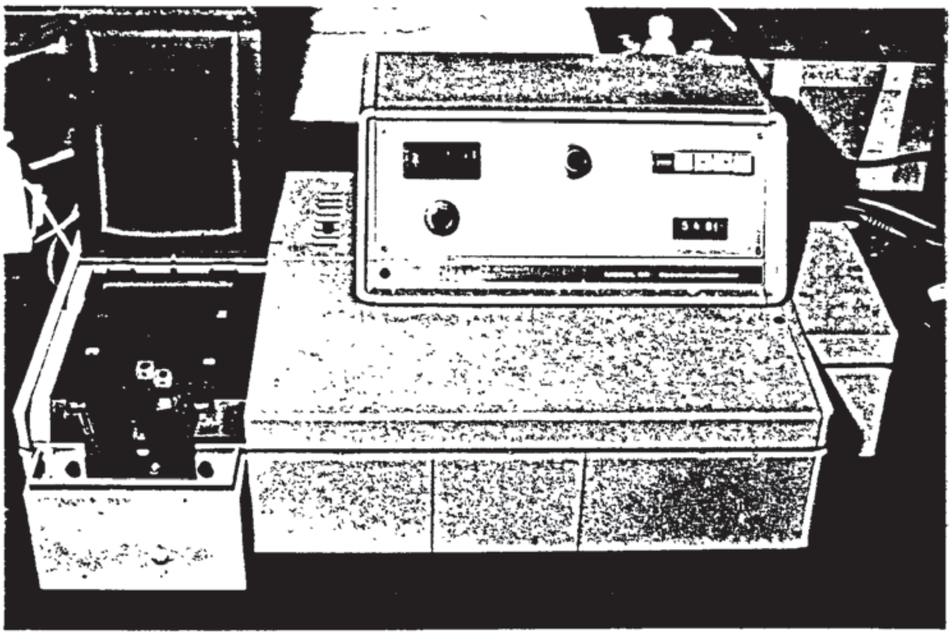


Figure 2.9
TWIN BEAM SPECTROPHOTOMETER

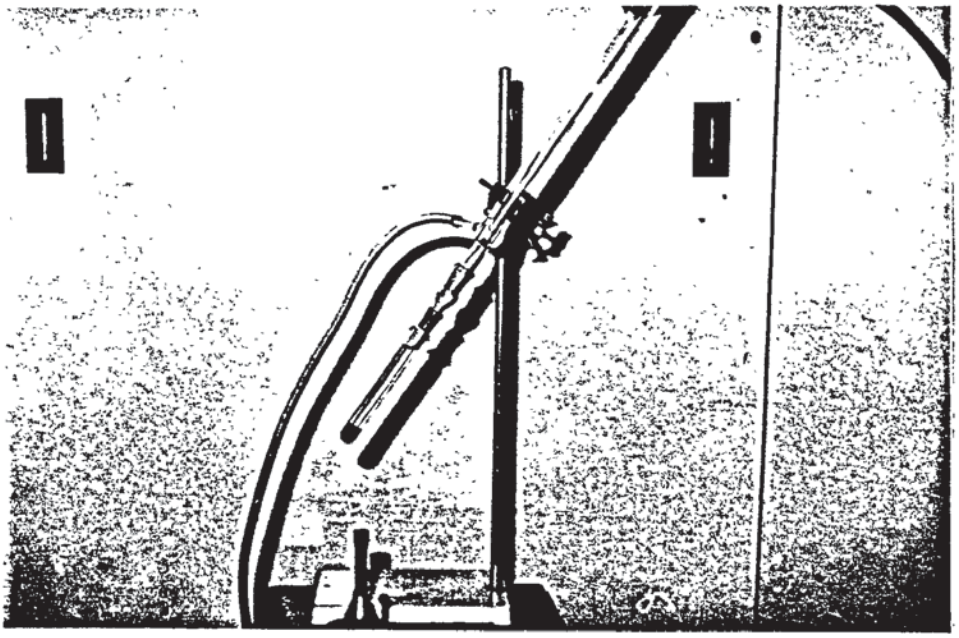


Figure 2.10
APPARATUS FOR TOTAL CHLORIDE CONTENT DETERMINATION

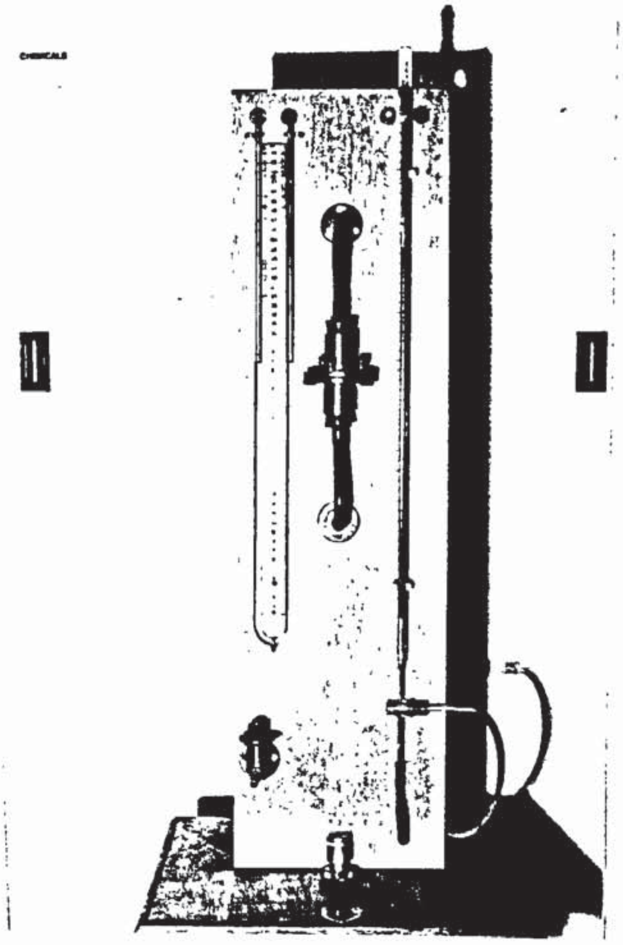


Figure 2.11
MODIFIED LEA AND NURSE APPARATUS

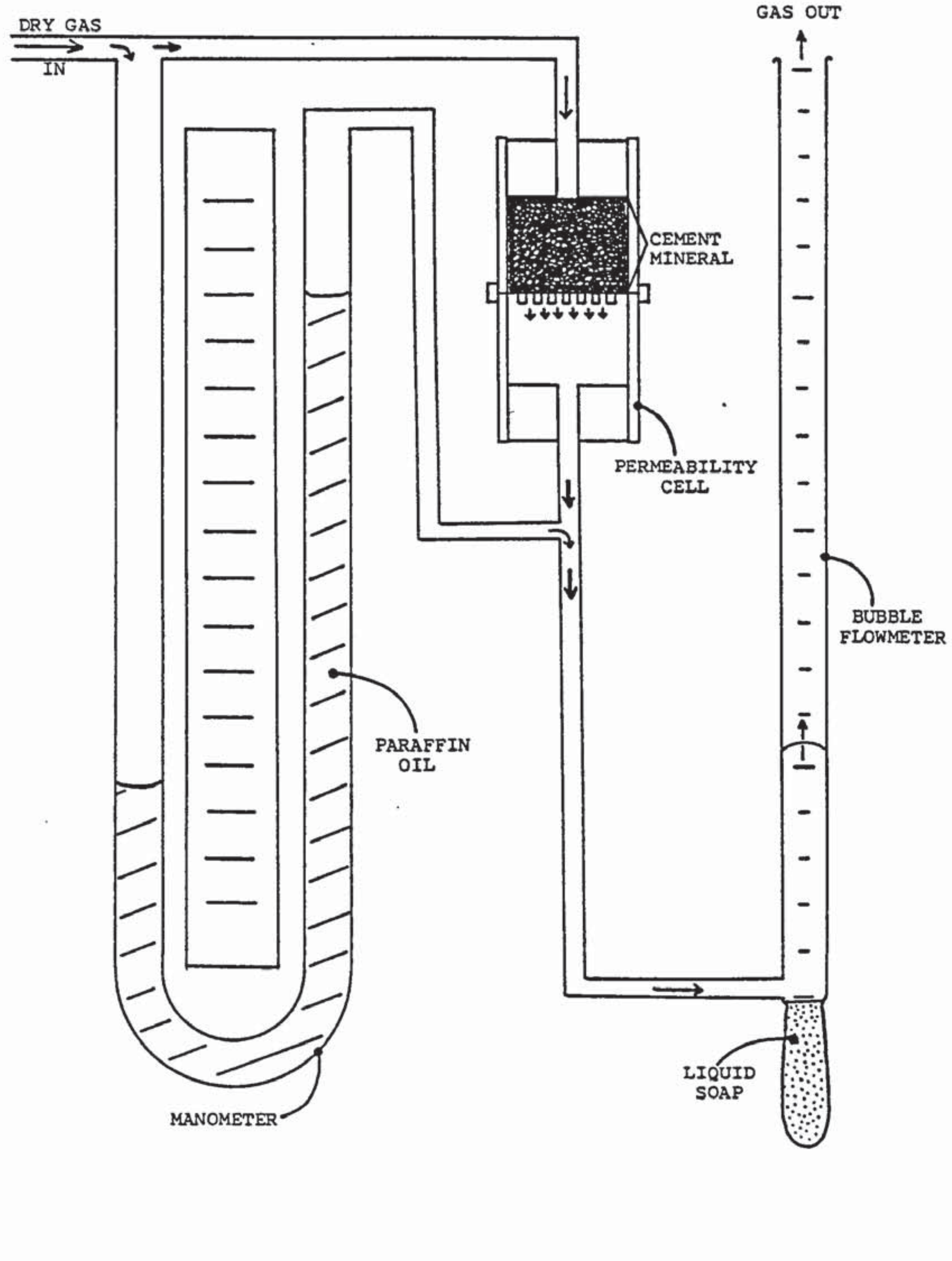


Figure 2.12
DIAGRAMMATIC REPRESENTATION OF MODIFIED
LEA AND NURSE APPARATUS

Figure 2.13
DENSITY BOTTLE

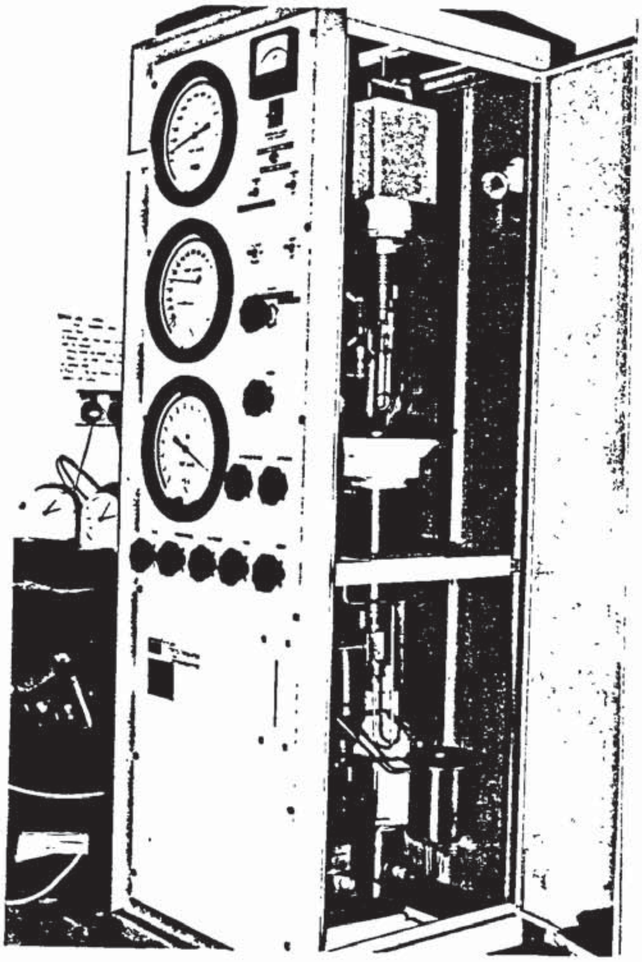


Figure 2.14
MERCURY INTRUSION POROSIMETER

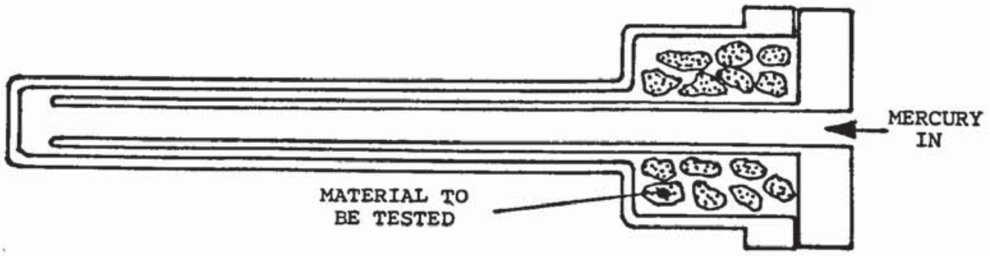


Figure 2.15
POROSIMETER CELL

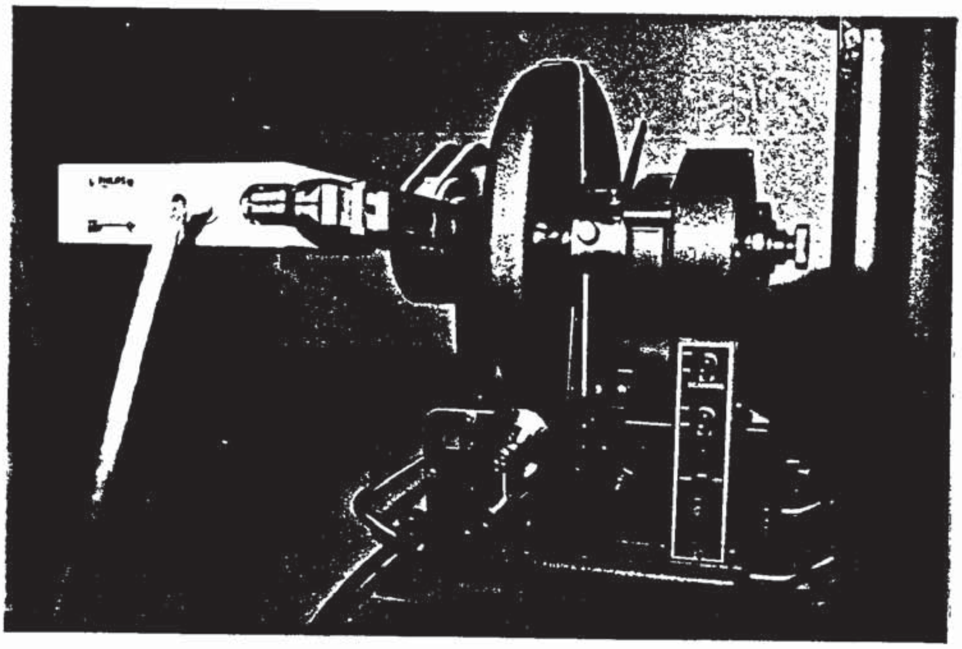


Figure 2.16
X-RAY SPECTROMETER

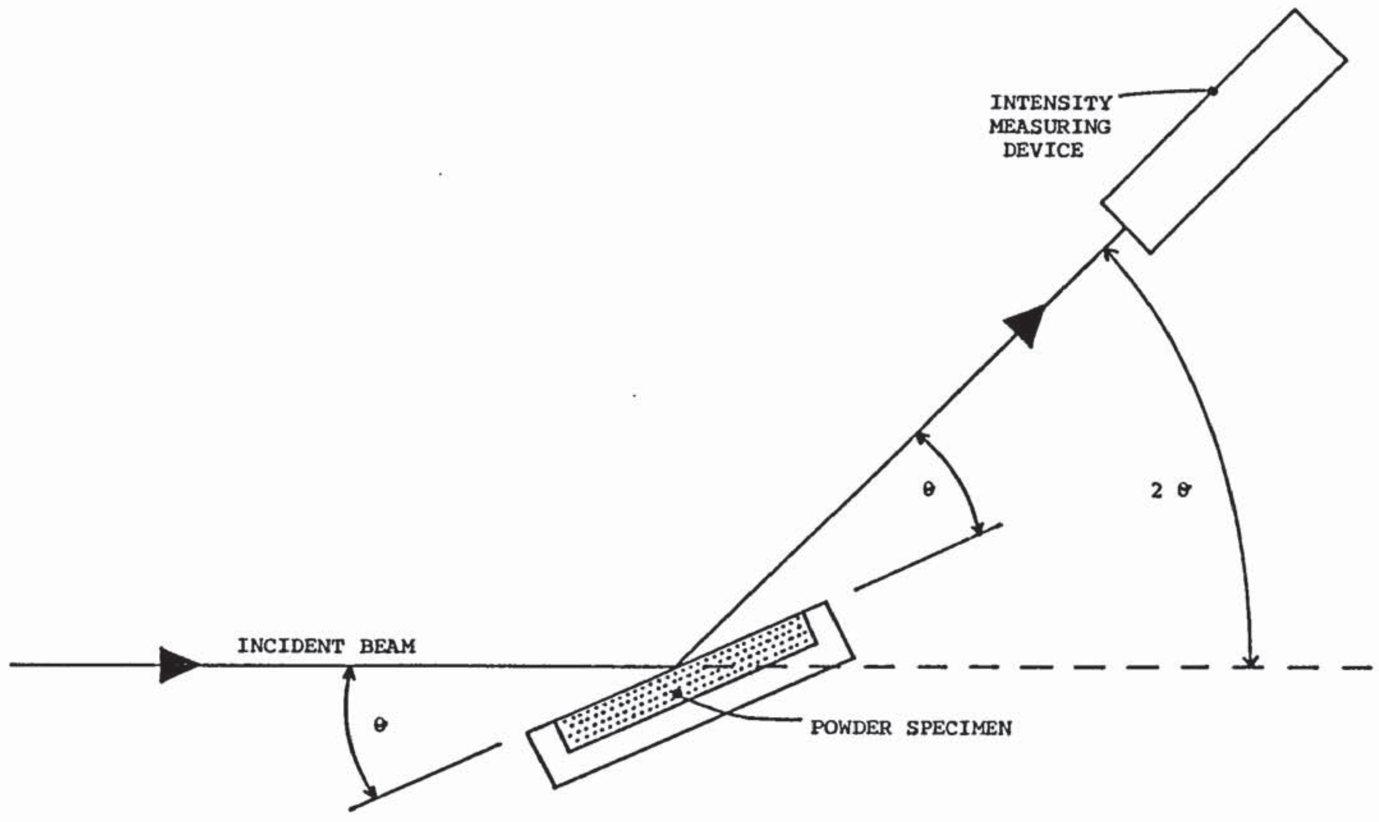
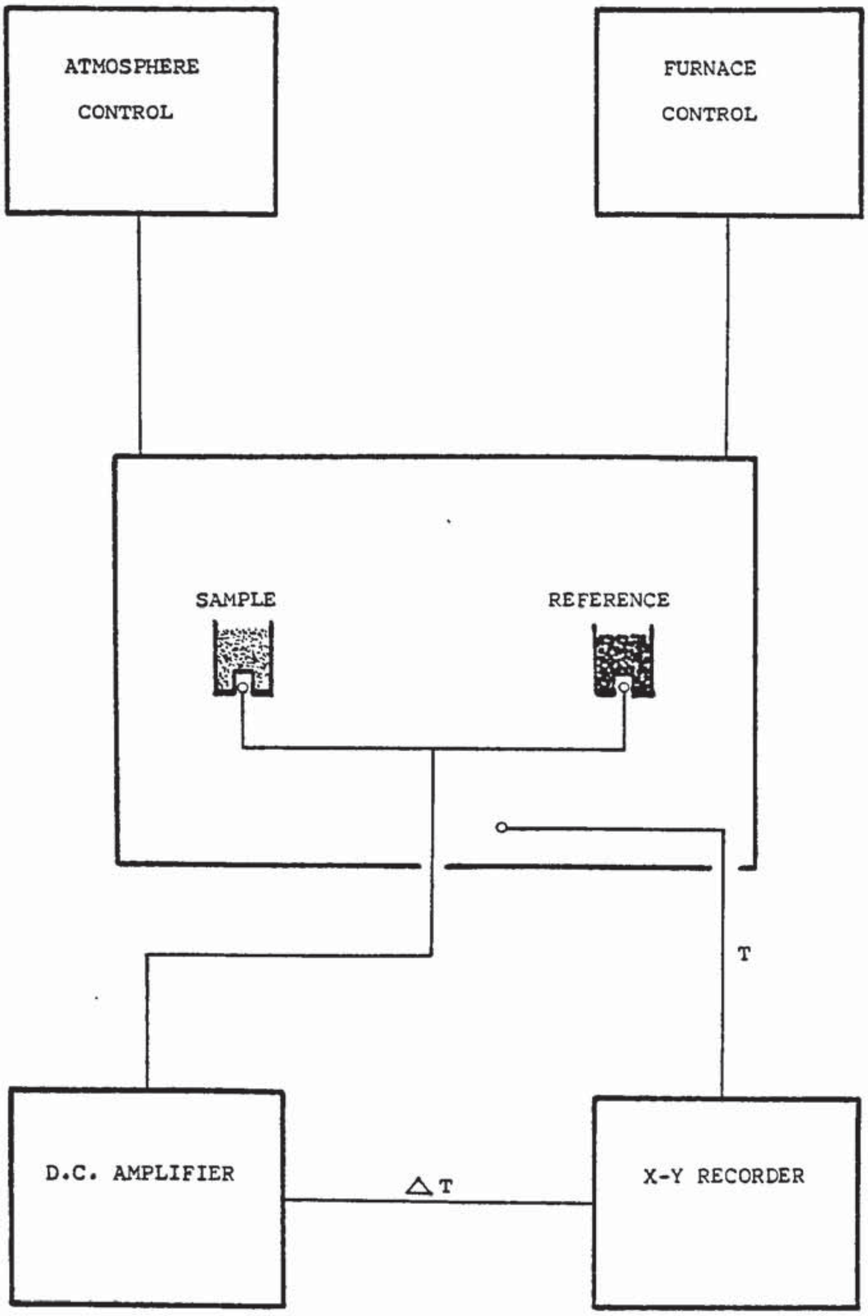


Figure 2.17
GEOMETRIC ARRANGEMENT OF X-RAY SPECTROMETER



(o = thermocouple)

Figure 2.18
SCHEMATIC DIAGRAM OF DIFFERENTIAL THERMAL ANALYSER

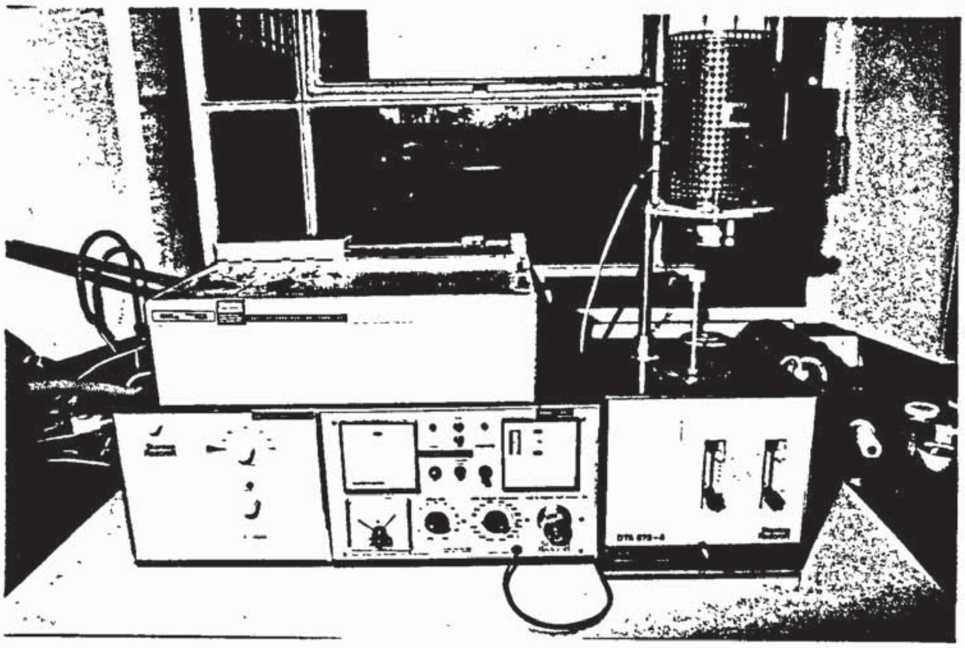


Figure 2.19
DIFFERENTIAL THERMAL ANALYSER

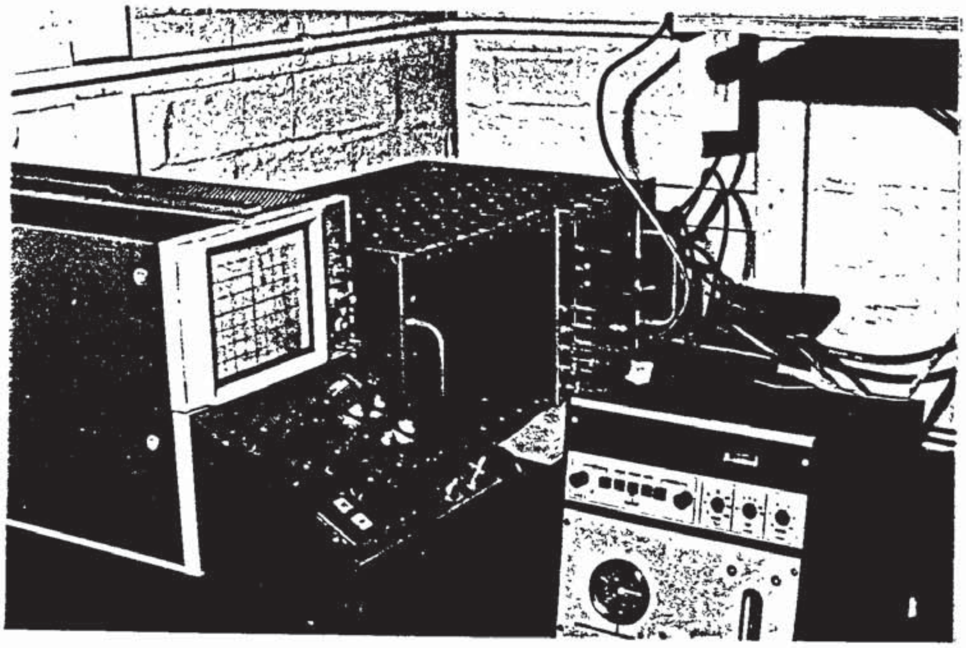


Figure 2.20
MÖSSBAUER SPECTROMETER

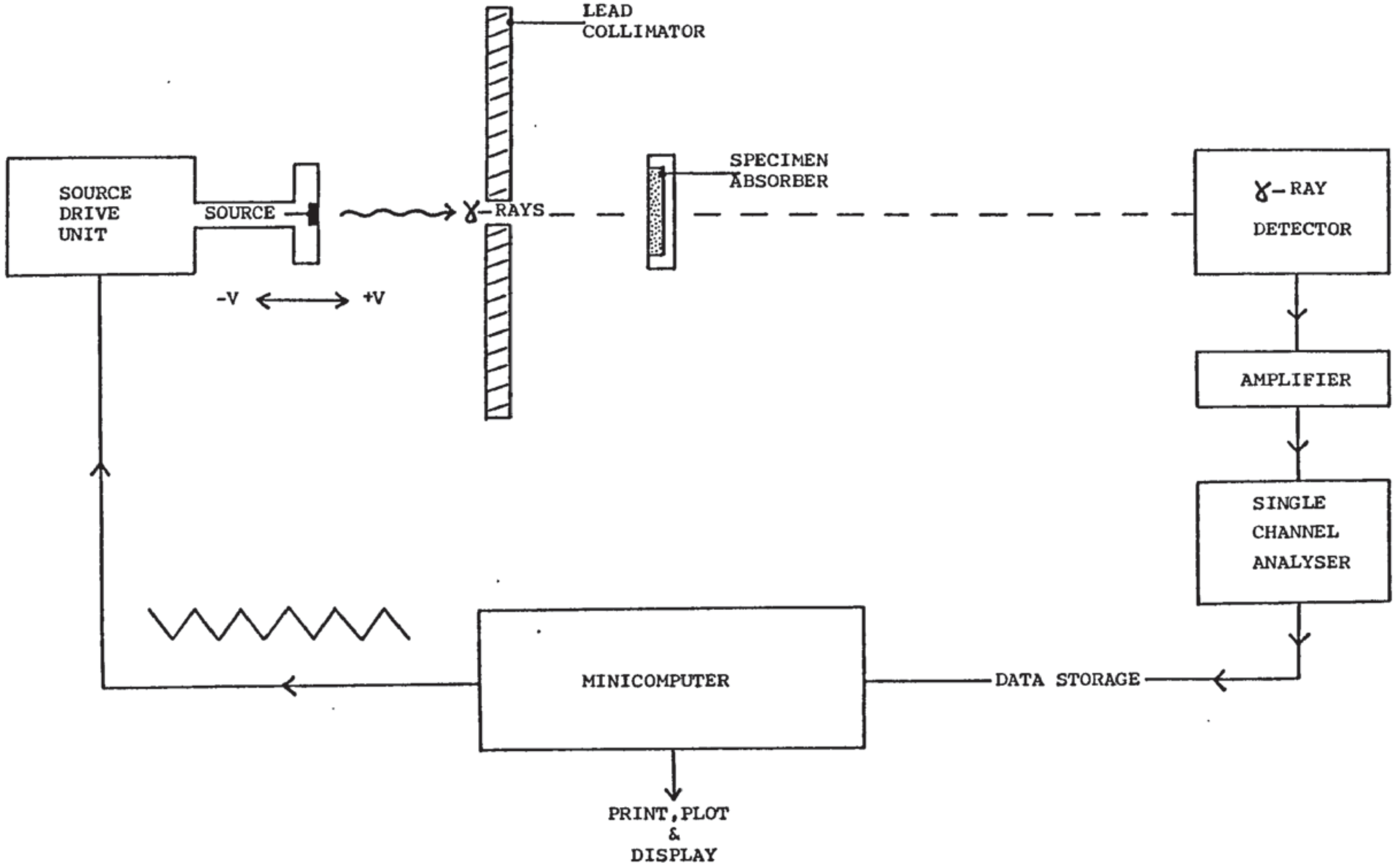


Figure 2.21
SCHEMATIC DIAGRAM OF MÖSSBAUER SPECTROMETER

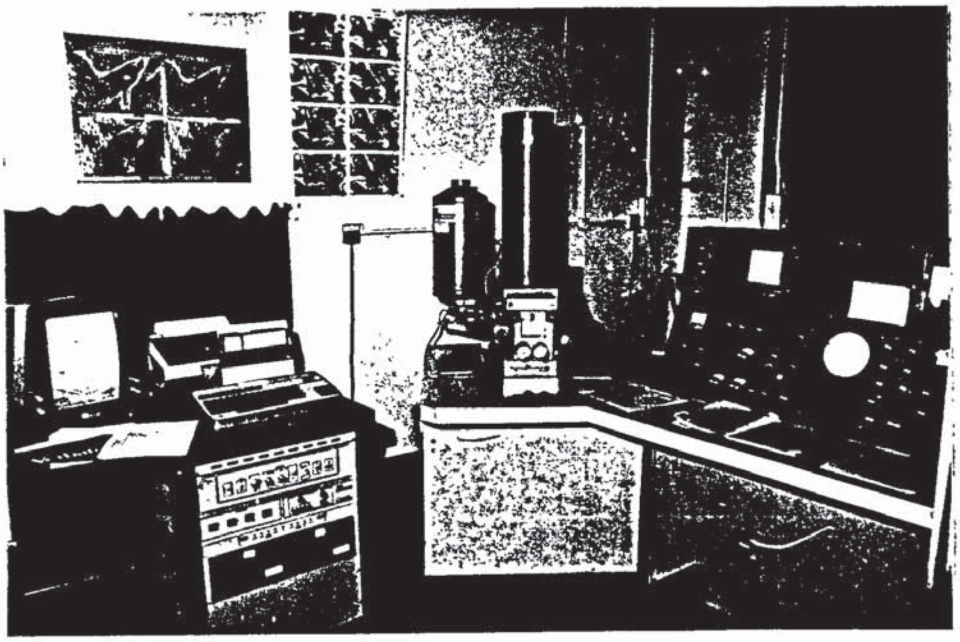


Figure 2.22
SCANNING ELECTRON MICROSCOPE COUPLED TO ENERGY DISPERSIVE X-RAY ANALYSER

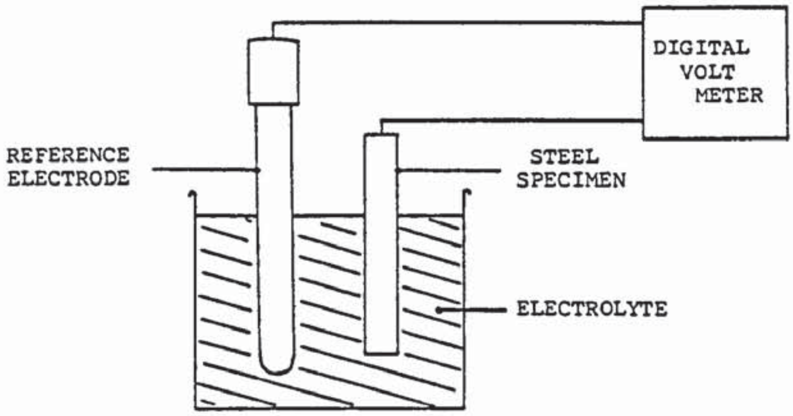
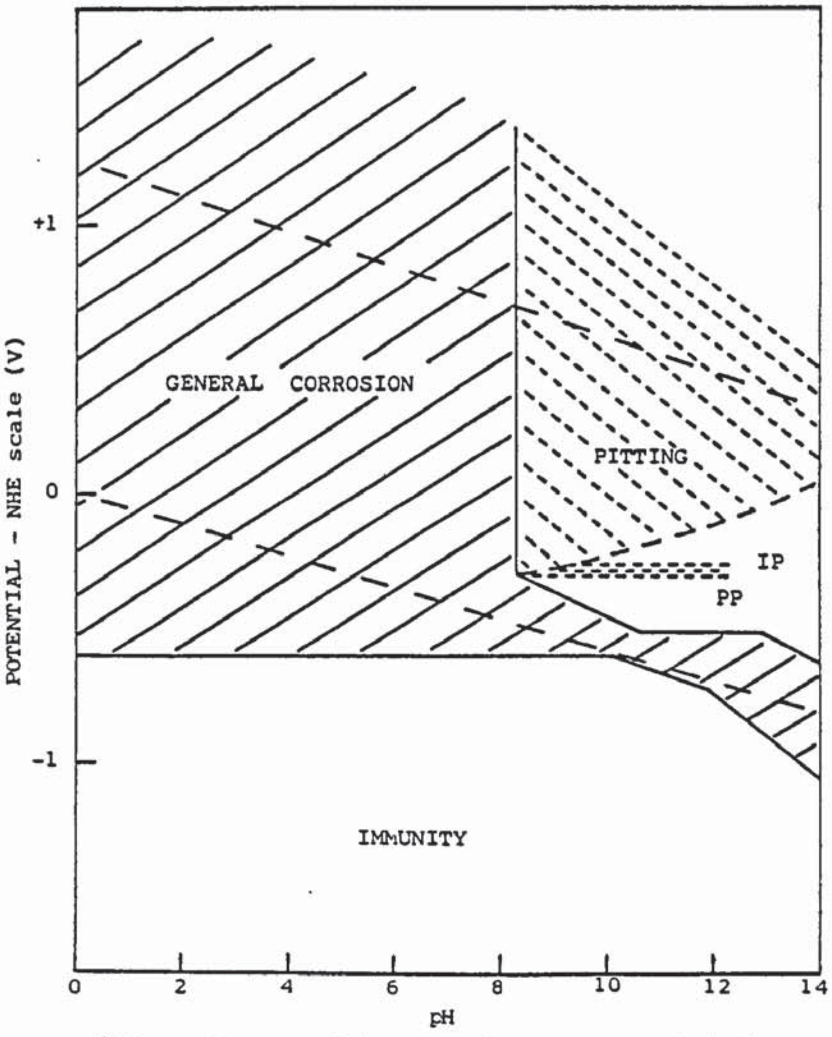


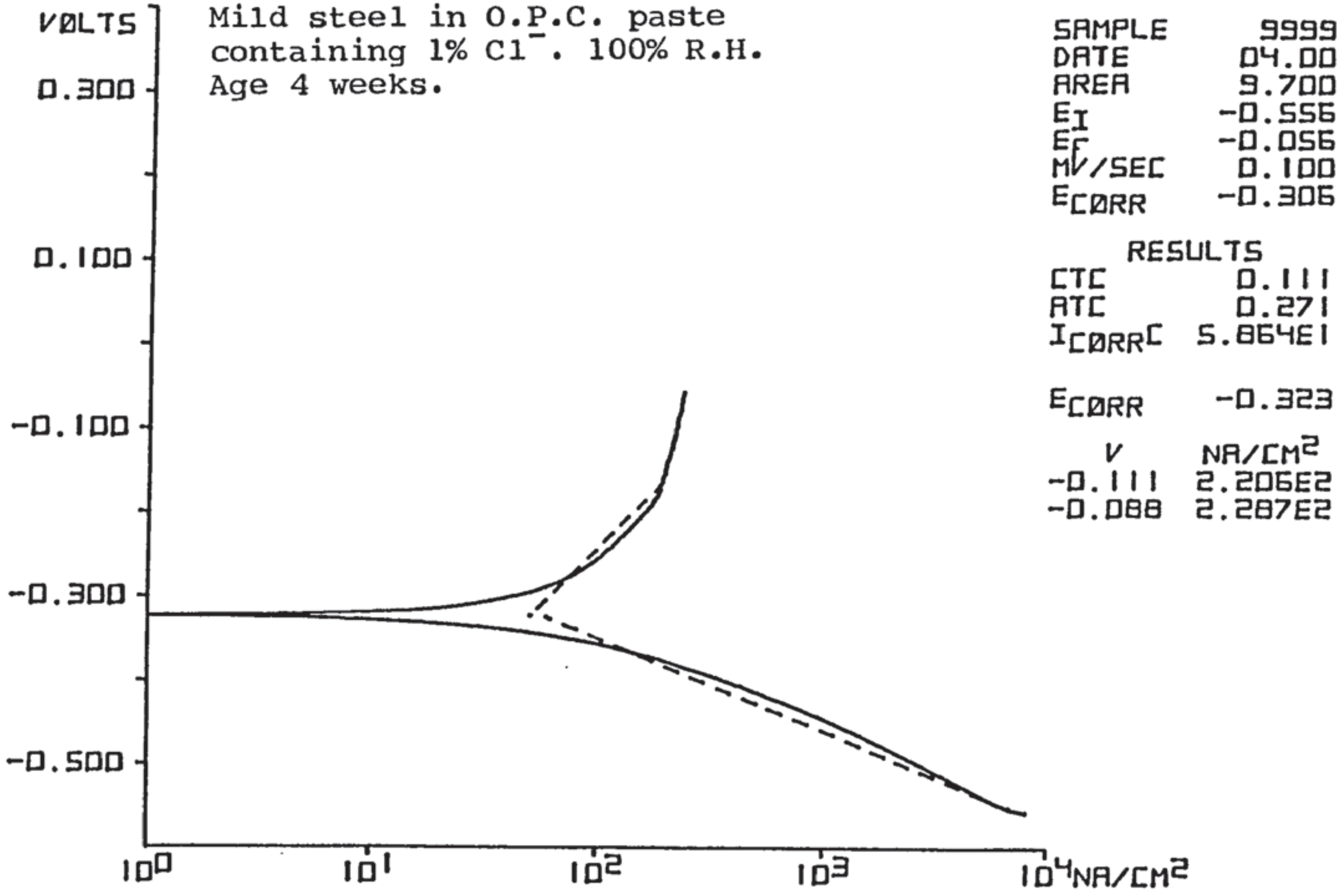
Figure 2.23
MEASUREMENT OF REST POTENTIAL



(PP, perfect passivity; IP, imperfect passivity)

FOR RAPIDLY STIRRED SOLUTIONS

Figure 2.24
PLOT OF POTENTIAL AGAINST pH FOR IRON
IN A 1 MOLAR SOLUTION OF CHLORIDE IONS


Mild steel in O.P.C. paste
containing 1% Cl^-. 100% R.H.
Age 4 weeks.

```
SAMPLE          9999
DATE           04.00
AREA           9.700
EI            -0.556
EF            -0.056
MV/SEC         0.100
ECØRR         -0.306

      RESULTS
CTC            0.111
ATC            0.271
ICØRRC      5.864E1

ECØRR         -0.323

   V       NA/CM2
-0.111    2.206E2
-0.088    2.287E2
```

Figure 2.25
TAFEL PLOT PRODUCED BY P.A.R.
POTENTIOSTAT

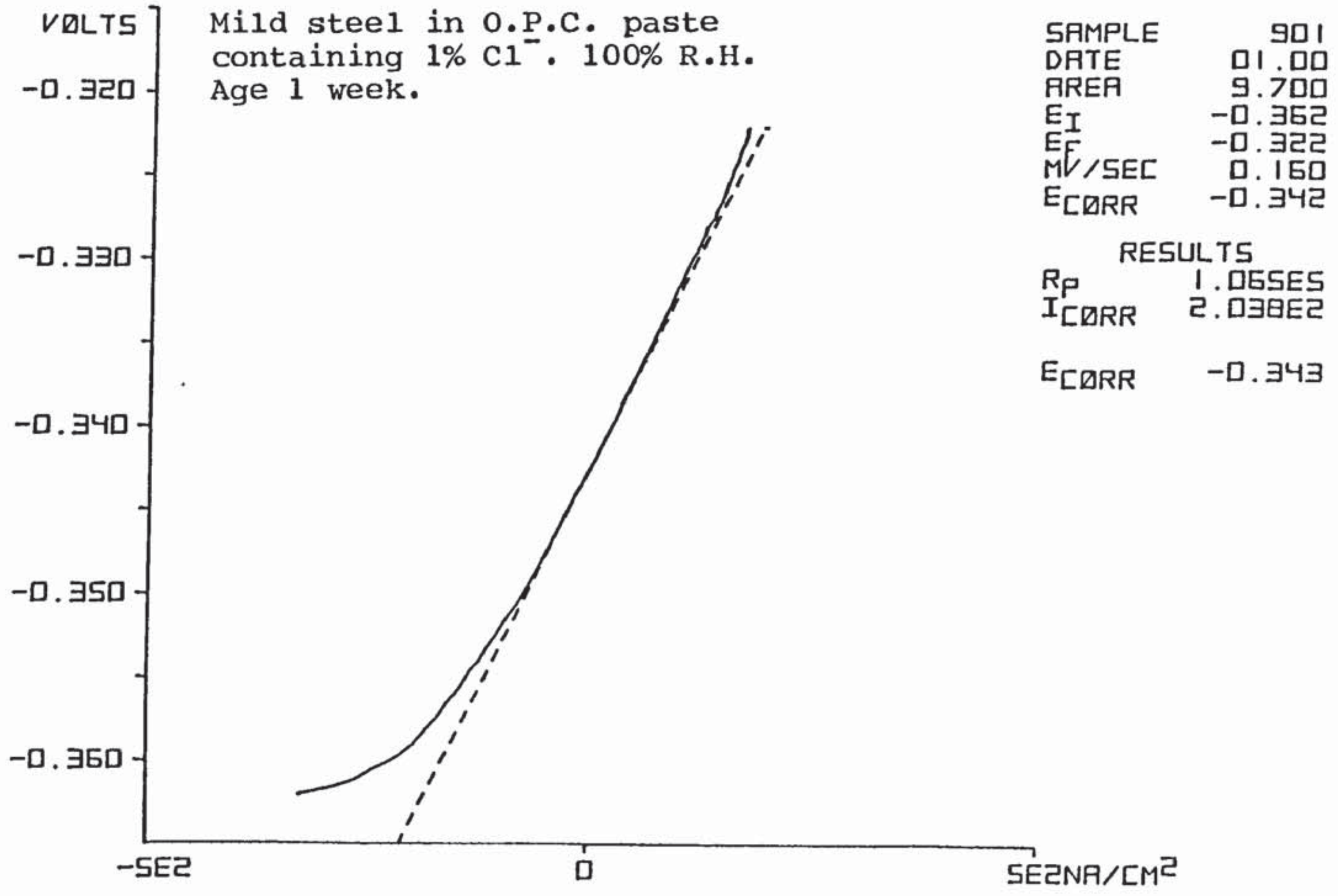


Figure 2.26
POLARISATION RESISTANCE PLOT PRODUCED
BY P.A.R. POTENTIOSTAT

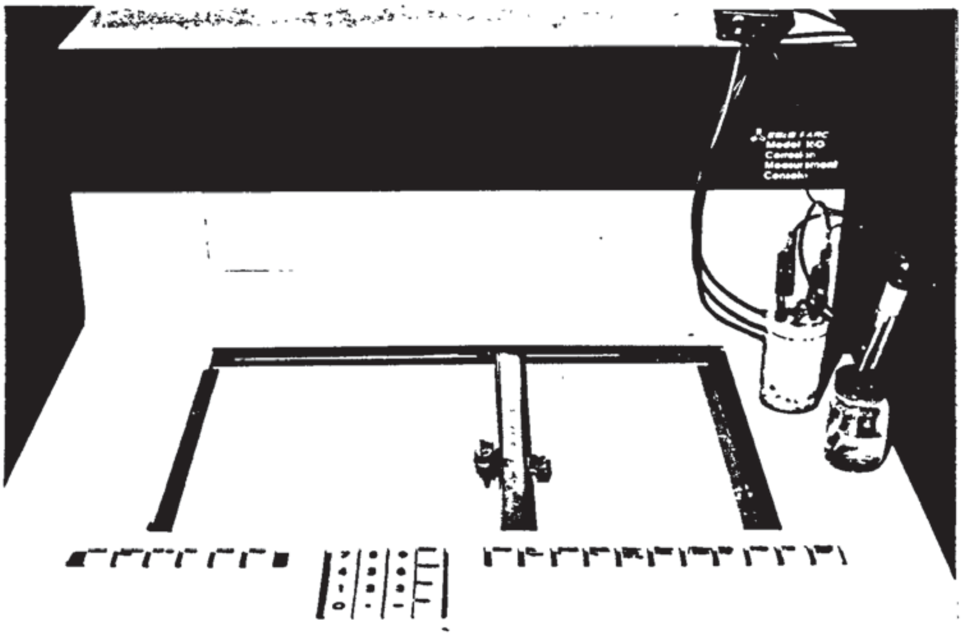


Figure 2.27
P.A.R. POTENTIOSTAT

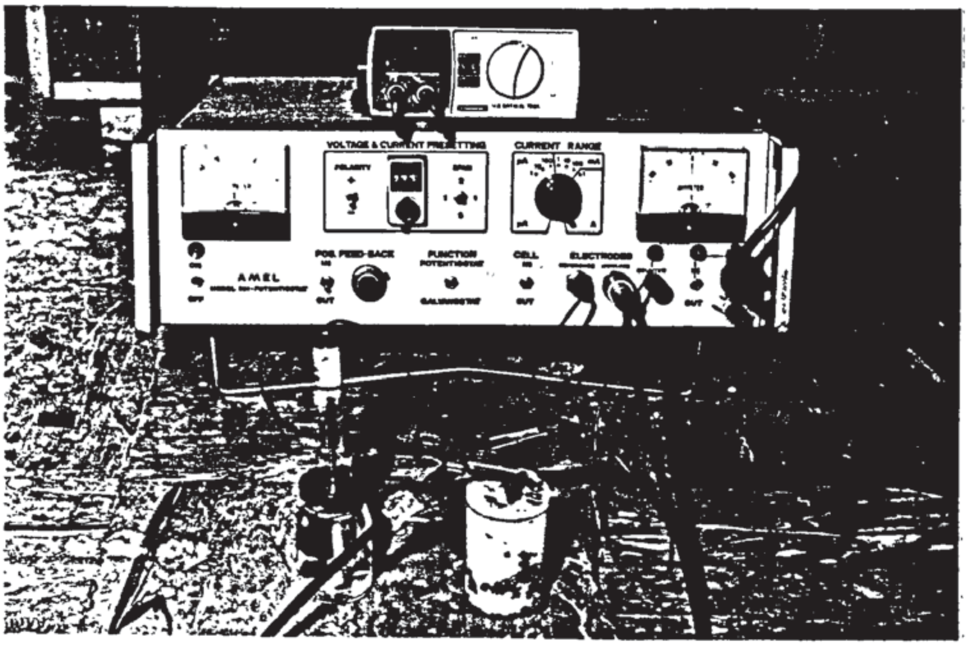


Figure 2.28
APPARATUS FOR MANUAL DETERMINATION OF
POLARISATION RESISTANCE

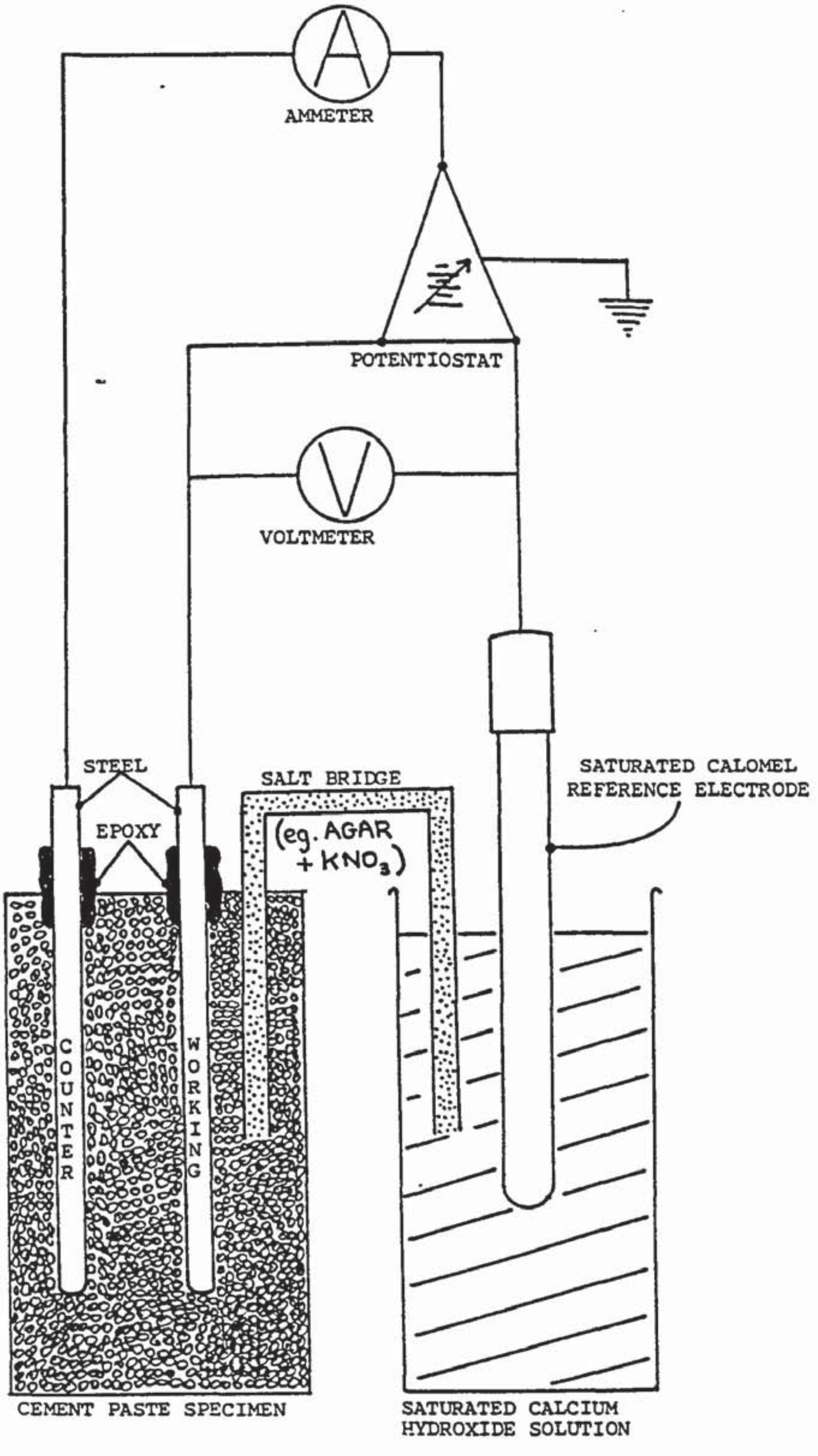


Figure 2.29
ARRANGEMENT FOR THE MANUAL DETERMINATION OF POLARISATION RESISTANCE

CHAPTER 3

THE EFFECT OF EXTERNAL AND INTERNAL CHLORIDES ON THE CHEMISTRY OF CEMENT PASTES

3.1 INTRODUCTION

Chloride ions may enter hardened cement paste and concrete by two means, they may be added during mixing either deliberately as an admixture or as a contaminant in the original mix constituents, or they may enter the cement matrix after hydration from an external source such as de-icing salts or sea water. (54) Once chloride is within the cement matrix, it tends to depassivate embedded steel by breaking down the protective layer of oxide which is normally formed in a highly alkaline medium such as cement or concrete. (55)

An important factor in the effect chloride ions have on the inhibitive quality of the cement matrix is the proportion of tricalcium aluminate present in the cement which may vary from around 14% in an ordinary Portland cement to less than 3.5% in a sulphate resisting Portland cement. Tricalcium aluminate reacts with chloride to form insoluble complex salts so reducing the number of free ions in the pore solution. (56) Roberts noted in 1962 that steel embedded in sulphate resisting Portland cement showed a higher rate of corrosion than that in ordinary Portland cement containing the same amount of chloride. (9) From this he suggested that the use of calcium chloride as a set accelerator should be avoided with sulphate resisting Portland cement. He also observed that the extent of corrosion increased with larger additions of chlorides.

In unstirred chloride solutions the electrode potential and corrosion rate of steel do not give reproducible values due to uneven diffusion of oxygen to the surface. By agitating the solutions, Brasher found that the electrode potential reached a steady reproducible value and that the potential and corrosion rate for any one steel specimen was altered only by the chloride concentration. (57) The limiting concentration of chloride for steel prepared with emery paper and agitated with air in neutral solutions was found to be 10^{-1} molar and for a similar specimen agitated with oxygen, 10^{-2} molar. Below these concentrations the steel was seen to be passive and above them corrosion took place.

The effect of hydroxyl ion concentration (pH) is another important factor influencing the passivity of steel. Gouda showed that for polished steel to demonstrate permanent passivation in an aqueous solution it had to be at a pH of at least 12. (58) For pickled steel the pH must be higher than 12 and for rusted steel even more alkaline again if passivity is to be maintained. For steel in a particular concrete it was shown that the critical concentration of sodium chloride above which corrosion took place was around 1% if added in the mix water and 4% from the surrounding medium as the steel would have passivated prior to the chloride being present. The threshold level of sodium chloride as an admixture has since been shown to be nearer 0.75% for clean steel and 0.15% for rust covered steel, the mixes used in both pieces of work being similar in composition (1 cement : 2.9 or 2.3 sand : 3.4 gravel) with water-cement ratios of 0.6.(59) Further work by Gouda with steel in alkaline solutions has shown a relationship between hydroxyl ion concentration and the respective threshold chloride level.(60) As the pH of a solution is increased from 12 to 14 so the threshold chloride concentration alters from 250 to over 4 000 parts per million. A plot of the logarithm of threshold chloride level against pH between 12 and 13.3 has been shown to be effectively linear. (See figure 3.1)

Chloride is one of the most common depassivating ionic species to be found in steel reinforced concrete and, therefore, of great interest. With cement being an alkaline medium the level of hydroxyl ion is as important in determining the stability of the oxide film as is the level of chloride. The source of the chloride and stage of hydration at which it is present are also likely to be of major importance. This chapter aims to study the effects of chloride from internal and external sources on the pore solutions of two cements of differing tricalcium aluminate content.

3.2 PREVIOUS WORK

It has been known for many years that chloride salts may be detrimental to concrete. The most common effect is their tendency to increase the corrosion rate of embedded steel b work has shown that chlorides may also alter the mechanical characteristics of the cement matrix. Neville demonstrated that hydrated cements immersed in saturated calcium chloride solutions exhibit severe leaching of hydroxyl ion combined with expansion and loss of strength.(61)

Chloride ions can react with the calcium hydroxide, produced by the hydration of the calcium silicates, to form complex salts so reducing the alkalinity of the pore solution. The leaching effect upon the level of calcium hydroxide is thought to increase the porosity of the cement and therefore make it more susceptible to frost damage. (62)

Work carried out by Kawadkar and Krishnamoorthy studying the behaviour of concrete subjected to concentrated solutions of sodium chloride showed the microstructure and strength of the cement to be adversely affected. (63) The effects were greater at higher hydrostatic pressures suggesting that submerged marine structures may be open to severe degradation of the cement matrix.

By far the most common source of internal chloride is the use of calcium chloride as a set accelerator. Skalny and Odler attempted to establish its mechanism with a range of chloride salts using differential thermal analysis. (64) From their results they concluded that a 2% addition of chloride by weight of the cement accelerated the hydration of both tricalcium and dicalcium silicate. The chlorides also caused a decrease in the concentration of sulphates due to a more rapid formation of sulphate containing phases. The main product of the hydration of tricalcium silicate was found to be a tobermoritic phase (Calcium-Silicate-Hydrate gel) though the disappearance of hydroxide and chloride indicated the presence of $CaCl_2Ca(OH)_2.H_2O$. The presence of gypsum was seen to cause the formation of ettringite rather than calcium chloroaluminate until all the gypsum was consumed.

A major problem in all such studies has been to develop a method for determining the level of ion activity in the pore water. Chloride levels have been measured by dissolving the free ions in solvents such as water, ethanol and acetone and it has been shown that, given time, water will dissolve all the chloride present in a cement paste. (65) Brown and Bolling determined free chloride ion activity by steeping cement specimens in water for forty eight hours and measuring the level in the solvent by means of a specific ion electrode (66) while Ramachandran studied the effects of calcium chloride on the hydration of tricalcium silicate by leaching specimens with both water and ethanol. (67)

An alternative method developed by Theissing et al involves placing hydrated cement specimens in chloride solutions and allowing the chloride concentration in the pores and the external solution to equilibrate. The amount of combined chloride may then be calculated as follows

$$Cl_c = Cl_t - W_p \times Cl_e$$

where

Cl_c = combined chloride content

Cl_t = total chloride content of the cement

W_p = amount of evaporable water

Cl_e = concentration of the equilibrium solution

The main drawbacks of this technique are that it is time consuming and unreliable at low chloride concentrations where the concentration gradient is small and there is a risk of interference by background chloride levels. (68)

Problems arise where the activity of more than one ionic species is to be determined. Much work has been carried out on young cement pastes less than two hours old and on mixes of high water-cement ratios (between 1 and 2) which have been kept agitated for up to a week. (69)(70) In each case, free water may be filtered out and analysed giving information on the very early stages of hydration.

The development of pressure extraction techniques by Longuet et al has allowed pore solutions from fully hydrated cement pastes to be analysed. (71) It is this method that has been employed in this chapter to provide samples of pore solutions for subsequent analysis.

3.3 EXPERIMENTAL PROCEDURE

Portions of the two cements to be used were sieved and sufficient cement weighed out to make either three cylinders (49 millimetres diameter by 75 millimetres depth) or twenty five discs (49 millimetres diameter by 10 millimetres depth) with any one mix. The required amount of mixing water was weighed and in the case of the cylinders containing internal chlorides, the required amount of sodium chloride was dissolved in the water prior to mixing. Once mixed, the cement pastes were poured into the moulds and vibrated as described in chapter 2 (para.2.3). Figure 3.2 shows the types of moulds used and the forms of specimen produced. Details of the cements are given in chapter 2 (para.2.2). All the mixes were of 0.5 water-cement ratio. The cylinders containing chloride were cured in their moulds at 100% relative humidity and 25 degrees Centigrade until pressing. The discs were cured in the same manner as the cylinders for the first forty eight hours and then placed into 2% sodium chloride solution which was replaced weekly until pressing. Sufficient specimens were produced to allow three samples of pore solution to be expressed in each case ie. three cylinders or 3 x 8 discs. Larger volumes of pore solution were obtained by breaking the discs into small pieces which then reformed into a cylinder during pressing. (See figure 3.3) Care was taken to remove the surface water from the discs prior to testing to ensure only the absorbed chloride would be expressed. The method of expression is described in chapter 2 (para.2.5).

The triplicate specimens of pore solution produced by expression were analysed for hydroxyl ion (pH) and chloride ion content as described in chapter 2 (para.2.6). A sample of cement paste taken from each specimen prior to pressing was used for the determination of evaporable/non-evaporable water content (para.2.7), total chloride content (para.2.8) and differential thermal analysis (para.2.13). Appendix 11 provides a key to the differential thermal analysis peaks obtained.

3.4 RESULTS AND DISCUSSION

The values obtained from the expressed pore solutions for hydroxyl ion (pH) and free/total chloride ion activity are given in tables 3.1 to 3.3. Chloride ion levels have been expressed in terms of millimoles of chloride per gramme of unhydrated cement (mM/g). Free chloride levels have also been expressed in terms of moles per litre (M/l) ie. the chloride molarity of the pore solutions. The water content of the specimens has been expressed as grammes of water per gramme of unhydrated cement (g/g) and separated into evaporable (free) and non-evaporable (bound). (Para.2.7)

Figures 3.4 and 3.5 show the differential thermograms obtained for each type of specimen and for specimens of both cements containing no chloride. Figures 3.6 and 3.7 show the effect of an external source of chloride ions on the ratio of free to bound chloride and pore solution pH for discs of the two cements over the period 50 to 100 days.

During their period of immersion in sodium chloride solution the cement discs suffered severe leaching of calcium hydroxide resulting in the appearance of a layer of calcium carbonate on the surface of the baths and the formation of small, whisker-like growths from larger external pores. Despite regular renewal of the solutions they continued to become highly alkaline.

For the cylinders containing chloride as an admixture the difference between the two cements is very clear. Although the paste specimens of both cements had been made with the same level of internal chloride, within 50 days those made with ordinary Portland cement had a far lower level of free chloride than those with sulphate resisting Portland cement. This resulted in a considerable difference between their respective ratios of free to total chloride (16.2% for O.P.C., 40.6% for S.R.P.C.). By studying the differential thermograms and comparing them to standard data (41), it is possible to infer the reason for the lower free chloride level with the ordinary Portland cement. The 50 day old samples containing chloride have lost some of their ettringite phase (~ 200°C) which has reacted to produce Friedel's salt, an insoluble calcium chloroaluminate phase (~ 320°C). This has happened to smaller extent with the sulphate resisting Portland cement. Due to the differing amounts of tricalcium aluminate present in the two cements the ordinary Portland cement is left with around 0.5% free sodium chloride and the sulphate resisting Portland cement nearer 1.25%. The sulphate resisting Portland cement also exhibits a small drop in pH compared with the ordinary Portland cement. Therefore when chloride is added to cements during hydration ordinary Portland cement is far more capable of removing free chloride and maintaining a high pH.

Where chloride is introduced into cement after the initial hydration has taken place the difference between the two cement types would appear not to be so clearly defined. After 50 days there is only a small advantage to ordinary Portland cement with the two cements having identical chloride levels and around 15% difference between the free to bound ratios. The pH level of each has dropped severely, aggravated by leaching, to a similar value. The thermograms for the 50 day old specimens exposed to external chlorides show the extent to which the calcium chloroaluminates peak ($\sim 320^{\circ}C$) has increased in size for the ordinary Portland cement and the small amount of ettringite ($\sim 200^{\circ}C$) the sulphate resisting Portland cement has remaining.

After 100 days the ratio of free to bound chloride has dropped slightly and by a similar amount for both cements (see figure 3.6). The probable reason for this can be seen by studying the levels of free chloride in the pores. At 100 days the level in both cements is nearly in equilibrium with the external solution so that the rate of increase in the concentration will have slowed down. As the remaining ettringite reacts with the chloride the free to bound ratio is reduced. The pH of the pore solution in the sulphate resisting Portland cement discs drops at a faster rate than that for the ordinary Portland cement discs (see figure 3.7), possibly due to a more open pore structure, and at 100 days is equivalent to the pH of saturated calcium hydroxide solution (pH = 12.45 at 25°C). It may be assumed that the pH of the pore solution would remain at this 'equilibrium' level for as long as the external solution remained saturated with calcium hydroxide leached from the cement paste. If the pH of the pore solution in the ordinary Portland cement specimens continued to drop at a steady rate it would take a further 1 000 days to reach this possible equilibrium point.

The major difference between the two cements at 100 days is the amount of bound chloride each contains. The ordinary Portland cement has nearly 25% more bound chloride than the sulphate resisting Portland cement due to its greater initial proportion of tricalcium aluminate. If the levels of free chloride and hydroxyl ion (pH) present in these specimens are compared with the data provided by Gouda as shown in figure 3.1, certain inferences can be made as to the condition that embedded steel would be in in such environments. Only the specimens of ordinary Portland cement with internal chloride added during mixing prove to have a pore solution analysis consistent with maintaining the passivity of steel. The equivalent specimens made with sulphate resisting Portland cement have a chloride/pH level twice that of the suggested threshold. This clearly illustrates the risk of using chloride based admixtures with sulphate resisting Portland cement. For the remaining specimens where the chlorides have entered from an external source, the levels of free chloride are 20 to 25 times greater than the respective threshold levels. Even taking into account the work by Gouda suggesting that four times as much chloride is required from an external source to produce the same effect as internal chloride, the levels for those specimens exposed to 2% sodium chloride solution are five times more severe than those caused by the addition of 2% sodium chloride as an admixture in the mixing water. (59)

3.5 CONCLUSIONS

Where small addtions of sodium chloride have been made to cement pastes during mixing, sulphate resisting Portland cement has proved to be less capable than ordinary Portland cement in reducing the resultant free chloride level due to its lower initial level of tricalcium aluminate. For an addition of 2% sodium chloride in the mixing water, sulphate resisting Portland cement has a free chloride level 2½ times greater than ordinary Portland cement at an age of 50 days. There is also a resulting reduction in the hydroxyl ion concentration of the sulphate resisting Portland cement pore solution. For these reasons the use of chloride based admixtures with sulphate resisting Portland cement should be avoided even at very low concentrations and great care is needed to ensure that there is no chloride contamination in the aggregates or mixing water.

Where hydrated cement pastes are cured in sodium chloride solutions the advantage of the higher tricalcium aluminate level in ordinary Portland cement is less apparent.

By 100 days the free chloride concentrations of both types of cement are very similar and are approaching the concentration of the external solution. The hydroxyl ion concentrations of the pore solutions are greatly lowered, aggravated by severe leaching by the surrounding solution. The pH of the sulphate resisting Portland cement pore solution drops at a faster rate than that of the ordinary Portland cement, possibly assisted by a more open pore structure. For this reason ordinary Portland cement would be slightly more suitable than sulphate resisting Portland cement for use in chloride environments although neither performs sufficiently well to protect embedded steel. For steel to be protected in such environments the permeability of the cement matrix needs to be reduced by the inclusion of aggregates and a good depth of cover must be maintained.

(Chloride concentration of external solution = 0·342M)

SPECIMEN	O.P.C. CYLINDERS CONTAINING 2% SODIUM CHLORIDE. CURED IN 100% R.H. 50 DAYS.				S.R.P.C. CYLINDERS CONTAINING 2% SODIUM CHLORIDE. CURED IN 100% R.H. 50 DAYS.			
WATER CONTENT (g/g_{cem})	FREE= 0.3135 BOUND= 0.1829 TOTAL= 0.4964			AVERAGE RESULTS	FREE= 0.3148 BOUND= 0.1817 TOTAL= 0.4965			AVERAGE RESULTS
TOTAL CHLORIDE (mM/g_{cem})	0.171	0.171	0.171	0.171	0.171	0.171	0.171	0.171
FREE CHLORIDE (M/1)	0.088	0.088	0.087	0.088	0.224	0.222	0.212	0.219
FREE CHLORIDE (mM/g_{cem})	0.028	0.028	0.027	0.028	0.071	0.070	0.067	0.069
pH	13.78	13.77	13.78	13.78	13.65	13.65	13.65	13.65
$\frac{\text{FREE } Cl^-}{\text{TOTAL } Cl^-}$	16.4%	16.4%	15.8%	16.2%	41.5%	41.0%	39.2%	40.6%

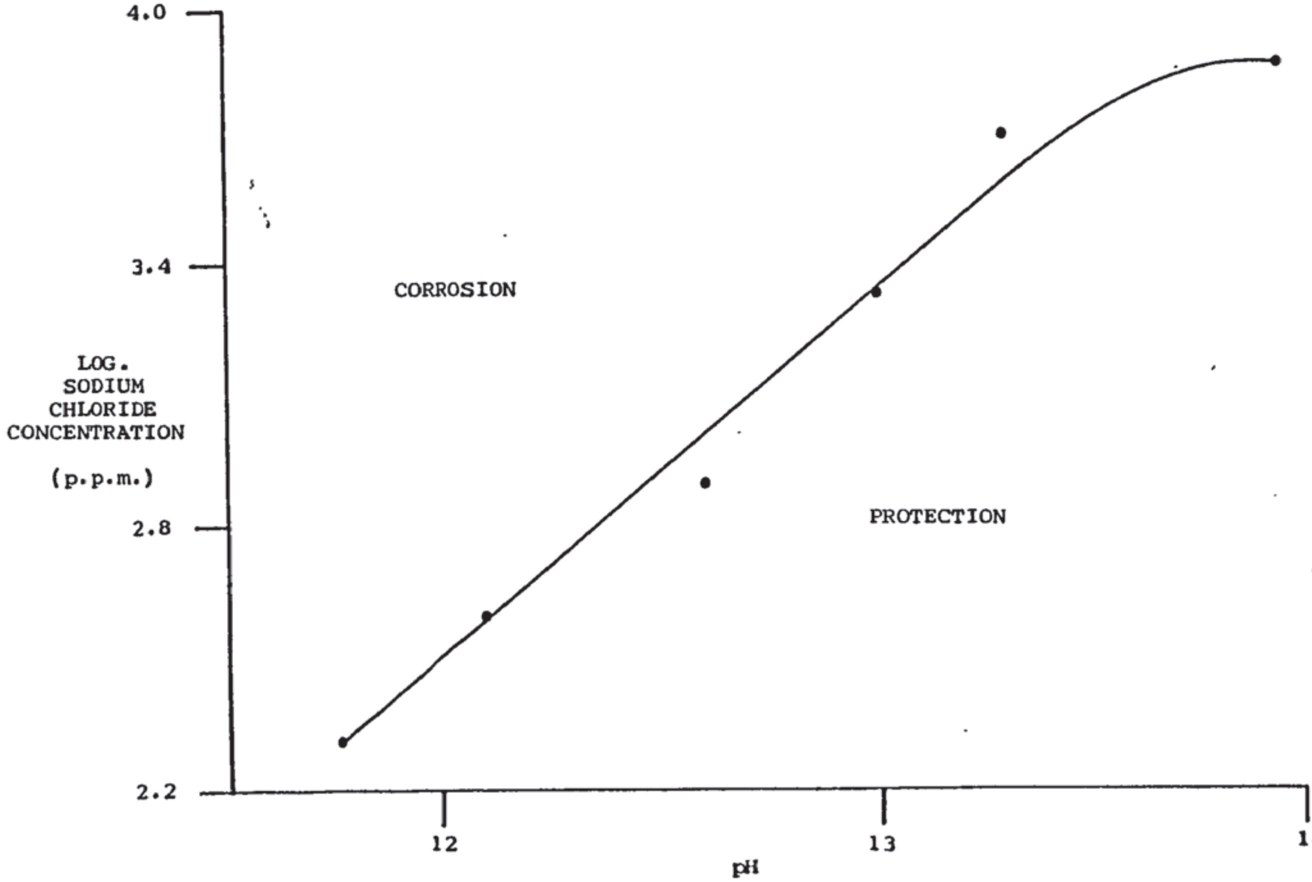
Table 3.1 RESULTS FOR CEMENT PASTE CYLINDERS CONTAINING INTERNAL CHLORIDE (50 DAYS)

SPECIMEN	O.P.C. DISCS CURED IN 2% SODIUM CHLORIDE SOLUTION. 50 DAYS.				S.R.P.C. DISCS CURED IN 2% SODIUM CHLORIDE SOLUTION. 50 DAYS.			
WATER CONTENT (g/g_{cem})	FREE= 0.3195 BOUND= 0.1820 TOTAL= 0.5015			AVERAGE RESULTS	FREE= 0.3169 BOUND= 0.1819 TOTAL= 0.4988			AVERAGE RESULTS
TOTAL CHLORIDE (mM/g_{cem})	0.196	0.183	0.225	0.201	0.153	0.168	0.174	0.165
FREE CHLORIDE (M/l)	0.288	0.273	0.273	0.278	0.265	0.273	0.280	0.273
FREE CHLORIDE (mM/g_{cem})	0.092	0.087	0.087	0.089	0.084	0.087	0.089	0.087
pH	12.59	12.62	12.63	12.61	12.54	12.52	12.56	12.54
$\frac{\text{FREE Cl}^-}{\text{TOTAL Cl}^-}$	46.9%	47.5%	38.7%	44.4%	54.9%	51.8%	51.1%	52.6%

Table 3.2 RESULTS FOR CEMENT PASTE DISCS EXPOSED TO EXTERNAL CHLORIDE (50 DAYS)

SPECIMEN	O.P.C. DISCS CURED IN 2% SODIUM CHLORIDE SOLUTION. 100 DAYS.				S.R.P.C. DISCS CURED IN 2% SODIUM CHLORIDE SOLUTION. 100 DAYS.			
WATER CONTENT (g/g_{cem})	FREE= 0.3158 BOUND= 0.1851 TOTAL= 0.5009			AVERAGE RESULTS	FREE= 0.3173 BOUND= 0.1825 TOTAL= 0.4998			AVERAGE RESULTS
TOTAL CHLORIDE (mM/g_{cem})	0.260	0.235	0.244	0.246	0.187	0.208	0.201	0.199
FREE CHLORIDE (M/1)	0.313	0.332	0.317	0.321	0.313	0.306	0.302	0.307
FREE CHLORIDE (mM/g_{cem})	0.099	0.105	0.100	0.101	0.099	0.097	0.096	0.097
pH	12.58	12.60	12.61	12.60	12.40	12.38	12.52	12.43
$\frac{\text{FREE Cl}^-}{\text{TOTAL Cl}^-}$	38.1%	44.7%	41.0%	41.3%	52.9%	46.6%	47.8%	49.1%

Table 3.3 RESULTS FOR CEMENT PASTE DISCS EXPOSED TO EXTERNAL CHLORIDE (100 DAYS)



(AFTER GOUDA)(60)

Figure 3.1
THRESHOLD CONCENTRATIONS OF CHLORIDE ION RESULTING IN THE DEPASSIVATION OF STEEL IN ALKALINE SOLUTIONS (AFTER GOUDA)

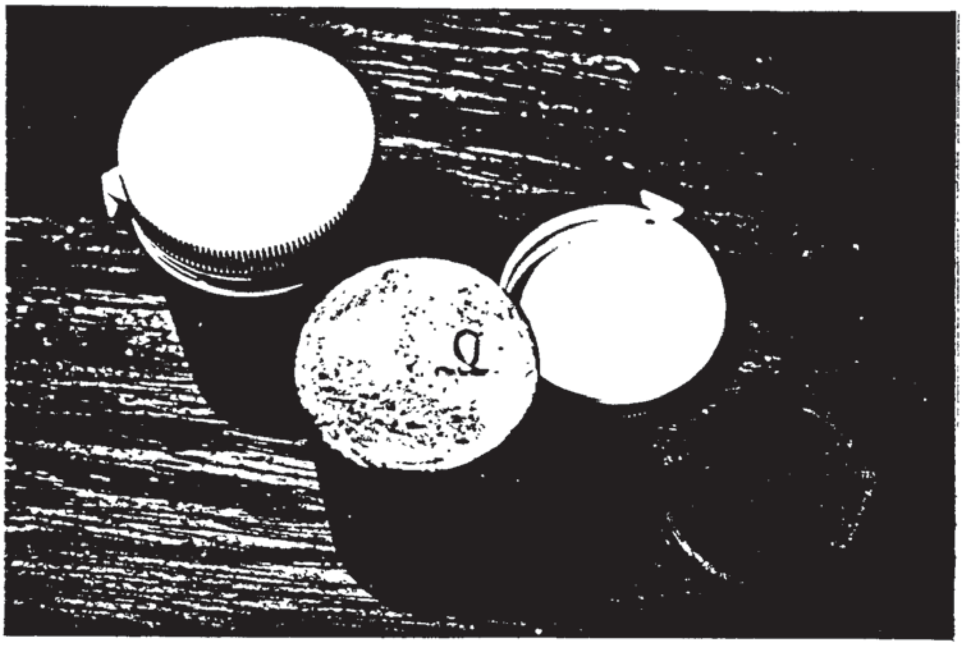


Figure 3.2
TYPES OF MOULDS USED AND SPECIMENS PRODUCED

Figure 3.3
CYLINDER AND DISCS BEFORE AND AFTER PRESSING

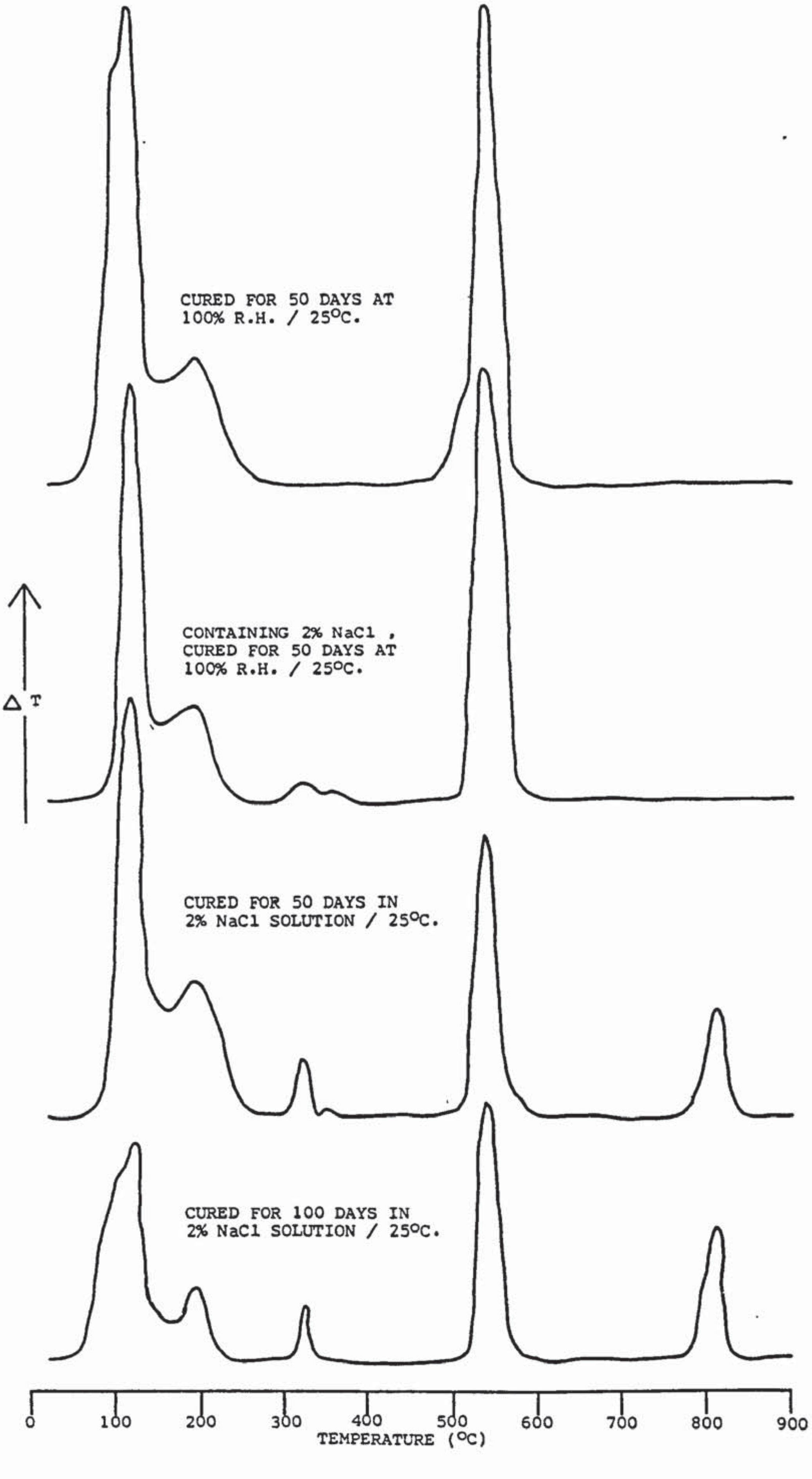


Figure 3.4

DIFFERENTIAL THERMOGRAMS FOR ORDINARY PORTLAND CEMENT SPECIMENS CONTAINING INTERNAL AND EXTERNAL CHLORIDES

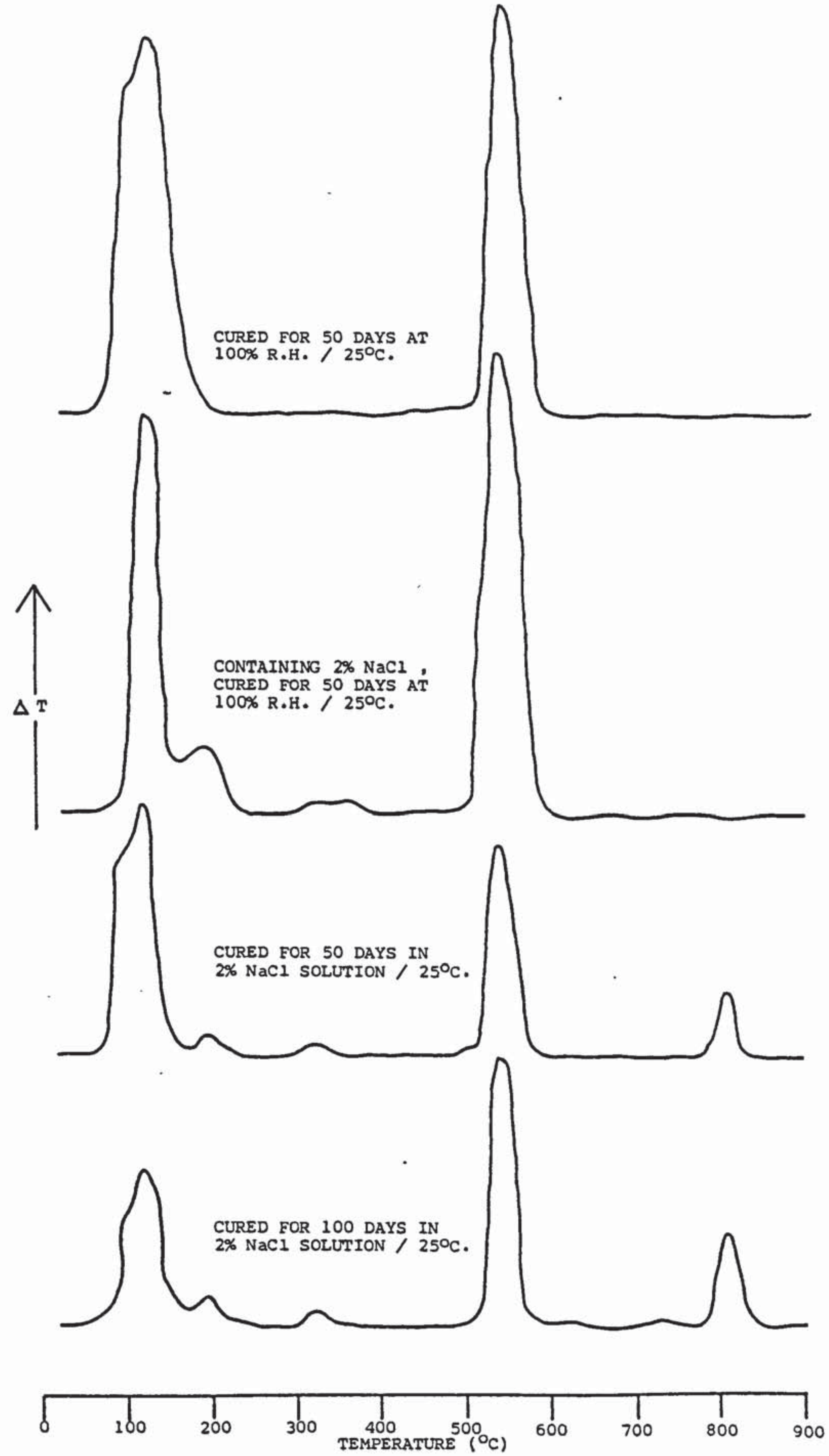


Figure 3.5
DIFFERENTIAL THERMOGRAMS FOR SULPHATE RESISTING PORTLAND CEMENT SPECIMENS CONTAINING INTERNAL AND EXTERNAL CHLORIDES

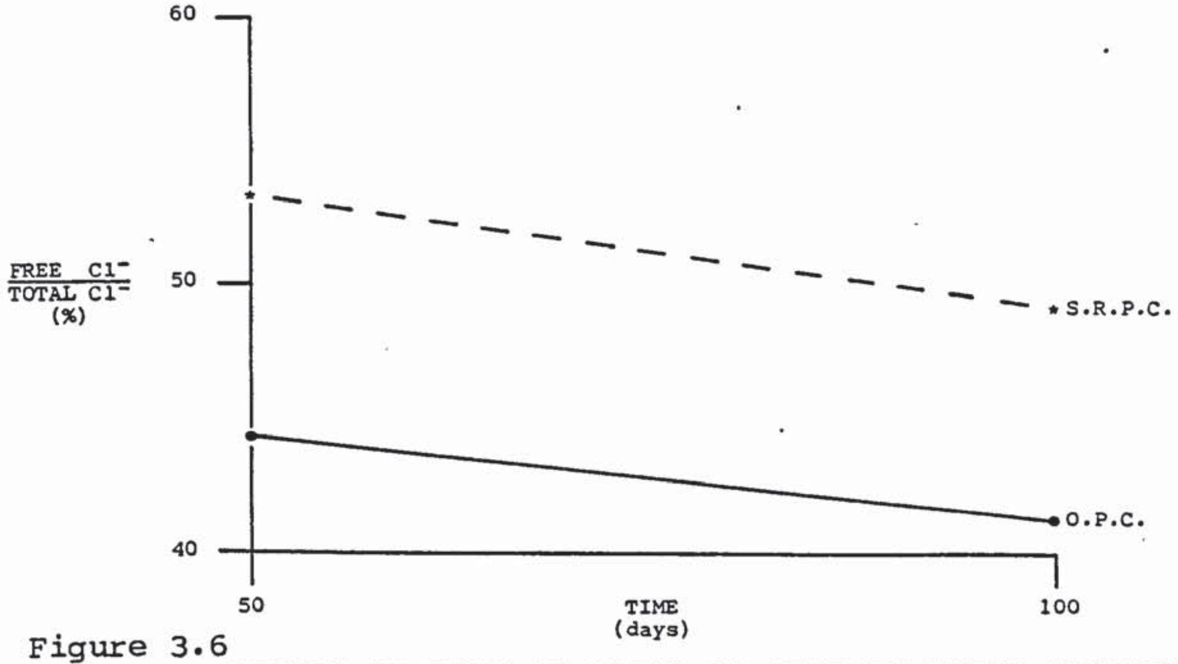


Figure 3.6

EFFECT OF TIME ON RATIO OF FREE TO TOTAL CHLORIDE ION FOR DISCS IMMERSED IN SODIUM CHLORIDE SOLUTION

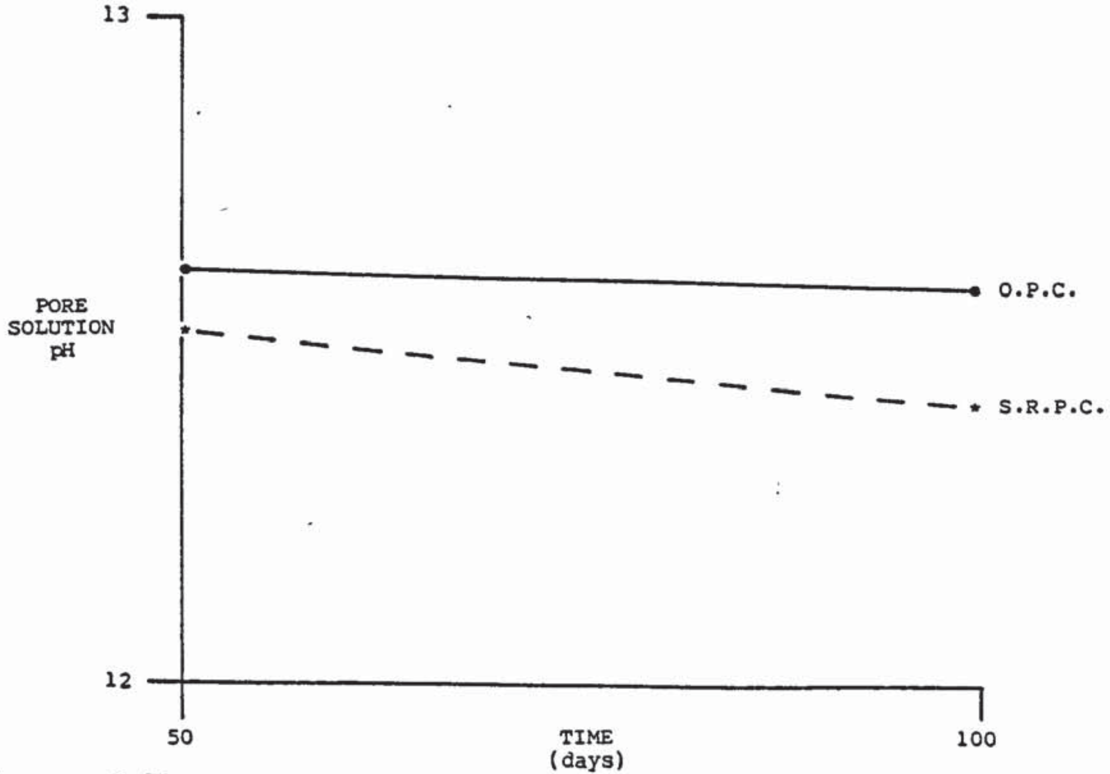


Figure 3.7

EFFECT OF TIME ON pH OF PORE SOLUTION FOR DISCS IMMERSED IN SODIUM CHLORIDE SOLUTION

CHAPTER 4

THE PRODUCTION AND CHARACTERISATION OF PURE CEMENT COMPOUNDS

4.1 INTRODUCTION

Portland cement is a complex mixture of many compounds, some of which play a major part in the hydration or chemical characteristics of the cement. It is manufactured commercially by heating together a mixture of limestone and clay up to a temperature of 1300 to 1500 degrees Centigrade. Although twenty to thirty percent of the mix becomes molten during the process the majority of the reactions which take place are solid-state in nature and therefore liable to be slow. Once cooled, the resulting clinker is ground to a fine powder and a small amount of gypsum (calcium sulphate dihydrate) is added to slow down the rate at which the cement hydrates to a workable level. (72)

The work of early investigators using optical and x-ray techniques, starting in 1882 with Le Chatelier, has shown that most Portland cement clinkers contain four principal compounds. (73) These are tricalcium silicate ($3CaO.SiO_2$), β-dicalcium silicate ($2CaO.SiO_2$), Tricalcium aluminate ($3CaO.Al_2O_3$) and a ferrite phase from the ($2CaO.Fe_2O_3$ - $6CaO.2Al_2O_3.Fe_2O_3$) solid solution series which at one time was considered to have the fixed composition ($4CaO.Al_2O_3.Fe_2O_3$). These phases were named ALITE, BELITE, CELITE and FELITE respectively by Tornebohm in 1897. (74)

From work carried out by Jeffery in 1952 it was concluded that alite as present in Portland cement clinker had the composition $(54CaO.16SiO_2.Al_2O_3.MgO)$ where small amounts of magnesia and alumina had been substituted into the lattice structure. (75) The morphology of this compound was found to be monoclinic. Jeffery also showed that pure, unsubstituted tricalcium silicate occurred in three distinct morphologies, these being trigonal, monoclinic and triclinic. Work by Midgley et.al in 1964 showed that alite in Portland cement could also occur as all three of the polymorphs. (76) Of the sixty two cements that were examined, one was triclinic, fifty six were monoclinic and five trigonal. Later work by Nurse et.al found that these various morphologies seemed to have little or no effect on the mechanical properties of the hydrated compounds. (77)

Alite normally accounts for over forty percent of the content of Portland cement and is the hydrating compound responsible for early strength. For these reasons the vast majority of work carried out on cement compounds has concentrated on alite, principally on the role of ionic substitutions by species such as magnesium and aluminium. (78) The synthesis of alite has on the whole been restricted to pure, triclinic tricalcium silicate.

The initial intention of this work was to develop a simple method for the manufacture of large amounts of relatively pure triclinic tricalcium silicate. This aim was, however, changed to the production of a substituted tricalcium silicate solid solution similar in structure to those found in true Portland cements. The reasons for the change in direction are made clear in the experimental section of this chapter. A method for the production of tricalcium aluminate has also been developed. This chapter also covers the characterisation of the cement compounds prior to use. Experimental work carried out with these compounds appears in Chapter 5.

4.2 PREVIOUS WORK

Many early attempts at producing small amounts of individual cement compounds from commercial cement clinkers were based upon geological techniques of physical or chemical separation taking advantage of properties such as density or solubility. Guttmann and Gille successfully separated a small quantity of alite by centrifuging powdered cement clinker in heavy liquids. (79) This was possible as tricalcium silicate crystals grow to a larger size than the other constituents. Other techniques used include the dissolution of silicate phases by salicylic acid and magnetic separation of the ferrite phase. (80) Because cement forms small, inhomogeneous crystals which exhibit a range of properties, such methods have never proved to be totally successful.

A method of chemically synthesizing tricalcium silicate, developed by Hansen in 1928, has been employed in one form or another by many workers up to the present day.(81) In this method a stoichiometric mix of calcium carbonate and silica is first decarbonated in a furnace at 1000 degrees Centigrade converting the calcium carbonate to calcium oxide (lime). The mixture is then allowed to cool and is pelletised in a press at around 25megaPascals. The pellets are fired in a platinum boat at 1500 to 1550 degrees Centigrade for several hours. The material is crushed, reformed into pellets and refired until no dusting occurs on cooling. During firing the lime and silica slowly combine together. This is assisted by the fineness of the particles and the closeness to which they have been packed. If this slow, solid-state reaction is not given sufficient time the majority of the fired pellets will be β-dicalcium silicate. On cooling this undergoes a polymorphic inversion to γ-dicalcium silicate, a weak and undesirable phase. It is this inversion that results in the powdering. The reaction may be considered to be complete when no powdering occurs on cooling.

The major impurity liable to occur in tricalcium silicate manufactured by solid-state reaction is therefore likely to be unconverted dicalcium silicate and the remaining free lime associated with it. Determination of the free lime content by chemical extraction is therefore a convenient method of determining the purity of a particular sample. (82)

Most workers in the field have used small quantities of very pure, triclinic tricalcium silicate often supplied to them by cement industry research laboratories. The methods used by those workers who synthesize their own tricalcium silicate were studied by Odler and Dörr in order to evaluate the best combinations of starting ingredients and firing schedules. (83) They found that the experimental conditions recommended by the various workers involved varied greatly. As a source of calcium oxide or lime (CaO) most used calcium carbonate though some used calcium hydroxide or calcium oxalate. Sources of silica that were recommended include pure silica, amorphous silica, precipitated silica, silica gel, quartz and ethyl silicate. The firing temperatures varied between 1450 and 1600 degrees Centigrade lasting for nine to forty hours and repeated two to six times. At 1000 degrees Centigrade any combination of the two sources will decompose to leave calcium oxide and silicon oxide though these will be at different degrees of dispersion. It is usually necessary to grind and pelletise the mix in order to bring the constituents into close enough contact to undergo the solid-state reaction successfully. However, Odler and Dörr found that by using freshly precipitated calcium oxalate and finely divided silica gel they could produce tricalcium silicate from a single twenty four hour firing at 1520 degrees Centigrade without the need to compact the mix constituents into pellets.

It is this method that was taken as a starting point for the development of simple techniques for the production of relatively large quantities of tricalcium silicate/alite and tricalcium aluminate.

4.3 EXPERIMENTAL PROCEDURE

The initial goal of the experimental work was to reproduce successfully the work of Odler and Dörr by synthesizing pure, triclinic tricalcium silicate from calcium oxalate and silica gel.(83) As a lime source freshly precipitated calcium oxalate was used which has a very large specific surface of around 70 000 square centimetres per gramme. Silica gel of laboratory reagent grade was obtained with a particle size of less than 75 micrometres. The calcium oxalate was produced by mixing aqueous solutions of ammonium oxalate and calcium nitrate. The addition of a small amount of ammonia in solution causes the calcium oxalate to precipitate out as it is virtually insoluble in an alkaline environment. If a portion of the remaining solution is evaporated small white crystals are formed which are easily identifiable as ammonium nitrate, a very soluble compound of low melting point (170 degrees Centigrade). The added ammonia remains unaffected, its only purpose being to make the solution more alkaline. By allowing the precipitate to settle and decanting the remaining solution by means of a syphon tube it is possible to remove most of the unwanted ammonia and ammonium nitrate. That which remains is vapourised during the firing process. The equation for the precipitation reaction is as follows

$$\underset{\text{AMMONIUM OXALATE SOLUTION}}{(COONH_4)_2 \cdot H_2O\ aq.} + \underset{\text{CALCIUM NITRATE SOLUTION}}{Ca(NO_3)_2 \cdot 4H_2O\ aq.} + \underset{\text{AMMONIA SOLUTION}}{NH_3\ aq.} \longrightarrow$$

$$\underset{\text{CALCIUM OXALATE SOLUTION}}{CaC_2O_4 \cdot 3H_2O \downarrow} + \underset{\text{WATER}}{2H_2O} + \underset{\text{AMMONIA}}{NH_3\ aq.} + \underset{\text{AMMONIUM NITRATE}}{2NH_4NO_3\ aq.}$$

Silica gel was added in a one to three stoichiometric mix with the slurry of calcium oxalate. The slurry was then cake dried in an oven at 130 degrees Centigrade prior to firing. The cake was broken into pieces roughly one centimetre square and packed into an alumina crucible lined with platinum foil. The platinum prevents impurities from getting to the cake which at the firing temperature would cause fluxing of the mix resulting in damage to the furnace. On occasions where the platinum foil failed to prevent fluxing, damage to the floor of the furnace occurred and the platinum required cleaning in hydrofluoric acid. Figure 4.2 shows the lined crucible in the mouth of the electric muffle furnace used.

With a stoichiometric mix for the production of triclinic tricalcium silicate the stages are as follows

$$\underset{\text{CALCIUM OXALATE}}{3(CaC_2O_4\cdot 3H_2O)} \underset{}{+} \underset{\text{SILICA GEL}}{SiO_2\cdot 2H_2O} \xrightarrow{1000^{\circ}C}$$

$$\underset{\text{CALCIUM OXIDE}}{3CaO} + \underset{\text{SILICON OXIDE}}{SiO_2} + \underset{\text{CARBON DIOXIDE}}{6CO_2\uparrow} + \underset{\text{CARBON MONOXIDE}}{6CO\uparrow} + \underset{\text{WATER}}{H_2O\uparrow}$$

$$\underset{\text{CALCIUM OXIDE}}{3CaO} + \underset{\text{SILICON OXIDE}}{SiO_2} \xrightarrow{1550^{\circ}C} \underset{\text{CALCIUM OXIDE}}{CaO} + \underset{\text{DICALCIUM SILICATE}}{2(CaO)SiO_2}$$

$$\xrightarrow[\text{slowly}]{1550^{\circ}C} \underset{\text{TRICALCIUM SILICATE}}{3(CaO)SiO_2}$$

Initially the mix was fired for eighteen hours at 1550 degrees Centigrade and allowed to cool before removal from the furnace. The product thus formed was a powder with a slight pink hue which when analysed by x-ray diffraction proved to be a mixture of γ-dicalcium silicate and calcium oxide, suggesting that insufficient time had been allowed for tricalcium silicate to be formed. The x-ray analysis of this mixture is shown in figure 4.1. Further quantities of the raw mix were fired for periods of up to forty eight hours but yielded the same products. To prevent the inversion to γ-dicalcium silicate, rapid air cooling from the firing temperature was tried. This initially yielded pieces of material similar to those put in but smaller due to the loss of mass at 1000 degrees Centigrade. However, as their temperature approached ambient these pieces also powdered to γ-dicalcium silicate. Occasionally, small crystals of a slight green hue would be left adhered to the platinum. These were later found to be tricalcium silicate.

As no combination of heating and cooling cycles would produce tricalcium silicate in a single burn, repeat firings were tried. The powder obtained from the first firing was formed into pellets in a specimen press and refired for a further day. Again, on cooling, the pellets would powder at around 200 degrees Centigrade. Second and third firings were equally unsuccessful.

Due to this continuing lack of success it was decided to attempt to produce a substituted tricalcium silicate similar to that found naturally in commercial Portland cement clinkers. Various compositions have been suggested for synthetic substituted alites.(84) The one that was finally chosen for this work was 'Jeffery's alite' ($54(CaO)16(SiO_2)Al_2O_3.MgO$) as suggested by Jeffery in 1952.(75) This is a tricalcium silicate solid solution which is monoclinic in structure and essentially similar to the alite found in most commercial Portland cement. High purity polishing grade aluminium oxide of 0.3 micrometre particle size and analytical grade light magnesium oxide were the two compounds introduced for the substitution. The new reaction path was as follows

$$54(CaC_2O_4\cdot 3H_2O) + 16(SiO_2\cdot 2H_2O) + Al_2O_3 + MgO \xrightarrow{1000^\circ C}$$

CALCIUM OXALATE + SILICA GEL + ALUMINA + MAGNESIA

$$54CaO + 16SiO_2 + Al_2O_3 + MgO + 54CO_2\uparrow + 54CO\uparrow + 194H_2O\uparrow$$

CALCIUM OXIDE + SILICON OXIDE + ALUMINA + MAGNESIA + CARBON DIOXIDE + CARBON MONOXIDE + WATER

$$\xrightarrow{1550^\circ C} 54(CaO)16(SiO_2)Al_2O_3\cdot MgO$$

SUBSTITUTED TRICALCIUM
SILICATE SOLID SOLUTION

An eighteen hour burn was sufficient to produce pieces alite which exhibited no dusting on cooling. Shorter burns still produced alite with no dusting although quantities of the calcium oxide and silica had failed to combine. No intermediate dicalcium silicate stage could be detected but should by no means be ruled out.

Following the success in producing alite, a method for the production of tricalcium aluminate was developed. A simple three to one mix of calcium oxalate and fine aluminium oxide proved to be adequate for the production of pure tricalcium aluminate by means of a single burn.

$$3(CaC_2O_4\cdot 3H_2O) + Al_2O_3 \xrightarrow{1000^\circ C}$$

CALCIUM OXALATE+ALUMINA

$$\underset{\text{CALCIUM OXIDE}}{3CaO} + \underset{\text{ALUMINA}}{Al_2O_3} + \underset{\text{CARBON DIOXIDE}}{3CO_2\uparrow} + \underset{\text{CARBON MONOXIDE}}{3CO\uparrow} + \underset{\text{WATER}}{9H_2O\uparrow}$$

$$\xrightarrow{1450^{\circ}C} \underset{\text{TRICALCIUM ALUMINATE}}{3(CaO)Al_2O_3}$$

There is no intermediate stage in this reaction.

Sufficient quantities of each mineral were prepared for subsequent use in the work described in Chapter 5. The minerals were ground to fine powders in a stainless steel ball mill, as shown in figure 4.3. The individual batches of each mineral were ball milled together in a small quantity of acetone and each characterised as a single large batch in terms of crystal structure (para.2.12), density and fineness (para.2.9) and free lime (calcium oxide) content (para.2.11).

4.4 RESULTS AND DISCUSSION

X-ray analysis of the cement compounds was carried out on small samples from the individual firings as a form of quality control and the results obtained compared with standard data.(85) Such samples were hand ground in an agate mortar and pestle and passed through a 200 micrometre sieve prior to analysis. In this state the alite was off-white in appearance and the tricalcium aluminate pure white. All the batches of each mineral that passed the analysis were ball milled together for several days. A small quantity of acetone was added to prevent the powder compacting against the walls of the mill. Once milled, the powder was washed from the mill with more acetone and passed through a coarse sieve to remove the balls. As soon as the acetone had evaporated the mineral was ready for final characterisation. Both minerals were now grey in appearance due to trace amounts of iron that had been picked up during the milling operation. This iron showed up in the final x-ray analysis carried out on each entire batch. The changes in appearance that occur during the production of alite are shown in figure 4.4. X-ray traces obtained for both the alite and tricalcium aluminate are shown in figure 4.1.

To determine the approximate purity of the specimens, free lime determinations were carried out, lime being by far the most common form of impurity as discussed earlier. The values of free lime obtained were 0.058% for the alite and 0.072% for the tricalcium aluminate. Hence, both minerals may be considered to have a purity in excess of 99%. The calculations involved in these determinations are given in Appendix 7.

The density of each mineral, as well as being an interesting characteristic, needed to be determined prior to the measurement of fineness. The values obtained were 3140 and 2860 kilogrammes per cubic metre for the alite and tricalcium aluminate respectively. The fineness values obtained by a gas permeability method were 2100 square centimetres per gramme for the alite and 3510 square centimetres per gramme for the tricalcium aluminate (see Appendix 5). These values compare with the British Standard values of 2250 and 3250 square centimetres per gramme for ordinary and rapid hardening Portland cement. (86)

In addition to the above characteristics the twenty eight day compressive strength of hydrated alite was measured using duplicate cylinders twenty five millimetres in both diameter and length, made with a water to mineral ratio of 0.6 and cured under calcium hydroxide solution. Each cylinder was compressed lengthwise at a loading rate of 35 Newtons per second in a universal testing machine fitted with a special ball mounted platten (see figure 4.5) and the maximum sustained load converted to an estimated cube strength as shown in Appendix 10. The average value so obtained was 23 megaNewtons per square metre which compares well with the value of 25 megaNewtons per square metre obtained by Jeffery on a similar specimen. (75)

All the characterisations obtained for the two minerals are summarised in table 4.1.

The alite hydrated rapidly when mixed with water and a 0.6 water-mineral ratio was used so as to maintain an adequate workability for long enough to compact the mix. The reaction of the tricalcium aluminate to water was sufficiently violent to crack a glass test tube. The heat evolved by only a few grammes soon made the tube too hot to hold. Great care was taken to keep the minerals away from moisture prior to their use described in Chapter 5.

4.5 CONCLUSIONS

Relatively large quantities of alite ($Ca_{54}Si_{16}O_{90}Al_2Mg$) and tricalcium aluminate ($Ca_3Al_2O_6$) with purities of greater than 99% can be synthesized from starting mixes of freshly precipitated calcium oxalate and finely divided sources of silica gel, aluminium oxide and magnesium oxide.

Such minerals can be prepared and characterised so as to be comparable with commercial Portland cements and are suitable for the preparation of specimens for subsequent work.

It is most likely that many other cement minerals may be synthesized by suitably adapting this basic method although the manufacture of pure triclinic tricalcium silicate has, in this work, been unsuccessful.

	MORPHOLOGY	FREE LIME	DENSITY (Kg/m^3)	SPECIFIC SURFACE (cm^2/g)	ESTIMATED CUBE STRENGTH (MN/m^2)
ALITE	MONOCLINIC	0.058%	3140	2100	23.3
TRICALCIUM ALUMINATE	CUBIC	0.072%	2860	3510	-

Table 4.1
PHYSICAL AND CHEMICAL CHARACTERISTICS OF SYNTHESIZED ALITE AND TRICALCIUM ALUMINATE

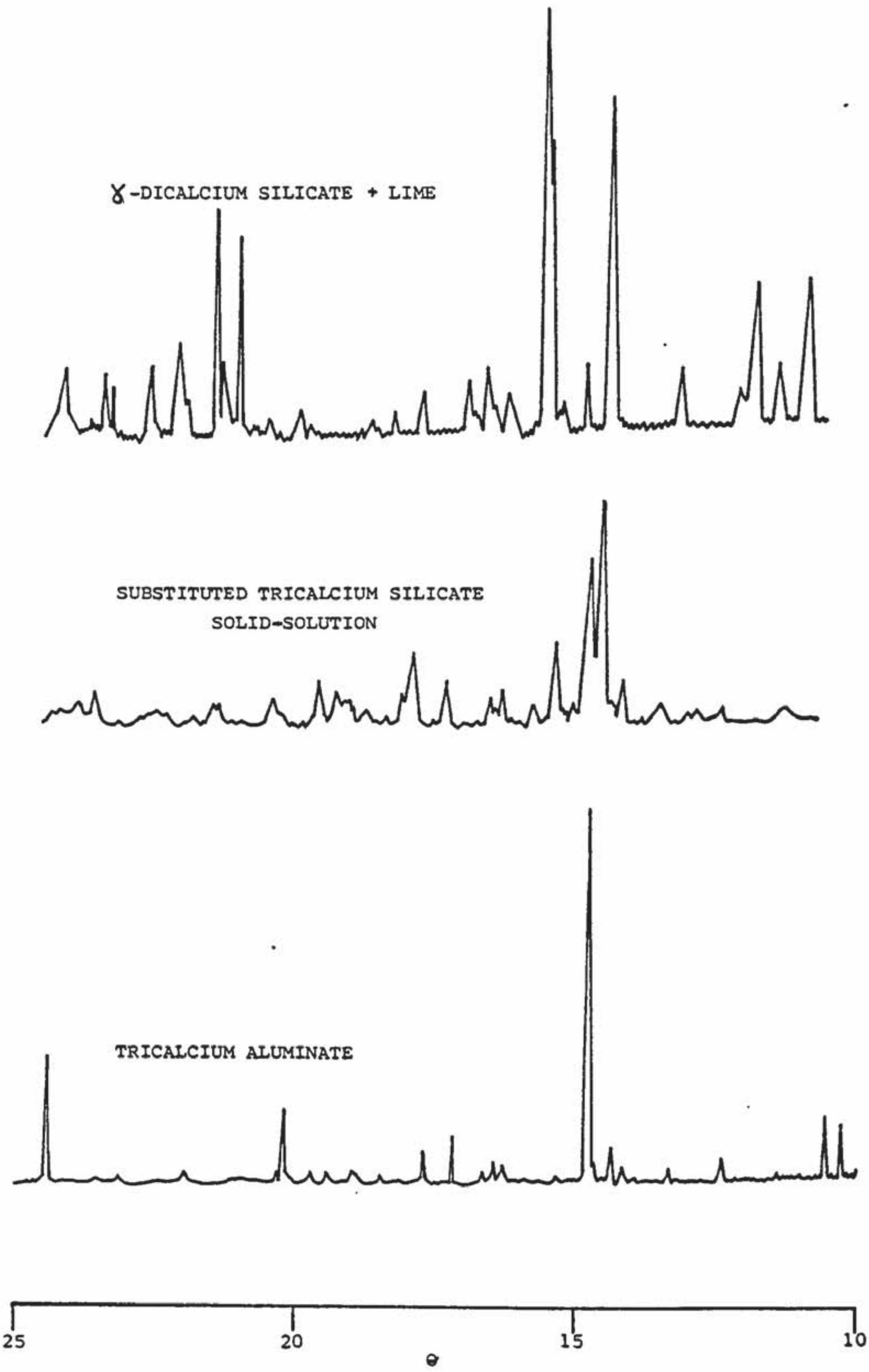


Figure 4.1
X-RAY DIFFRACTOMETER TRACES OF CEMENT MINERALS PRODUCED

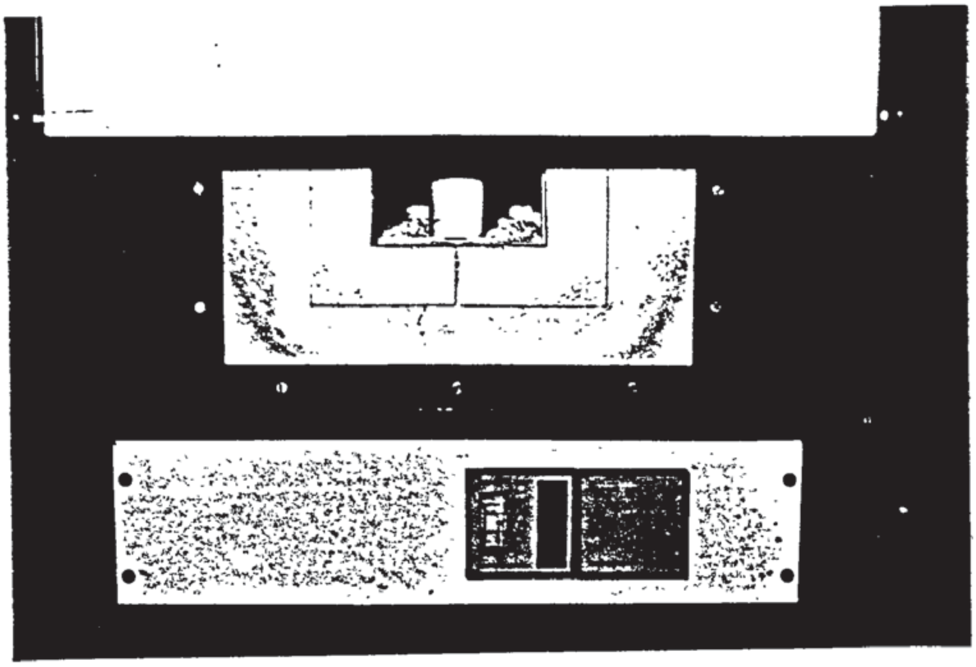


Figure 4.2
PLATINUM LINED CRUCIBLE IN MOUTH OF MUFFLE FURNACE

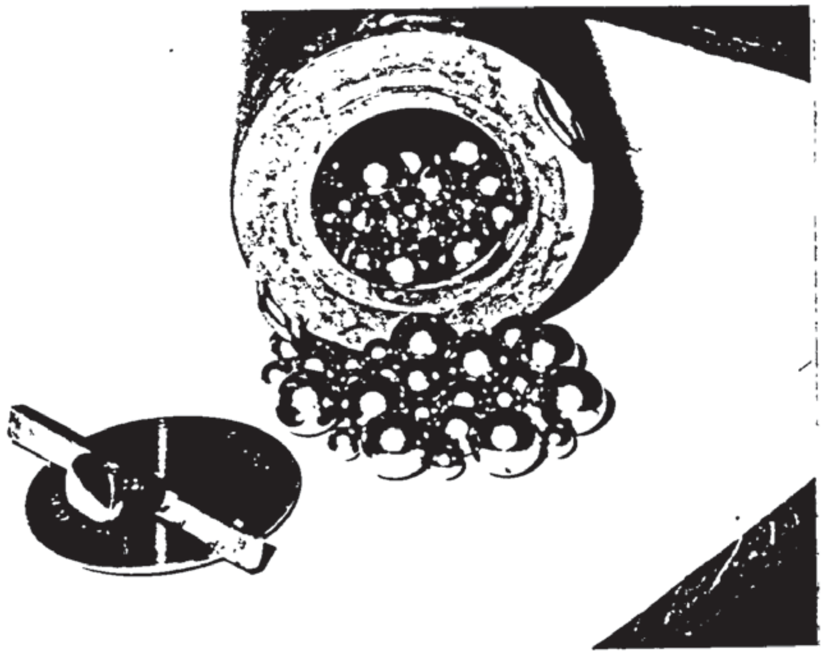


Figure 4.3
STAINLESS STEEL BALL MILL WITH FULL CHARGE OF BALLS

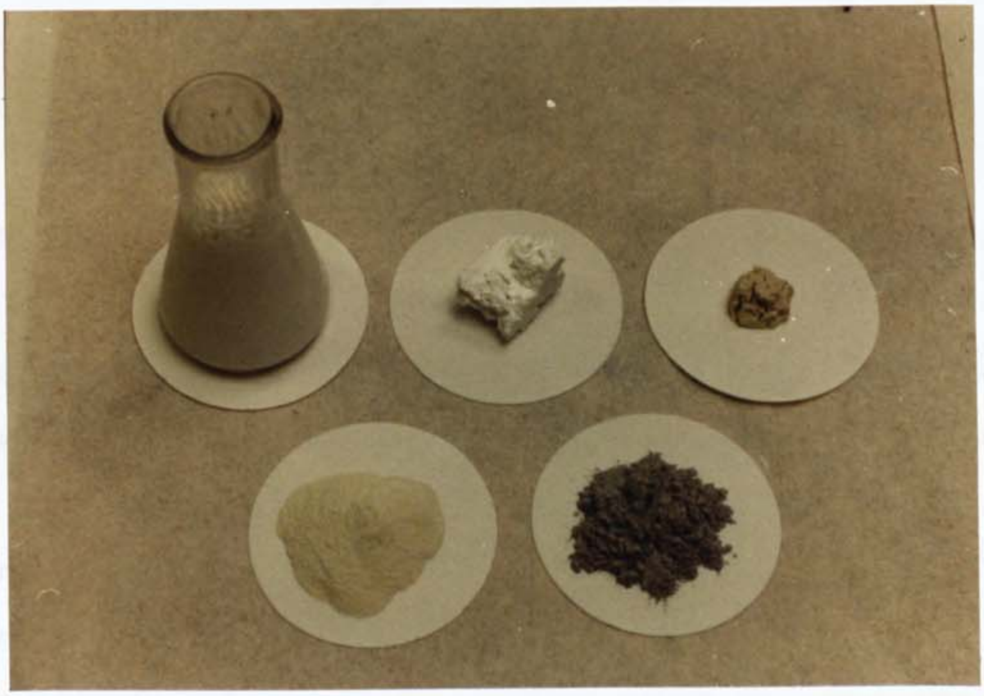


Figure 4.4
FIVE STAGES IN THE PRODUCTION OF ALITE

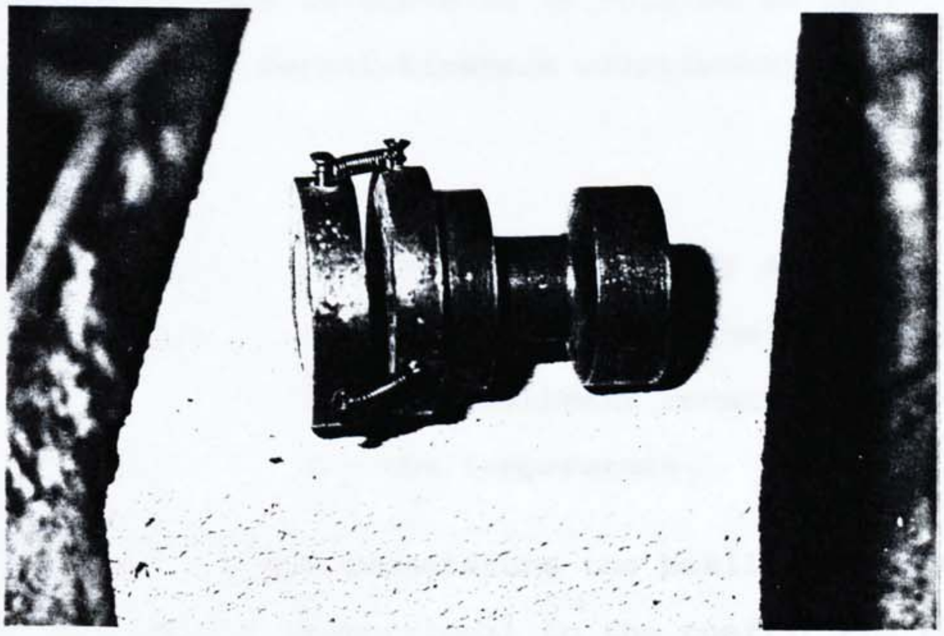


Figure 4.5
SMALL BALL-MOUNTED PLATTEN FOR ALITE COMPRESSION TESTS

CHAPTER 5

DIFFUSION OF CHLORIDE THROUGH HYDRATED CEMENT MINERALS

5.1 INTRODUCTION

As has already been discussed in chapter 3, chloride ions may enter concrete structures either during hydration as an admixture or contaminant or after hydration from an external source such as sea water or de-icing salts. (87)(88) In the case of external chlorides the process by which the chloride ions may reach reinforcing steel is often one of diffusion.

For chloride ions to affect the passivity of embedded steel they must be capable of moving freely around the interface between the steel and cement or concrete. (89) The mobility of ions is shown to be related to their diffusivity by the Nernst-Einstein relationship which states that :

$$D = ukT$$

where D = the coefficient of diffusion
u = the mobility of the particles
k = the Boltzmann constant
T = the temperature

Therefore, for a given temperature the mobility of the ionic species is directly proportional to the coefficient of diffusion. (90)

The laws of diffusion developed by Fick in the middle of the last century allow the determination of diffusion kinetics from measurable quantities. Fick's first law states that the flux is proportional to the concentration gradient, the diffusion coefficient being the constant of proportionality in the relationship. As the units of flux are mass over area by time and those of concentration are mass over volume then the diffusion coefficient has units of area over time and may be expressed in terms of square centimetres per second. (91) By measuring the diffusion coefficient of an ionic species through a permeable material at several temperatures it is possible to determine an activation energy (or enthalpy of activation), the minimum energy required by the ions to initiate movement through the material. (92)

In this work the diffusivity of chloride through hydrated alite (substituted tricalcium silicate) and blended alite/tricalcium aluminate discs has been measured and the values compared with similarly obtained results for commercial cement pastes. Previous work on chloride diffusion through ordinary and sulphate resisting Portland cements has shown there to be differences in their diffusivities. (93) By studying pure and blended alite it should be possible to examine further the relative effects of tricalcium aluminate content and pore structure on the diffusion kinetics of Portland cement pastes.

Specimens of steel embedded in alite paste and exposed to various levels of internal and external chloride ion have also been studied and compared with steel in saturated calcium hydroxide solutions containing dissolved chloride. As the hydration of alite produces only Calcium-Silicate-Hydrate gel and calcium hydroxide, steel specimens exposed to either alite paste or calcium hydroxide solution should be in exactly the same chemical environment. Any difference in their resistance to depassivation by chloride ions must be due to physical dissimilarities between the two media.

5.2 PREVIOUS WORK

Two significantly different methods have been applied successfully to the determination of diffusion kinetics for Portland cements. That employed by Collepardi et al involved exposing the end faces of cement cylinders, cast in-vacuo to eliminate air bubbles, to 3% calcium chloride solution. (94) Samples of cement and concrete were exposed to chloride ions by such means at 10, 25 and 40 degrees Centigrade. Periodically samples were removed from the solution and cut into equal slices perpendicular to the exposed surface. The total chloride ion content of each slice was then determined by chemical analysis. Diffusion coefficients were calculated using a solution of Fick's second law as applied to non-steady-state conditions for a semi-infinite solid. The equation used was as follows :

$$\frac{Cx}{Cs} = 1 - \mathrm{erf}\left\{ \frac{x}{2}\sqrt{Dt} \right\}$$

for the boundary conditions

$Cx = 0$ at $t = 0$

$0 < x < \infty$

$Cx = Cs$ at $x = 0$

$0 < t < \infty$

where Cx = chloride ion concentration of slice

Cs = chloride ion concentration of external solution

x = thickness of slice measured from original exposed surface

t = time of exposure

D = diffusion coefficient

The value of erf $(x/2\sqrt{Dt})$ versus $(x/2\sqrt{Dt})$ can be found in mathematical tables. Values of Cs and D were obtained by extrapolating the curve of Cx versus x to the point x=0. Values for the diffusion coefficient of chloride ions through Portland and pozzolanic cements and concretes were so obtained. Activation energies for the cement pastes were calculated from the temperature dependance of the diffusion coefficients.

Work carried out by Page et al also commenced with the casting of fault free cement paste cylinders. (93) This they achieved by completely filling sealable plastic moulds with paste and rotating them about a horizontal axis so as to prevent segregation. After initial curing such cylinders were tested non-destructively by ultrasonic pulse velocity determinations to ensure the absence of voids and other major faults. Rather than exposing the entire cylinders to chloride solutions, discs of around 3 millimetres in thickness were cut from the centre portions of the cylinders with a diamond saw. These were then exposed to chloride solutions in specially designed glass cells comprising of two compartments with the cement discs fitted in between. In one compartment was placed saturated calcium hydroxide solution while the other held one molar sodium chloride solution, also saturated with calcium hydroxide. By measuring the level of chloride ion in the low concentration side with time they were able to determine values for the diffusion coefficient from a solution of Fick's first law as applied to quasi-steady-state diffusion. D was therefore calculated from the slope of the rectilinear plot of the chloride ion concentration in the low side against time. Values of activation energy were also obtained from best-fit Arrhenius plots of the diffusion data.

It is this second method that has been employed in the study of the diffusion kinetics of hydrated cement minerals as described in this chapter for both the simplicity of the method and the small amounts of material required.

5.3 EXPERIMENTAL PROCEDURE

The cement minerals were prepared and characterised as described in chapter 4 and required no further treatment prior to use other than a final sieving. A method had to be developed for the making of high quality cement mineral discs without wasting large amounts of material. The method that was finally adopted involved casting individual discs around 5 millimetres thick and of the required diameter in the same type of mould as used for the production of discs in chapter 3 (para.3.3). In order to save material mixing took place in the mould itself followed by vibration to remove entrapped air. Owing to the speed at which alite hydrates a water to mineral ratio of 0.6 was selected so as to give adequate workability and it was necessary to carry out the mixing and vibrating in as short a time as possible while still being thorough. The same procedure was adopted in the production of blended alite/tricalcium aluminate discs except that gypsum (calcium sulphate dihydrate) was added as one third the weight of tricalcium aluminate present so as to prevent the tricalcium aluminate from reacting violently on contact with the water. Two levels of tricalcium aluminate, 3% and 12%, were blended with alite. These are similar to the contents of sulphate resisting and ordinary Portland cements. The correct proportions of each mineral were blended together in a ball mill prior to mixing with water. After an initial curing of 48 hours in a 100% relative humidity environment the discs were carefully demoulded and stored under calcium hydroxide solution until 60 days old and in effect fully hydrated. Prior to use the discs were ground on both sides by hand on graded emery paper until of an even thickness of around 2 to 3 millimetres. Figure 5.1 shows an alite disc before and after hand grinding. Once 60 days old and ground to an even thickness the cement paste discs were ready for mounting into the glass diffusion cells as shown in figure 5.3. Each disc was mounted between the ground flanges of two half cells. Lightly greased rubber gaskets were placed between the discs and the flanges, and the cells held together with elastic bands. The joints were further supported with P.T.F.E. tape. The gaskets ensured a leak tight fit and allowed a known area of the discs to be exposed. The high concentration side of each cell was filled with 1 molar sodium chloride solution saturated with calcium hydroxide while the low concentration side was filled with a known volume of saturated calcium hydroxide solution. The cells were then sealed with stoppers to prevent atmospheric carbon dioxide from reacting with the solutions and supported in water baths at the experimental temperature by plastic cradles as shown in figure 5.4.

After an initial period of time over which the diffusion through the discs became established, 0.1 millilitre aliquots of solution were taken from the low concentration side of each cell and analysed for chloride ion content colorimetrically as described in chapter 2 (para.2.6). By plotting the chloride level in the low concentration side of each cell with time, straight lines were obtained the slopes of which were proportional to the respective chloride fluxes (see figure 5.5). From these, values of diffusion coefficient and ultimately activation energy were obtained.

In addition to the discs, a small number of duplicate embedded steel specimens were made for rest-potential studies. Discs of steel 1 centimetre in diameter with a soldered electrical connection were mounted in epoxy resin and a layer of alite 3 millimetres thick cast over them. Some were then exposed to calcium hydroxide solutions containing various levels of chloride ion while others were made with chloride in the mixing water and cured in moist air. Another group had the steel coupled to an external strip of stainless steel gauze with an area of 5 square centimetres and the whole unit exposed to chloride in calcium hydroxide solution thus reproducing the conditions of small anode and large cathode experienced by non-embedded steel. A control group of non-embedded steel specimens was also exposed to solutions containing chloride ions. Figure 5.2 shows two embedded specimens made with internal chloride and exposed to 100% relative humidity. The solutions were replaced regularly and the values of rest-potential for each specimen were taken weekly for ten weeks at which point all the specimens were opened and the condition of the steel observed.

5.4 RESULTS AND DISCUSSION

The values of chloride concentration measured in the low concentration side of each cell were plotted against time giving linear relationships as shown in figure 5.5. The time delay 'to' is the initiation period during which the diffusion becomes established across the thickness of the disc. During the duration of the experiments the chloride concentration of the high concentration side may be considered to be effectively constant. It is assumed then that conditions of quasi-steady-state diffusion are operating across the discs and therefore that the chloride ion flux and activity are constant throughout the discs. The flux (J) of chloride ion (in moles per square centimetre per second) entering the low concentration side of the cell is related by Fick's first law to the diffusion coefficient and the concentration gradient.

$$J = \frac{V}{A}\frac{dC_2}{dt} = \frac{D}{l}(C_1 - C_2)$$

where V = volume of the low concentration side (cubic centimetres)

A = cross-sectional area of the disc (square centimetres)

C_1 = chloride concentration in high side (= 1 mole/litre)

C_2 = chloride concentration in low side (mole/litre)

t = time (seconds)

l = thickness of disc (centimetres)

D = diffusion coefficient (square centimetres per second)

This may be simplified for the conditions $t > to$, $C_1 \gg C_2$ to :

$$C_2 \cong \frac{DAC_1}{1V} (t - to)$$

(See Appendix 12)

Thus D may be calculated from the gradient of the rectilinear plot of C_2 versus t :

$$D = \text{GRADIENT} \times 35.5 \times \frac{1}{A} \times \frac{V}{1000} \times \frac{1}{(C_1 - C_2)} \qquad (cm^2 s^{-1})$$

The values of D thus obtained along with the other relevant data for all 35 discs tested are given in tables 5.1 to 5.7.

As the alite discs were tested at five temperatures it was possible to obtain a value of activation energy by producing an Arrhenius plot of $\log_{10}$ diffusion coefficient against the reciprocal of absolute temperature as shown in figure 5.6. The 'best-fit' straight lines for both the diffusion and Arrhenius plots were obtained by linear regression analysis and the correlation and error by standard statistical methods.(95) Worked examples of the calculations required are given in appendix 13.

Mercury intrusion porosimetry as described in chapter 2 (para.2.10) was used to produce pore size distribution curves for the mineral discs. Figures 5.7 and 5.8 show the results obtained. Little or no difference was found between the distributions obtained before and after exposure to chloride solutions for similar discs.

Differential thermal analysis as described in chapter 2 (para.2.13) was performed on samples of the discs before and after chloride diffusion and the thermograms obtained are shown in figures 5.9 and 5.10. Appendix 11 provides a guide to the peaks obtained by differential thermal analysis.

The results obtained from the steel/alite specimens are shown in figures 5.11 to 5.14. For each type of specimen plots of rest potential against time are shown for the duplicate specimens at each chloride ion concentration. Figures 5.15 to 5.19 show the condition of the steel in several of the specimens after ten weeks while figures 5.20 and 5.21 show electron photomicrographs of alite cast against an abraded steel substrate for 9 and 90 days.

The correlations obtained for the plots of chloride concentration against time were greater than 0.9 for all the discs tested. Five discs were used for each determination so that a representative average value could be obtained. In the case of the alite discs, all twenty five values of diffusion coefficient were used to produce the Arrhenius plot from which the activation energy was obtained.

The value of activation energy for 0.6 water-mineral ratio hydrated alite discs may be compared with the values obtained by other workers for discs made from ordinary Portland cement.(93) The value of 33.4 ± 4.9 kJ/mole obtained for the alite discs lies between the values of 32.0 ± 2.4 and 44.6 ± 4.3 kJ/mole obtained by Page et al for ordinary Portland cement pastes of 0.6 and 0.5 water-cement ratios respectively. These contrast with values in the region of 17.6 kJ/mole for the diffusion of chloride ions in normal electrolyte solutions.(96)

The similarity of the activation energies for alite and conventional cement pastes suggests that it is the Calcium-Silicate-Hydrate gel matrix, produced by the hydration of alite, that is responsible for controlling the diffusion of chloride ions in cement pastes and concretes and that it is through this matrix that the chloride ions move.

The values of diffusion coefficient (D-value) obtained for alite compare more closely with those previously obtained for ordinary Portland cement of 0.5 rather than 0.6 water-cement ratio.(93) This may be due in some part to a greater similarity of water-alite ratio between the two materials. Comparison of mercury intrusion porosimetry data shows the alite paste to have a very fine pore structure, having a similar total porosity to a 0.5 water-cement ratio ordinary Portland cement paste (see figure 5.7). While the ordinary Portland cement pastes have an effective maximum pore diameter of around 100 nanometres, the alite paste has few pores with a diameter greater than 25 nanometres. This suggests that although the chloride is diffusing through the Calcium-Silicate-Hydrate gel (as indicated by the activation energy), the rate at which it does so is not soley determined by the pore-size distribution or total porosity.

The diffusion coefficients obtained for 0.6 water-mineral ratio discs of alite blended with 3% and 12% tricalcium aluminate (plus gypsum) at 25 degrees Centigrade were 5.01E-08 ($\pm 5.01\text{x}10^{-8}$) and 3.80E-08 ($\pm 3.80\text{x}10^{-8}$) square centimetres per second respectively. These may be compared with the value for pure alite at 25 degrees Centigrade of 6.67E-08 ($\pm 6.67\text{x}10^{-8}$) square centimetres per second. The total porosities and pore-size distributions obtained for the blended minerals are greater and more open than for the pure alite, resembling traces for ordinary and sulphate resisting Portland cements of 0.5 water-cement ratio (see figure 5.8).

The discs containing 3% tricalcium aluminate show a larger total porosity than those containing 12% tricalcium aluminate and it may therefore be only to be expected that they demonstrated a higher coefficient of diffusion. However, both blended materials allowed less chloride to diffuse through than the pure alite at the same temperature and water-mineral ratio despite the 'tighter' pore structure of the pure mineral. The inference to be made from this is that the tricalcium aluminate content does affect the rate of diffusion through cement pastes and concretes and that this difference cannot be explained soley in terms of its effect on the porosity.

Differential thermograms for hydrated pastes of alite and alite blended with tricalcium aluminate carried out before and after exposure to chloride solutions show chemical differences between the materials (see figures 5.9 and 5.10). The pure hydrated alite consists soley of Calcium-Silicate-Hydrate gel ($\sim 130^{o}C$) and calcium hydroxide ($\sim 550^{o}C$) as would be expected. Exposure to chloride solution has caused no apparent chemical change.

The blended minerals show peaks at ~ 200 degrees Centigrade consistant with the presence of ettringite. The mineral containing 3% tricalcium aluminate shows a lower proportion of ettringite than that containing 12% tricalcium aluminate. After exposure to chloride solutions each has produced a peak at ~320 degrees Centigrade indicating calcium chloroaluminate, the proportion produced being related to the initial tricalcium aluminate content.

Whether or not the chemical complexation of chloride ions by tricalcium aluminate hydrates is sufficiently extensive to alter significantly the amount of chloride passing through a disc of hydrated mineral is uncertain. The differences between the diffusion coefficients for the pure and blended alite are small and in these unusual circumstances may well be due to the removal of chloride ions by complexation.

In order to see whether or not the C-S-H gel plays any part in the complexation of chloride ions, two small cylinders of 0.6 water-mineral ratio alite were cast containing 1% and 2% chloride ion by weight of alite. These were cured for 200 days at 100% relative humidity and then placed into the pore solution expression device (see chapter 2 para.2.5) in order to obtain samples of the pore solutions for subsequent analysis. The results obtained and calculations carried out are given in appendix 14. The values of free to total chloride ion ratio calculated from each specimen (expressed as percentages) were 99.65% and 99.84% for the 1% and 2% chloride ion additions respectively. This indicates that the alite used in this work gave little or no contribution to the binding of chloride ions.

The small scale electrochemical study of steel embedded in alite has resulted in some interesting indications as to the differences between cement pastes and conventional electrolyte solutions.

A control group of duplicate mild steel specimens were exposed to saturated calcium hydroxide solutions containing 0, 250, 1 000, and 2 000 parts per million of chloride ion (see figure 5.11). Those exposed to calcium hydroxide solution containing no chloride remained passive for the 10 week period of the test, the steel being clean and bright upon removal from the solution (see figure 5.15). All those exposed to a chloride bearing solution were corroding rapidly by the end of the test, corrosion having been initiated more quickly for those exposed to the higher chloride ion concentrations (see figure 5.16).

A second set of specimens were made with steel embedded in 0.6 water-mineral ratio alite containing the same five levels of chloride ion (see figure 5.12). Theoretically, the chemical environment to which the steel was exposed should have been the same as for the control group, the hydration products of alite being C-S-H gel and calcium hydroxide. Any difference in the behaviour of the steel must be due to the physical presence of the C-S-H gel and any associated lime-rich layer produced on the surface of the steel. The rest potential/time traces suggest that all the steel specimens were corroding, however, upon opening up the specimens all were found to be bright and clean (see figure 5.17). Similar effects were found with embedded steel specimens exposed to saturated calcium hydroxide solution containing chloride ions (see figures 5.13 and 5.18).

A decreasing potential can be due to one of two effects, either the anode reaction is less polarised (anodic control) in which case corrosion occurs more rapidly or the cathode reaction is more polarised (cathodic control) due to an inadequate supply of oxygen and corrosion occurs more slowly.. It is the latter which must be occurring in these instances. Figures 5.20 and 5.21 show the surfaces of alite pastes that have been cast against the same abraded steel surfaces for 9 and 90 days. At 9 days the pattern of the steel surface cannot be seen on the alite and it is still possible to identify the individual particles of the mineral. By 90 days the individual mineral particles were no longer clearly defined and the pattern of the abraded steel substrate reflected in the surface of the alite paste. Energy dispersive x-ray analysis yields only the presence of calcium suggesting the existence of a lime-rich Portlandite layer.(97) The high quality barrier so produced would appear to have been sufficiently impervious to reduce drastically the amount of oxygen reaching the surface of the steel.

A fourth set of specimens were made with embedded steel electrically coupled to external stainless steel electrodes and exposed to various levels of chloride ion in saturated calcium hydroxide solution (see figure 5.14). The stainless steel electrodes act as large cathodes provided with an adequate oxygen supply while the steel may be considered to be a potential anodic site. Once again, none of the steel electrodes proved to have suffered corrosion when opened (see figure 5.19). Due to the inclusion of a large cathode exposed to oxygen the rest potentials remained in the region of 300 to 400 millivolts reflecting the condition of the steel.

The diffusion results suggest that those specimens exposed to solutions containing chloride ions would have had chloride ions present at the surface of the steel within the 10 week exposure period, the depth of cover being around 3 millimetres, even allowing for a slower rate of diffusion across the cast surface.(93) This being the case, it is clear that the environment provided to steel by hydrated alite is capable of maintaining passivity in the presence of chloride ions, even though the pore solution is no more than saturated calcium hydroxide solution of pH 12.45 (25°C).

5.5 CONCLUSIONS

The activation energy obtained for the diffusion of chloride ions through hydrated alite is similar to those values obtained by other workers for commercial Portland cement pastes indicating that chloride diffusion occurs through the Calcium-Silicate-Hydrate gel matrix.

The addition of tricalcium aluminate (plus gypsum) to alite pastes enlarges the pore structure but results in a slight reduction of the diffusion coefficients (as measured at 25°C), possibly due to the complexation of chloride ions by the tricalcium aluminate hydrate.

Alite of the composition and morphology of that used in this work does not complex chloride ions to any significant degree (less than 0.5% of total).

Blended cement mineral pastes of 0.6 water-mineral ratios have comparable pore structures to 0.5 water-cement ratio commercial Portland cement pastes of similar initial tricalcium aluminate content.

Hydrated alite can maintain the passivity of embedded steel in the presence of chloride ions, even at levels which result in corrosion to steel in saturated calcium hydroxide solution. The low permeability of the hydrated alite results in a lowering of the rest potential of the embedded steel due to an inadequate supply of oxygen to maintain the cathodic reaction.

	CHLORIDE CONCENTRATION (M/1)				
TIME (seconds)	DISC 1	DISC 2	DISC 3	DISC 4	DISC 5
237 600	0.0015	0.0020	0.0015	0.0015	0.0015
583 200	0.0065	0.0055	0.0025	0.0035	0.0055
842 400	0.0120	0.0095	0.0040	0.0080	0.0085
1 015 200	0.0140	0.0140	0.0055	0.0100	0.0100
1 188 000	0.0175	0.0150	0.0085	0.0150	0.0135
VOLUME OF CELL (mls)	85	90	90	80	80
THICKNESS OF DISC (cms)	0.277	0.270	0.281	0.275	0.272
GRADIENT	1.69E-8	1.33E-8	6.90E-9	1.38E-8	1.21E-8
CORRELATION	0.997	0.990	0.938	0.965	0.994
D-VALUE	4.14E-8	3.36E-8	1.81E-8	3.16E-8	2.74E-8

AVERAGE D-VALUE 3.04E-8 cm^2s^{-1}

Table 5.1
ALITE CHLORIDE ION DIFFUSION RESULTS - 7°C

	CHLORIDE CONCENTRATION (M/l)				
	DISC 1	DISC 2	DISC 3	DISC 4	DISC 5
TIME (seconds)					
235 200	0.0025	0.0020	0.0020	0.0020	0.0020
408 000	0.0055	0.0055	0.0045	0.0060	0.0030
580 800	0.0095	0.0095	0.0085	0.0105	0.0040
840 000	0.0175	0.0150	0.0135	0.0165	0.0070
1 012 800	0.0190	0.0190	0.0150	0.0195	0.0085
VOLUME OF CELL (mls)	80	80	80	80	95
THICKNESS OF DISC (cms)	0.295	0.310	0.303	0.296	0.360
GRADIENT	2.28E-8	2.19E-8	1.76E-8	2.29E-8	8.64E-9
CORRELATION	0.991	1	0.993	0.998	0.990
D-VALUE	5.59E-8	5.65E-8	4.43E-8	5.64E-8	3.07E-8

AVERAGE D-VALUE 4.88E-8 cm^2s^{-1}

Table 5.2
ALITE CHLORIDE ION DIFFUSION RESULTS - 15°C

	CHLORIDE CONCENTRATION (M/1)				
TIME (seconds)	DISC 1	DISC 2	DISC 3	DISC 4	DISC 5
235 200	0.0025	0.0035	0.0030	0.0025	0.0025
408 000	0.0085	0.0065	0.0090	0.0070	0.0060
494 000	0.0100	0.0085	0.0095	0.0075	0.0075
580 800	0.0140	0.0105	0.0140	0.0100	0.0100
840 000	0.0215	0.0175	0.0200	0.0170	0.0175
VOLUME OF CELL (mls)	80	80	80	80	80
THICKNESS OF DISC (cms)	0.304	0.291	0.319	0.294	0.314
GRADIENT	3.14E-8	2.34E-8	2.80E-8	2.36E-8	2.50E-8
CORRELATION	0.997	0.995	0.990	0.993	0.993
D-VALUE	7.94E-8	5.66E-8	7.43E-8	5.77E-8	6.53E-8

AVERAGE D-VALUE 6.67E-8 cm^2s^{-1}

Table 5.3
ALITE CHLORIDE ION DIFFUSION RESULTS - 25°C

	CHLORIDE CONCENTRATION (M/1)				
TIME (seconds)	DISC 1	DISC 2	DISC 3	DISC 4	DISC 5
85 200	0.0030	0.0030	0.0025	0.0025	0.0030
171 600	0.0060	0.0055	0.0065	0.0055	0.0055
256 800	0.0115	0.0065	0.0085	0.0070	0.0100
343 200	0.0150	0.0140	0.0135	0.0100	0.0105
609 300	0.0270	0.0215	0.0255	0.0205	0.0200
VOLUME OF CELL (mls)	85	80	85	80	80
THICKNESS OF DISC (cms)	0.285	0.280	0.301	0.287	0.301
GRADIENT	4.64E-8	3.64E-8	4.40E-8	3.42E-8	3.21E-8
CORRELATION	0.998	0.991	0.997	0.994	0.991
D-VALUE	1.17E-7	8.48E-8	1.17E-7	8.15E-8	8.17E-8

AVERAGE D-VALUE 9.64E-8 cm^2s^{-1}

Table 5.4
ALITE CHLORIDE ION DIFFUSION RESULTS - 35°C

	CHLORIDE CONCENTRATION (M/1)				
	DISC 1	DISC 2	DISC 3	DISC 4	DISC 5
TIME (seconds)					
84 000	0.0060	0.0055	0.0045	0.0060	0.0035
108 600	0.0075	0.0060	0.0060	0.0075	0.0040
170 400	0.0140	0.0120	0.0115	0.0145	0.0075
193 200	0.0150	0.0140	0.0120	0.0160	0.0080
255 600	0.0205	0.0185	0.0160	0.0215	0.0120
VOLUME OF CELL (mls)	80	80	80	80	85
THICKNESS OF DISC (cms)	0.281	0.307	0.292	0.285	0.338
GRADIENT	8.61E-8	8.00E-8	6.27E-8	9.29E-8	4.99E-8
CORRELATION	0.997	0.995	0.993	0.997	0.993
D-VALUE	2.01E-7	2.04E-7	1.52E-7	2.20E-7	1.49E-7

AVERAGE D-VALUE 1.85E-7 cm^2s^{-1}

Table 5.5
ALITE CHLORIDE ION DIFFUSION RESULTS - 45°C

	CHLORIDE CONCENTRATION (M/1)				
TIME (seconds)	DISC 1	DISC 2	DISC 3	DISC 4	DISC 5
279 600	0.0055	0.0030	0.0035	0.0050	0.0030
428 400	0.0100	0.0055	0.0065	0.0100	0.0060
603 900	0.0145	0.0080	0.0085	0.0145	0.0095
859 800	0.0215	0.0130	0.0135	0.0200	0.0130
1 034 400	0.0265	0.0185	0.0185	0.0250	0.0185
VOLUME OF CELL (mls)	78	79	82	79	79
THICKNESS OF DISC (cms)	0.264	0.283	0.297	0.256	0.269
GRADIENT	2.75E-8	1.99E-8	1.91E-8	2.56E-8	1.95E-8
CORRELATION	1	0.990	0.991	0.997	0.992
D-VALUE	5.89E-8	4.62E-8	4.84E-8	5.38E-8	4.31E-8

AVERAGE D-VALUE 5.01E-8 cm^2s^{-1}

Table 5.6
ALITE/3% TRICALCIUM ALUMINATE CHLORIDE ION DIFFUSION RESULTS - 25°C

	CHLORIDE CONCENTRATION (M/l)				
	DISC 1	DISC 2	DISC 3	DISC 4	DISC 5
TIME (seconds)					
279 600	0.0045	0.0050	0.0060	0.0045	0.0060
428 400	0.0060	0.0060	0.0120	0.0065	0.0065
603 900	0.0070	0.0080	0.0145	0.0085	0.0085
859 800	0.0115	0.0125	0.0235	0.0130	0.0125
1 034 400	0.0175	0.0170	0.0290	0.0165	0.0165
VOLUME OF CELL (mls)	79	80	70	76	79
THICKNESS OF DISC (cms)	0.274	0.283	0.214	0.299	0.280
GRADIENT	1.64E-8	1.59E-8	2.97E-8	1.58E-8	1.41E-8
CORRELATION	0.958	0.980	0.994	0.995	0.977
D-VALUE	3.69E-8	3.74E-8	4.62E-8	3.73E-8	3.24E-8

AVERAGE D-VALUE 3.80E-8 cm^2s^{-1}

Table 5.7
ALITE/12% TRICALCIUM ALUMINATE CHLORIDE ION DIFFUSION RESULTS - 25°C

Figure 5.1
ALITE DISCS BEFORE AND AFTER GRINDING

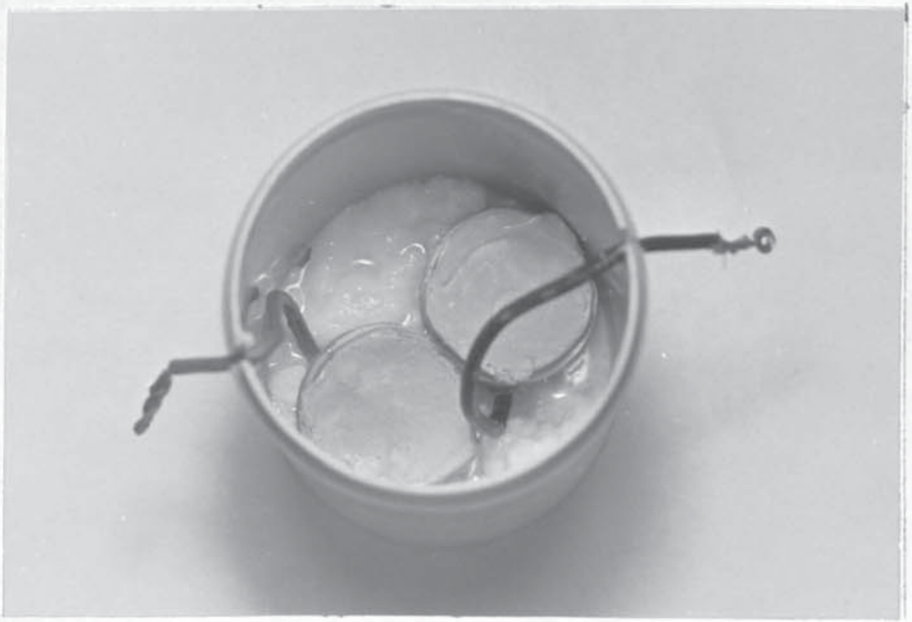


Figure 5.2
DUPLICATE STEEL SPECIMENS IN ALITE WITH INTERNAL CHLORIDES. 100% R.H.

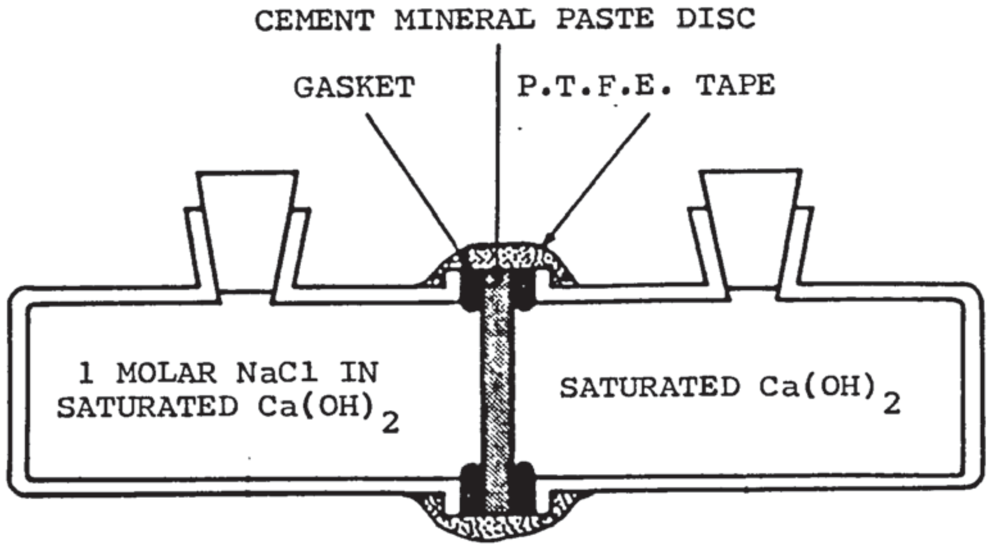


Figure 5.3
CHLORIDE DIFFUSION CELL

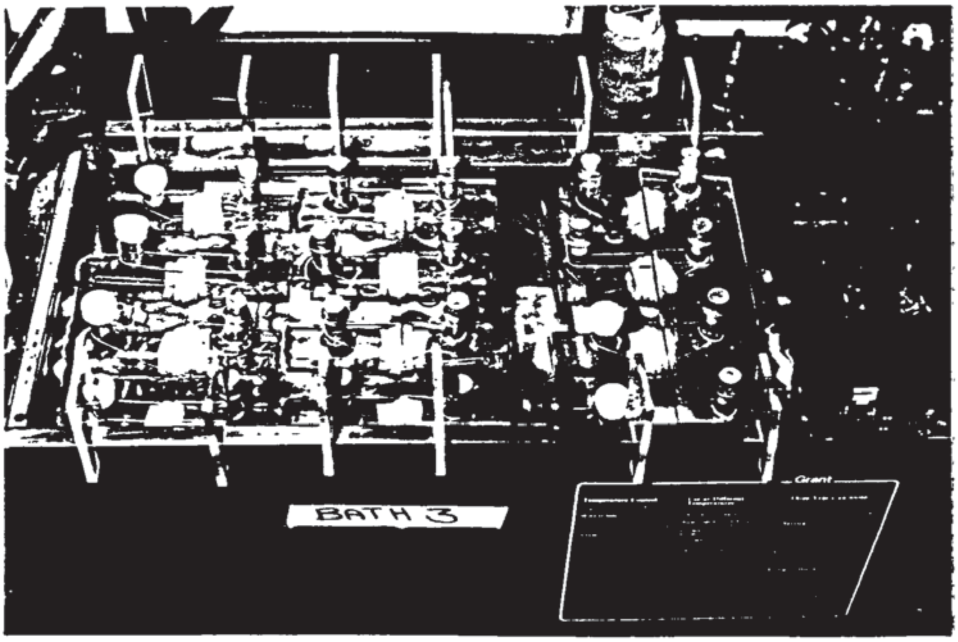


Figure 5.4
CELLS SUPPORTED BY CRADLE IN WATER BATH

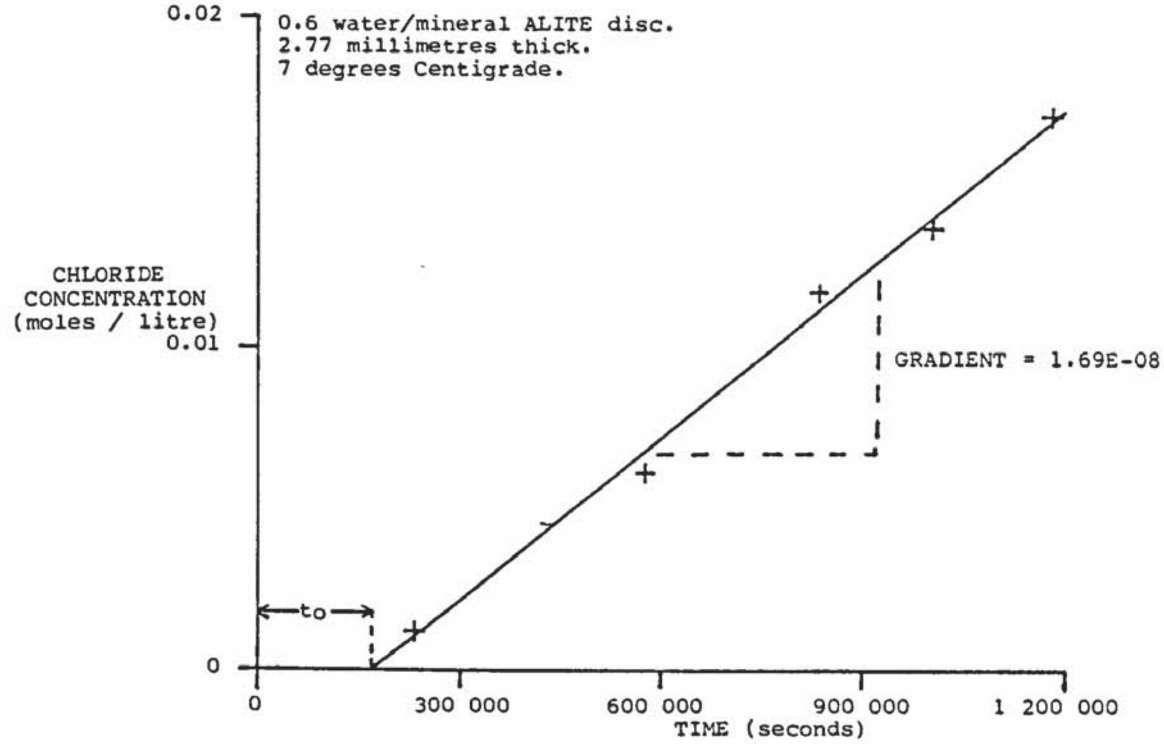


Figure 5.5
CHLORIDE DIFFUSION THROUGH AN ALITE DISC

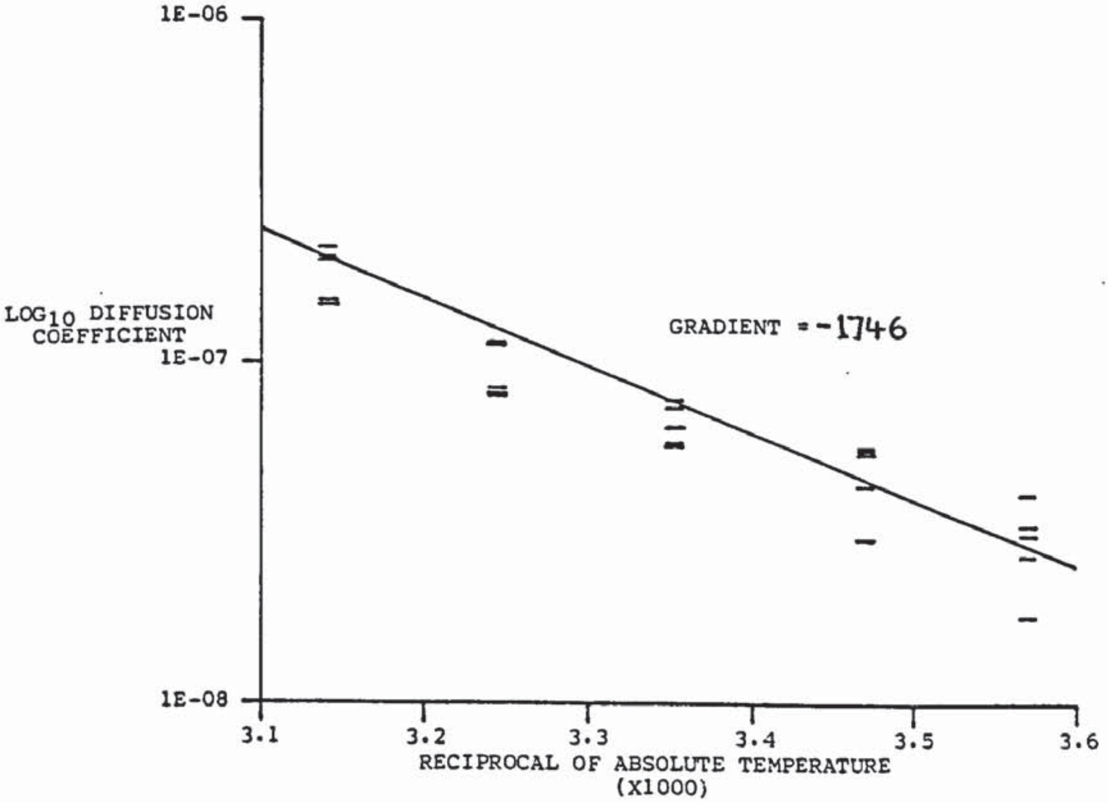


Figure 5.6
ARRHENIUS PLOT FOR ALITE

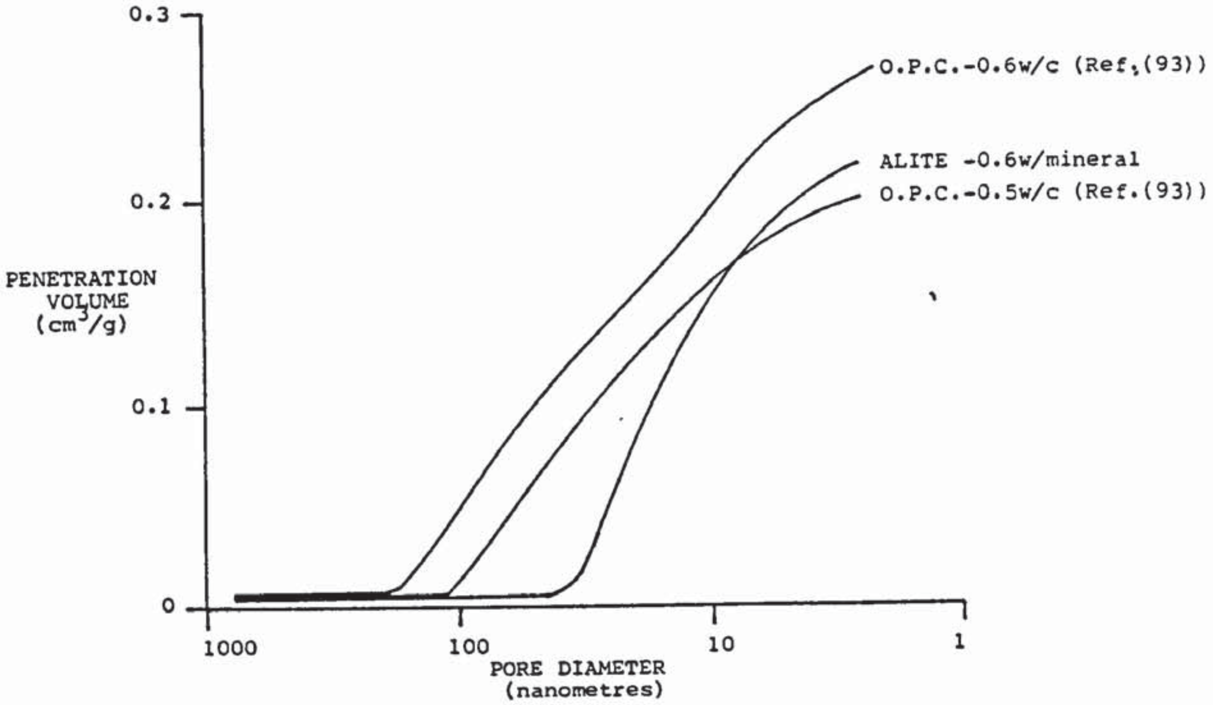


Figure 5.7
PORE SIZE DISTRIBUTIONS FOR ALITE AND O.P.C. DISCS

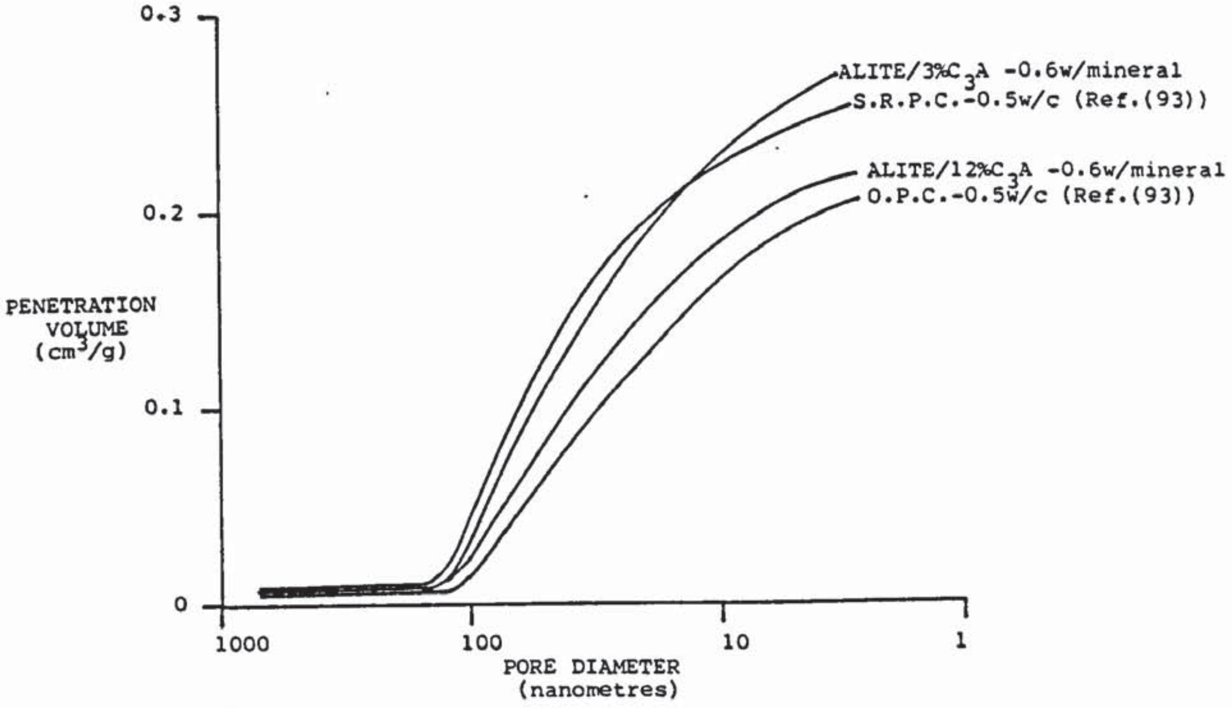


Figure 5.8
PORE SIZE DISTRIBUTIONS FOR BLENDED MINERAL DISCS COMPARED WITH PORTLAND CEMENT PASTES

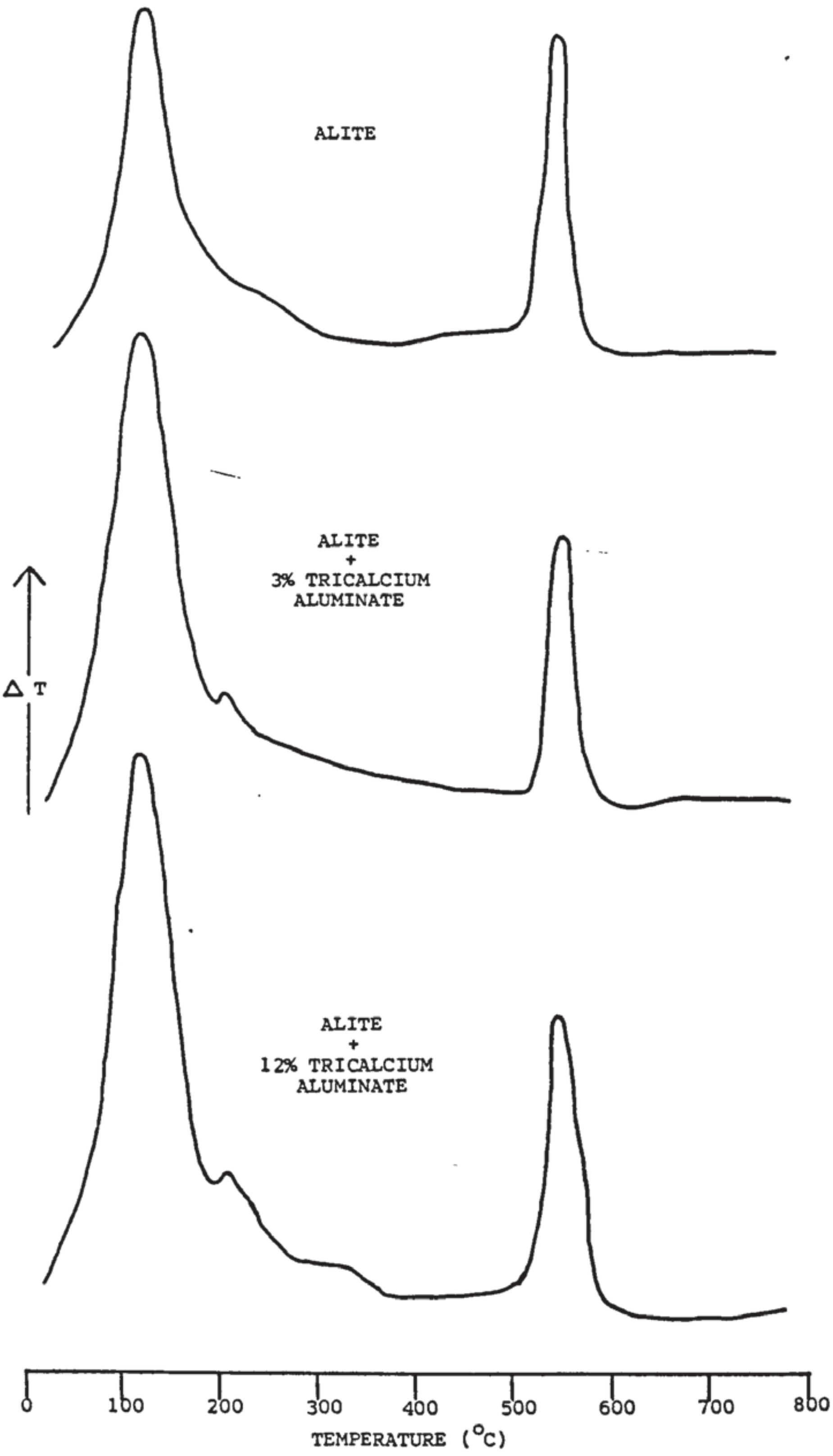


Figure 5.9
DIFFERENTIAL THERMOGRAMS FOR HYDRATED CEMENT MINERAL DISCS BEFORE CHLORIDE DIFFUSION MEASUREMENTS

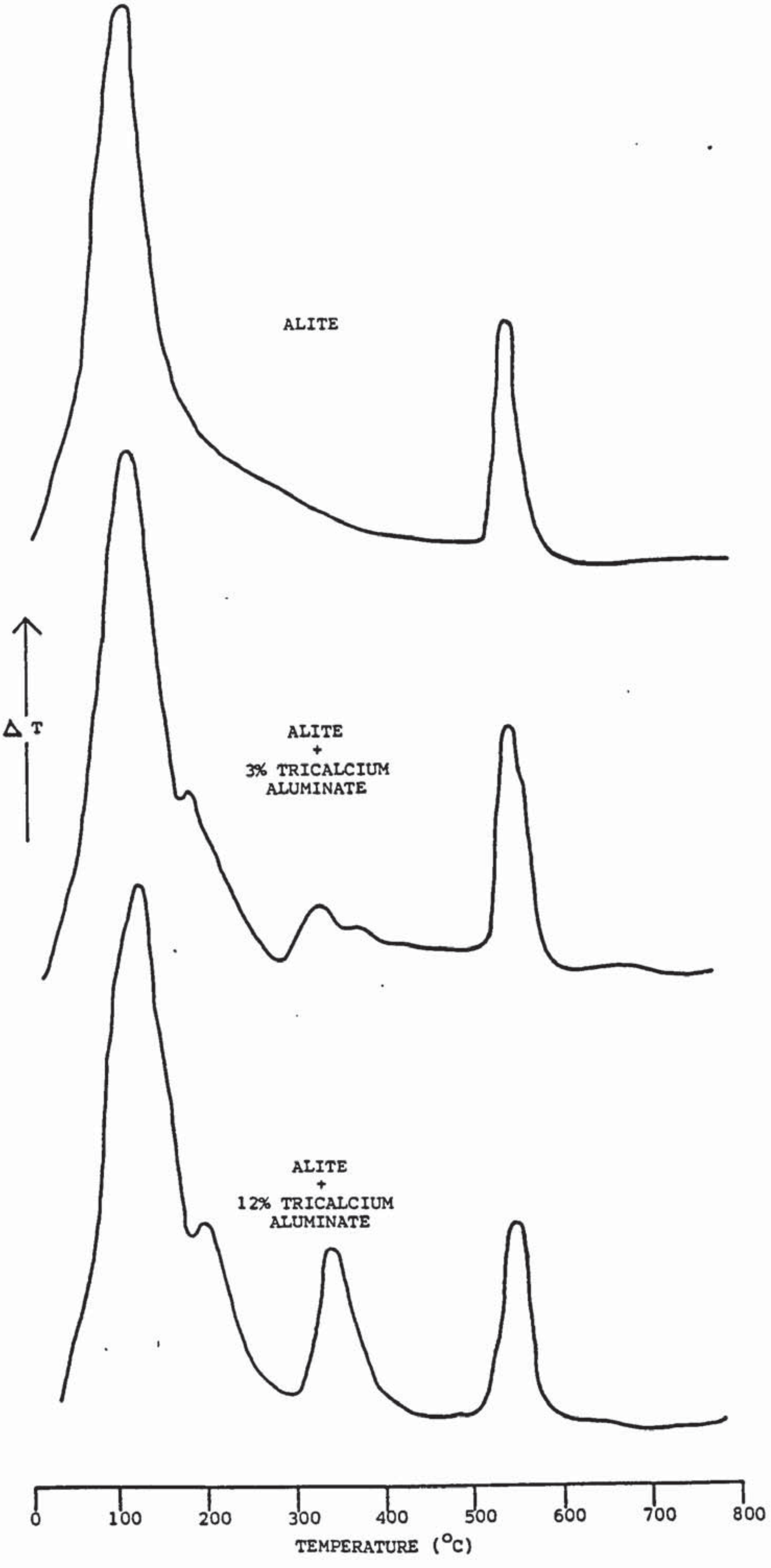


Figure 5.10
DIFFERENTIAL THERMOGRAMS FOR HYDRATED CEMENT MINERAL DISCS AFTER CHLORIDE DIFFUSION MEASUREMENTS

ALL POTENTIALS MEASURED VERSUS SATURATED CALOMEL ELECTRODE.

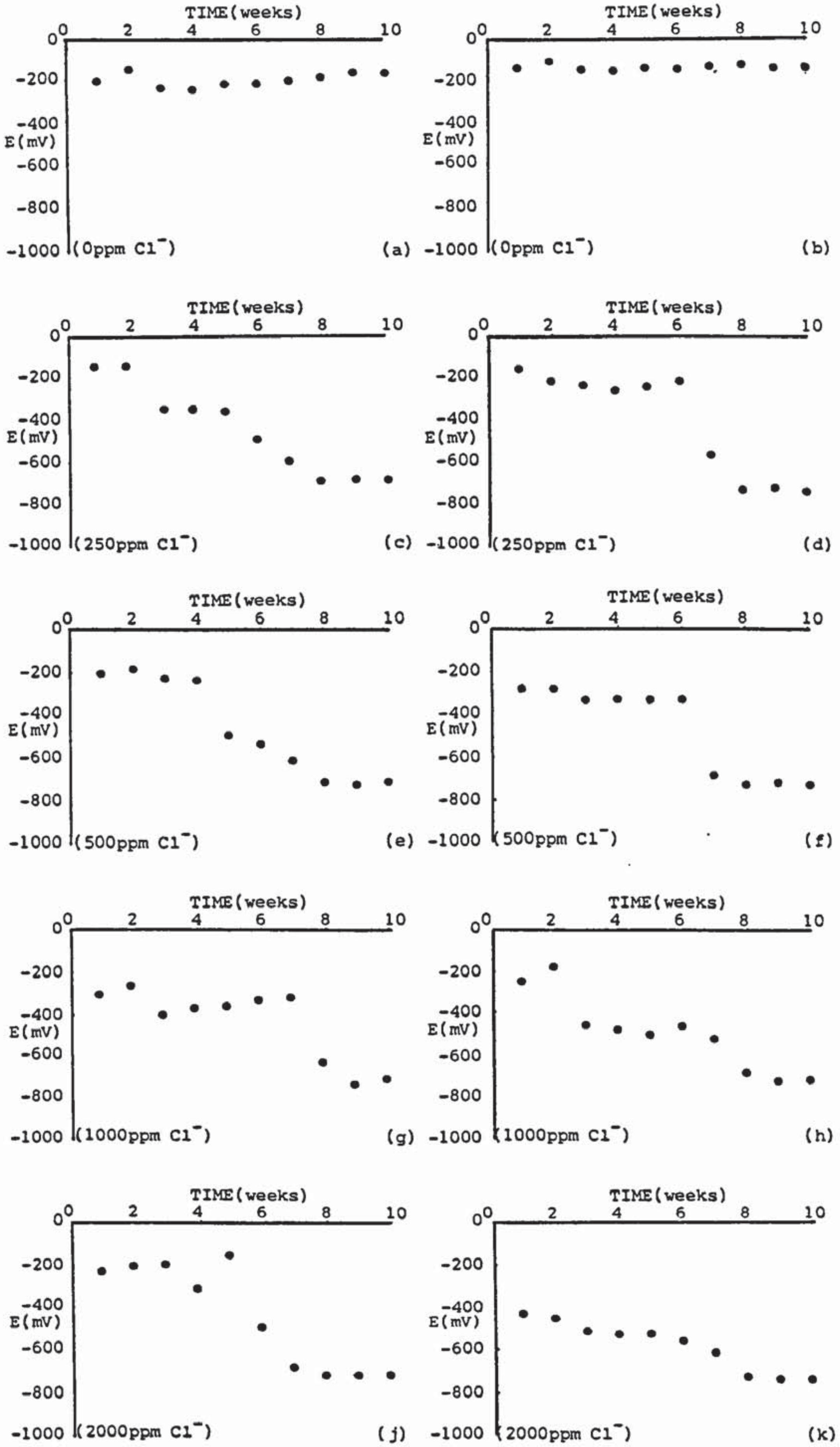


Figure 5.11 POTENTIAL/TIME PLOTS FOR STEEL IN CALCIUM HYDROXIDE SOLUTION CONTAINING 0-2000ppm CHLORIDE ION (by weight of cement)

ALL POTENTIALS MEASURED VERSUS SATURATED CALOMEL ELECTRODE.

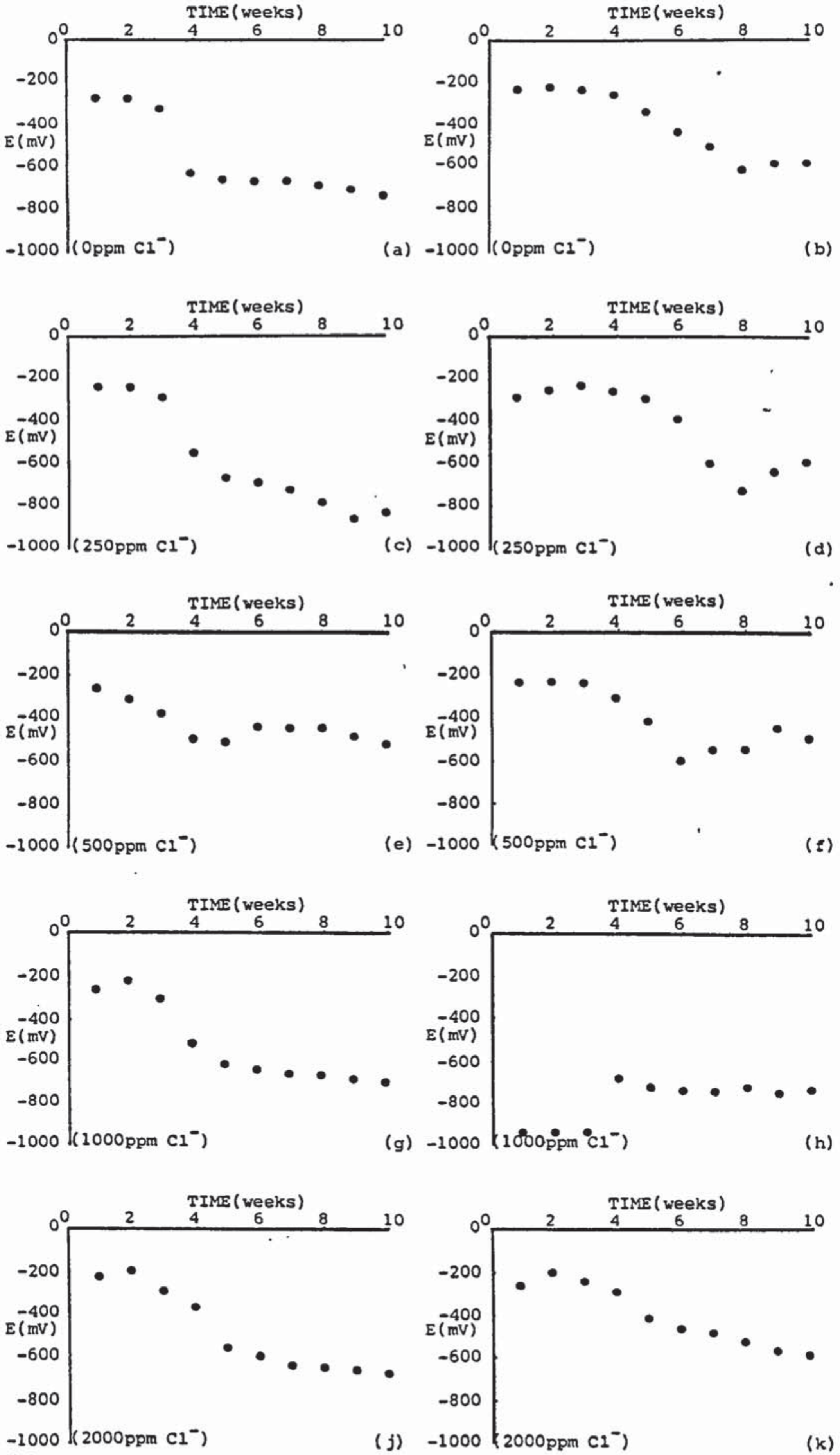


Figure 5.12 POTENTIAL/TIME PLOTS FOR STEEL IN ALITE CONTAINING 0-2000ppm CHLORIDE ION. 100% R.H.

ALL POTENTIALS MEASURED VERSUS SATURATED CALOMEL ELECTRODE.

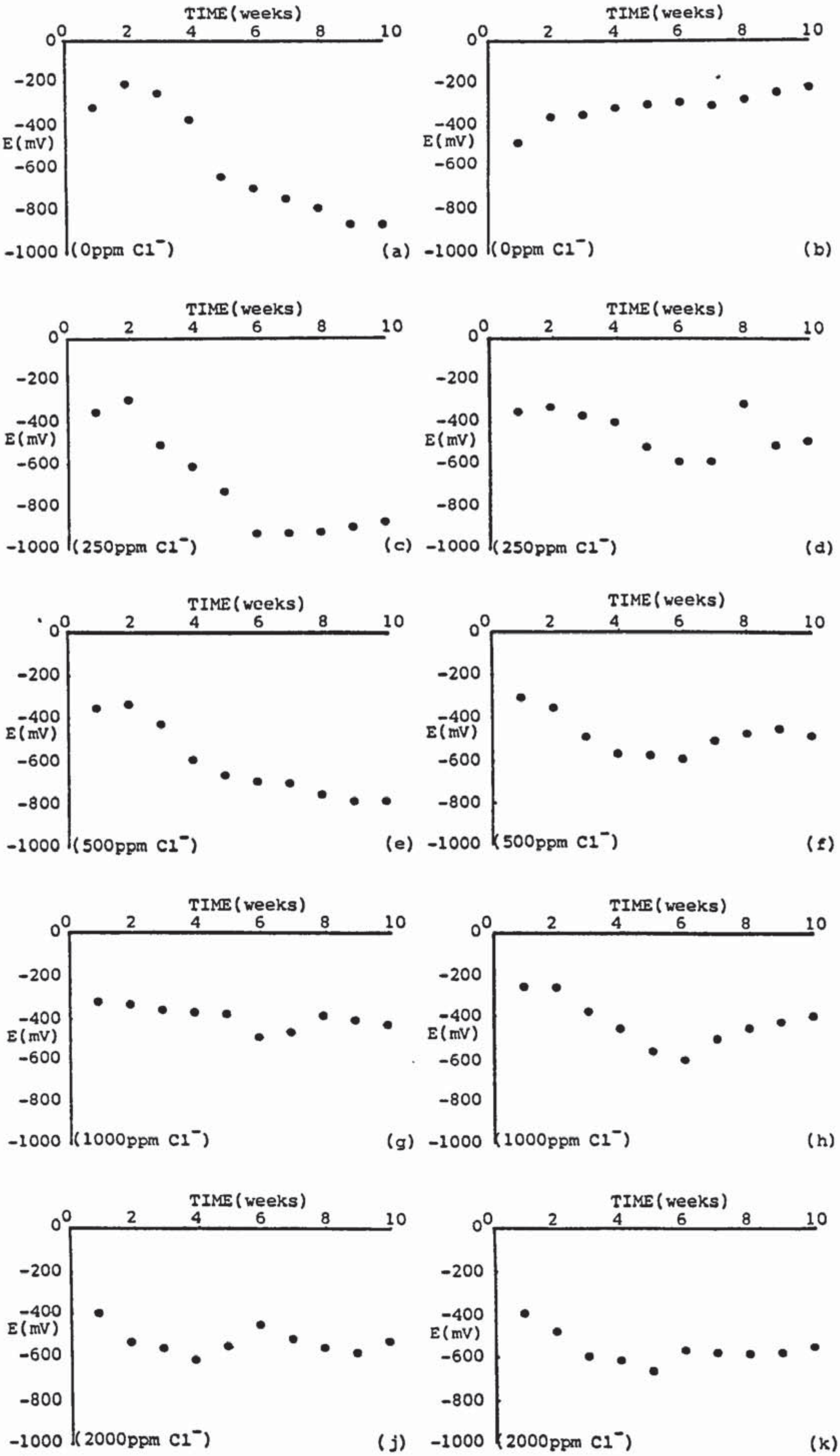


Figure 5.13 POTENTIAL/TIME PLOTS FOR STEEL IN ALITE EXPOSED TO CALCIUM HYDROXIDE SOLUTION CONTAINING 0-2000ppm CHLORIDE ION

ALL POTENTIALS MEASURED VERSUS SATURATED CALOMEL ELECTRODE.

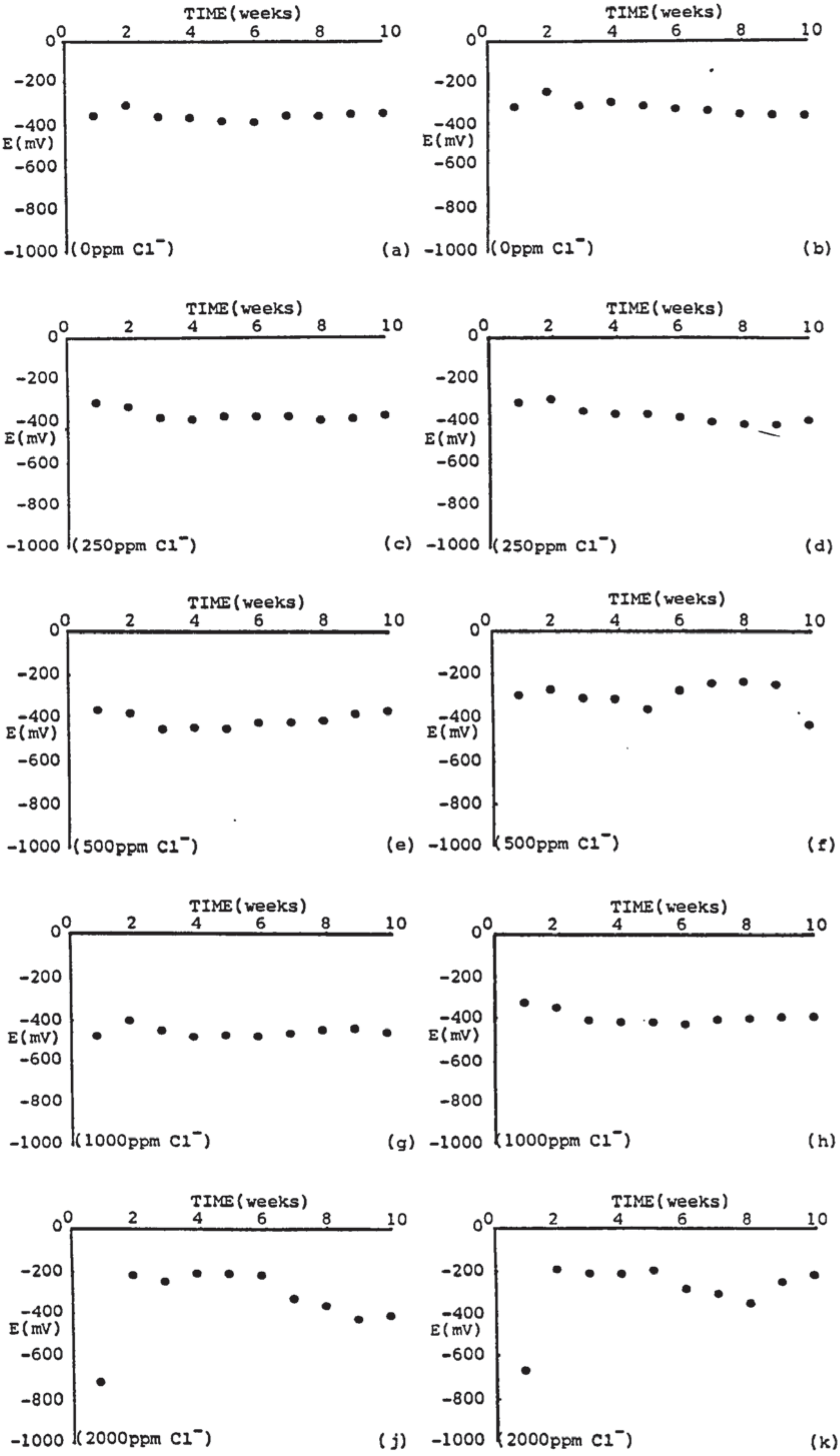


Figure 5.14 POTENTIAL/TIME PLOTS FOR STEEL IN ALITE COUPLED TO STAINLESS STEEL, EXPOSED TO CALCIUM HYDROXIDE SOLUTION CONTAINING 0-2000ppm CHLORIDE ION

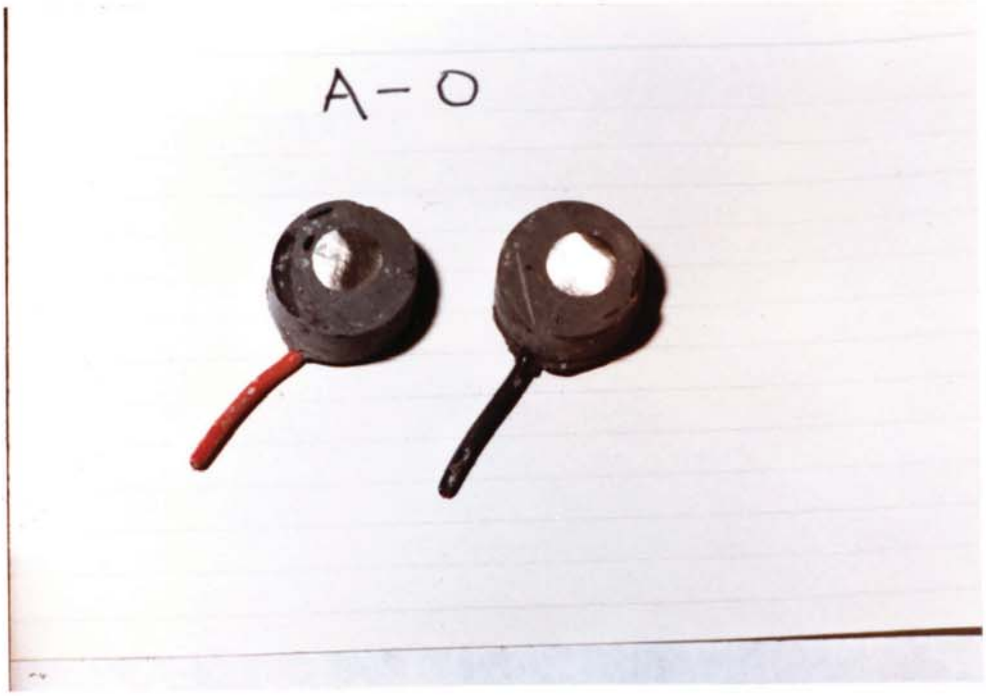


Figure 5.15
MILD STEEL IN CALCIUM HYDROXIDE SOLUTION (10 WEEKS)

Figure 5.16
MILD STEEL IN CALCIUM HYDROXIDE SOLUTION PLUS 250 ppm Cl^- (10 WEEKS)

Figure 5.17
MILD STEEL IN ALITE CONTAINING 2000 ppm Cl^-
(10 WEEKS)

Figure 5.18
MILD STEEL IN ALITE, IN CALCIUM HYDROXIDE
SOLUTION CONTAINING 2000 ppm Cl^- (10 WEEKS)

Figure 5.19
MILD STEEL IN ALITE COUPLED TO STAINLESS STEEL, IN CALCIUM HYDROXIDE SOLUTION CONTAINING 2000 ppm Cl^- (10 WEEKS)

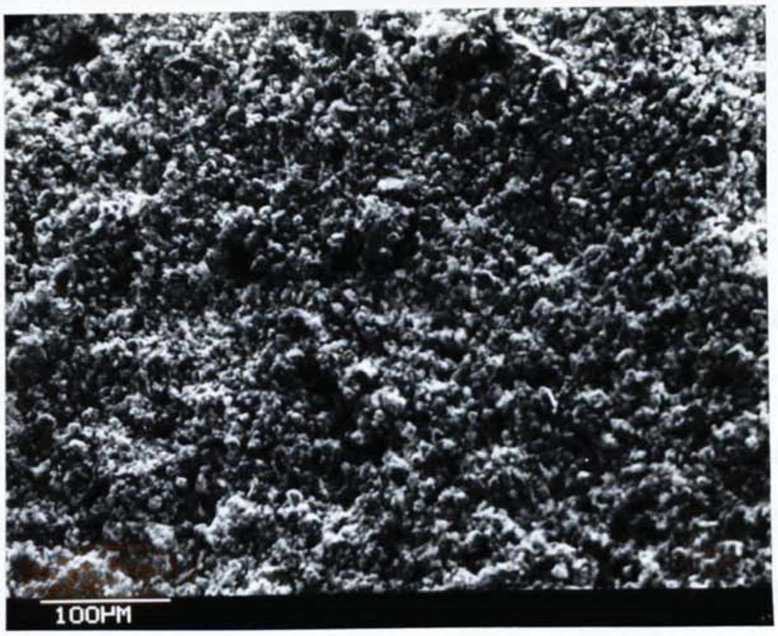


Figure 5.20
ELECTRON PHOTOMICROGRAPH OF HYDRATED ALITE CAST AGAINST AN ABRAIDED STEEL SUBSTRATE (9 DAYS)

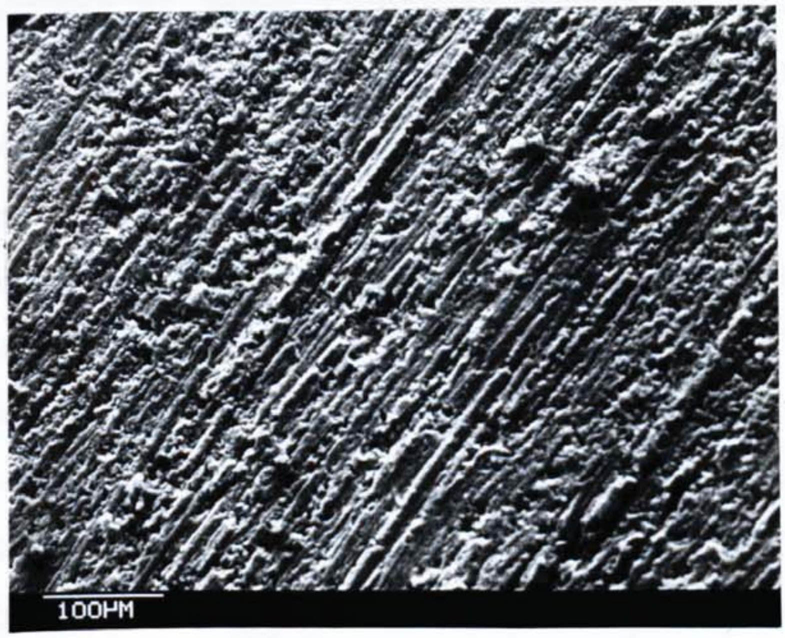


Figure 5.21
ELECTRON PHOTOMICROGRAPH OF HYDRATED ALITE CAST AGAINST AN ABRAIDED STEEL SUBSTRATE (90 DAYS)

CHAPTER 6

THE EFFECT OF SURFACE CONDITION AND ENVIRONMENT ON THE BEHAVIOUR OF STEEL IN CONCRETE

6.1 INTRODUCTION

The effectiveness of Portland cement in preventing the corrosion of embedded steel has been recognised for over a century but more recently it has been noted that the passive condition of steel embedded in good quality mortars and concretes is more stable than would be expected from electrochemical studies of steel immersed in static solutions of similar ionic contents to pore solution. (98) This may be in some part due to the presence of a portlandite-rich layer at the steel-cement interface. (99) The alkalinity of the liquid phase of Portland cement pastes has been found to reach levels in excess of pH 13 due to the presence of small amounts of sodium hydroxide and potassium hydroxide and even where the pore solution pH is reduced by effects such as leaching the alkalinity tends to be buffered at around pH 12.5 due to the abundance of sparingly soluble calcium hydroxide produced during hydration. (18)

Pourbaix has shown the wide range of potentials over which iron may remain passive in such an alkaline environment due to the formation of a thin surface coating of stable oxide. (46) Rest potential measurements in de-aerated calcium hydroxide solution have demonstrated that even a limited supply of oxygen can provide the necessary degree of anodic polarisation to maintain the passive condition of the steel. (100) Passivation by the alkaline environment is the primary means of corrosion protection for embedded steel and it can be demonstrated by simple electrochemical methods that this can be true regardless of whether the steel is bright or carrying a light deposit of corrosion product when introduced into the cement paste or concrete. Indeed, it is common for steel reinforcement that has had a light deposit of rust prior to casting to appear grey and uncorroded upon removal after prolonged exposure to concrete.(101) This would indicate that the nature of the surface corrosion is altered and it would therefore be of interest to determine the composition of such rust films before and after exposure to concrete.

The use of x-ray diffraction in the analysis of iron corrosion products has been employed for this purpose although the amorphous character of the fine crystals produced can prevent successful analysis.(102) Mössbauer spectroscopy is a technique ideally suited to the characterisation of iron corrosion products. It is not affected by the size of crystals present and can differentiate between the different forms of iron oxides and hydroxides.

The vast majority of work carried out on steel embedded in Portland cement mortars and concretes has understandably involved the use of clean or 'as-received' mild steel reinforcements. By employing clean steel a uniform and consistent surface can be ensured while 'as-received' steel may be regarded as more realistic in terms of on-site usage. Studies of steel bearing both atmospheric corrosion and mill scale have provided vital information as to the galvanic couples that can be produced.(104)

The aim of this chapter has been to study the electrochemical behaviour of mild steel with several surface conditions that has been embedded in good quality concrete and exposed to various environments. An attempt has also been made to determine the changes that occur in the surface layers of the steel.

6.2 PREVIOUS WORK

The most common type of specimen employed for the study of the behaviour of steel reinforcement in concrete is in the form of a steel bar embedded in cement paste, mortar or concrete. Once the specimens have been made it is necessary to select a method of monitoring the behaviour of the steel. The simplest method is to remove the steel after a period of exposure and observe the changes that have taken place but as this method is, by its very nature, destructive it is generally only used as a source of secondary information when the main sequence of corrosion monitoring has been completed.

The various electrochemical methods currently available are, for the most part, ably suited to the task of monitoring the behaviour of embedded steel. Those methods which involve the use of impressed voltage or current can result in permanent changes in the electrochemical nature of the steel and are prone to interference due to concentration polarisation.(105) It is possible to measure the current flow between a galvanic couple produced by two steel electrodes of different electrochemical condition which are embedded in the same concrete specimen but this technique does not provide information on either of the individual sections of steel. (106) Those methods which are essentially non-destructive when used to study embedded steel include half-cell potential (also known as rest potential and corrosion potential), linear polarisation, A.C. impedance and electrochemical noise. (107)(108)

The A.C. impedance and electrochemical noise techniques have only recently been developed for use with steel embedded in concrete and the results obtained so far have proved to be very interesting. Measurements with A.C. impedance may be carried out by applying a small amplitude perturbation of ± 10 to 20 millivolts as a sine wave of known frequency in the range 100 kilohertz to 1 megahertz and the required calculations are normally carried out by computer. As the applied voltage is both small and alternating no potential shift should be experienced by the steel electrodes and representative values of corrosion rate may be obtained. (109)

Electrochemical noise may be observed for steel embedded in concrete as fluctuations of both current and potential. The sources of the noise are thought to be effects such as thermal agitation of charge carriers or the process of passive film formation. Work has been concentrated on the noise associated with rest potentials of embedded steel which has been measured by means of a high resolution voltmeter connected to a data acquisition system. By such a method it is possible with the aid of computers to obtain corrosion rate data from the rest potentials of embedded steel. (110)

Rest potential and polarisation resistance measurements are commonly used together for the monitoring of steel in concrete in the laboratory. Both are quick and easy to carry out, non-destructive in nature and the interpretation of the results can be performed manually. (111) For these reasons both techniques have been employed in chapter 7 of this work. Rest potential half-cell measurements are by far the most simple to carry out, the only equipment required being a reference electrode and a high impedance voltmeter. (112) Rest potentials can be measured instantaneously without the need to know the area of the steel electrode and for these reasons the method is widely used for 'in-situ' testing of reinforced concrete structures and where a large number of specimens are to be monitored regularly over a long period of time. (113) For large areas of reinforced concrete it is possible to carry out potential mapping by moving the reference electrode through several positions in a grid and so determine the positions of possible anodic sites. (114) (115)

The main disadvantage of potential measurements is that they only indicate the balance between the anodic and cathodic areas of the steel and cannot be used to determine actual corrosion rates except in the case of electrochemical noise measurements. Where there is a severe restriction of oxygen access to the embedded steel such as in submerged marine structures it is possible to detect potentials which may be interpreted as a sign of corrosion but are in fact due to a limitation of the cathodic reaction. (106)

Most forms of work carried out on the behaviour of steel in pastes, mortars and concretes have involved the use of steel with a uniform surface condition, usually cleaned and degreased, exposed to different environments. The advantages of using cleaned steel are that a uniform initial surface condition can be ensured and corrosion rates can be determined by weight loss measurements. (102) A great deal of work has also been carried out on comparisons between clean steel, 'as-received' steel and various coated steels such as galvanised and epoxy coated. (13)(116)

Where clean and rusted steels embedded in concrete have been compared differences in their ability to resist depassivation by chloride ions have been noted. During a study of pre-tensioned wires in concrete containing calcium chloride Roberts noted that where the wires had been allowed to form a uniform layer of atmospheric corrosion product much less pitting corrosion occurred in the presence of calcium chloride than with similar wires that had been cleaned prior to use. (9) Other wires that had only been partly rusted showed no such advantage. Roberts inferred from his results that the nature of the rust, which would be influenced by such factors as the speed of formation, density and degree and nature of atmospheric pollutants present, must exert some form of influence on the behaviour of the steel when embedded in concrete.

More recent work by John et al appears to contradict the findings of Roberts. (117) Bright and pre-rusted steel bars were embedded in concrete and exposed to a marine environment. Both types of steel exhibited pitting corrosion but the pre-rusted steel bars were found to have corroded to a far greater degree. The extent of the difference between the two types of steel was found to be dependent upon the quality of the concrete.

The work described in this chapter is an attempt to promote further understanding of the effects that different types of surface corrosion have on the behaviour of steel embedded in concrete and exposed to various environments.

6.3 EXPERIMENTAL PROCEDURE

Mild steel bar of 10 millimetres diameter was cut into lengths of 140 millimetres and the cut ends finished on a lathe. Into one end was drilled a 2 millimetre diameter hole to a depth of around 3 to 4 millimetres for the purpose of electrical connection. This was achieved by heating the recess end of each bar in a gas flame for a short time and then introducing the bared end of an insulated copper wire with flux core solder. The procedure was completed by quenching the end of the specimen with deionised water. Care was taken not to overheat the specimens and any with heat discolouration present over more than the first 15 to 20 millimetres of their length were discarded.

All the specimens so prepared were grit blasted and degreased in 'Inhibisol' so as to produce a consistant surface condition. At this point one quarter of the bars were stored in a desiccator over silica gel for a period of around two weeks so as to be sure that a uniform oxide film had formed. The remaining bars were split into three groups and each exposed to a different corrosive environment. One group was kept in deionised water vapour, one in 1 molar ferrous sulphate solution and the third in 1 molar sodium chloride solution. All three groups were maintained at 25 degrees Centigrade during the two weeks of exposure.

The specimens exposed to solutions were submerged twice a day and then left in the vapour above allowing excess solution to drain away.

In an attempt to avoid the problems of crevice attack a novel system of masking was employed at the electrical junction end of each specimen. A cement paste slurry of 0.4 water-cement ratio was applied in the form of a collar around the first 20 to 30 millimetres of each specimen. The thickness of cover was maintained at around 2 millimetres. Once the cement paste was hardened a covering of air-cure epoxy resin was applied so as to seal totally the top of the steel specimen. Care was taken to ensure that the epoxy did not come into contact with the bottom edge of the cement paste collar. In such a manner the electrical connection was isolated from the body of each specimen while the thin cement paste collar ensured that no crevice existed at the interface with the concrete.

The concrete employed was a simple mix of 3 parts of coarse aggregate, 2 parts of fine aggregate, 1 part cement and a water-cement ratio of 0.5. The coarse aggregate used was a 10 millimetre quartzite and the fine aggregate a 'zone 2' concreting sand. The cement used was the same ordinary Portland cement that has been employed in other chapters. Analyses of both the cement and steel are given in chapter 2 (tables 2.1 and 2.2). The procedures employed for mixing, casting and vibrating are given in chapter 2 (para.2.3). The concrete was cast in commercial steel cylinder moulds to produce specimens of 80 millimetre diameter by 160 millimetre length. The steel was introduced centrally during the final vibration by means of a jig designed to ensure correct insertion. The top 5 millimetres of the masked ends were left protruding from the surface of each specimen. Once demoulded the top surface and first 4 centimetres of the side were coated with several layers of rubberised paint. The purpose of this coating was to ensure that the shortest path between the embedded steel and the environment was through the sides of the specimen. It also had the advantage of eliminating the need to keep the specimens exposed to solutions fully submerged at all times as the level of solution would have to drop several centimetres before the uncoated concrete was exposed to the atmosphere. The finished form of specimen is shown in figures 6.1 and 6.2.

Due to the limited number of moulds available only five specimens could be cast with any one batch of concrete. To ensure consistent quality sufficient concrete was produced with each mix to make the specimens and a standard 100 millimetre test cube. All 32 test cubes so produced were tested for compressive strength at 28 days as described in chapter 2 (para.2.4). The results obtained are given in Appendix 1.

For each of the four steel surface conditions 40 concrete embedded specimens were produced and these were split into four groups of ten and exposed to different environments. The environments studied were saturated calcium hydroxide solution, saturated calcium hydroxide solution containing 1 mole per litre of sodium chloride, artificial seawater and 100% relative humidity. All environments were maintained at 25 degrees Centigrade and the solutions replaced weekly for the first three months and monthly thereafter. The baths were designed so that there was 1 litre of solution for each specimen except in the case of artificial seawater where there was 2 litres per specimen. The pH of the artificial seawater was measured regularly with a pH meter and replaced when the pH dropped below 8.2. The artificial seawater used was made in the laboratory from deionised water containing the following additions by weight of water :

2.45% sodium chloride
0.52% magnesium chloride
0.41% sodium sulphate
0.12% calcium chloride
0.07% potassium chloride
0.02% sodium hydrogen carbonate

This is based on the artificial seawater given in A.S.T.M. standards but some of the less common constituents have been omitted. (118) It is a simple but adequate alternative to seawater, containing as it does the most plentiful ionic species to be found in true seawater. It is important to realise that the proportions of these ions in natural seawater alter with geographical location, time, temperature and depth. (119)

Rest potential measurements were taken weekly versus a saturated Calomel reference electrode by means of a high impedance digital voltmeter as described in chapter 2 (para. 2.16). Both the electrodes and the meter were checked regularly against other reference electrode and meter combinations to ensure correct operation. Those specimens exposed to solutions had their rest potentials determined by placing the reference electrode into the solutions and coupling the steel to the meter by means of the soldered electrical connection. The specimens exposed to 100% relative humidity were provided with small salt bridges containing cement paste through which the reference electrode could be coupled. The rest potentials obtained were plotted against time for each individual specimen. Two of each type of specimen for each environment were opened after 84 weeks and their appearance compared with the rest potential data. The remaining specimens were left on test and are presently approaching two years of age.

Samples of the surface corrosion products were scraped from the three types of rusted specimen both before and after exposure in concrete and subjected to Mössbauer spectroscopy in an attempt to determine any differences between the three corrosion products and any changes that occurred during exposure. Energy dispersive x-ray analysis was also carried out on the four types of steel prior to exposure.

6.4 RESULTS AND DISCUSSION

The majority of the results obtained in this work are in the form of plots of rest potential against time. Each specimen is shown on an individual plot and owing to the large number involved they are to be found in Appendix 15. Although the data was recorded weekly it has been plotted monthly and the reason the results have only been given up to one year is because of the time involved in the production of such figures. At the time of writing the majority of the specimens are still on test and approaching two years of age. Their electrochemical behaviour, except where stated, has remained similar to that at one year.

A representative set of specimens were removed after 84 weeks and split open by axial loading for observation. Energy dispersive x-ray analysis (E.D.X.A.) of the four surface conditions prior to embedment was carried out and the traces obtained are given in figure 6.3. Mössbauer spectroscopy was used to characterise the three types of surface corrosion, both before and after being embedded in concrete, and the traces obtained may be found in figures 6.4 and 6.5. The cement/steel interfaces of the opened specimens were studied by means of the scanning electron microscope (S.E.M.) in an attempt to distinguish any differences in the interfacial zones produced against the different surfaces.

Parts 1 to 3 of Appendix 15 contain the potential-time curves for the concrete specimens containing steel with the three pre-rusted surfaces. For those specimens exposed to solutions the potentials settled to values between -200 millivolts where one would expect the steel to be passive to -500 millivolts where it is possible that there is either a low oxygen access and the steel is passive or a high oxygen access and the steel is undergoing localised breakdown of the passive film resulting in pitting. Two notable exceptions to this occur with specimens containing steel bearing the 'sulphate rust' that had been exposed to saturated calcium hydroxide solution containing 1 mole per litre of sodium chloride (part 2.2, plots e) and g)). The steel shown in plot e) has slowly dropped to a potential of around -900 millivolts indicating that the steel is active and undergoing generalised corrosion but due to restricted oxygen access the overall corrosion rate is low. Such a condition is referred to as low potential active. Plot g) drops to -900 millivolts within 12 weeks and then returns to around -500 millivolts. Plot e) also demonstrated an increase in potential and by 80 weeks was back in the -500 millivolt region. This type of behaviour was not observed in any of the other pre-rusted specimens but, as will be seen, has proved to be quite common with those specimens containing clean and degreased steel which has been exposed to chloride environments. The behaviour of all four steel surface conditions to the 100% relative humidity environment has been totally passive in nature (see parts 1.4, 2.4, 3.4 and 4.4). The potentials have all settled quickly to a value above -200 millivolts and remained there for the period of exposure assisted by an unrestricted oxygen supply. It is interesting to note the differences between the initial potentials of the four surface conditions at the moment of embedment. The clean and 'chloride rust' steels exhibited initial potentials of between -300 and -400 millivolts, the 'sulphate rust' had a low initial potential of around -600 millivolts while the 'water vapour rust' specimens showed the most noble initial potentials of all at around -200 millivolts. When exposed to 100% relative humidity the 'water vapour rust' specimens continued to be the most noble during the period of exposure but showed no such effect in any of the other environments.

The greatest extremes of behaviour were exhibited by the clean and degreased steel specimens exposed to solutions (parts 4.1 to 4.3). For each solution around half the specimens remained at a potential of between -200 to -400 millivolts while the others dropped to nearly -1 volt. Where the solutions contained chloride ions a majority of the low potential specimens returned to values of around -400 millivolts within 30 to 40 weeks. It is significant that none of the specimens at a low potential which were exposed to saturated calcium hydroxide solution exhibited this increase in potential. The fact that some of the specimens dropped in potential to the low potential active region indicates that the supply of oxygen must have been very limited resulting in a restriction of the cathodic processes and leading to a very low corrosion rate. The return of some of the low potential active specimens to a higher potential suggests there to be a very fine balance between the passive and low potential active conditions which must depend on small changes in the availability of oxygen and is somehow related to the presence of chloride ions. Further information might be forthcoming from close examination of the steel itself.

It was first necessary to characterise the nature of the four surface conditions. By comparing the two types of analysis carried out on the steel surfaces prior to embedment it is possible to see the different types of information they provide. The energy dispersive x-ray traces for all four types of steel (figure 6.3) all possess a central group of peaks between 6.4 and 7.1 KeV which represent iron. The small peak at around 12 KeV would appear to be gold and is probably due to x-rays emitted from the electrical fittings of the equipment. The most interesting features of these traces are the extra peaks at 2.3 and 2.6 KeV. They indicate that a certain amount of sulphate and chloride has been included into the corrosion products of those specimens exposed to solutions containing sulphate and chloride ions respectively. The small peaks present at 1.5 and 1.8 KeV on each trace but which are especially clear on the clean and degreased steel represent aluminium and silicon. This is thought to be due to small amounts of alumina and silica that were picked up during the grit blasting process.

Mössbauer spectroscopy was carried out only on the three 'rusts'. Although it is possible to perform such analyses on clean steel substrates there was insufficient time to develop the techniques required. Whereas the E.D.X.A. results could only indicate iron plus any other elements present within its range of detection, Mössbauer spectroscopy can show which oxides and hydroxides are present and their relative proportions. The traces obtained prior to embedment as shown in figure 6.4 all share a large central doublet indicating superparamagnetic α-FeOOH with γ-FeOOH. The peaks to the left and right of this central doublet are mainly due to γ-Fe_2O_3 and Fe_3O_4. (43) The proportion of oxides to hydroxides appears to become smaller as one moves down from the 'water vapour rust' through the 'sulphate rust' until with the 'chloride rust' there is only α-FeOOH and γ-FeOOH present.

A second set of Mössbauer analyses were carried out on material removed from the surfaces of the three types of pre-rusted steel after 84 weeks exposure in concrete. No differences were apparent between the four environments and so only one set of results has been reproduced in figure 6.5. All three structures have become similar in composition, this being α-FeOOH, γ-FeOOH, γ-Fe_2O_3 and Fe_3O_4. The set of smaller peaks present around channel numbers 225, 350, 475, 575, 700 and 800 are due to α-FeOOH and would suggest that the proportion of this component has increased for all three specimens.

The appearance of the bars also underwent a change during the period of embedment. The bars with 'water vapour rust' were originally very dark brown in colour with an uneven surface, the 'chloride rust' was black and rough and the 'sulphate rust' comparitively smooth and yellow-brown in colour. When removed from exposure both the 'chloride' and 'water vapour' pre-rusted bars were much smoother and had become dark grey in colour whilst the 'sulphate rust' specimens were mostly dark grey but with yellow streaks along their lengths. (See figures 6.6 to 6.8). The appearance of the bars was the same irrespective of the external environment they had been exposed to. The cement interfaces were also characteristic, being rather rough with an open, porous structure for the 'chloride' and 'water vapour rust' specimens while the tracks left by the 'sulphate rust' bars were partly smooth and partly porous. The smooth, continuous areas corresponded to the regions of the bars that had remained yellow-brown in colour. Figures 6.10 to 6.12 show scanning electron micrographs of the interfacial layers produced against bars with 'water vapour rust', 'sulphate rust' and clean and degreased surfaces. The interfacial layer produced by 'chloride rust' was found to be identical in appearance to that formed against 'water vapour rust' and for that reason is not shown.

When removed from the concrete all the clean and degreased bars were a dull, medium grey in appearance including those which had exhibited a low potential (see figure 6.9). This confirms that their low potential was due to a restricted supply of oxygen which had resulted in a slowing down of the cathodic reaction. The clean and degreased bars that had been in a chloride environment began to show signs of general surface corrosion within a short time of being exposed to the atmosphere. The cement interface associated with the clean bars was smooth and continuous (see figure 6.12) and when analysed by E.D.X.A. yielded only calcium suggesting the existence of a lime-rich layer. It is most likely that the cause of the oxygen restriction was partly due to the compact and fault-free nature of this interfacial zone.

An interesting discovery was made concerning those bars with a clean and degreased surface that were exposed to chloride environments and had at first dropped to a low potential around -1 volt and then climbed back to a value of between -300 to -500 millivolts. On close examination it was found that they all possessed a single small corrosion pit of between 3 to 5 millimetres in diameter, presumably caused by a concentration of chloride ions at that particular area of the surface (see figure 6.13). Associated with each pit was a small rupture of the interfacial zone apparently due to the volume increase of the corrosion products. The mechanism for this apparent repassivation of the steel might therefore be the reinstatement of an adequate oxygen supply due to the introduction of a fault in the otherwise faultless interfacial zone. It is most likely that the two 'sulphate rust' specimens that exhibited similar behaviour underwent the same procedure. The breach of the interfacial zone would appear to be caused by the formation of a pit which has been initiated by the presence of chloride ions at the surface of the steel.

None of the specimens that were opened exhibited any form of crevice attack and when the cement/epoxy masking was removed the tops of the bars proved to be in good condition (see figure 6.14). This method of stopping-off the tops of the bars would therefore appear to be effective for periods of at least 18 months and possibly longer.

Samples of concrete were taken from areas adjacent to the steel in those specimens exposed to chloride environments and total chloride ion content determinations carried out as described in chapter 2 (para.2.8). The average values obtained were 2.3% chloride ion by weight of cement for those specimens exposed to saturated calcium hydroxide solution containing 1 mole per litre of sodium chloride and 1.7% chloride ion by weight of cement for the artificial seawater environment. This indicates that chloride ions had penetrated the concrete cover during the period of exposure and the difference between the two values is most probably due to the deposition of magnesium hydroxide in the pores of those specimens exposed to artificial seawater which is known to hinder the penetration of solutions in marine structures. (120)

6.5 CONCLUSIONS

The corrosion products formed by the three environments studied were different in appearance and structure. Where a 'contaminant' was present in the exposure environment it became included into the structure of the corrosion products. It is therefore reasonable to assume that where steel reinforcements are stored near a source of sulphate or chloride ions such as ground water, atmospheric pollution or marine environments, the corrosion products formed on the surface will be characteristic of that environment.

Of the two methods studied for the characterisation of the steel surfaces, Mössbauer spectroscopy provided the most information concerning the structure of the corrosion products while energy dispersive x-ray analysis indicated only the presence of chloride and sulphate ions as 'contaminants'.

During the prolonged exposure to concrete the structures of the three steel corrosion products changed both in appearance and in composition to a smooth, dark grey condition with no apparent sign of corrosion. The composition of this product would appear to be α-FeOOH, γ-FeOOH, γ-Fe_2O_3 and Fe_3O_4. The steel originally pre-rusted in water vapour exhibited a darker grey appearance than the others and this may be due to a larger proportion of Fe_3O_4 (magnetite) in its composition. Steel pre-rusted in ferrous sulphate solution maintains some of its original appearance in the form of yellow-brown streaks which are associated with smooth, continuous areas of the interfacial zone.

Differences observed in the interfacial zones of opened specimens appear to be associated with the surface texture of the steel. Clean, degreased steel with a light, even abrasion produces a smooth continuous interfacial zone which can result in a restriction of the oxygen supply to the surface of the steel causing it to assume a low potential active condition. Embedded steel in this state that was coupled to external steel work such as the superstructure of an oil rig would behave as a large anode and apart from a small amount of corrosion on the embedded steel, the entire structure would remain protected. If, however, the oxygen supply to the embedded steel was plentiful its potential could easily become more noble than that of the exposed steel resulting in a large cathode, small anode situation and potentially disastrous corrosion of the exposed steel.

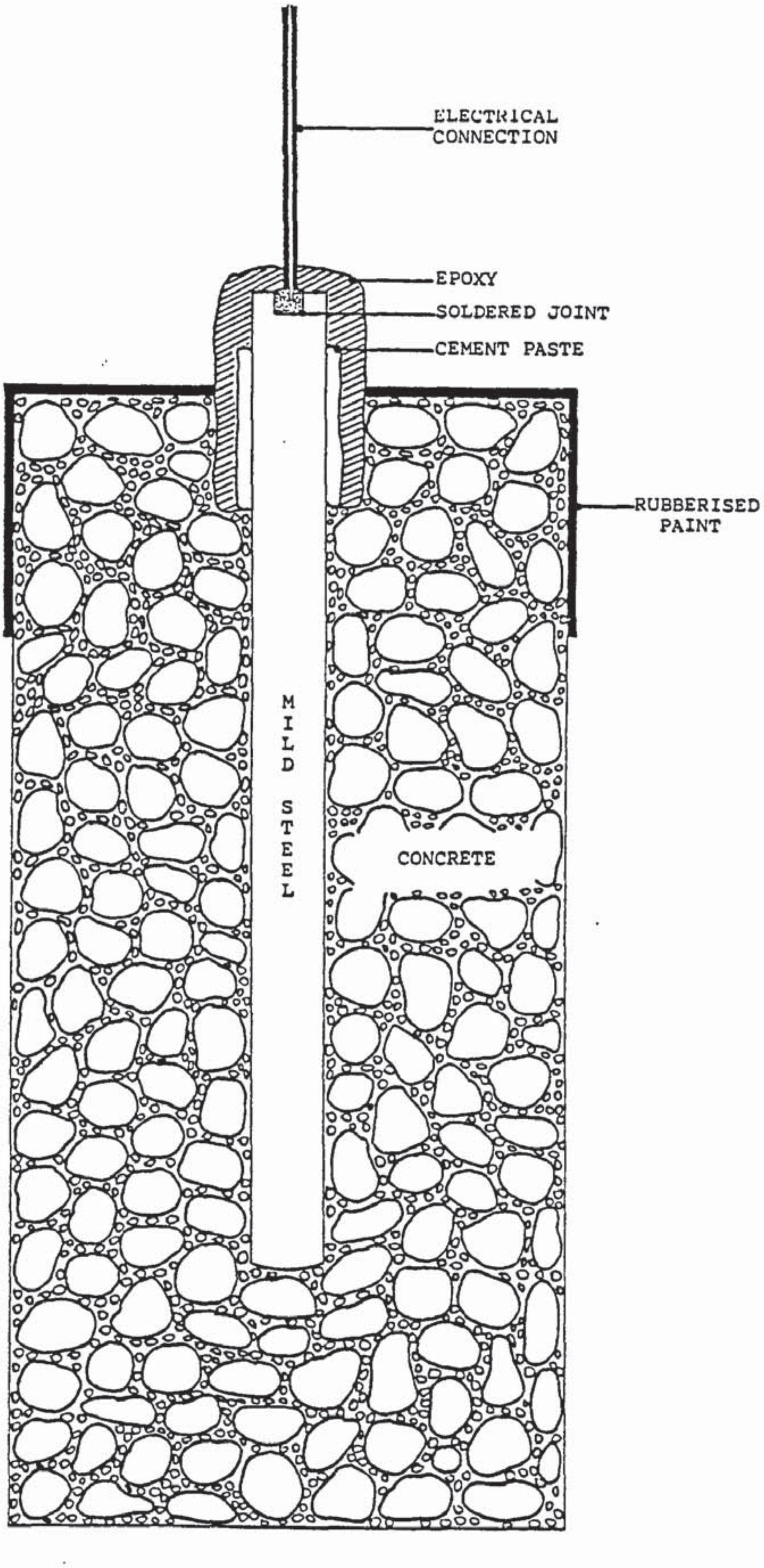
The ability of some of the low potential active specimens to return to a higher potential would suggest that there is a fine balance between the passive and low potential active conditions dependent upon small variations in the availability of oxygen to the steel surface. The effect was only observed on specimens exposed to chloride environments and those specimens examined proved to possess a single, small corrosion pit associated with a rupture in the interfacial zone. It is possible that the action of chloride ions at a point on the steel surface eventually resulted in the reinstatement of the oxygen supply and an associated increase in potential.

Concrete specimens containing the three types of pre-rusted steel have shown little difference in behaviour during the period of exposure to solutions, whether containing chloride ions or not. Those exposed to artificial seawater or calcium hydroxide/sodium chloride solution had chloride ions present at the steel surface at 84 weeks although there was a lower total chloride ion level for the artificial seawater specimens, possibly due in part to blocking of the pores by magnesium hydroxide.

The duplex cement/epoxy masking system employed for the embedded steel specimens would appear to have been successful in avoiding crevice attack and there have been no signs of breakdown with those specimens still on test. The only apparent problem associated with the technique is the uncertain surface area that is exposed to the concrete. Although this is unimportant for rest potential measurements it might result in inaccuracies where other electrochemical techniques are employed which require the area to be known. This would be especially true where a large proportion of the total specimen area was masked.

Figure 6.1

SECTIONAL REPRESENTATION OF EMBEDDED STEEL SPECIMEN



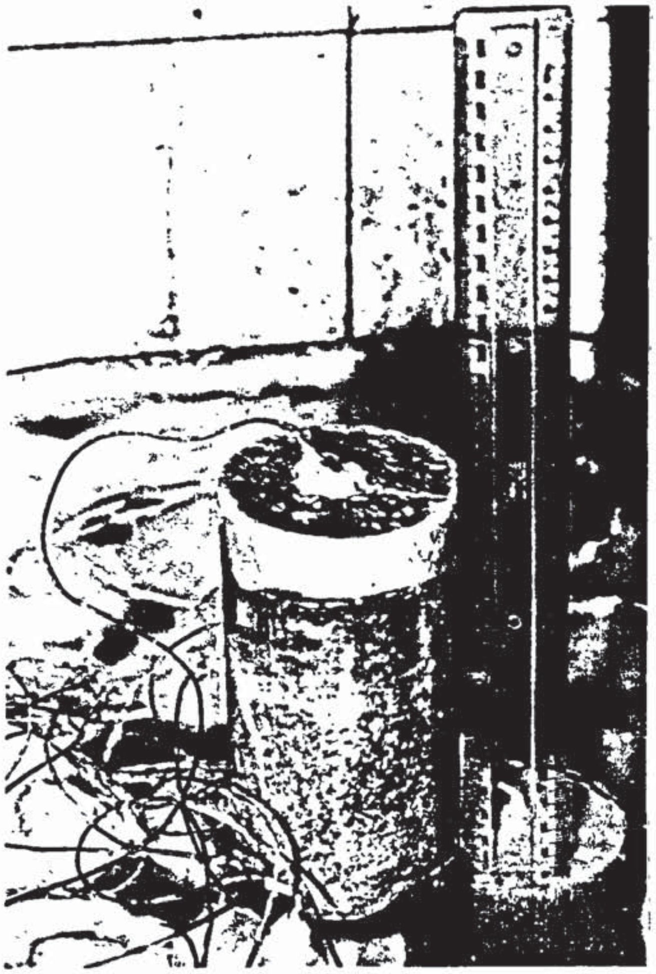


Figure 6.2
EMBEDDED STEEL SPECIMEN

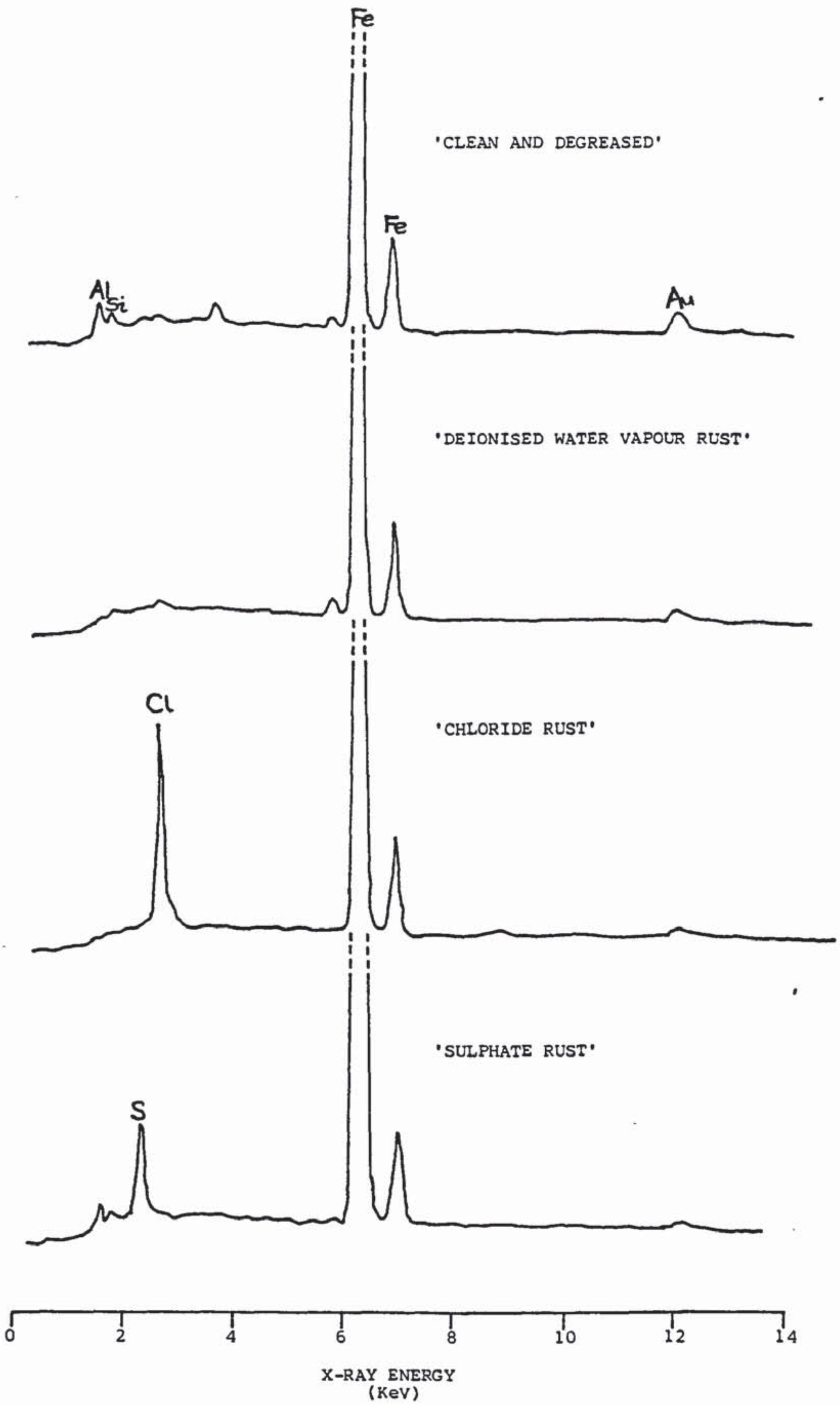


Figure 6.3
E.D.X.A. TRACES FOR ALL FOUR STEEL SURFACE CONDITIONS PRIOR TO EMBEDMENT

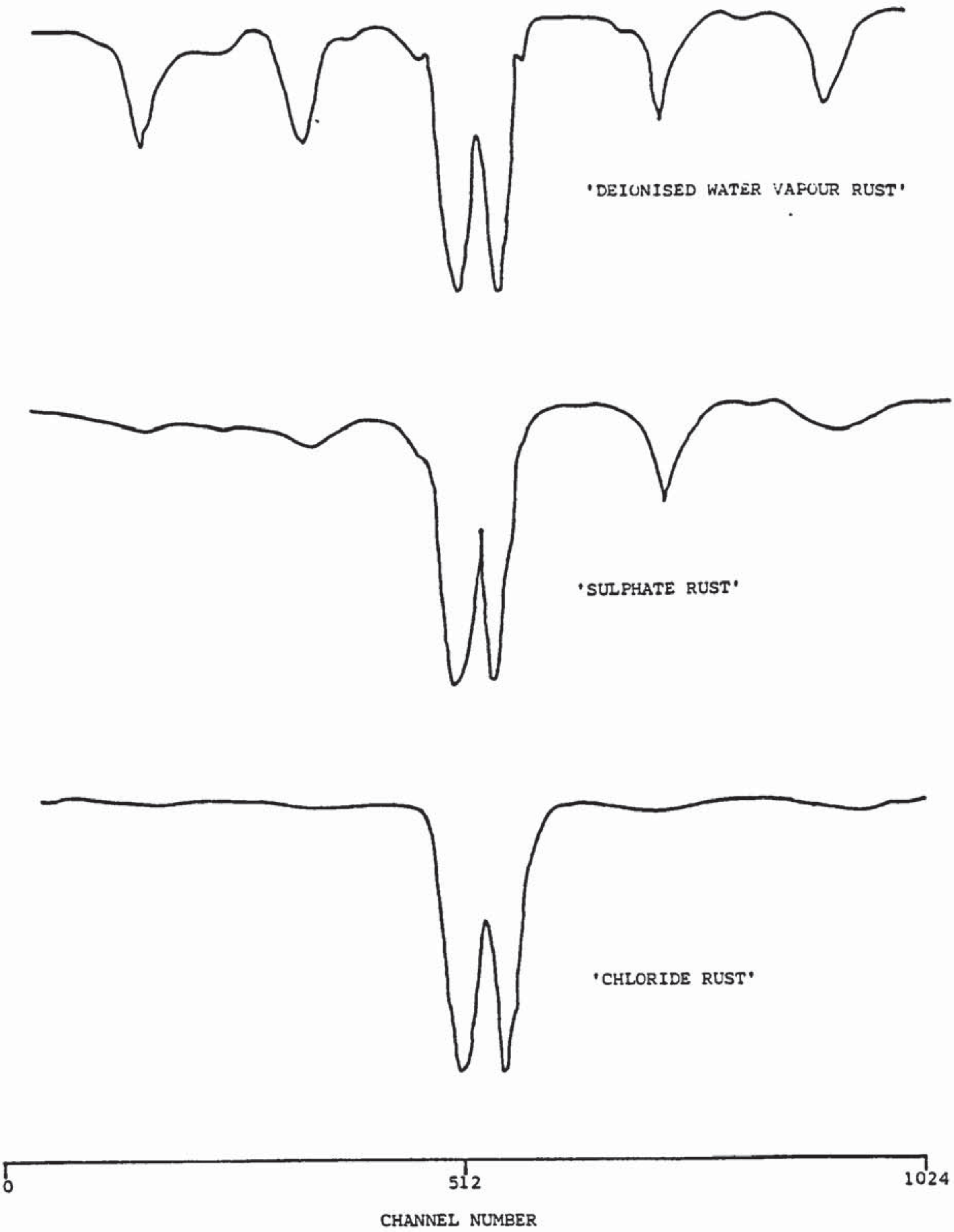


Figure 6.4
MÖSSBAUER SPECTROGRAPHS OF THE THREE SURFACE CORROSION PRODUCTS PRIOR TO EMBEDMENT

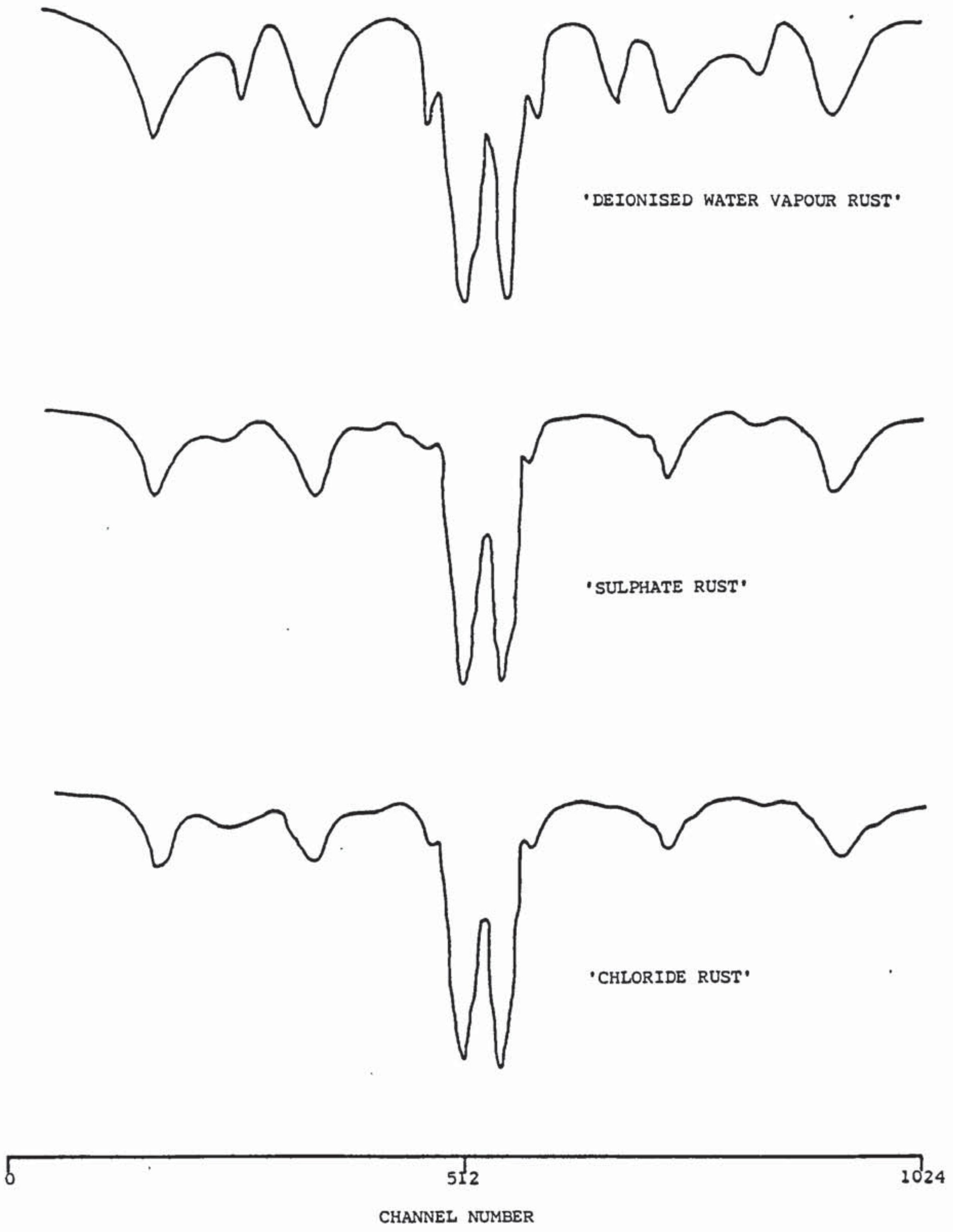


Figure 6.5 MÖSSBAUER SPECTROGRAPHS OF THE THREE SURFACE CORROSION PRODUCTS AFTER BEING EMBEDDED IN CONCRETE FOR 84 WEEKS

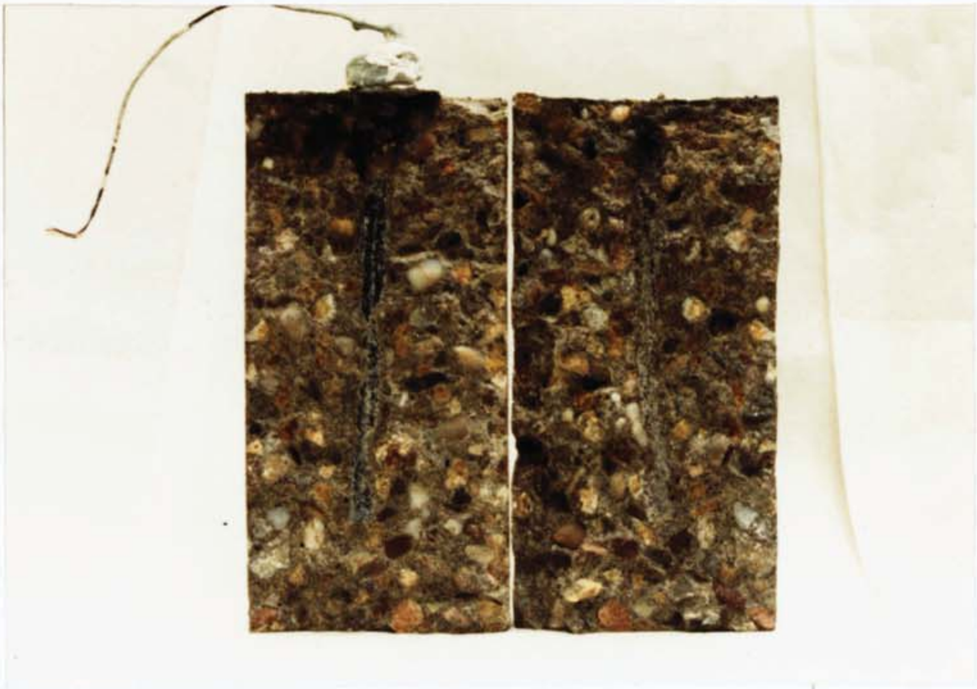


Figure 6.6
OPENED SPECIMEN CONTAINING STEEL WITH 'WATER VAPOUR RUST' (84 WEEKS)

Figure 6.7
OPENED SPECIMEN CONTAINING STEEL WITH 'CHLORIDE RUST' (84 WEEKS)

Figure 6.8
OPENED SPECIMEN CONTAINING STEEL WITH 'SULPHATE RUST' (84 WEEKS)

Figure 6.9
OPENED SPECIMEN CONTAINING STEEL WITH CLEAN AND DEGREASED STEEL (84 WEEKS)

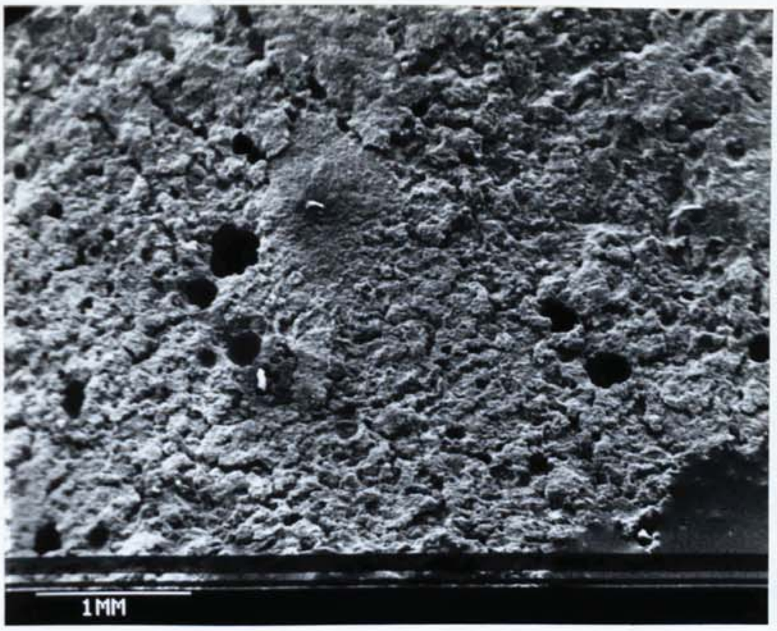


Figure 6.10
INTERFACIAL LAYER FORMED AGAINST 'WATER VAPOUR RUST' (x 20)

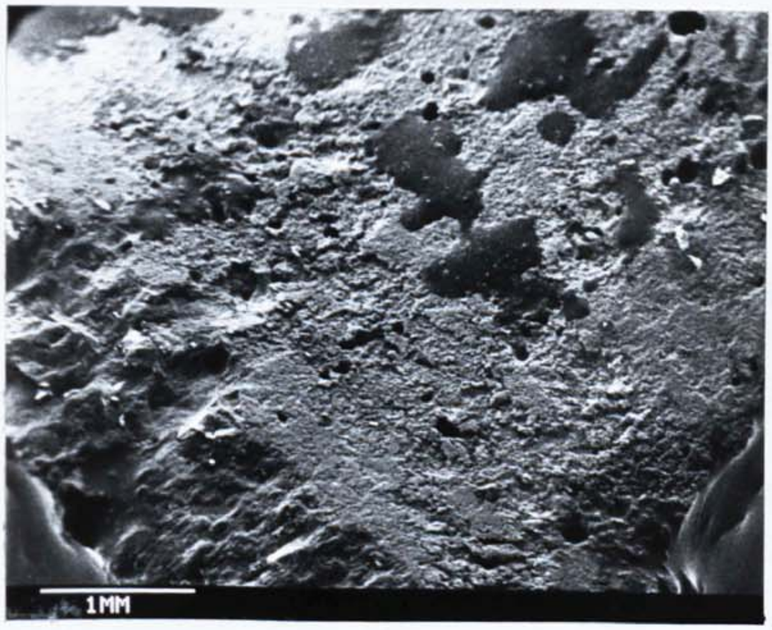


Figure 6.11
INTERFACIAL LAYER FORMED AGAINST 'SULPHATE RUST' (x 20)

Figure 6.12
INTERFACIAL LAYER FORMED AGAINST CLEAN AND DEGREASED STEEL (x20)

Figure 6.13
SMALL AREA OF CORROSION ON EMBEDDED CLEAN STEEL BAR EXPOSED TO A CHLORIDE ENVIRONMENT (84 WEEKS)

Figure 6.14
APPEARANCE OF STEEL BENEATH MASKING (84 WEEKS)

CHAPTER 7

THE EFFECT OF INHIBITORS ON CEMENT PASTE CHEMISTRY AND THE BEHAVIOUR OF EMBEDDED STEEL

7.1 INTRODUCTION

The presence of chloride ions can, as has already been discussed in chapter 3, destroy the passivity of steel in a concrete environment. For passivity to be maintained in the presence of chloride ions a higher concentration of hydroxyl ion in the pore solution is required as indicated by the relationship produced by Gouda (see figure 3.1).

The permeability of the concrete is a major factor in protecting embedded steel from chloride ion attack but where aerated concretes are used or designs require low depths of cover the steel requires additional protection either by treating the steel itself or by improving the ability of the concrete to maintain passivity. Great commercial competition exists between the various coatings and cathodic protection systems which may be used to protect the steel. A further method that has been used to increase the protection offered by concrete is the incorporation of corrosion inhibitors. These may be organic or inorganic substances which when added to the concrete are capable of reducing the corrosion rate of embedded steel to a very low value. A review of these materials has been published. (121)

There are two classes of inhibitor, anodic and cathodic, which inhibit either the anodic or cathodic half of the corrosion reaction. The inhibitors most commonly used in concrete are calcium nitrite, sodium nitrite and sodium benzoate all of which are anodic in action. The mechanism of the action of calcium nitrite on the corrosion of steel in alkaline aqueous solutions containing chloride ions has been examined by Rosenberg and Gaidis by means of polarisation studies.$^{(122)}$

For steel surrounded by an aerated solution containing salt the immediate anodic product is the ferrous ion and cathodic product, the hydroxyl ion. An insoluble product is precipitated at a point between the anodic and cathodic sites. The presence of an anodic inhibitor causes the insoluble iron compound to be precipitated at the weak points in the oxide film where ferrous ions are emerging. Thus the anodic sites are plugged and metal dissolution arrested. Anodic inhibitors which are alkaline when in solution require the presence of oxygen for inhibition to take place but nitrites are effective at maintaining a stable film of ferric oxide even in the absence of oxygen.

All anodic inhibitors have a critical concentration in solution above which inhibition is to be expected. However, if the concentration of the inhibitor falls below this value corrosion of the metal is concentrated on a few points. In the case of iron corroding under cathodic control, as the number of anodic areas is reduced by the action of the inhibitor, anodic polarisation increases while the cathodic area remains effectively the same. This causes the current density at the remaining anodic areas to be increased leading to rapid localised pitting corrosion. Such attack is most serious when the level of inhibitor is slightly sub-critical. Sodium benzoate may be considered to be a safe inhibitor in this sense as it acts on a large area of metal at all times and for this reason is used as a corrosion inhibitor in motor vehicle 'anti-freeze' mixtures. (123)

Where inhibitors have been added to concrete containing steel it is important to know to what extent such substances react with cement compounds or are leached out by external solutions. To study such effects specimens of cement paste containing various levels of inhibitor and chloride ion have been exposed to two environments and the chemistry of the pore solutions analysed. Other specimens containing embedded steel with various levels of inhibitors and chloride ion have been monitored for several weeks in terms of rest potential and polarisation resistance.

7.2 PREVIOUS WORK

Much work has been carried out on the mechanisms of inhibition and the action of inhibitors on steel in both neutral and alkaline solutions, notably by Mayne with both Hancock and Gilroy and by Brasher et al. (124-126) Reviews of such work and of the use of inhibitors in various aggressive environments are given in reference 127.

The effect of inhibitive and other admixtures in the alkaline environment of Portland cement paste was studied by Roberts in 1968. (128) Roberts produced Portland cement pastes of high water cement ratios, typically between 1 and 2. Various amounts of different admixtures were included into the pastes which were then kept agitated so as to maintain the mixture as a slurry. This allowed the removal of liquid for chemical analysis for up to seven days so giving information as to the relative levels of various ionic species during the early stages of hydration. The inhibitive admixtures studied were sodium nitrite and sodium benzoate.

The main observation made in this study was the degree to which the level of each salt was reduced within the first few days due to reaction with the tricalcium aluminate in the cement to form complex hydrated calcium aluminate salts. This has the effect of reducing the concentrations of the inhibitors in solution and consuming some of the tricalcium aluminate which might otherwise combine with and remove chloride ions. A by-product of this reaction between sodium nitrite or benzoate and cement is sodium hydroxide and the effect of the liberated hydroxyl ions on the alkalinity of the cement paste solution was clearly demonstrated.

Work carried out in the same year by Treadaway and Russell concentrated on the use of sodium nitrite and benzoate as admixtures and their effects on steel both in alkaline solutions and concrete. (102) Immersion tests were carried out on steel coupons in alkaline solutions of sodium hydroxide intended to simulate the aqueous phase in concrete and in 'real' pore solutions obtained by hydrating cement with excess water and filtering out the solid phase after several days in the manner employed by Roberts. Both types of solution had various additions of sodium nitrite, sodium benzoate and calcium chloride and were aerated during the exposure period of immersion. Once the exposure was complete the steel specimens were removed from the solutions and any corrosion products cleaned off and analysed by x-ray diffraction. The final traces of corrosion products were dissolved away with Clarke's solution allowing the corrosion rate to be determined by weight loss measurements. Further tests were made by electrochemical means on steel specimens embedded in concrete cylinders containing various levels of sodium nitrite and calcium chloride. Once the specimens had been cured for four days they were connected to a polarisation cell and anodic polarisation measurements taken for twenty minutes. Both the immersion tests and the electrochemical measurements demonstrated the effect of sub-critical levels of sodium nitrite leading to high rates of corrosion. Cubes containing various inhibiting admixtures were tested for compressive strength up to 28 days and the reduction in strength caused by additions of sodium nitrite and more especially sodium benzoate clearly indicated. Their findings led them to list four factors which they felt should be taken into consideration when evaluating an inhibitor. These were the amount of inhibitor required, the rate of consumption of the inhibitor, the type of attack promoted in the presence of the inhibitor and the effect of the inhibitor on concrete strength.

On the basis of these requirements they considered neither nitrite nor benzoate to be individually suitable. The evidence obtained by their work led them to recommend the use of a mixed inhibitor containing both nitrite and benzoate, ideally in the form of a slurry coating to the rebar containing the inhibitors and so helping to overcome the possible loss of strength.

Lundquist Jr., Rosenberg and Gaidis have studied the behaviour of calcium nitrite as an inhibitor in reinforced concrete containing chloride ions by means of various electrochemical procedures and shown that 2 to 4% additions of calcium nitrite may reduce the corrosion rate of steel by a factor of 15 or more compared with that in saturated sodium chloride solution. (129) It must at all times be remembered that the effectiveness of added nitrite ions is directly related to the concentration of chloride ions present, with higher chloride ion levels requiring larger amounts of added nitrite to maintain inhibition. (130)

Lundquist Jr. et al reviewed the electrochemical techniques that had been used in the study of corrosion inhibitors in concrete including corrosion potential (rest potential), polarisation resistance (linear polarisation), impressed current and impressed voltage. Of these, only corrosion potential and polarisation resistance are essentially non-destructive with time and able to avoid interference due to concentration polarisation. (105)

Gonzalez, Algaba and Andrade have employed linear polarisation for the study of steel embedded in carbonated and non-carbonated mortars containing various admixtures including corrosion inhibitors. (50) The calculated electrochemical weight losses for individual steel specimens were compared with weight loss determinations and a linear relationship obtained.

By being able to analyse specimens of 'true' pore solution from well hydrated cement pastes it is hoped that the work described in this chapter will continue the study of the effects of inhibitors on pore solution chemistry looking particularly at the levels of free inhibitor with time and environment and their effect on pore solution alkalinity. Additional specimens containing steel electrodes have allowed a small scale electrochemical study to be carried out.

7.3 EXPERIMENTAL PROCEDURE

The experimental procedures followed for the making-up of cement paste cylinders and discs and the subsequent expression of pore solution were the same as those employed in chapter 3. Portions of ordinary Portland cement were sieved and weighed out for the making of either three cylinders or twenty five discs with a water-cement ratio of 0.5 for each mix and age with each specimen containing an addition of inhibitor. This addition was either 2% calcium nitrite, 1.84% sodium nitrite or a mixture of 1.84% sodium nitrite with 2% sodium benzoate (all percentages by weight of dry cement). 2% calcium nitrite and 1.84% sodium nitrite are each equivalent to 1.23% nitrite ion.

Those specimens to be cast with internal chlorides had an addition of 0.4% sodium chloride. All additions were dissolved in the water prior to mixing. Both calcium and sodium nitrite have been studied as each are used in certain parts of the world, calcium nitrite being commonly used in North America while sodium nitrite is more common in Western Europe.

Once thoroughly mixed the cement pastes were cast into the moulds and vibrated as described in chapter 2 (para.2.3). The cylinders were cured at 100% relative humidity and 25 degrees Centigrade until tested. The discs, none of which contained internal chlorides, were demoulded at 48 hours and placed in 2% sodium chloride solution (equivalent to 0.3419 moles per litre) until tested. A sufficient number of specimens were produced to allow triplicate pressings to be carried out for each mix and age. The method of expression is fully described in chapter 2 (para.2.5).

The triplicate specimens of pore solution produced were analysed for levels of hydroxyl ion, chloride ion, nitrite ion and benzoate ion (para.2.6). Samples of cement paste taken from the specimens prior to pressing were used for evaporable/non-evaporable water content (para.2.7), total chloride determination (para.2.8) and differential thermal analysis (para.2.13). Further cement paste cylinders containing mild steel electrodes were made with additions of 1.84% sodium nitrite, 0.92% sodium nitrite, 1.84% sodium nitrite plus 2% sodium benzoate, 0.92% sodium nitrite plus 1% sodium benzoate and no inhibitor, all in combination with either 1 or 2% chloride ion as sodium chloride. These were maintained at 20 degrees Centigrade and 100% relative humidity while rest potential (para.2.16) and linear polarisation measurements (para.2.17) were made over a period of fifteen weeks. Before being embedded in the cement paste the steel electrodes were cleaned, degreased and masked with epoxy resin so that each exposed an area of 10 square centimetres to the cement paste. A salt bridge was also cast into each specimen so as to allow the electrical connection of a reference electrode. Figures 7.1 and 7.2 show the form of the specimen used.

7.4 RESULTS AND DISCUSSION

The values obtained from the expressed pore solutions for hydroxyl ion, chloride ion, nitrite ion and benzoate ion along with determinations of free and bound water contents are given in Appendix 16. The total levels of chloride, nitrite and benzoate ions are quoted as the amount added during mixing except for the level of total chloride ion in those specimens exposed to 2% sodium chloride solution where the value has been determined as described in chapter 2 (para.2.8). Differential thermograms were obtained for each type of specimen at 50 and 100 days. The 100 day thermograms are given in figures 7.3 to 7.5. The only essential differences between the 50 and 100 day thermograms was the ratio of the Calcium-Silicate-Hydrate gel and calcium hydroxide peak heights. A guide to differential thermogram peaks is given in Appendix 11.

The potential against time and polarisation resistance against time curves obtained for the specimens containing embedded steel are given in figures 7.6 and 7.7. The linear polarisation results have been given in terms of polarisation resistance (Rp) rather than corrosion intensity (Icorr) so as to avoid the need to select suitable and realistic values of Tafel constants for the Stern-Geary relationship (see chapter 2 para.2.17). Rp is inversely proportional to Icorr and as such gives an indication of the corrosion rate.

Working through the results given in Appendix 16 the first effects to be noticed are the low values of free to total percentage of nitrite ion. With 2% calcium nitrite at 100% relative humidity the value is down to below 8% at 50 days and nearer 5% by 100 days. These compare with values of around 5% and 4% for similar specimens containing sodium nitrite for the two periods. The equivalent specimens containing the mixed inhibitor have a free to bound nitrite ion value of just below 4% at both 50 and 100 days.

The pH of the pore solutions for the three types of chloride-free specimen are all above 13.5 and have all increased slightly over the 50 to 100 day period. If the pH values are compared with those obtained for a similar ordinary Portland cement paste containing internal chlorides shown in chapter 3, table 3.1 (around pH 13.8) it will be seen that all those specimens containing only inhibitor have a slightly less alkaline pH.

The values of pH for the three types of specimen containing a low level of internal chloride are slightly higher than for the equivalent specimens with no chloride and it is therefore possible that the presence of chloride ions is required for the complexation of inhibitor with the tricalcium aluminate phase to take place and produce an increase in the pH. The levels of pH are still lower than those obtained for specimens containing only internal chlorides as shown in table 3.1.

The ratios of free to total nitrite in the specimens containing internal chlorides are all slightly higher than those for the specimens with no chlorides. This is possibly due to some of the tricalcium aluminate, which might otherwise have bound nitrite ions, complexing with the free chloride. The ratios of free to total chloride ion reduce with time and are similar to those obtained for inhibitor-free cement paste as given in table 3.1, despite the fact that these have two and a half times as much internal chloride ion. The exceptions are those specimens containing 2% calcium nitrite which have a 50 day value of around 23% compared with nearer 17%. This drops to around 10% by 100 days in line with the other specimens. Thus it would appear that calcium nitrite reduces the initial rate of chloride binding although there is no long term effect. The reasons for this are not clear and as will be seen, no such effect occurs with similar specimens exposed to plentiful supplies of external chloride ion.

The percentages of free to total benzoate ion in the mixed inhibitor specimens containing either no chlorides or a low level of internal chloride ion are all around 35% throughout the period of testing. It is apparent from this that benzoate ions are less capable than nitrite ions of binding with tricalcium aluminate and that complexation that does occur must take place within the first 50 days and is unaffected by small amounts of internal chloride ion.

The most striking results were those that were obtained for the specimens exposed to 2% sodium chloride solution for 50 and 100 days. These may be directly compared to the results obtained for similar specimens of ordinary Portland cement pastes exposed to the same strength chloride solution but containing no inhibitors given in tables 3.2 and 3.3. It is important to note that the values of total nitrite and benzoate ion do not allow for any loss due to leaching which undoubtedly occurs, especially in the case of sodium benzoate.

The values of free to total nitrite for all three types of specimen at 50 days are lower than for the comparable specimens with internal chlorides. The 50 day values for the specimens containing sodium nitrite and the mixed inhibitor are slightly higher than for the comparable specimens containing no chloride. The specimens containing calcium nitrite have an average value of 6.8% compared with 7.7% for the chloride-free specimens. Despite this drop the specimens containing calcium nitrite still have a higher level of free nitrite ion than either of the other two types. This remains the case at 100 days although the free to total nitrite levels in all three types have dropped to around 2%, the worst being 1.4% for the mixed inhibitor system. This large drop has almost certainly been assisted by leaching of the nitrite into the surrounding solution.

If the levels of total and free chloride for the specimens exposed to 2% sodium chloride are compared with the values in tables 3.2 and 3.3 it can be seen that over the 100 day period those containing inhibitors have bound a larger amount of free chloride than those containing none although all but the calcium nitrite specimens were slow starters. Most effective over 100 days have been the specimens containing calcium nitrite and least effective those with the mixed inhibitor. The 100 day free chloride values are similar for all the specimens both with and without inhibitors.

The pH values of the pore solutions for those specimens containing inhibitors are significantly higher than for the similar inhibitor-free specimens exposed to external chlorides. All those with inhibitors have similar values of pH 13.3 at 50 days and pH 13 at 100 days compared with values of around 12.6 for the inhibitor-free specimens. It is interesting to note that the addition of sodium benzoate to form a mixed inhibitor has not produced an added increase in the pH. It has in fact resulted in a decrease in the chloride binding ability of the cement paste and a reduction in the level of free nitrite ion.

The level of free benzoate ion in the mixed inhibitor specimens exposed to external chlorides has dropped dramatically from 35% to less than 10% in the first 50 days. By 100 days this ratio is down to 5.5%. The differential thermograms obtained for those specimens containing mixed inhibitor show the interesting effect of an endothermic peak at 475 degrees Centigrade (see figure 7.5). The relative size of this peak has proved to be proportional to the amount of free benzoate present in the specimens. The fact that it has all but vanished by 100 days for the specimens exposed to external chloride solution (and was in fact not much larger at 50 days) suggests that the balance of the free benzoate has been leached into the surrounding solution. High levels of nitrite, benzoate and hydroxyl ion were detectable in the external solutions throughout the period of exposure despite the solutions being replaced weekly.

The results obtained from the limited number of cement paste specimens containing embedded steel in combination with inhibitors and internal chloride are not as clear as they might be (see figures 7.6 and 7.7). The rest potential against time curves suggest that the specimens displaying the best passive behaviour for both levels of internal chloride were those containing no inhibitor at all. For the polarisation resistance against time curves (where a high value is consistent with passivity) the behaviour would appear to be the same at 1% of chloride ion and it is only at 2% chloride where there would appear to be some slight gain, namely by the mixed nitrite-benzoate inhibitor both at 'full' and 'half' strength. Indeed, all the electrochemical data suggests the superiority of the mixed inhibitor.

When a number of the specimens were opened at 30 weeks all the steel electrodes were suffering from some form of crevice attack at the steel/epoxy interface except for those specimens containing the mixed inhibitor (see figures 7.8 and 7.9). Other specimens which were opened at 15 weeks showed no signs of corrosion at all. It would appear therefore that the mixed nitrite-benzoate inhibitor is superior to nitrite alone where internal chlorides are present. The exception would seem to be where there was a risk of leaching by an external solution which would remove much of the free benzoate ion and result in a free nitrite ion level lower than would be the case for an addition of nitrite alone.

7.5 CONCLUSIONS

The addition of calcium nitrite to ordinary Portland cement paste results in a higher concentration of free nitrite ions than would an equivalent addition of sodium nitrite. Sodium nitrite is, however, more effective than calcium nitrite at maintaining a high pore solution pH.

For all the inhibitor systems studied in this work, a small addition of internal chloride ion (0.4% sodium chloride) increases the pH and concentration of free nitrite ions in the pore solution.

A mixed addition of sodium nitrite and sodium benzoate would appear to be the most effective inhibitor where steel embedded in ordinary Portland cement paste is to be exposed to internal chlorides. However, where there is a likelihood of leaching, especially by a chloride-bearing solution, a single addition of sodium or calcium nitrite would result in a higher level of free nitrite ion.

Figure 7.1
EMBEDDED STEEL SPECIMEN FOR POLARISATION RESISTANCE MEASUREMENTS

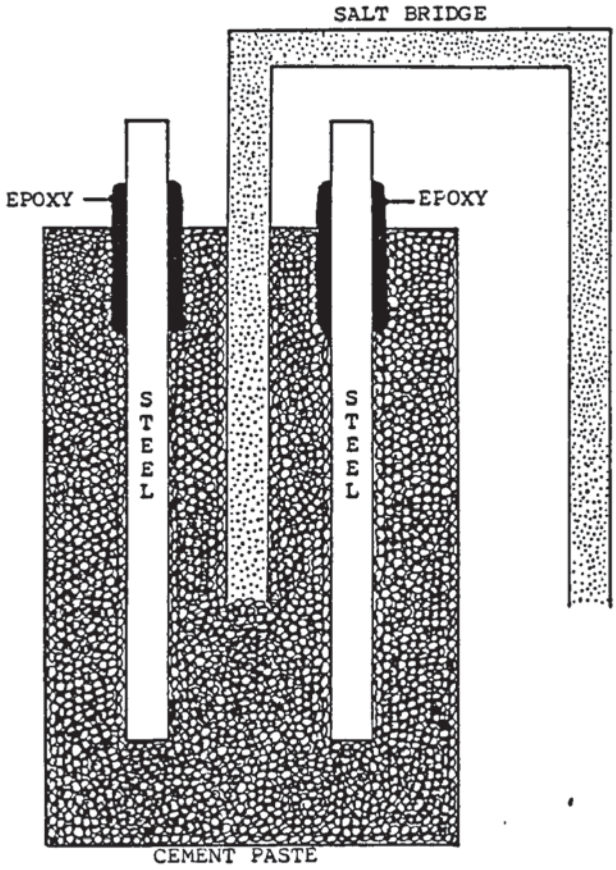


Figure 7.2
SECTIONAL DIAGRAM OF
EMBEDDED STEEL SPECIMEN

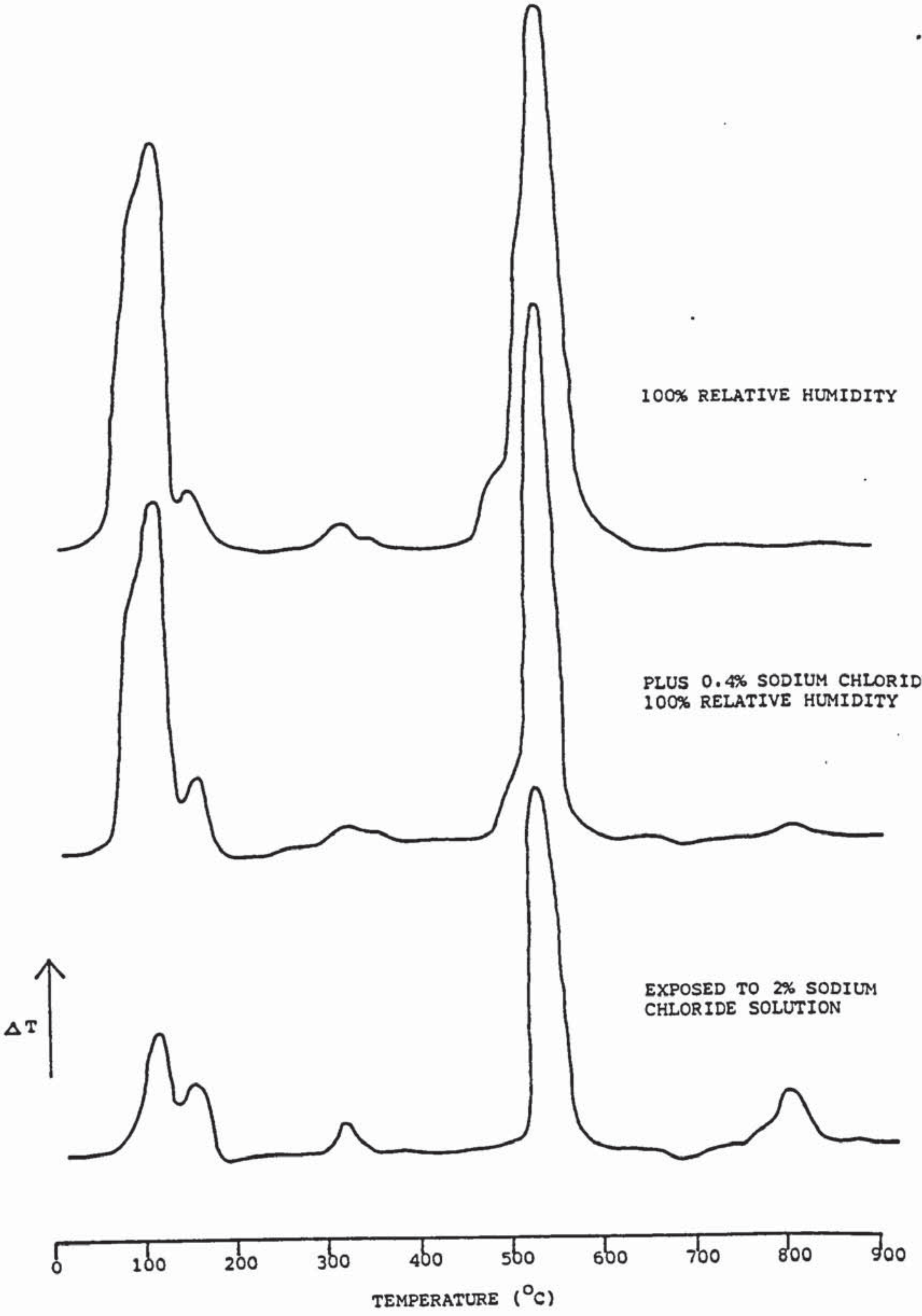


Figure 7.3
DIFFERENTIAL THERMOGRAMS OF CEMENT PASTE SPECIMENS CONTAINING 2% CALCIUM NITRITE (100 DAYS)

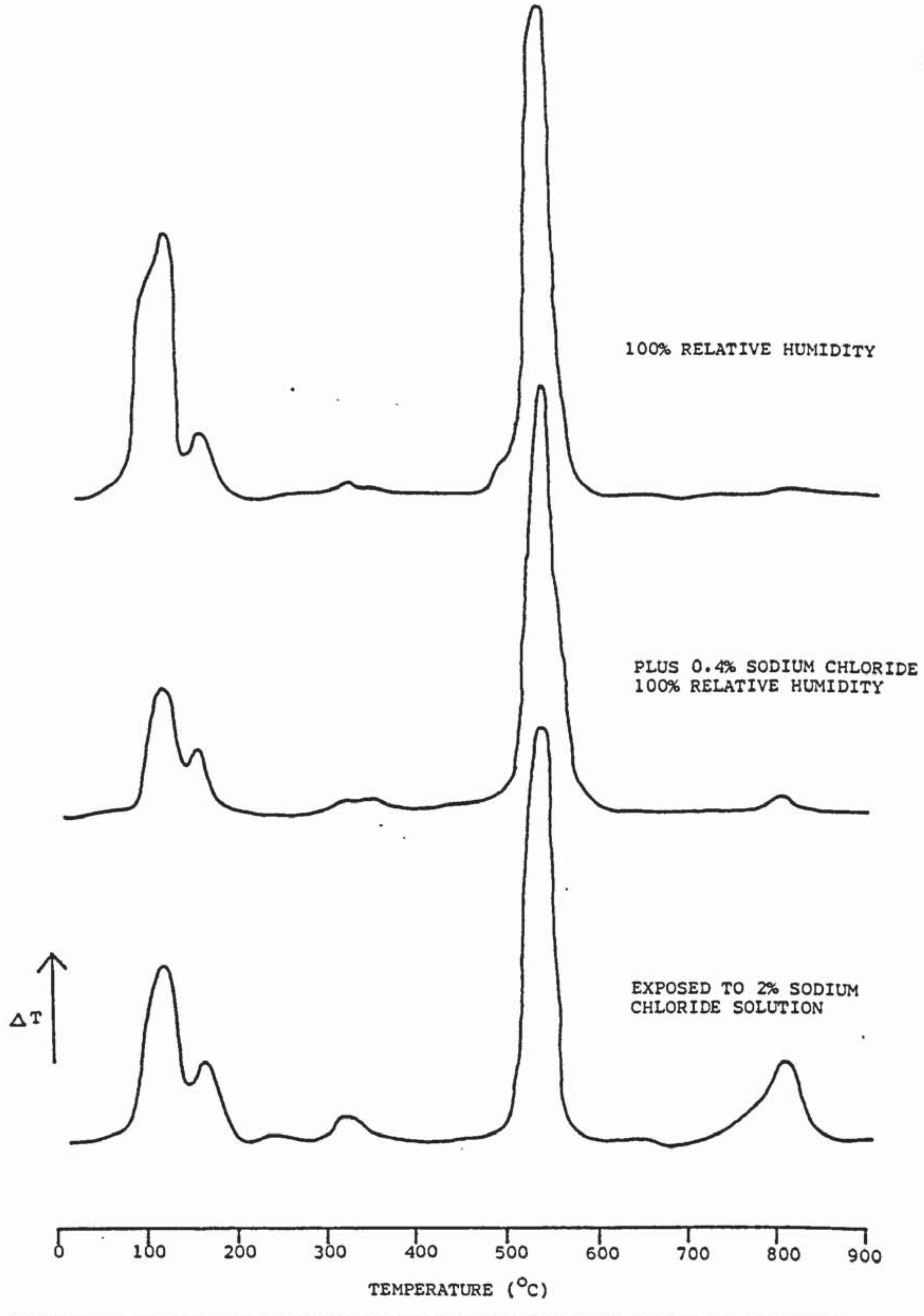


Figure 7.4
DIFFERENTIAL THERMOGRAMS OF CEMENT PASTE SPECIMENS CONTAINING 1.84% SODIUM NITRITE (100 DAYS)

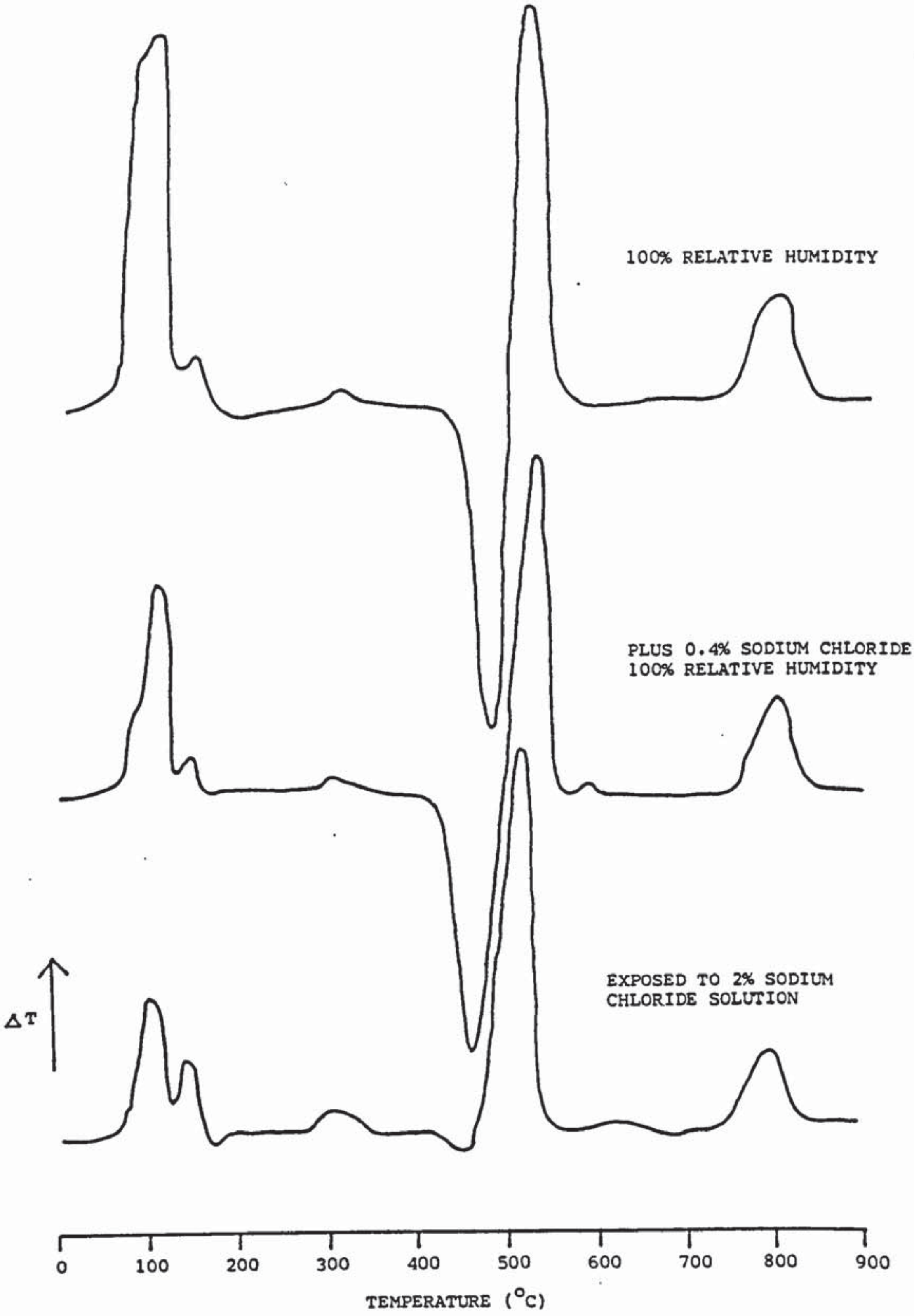
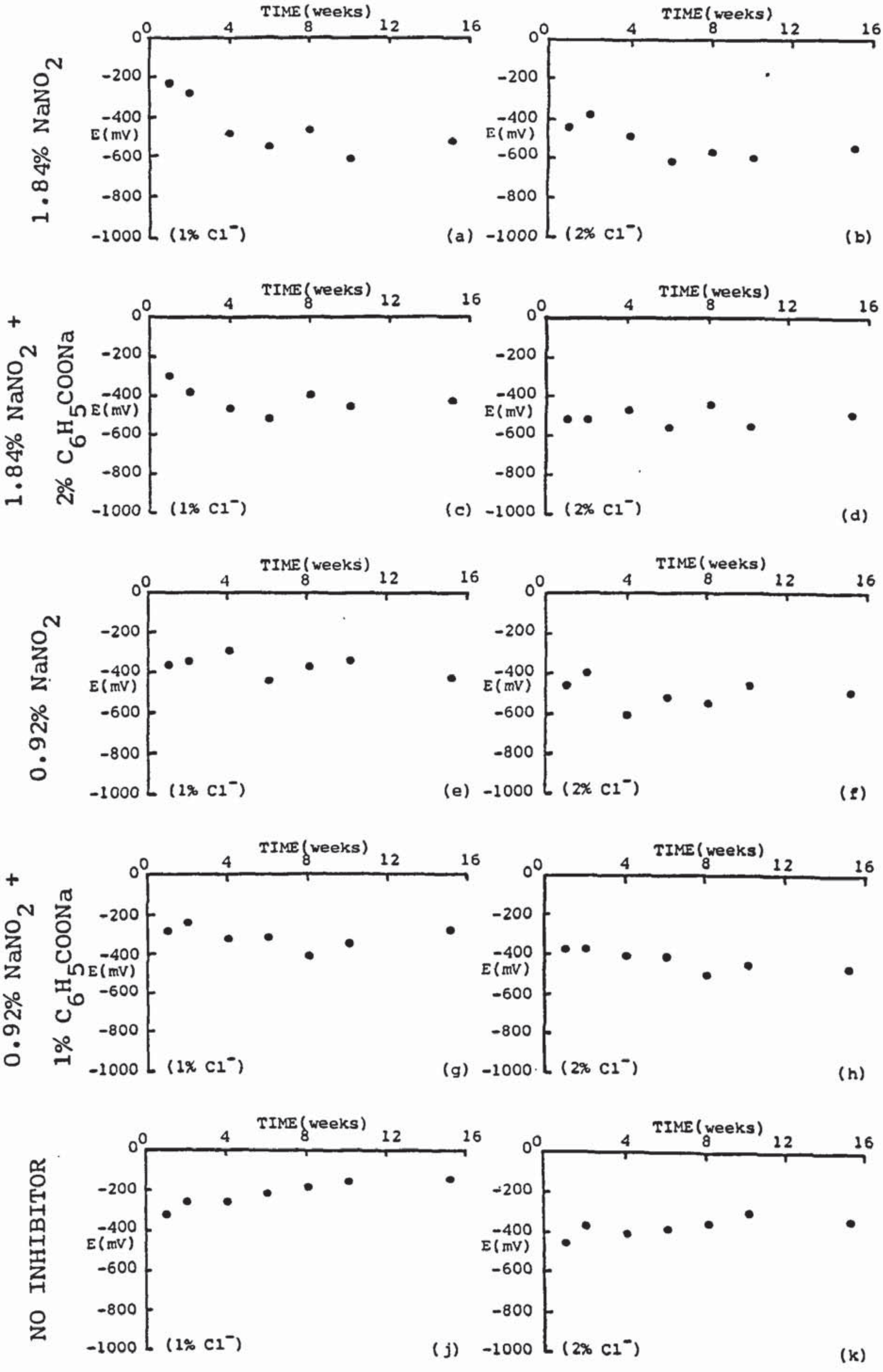


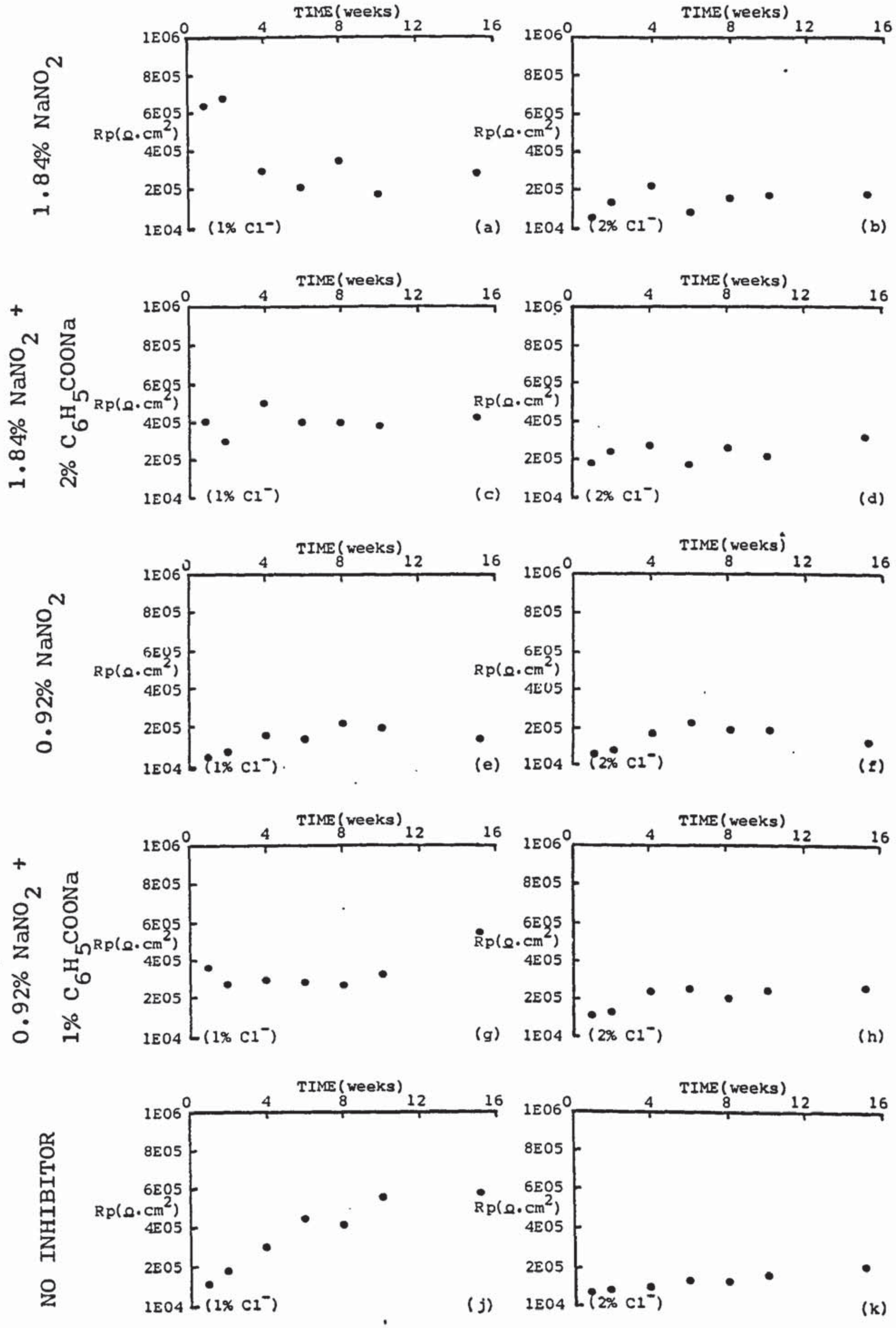
Figure 7.5
DIFFERENTIAL THERMOGRAMS OF CEMENT PASTE SPECIMENS CONTAINING 1.84% SODIUM NITRITE PLUS 2% SODIUM BENZOATE (100 DAYS)

ALL POTENTIALS MEASURED VERSUS SATURATED CALOMEL ELECTRODE.



ALL POINTS ARE THE AVERAGE OF THREE RESULTS FROM SEPARATE SPECIMENS.

Figure 7.6 POTENTIAL/TIME CURVES FOR STEEL IN CEMENT PASTE CONTAINING INHIBITORS AND CHLORIDE IONS



ALL POINTS ARE THE AVERAGE OF THREE RESULTS FROM SEPARATE SPECIMENS.

Figure 7.7 POLARISATION RESISTANCE/TIME CURVES FOR STEEL IN CEMENT PASTE CONTAINING INHIBITORS AND CHLORIDE IONS

Figure 7.8
EMBEDDED STEEL SPECIMEN SHOWING CREVICE ATTACK
(0.92% sodium nitrite plus 1% Cl^-, 30 weeks)

Figure 7.9
EMBEDDED STEEL SPECIMEN SHOWING NO CREVICE ATTACK (1.84% sodium nitrite, plus 2% sodium benzoate, plus 2% Cl^-, 30 weeks)

CHAPTER 8

GENERAL CONCLUSIONS AND RECOMMENDATIONS FOR FURTHER WORK

8.1 GENERAL CONCLUSIONS

An attempt has been made to study some of the factors that affect the behaviour of steel embedded in a cementitious environment. It has been shown that cements of differing tricalcium aluminate content are affected in different ways by internal and external sources of the depassivating chloride ion. Ordinary Portland cement paste exposed to chloride ions from an internal source can complex around 50% more free chloride ions than a similar paste made with sulphate resisting Portland cement. When exposed to an external chloride solution the ordinary Portland cement performs better initially but eventually both cement pastes approach a free chloride ion level in equilibrium with the external solution. Ordinary Portland cement is generally more effective at maintaining a high pH but when exposed to an external solution both it and the sulphate resisting Portland cement gradually lose calcium hydroxide by leaching and approach a buffered pH of around 12.5. The pH of sulphate resisting Portland cement paste drops at a faster rate than the ordinary Portland cement, possibly due to a more open pore structure.

Previous workers have examined aspects of the mechanism by which chloride ions from external sources diffuse through hydrated Portland cement matrices. In an attempt to further the understanding of the mechanism involved an activation energy was determined for the diffusion of chloride ions through discs of hydrated alite prepared in the laboratory. The value of 33·4 ± 4·9 kiloJoules per mole obtained proved to be similar to those previously obtained by other workers for unblended Portland cement pastes. This suggests that the diffusion of chloride ions through Portland cement pastes is by means of a single activated step associated with the Calcium-Silicate-Hydrate gel.

The method used to produce pure alite proved suitable for the production of tricalcium aluminate and several hydrated alite discs were prepared containing 3% and 12% additions of tricalcium aluminate. When tested at 25 degrees Centigrade they proved to have slightly lower diffusion coefficients than the equivalent pure alite discs, possibly due to some complexation of the chloride ions. Whereas the pore structure of the pure hydrated alite was tight and compact, the structures of the blended mineral hydrates were found to be more open and similar to commercial cements. Hydrated alite cylinders containing sources of internal chloride ions had their pore solution expressed and analysed after 200 days and it was found that there was no significant binding of the ions by the mineral.

As fully hydrated alite should consist solely of Calcium-Silicate-Hydrate gel and calcium hydroxide (portlandite), any difference in the behaviour of mild steel exposed to hydrated alite or calcium hydroxide solution, each containing chloride ions, must be a result of the presence of the gel. Abraded steel in saturated calcium hydroxide solution containing no chloride ions remained passive during the period of testing but as soon as even 250 ppm of chloride ion were present, severe corrosion occurred.

Similar mild steel specimens exposed to hydrated alite containing internal and external sources of chloride ion demonstrated drops in potential which would indicate that the steel was either passive and in a low oxygen environment or undergoing localised breakdown of the passive film with high oxygen access. However, upon removal of the alite cover, none of the specimens had proved to have corroded despite the fact that the depth of cover was less than 5 millimetres. The lowering of the potential was most likely due to a restriction of oxygen access, assisted by the presence of a high quality, lime-rich interfacial layer. A further set of steel specimens embedded in hydrated alite but coupled to large external stainless steel cathodes with an abundant supply of oxygen demonstrated noble passive potentials throughout the test period and the steel remained unattacked.

In reality, steel is not normally clean and bright when embedded in concrete and it was therefore thought necessary to compare the long term behaviour of clean steel with embedded steel specimens bearing corrosion products formed in different environments. The nature of the corrosion products produced on the three types of pre-rusted bar proved to be characteristic of the environments they were formed in. When exposed to 100% relative humidity all four types of steel behaved in a totally passive manner for the entire period of testing. When exposed to saturated calcium hydroxide solution, both with and without 1 mole per litre of sodium chloride, and artificial seawater all the pre-rusted bars behaved in a manner consistent with passivation or localised corrosion depending upon the availability of oxygen. Chloride ions were detected as present in the regions adjacent to the steel for those specimens exposed to chloride-bearing solutions, the specimens exposed to artificial seawater proving to have a lower total chloride ion content than those exposed to saturated calcium hydroxide solution containing sodium chloride, possibly due, in some part, to blocking of the pores by magnesium hydroxide. When removed from the concrete after 84 weeks the pre-rusted bars proved to be, for the most part, coated with a comparitively smooth, hard, dark grey material which when analysed by Mössbauer spectroscopy appeared to be similar in structure for all specimens being a mixture of α-FeOOH, γ-FeOOH, γ-Fe_2O_3 and Fe_3O_4.

The cement/steel interfacial zones associated with the bars pre-rusted in deionised water vapour and 1 molar sodium chloride solution were open and porous in structure while the interface associated with the bars pre-rusted in 1 molar ferrous sulphate solution were partly porous and partly smooth and continuous, the continuous regions being associated with areas of the bars that had maintained their original appearance. The inference made from this being that the continuous form of interface was less effective than the porous, discontinuous form at converting the rust to the dark grey coating.

The clean steel that had been grit blasted and degreased demonstrated certain unusual behaviour patterns when exposed to solutions. Around half of the specimens dropped to a low potential approaching -1 volt, in some cases within a few days, a condition where the steel is active but low oxygen access results in only slight generalised corrosion. This may be referred to as the low potential active condition. Some of those exposed to solutions containing chloride ions later returned to higher potentials after 30 to 40 weeks. When opened, the clean steel specimens proved to be free from rust, including those at a low potential, and the surface to be a dull grey all over, the exceptions being those specimens which had returned to a higher potential. These were found to each possess a single small area of localised corrosion which had, in turn, resulted in a small rupture in the interfacial zone which was otherwise smooth and continuous. It would appear, therefore, that the faultless nature of the interfacial zone, coupled with the lower oxygen environments of the solution, had resulted in some of the specimens dropping in potential due to there being an inadequate oxygen supply to fully maintain the cathodic reaction at the surface of the steel. However, where chloride ions were present, some had penetrated to the surface of the steel, possibly assisted by a small fault, resulting in the formation of a pit. The associated corrosion products had then ruptured the interfacial zone, increasing the oxygen supply by the small amount required to tip the balance from active to passive.

The method employed for masking the ends of the steel bars proved to be totally successful in so far as avoiding crevice attack and should prove to be suitable for many other applications where electrochemical measurements are to be made, provided the masking accounts for only a small percentage of the total area of the specimen. One complaint that might be made concerning this work is that the quality of the concrete cover (as determined by compressive strength measurements) is higher than would typically be encountered on site. It does, however, demonstrate what can be expected with a good quality concrete cover.

Where an adequate depth of cover is not possible due to design constraints or where reinforced concrete is to be exposed to a particularly aggressive environment it may be necessary to improve the corrosion resistance of the embedded steel. One way of accomplishing this is to include inhibitors into the mix, typically anodic inhibitors such as calcium nitrite, sodium nitrite and sodium benzoate. Specimens of ordinary Portland cement paste, containing single additions of calcium nitrite and sodium nitrite and a combined addition of sodium nitrite plus sodium benzoate, were exposed to 100% relative humidity and internal and external sources of chloride ion. The analysis carried out on the expressed pore solutions showed the extent to which such inhibitors are removed by complexation or leached out by external solutions.

The amount of free nitrite ion remaining in the specimens exposed to 100% relative humidity for 100 days was around 4% of the original addition while the free benzoate ion maintained a level nearer to 35% of the original amount. The inclusion of a small amount of internal chloride ion resulted in the free nitrite ion levels increasing slightly to around 5%, possibly due to preferential complexation of the chloride ions by the tricalcium aluminate phase, while the free benzoate ion level remained very much the same. When exposed to external solutions containing sodium chloride the free nitrite ion levels dropped within 100 days to around 2% and the free benzoate to less than 6% of the original additions. This was aided, no doubt, by leaching the ions into the surrounding solution.

From the pore solution analysis results obtained it would appear that the addition of calcium nitrite to ordinary Portland cement paste results in a slightly higher free nitrite ion level than would be the case for an addition of sodium nitrite containing the same concentration of nitrite ions. Sodium nitrite, on the other hand, is more effective than calcium nitrite at maintaining the alkalinity of the pore solutions.

An electrochemical study was made of abraded mild steel specimens embedded in ordinary Portland cement paste containing different levels of single and mixed inhibitors and internal chlorides and exposed to 100% relative humidity. The results suggested that the most effective inhibitor system of those studied was a mixed addition of sodium nitrite and sodium benzoate. The pore solution data would, however, indicate that where there was a possibility of leaching by an external solution, such as in a marine environment, a single addition of sodium nitrite or calcium nitrite would ultimately result in a higher level of free nitrite ion while still maintaining the pH.

8.2 RECOMMENDATIONS FOR FURTHER WORK

A study could be carried out of the relative free to bound chloride ion levels in pastes made with different commercial Portland cements and alite pastes containing varying amounts of tricalcium aluminate so as to determine to what extent chloride ion binding is a function of tricalcium aluminate content. It may be possible to grade commercial cements by their chloride ion binding capacity and ability to maintain pore solution alkalinity.

Portland cement paste specimens could also be exposed to solutions containing both chlorides and sulphates and analyses carried out to determine if either react preferentially with the tricalcium aluminate phase. Chloride diffusion measurements could be carried out on discs previously exposed to internal and external sources of chlorides and sulphates.

Many further studies could be performed with alite, especially in combination with other cement minerals which it might be possible to produce by the same basic method. The diffusion of species such as chloride ions, hydroxyl ions and oxygen through such materials would provide essential information as to the mechanisms involved. Diffusion measurements through alite cast against different steel substrates could provide much information with regard to the nature of the steel/cement interfacial zone.

More work needs to be carried out on the nature of rusted steel both before and after being embedded in concrete. Mössbauer spectroscopy could be employed to determine the structure of corrosion products produced on reinforcing steels that have been taken from site conditions. If such information were coupled with exposure tests it might ultimately lead to more comprehensive recommendations concerning the site storage and treatment of reinforcements prior to use.

It might be possible to develop the method employed for the masking of steel bars in chapter 6 as a repair system for exposed reinforcements or even as an alternative coating system to galvanising or epoxy resin.

There is a need for a long term study of clean and pre-rusted steels embedded in concretes containing many types and levels of corrosion inhibitors and exposed to various aggressive environments. The practice of applying inhibitors to reinforcements in a slurry so as to overcome leaching and loss of compressive strength could also be looked at with special regard to the diffusion of the inhibitors into the body of the concrete and possible reductions in the steel/concrete bond strength.

APPENDIX 1

TWENTY EIGHT DAY COMPRESSIVE STRENGTH MEASUREMENTS OF CONCRETE USED FOR THE PRODUCTION OF SPECIMENS IN CHAPTER 6

Worked example :

Maximum load = 733 KN

Cross-sectional area = 10 000 mm^2

$$\text{COMPRESSIVE STRENGTH} = \frac{733\ \text{KN}}{10\ 000\ \text{mm}^2}$$

$$= 73.3\ \text{MN/m}^2$$

Result for all cubes :

The results for all thirty two cubes tested (given in MN/m^2) are given below

73	70	70	73	71	73	75	71
71	70	69	74	76	71	70	72
73	70	73	70	73	71	77	76
74	70	76	74	73	71	77	73

Average compressive strength = 72.5 MN/m^2

Standard Deviation = 2.25

APPENDIX 2

EXAMPLE CALCULATIONS FOR HYDROXYL, CHLORIDE, NITRITE AND BENZOATE IONS IN PORE SOLUTIONS AND CALIBRATION CURVES FOR THE SPECTROPHOTOMETRIC DETERMINATION OF CHLORIDE AND NITRITE ION CONCENTRATIONS

HYDROXYL ION (pH) :

For a 0.1 ml aliquot.

Titre (10 mM nitric acid) = 4.45 mls

$$(OH^-) = (4.45 \times 0.01 \times 10)M = 0.445\ M$$

$$\begin{aligned} pH &= 14 + \log_{10}(OH^-) \\ &= 14 + \log_{10}(0.445) \\ &= 14 + (-0.35) \\ &= 13.65 \end{aligned}$$

CHLORIDE ION :

For a 0.1 ml aliquot made-up to 10 mls.

Spectrophotometer reading = 0.774 ABS.

From calibration curve $\equiv$ 410 μM Cl^-

As the solution has been diluted by a factor of 100

$$\begin{aligned} (Cl^-) &= ((4.10E-04) \times 100)M \\ &= 0.0410\ M \\ &= 41.0\ mM \end{aligned}$$

NITRITE ION :

For a 0.1 ml aliquot made-up to 100 mls.

Spectrophotometer reading = 0.339 ABS.

From calibration curve ≡ 2.175 µM NO_2^-

As the solution has been diluted by a factor of 1000

(NO_2^-) = ((2.175E-06)x1000)M

= 0.002175 M

= 2.175 mM

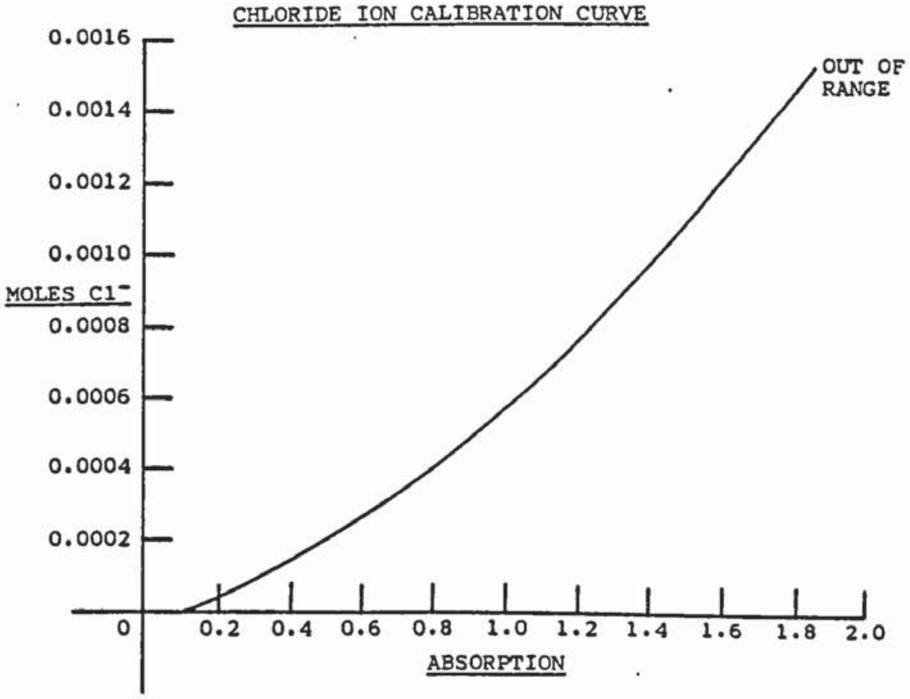
BENZOATE ION :

For a 0.1 ml aliquot (neutralised to phenolphthalein with sulphuric acid).

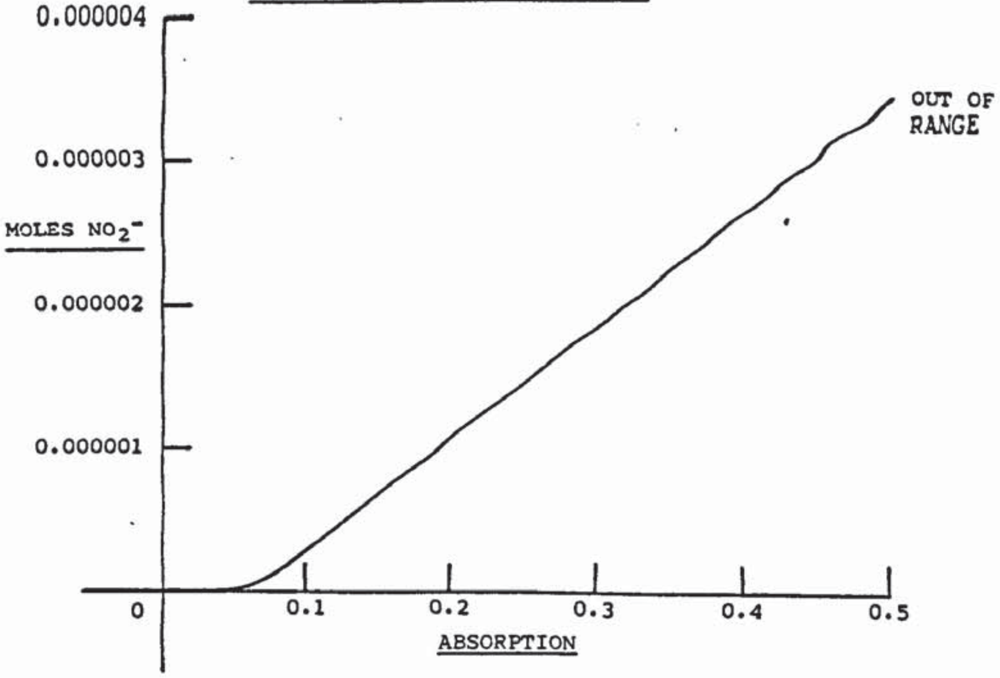
Titre (10 µM sulphuric acid in ether) = 0.78 mls

$(C_6H_5COO^-)$ = (0.78x0.00001x10x2)M

= 0.1560 mM



CHLORIDE ION CALIBRATION CURVE



NITRITE ION CALIBRATION CURVE

APPENDIX 3

CALCULATION OF EVAPORABLE AND NON-EVAPORABLE WATER

Original mass of specimen = 2.2181g = W_o

Mass of specimen at 105°C = 1.7639g = W_{105}

Mass of specimen at 950°C = 1.4538g = W_{950}

% Loss-on-ignition = 2.44% = i

% Admixture content = 2.00% = a

$$\text{EVAPORABLE WATER(\%)} = \frac{W_o - W_{105}}{W_{950}}(100 - i + a)$$

$$= \frac{2.2181-1.7639}{1.4538}(100-2.44+2)$$

$$= 31.10\%$$

$$\text{NON-EVAPORABLE WATER(\%)} = \frac{W_{105}(100 - i + a) - W_{950}(100 + a)}{W_{950}}$$

$$= \frac{1.7639(100-2.44+2)-1.4538(100+2)}{1.4538}$$

$$= 18.80\%$$

Actual water-cement ratio = 0.3110 + 0.1880

= 0.4990

APPENDIX 4

DETERMINATION OF TOTAL CHLORIDE CONTENT

Weight of sample to be tested = 2.4142g

Equivalent weight at $950^{\circ}C$ = $2.4142 \times \frac{a}{b}$

where b and a are the weights of a second sample of cement at $105^{\circ}C$ and $950^{\circ}C$ respectively after corrections for admixture content and loss-on-ignition

$$= 2.4142 \times \frac{2.3419}{2.7778}$$

$$= 2.0354g$$

Spectrophotometer reading = 0.788 ABS.

Molarity of chloride ≡ 0.00042 M

Dilution factor = 100

(Cl^{-}) in the solution = 0.042 M

$$\text{TOTAL CHLORIDE CONTENT} = \frac{(0.042)}{(2.0354)\ (100)}$$

$$= 0.2063 \text{ mM/g}$$

APPENDIX 5

WORKED EXAMPLES OF DENSITY AND FINENESS CALCULATIONS

Density of displacement liquid :

$$\rho L = \frac{W_2}{W_1} \times \rho W$$

Temperature = 19°C

Mass of bottle = 31.4494g

Mass of bottle filled with pure water = 80.9570g

Mass of bottle filled with displacement liquid = 74.0951g

Density of water = 0.9984 g/cm^3

$$\rho L = \frac{(74.0951-31.4494)}{(80.9570-31.4494)} \times 0.9984$$

DENSITY OF DISPLACEMENT LIQUID, ρL = 0.8600 g/cm^3

Density of alite :

$$\rho = \frac{W_4 \times \rho L}{W_3 + W_4 - W_5} \times 1000$$

Temperature = 19°C

Mass of bottle = 31.4494g

Mass of bottle filled with displacement liquid = 74.0951g

Mass of bottle and sample = 40.7412g

Mass of bottle, sample and displacement liquid = 80.8428g

Density of displacement liquid = 0.8600 g/cm^3

$$\rho = \frac{9.2918 \times 0.8600}{74.0951+9.2918-80.8428} \times 1000$$

DENSITY OF ALITE (to nearest 10 kg/m^3), ρ = 3140 kg/m^3

Fineness determination of alite :

$$S = \frac{14}{\rho\,(1-\epsilon)}\sqrt{\frac{\epsilon^3.Ai}{v.Q}} \times 100$$

Temperature = 19°C

Density of alite = 3.14 g/cm^3

Porosity of powder bed = 0.475

Cross-sectional area = 5.067 cm^2

Hydraulic gradient = 16.684

Kinematic viscosity of nitrogen (19°C) = 14 Ns/m^2

Rate of flow = 0.1064 cm^3/s

$$S = \frac{14}{3.14(1-0.475)}\sqrt{\frac{0.475^3 \times 5.067 \times 16.684}{14 \times 0.1064}} \times 100$$

SPECIFIC SURFACE OF ALITE, S = 2095 cm^2/g

APPENDIX 6

EXAMPLE CALCULATION OF PORE SIZE DISTRIBUTION

Porosimeter data and calculations for 0.6 w/c ALITE :

APPLIED PRESSURE (p.s.i.)	PENETRATION COUNTER INDICATION	PORE DIAMETER (nm)	VOLUME OF PORES OF INDICATED DIAMETER AND LARGER (cm^3/g)
1	9	124 000	1.37E-03
2	17	62 450	2.58E-03
100	74	1 249	1.12E-02
600	80	208	1.22E-02
1 500	86	83	1.31E-02
2 500	92	50	1.39E-02
4 000	111	31	1.69E-02
6 000	385	21	5.85E-02
9 000	951	14	0.1445
12 000	1 207	10	0.1833
18 000	1 380	7	0.2096
22 000	1 428	6	0.2169
28 000	1 461	5	0.2220
38 000	1 503	4	0.2283
48 000	1 507	3	0.2289

Contact angle = 117^o

Penetration counter indication corrected by subtracting readings from 'blank' run.

APPENDIX 7

DETERMINATION OF FREE LIME CONTENT

Standardisation :

Weight of CaO standard = 0.1238g = w

Volume of 0.1M HCl titre = 36.00mls = ts

Cement mineral analysis :

FOR 1g OF ALITE :

Volume of 0.1M HCl titre = 0.17mls = t

$$\text{FREE LIME (\%)} = t \times \frac{100w}{ts}$$

$$= 0.17 \times \frac{100(0.1238)}{36}$$

$$= 0.058\%$$

FOR 1g OF TRICALCIUM ALUMINATE :

Volume of 0.1M HCl titre = 0.21mls = t

$$\text{FREE LIME (\%)} = 0.21 \times \frac{100(0.1238)}{36}$$

$$= 0.072\%$$

APPENDIX 8

X-RAY ANALYSIS OF TRICALCIUM ALUMINATE

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

$\lambda = 1.542$

$n = 1$

2θ	PEAK INTENSITY	'd'- VALUE
21	m	4.23
22	ms	4.04
32	ms	2.79
33	vvs	2.70
41	m	2.20
47.5	s	1.91
59	s	1.56

ALL MAJOR PEAKS IDENTIFIED.

APPENDIX 9

COMPARISON OF Rp VALUES OBTAINED BY AUTOMATIC AND MANUAL METHODS

Specimen : O.P.C./0.5 w-c/2%Cl^- by weight of cement/21 days

P.A.R. potentiostat :

Value of Rp obtained = 4.764E04 Ωcm^2

AMEL potentiostat : I.R. compensation not required.

Area of working electrode = 9.70 cm^2

Degree of polarisation = +10mV from E_{corr}

Current 30 seconds after polarisation = 2400nA

$$\text{Current per area} = \frac{2.40E-06}{9.70} = 2.47E-07\ A/cm^2$$

$$\text{Polarisation resistance, Rp} = \frac{0.01}{2.47E-07} = 4.05E04\ \Omega cm^2$$

The two values of Rp obtained are within 15% of each other.

APPENDIX 10

TWENTY EIGHT DAY COMPRESSIVE STRENGTH OF ALITE

Water-cement ratio = 0.6

Age = 28 days - cured in $Ca(OH)_2$ sol^n

Diameter = 25mm

Length = 25mm

Area of loading = 4.90E-04 m^2

Loading rate = 35 N/sec (≡ 4.3 $N/mm^2/min$)

	(1)	(2)
MAXIMUM SUSTAINED LOAD	10.76 kN	9.14 kN
CYLINDER STRENGTH	$\frac{10.76}{4.9087E-04}$ = 21920 kN/m^2	$\frac{9.14}{4.9087E-04}$ = 18620 kN/m^2
CORRECTED CYLINDER STRENGTH	= (21920 x 0.92) = 20166 kN/m^2	= (18620 x 0.92) = 17130 kN/m^2
ESTIMATED CUBE STRENGTH	= (20166 x 1.25) = 25207 kN/m^2	= (17130 x 1.25) = 21413 kN/m^2

AVERAGE CUBE STRENGTH

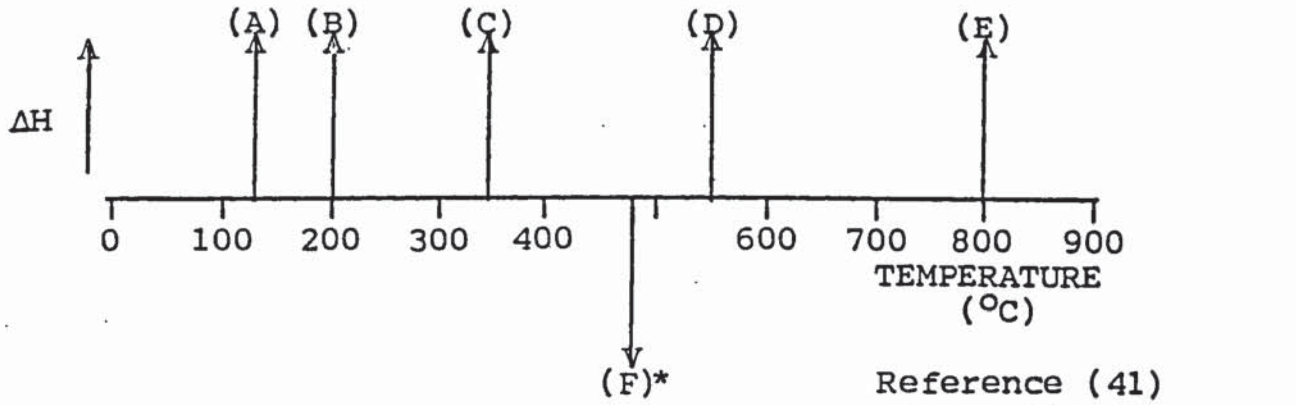
$$= \frac{25207 + 21413}{2}$$

$$= 23310\ kN/m^2$$

$$= 23.31\ MN/m^2$$

APPENDIX 11

INDEX OF PEAKS OBTAINED BY DIFFERENTIAL THERMAL ANALYSIS



Reference (41)
except '*' -
this work, chapter 7

(A) CALCIUM-SILICATE-HYDRATE GEL (C-S-H GEL)

(B) CALCIUM SULPHOALUMINATE HYDRATE (ETTRINGITE)

(C) CALCIUM CHLOROALUMINATE HYDRATE (FRIEDEL'S SALT)

(D) CALCIUM HYDROXIDE (PORTLANDITE)

(E) SODIUM CHLORIDE

(F) SODIUM BENZOATE

APPENDIX 12

PROOF OF THE EQUATION USED IN THE DETERMINATION OF DIFFUSION COEFFICIENTS

$$J = \frac{V}{A} \cdot \frac{dC_2}{dt} = \frac{D}{l}(C_1 - C_2)$$

$$\frac{dC_2}{dt} = \frac{DA}{lv}(C_1 - C_2)$$

$$\frac{d(C_1 - C_2)}{(C_1 - C_2)} = -\frac{DA}{lv}\,dt$$

$$\Big[\log_e(C_1 - C_2)\Big]_{C_2=0}^{C_2=C_2} = -\frac{DA}{lv}\Big[t\Big]_{to}^{t}$$

$$\log_e\left(\frac{C_1 - C_2}{C_1}\right) = -\frac{DA}{lv}(t - to)$$

$$\log_e\left(\frac{C_1}{C_1 - C_2}\right) = \log_e\left(1 + \frac{C_2}{C_1 - C_2}\right)$$

$$= \frac{DA}{lv}(t - to)$$

EXPAND THE LOGARITHM :

$$\frac{C_2}{C_1 - C_2} = \frac{DA}{lv}(t - to) + \cdots\cdots\cdots\cdots\cdots\cdots$$

For $t > to$, $C_1 \gg C_2$:

$$C_2 \cong \frac{DAC_1}{lv}(t - to)$$

APPENDIX 13

DETERMINATION OF GRADIENT, CORRELATION AND ERROR FOR CHLORIDE DIFFUSION DATA BY LINEAR REGRESSION ANALYSIS AND OTHER STATISTICAL METHODS

The statistical methods shown here have been used to obtain 'best-fit' straight lines for the chloride diffusion data given in chapter 5. The worked example given is for the Arrhenius plot of $\log_{10}$ diffusion coefficient against the reciprocal of absolute temperature used to determine the activation energy.

These methods require summations of the data in various forms as given below.

$\Sigma x = 8.3910\text{E}-2$

$\Sigma y = -178.9792$

$\Sigma x^2 = 2.8230\text{E}-4$

$\Sigma y^2 = 1283.3497$

$\Sigma xy = -0.6019$

n = number of points
= 25

GRADIENT (b) :

$$b = \frac{\Sigma xy - \dfrac{(\Sigma x)(\Sigma y)}{n}}{\Sigma x^2 - \dfrac{(\Sigma x)^2}{n}}$$

$$= -1746$$

CORRELATION (r) :

$$r = \frac{\Sigma xy - \frac{(\Sigma x)(\Sigma y)}{n}}{\sqrt{\left[\Sigma x^2 - \frac{(\Sigma x)^2}{n}\right]\left[\Sigma y^2 - \frac{(\Sigma y)^2}{n}\right]}}$$

$$= -0.9405$$

CONFIDENCE LIMITS (95%) :

Residual variance, s_r^2

$$s_r^2 = \frac{1}{n-2} \quad SSy - \frac{(SPxy)^2}{SSx}$$

where $SSy = \Sigma y^2 - \frac{(\Sigma y)^2}{n} = 2.0075$

$$SPxy = \Sigma xy - \frac{\Sigma x . \Sigma y}{n} = 1.017E-3$$

$$SSx = \Sigma x^2 - \frac{(\Sigma x)^2}{n} = 5.820E-7$$

$$s_r^2 = 1.0017E-2$$

$$s_b^2 = \frac{s_r^2}{SSx}$$

$$= 17212$$

$$s_b = 131.1946$$

$b = -1746 \pm (131.1946)(1.96)$ -from t-distribution table

$$= -1746 \pm 257$$

ACTIVATION ENERGY (Q) :

$$b = \frac{-Q}{2.3R}$$

where Q = activation energy

R = gas constant (8.31434)

$$Q = (1746 \pm 257)(2.3)(8.31434)$$

$$= 33.4 \pm 4.9 \text{ kJ/mole}$$

APPENDIX 14

DETERMINATION OF HYDROXYL ION CONCENTRATION AND FREE/TOTAL CHLORIDE ION CONCENTRATIONS IN HYDRATED ALITE PASTES

TOTAL CHLORIDE

Added as sodium chloride during mixing

a) 1% Cl^- by weight of alite = 0.2817 millimoles per gramme

b) 2% Cl^- by weight of alite = 0.5634 millimoles per gramme

PORE SOLUTION HYDROXYL ION CONCENTRATION (pH)

Found by titration with 0.01 M HNO_3 (see Appendix 2)

Average titre

a) 0.27 millilitres $\equiv$ pH 12.43

b) 0.30 millilitres $\equiv$ pH 12.48

EVAPORABLE AND NON-EVAPORABLE WATER

Carried out on similar specimen containing no chloride (see Appendix 3)

Initial weight of specimen = 2.6275 grammes

Weight at 105°C = 1.9395 grammes

Weight at 950°C = 1.6422 grammes

Loss-on-ignition = none

Evaporable water = 0.6880 grammes = 0.4189 g/g_{alite}

Non-evaporable water = 0.2973 grammes = 0.1810 g/g_{alite}

FREE CHLORIDE

(see Appendix 2)

Average absorption (dilution factor = 1000)

a) 1.079 ABS = 0.672 MCl^- = 0.2807 millimoles per gramme

b) 1.705 ABS = 1.343 MCl^- = 0.5625 millimoles per gramme

RATIO OF FREE TO TOTAL CHLORIDE (%)

a) 99.65%

b) 99.84%

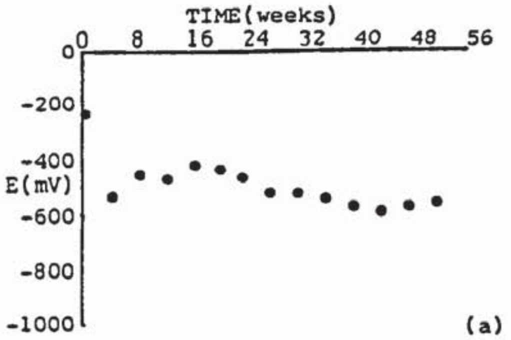
APPENDIX 15

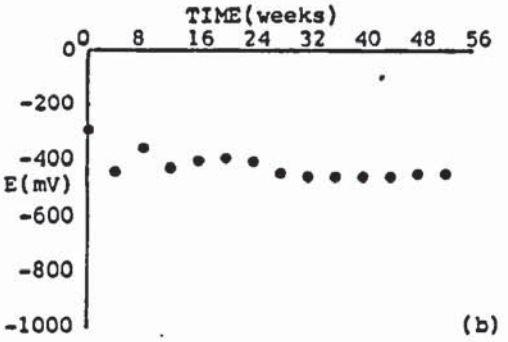
TRACES OF REST POTENTIAL AGAINST TIME FOR MILD STEEL WITH FOUR DIFFERENT SURFACE CONDITIONS, EMBEDDED IN CONCRETE AND EXPOSED TO FOUR DIFFERENT ENVIRONMENTS

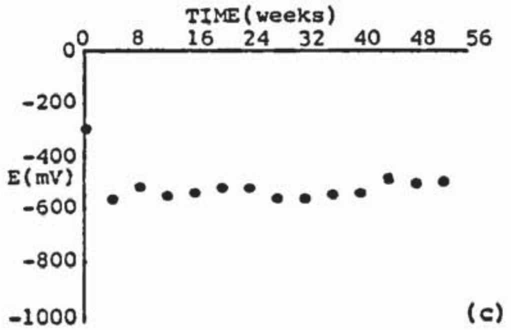
Part 1 Mild steel bearing rust produced in deionised water vapour

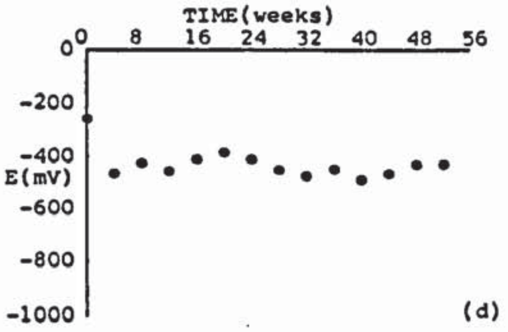
Part 1.1 Exposed to saturated calcium hydroxide solution

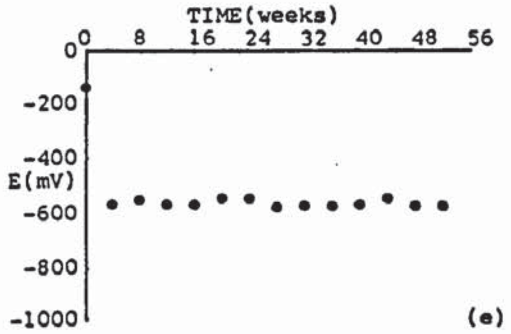
ALL POTENTIALS MEASURED VERSUS SATURATED CALOMEL ELECTRODE.

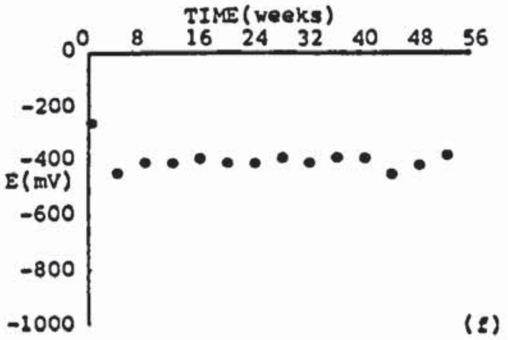


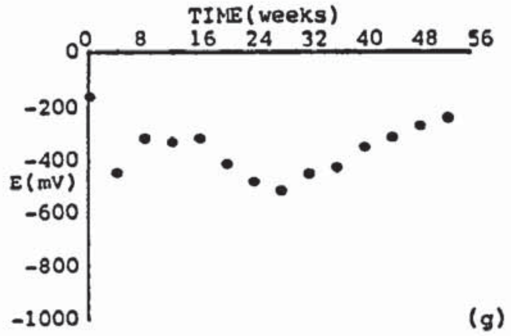


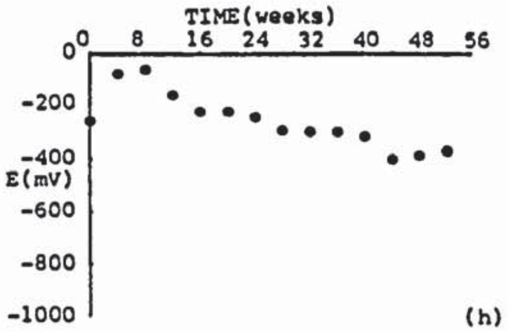


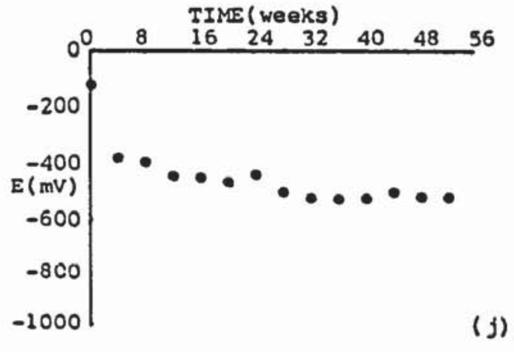


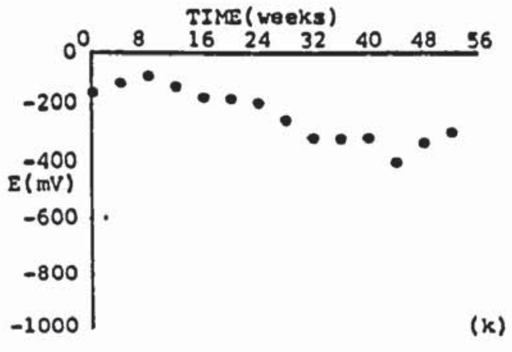






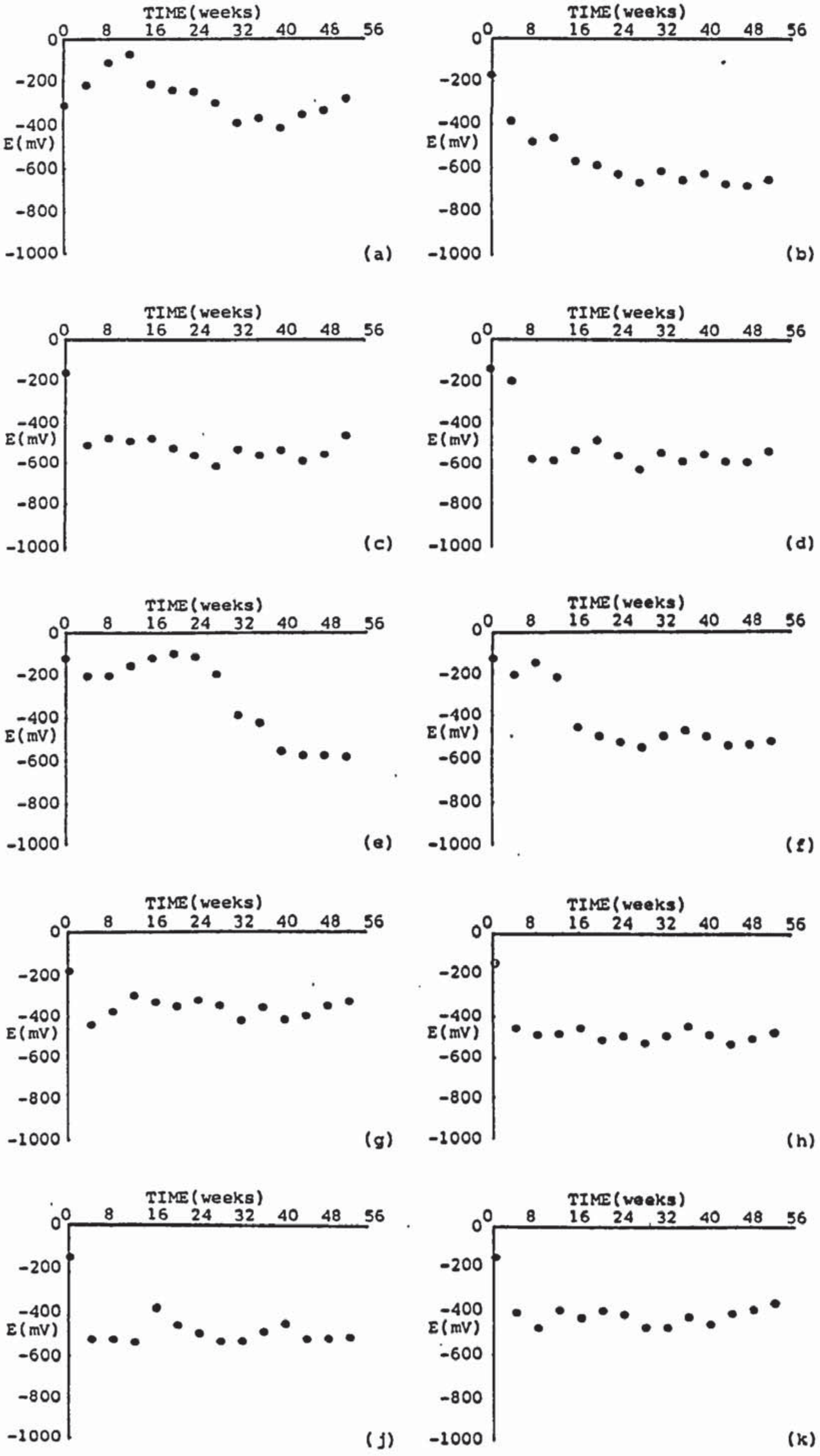






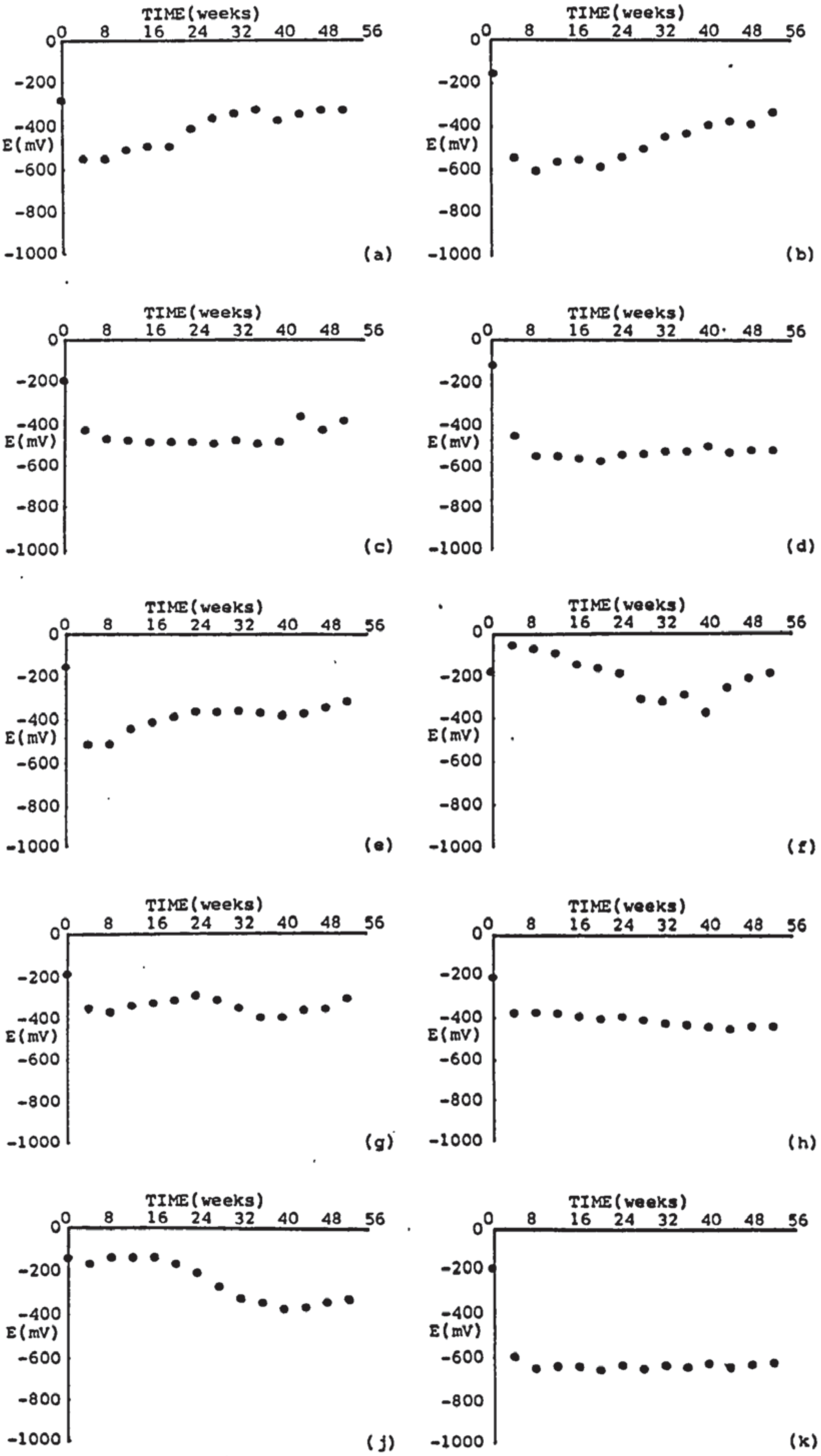
Part 1.2 Exposed to saturated calcium hydroxide solution containing 1M sodium chloride

ALL POTENTIALS MEASURED VERSUS SATURATED CALOMEL ELECTRODE.



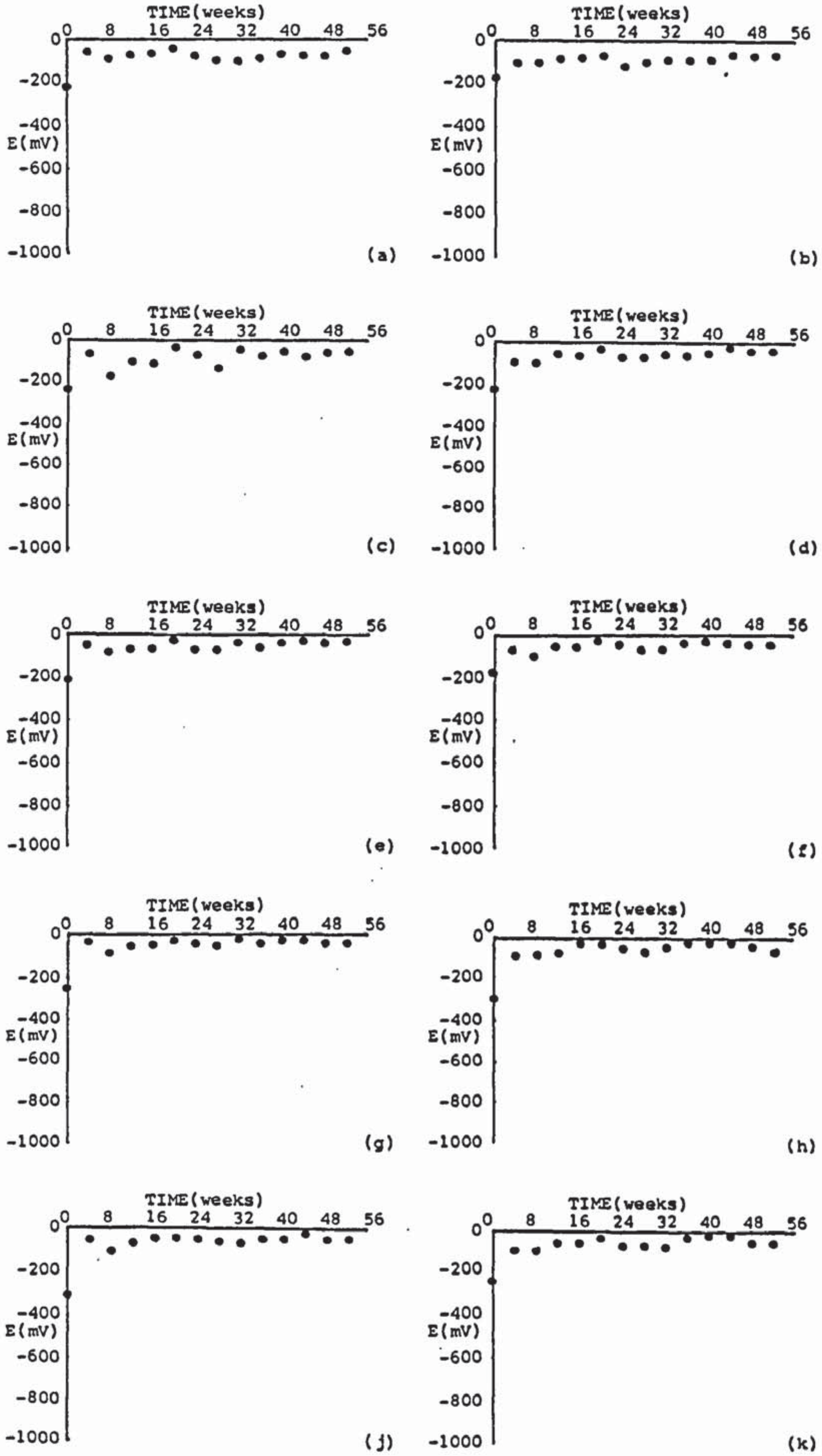
Part 1.3 Exposed to artificial seawater

ALL POTENTIALS MEASURED VERSUS SATURATED CALOMEL ELECTRODE.



Part 1.4 Exposed to 100% relative humidity

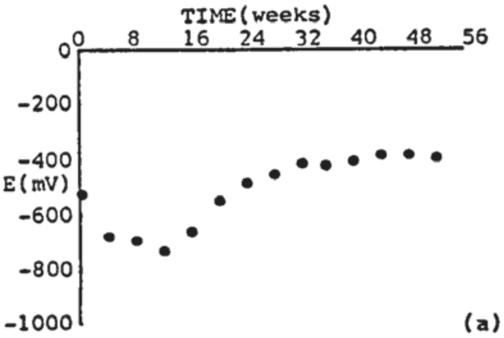
ALL POTENTIALS MEASURED VERSUS SATURATED CALOMEL ELECTRODE.

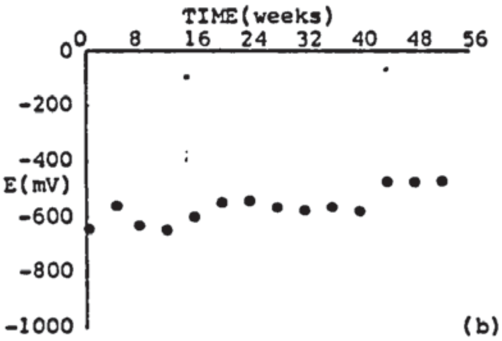


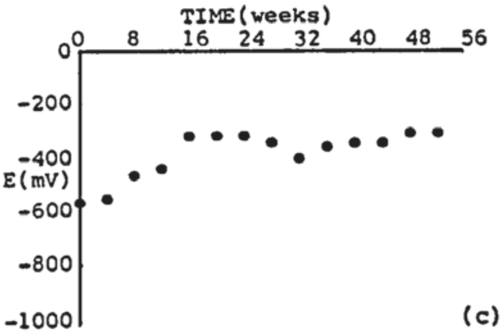
Part 2 Mild steel bearing rust produced in 1 molar ferrous sulphate solution

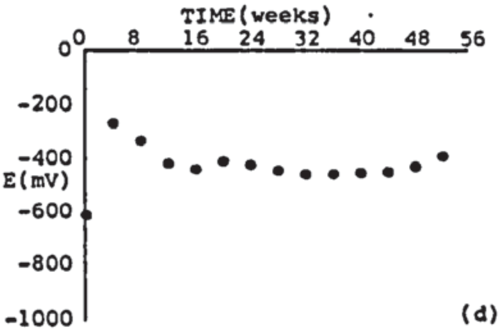
Part 2.1 Exposed to saturated calcium hydroxide solution

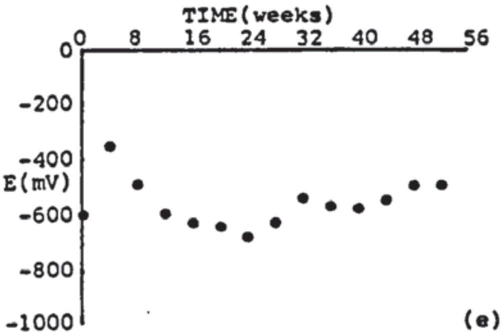
ALL POTENTIALS MEASURED VERSUS SATURATED CALOMEL ELECTRODE.

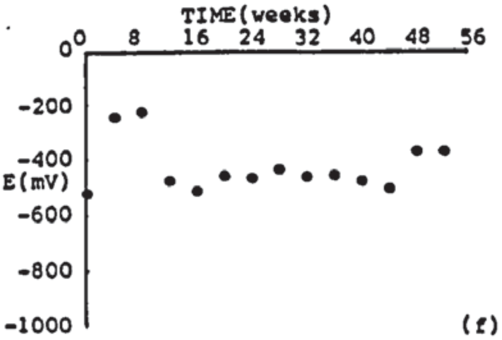


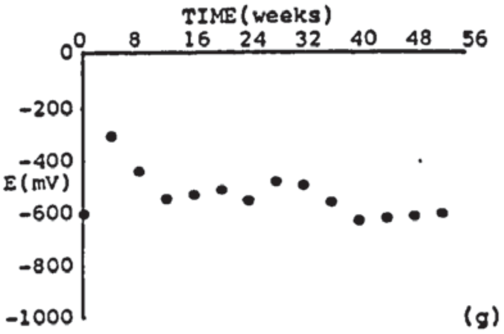


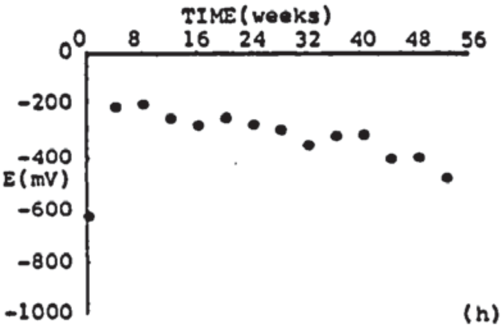


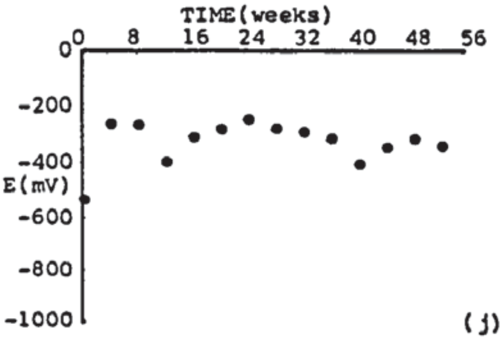


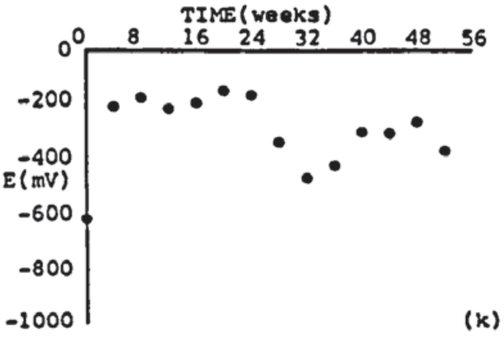






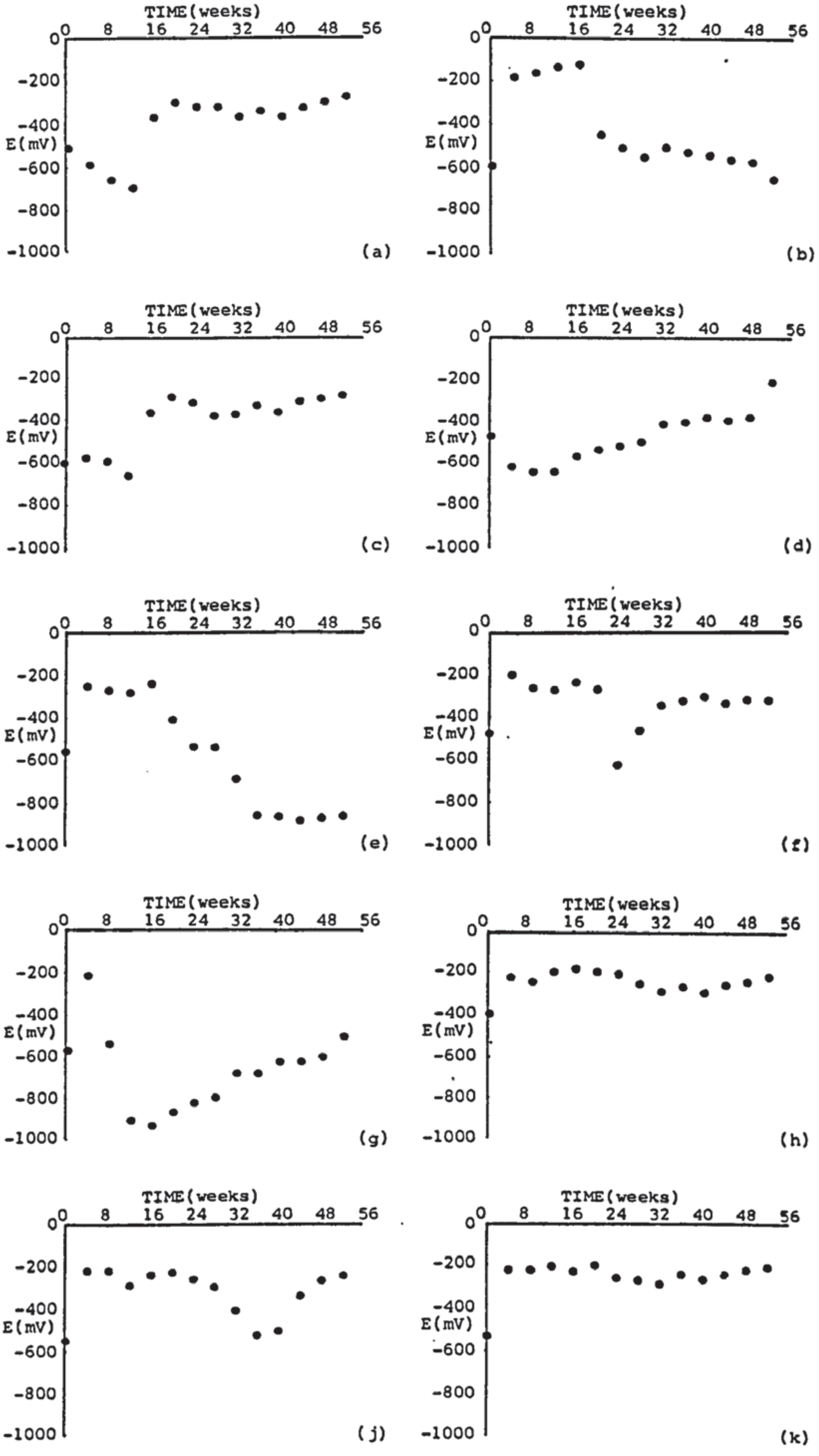






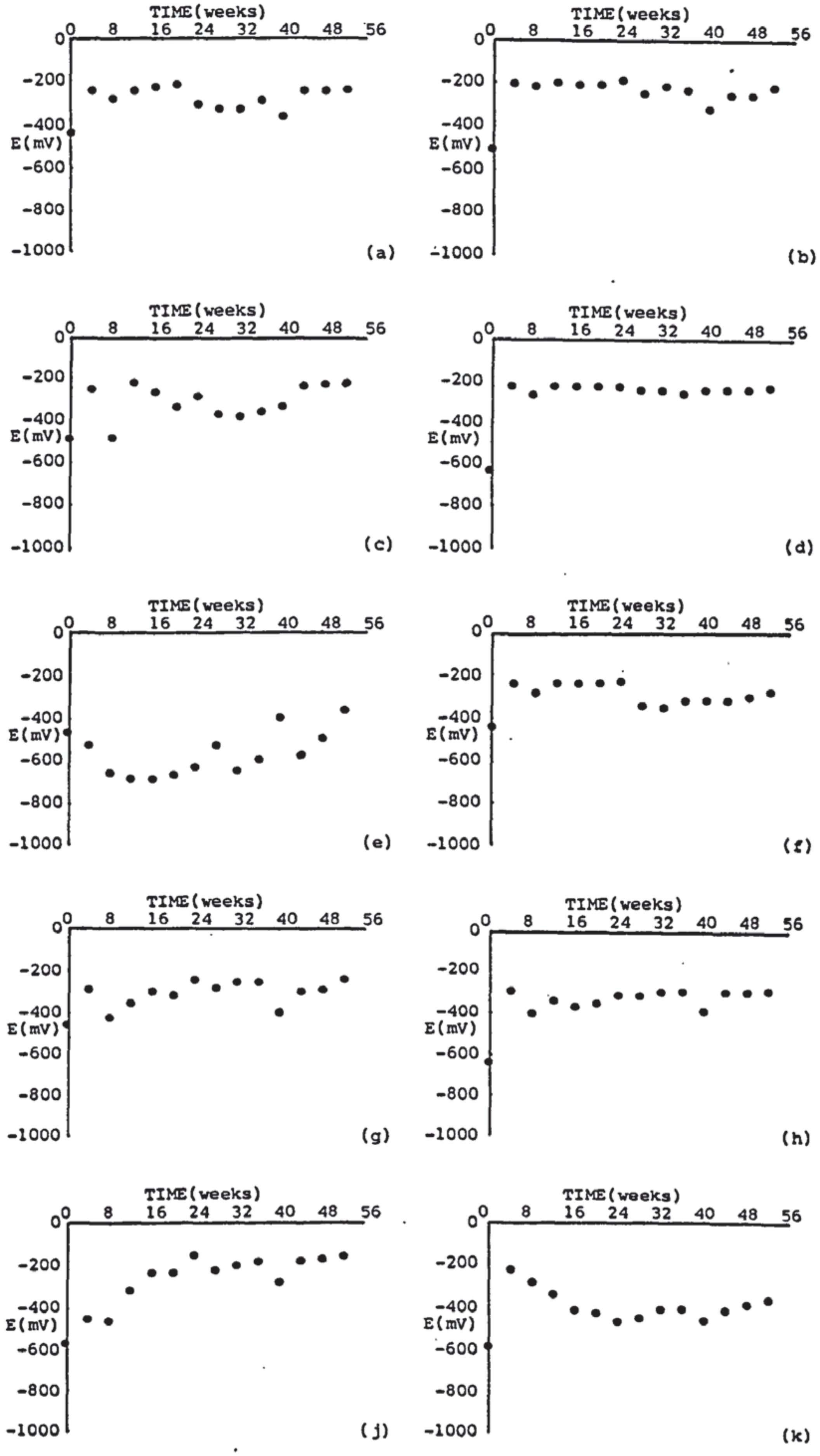
Part 2.2 Exposed to saturated calcium hydroxide solution containing 1M sodium chloride

ALL POTENTIALS MEASURED VERSUS SATURATED CALOMEL ELECTRODE.



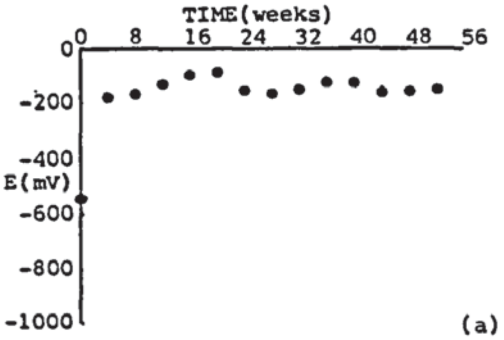
Part 2.3 Exposed to artificial seawater

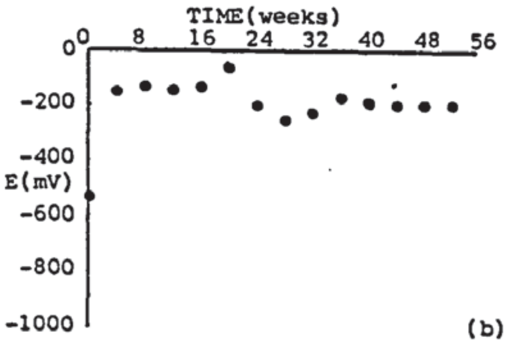
ALL POTENTIALS MEASURED VERSUS SATURATED CALOMEL ELECTRODE.

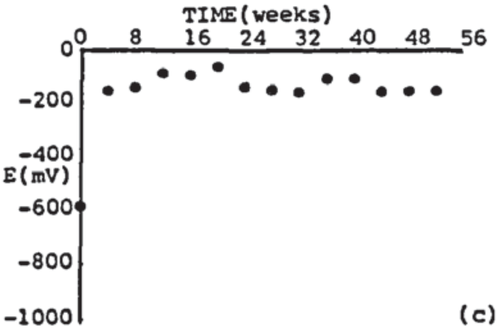


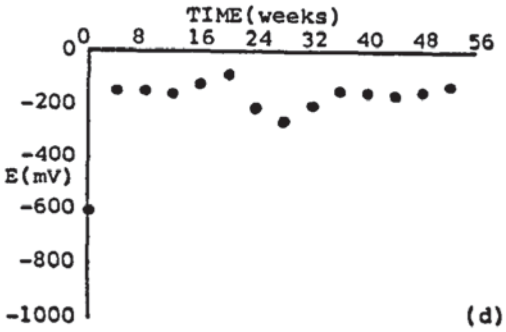
Part 2.4 Exposed to 100% relative humidity

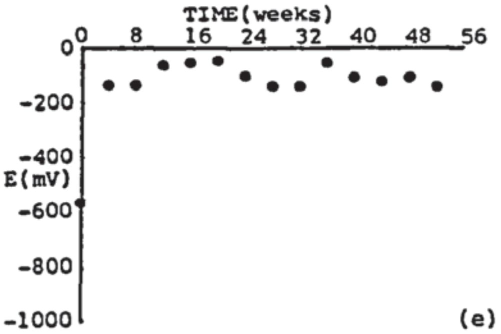
ALL POTENTIALS MEASURED VERSUS SATURATED CALOMEL ELECTRODE.

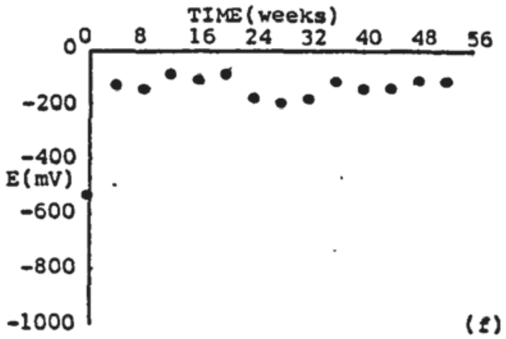


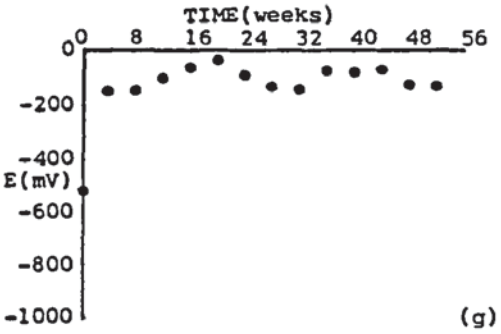


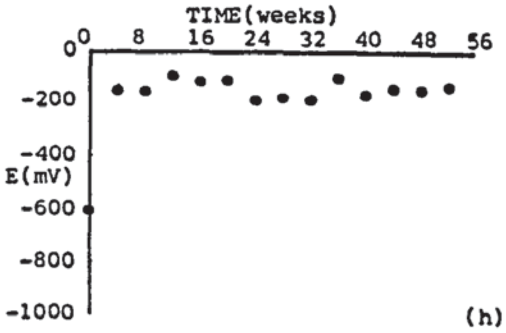


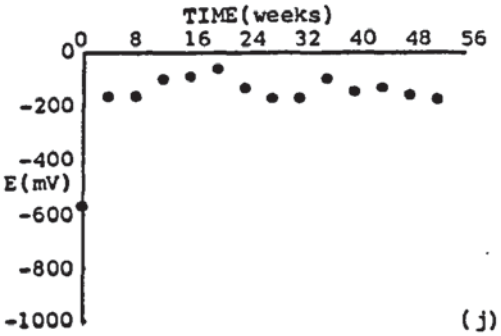


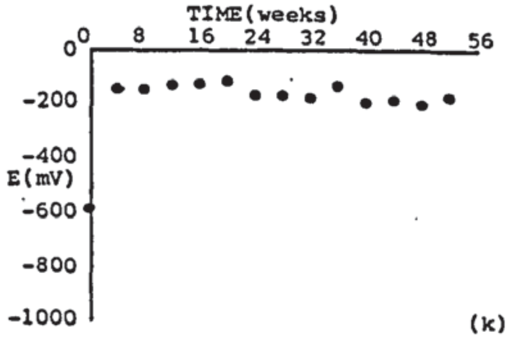








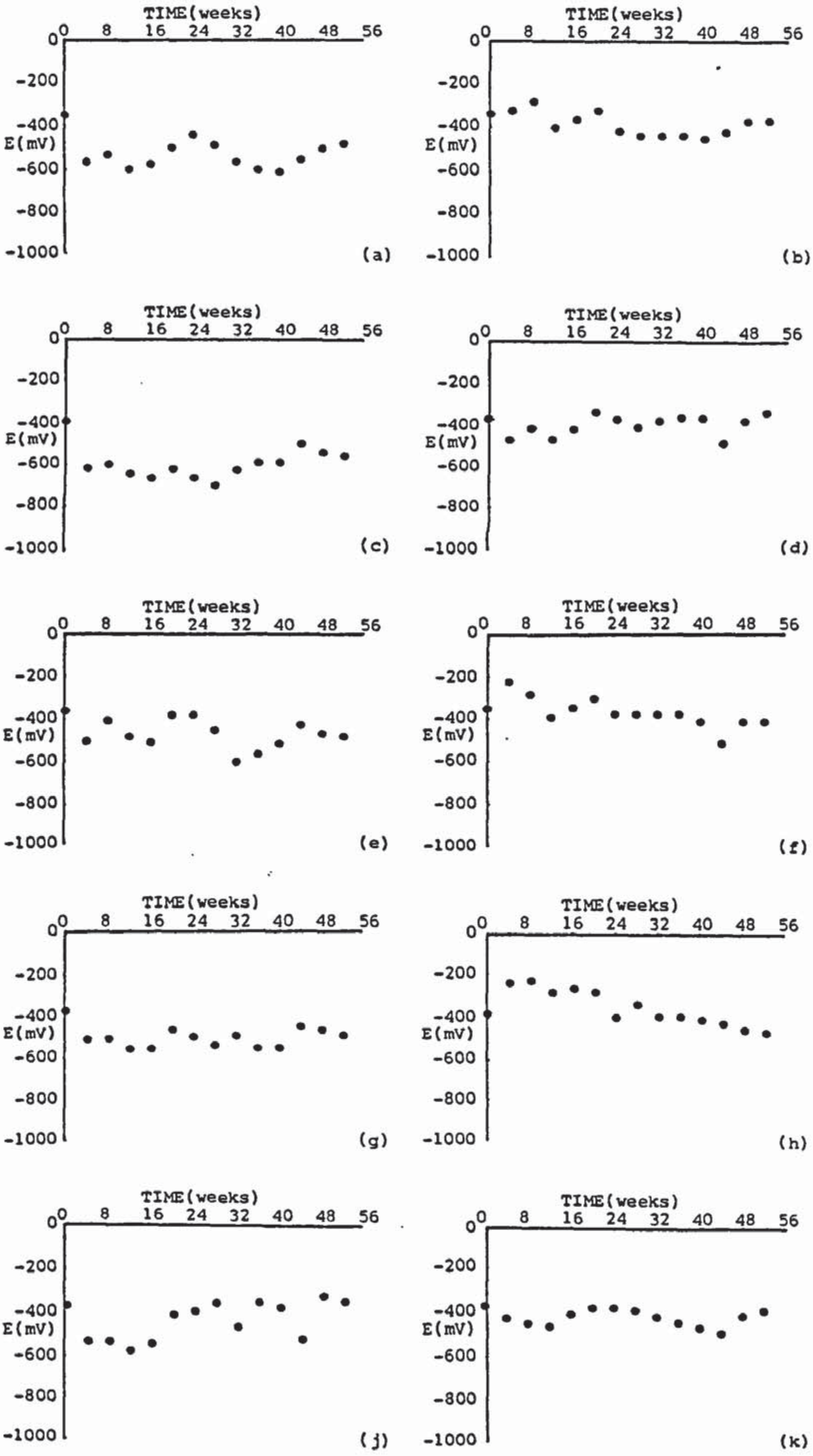




Part 3 Mild steel bearing rust produced in 1 molar sodium chloride solution

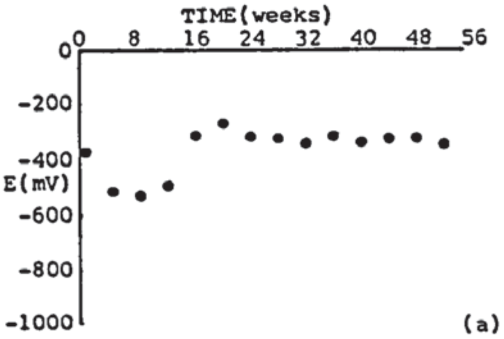
Part 3.1 Exposed to saturated calcium hydroxide solution

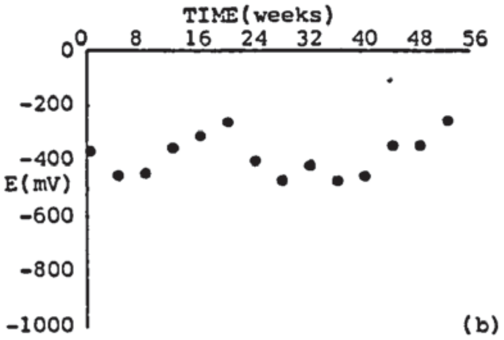
ALL POTENTIALS MEASURED VERSUS SATURATED CALOMEL ELECTRODE.

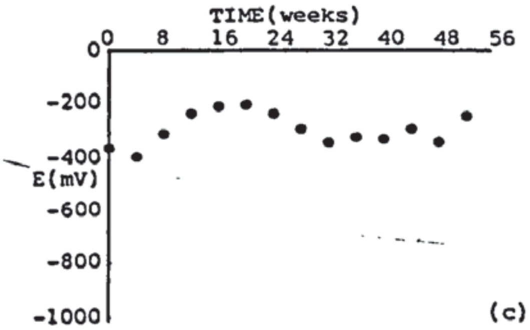


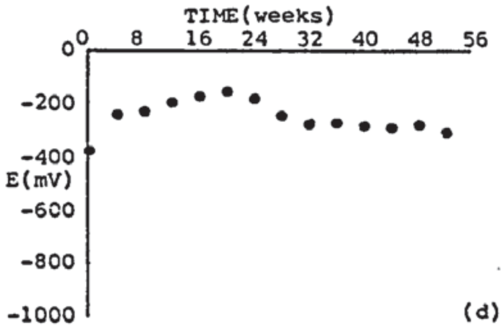
Part 3.2 Exposed to saturated calcium hydroxide solution containing 1M sodium chloride

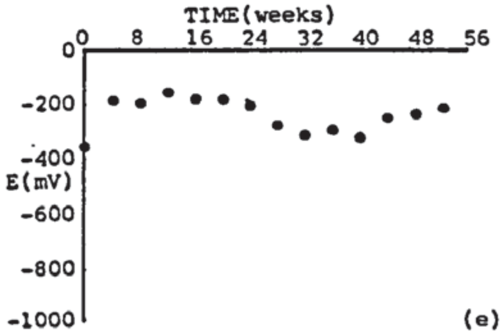
ALL POTENTIALS MEASURED VERSUS SATURATED CALOMEL ELECTRODE.

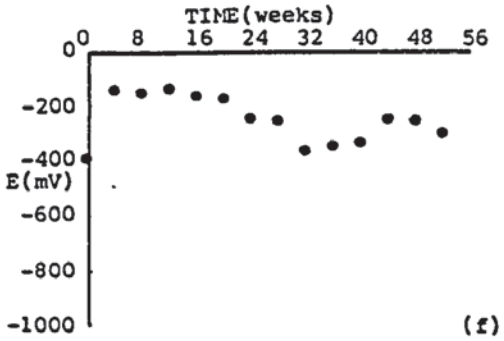


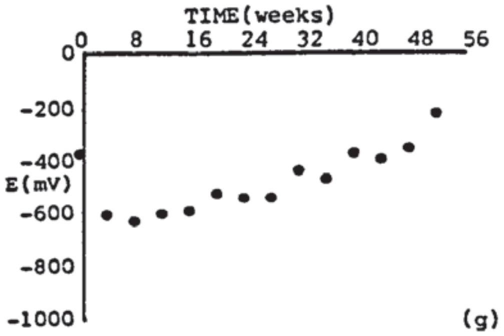


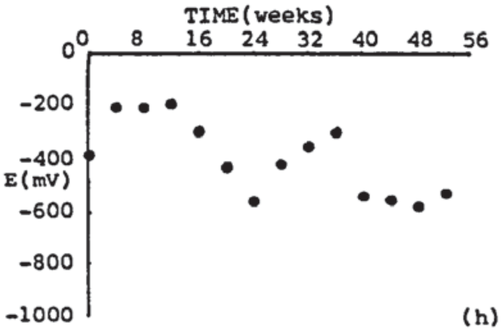


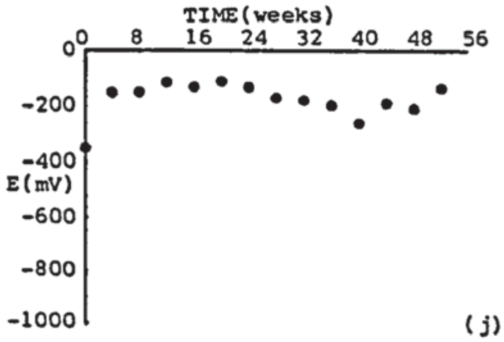


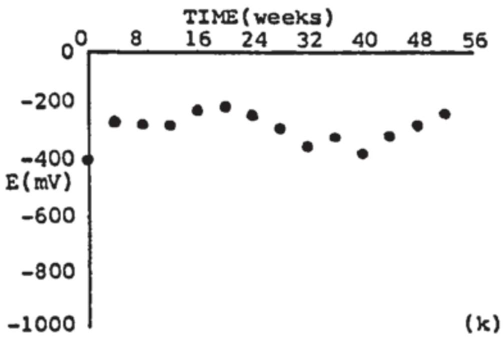






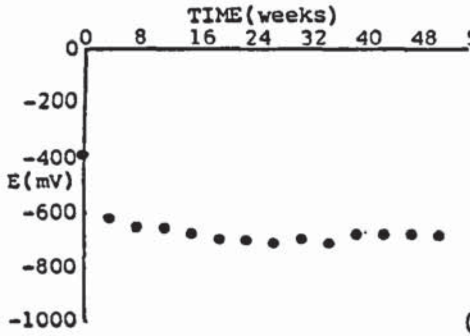






Part 3.3 Exposed to artificial seawater

ALL POTENTIALS MEASURED VERSUS SATURATED CALOMEL ELECTRODE.



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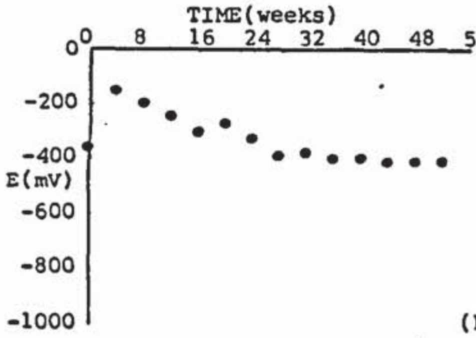

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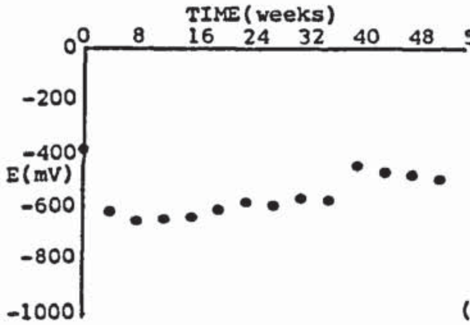

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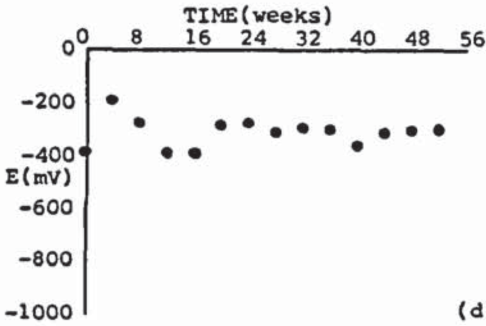

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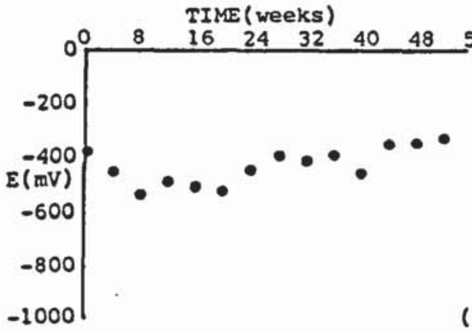

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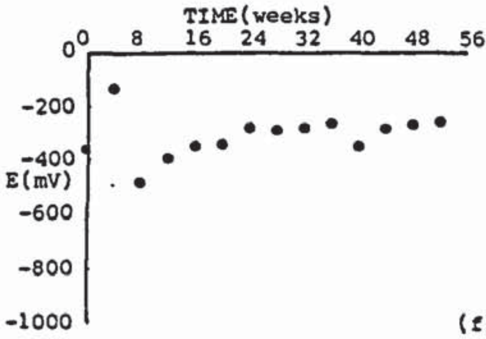

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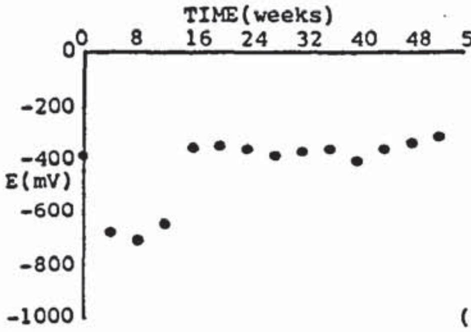

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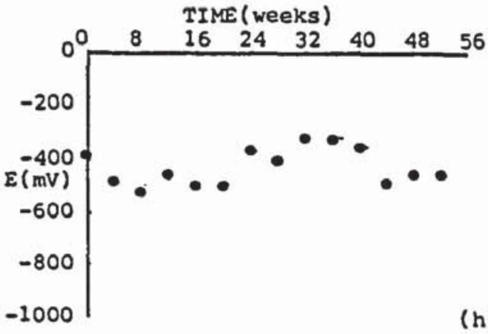

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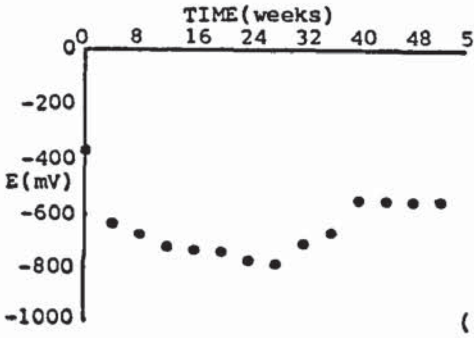

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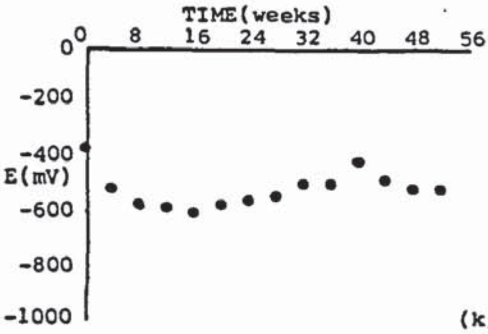
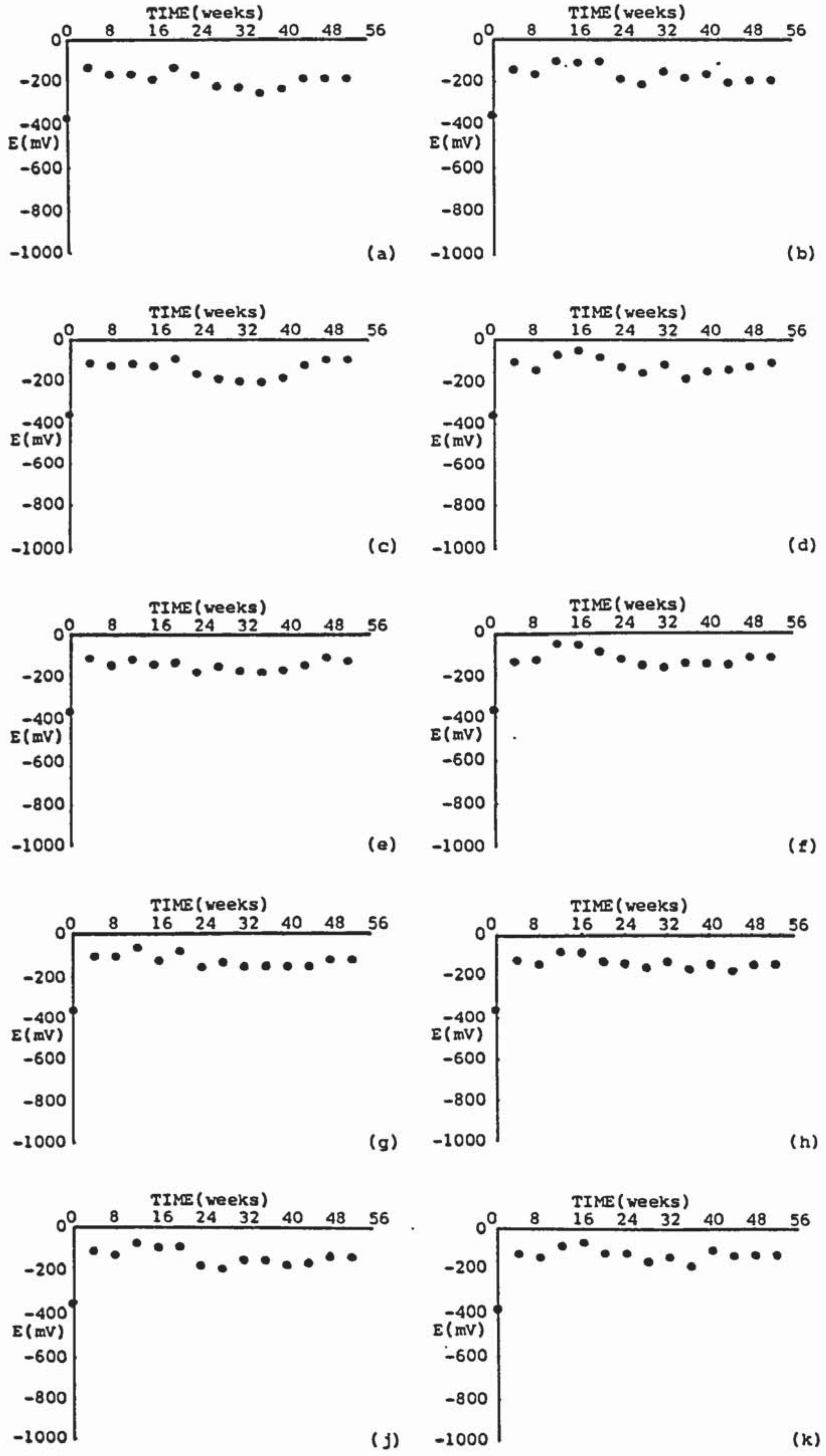


(k)

Part 3.4 Exposed to 100% relative humidity

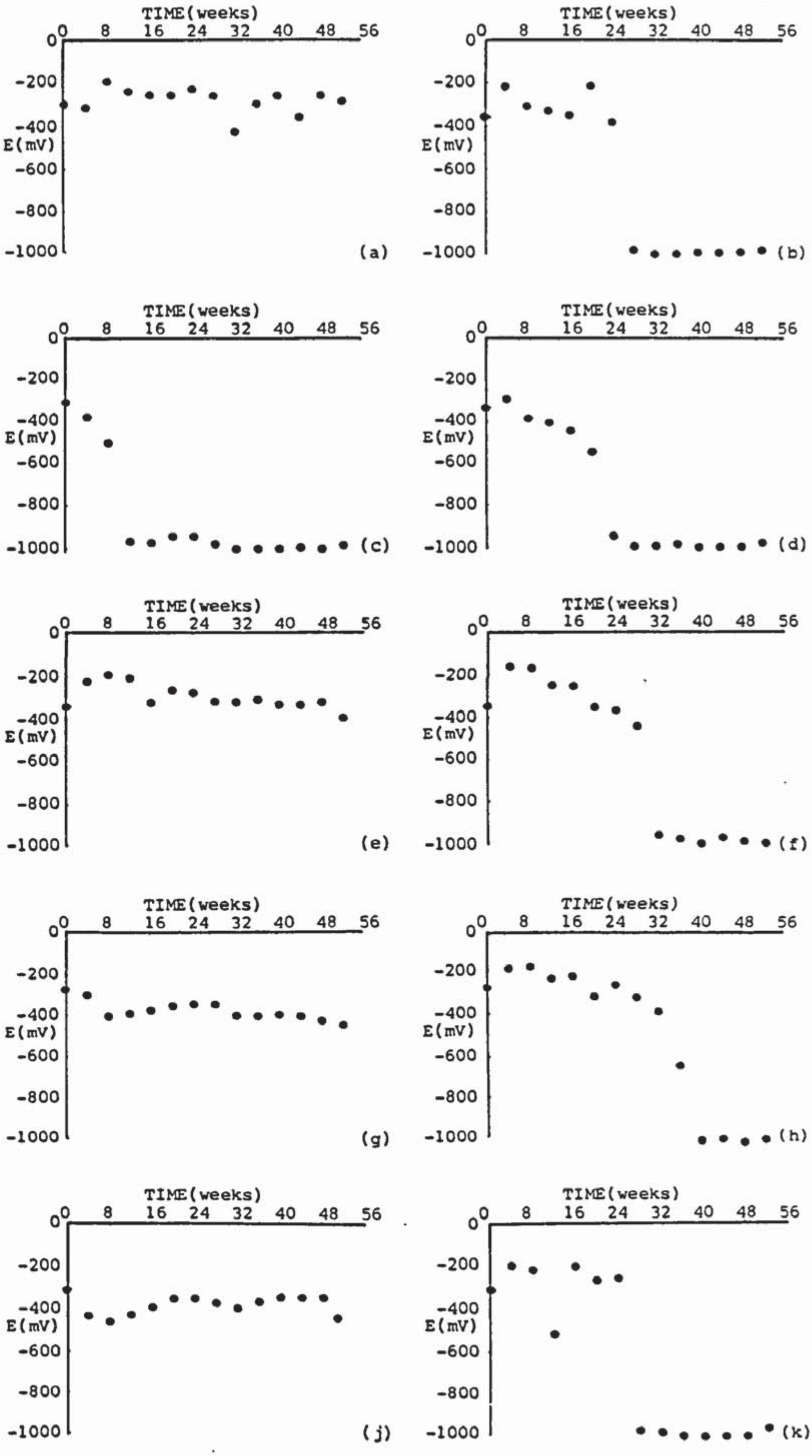
ALL POTENTIALS MEASURED VERSUS SATURATED CALOMEL ELECTRODE.



Part 4 Clean and degreased steel

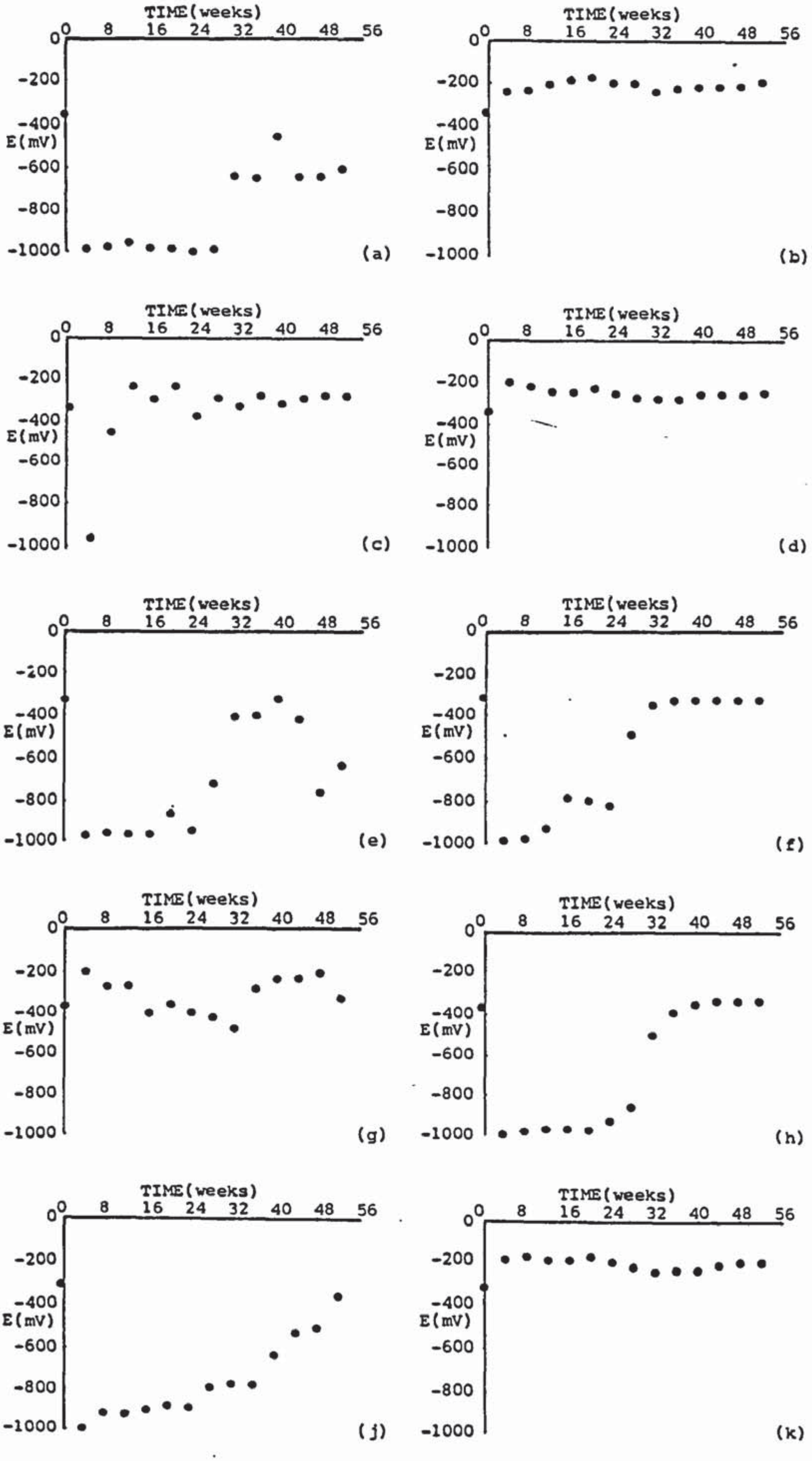
Part 4.1 Exposed to saturated calcium hydroxide solution

ALL POTENTIALS MEASURED VERSUS SATURATED CALOMEL ELECTRODE.



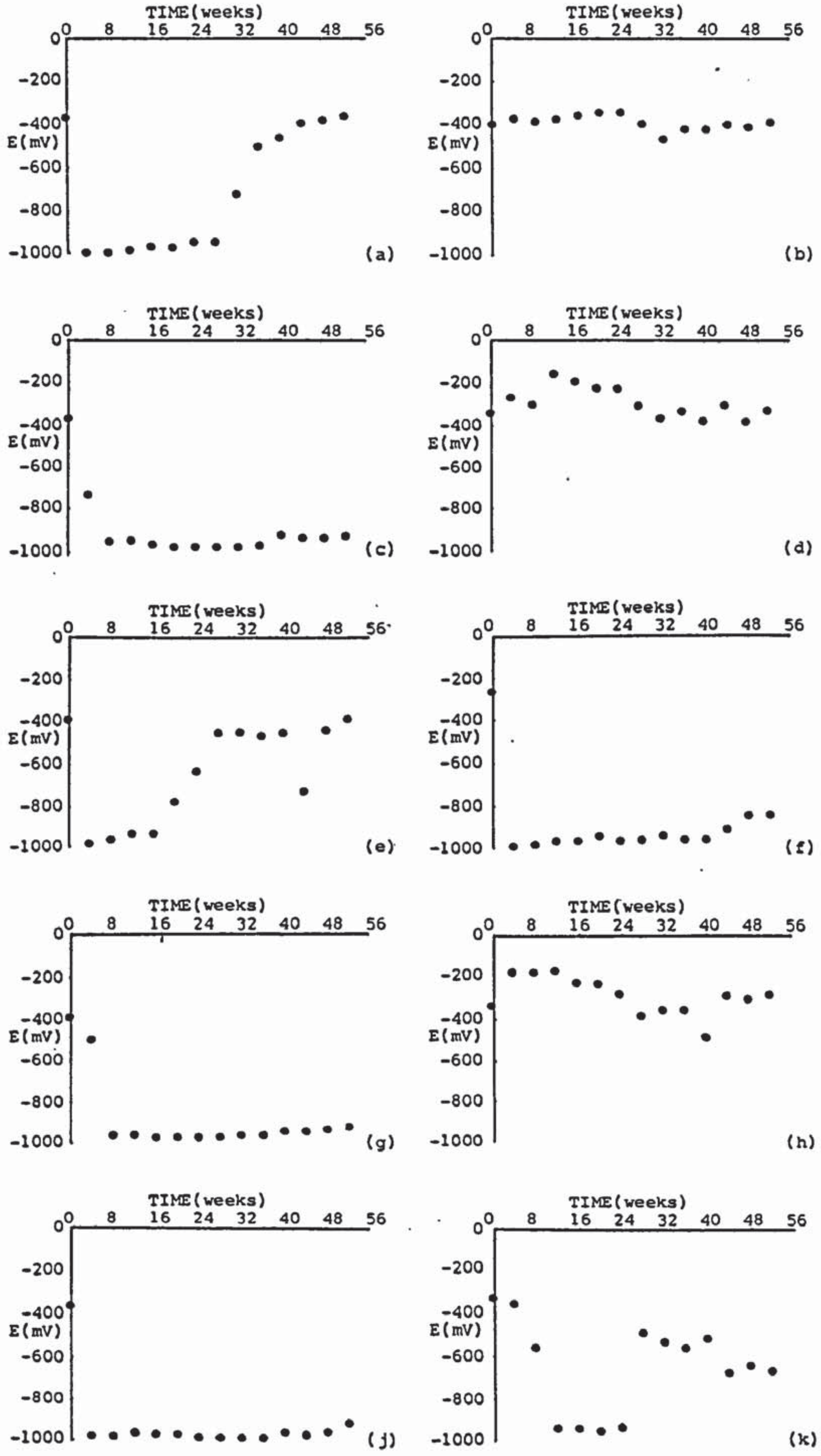
Part 4.2 Exposed to saturated calcium hydroxide solution containing 1M sodium chloride

ALL POTENTIALS MEASURED VERSUS SATURATED CALOMEL ELECTRODE.



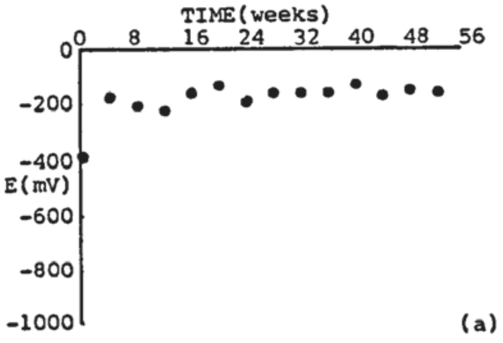
Part 4.3 Exposed to artificial seawater

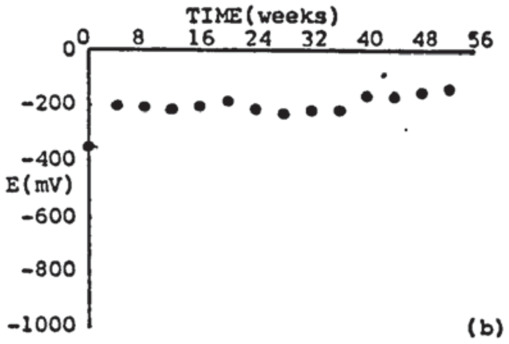
ALL POTENTIALS MEASURED VERSUS SATURATED CALOMEL ELECTRODE.

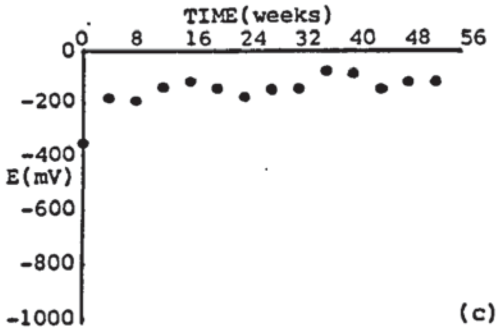


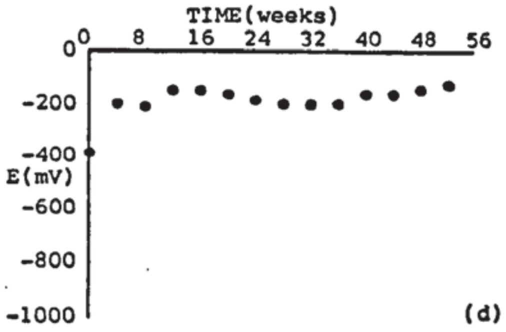
Part 4.4 Exposed to 100% relative humidity

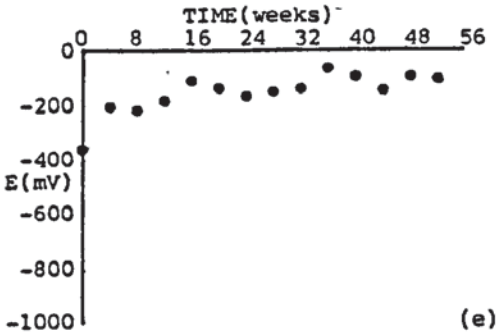
ALL POTENTIALS MEASURED VERSUS SATURATED CALOMEL ELECTRODE.

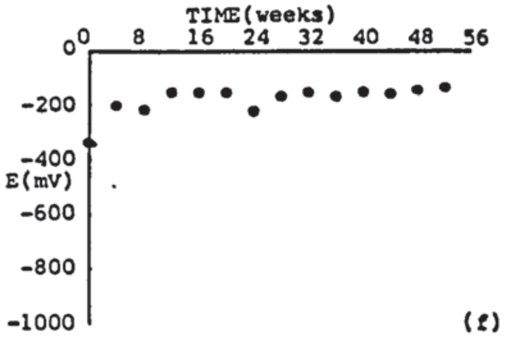


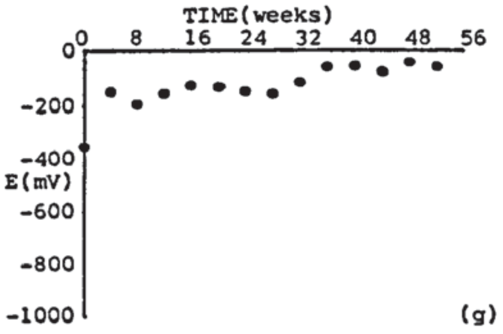


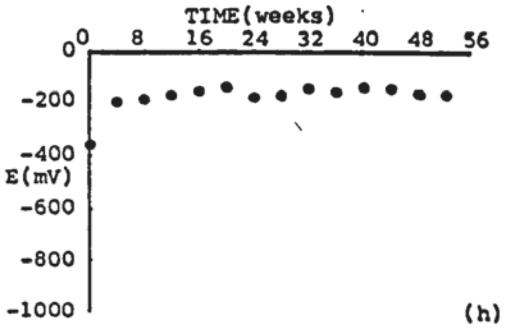


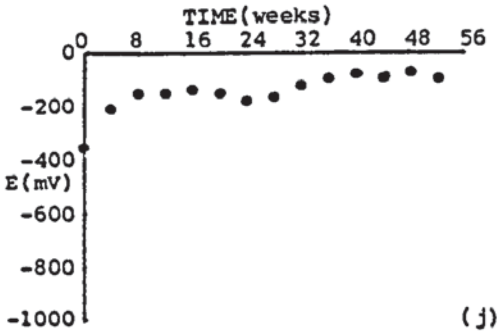


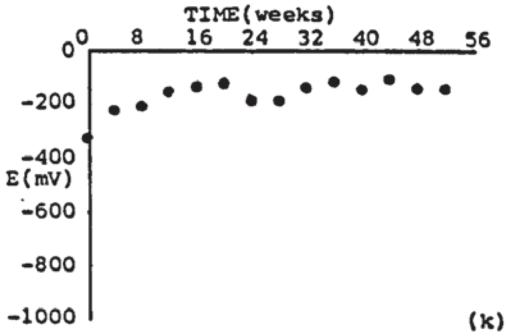












APPENDIX 16

PORE SOLUTION AND CEMENT PASTE ANALYSES FOR 0.5 WATER-CEMENT RATIO ORDINARY PORTLAND CEMENT PASTES CONTAINING INHIBITORS AND EXPOSED TO INTERNAL AND EXTERNAL SOURCES OF CHLORIDE ION FOR 50 AND 100 DAYS

SPECIMEN	CYLINDERS CONTAINING 2% CALCIUM NITRITE.CURED IN 100% R.H. 50 DAYS.			
WATER CONTENT (g/g_{cem})	FREE=0.3159 BOUND=0.1824 TOTAL=0.4983			AVERAGE RESULTS
TOTAL CHLORIDE (mM/g_{cem})	-	-	-	-
FREE CHLORIDE (mM/g_{cem})	-	-	-	-
FREE/TOTAL CHLORIDE (%)	-	-	-	-
TOTAL NITRITE (mM/g_{cem})	0.1333	0.1333	0.1333	0.1333
FREE NITRITE (mM/g_{cem})	0.0104	0.0103	0.0103	0.0103
FREE/TOTAL NITRITE (%)	7.8	7.7	7.7	7.7
TOTAL BENZOATE (mM/g_{cem})	-	-	-	-
FREE BENZOATE (mM/g_{cem})	-	-	-	-
FREE/TOTAL BENZOATE (%)	-	-	-	-
pH	13.54	13.54	13.55	13.54

SPECIMEN	CYLINDERS CONTAINING 2% CALCIUM NITRITE.CURED IN 100% R.H. 100 DAYS.			
WATER CONTENT (g/g_{cem})	FREE=0.3164 BOUND=0.1828 TOTAL=0.4992			AVERAGE RESULTS
TOTAL CHLORIDE (mM/g_{cem})	-	-	-	-
FREE CHLORIDE (mM/g_{cem})	-	-	-	-
FREE/TOTAL CHLORIDE (%)	-	-	-	-
TOTAL NITRITE (mM/g_{cem})	0.1333	0.1333	0.1333	0.1333
FREE NITRITE (mM/g_{cem})	0.0064	0.0066	0.0065	0.0065
FREE/TOTAL NITRITE (%)	4.8	5.0	4.9	4.9
TOTAL BENZOATE (mM/g_{cem})	-	-	-	-
FREE BENZOATE (mM/g_{cem})	-	-	-	-
FREE/TOTAL BENZOATE (%)	-	-	-	-
pH	13.60	13.60	13.60	13.60

SPECIMEN	CYLINDERS CONTAINING 1.84% SODIUM NITRITE.CURED IN 100% R.H. 50 DAYS.			
WATER CONTENT (g/g_{cem})	FREE=0.3165 BOUND= 0.1821 TOTAL= 0.4986			AVERAGE RESULTS
TOTAL CHLORIDE (mM/g_{cem})	-	-	-	-
FREE CHLORIDE (mM/g_{cem})	-	-	-	-
FREE/TOTAL CHLORIDE (%)	-	-	-	-
TOTAL NITRITE (mM/g_{cem})	0.1333	0.1333	0.1333	0.1333
FREE NITRITE (mM/g_{cem})	0.0064	0.0062	0.0059	0.0062
FREE/TOTAL NITRITE (%)	4.8	4.7	4.4	4.6
TOTAL BENZOATE (mM/g_{cem})	-	-	-	-
FREE BENZOATE (mM/g_{cem})	-	-	-	-
FREE/TOTAL BENZOATE (%)	-	-	-	-
pH	13.70	13.70	13.70	13.70

SPECIMEN	CYLINDERS CONTAINING 1.84% SODIUM NITRITE.CURED IN 100% R.H. 100 DAYS.			
WATER CONTENT (g/g_{cem})	FREE= 0.3172 BOUND= 0.1816 TOTAL= 0.4988			AVERAGE RESULTS
TOTAL CHLORIDE (mM/g_{cem})	-	-	-	-
FREE CHLORIDE (mM/g_{cem})	-	-	-	-
FREE/TOTAL CHLORIDE (%)	-	-	-	-
TOTAL NITRITE (mM/g_{cem})	0.1333	0.1333	0.1333	0.1333
FREE NITRITE (mM/g_{cem})	0.0056	0.0057	0.0053	0.0055
FREE/TOTAL NITRITE (%)	4.2	4.3	4.0	4.1
TOTAL BENZOATE (mM/g_{cem})	-	-	-	-
FREE BENZOATE (mM/g_{cem})	-	-	-	-
FREE/TOTAL BENZOATE (%)	-	-	-	-
pH	13.73	13.72	13.72	13.72

SPECIMEN	CYLINDERS CONTAINING 1.84% SODIUM NITRITE & 2% SODIUM BENZOATE. CURED IN 100% R.H. 50 DAYS.			
WATER CONTENT (g/g_{cem})	FREE= 0.3154 BOUND= 0.1823 TOTAL= 0.4977			AVERAGE RESULTS
TOTAL CHLORIDE (mM/g_{cem})	-	-	-	-
FREE CHLORIDE (mM/g_{cem})	-	-	-	-
FREE/TOTAL CHLORIDE (%)	-	-	-	-
TOTAL NITRITE (mM/g_{cem})	0.1333	0.1333	0.1333	0.1333
FREE NITRITE (mM/g_{cem})	0.0053	0.0050	0.0051	0.0051
FREE/TOTAL NITRITE (%)	4.0	3.8	3.8	3.8
TOTAL BENZOATE (mM/g_{cem})	0.1389	0.1389	0.1389	0.1389
FREE BENZOATE (mM/g_{cem})	0.0492	0.0498	0.0486	0.0492
FREE/TOTAL BENZOATE (%)	35.4	35.9	35.0	35.4
pH	13.62	13.62	13.63	13.62

SPECIMEN	CYLINDERS CONTAINING 1.84% SODIUM NITRITE & 2% SODIUM BENZOATE. CURED IN 100% R.H. 100 DAYS.			
WATER CONTENT (g/g_{cem})	FREE=0.3153 BOUND=0.1826 TOTAL= 0.4979			AVERAGE RESULTS
TOTAL CHLORIDE (mM/g_{cem})	-	-	-	-
FREE CHLORIDE (mM/g_{cem})	-	-	-	-
FREE/TOTAL CHLORIDE (%)	-	-	-	-
TOTAL NITRITE (mM/g_{cem})	0.1333	0.1333	0.1333	0.1333
FREE NITRITE (mM/g_{cem})	0.0050	0.0053	0.0050	0.0051
FREE/TOTAL NITRITE (%)	3.8	4.0	3.8	3.8
TOTAL BENZOATE (mM/g_{cem})	0.1389	0.1389	0.1389	0.1389
FREE BENZOATE (mM/g_{cem})	0.0479	0.0479	0.0479	0.0479
FREE/TOTAL BENZOATE (%)	34.5	34.5	34.5	34.5
pH	13.63	13.63	13.62	13.63

SPECIMEN	CYLINDERS CONTAINING 0.4% SODIUM CHLORIDE & 2% CALCIUM NITRITE. CURED IN 100% R.H. 50 DAYS.			
WATER CONTENT (g/g_{cem})	FREE=0.3151 BOUND=0.1826 TOTAL=0.4977			AVERAGE RESULTS
TOTAL CHLORIDE (mM/g_{cem})	0.0684	0.0684	0.0684	0.0684
FREE CHLORIDE (mM/g_{cem})	0.0161	0.0161	0.0158	0.0160
FREE/TOTAL CHLORIDE (%)	23.5	23.5	23.1	23.4
TOTAL NITRITE (mM/g_{cem})	0.1333	0.1333	0.1333	0.1333
FREE NITRITE (mM/g_{cem})	0.0109	0.0109	0.0109	0.0109
FREE/TOTAL NITRITE (%)	8.2	8.2	8.2	8.2
TOTAL BENZOATE (mM/g_{cem})	-	-	-	-
FREE BENZOATE (mM/g_{cem})	-	-	-	-
FREE/TOTAL BENZOATE (%)	-	-	-	-
pH	13.69	13.69	13.68	13.69

SPECIMEN	CYLINDERS CONTAINING 0.4% SODIUM CHLORIDE & 2% CALCIUM NITRITE.CURED IN 100% R.H. 100 DAYS.			
WATER CONTENT (g/g_{cem})	FREE=0.3157 BOUND= 0.1831 TOTAL= 0.4988			AVERAGE RESULTS
TOTAL CHLORIDE (mM/g_{cem})	0.0684	0.0684	0.0684	0.0684
FREE CHLORIDE (mM/g_{cem})	0.0068	0.0069	0.0069	0.0069
FREE/TOTAL CHLORIDE (%)	9.9	10.1	10.1	10.1
TOTAL NITRITE (mM/g_{cem})	0.1333	0.1333	0.1333	0.1333
FREE NITRITE (mM/g_{cem})	0.0096	0.0089	0.0097	0.0094
FREE/TOTAL NITRITE (%)	7.2	6.7	7.3	7.1
TOTAL BENZOATE (mM/g_{cem})	-	-	-	-
FREE BENZOATE (mM/g_{cem})	-	-	-	-
FREE/TOTAL BENZOATE (%)	-	-	-	-
pH	13.66	13.65	13.67	13.66

SPECIMEN	CYLINDERS CONTAINING 0.4% SODIUM CHLORIDE & 1.84% SODIUM NITRITE. CURED IN 100% R.H. 50 DAYS.			
WATER CONTENT (g/g_{cem})	FREE= 0.3168 BOUND= 0.1822 TOTAL= 0.4990			AVERAGE RESULTS
TOTAL CHLORIDE (mM/g_{cem})	0.0684	0.0684	0.0684	0.0684
FREE CHLORIDE (mM/g_{cem})	0.0120	0.0117	0.0120	0.0119
FREE/TOTAL CHLORIDE (%)	17.5	17.1	17.5	17.4
TOTAL NITRITE (mM/g_{cem})	0.1333	0.1333	0.1333	0.1333
FREE NITRITE (mM/g_{cem})	0.0070	0.0070	0.0069	0.0070
FREE/TOTAL NITRITE (%)	5.3	5.3	5.2	5.3
TOTAL BENZOATE (mM/g_{cem})	-	-	-	-
FREE BENZOATE (mM/g_{cem})	-	-	-	-
FREE/TOTAL BENZOATE (%)	-	-	-	-
pH	13.78	13.75	13.76	13.76

SPECIMEN	CYLINDERS CONTAINING 0.4% SODIUM CHLORIDE & 1.84% SODIUM NITRITE.CURED IN 100% R.H. 100 DAYS.			
WATER CONTENT (g/g_{cem})	FREE= 0.3167 BOUND= 0.1824 TOTAL= 0.4991			AVERAGE RESULTS
TOTAL CHLORIDE (mM/g_{cem})	0.0684	0.0684	0.0684	0.0684
FREE CHLORIDE (mM/g_{cem})	0.0076	0.0074	0.0078	0.0076
FREE/TOTAL CHLORIDE (%)	11.1	10.8	11.4	11.1
TOTAL NITRITE (mM/g_{cem})	0.1333	0.1333	0.1333	0.1333
FREE NITRITE (mM/g_{cem})	0.0065	0.0067	0.0067	0.0066
FREE/TOTAL NITRITE (%)	4.9	5.0	5.0	5.0
TOTAL BENZOATE (mM/g_{cem})	-	-	-	-
FREE BENZOATE (mM/g_{cem})	-	-	-	-
FREE/TOTAL BENZOATE (%)	-	-	-	-
pH	13.79	13.77	13.76	13.77

SPECIMEN	CYLINDERS CONTAINING 0.4% SODIUM CHLORIDE, 1.84% SODIUM NITRITE & 2% SODIUM BENZOATE. CURED IN 100% R.H. 50 DAYS.			
WATER CONTENT (g/g_{cem})	FREE=0.3158 BOUND=0.1825 TOTAL= 0.4983			AVERAGE RESULTS
TOTAL CHLORIDE (mM/g_{cem})	0.0684	0.0684	0.0684	0.0684
FREE CHLORIDE (mM/g_{cem})	0.0129	0.0120	0.0126	0.0125
FREE/TOTAL CHLORIDE (%)	18.9	17.5	18.4	18.3
TOTAL NITRITE (mM/g_{cem})	0.1333	0.1333	0.1333	0.1333
FREE NITRITE (mM/g_{cem})	0.0069	0.0066	0.0068	0.0068
FREE/TOTAL NITRITE (%)	5.2	5.0	5.1	5.1
TOTAL BENZOATE (mM/g_{cem})	0.1389	0.1389	0.1389	0.1389
FREE BENZOATE (mM/g_{cem})	0.0505	0.0518	0.0493	0.0505
FREE/TOTAL BENZOATE (%)	36.4	37.3	35.5	36.4
pH	13.65	13.65	13.65	13.65

SPECIMEN	CYLINDERS CONTAINING 0.4% SODIUM CHLORIDE, 1.84% SODIUM NITRITE & 2% SODIUM BENZOATE CURED IN 100% R.H. 100 DAYS.			
WATER CONTENT (g/g_{cem})	FREE= 0.3153 BOUND= 0.1827 TOTAL= 0.4980			AVERAGE RESULTS
TOTAL CHLORIDE (mM/g_{cem})	0.0684	0.0684	0.0684	0.0684
FREE CHLORIDE (mM/g_{cem})	0.0074	0.0073	0.0075	0.0074
FREE/TOTAL CHLORIDE (%)	10.8	10.7	11.0	10.8
TOTAL NITRITE (mM/g_{cem})	0.1333	0.1333	0.1333	0.1333
FREE NITRITE (mM/g_{cem})	0.0062	0.0065	0.0067	0.0065
FREE/TOTAL NITRITE (%)	4.7	4.9	5.0	4.9
TOTAL BENZOATE (mM/g_{cem})	0.1389	0.1389	0.1389	0.1389
FREE BENZOATE (mM/g_{cem})	0.0485	0.0504	0.0492	0.0494
FREE/TOTAL BENZOATE (%)	34.9	36.3	35.4	35.6
pH	13.67	13.66	13.67	13.67

SPECIMEN	DISCS CONTAINING 2% CALCIUM NITRITE. CURED IN 2% SODIUM CHLORIDE SOL. 50 DAYS.			
WATER CONTENT (g/g_{cem})	FREE= 0.3161 BOUND= 0.1827 TOTAL= 0.4988			AVERAGE RESULTS
TOTAL CHLORIDE (mM/g_{cem})	0.2063	0.2045	0.2071	0.2060
FREE CHLORIDE (mM/g_{cem})	0.0648	0.0585	0.0601	0.0611
FREE/TOTAL CHLORIDE (%)	31.4	28.6	29.7	29.7
TOTAL NITRITE (mM/g_{cem})	0.1333	0.1333	0.1333	0.1333
FREE NITRITE (mM/g_{cem})	0.0086	0.0088	0.0096	0.0090
FREE/TOTAL NITRITE (%)	6.5	6.6	7.2	6.8
TOTAL BENZOATE (mM/g_{cem})	-	-	-	-
FREE BENZOATE (mM/g_{cem})	-	-	-	-
FREE/TOTAL BENZOATE (%)	-	-	-	-
pH	13.25	13.26	13.23	13.25

SPECIMEN	DISCS CONTAINING 2% CALCIUM NITRITE.CURED IN 2% SODIUM CHLORIDE SOL. 100 DAYS.			
WATER CONTENT (g/g_{cem})	FREE= 0.3163 BOUND= 0.1826 TOTAL= 0.4989			AVERAGE RESULTS
TOTAL CHLORIDE (mM/g_{cem})	0.3468	0.3521	0.3417	0.3469
FREE CHLORIDE (mM/g_{cem})	0.1044	0.1059	0.1044	0.1049
FREE/TOTAL CHLORIDE (%)	30.1	30.1	30.6	30.2
TOTAL NITRITE (mM/g_{cem})	0.1333	0.1333	0.1333	0.1333
FREE NITRITE (mM/g_{cem})	0.0030	0.0032	0.0031	0.0031
FREE/TOTAL NITRITE (%)	2.3	2.4	2.3	2.3
TOTAL BENZOATE (mM/g_{cem})	-	-	-	-
FREE BENZOATE (mM/g_{cem})	-	-	-	-
FREE/TOTAL BENZOATE (%)	-	-	-	-
pH	12.98	12.99	12.98	12.98

SPECIMEN	DISCS CONTAINING 1.84% SODIUM NITRITE.CURED IN 2% SODIUM CHLORIDE SOL. 50 DAYS.			
WATER CONTENT (g/g_{cem})	FREE= 0.3167 BOUND= 0.1825 TOTAL= 0.4992			AVERAGE RESULTS
TOTAL CHLORIDE (mM/g_{cem})	0.1810	0.1754	0.1768	0.1777
FREE CHLORIDE (mM/g_{cem})	0.0697	0.0633	0.0681	0.0670
FREE/TOTAL CHLORIDE (%)	38.5	36.1	38.5	37.7
TOTAL NITRITE (mM/g_{cem})	0.1333	0.1333	0.1333	0.1333
FREE NITRITE (mM/g_{cem})	0.0058	0.0069	0.0067	0.0065
FREE/TOTAL NITRITE (%)	4.4	5.2	5.0	4.9
TOTAL BENZOATE (mM/g_{cem})	-	-	-	-
FREE BENZOATE (mM/g_{cem})	-	-	-	-
FREE/TOTAL BENZOATE (%)	-	-	-	-
pH	13.33	13.30	13.31	13.31

SPECIMEN	DISCS CONTAINING 1.84% SODIUM NITRITE,CURED IN 2% SODIUM CHLORIDE SOL. 100 DAYS.			
WATER CONTENT (g/g_{cem})	FREE= 0.3169 BOUND= 0.1827 TOTAL= 0.4996			AVERAGE RESULTS
TOTAL CHLORIDE (mM/g_{cem})	0.3188	0.3143	0.3168	0.3166
FREE CHLORIDE (mM/g_{cem})	0.1030	0.1046	0.1038	0.1038
FREE/TOTAL CHLORIDE (%)	32.3	33.3	32.8	32.8
TOTAL NITRITE (mM/g_{cem})	0.1333	0.1333	0.1333	0.1333
FREE NITRITE (mM/g_{cem})	0.0024	0.0028	0.0026	0.0026
FREE/TOTAL NITRITE (%)	1.8	2.1	2.0	2.0
TOTAL BENZOATE (mM/g_{cem})	-	-	-	-
FREE BENZOATE (mM/g_{cem})	-	-	-	-
FREE/TOTAL BENZOATE (%)	-	-	-	-
pH	13.00	13.00	13.01	13.00

SPECIMEN	DISCS CONTAINING 1.84% SODIUM NITRITE & 2% SODIUM BENZOATE. CURED IN 2% SODIUM CHLORIDE SOL. 50 DAYS.			
WATER CONTENT (g/g_{cem})	FREE= 0.3164 BOUND= 0.1826 TOTAL= 0.4990			AVERAGE RESULTS
TOTAL CHLORIDE (mM/g_{cem})	0.1609	0.1624	0.1612	0.1615
FREE CHLORIDE (mM/g_{cem})	0.0680	0.0696	0.0680	0.0685
FREE/TOTAL CHLORIDE (%)	42.3	42.9	42.2	42.5
TOTAL NITRITE (mM/g_{cem})	0.1333	0.1333	0.1333	0.1333
FREE NITRITE (mM/g_{cem})	0.0059	0.0057	0.0060	0.0059
FREE/TOTAL NITRITE (%)	4.4	4.3	4.5	4.4
TOTAL BENZOATE (mM/g_{cem})	0.1389	0.1389	0.1389	0.1389
FREE BENZOATE (mM/g_{cem})	0.0133	0.0133	0.0133	0.0133
FREE/TOTAL BENZOATE (%)	9.6	9.6	9.6	9.6
pH	13.23	13.21	13.22	13.22

SPECIMEN	DISCS CONTAINING 1.84% SODIUM NITRITE & 2% SODIUM BENZOATE. CURED IN 2% SODIUM CHLORIDE SOL. 100 DAYS.			
WATER CONTENT (g/g_{cem})	FREE= 0.3164 BOUND= 0.1828 TOTAL= 0.4992			AVERAGE RESULTS
TOTAL CHLORIDE (mM/g_{cem})	0.2635	0.2587	0.2619	0.2614
FREE CHLORIDE (mM/g_{cem})	0.1036	0.1028	0.1031	0.1032
FREE/TOTAL CHLORIDE (%)	39.3	39.7	39.4	39.5
TOTAL NITRITE (mM/g_{cem})	0.1333	0.1333	0.1333	0.1333
FREE NITRITE (mM/g_{cem})	0.0019	0.0020	0.0019	0.0019
FREE/TOTAL NITRITE (%)	1.4	1.5	1.4	1.4
TOTAL BENZOATE (mM/g_{cem})	0.1389	0.1389	0.1389	0.1389
FREE BENZOATE (mM/g_{cem})	0.0070	0.0082	0.0076	0.0076
FREE/TOTAL BENZOATE (%)	5.0	5.9	5.5	5.5
pH	13.02	13.00	13.01	13.01

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