CEMENT COMPOSITION EFFECT ON CORROSION OF STEEL IN CONCRETE

by

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SUMMARY

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"CEMENT COMPOSITION EFFECT ON
CORROSION OF STEEL IN CONCRETE"

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A study of several chemical, electrochemical and environmental factors which affect the risk of embedded steel corroding in cement pastes and concrete has been carried out. The effect of the modification of the cement by the addition of blending agents such as pulverised fuel ash and ground granulated blast furnace slag has also been considered.

The effects of deliberate internal additions of chloride ions, on the pore solution chemistry of Portland cement pastes were studied, using a pore solution expression device. This equipment was used to obtain samples of pore solution from hardened cement pastes for subsequent analysis for certain ionic species.

Diffusion coefficients for chloride ions at 25°C were obtained for hardened Portland cement pastes, using a quasi-steady state diffusion technique. Activation energies for the diffusion process, were obtained for several of the cements studied.

The electrochemical behaviour of embedded steel in hardened cement pastes was examined using several techniques. Firstly the technique of AC Impedance was employed and secondly Linear Polarisation.
Rest potential measurements were also made in some cases.

A petrographic examination of a number of concrete samples from existing structures in the Middle east was carried out using a thin section technique. This enabled an assessment of the condition of the concrete to be made and made it possible to attempt to relate environmental conditions to the condition of the concrete.

The author also participated in the setting up of a field trial exposure programme in the Middle East and the UK. The aim of this was to have standardised laboratory produced concrete exposed to the two very different climatic conditions and thereby have a realistic comparison of the effects of each climate on the same type of concrete.

KEY WORDS cement, corrosion, steel, diffusion, chlorides

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CHAPTER 1

INTRODUCTION

1.1 The History of Reinforced Concrete

Concrete is a building material composed of cement, stone, sand and water. It is a material with its roots in even earlier civilisations than the Egyptians. The form in which we know it today, however, has a development span of approximately a century and a half. There have been quite remarkable developments in the last decade or two, with new kinds of concrete handling techniques and new designs for concrete structures. Even so some of the earlier developments, are in their way, just as worthy of note.

We may never know who made the first concrete because early attempts probably resulted in a very friable material, all traces of which will have long since disappeared. The oldest concrete so far discovered dates from around 5600BC and was found in Yugoslavia [1]. It was used to construct hut floors by Stone-Age men. After this there seem to be no further examples until Egyptian times. A form of concrete was used in the Great Pyramid at

Giza in Ancient Egypt in 2500BC. For many years concrete was used just as an infill material for stone walls and only much later did it develop as a structural material in its own right. The art of making concrete eventually spread from Egypt around the Eastern Mediterranean and by 500BC was being used in Ancient Greece. So called "Pseudo-concrete" preceded real concrete and consisted of roughly broken stone held together with a mortar of lime and sand. It is known as "pseudo-concrete" because the mortar was too weak to bind the whole together as a compact mass.

It is thought that the Romans copied and developed the idea of making concrete from the Greeks. Examples of early Roman concrete dating back to 300BC have been found. In fact the word concrete comes from the Latin 'concretus' meaning compounded. During the second century BC the Romans quarried a pink sand-like material from a source near Pozzuoli. When added to lime they found that the mixture resulted in a much stronger concrete than they had produced before. The material they had quarried was in fact a fine volcanic ash containing silica and alumina which combined chemically with the lime to produce what became known as pozzolanic cement.

The Romans attempted to reinforce some of their concrete structures with bronze strips and rods. This was because although concrete is quite strong in compression, it has considerably lower tensile strength and in most structures the applied loading is tensional. Bronze however was not a good choice of reinforcement material. Although there was some improvement in the tensile strength of the concrete, the bronze had a higher rate of thermal expansion than the concrete and caused spalling and cracking. Nowadays steel is used as the reinforcement material, because of its compatible coefficient of thermal expansion with concrete over the range of normal temperatures.

Because of the failure of bronze as a reinforcement material the Romans had to design their structures in compression and this resulted in walls of massive thickness sometimes in excess of 8 metres. This led to the development of lightweight concrete which used crushed pumice (a porous volcanic rock) as an aggregate. With the decline of the Roman empire the knowledge of concrete technology was lost for a time until reintroduced by the Normans in Britain. Again in Medieval and Renaissance periods very little concrete was used and it was not until the middle of the Eighteenth century that a further revival came about. In 1756 a Leeds engineer John Smeaton was commissioned to build the third Eddystone lighthouse.

Smeaton decided to build the lighthouse from blocks of stone but needed a material to bind them together. The only cements available in 1756 were weak and slow setting and would be washed away by the sea before they had hardened. He decided to investigate the properties of mortars by trying out different sorts from all over the country. He eventually settled on a mixture of burnt limestone from South Wales and a pozzolana from Civitaveccha When the two were combined they produced a cement with superior hardening properties when used under water. Thus Smeaton produced the first good quality cement since the downfall of the Roman empire. Smeaton outlined his research in a book entitled "A Narrative of the Eddystone Lighthouse". As a result of reading this book Joseph Aspdin carried on where Smeaton left off and tried to produce a new and better cement. On 21 October 1824 Aspdin took out a Patent for the manufacture of the world's first Portland cement (so called because it resembled Portland stone in colour). Aspdin's cement was the most superior of the day but since then considerable improvements have been made in the cement making process so that present day Portland cement resembles that produced by Aspdin in basic ingredients only.

As early as 1830 the first idea of reinforced concrete was mentioned in a publication entitled "Encyclopaedia of Cottage, Farm and Village Architecture", which suggested that a lattice of iron tie rods could be embedded in concrete to form a roof. The man who is generally credited with the invention of reinforced concrete however is William Wilkinson. In his patent application of 1854 he states that "a number of strips of hoop iron are to be laid on edge and embedded in mass concrete at distances of about 2 feet (600mm) - the distance may vary depending on the desired strength of the floor, if set in a low position the strips will act with more power as tension rods."

By the 1890s concrete was being used extensively for dockworks, river banks and bridges, but in all this time Wilkinson's ideas had not attracted much attention and it was the French who were to pioneer further development. The most famous of the French workers was Francois Hennebique. The popularity of his system of reinforced concrete was such that by 1910 over 40,000 structures of various kinds had been completed.

Until this time all concrete had been compacted by hand, but in 1917 another Frenchman, Eugene Freyssinet discovered the value of mechanical vibration. He is better known, however, for pioneering the system of prestressing that still bears his name. Between the First and Second World Wars attention was focussed on the development of prestressed concrete. Prestressing involves creating preliminary compressive stresses in the concrete, with the primary object of avoiding cracking under the conditions of working load. In most cases the prestress is applied by stretched steel wires or bars. The steel is said to be pre-tensioned if it is stretched before the concrete is set, and post-tensioned if it is stretched after the concrete has hardened. Prestressing permits the design of slender yet strong units with a saving in time and materials. Work is still being carried on to improve the performance and cost effectiveness of concrete. Specialist cements have been developed for use in demanding conditions, for example sulphate Resisting Portland Cement (SRPC) for use in environments where sulphate attack may be a problem. Although Portland Cement is a relatively cheap building material, its scale of use means that even a small percentage saving in material can result in a worthwhile finanical gain. Partly towards this end there has been an increasing trend to use waste materials such as Pulverised Fuel Ash (PFA) and Ground Granulated

Blast Furnace Slag (GGBFS) as partial cement replacements. More recently Microsilica, a by-product from the metallurgical industry, has begun to be considered as a partial replacement. When considering the financial incentives to use these materials it must also be ascertained whether they produce a concrete of as good a quality as a conventional Ordinary Portland Cement. One of the aims of this work therefore is to assess the performance of a range of these new blended cements.

1.2 The Nature of Concrete

Concrete is not a completely solid material. It is in fact porous by nature. Many factors can affect the physical pore structure and the chemical composition of the pore solution of concrete. Consequently the nature of concrete as a corrosive medium is difficult to define in general terms. The most important and active constituent of concrete is the cement which acts as a hydraulic binder. Portland cement in unhydrated form is made up of four minerals. These are approximately tricalcium silicate ($3CaOSiO_2$), dicalcium silicate ($2CaOSiO_2$), tricalcium aluminate ($3CaOAl_2O_3$) and tetracalcium alumino-ferrite ($4CaOAl_2O_3Fe_2O_3$). Cement chemists use an abbreviated notation for these cement minerals and these are C_3S, C_2S, C_3A and C_4AF respectively. When mixed with water the constituent materials of Portland cement undergo complex hydration reactions. These transform the paste over a period of time to a hardened matrix of hydration products. The most important reactions, so far as the development of physical structure and mechanical strength are concerned, are those involving C_3S and C_2S which are converted to a gel of calcium silicate hydrates of ill-defined composition and structure (CSH gel) and to calcium hydroxide produced mainly in the form of well developed portlandite crystals [2]. In a fully hydrated sample C-S-H gel would account for $\sim$ 70% of the weight of the cement paste and calcium hydroxide for $\sim$ 20% [3].

The aqueous phase rapidly acquires a high pH value. After a few weeks of hydration pH values much in excess of 13 are produced [4,5]. In all but extremely oxygen starved environments, the main mechanism of corrosion protection afforded by concrete involves passivation of the embedded steel. This results from the chemically inhibitive influence of hydroxyl ions.

1.3 The Corrosion of Steel in Concrete

Under normal conditions well made concrete will provide adequate protection to the reinforcement against corrosion. However, corrosion still remains the most common cause of deterioration of reinforced concrete. The corrosion of steel in concrete has many similarities with corrosion under other circumstances. The presence of an electrolyte (the aqueous phase in concrete) and access of oxygen are required. The final result of the corrosion process is the formation of a corrosion product layer on the steel reinforcement which exerts sufficient tensile forces within the concrete, to crack and spall the concrete cover. The presence of calcium hydroxide solution in set concrete produces an alkaline environment for the steel. This promotes a protective oxide film on the surface of the steel rendering it passive. For corrosion to take place this protective film must be flawed and there must be access of oxygen. The stability of the film depends on the maintenance of a certain minimum pH value and under such conditions the presence of oxygen will not cause corrosion. The access of carbon dioxide reduces the pH to 10 and lower and reduces the alkaline protection of the concrete. Access of oxygen will then cause corrosion.

The corrosion of steel is an electrochemical process associated with the presence of anodic and cathodic areas arising from inhomogeneities in the surrounding liquid medium or even on the steel surface itself.

The reactions involved in the corrosion process are:-

ANODE

$$2\ Fe\ (metal) \longrightarrow 2\ Fe^{++} + 4\ e^-$$

CATHODE :

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

The ferrous ions and hydroxyl ions then combine to produce ferrous hydroxide

$$2\ Fe^{++} + 4\ OH^- \longrightarrow 2\ Fe\ (\ OH\ )_2$$

followed by oxidation of the ferrous ion to the ferric state.

The extent to which these reactions proceed depends upon the conductivity of the electrolyte and the difference in potential between the anodic and cathodic areas.

anodic zones raises the potential to a value close

For steel in concrete, the strong polarisation of the anodic zone raises the potential to a value close to that of the cathode and as predicted by the Pourbaix E-pH diagram [6], the surface of the steel is passivated by the formation of an oxide layer [7].

The overall corrosion reaction may be slowed by reducing the rate at which oxygen reaches the cathode, thereby retarding the cathodic process. This may well occur when the concrete is saturated as a result of being fully submerged for long periods in water [8] the oxygen access at the cathode

In addition to the loss of passivation caused by carbonation, corrosion can be promoted by the presence of aggressive ions such as chloride ions in the concrete. Chlorides may be introduced into the concrete during manufacture or during service. During manufacture chlorides may be admitted as deliberate additions, such as calcium chloride, to accelerate setting and hardening, although this is now discouraged for concrete containing embedded metal [9]. Alternatively chlorides maybe introduced as contaminants in the aggregates or mixing water. This can be particularly important in certain parts of the world where the use of local materials is necessary [10, 11]. During service chlorides from the environment, such as seawater deicing salts etc. may penetrate the concrete [12, 13].

The presence of chloride ions raises the pH required to stabilise the passive film to a value in excess of that which may be produced by the pore solution, so stimulating corrosion [14].

1.4 Aims of Research

The influence of cement composition on the corrosion behaviour of steel in concrete containing chlorides and sulphates is thought to depend on a complex and imperfectly understood interaction of several variables [15]. In particular, variables which affect the activities and diffusion coefficients of free chloride and hydroxyl ions in the pore electrolyte are of prime importance.

As a result Aston University in collaboration with the Building Research Establishment has undertaken a fundamental investigation of these effects using a range of cements from both British and Middle Eastern sources. The results are expected to have practical significance, because of the increasing trend towards the use of marine dredged aggregates in Britain and secondly because of the use of saline local aggregates in the Arabian Gulf States.

Problems encountered in the Middle East are of a more severe nature than those in the United Kingdom because of complicating factors such as adverse climatic conditions and ground salt contamination e.g. sulphates.

When considering the use of chloride-bearing materials or when investigating the durability of reinforced concrete structures - it is of practical importance to consider the threshold level of chloride ion, which is necessary to stimulate the corrosion of steel in concrete. The range of variables which would influence this threshold level is so large that it is impossible to give a definitive value. However guidelines have been prepared by the Building Research Establishment based on a large number of surveys of reinforced structures in Britain [16]. In these the risk of corrosion has been assessed. For concrete made from ordinary Portland Cement it is proposed that a low risk is associated with chloride contents by weight of cement of $< 0.4\%$,an intermediate risk for chloride contents of 0.4 - 1.0% and a high risk for levels greater than 1.0%.

These limits are intended as a guide only and are not based on any mechanistic interpretations of the factors which determine the risk of corrosion in concrete containing a given quantity of chloride ion.As these factors are likely to influence the corrosion risk associated with given amounts of chloride ion present, it is necessary to examine their relative importance and roles.

The more important factors would seem to be:

1. Chlorides in the presence of other contaminent anions such as sulphates
2. Chlorides in concrete of varying water/cement ratio
3. Chlorides in concrete made from cements of different compositions
4. Chlorides introduced at or after the time of mixing
5. Chlorides in concrete cured or exposed in different conditions

In this work several of these factors were examined with the ultimate aim of providing a league of cements which would be suitable for use under varying degrees of exposure to chloride contamination.

The basic aims of the work are:-

1. To examine the chloride ion binding capacity of a range of cements of United Kingdom and Middle Eastern origin at several levels of initial contamination and in combination with sulphate ion contamination

2. To determine diffusion coefficients and activation energies for chloride ion transport through a range of cement pastes.

3. To assess relative rates of corrosion of steel in various cement pastes using electrochemical techniques.

4. To determine whether blending agents such as PFA and GGBFS have detrimental effects on the above factors.

5. To examine existing structures in the Middle East and formulate an exposure site programme in the Middle East to examine effects of climate in conjunction with previous factors.

1.5 Plan of Presentation

Each chapter consists of an introduction to the work carried out, comprising of previous work undertaken by other researchers, the theory associated with the subject and the basic aims of that section of work. The experimental work is then described, followed by a presentation and discussion of the results obtained. Finally conclusions are drawn and discussed.

Chapter 2 deals with the major experimental techniques used and describes the associated theory behind them. Minor techniques are included in the relevant chapters.

Chapter 3 describes the expression and analysis of the pore liquid from various hardened cement pastes containing deliberate additions of chloride.

Chapter 4 deals with the determination of diffusion coefficients and activation energies for chloride ion movement through cement pastes of various type.

Chapter 5 is concerned with the assessment of corrosion rates of steel embedded in cement pastes, with deliberate additions of chloride, using electrochemical methods.

Chapter 6 contains an examination of specimens of concrete from existing structures in the Middle East. An exposure site programme involving the manufacture of specimens in the UK for exposure in the Middle East is described.

Chapter 7 is a discussion of the general conclusions arrived at and suggestions for further work.

CHAPTER 2

MATERIALS AND EXPERIMENTAL TECHNIQUES

2.1 Materials

2.1.1 Cements

A range of cements and cement blends was used in this research, both of British and Middle Eastern origins. Many of the British cements were in stock but the remainder and also the Middle Eastern cements were supplied by the Building Research Establishment. Although quite a large number of cements were used in total during this work, five cements were concentrated on specifically throughout the work with the aim of producing an order of suitability for use in environments where aggressive ions are likely to be encountered.

The cements used were all stored in airtight drums until required.

A list of the cements used together with their chemical compositions is given in table 2.1.

2.1.2 Pulverised Fuel Ash

Pulverised fuel ash (PFA) from Stourport Power Station was blended with a well characterised ordinary cement (OPC B) to a level of 30% of the total weight for work in chapters 3,4 and 5.

Eggborough PFA was blended with OPC D to a level of 5% of the total weight for work in chapters 4 and 5. This cement was supplied already blended with the PFA. OPC A was also supplied with 5% PFA added. Chemical analyses are shown in Table 2.1

2.1.3 Blast Furnace Slag

Ground granulated blast furnace slag (GGBFS) supplied by the Frodingham Cement Co Ltd was added to OPC B to a level of 65% of the total weight for work in chapters 3,4 and 5. OPC F was supplied already blended with 5% BFS for work in chapters 4 and 5. Chemical analyses are given in table 2.1.

2.1.4 Silica

Microsilica supplied by Elkem Ltd was blended with OPC B to a level of 10% for work in chapter 4 A chemical analysis is given in table 2.1.

2.1.5 Concrete

Samples of concrete from existing Middle Eastern structures were supplied by the Building Research Establishment for petrographic examination. These are discussed in chapter 6.

2.2 Specimen Preparation

2.2.1 Preparation of Specimens for the extraction of Pore Liquid

The required amount of cement was taken from air tight bins where it was stored and sieved using a 150 micron mesh. It was then mixed by hand with the appropriate volume of water in a glass beaker to obtain the desired water/cement ratio. Mixing continued vigorously until a homogenous paste was obtained. When thoroughly mixed the paste was carefully poured into plastic cylindrical moulds, (49mm in diameter and 75mm in height) to avoid trapping excess air, and levelled off at the top using a wooden spatula. The filled cylinder was then vibrated for 2-3 minutes using a small vibrator. The vibrator was then switched off and the resulting mixture of air bubbles and cement paste which formed at the surface of the cement paste was carefully removed using the spatula. Fresh cement paste was used to replace that taken away and vibration was carried out for a further 2-3 minutes. Again the aerated mixture at the surface was removed and replaced by fresh cement. The surface was levelled off and the cylinder was capped with a sealable top.

The sealed cylinder was then placed in a ball mill and rotated for 24 hours to avoid segregation within the paste. Rotation took place in the plane parallel to the ends of the cylinder. After this period the cylinder was removed from the ball mill and the hardened cement paste carefully cut free from the disposable plastic mould. The cylinder was then marked for identification and stored in sealable plastic bags with a wad of moist cotton wool to maintain the high humidity, and in turn these bags were kept in the curing room at a constant temperature of 22°C and high relative humidity. The samples were kept in such a manner until the required age for testing had been reached.

When it was desired to make the addition of agents such as chlorides and sulphates these were introduced into the samples via the mixing water.

2.2.2 Preparation of Specimens for Chloride Ion Diffusion Measurement

Samples were prepared in much the same way as for the extraction of pore liquid. However, after demoulding the cylinders were stored under saturated calcium hydroxide solution and placed in a curing room at a constant temperature of 22°C. The samples were cured in this condition for sixty days. Ultrasonic pulse velocity (UPV) measurements were carried out to verify the quality of the cylinders, i.e. the density,and discs of between 2 and 3mm were cut using a Microslice diamond tipped circular saw. This was lubricated with deionised water. The ends of the cylinders, approximately 10-15mm were discarded to prevent the discs cut from this region having any deficiencies due to segregation Once cut the discs were given a gentle polish on 600 grade grinding paper using deionised water as a lubricant. The thickness of the discs was then measured in several places to obtain an average value, using a micrometer. The discs were then ready to be assembled into the cells used for the diffusion experiments.

2.2.3 Preparation of Petrographic Specimens

The initial condition in which the samples of the Middle Eastern concrete arrived was one of assorted size and irregular shape. So first of all these had to be cut down to a manageable size. A slice of between 10mm and 15mm was taken after producing a flat edge using a circular saw. This was then trimmed so as to fit a glass slide and then washed in warm water and oven dried. (The water temperature and oven temperature did not go above $50^{o}C$ otherwise detrimental reactions within the concrete may have occurred).

Whilst the specimen was being dried, preparation of the glass slide could be carried out. Glass slides cannot be produced to an exact standard size by the manufacturer and this can cause inherent errors in the lapping operation if it is not compensated for. So for this reason the slide is ground down to a thickness of 1mm using a Logitech lapping wheel. When the slide is done it is washed with warm water and detergent and then dried.

Once the concrete sample was dried it was ready for the next stage of preparation. Specimens which were in a poor condition i.e. those which were cracked or looked as though they might have cracked during subsequent preparation needed to be impregnated with resin. The specimens were arranged in a container and resin which was mixed with 10% by volume of hardener and dye if required was poured onto them. These were then placed in a desiccator and a vacuum was applied. When all the frothing of the resin died down this indicated that the penetration of the resin into the specimen was complete. The specimens were then put into the oven to set. This was a fairly slow process. When the resin had set the specimen was exposed using a large Abwood grinder. This had to be done at a fairly slow and constant speed to avoid 'ripping' the concrete rather than grinding it. Also when flint-like aggregates are present there is a danger of sparks igniting the oil which is used as a lubricant.

When the surface of the concrete was exposed the excess resin from the edges was sawn off. The opposite face of the specimen could also be ground to save polishing time later if desired. The specimen was then put on the 'Logitech' grinder to polish the exposed surface. The grinding agent used was an alumina powder in a mineral oil vehicle. After grinding, the specimen was placed in a beaker of Ardrox solvent and put in an ultrasonic bath for approximately 3 minutes before being removed and rinsed with Ardrox. Ardrox is a degreasing compound similar to acetone.

Both the glass slide and the specimen were then given a rub down on a glass block, (the surface of which was coated with fine alumina and mineral oil) before being washed and rinsed with methylated spirit and then put on a hotplate to dry. Glue which hardened in response to ultra violet light was applied to the specimen and the glass slide was carefully placed on top to avoid trapping air. The slide and specimen were then put into a press which was pumped up to a pressure of approximately 2MPa making sure the specimen stayed fairly central on the slide. The slide and attached specimen were then placed under ultra violet light for several minutes to set the glue.

The excess specimen could now be cut off using a Logitech saw with an automatic feed attachment. The specimen was now down to approximately 1mm in thickness. The slide and specimen were then put on the Logitech lapping wheel to polish the specimen down to a thickness approaching 30 microns. After washing with Ardrox the specimen was ground on a C15 oil slab by hand and then on a C9 oil slab. (C15 and C9 refer to coarseness of the grinding powder used. C15 being coarser than C9) When the specimen was down to 30 microns it was cleaned in the ultrasonic cleaner. The slide was finished by washing with Ardrox and then trimming off the excess glue and resin from around the specimen with a razor blade. A cover slip was trimmed to size, washed with Teepol and water and then methylated spirits and finally dried with compressed air. With both the slide and cover slip on the hotplate hystorone was applied to the specimen and the cover slip was put onto the specimen in the same way that the glass slide was.

2.2.4 Preparation of Specimens for use in Electrochemical Work

Two designs of specimen were used for this work. One was as used in work carried out by the

Building Research Establishment, Figure 2.1, and the second was as used in previous work within the department, Figure 2.2. The main differences between the two types of specimen are the size and the method of stopping off the electrodes so that a known area of steel is exposed to the cement paste. In the first design the cement was sieved using a 150mm mesh and mixed by hand with deionised water to form a homogeneous paste. Any additions such as chlorides were introduced in the mixing water. Electrodes had previously been prepared. These consisted of 6mm diameter mild steel for (analysis is given in table 2.2) which were cut to length and cleaned mechanically with an abrasive paper and then chemically using Ardrox and acetone. Heat-shrink plastic tubing was applied to the steel electrode so that only a known area of steel would be in contact with the cement paste when the cell was assembled. The electrodes were then inserted into holes in a 100mm diamter plywood disc.

The mixed cement paste was cast into 600ml volume polyethylene beakers taking care to avoid trapping the cement paste, the plywood disc seating itself on the inner lip of the beaker. An agar/potassium nitrate salt bridge was then inserted into the cement paste between the two electrodes via another hole in the plywood disc. The other end of the salt bridge being immersed in saturated calcium hydroxide solution.

The completed cells were stored in a watertight box at high humidity and left to harden.

The second design of electrochemical specimen ulitised the disposable plastic moulds which were mentioned in the previous sections on specimens for pore liquid extraction and diffusion measurement. The electrodes were not stopped off at the bottom in this case and epoxy resin was used instead of heat shrink tubing. Instead of the plywood disc the cap of the disposable mould was used to hold the electrodes and salt bridge in place during setting of the cement paste. The manufacture of the electrode and the assembly of the cells was in all other respects similar to that in the first design. However once the cement paste had set the plastic moulds were stripped off and the cells stored in the same way as previously described.

2.3 Extraction of Pore Liquid from Hardened Cement Pastes

Following work in France [17] and America [18] it was found that it is possible to extract unbound water which is present in the pores of hydrated cement paste in sufficient quantities to allow analyses to be performed. On the basis of this success the construction of a press designed along the lines of the equipment used by Diamond [18] was commenced by 'Aston Services' to specifications provided by Dr. C.L. Page and Mr. J. Slimak. This piece of equipment was available to the author at the commencement of the project. This is shown in Figures 2.3 and 2.4.

The press is capable of accepting the cylinders described in section 2.2.1 and also pulverised concrete of the same volume. It consists of a platen into which a concentric groove has been cut, that has an outlet to a collection system. The cement specimen sits on the platen, inside the groove and is surrounded by the die body which provides the radial pressure. A piston assembly provides the axial pressure. A Polytetrafluroethylene (PTFE) disc placed between the specimen and the piston assembly prevents pieces of the specimen breaking off and getting lodged between the die body and the piston assembly. It also helps to distribute evenly the load over the top of the specimen. The press is capable of creating a pressure of 375 MPa; however liquid is often expressed well within this limit.

In this work several methods of collection of the pore liquid were tried, including drawing the liquid off under vacuum and blowing nitrogen through the apparatus whilst it was under load. In some cases, particularly with young pastes, the pressure alone was sufficient to expel the solution.

However the method eventually settled upon was that used by Diamond [18] in which the liquid is drawn off by means of a syringe whilst the press is under load. All the internal parts of the press received a generous coating of PTFE spray. The press was then assembled with the cement cylinder inside. The pressure was applied slowly and after excess air had been expelled from the apparatus a plastic syringe was attached to the PTFE drain tube with another piece of plastic tubing. Pressure continued to be applied and the liquid was drawn off using the syringe. The necessary pressure to be applied depended on factors such as the age of the specimen, the water cement ratio, type of cement etc. When sufficient liquid had been collected in the syringe it was transferred to a small airtight plastic vial for storage until the analysis could be performed. A plastic collection and storage system had to be used because of the highly alkaline nature of the pore liquid. If glass containers had been used there would have been the possibility of silicate pick up from the glass.

When the liquid had been collected the press was dismantled and the cement slug removed. The press was cleaned thoroughly with water to remove any aggressive ions which might corrode it. This was followed by an application of ethanol and then acetone to drive off any remaining water. Finally the parts which came into contact with the cement were sprayed with PTFE again. Any stubborn debris which remained in the die body was removed with a fine abrasive paper.

2.4 Determination of Diffusion Coefficients for Chloride Ions in Hydrated Cement Pastes

Work on the measurement of diffusion rates for some cements was initiated several years ago [19] and this work carried on the investigation using the same technique. The discs described in section 2.2.2 were assembled in glass cells, the arrangement of which is shown in figures 2.5 and 2.6. The assembled cells were then placed in water baths set at the temperature for which the diffusion coefficient was to be determined. For each set of conditions i.e. type of cement, water/cement ratio, levels of additives etc 4 or 5 replicate cells were used to obtain an average value. An incubation period which varied according to the temperature was allowed to give the chloride ions in the initially concentrated half of the cell time to pass through the cement disc into the initially dilute half of the cell. 100µl alquots were then taken from the dilute half of the cell using automatic pipettes with disposable tips. The chloride concentration of these samples was determined by a standard colcrimetric test [20]. The aliquots for testing were taken at intervals which were dependant upon the temperature. The higher the temperature the more rapid the movement of the chloride ions. The aliquots were small and their removal from the cell was not significant in relation to the total cell volume.

After an initial delay (to) during which chloride diffusion becomes established across the disc, there is a linear increase with time in the chloride concentration (C_2) of the solution in compartment 2 of the cell. The concentration (C_1) in compartment 1 effectively remains constant over the period of measurement. This is consistent with conditions of quasi-steady-state diffusion across the disc and implies that the flux through all sections of the disc normal to the diffusion direction is constant and that the activity of chloride ions is effectively unchanging at all points in the disc.

The effective diffusivity (D) can be calculated from the slope of a rectilinear plot of C_2 versus t according to the equation:

$$D = \frac{V_2 L C_2}{A\ C_1} \left(\frac{1}{t-to}\right)$$

where* D is the effective diffusivity of chloride ions through the disc in m^2s^{-1}, V_2 is the volume of solution in compartment 2 in m^3, A is the cross sectional area of exposed disc in m^2, L is the thickness of the disc in m, C_1 and C_2 are the solution concentrations, to is the time taken to establish diffusion across the disc in seconds and t is the time of measurement of concentration in seconds.

The values of effective diffusivity of chloride ions can be plotted against the reciprocal of absolute temperature according to the Arrhenius equation

$$D = Do \exp \left(\frac{-Q}{RT}\right)$$

where; D is the effective diffusivity in $cm^2 s^{-1}$,

Q is the activation energy for the diffusion of chloride ions in the paste in KJ $mole^{-1}$, T is the absolute temperature in $^{\circ}K$, R is the universal gas content (KJ $mole^{-1}$), and Do is a constant. Provided the effective diffusivity can be fitted to a unique straight line, the activation energy of a single dominant process can be obtained.

2.5 Polarisation Resistance Technique

The electrochemical technique of Polarisation Resistance (also known as Linear Polarisation) was developed by Stern et al [21-24] and is a method for measuring corrosion rates. The technique is performed by applying a controlled potential scan over a small range (20mV below and 20mV above the E corr value).

The resultant current is plotted against potential as shown in Fig. 2.7. The gradient of the curve produced at E corr is the polarisation resistance value Rp.

However Andrade [25] has proposed that the slope should be determined at Ecorr by joining it with a point 10mV more noble and measuring the resultant secant. The polarisation resistance can be used in the Stern-Geary equation [21] to calculate the corrosion current density i corr. The polarisation resistance value is used in the same way as the charge transfer resistance value Rt (see section 2.6) obtained by the AC impedance technique. Linear Polarisation is a very rapid technique. At a scan rate of 0.16mV/s a range of 40mV can be scanned in less than 5 minutes. It is important to choose a suitable sweep rate for the system under investigation, as pointed out by Gonzalez et al [26]. If the sweep rate is too high an I corr higher than the real value may be yielded, when the transient component of the intensity is still significant. A sweep rate which is too low may alter the electrode during the course of the scan and give too low an I corr value.

Andrade et al have used the linear polarisation technique over a number of years for estimating the corrosion rate of reinforcements in concrete. In the majority of cases they have found an acceptable agreement between gravimetric weight loss studies and values obtained from Rp measurement using a sweep rate of 0.16mV/sec [27-34].

Other authors [35-38] have studied the limitations and accuracy of the technique. As with other electrochemical techniques Rp measurement is not accurate and the corrosion rate can be in error by a factor of two as suggested by Stern. However, it is still a very useful technique and the studies on its limitations have only served to enhance the reliability.

The instrument used in this work was a Princeton Applied Research Corporation Corrosion Console connected to the specimens under study and a Standard Calomel Reference Electrode. This instrument scans and also produces a playback of the scan providing a hard copy of the plot. If the required data such as Tafel Constants are fed into the instrument it will produce a value for polarisation resistance directly and also corrosion rate.

Tafel constants typically do not vary over a wide range. As a result an estimated value of 0.1 V/decade for each Tafel constant can frequently be used. In the worst case the calculated corrosion rate will be within a factor of 2.2 of the value that would have been found using the true Tafel constants, ignoring other experimental errors [39].

The theoretical background for linear polarisation measurements was provided by Stern and Geary [21]. In a corroding system, two electrochemical reactions are present:-

$$M^{+} + e^{-} \rightleftharpoons M$$

$$Z^{+} + e^{-} \rightleftharpoons Z$$

where M is the corroding metal and Z is usually a species in solution. The current-potential relationship of such a mixed-couple system is shown in Fig.2.8. The equilibrium potentials of the couples in the above equations are labelled $E_{eq,M}$ and $E_{eq,Z}$ respectively. When the corrosion potential is sufficiently removed from $E_{eq,M}$ and $E_{eq,Z}$ the rate of reduction of M^{+} becomes insignificant compared to the rate of oxidation of M, and the rate of oxidation of Z becomes insignificant with respect to the rate of reduction of Z^{+}.

The corrosion potential is the potential at which the rate of oxidation of M (defined by current $i_{O,M}$) is equal to the rate of reduction of Z^+ (defined by current $i_{R,Z}$). The terms 'rate' and 'current' are used to mean the same thing. Since the net current is the difference between the two currents, the current measured with an external device will be zero.

$$i \text{ measured} = i_{O,M} - i_{R,Z} = 0 \text{ at } E_{corr}$$

$$\text{and } i_{corr} = i_{O,M} = i_{R,Z}$$

To calculate the corrosion rate i_{corr} must be determined. When a potential is imposed on the metal specimen from an external voltage source, such as a potentiostat a current will pass according to the following equation.

$$i \text{ measured} = i_{O,M} - i_{R,Z}$$

Assuming the anodic and cathodic currents obey the Tafel equations

$$\eta = B_a \log \frac{i_{O,M}}{i_{corr}}$$

$$\text{and} \quad \eta = -B_c \log \frac{i_{R,Z}}{i_{corr}}$$

where η = overvoltage, the difference between the potential imposed on the specimen and the corrosion potential

$$\eta = E_{app} - E_{corr}$$

The Tafel equations may be rearranged to give

$$\log \frac{i_{O,M}}{i_{corr}} = \eta/Ba$$

and

$$\log \frac{i_{R,Z}}{i_{corr}} = -\eta/Bc$$

Since log X = Y is the same as $10^{Y} = X$ these equations may be rewritten as

$$10^{\eta/Ba} = \frac{i_{O,M}}{i_{corr}}$$

and

$$10^{-\eta/Bc} = \frac{i_{R,Z}}{i_{corr}}$$

Substitution of these equations into i measured = $i_{O,M} - i_{R,Z}$ gives

$$i \text{ measured} = i_{corr} \left(10^{\eta/Ba} - 10^{-\eta/Bc}\right)$$

10^{x} can be approximated by the following power series

$$10^{x} = 1 + 2.3x + \frac{(2.3x)^2}{2!} + \ldots\ldots + \frac{(2.3x)^n}{n!}$$

If x in this series is small, the third and later terms of the series can be neglected without introducing a significant error.

Substituting η/Ba and $-\eta/Bc$ for x gives

$$10^{\eta/Ba} = 1 + 2.3\,\eta/Ba$$

$$10^{-\eta/Bc} = 1 - 2.3\,\eta/Bc$$

Substitute these equations into the ones defining i measured and simplify to give

$$i \text{ measured} = 2.3\, i_{corr}\, \eta\, \frac{Ba + Bc}{Ba\,Bc}$$

Rearrangement to solve for polarisation resistance gives

$$\eta / i \text{ measured} = \frac{Ba\,Bc}{2.3\, i_{corr}\, (Ba + Bc)}$$

$$\text{or} \quad \Delta E/\Delta I = \frac{Ba\,Bc}{2.3\, (i_{corr})(Ba + Bc)}$$

where $\Delta E/\Delta I$ is the polarisation resistance.

2.6 AC Impedance Measurement

This technique of using impedance measurements to obtain corrosion rates has recently been of increasing interest. The equipment necessary to carry out this technique was supplied by the BRE and consisted of a Hewlett-Packard 3582A Spectrum Analyser, a Hewlett-Packard HP85 Mini Computer and a corrosion cell amplifier designed and built by the BRE.

The basic concepts of the technique can be difficult to understand, particularly since most explanations tend to be highly mathematical.

However the following is an attempt to give as simple as possible an explanation of the basic principles. [40]

Electrochemical interfaces such as the surface of a corroding electrode can be seen as combinations of passive electrical circuit elements i.e. resistance, capacitance and inductance. If an alternating voltage is applied to these the resultant current can be determined using Ohms law,

$$V = IR$$

provided that R (resistance) is replaced by the appropriate expression for the reactance X of the passive element in question i.e.

$$V\ \text{peak} = I\ \text{peak}\ X$$

The reactance of a capacitor or an inductor can be expressed in several forms, the most usual using the complex number

$$j = \sqrt{-1}$$

$$X_r = R$$

$$X_c = \frac{1}{jWc}$$

$$X_L = jWL$$

where W = angular frequency ($W = 2\pi f$)

R = resistance

C = capacitance

L = inductance

This notation makes it possible to represent any reactance or the impedance of a combination of reactances, as a vector in the real-imaginary plane in the form of an Argand diagram (Fig 2.9).

An impedance can thus be completely defined by specifying the magnitude $|Z|$ and the angle $\emptyset$ its vector makes into the real positive axis or alternatively by specifying the magnitudes of its real Z' and imaginary Z'' components.

The two are equivalent since:-

$$Z' = Z \cos \emptyset \text{ and } Z'' = Z \sin \emptyset$$

or in complex number notation

$$Z = Z' + jZ''$$

Since the above reactance expressions contain W, the angular frequency of the applied waveform, the magnitude and phase angle of the impedance vector representing the response of a circuit containing reactive elements will vary as W varies. A useful means of representing the variation with frequency is the Nyquist diagram. This is an extension of the Argand diagram using frequency as a variable. The diagram consists of a set of points each representing the magnitude and direction of the impedance vector at a particular frequency. In order to appreciate the variation of the electrochemical cell impedance with frequency it is convenient to consider a hypothetical equivalent circuit - a combination of electrical circuit elements that behaves in a similar manner to the corroding electrode. The equivalent circuit proposed by Randles [41] Fig 2.10 has been found to have a wide application to many electrochemical applications.

The resistance R_Ω represents the solution and corrosion product film. The parallel combination of the resistor Rt and capacitor Cdl represents the corroding interface. Cdl is the electrochemical double layer capacity resulting from absorbed ions and water molecules and Rt is the charge transfer resistance. This quantity determines the rate of the corrosion reaction and is a measure of the electron transfer across the surface. In an activation controlled system this is the quantity measured by the linear polarisation resistance technique i.e Rt is then equivalent to Rp the linear polarisation resistance. These may be used in the Stern-Geary equation to calculate the corrosion current density i corr [21].

$$i\ \mathrm{corr} = \frac{BaBc}{2.3(Ba + Bc)} \cdot \frac{1}{Rt}$$

$$\text{or} \quad i\ \mathrm{corr} = \frac{\mathrm{Constant}}{Rt}$$

where Ba and Bc are the anodic and cathodic Tafel constants respectively.

In practice Rt and Cdl are non-linear elements, i.e. their numerical value depends on the magnitude of the applied voltage. This difficulty can be overcome by considering the response of the cell to a sinusoidal voltage of a single frequency W and a small enough amplitude for the non linearity of the cell response to be negligble. This is analogous to the use of the 10-20mV dc perturbation used in the linear polarisation technique.

The behaviour of the equivalent circuit in terms of a Nyquist plot is shown in Fig. 2.11.

The horizontal axis represents the real part of the cell impedance i.e. the resistance component and the vertical axis the imaginary component, i.e. the capacitive reactance. At high frequencies the capacitor Cdl conducts easily and effectively shorts out Rt, only the effect of the solution and film resistances R_Ω remains. This point marks the left hand intercept of the semi circle. As the frequency decreases Cdl conducts less and less and the response follows a semi circle. At low frequencies i.e. as zero frequency or d.c. is approached the capacitor ceases to conduct and the cell impedance becomes the sum of R_Ω and Rt. In practice the situation where the corrosion rate is purely activation controlled rarely occurs and complications due to concentration effects are usually present. To account for these it is necessary to include an additional circuit element W in series with Rt. This is known as the Warburg impedance and describes the impedance of the concentration related processes. The Warburg impedance has the complex number form:-

$$W = \frac{\sigma}{\sqrt{\omega}} - \frac{j\sigma}{\sqrt{\omega}}$$

where σ is the Warburg coefficient.

The most common method of interpreting data from AC impedance measurements is to use the Nyquist diagram. However, as previously mentioned, diffusion processes distort the semi circle at low frequencies making it almost impossible to obtain Rt from the diagram. However, Rt may be obtained by replotting the data on axes of Z"W against Z. Extrapolation of the linear region to the ordinate results in an intercept of (R_Ω + Rt) Fig 2.12 shows this type of plot [42]. There are several manufactured instruments available for the measurement of AC impedance but the system previously described seems to combine efficiency with ease of operation. In practice the equipment is set up as shown in Fig 2.13 and measurements were made at the following range of frequencies; 0 - 2.5Hz, 0 - 500Hz and 0 - 10KHz. The spectrum analyser measures the response from the cell and passes the data tothe mini computer which produces plots of -jZ" against Z' and Z' against Z"W from which the charge transfer resistance can be obtained.

2.7 Rest Potential Measurement

All the electrochemical specimens produced were subjected to rest potential measurement. This is a passive measurement and involves measuring the potential of the embedded electrodes with respect to a reference electrode set at OV. This was a Standard Calomel Electrode (SCE) immersed in saturated calcium hydroxide solution. The specimens and solution were linked by a salt bridge. The potentials were measured periodically and plotted against time.

2.8 Determination of Chloride Concentration in Solution using a Colorimetric Technique

This technique was used to determine free chloride concentrations in the solutions expressed from hardened cement pastes and also used to measure the concentration of the solutions in the diffusion work.

The variation in colour of a solution with varying concentrations of that solution forms the basis of colorimetric analysis [20] and is given by Beer-Lambert law. This law states that $It = Ic10^{-Ect}$

where It = intensity of transmitted light

Ic = intensity of incident light

E = molecular extinction coefficient

C = concentration of solution

t = optical path length

Hence for a constant path the log intensity of a beam of monochromatic light is inversely proportional to the concentration of the absorbing substance it passes through. The colour is formed when the solution is treated with a reagent and the intensity of the colour produced can be compared with a solution of known concentration.

A spectrophotometer Fig 2.14 was used to measure the intensity of colour of the solutions. This consists of a spectrometer which produces coloured light of any selected wavelength and a photometer which measures the intensity of light. The instrument passes one beam of light through the solution under analysis and a second beam through a reference solution (deionised water). The intensities after transmission are compared and a ratio is established. This is a measure of the opacity of the sample at the wavelength of the test. A calibration curve was prepared using solutions of known chloride concentration Fig. 2.15.

Hence from the curve one could read off the chloride concentration for any value of opacity which the spectrophotometer produced.

The main advantage of the spectrophotometer and the reason for its use here is that it provides a simple way of determining small concentrations.

The procedure for the determination of chloride concentration in solution depends upon the displacement of thiocyanate ions from mercuric thiocyanate by chloride ions. In the presence of ferric ions a coloured ferric thiocyanate complex is formed and its intensity is proportional to the chloride ion concentration:-

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

In general 0.1ml aliquots of the solution under investigation were taken using an automatic pipette These were then diluted to 10ml using 9.9mls of deionised water. 2mls of Mercuric thiocyanate in ehtanol were added followed by 2mls of a 0.25M Ferric ammonium sulphate in 9M Nitric acid solution. The solutions were then allowed to develop their colour fully over a period of 10 minutes. The solutions were then put into the spectrophotometer together with a reference solution of deionised water and the optical densities were measured at a wavelength of 460 nanometres. This value was then used to read off the concentration of the diluted solution from the previously prepared calibration curve. The concentration of the original solution was found by multiplying by the dilution factor.

In some instances the solutions were too concentrated to use at the dilutions stated and in those cases smaller aliquots were taken thereby increasing the dilution factor.

2.9 Determination of pH

In order to obtain the pH values of the solutions extracted from hardened cement pastes a small amount of the pore fluid was titrated with 0.01M nitric acid using phenolphthalein as an indicator.

The amount of expressed solution was not very large so a small aliquot 0.1ml was taken and diluted with 0.9ml of deionised water. A drop of phenolphthalein was added which gave the characteristic pink colour to the alkaline solution. This solution was then titrated with the nitric acid using a microburrette until the solution became colourless. The titre was recorded and used to calculate the pH of the solution.

2.10 Pore Size Distribution Measurements

Pore size distribution measurements were made on the blended cements under examination to see if there was any substantial difference between those and pure Portland cement.

The mercury intrusion method was used, the instrument being a Micromeritics Instrument Corporation porosimeter model 900/910 series of 351 N/mm² pressuring capacity.

The principle of the technique is to determine the quantity of non wetting liquid (mercury) that may be forced into the pores of the cement paste under various pressures. The system is first evacuated to remove gases and vapours, then the mercury penetrates the pores in relation to their size and the applied pressure. The pressure at which mercury enters a pore of a given size can be calculated using the Washburn pressure displacement equation [43].

$$P = -4\gamma \cos\theta / d$$

where P is the applied pressure

d is the pore diameter

γ is the surface tension of the mercury (485×10^{-6} N/mm)

and θ is the contact angle between the mercury and the material, (117).

The samples used were broken up discs approximately 1mm thick of hardened cement paste, cut from a cylindrical sample using a diamond cutting wheel. These were then oven dried at 105°C for several days before testing. These were determined as suitable conditions by Young and Diamond [44,45].

Table 2.1 Chemical Analyses of Cements and Blending Agents

Material	CaO	SiO_2	Al_2O_3	Fe_2O_3	SO_3	MgO	Na_2O	K_2O	Ignition Loss
OPC-A	62.8	20.8	5.1	3.4	2.9	1.3	-	0.96	1.6
OPC-B	63.0	20.3	7.1	2.7	3.3	1.3	0.47	0.60	0.8
SRPC A	64.0	20.2	4.1	5.3	2.6	1.4	0.28	0.39	1.1
OPC C	63.1	22.1	4.7	3.0	1.7	2.5	0.06	1.30	1.4
SRPC C	63.8	21.1	4.01	4.65	2.6	0.9	0.13	0.67	1.0
OPC D	65.5	22.74	5.90	1.59	1.6	1.23	0.43	0.50	0.6
OPC E	64.3	24.4	3.1	3.3	1.4	1.7	0.08	0.22	1.3
SRPC E	64.2	24.5	3.1	3.3	1.4	1.7	0.07	0.24	1.28
OPC F	64.4	21.19	5.36	3.27	2.53	0.89	0.36	0.58	1.2
SRPC B	63.9	20.3	4.18	5.21	2.69	1.5	0.32	0.36	1.33
BFS	42.4	33.3	10.8	0.3	-	8.7	0.37	0.50	-
PFA	2.9	46.6	24.0	9.5	0.9	2.1	2.00	3.80	3.3

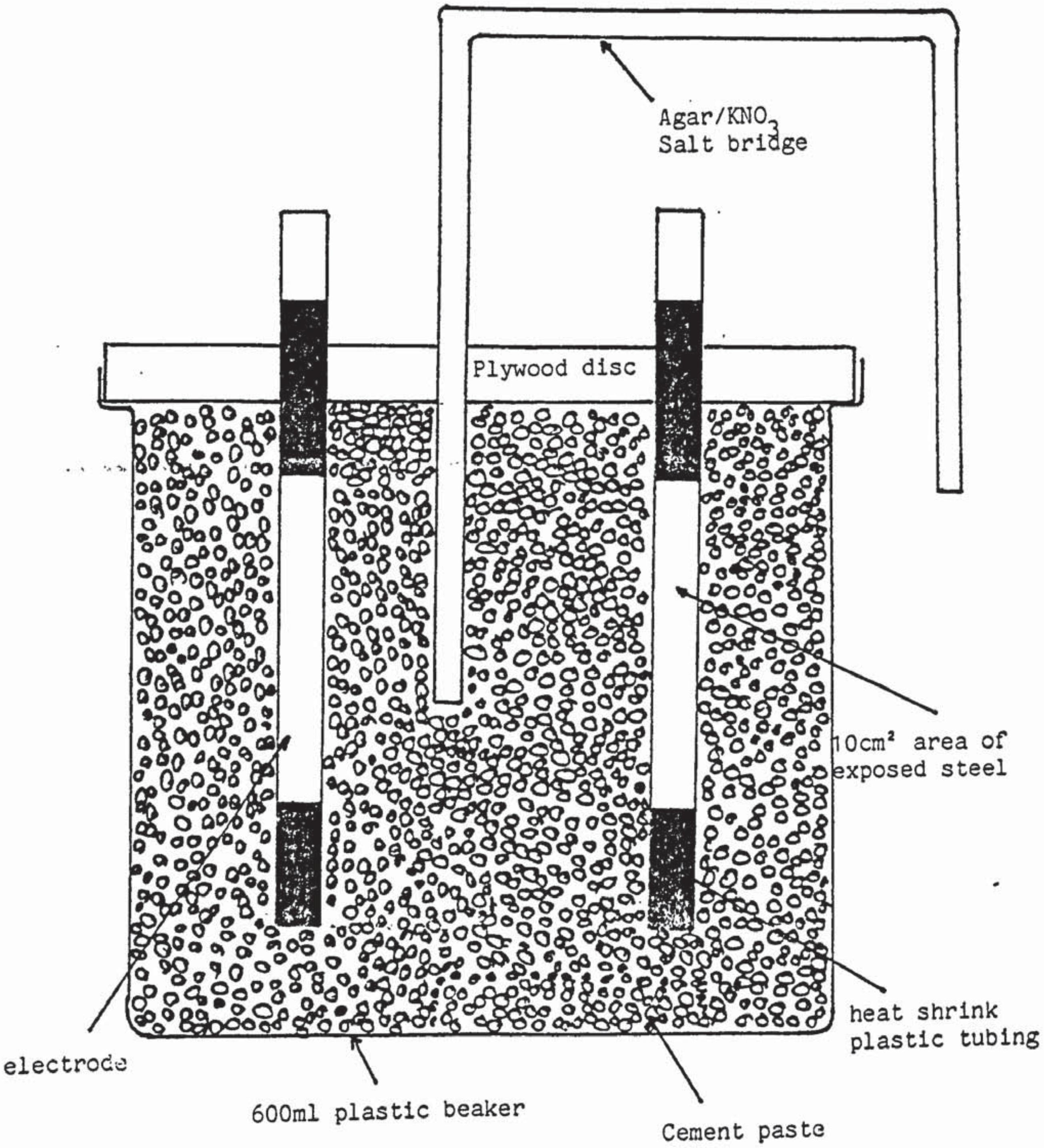


Fig 2.1 Specimen used for electrochemical studies as designed by the Building Research Establishment

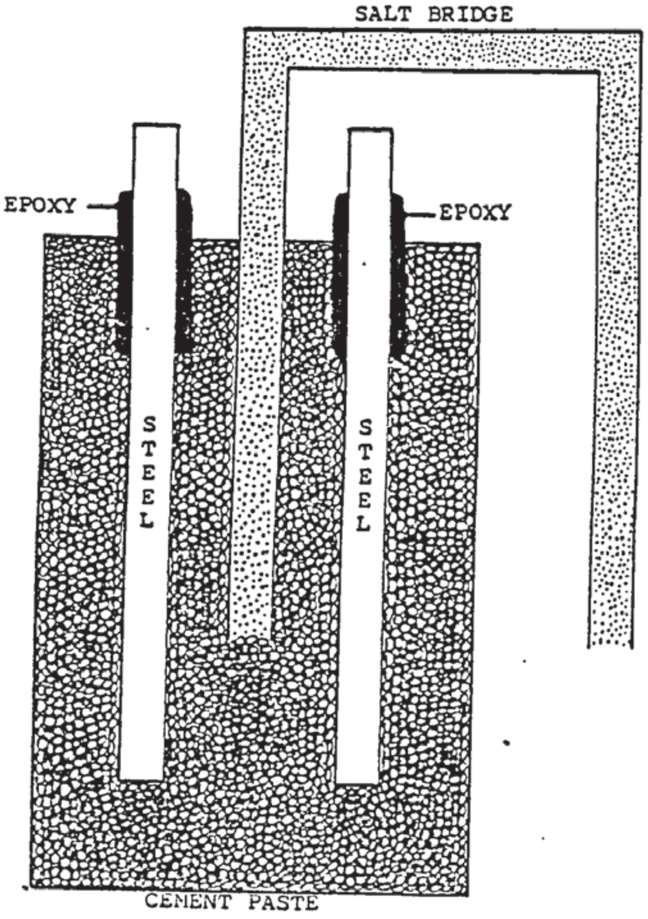


Fig. 2.2 Specimen used for electrochemical studies as designed at Aston University

Table 2.2 CHEMICAL ANALYSIS OF MILD STEEL

Element	%
Carbon	0.200
Sulphur	0.040
Silicon	0.270
Phosphorous	0.023
Manganese	0.860
Nickel	0.060
Chromium	0.150
Molybedum	0.010
Copper	0.160
Tin	0.035
Iron	Balance

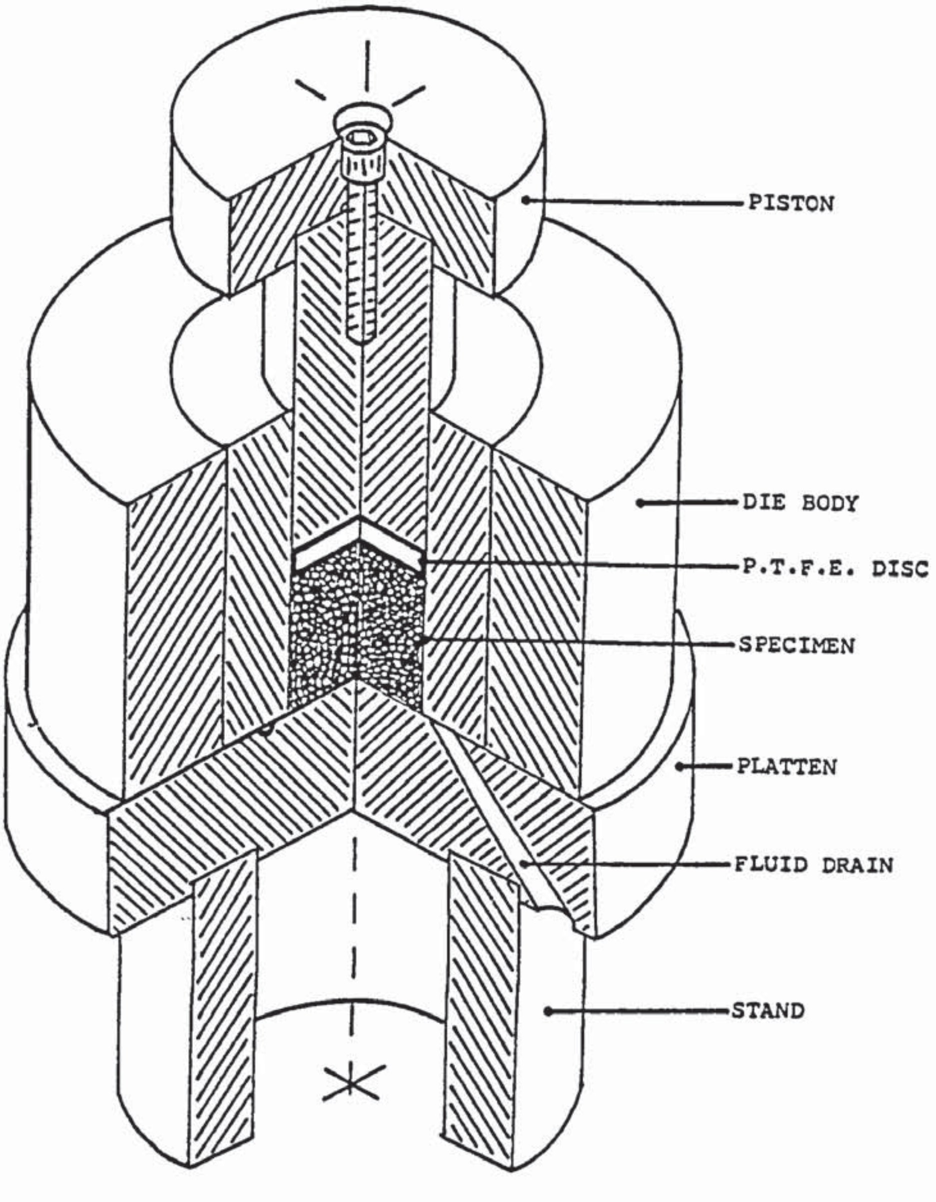


Fig 2.3 Sectional diagram of compression cell for the extraction of pore liquid

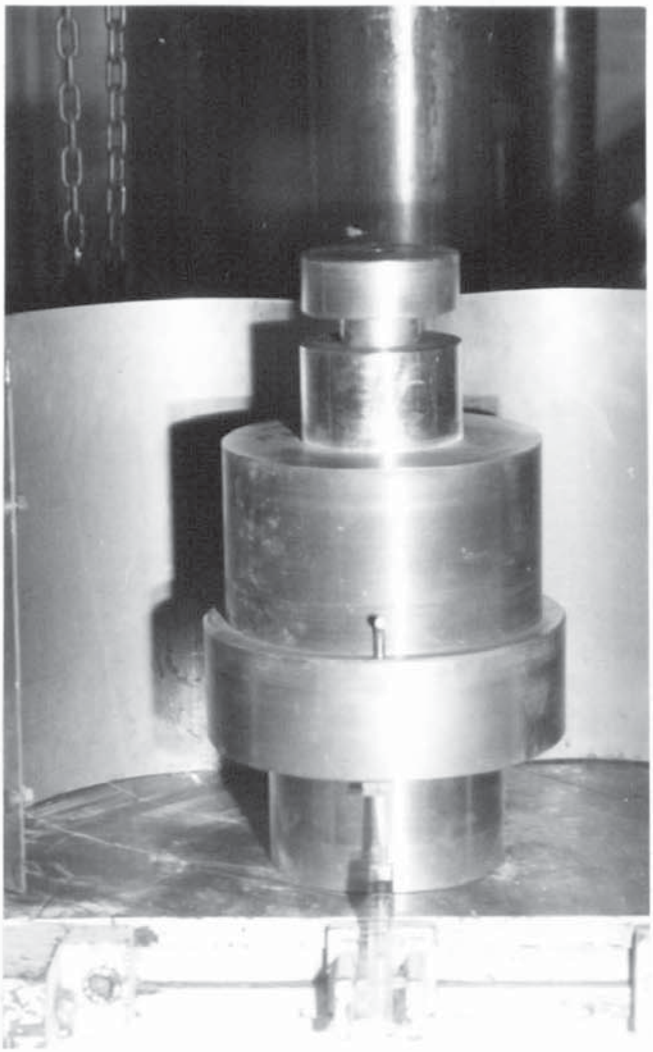


Fig. 2.4 Full view of compression cell

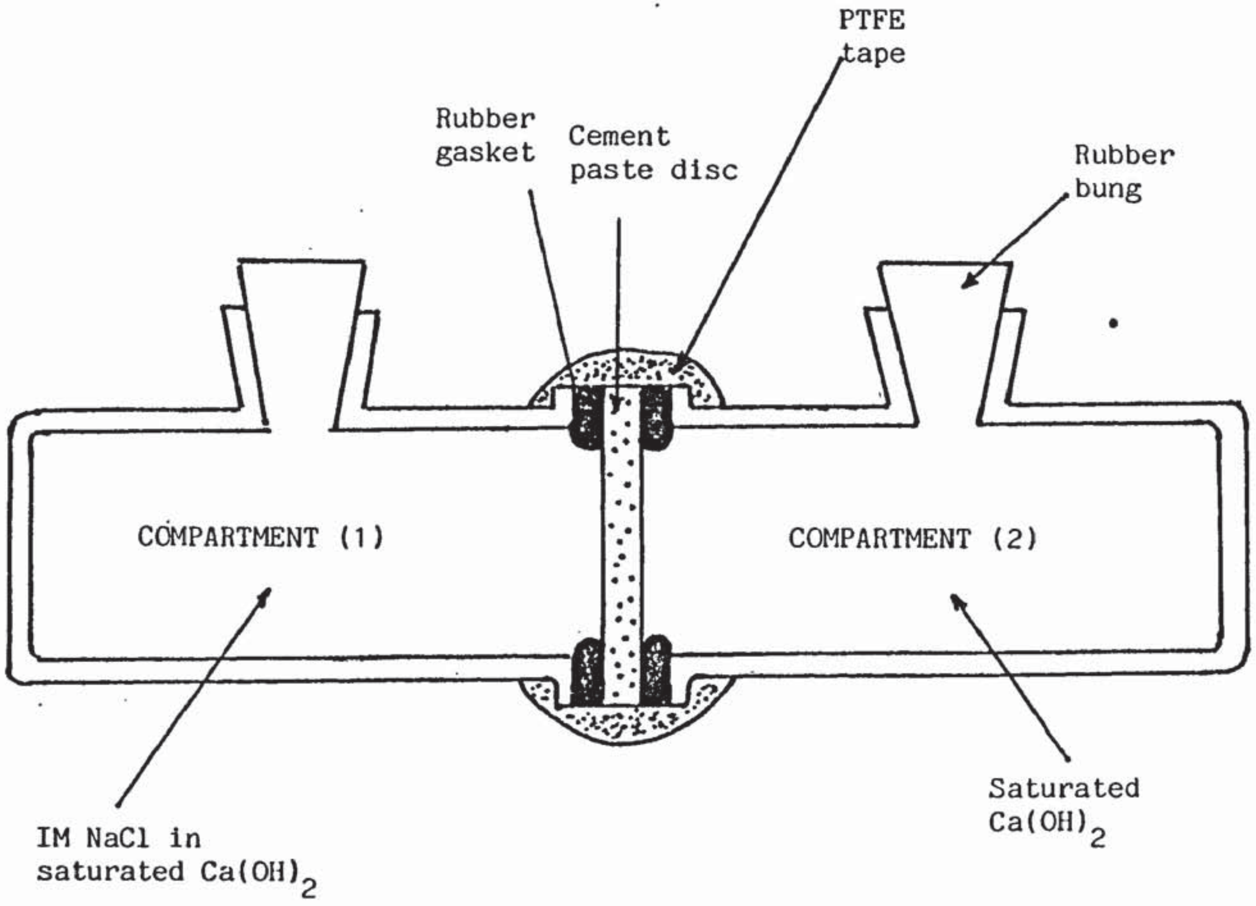


Fig 2.5 Diffusion cell (After Page, Short and El Tarras [18])

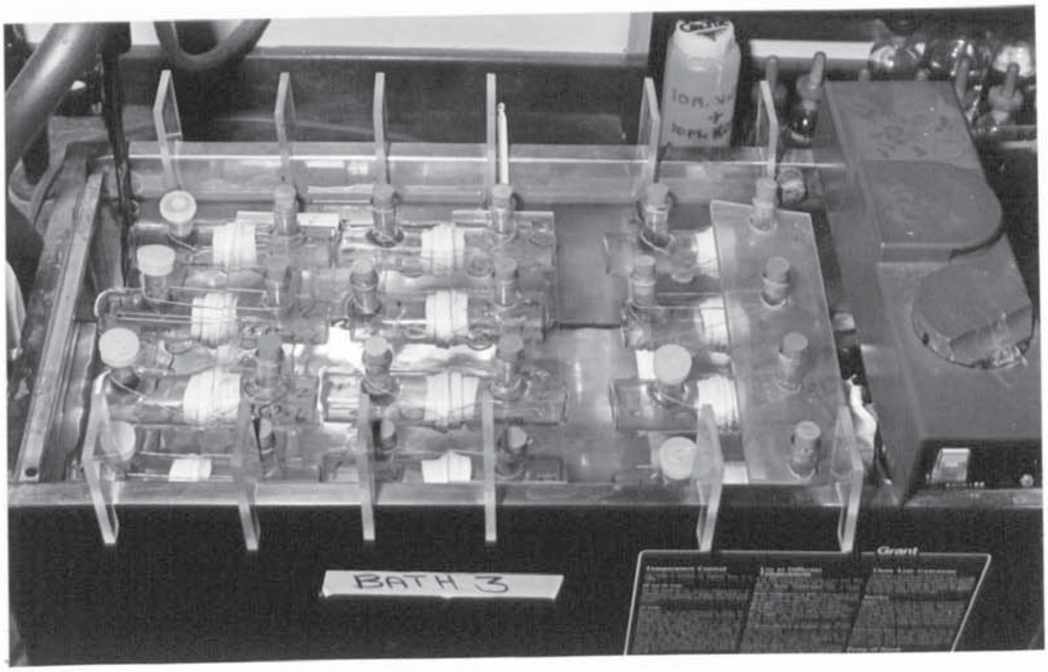


Fig. 2.6 Diffusion cells in a water bath

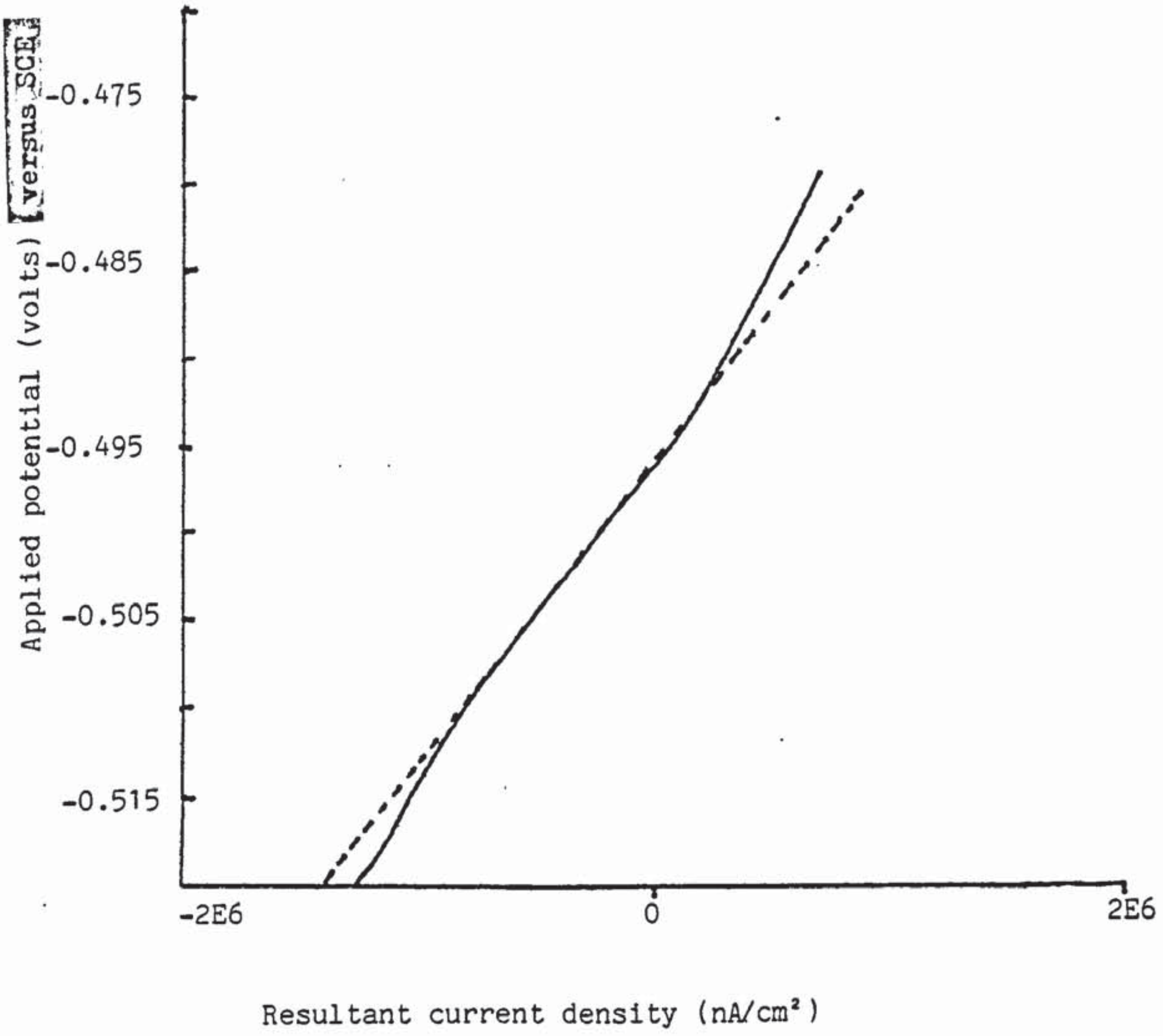


Fig 2.7 Typical polarisation resistance plot

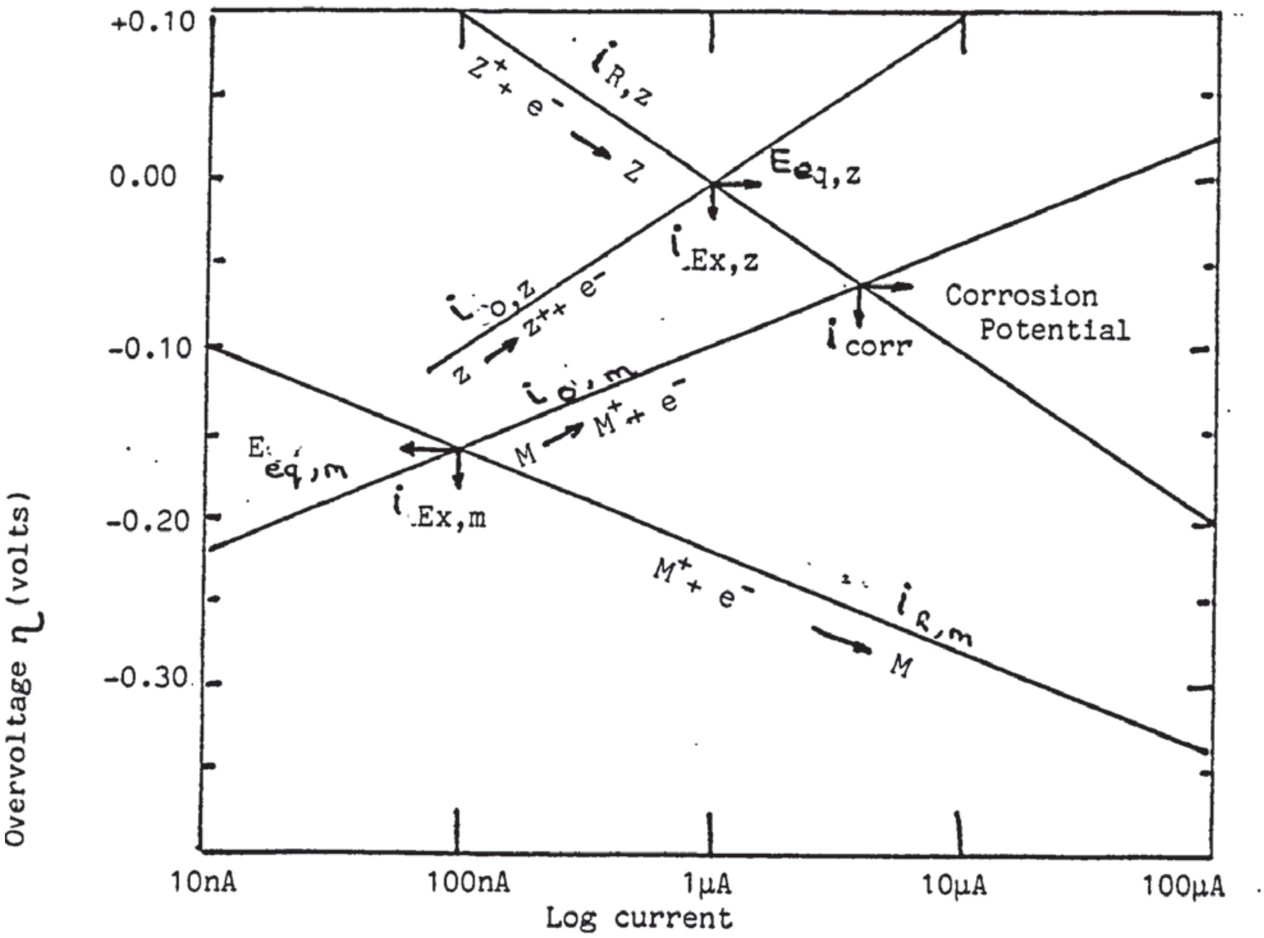


Fig 2.8 Potential current relationship for a mixed electrode system consisting of two electrochemical reactions

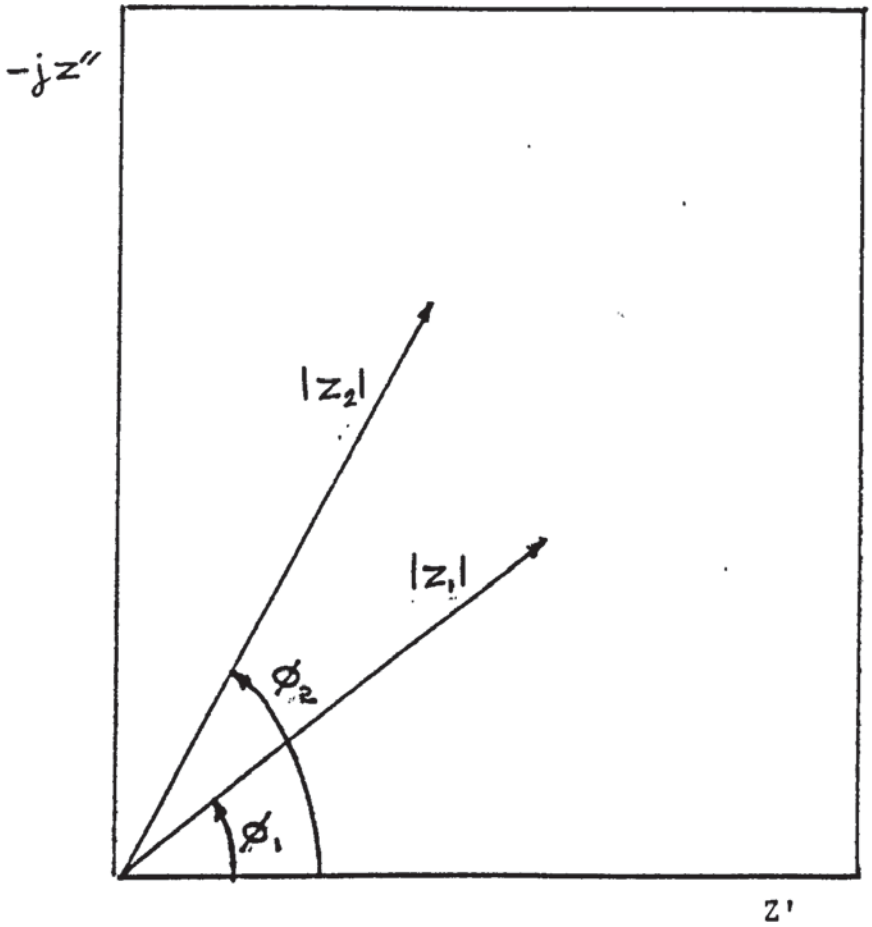


Fig 2.9 Argand Diagram

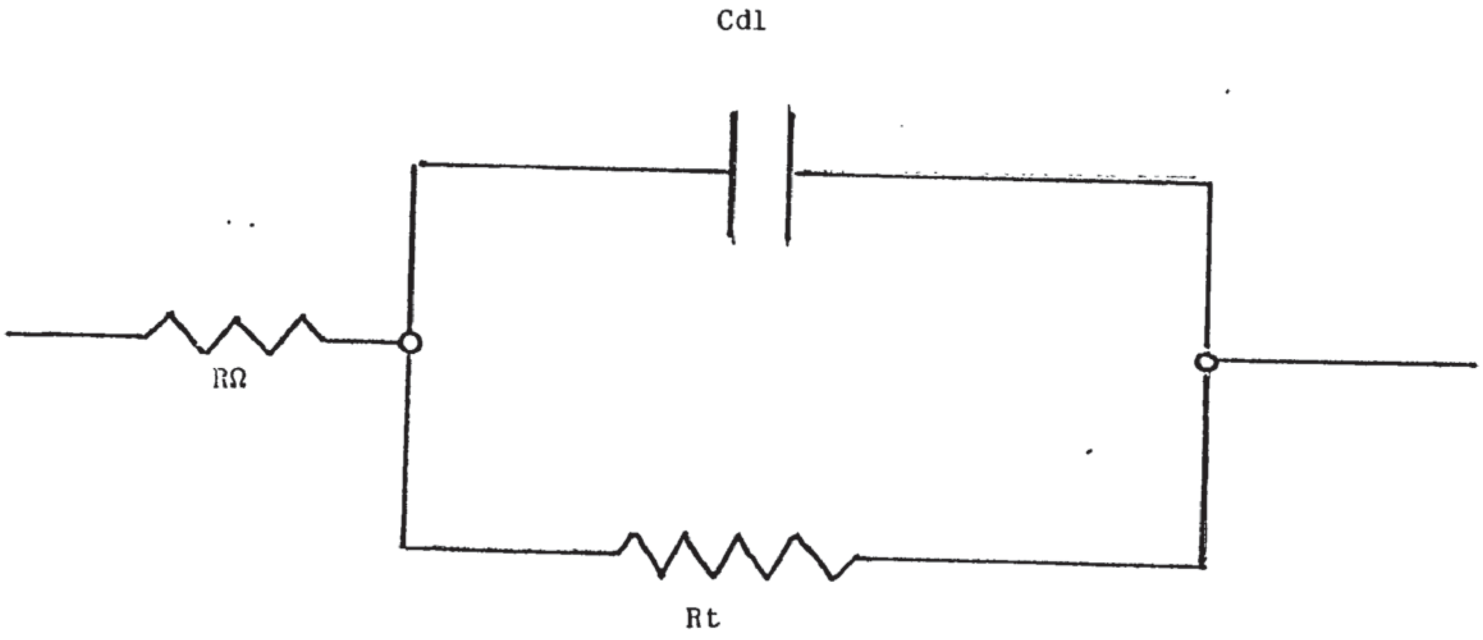


Fig 2.10 A simple Randles type equivalent circuit

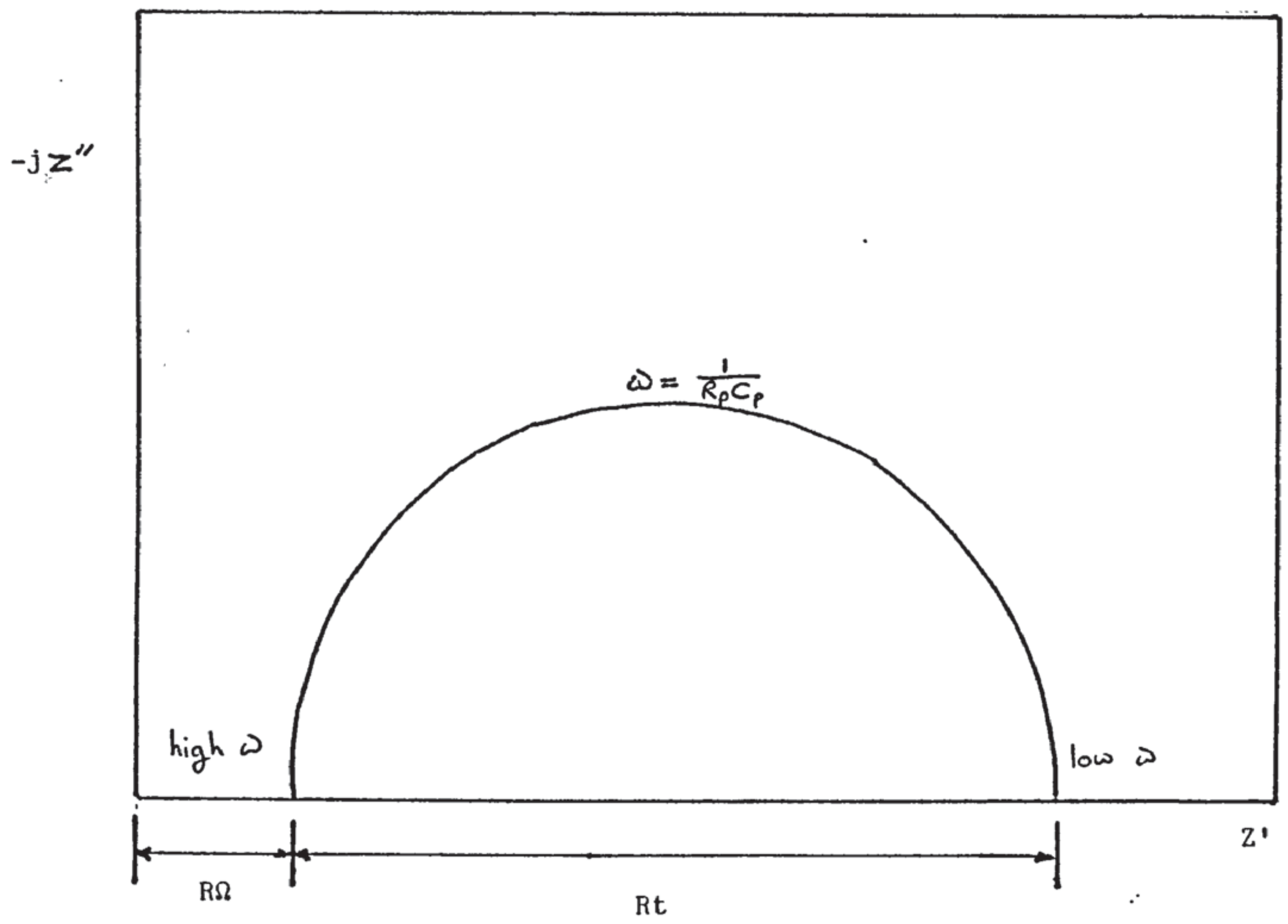


Fig 2.11 Nyquist diagram showing the complex plane response of a simple equivalent circuit

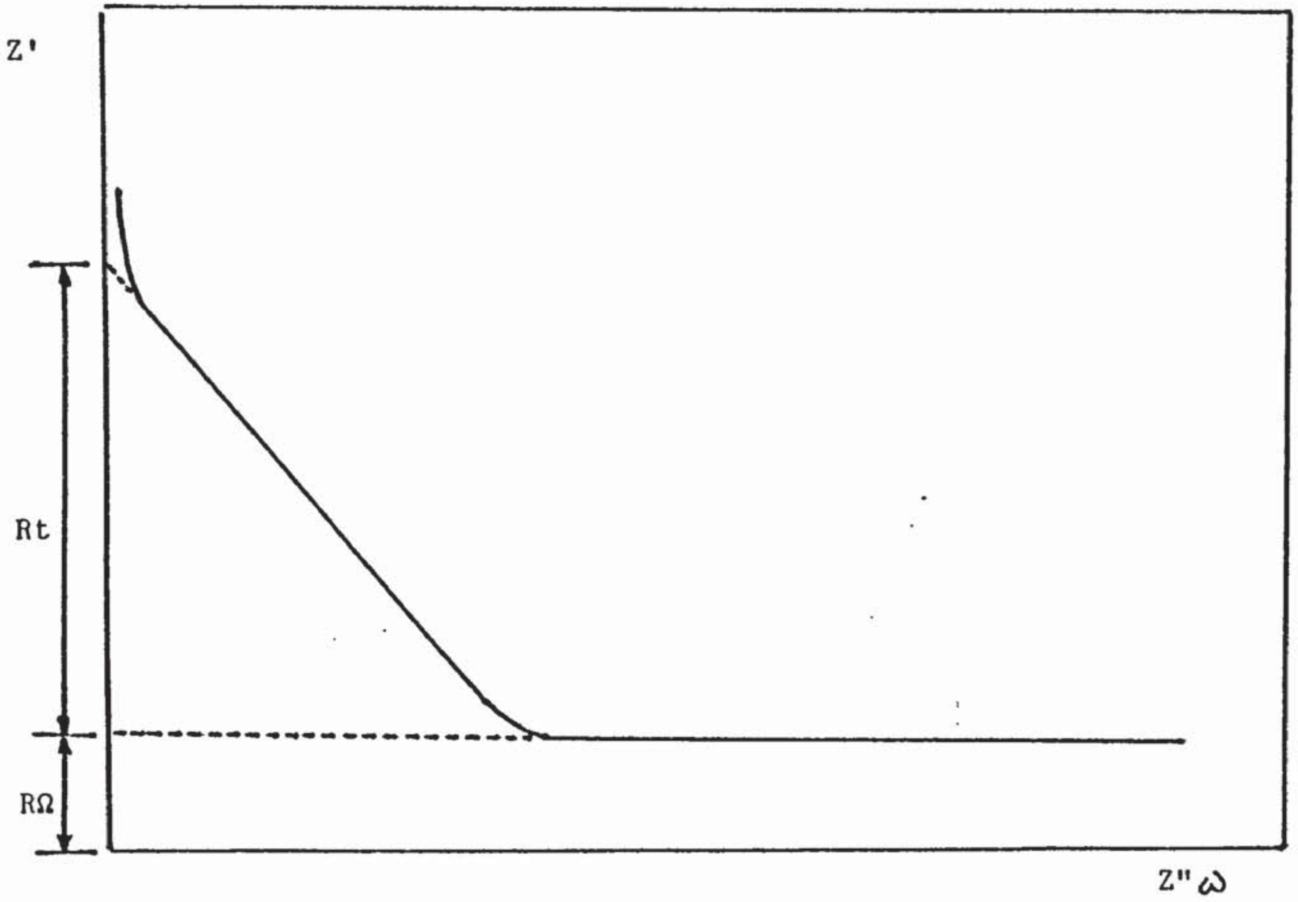


Fig 2.12 Plot of $\omega Z''$ v. Z' showing extrapolations to obtain Rt and RΩ

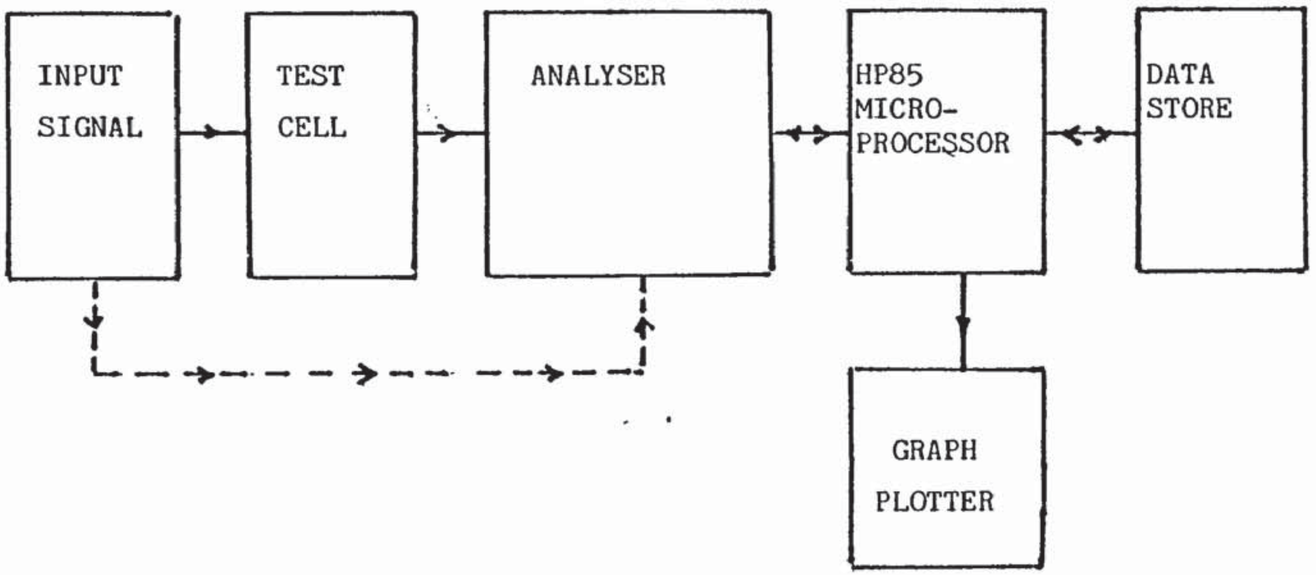


Fig 2.13 Block diagram of impedance instrumentation

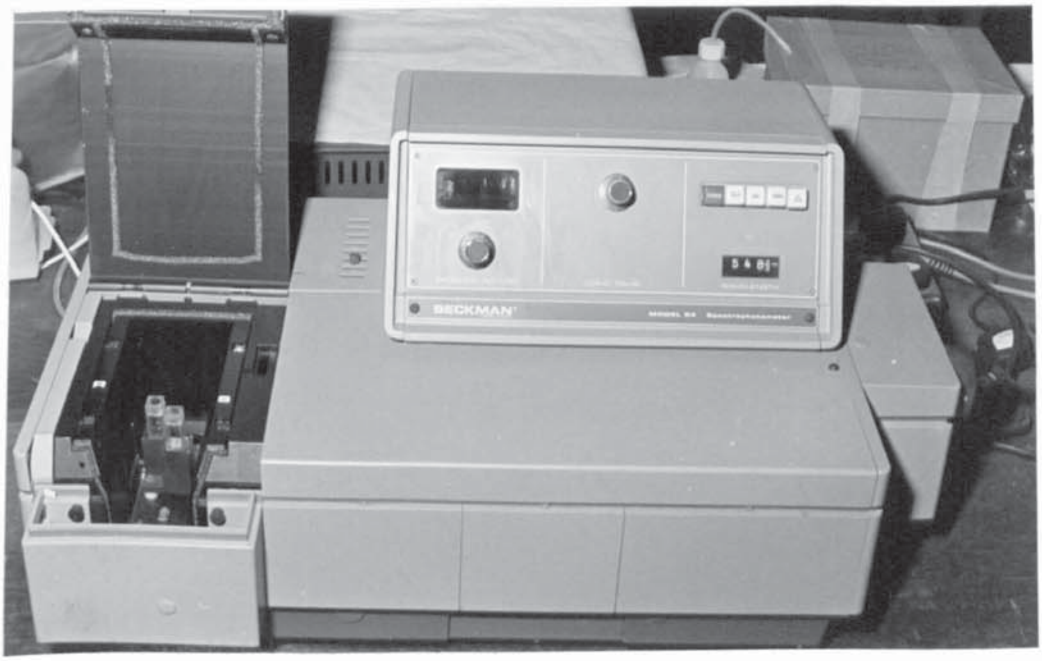


Fig 2.14   A Spectrophotometer

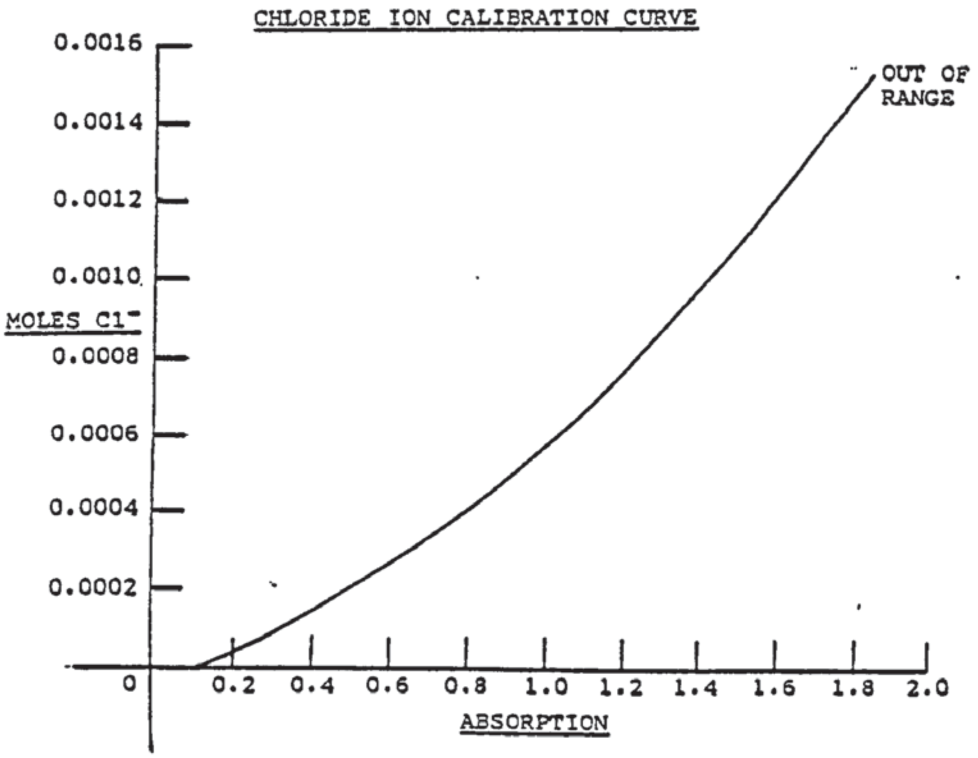


Fig 2.15 Calibration curve for the determination of chloride ion concentration in solution

CHAPTER 3

THE EXTRACTION AND ANALYSIS OF PORE LIQUID FROM HARDENED CEMENT PASTES

3.1 Introduction

As previously stated the aggressive ions responsible for the corrosion of reinforcing bar in concrete can find their way into the concrete by a number of means. These include penetration from the environment (eg a marine environment or one in which deicing salts are present), contamination of the constituents of the mix (eg the use of chloride bearing aggregates such as those dredged from the sea) and deliberate additions of admixtures such such as calcium chloride to increase the speed of setting and hardening.

The work in this chapter is concerned with making deliberate additions of (i) known amounts of chloride to cement pastes and (ii) known amounts of chloride in conjunction with sulphate in order to extract the pore liquid from the resultant hardened cement paste. After collection the pore solution was analysed to determine how much of the added chloride was free after hydration to cause possible damage to the reinforcement. It was then possible to produce a ranking of the cements studied on the basis of their ability to bind chloride and maintain a high pH.

A range of cements of both British and Middle Eastern origins was studied at various ages and with varying amounts of chloride additions.

The extraction of the pore liquid was performed by the use of a compression cell of a similar design to that used by other workers [18,46] as described in Chapter 2.

3.2 The Nature of The Pore Liquid

Concrete affords its protective nature to steel reinforcement by virtue of its normally high alkalinity [47] imparted to it by the presence of calcium hydroxide, sodium hydroxide and potassium hydroxide. It is well known that most cement pastes become rapidly saturated or supersaturated with respect to calcium hydroxide [48]. The hydroxyl concentration corresponding to pure saturated calcium hydroxide, 0.04M, acts as a base level for this important parameter of cement pore solutions. Values well in excess of this can be reached through the influence of alkali ions, but it is unlikely that values below this will occur except in special circumstances, such as where extensive carbonation has occurred.

Values for hydroxyl concentration in fresh pastes published prior to 1960 were tabulated by Greenberg and Mehra [49]. They were followed later by Lawrence [50], Roberts [51] and then several years later by Longuet, Burglen and Zelwer [4] who used the compression cell technique.

The values tabulated by Greenberg and Mehra were scattered for the first few hours after mixing but were generally in the range 0.04 to 0.15M. Pastes made from cements regarded as "low alkali" as published by Lawrence and Roberts generally ranged between 0.06 and 0.08M in the first few hours. This seems typical of cements of modest alkali contents. However, Lawrence's "high alkali" cement reached a hydroxyl concentration of 0.17M by the end of the first hour. This is a little more than four times the OH^- concentration of saturated calcium hydroxide.

After a rapid initial rise the measured hydroxyl concentrations of paste solutions appear to stabilise or decrease slightly until about 8 hours after mixing, when they begin to increase rapidly. Both Lawrences' and Roberts' data indicated that the increases continued until solutions could no longer be obtained. This was about a week for some of Roberts' higher water cement ratio pastes. The hydroxyl concentrations at the time at which values could no longer be obtained was 0.08 to 0.10M for pastes made from "low alkali" cements and as high as 0.26M for Lawrences' "high alkali" cement.

Longuet, Burglen and Zelwers' data show that hydroxyl concentrations of the order of 0.13 to 0.17M for three moderately high alkali cement paste solutions are obtained at 5 hours. After a few days values in excess of 0.40M were recorded and peak values of 0.70M were recorded for 28 day old pastes.

Because of these high levels of alkalinity then, steel in concrete encased properly should be passivated and be free from corrosion. Other problems can occur though due to this high alkalinity such as alkali attack on susceptible aggregates, known as alkali aggregate reaction (AAR). This problem is becoming of increasing interest in the UK possibly because of the trend towards the use of increasingly higher alkali cements and also the fact that several cases of damage to structures caused by this phenomenon have been reported in recent years. AAR has been the subject of several conferences in the last ten years [52,53] and is likely to be the subject of continued interest. It is generally agreed that the chemical reaction causing the distress involves an attack on susceptible aggregate grains by dissolved components of the pore fluid of the concrete. The mechanism of the attack is not agreed upon but the end result is an expansion of the outer surface of the aggregate particle leading to cracking of the aggregate and surrounding matrix [54,55,56]

When chloride is added to a concrete mix to promote accelerated hydration not all is combined in the reaction with cement minerals such as C_3A. Some is left as free chloride in the pore solution and it is this chloride which can make its way to the site of the reinforcement where it can cause pitting corrosion and in the case of prestressed reinforcement, stress corrosion [57] if present in too high concentrations.

Chlorides can be combined by hardening [illegible]

Chlorides may be combined by hardening cements in a number of ways. The dominant mechanism is combination with C_3A to form calcium chloroaluminate hydrate ($C_3A.CaCl_2.10H_2O$) and the amount combined will depend on the C_3A content of the cement [58]. Ramachandran has suggested [59] that a high proportion of chloride ions may form a chemisorbed complex with the C-S-H gel, although this has been disputed by later work of Diamond and Lopez-Flores [60]. Other mechanisms involving ion-exchange, and reaction with calcium hydroxide [61] are now largely discounted.

In Portland Cement at higher calcium chloride

In the past it has been generally assumed that free chloride in hardened cement paste can be determined by extraction with a solvent for the chloride. To determine free calcium chloride Rosenberg [62] used water, Tenoutasse [63] used ethanol, Schwiete, Ludwig and Albeck [58,64] and Ramachandran [65] also used ethanol. Wolhuter, Turkstra and Morris [66] used acetone.

None of these methods would appear to be as reliable as the compression cell technique. Rosenberg himself pointed out that water can cause hydrolysis of the compounds formed through the reaction of calcium chloride with the hydrated cement. As a result of replacing water by organic liquid the equilibrium constants of the prevailing reactions will change. Consequently the equilibrium concentrations of calcium chloride will also change. Also the solubility of calcium hydroxide in these organic liquids differs from that in water.

More recently Theissing, Hest-Wardenier and De Wind [67] claim to have produced a non destructive method to determine free chloride in hardened cement. However this method again relies on equilibrating cement samples in salt solutions and it is doubtful that the solution being analysed is truly representative of the pore solution.

There is an increasing trend of late towards the use of blending agents such as Pulverised Fuel Ash and ground Granulated Blast Furnace Slag to produce blended cements. The influence of these blending agents is to cause a small reduction in the alkalinity of the pore solution [68]. This reduced alkalinity has led to the suggestion that these cements will offer reduced corrosion protection to the embedded reinforcement [69]. However, experience over a long time has indicated that they may in fact be superior to OPC in chloride containing environments [70,71]. This may be partly explained by the fact that there is no reduction in the chloride binding capacity. However these findings may not necessarily be generally applicable to cements containing slags or pozzolanas from other sources[72].

Concrete structures in locations such as the Middle east are quite likely to be found subjected to environments which contain high levels of sulphates. Sulphate ions react preferentially with the C_3A phase in cement thus inhibiting the formation of Friedel's Salt. Pore solution pH increases as the hydroxyl ions enter the solution to balance the anions removed in the form of insoluble complex salts. The combination of sulphate and chlorides in the concrete environment would seem to indicate the possibility of increased corrosion risk.

The other possible effect of sulphates is to cause the possibility of increased alkali aggregate reaction because of the increase in pH of the pore solution.

3.3 Commissioning of the Pore Solution Expression Device

The initial work carried out using a pore solution expression device consisted of pressing samples (as described in Chapter 2) of hardened Ordinary Portland Cement of two different water cement ratios 0.4 and 0.6, several levels of added chloride (0%,0.1%,0.4%, 1.0% and 3% chloride by weight of cement added as sodium chloride). The samples were pressed at 28 days, 60 days and 84 days. Several methods of collection of the pore liquid were tried. Initially the solution was drawn off under vacuum whilst pressure was being applied to the specimen. This was followed by an attempt to force the liquid out of the press by blowing an unreactive gas(nitrogen) through the system whilst pressure was being applied.

However, the system which was eventually adopted was to draw off the liquid using a plastic syringe.

The solutions obtained were stored in sealed plastic vials and were analysed within several hours for free chloride using the spectrophotometer technique described in chapter 2. The pH was determined by titration, also as described in Chapter 2.

3.4 Programme of Extraction of Pore Liquid from a Range of Hardened Cement Pastes in order to establish a Rank Order

This programme consisted of the extraction of pore liquid from a number of United Kingdom and Middle Eastern cements. The following twelve cements were studied:-

i) Ordinary Portland Cement (OPC) A
ii) Sulphate Resisting Portland Cement (SRPC) A
iii) OPC B
iv) SRPC B
v) OPC C
vi) SRPC C
vii) OPC D blended with 5% pulverised fuel ash (PFA)
viii) OPC B blended with 30% PFA
ix) OPC E
x) SRPC E
xi) OPC B blended with 5% ground granulated blast furnace slag (GGBFS)
xii) OPC B blended with 65% GGBFS

Three series of experiments were set up:-

(i) Samples containing no admixtures

(ii) Samples containing 0.4%Cl by weight of cement added as sodium chloride

(iii) Samples containing 0.4%Cl by weight of cement added as sodium chloride 1.5% SO_3

The samples were all made in triplicate in the form of cylinders as described in Chapter 2. The water cement ratio was 0.5 and the age of the specimens at which the pore liquid was extracted was 84 days.

After collection the pore liquid was stored in sealed plastic vials, analysed for free chloride and subjected to pH determination within a few hours.

3.5 Extraction of Pore Liquid from Hardened Blended UK Cement Pastes

Because of the increasing use of blending agents added to cement a programme of extraction of pore liquid from several of these cements was undertaken in conjunction with diffusion studies and electrochemical studies on these cements. The aim was to determine whether the blending agents such as PFA and GGBFS would have any detrimental effects on the corrosion protection afforded to steel reinforcement by concrete. The cements studied were:

(i) OPC F

(ii) OPC F blended with 5% GGBFS

(iii) OPC D

(iv) OPC D blended with 5% PFA

(v) OPC A

(vi) OPC A blended with 5% PFA

The same cylindrical sample as described in Chapter 2 was used. The specimens were all made to a water cement ratio of 0.5 and were made in duplicate. Samples of pore liquid were stored in sealed plastic vials after collection until the analysis could be performed which was usually within a few hours. The solutions were analysed for free chloride using the technique previously mentioned and a titration was carried out to determine pH.

3.6 Results from Commissioning of Pore Solution Expression Device

Table 3.1 shows the results obtained for the early tests during which the pore solution expression device was commissioned. All results relate to an Ordinary Portland Cement (OPC B).

3.7 Results of Extraction of Pore Solution from British and Middle Eastern Hardened Cement Pastes in Order to Establish a Rank Order

Table 3.2 shows the results obtained when pore liquid was extracted from a range of hardened cement pastes of both British and Middle eastern origin. The results obtained were from specimens of water-cement ratio 0.5 and tested at an age of 84 days.

3.8 Results of Pore Solution Expression from a Range of UK Blended Cements

Table 3.3 shows the results of pore solution expression from a range of UK blended cements.

3.9 Discussion of Results obtained during commissioning of the Pore Solution Expression Device

The results discussed here were obtained in the early stages of the work using the pore solution expression device, when the optimum technique for sample collection was still being sought. In some cases this resulted in only small amounts of pore solution being obtained. Consequently there are some gaps in the data where there was an insufficient sample to determine both pH and chloride concentration. Similarly some solutions were out of the range limits for chloride concentration determination at the initial dilution level and there was not sufficient sample to allow for retesting at a higher dilution level. However these were early results which still showed encouraging trends and were useful in the planning of the larger programme which followed.

The first point which could be seen easily is that the pH of all the samples was very high. All were well in excess of pH13 (which is in agreement with Diamond's findings [48] and some were in excess of pH14.

The pH values of the solutions with an initially lower water-cement ratio (0.4 w/c) appeared in general to be higher than those of solutions which had an initially higher water-cement ratio (0.6 w/c). This was to be expected because the increase in pH above a value of 12.5 (the pH of a saturated calcium hydroxide solution) was due to sodium and potassium hydroxides. Increasing the level of water added initially to the cement dilutes these alkali hydroxide solutions.

At both water-cement ratios 0.4 and 0.6 increasing the level of added sodium chloride resulted in a progressive increase in pH value. At an initial level of 3% chloride ion by weight of cement the pH value was in excess of 14 for samples of water cements ratio of 0.4 at age 28 days. For samples of water cement ratio 0.6 the value was very close to 14 at this chloride addition level and age (This again would appear to confirm that water cement ratio is playing an important role). The pH increase was due to hydroxyl ions entering the solution to balance the anions removed in the form of insoluble complex salts. There would appear to be a slight decrease in pH with age when comparing specimens at age 80 days with specimens at age 28 days.

As expected the higher the initial addition level of chloride the more free chloride was present in the pore solution (Fig.3.1).

The ratio of chloride ion concentration to hydroxyl ion concentration was calculated as a guide to possible corrosion risk. A high level of free chloride ion concentration combined with a low hydroxyl ion concentration and hence a lower pH would give a higher ratio and would tend to indicate a greater potential corrosion risk.

There was a progressive increase in this ratio with increased initial addition levels of chloride (Fig 3.2) and also a slight general increase with age. There was also a small increase in the $[Cl^-]/[OH^-]$ ratio with increased water cement ratio at low level additions of chloride though the situation was reversed higher levels Fig.3.3.

3.10 Discussion of Results from Programme of Extraction of British and Middle Eastern Hardened Cement Pastes in order to establish a Rank Order

Table 3.2 shows the results of the analysis of the pore solution for the 12 cements studied. From the results it is clear that the different cements vary quite markedly in their alkalinity and their ability to complex chloride.

If the ratio of free chloride ion concentration to free hydroxyl ion concentration is considered it could be expected to have some value as an indicator to the degree of corrosion protection afforded to embedded steel. Within a ranking based on this ratio the major difference is between low C_3A cements such as SRPC. A(1.9%) and the other cements. This is probably because of its limited ability to form Friedel's salt $(3CaO.Al_2O_3.CaCl_2.10H_2O)$

However, there was also a substantial difference in the performance of the various OPC pastes. For example, OPC A had a C_3A content of 7.7% and had a lower chloride complexing ability than the OPC B which had a C_3A content of 14.3% (Fig 3.4)

The influence of the blending agents (GGBFS and PFA) caused a slight reduction in alkalinity of the pore solution. As previously stated combined additions of sodium chloride and sodium sulphate in all the cements studied, resulted in a substantial decrease in chloride binding ability.

This presumably reflects the tendency of sulphate ions to react preferentially with the C_3A phase thus inhibiting the formation of Friedel's salt (Fig.3.5).

An increase in pore solution pH was also observed as hydroxyl ions entered the solution to balance the anions removed in the form of insoluble complex salts. However, the net effect of 0.4% Cl^- and 1.5% SO_3 combined additions by weight of dry cement was to yield a higher free $[Cl^-]/[OH^-]$ ratio than was the case for 0.4%Cl^- in the absence of sulphate. This supports the argument that corrosion risks are likely to increase in circumstances where concrete is subjected to contamination with chlorides and sulphates, as is the case in the Middle East.

3.11 Discussion of Results of Programme of Expression of Pore Solution from a Range of UK Blended Cements

The level of addition of blending agent for this programme of work was much lower than for the work described in the previous section. The level of addition here was 5% GGBFS and 5% PFA compared with 65% BFS and 30% PFA in the previous section. Presumably this is too low a level to produce the significant reduction in alkalinity between blended and unblended cements which was observed in higher addition levels.

Both the PFA and GGBFS blended cements

That these 5 % blended cements are capable of slightly reducing the free Cl^- concentration whilst having little effect on pH, results in a slight reduction of the $[Cl^-]/[OH^-]$ ratio, compared to the unblended cements. Thus corrosion risks with these 5 % blended cements should be no worse than unblended cements. at this level.

The major variation of this ratio, however, again occurred between different cements rather than being caused by the addition of the blending agents. So at the 5% level of addition it would seem that blending with these particular fly ashes and slags has no adverse effect on the corrosion protection afforded by the alkalinity of the cement.

3.12 Conclusion

The results obtained from this work would seem to indicate that several of the factors studied play a role to a greater or lesser extent in determining the pH and free chloride ion concentration of the pore solution.

Increasing the initial addition level of sodium chloride increases the concentration of free chloride in the expressed pore solution.

The effect of sodium chloride addition was to increase the pH of the pore solution.

The pH of the pore solution is decreased as the water-cement ratio is increased.

Age plays a small part in that there is a slight decrease in the pH of the pore solution with increasing age.

The difference in alkalinity of the cement paste regardless of any additions is a major factor in assessing corrosion risk. The more alkaline the cement then generally the better it faired in the $[Cl^-]/[OH^-]$ ranking. Chloride complexing ability also varies considerably between the cements and manifests itself in the $[Cl^-]/[OH^-]$ ratio. Within a ranking based on this ratio there is a major difference between SRPC pastes and OPC pastes. There is also a significant difference between the different types of OPC pastes. These differences probably reflect the difference in C_3A contents of the cements.

The addition of PFA and BFS to OPC resulted in a modest decrease in the alkalinity of the cement but gave superior chloride complexing ability when 30 % PFA was added and 65 % BFS was added.

The overall result was that the ranking of the blended cements compared well with the corresponding OPC.

At an addition level of 5% PFA and BFS there was virtually no reduction in the alkalinity of the cement but chloride binding ability was still improved. In this respect the blended cement performed better than the corresponding pure OPC. On the basis of these results then there is no evidence to suggest that adding blending agents at this level is detrimental to corrosion protection.

Table 3.1 Results from the commissioning of pore solution expression device

Age of Specimen (Days)	Water-Cement Ratio W/C	% Cl^- by weight of cement	Titre 10m M Nitric Acid ml	$[OH^-]$ m mole 1^{-1}	pH	Spectro-photometer Reading absorbance	$[Cl^-]$ m mole 1^{-1}	$\frac{[Cl^-]}{[OH^-]}$
28	0.4	0	6.43	643	13.81	0.248	6	0.009
28	0.4	0	6.60	660	13.82	0.198	3	0.005
28	0.4	0	6.95	695	13.84	0.195	3	0.004
28	0.4	0.1	7.10	710	13.85	0.361	11	0.015
28	0.4	0.1	7.60	760	13.88	0.410	14	0.018
28	0.4	0.1	8.20	820	13.91	0.392	13	0.016
28	0.4	0.4	8.70	870	13.94	1.210	81	0.093
28	0.4	0.4	8.22	822	13.91	1.035	62	0.075
28	0.4	0.4	9.61	961	13.98	1.061	65	0.068
28	0.4	1.0	9.00	900	13.95	2.779	Out of limit	
28	0.4	1.0	8.90	890	13.95	2.779	Out of limit	
28	0.4	1.0	13.90	1390	14.14	2.783	Out of limit	
28	0.4	3.0	12.75	1275	14.11	2.777	Out of limit	
28	0.4	3.0	13.69	1369	14.14	2.777	Out of limit	
28	0.4	3.0	14.85	1485	14.17	2.777	Out of limit	

Table 3.1 continued

Age of Specimen (Days)	Water-Cement Ratio W/C	% Cl^- by weight of cement	Titre 10m M Nitric Acid m.l	$[OH^-]$ m mole l^{-1}	pH	Spectrro-photometer Reading absorbance	$[Cl^-]$ m mole l^{-1}	$\frac{[Cl^-]}{[OH^-]}$
28	0.6	0	5.14	514	13.71	0.381	13	0.025
28	0.6	0	5.95	595	13.77	0.377	12	0.020
28	0.6	0	5.85	585	13.77	0.375	12	0.021
28	0.6	0.1	4.99	499	13.70	0.360	11	0.022
28	0.6	0.1	4.83	483	13.68	0.379	13	0.027
28	0.6	0.1	4.88	488	13.69	0.457	17	0.035
28	0.6	0.4	5.00	500	13.70	0.698	34	0.068
28	0.6	0.4	5.61	561	13.75	0.684	33	0.059
28	0.6	0.4	5.64	564	13.75	0.650	31	0.055
28	0.6	1.0	7.46	746	13.87	1.666	135	0.181
28	0.6	1.0	6.81	681	13.83	1.856	Out of limit	
28	0.6	1.0	7.35	735	13.87	1.701	140	0.190
28	0.6	3.0	8.73	873	13.94	2.777	Out of limit	
28	0.6	3.0	10.00	1000	14.00	2.779	Out of limit	
28	0.6	3.0	9.85	985	13.99	2.779	Out of limit	
60	0.4	0	9.13	913	13.96	No sample		
60	0.4	0	7.97	797	13.90	No sample		

Table 3.1 continued

Age of Specimen (Days)	Water-Cement Ratio W/C	% Cl^- by weight of cement	Titre 10m M Nitric Acid ml	$[OH^-]$ m mole l^{-1}	pH	Spectro-photometer reading absorbance	$[Cl^-]$ m mole l^{-1}	$\frac{[Cl^-]}{[OH^-]}$
60	0.4	0	No sample obtained					
60	0.4	0.1	No sample obtained					
60	0.4	0.1	No sample obtained					
60	0.4	0.1	No sample obtained					
60	0.4	0.4	8.90	890	13.95	1.405	102	0.115
60	0.4	0.4	10.40	1040	14.02	1.305	89	0.086
60	0.4	0.4	11.60	1160	14.06	1.344	94	0.081
60	0.4	1.0	9.62	962	13.98	No sample		
60	0.4	1.0	12.28	1228	14.09	No sample		
60	0.4	1.0	10.61	1061	14.03	No sample		
60	0.4	3.0	11.00	1100	14.04	No sample		
60	0.4	3.0	9.50	950	13.98	No sample		
60	0.4	3.0	11.94	1194	14.08	No sample		
73	0.6	0	3.98	398	13.60	0.189	3	0.007
73	0.6	0	3.99	399	13.60	0.201	4	0.010
73	0.6	0	4.78	478	13.68	0.178	3	0.006
80	0.6	0.1	4.74	474	13.67	0.357	11	0.023

Table 3.1 continued

Age of Specimen (Days)	Water-Cement Ratio W/C	% Cl^- by weight of cement	Titre 10m M Nitric Acid ml	$[OH^-]$ m mole l^{-1}	pH	Spectro-photometer reading absorbance	$[Cl^-]$ m mole l^{-1}	$\frac{[Cl^-]}{[OH^-]}$
80	0.6	0.1	4.55	455	13.66	0.390	13	0.029
80	0.6	0.1	4.45	445	13.65	0.381	13	0.029
80	0.6	0.4	5.64	564	13.75	0.669	32	0.057
80	0.6	0.4	5.44	544	13.74	0.733	36	0.066
80	0.6	0.4	5.62	562	13.75	0.800	42	0.075
82	0.6	1.0	7.00	700	13.85	1.787	153	0.219
82	0.6	1.0	7.51	751	13.88	1.790	153	0.204
82	0.6	1.0	No sample obtained					
85	0.6	3.0	8.43	843	13.93	No sample		
85	0.6	3.0	8.15	815	13.91	No sample		
85	0.6	3.0	No sample obtained					

TABLE 3.2 Results of extraction of pore solution from British and Middle Eastern hardened cement pastes in order to establish a rank order

Normal dilution factor 100
* indicates dilution factor of 200
- indicates dilution factor of 400

Cement	Admixtures % by weight of cement	Titre 10mM Nitric Acid ml	$[OH^-]$ m mole l^{-1}	pH	Spectro-photometer reading absorbance	(Cl^-) m mole l^{-1}	$\frac{[Cl^-]}{[OH^-]}$
OPC A	0%Cl^-	5.97	597	13.78	0.198	3	0.005
	0%Cl^-	5.72	572	13.76	0.171	2	0.003
	0%Cl^-	6.06	606	13.78	0.174	2	0.003
OPC A	0.4%Cl^-	7.40	740	13.87	1.259	85	0.115
	0.4%Cl^-	7.44	744	13.87	1.241	83	0.112
	0.4%Cl^-	7.34	734	13.87	1.228	82	0.112
OPC A	0.4%Cl^-/1.5/SO_3	13.91	1391	14.14	1.372*	194	0.139
	0.4%Cl^-/1.5/SO_3	13.00	1300	14.11	1.413*	260	0.200
	0.4%Cl^-/1.5/SO_3	12.68	1268	14.10	1.352*	190	0.150
SRPC A	0%Cl^-	3.48	348	13.54	0.181	3	0.009
	0%Cl^-	3.51	351	13.35	0.170	2	0.006
	0%Cl^-	3.50	350	13.54	0.164	2	0.006
SRPC A	0.4%Cl^-	5.07	507	13.71	1.400	110	0.217
	0.4%Cl^-	4.98	498	13.70	1.558	121	0.243
	0.4%Cl^-	4.80	480	13.68	1.385	100	0.208

TABLE 3.2 continued

Cement	Admixtures % by weight of cement	Titre 10mM Nitric Acid ml	$[OH^-]$ m mole l^{-1}	pH	Spectro-photometer reading absorbance	$[Cl^-]$ m mole l^{-1}	$\frac{[Cl^-]}{[OH^-]}$
SRPC A	$0.4\%Cl^-/1.5\%SO_3$	10.04	1004	14.00	1.697*	280	0.279
	$0.4\%Cl^-/1.5\%SO_3$	9.95	995	13.99	1.551*	240	0.241
	$0.1\%Cl^-/1.5\%SO_3$	9.91	991	13.99	1.597*	252	0.254
OPC B	$0\%Cl^-$	4.74	474	13.68	0.191	3	0.006
	$0\%Cl^-$	4.94	494	13.69	0.194	3	0.006
	$0\%Cl^-$	4.61	461	13.66	0.178	3	0.007
OPC B	$0.4\%Cl^-$	6.93	693	13.84	0.722	36	0.052
	$0.4\%Cl^-$	6.44	644	13.81	0.763	38	0.059
	$0.4\%Cl^-$	6.40	640	13.81	0.875	48	0.075
OPC B	$0.4\%Cl^-/1.5\%SO_3$	9.70	970	13.99	1.333*	184	0.190
	$0.4\%Cl^-/1.5\%SO_3$	11.01	1101	14.04	1.043*	126	0.144
	$0.4\%Cl^-/1.5\%SO_3$	10.99	1099	14.04	1.151*	148	0.135
SRPC B	$0\%Cl^-$	3.46	346	13.54	0.183	3	0.009
	$0\%Cl^-$	3.34	334	13.52	0.169	2	0.006
	$0\%Cl^-$	3.42	342	13.53	0.174	2	0.006

TABLE 3.2 continued

Cement	Admixtures % by weight of cement	Titre 10mM Nitric Acid ml	$[OH^-]$ m mole l^{-1}	pH	Spectro-photometer reading absorbance	$[Cl^-]$ m mole l^{-1}	$\frac{[Cl^-]}{[OH^-]}$
SRPC B	0.4%Cl^-	4.29	429	13.63	1.538	118	0.275
	0.4%Cl^-	4.51	451	13.65	1.511	115	0.256
	0.4%Cl^-	4.26	426	13.63	1.517	116	0.272
SRPC B	0.4%Cl^-/1.5%SO_3	7.89	789	13.90	1.104^+	272	0.345
	0.4%Cl^-/1.5%SO_3	8.15	815	13.91	1.156^+	296	0.363
	0.4%Cl^-/1.5%SO_3	7.97	797	13.90	1.139^+	292	0.366
OPC C	0%Cl^-	6.04	604	13.78	0.187	3	0.005
	0%Cl^-	5.95	595	13.78	0.186	3	0.005
	0%Cl^-	5.99	599	13.78	0.174	2	0.003
OPC C	0.4%Cl^-	6.90	690	13.84	1.429	105	0.152
	0.4%Cl^-	6.92	692	13.84	1.509	115	0.166
	0.4%Cl^-	6.82	682	13.83	1.475	111	0.163
OPC C	0.4%Cl^-/1.5%SO_3	11.71	1171	14.07	1.164^+	300	0.256
	0.4%Cl^-/1.5%SO_3	11.94	1194	14.08	1.161^+	300	0.251
	0.4%Cl^-/1.5%SO_3	11.89	1189	14.08	1.147^+	296	0.249

Table 3.2 continued

Cement	Admixtures % by weight of cement	Titre 10mM Nitric Acid m l	$[OH^-]$ m mole l^{-1}	pH	Spectro-photometer reading absorbance	$[Cl^-]$ m mole l^{-1}	$\frac{[Cl^-]}{[OH^-]}$
SRPC C	0%Cl^-	5.84	584	13.77	0.189	3	0.005
	0%Cl^-	6.08	608	13.78	0.166	2	0.003
	0%Cl^-	6.13	613	13.79	0.170	2	0.003
SRPC C	0.4%Cl^-	6.71	671	13.83	1.605	126	0.188
	0.4%Cl^-	6.80	680	13.83	1.622	128	0.188
	0.4%Cl^-	6.79	679	13.83	1.591	125	0.184
SRPC C	0.4%Cl^-/1.5%SO_3	11.00	1100	14.04	1.082^+	268	0.244
	0.4%Cl^-/1.5%SO_3	11.33	1133	14.05	1.138^+	292	0.258
	0.4%Cl^-/1.5%SO_3	11.45	1145	14.06	1.080^+	268	0.234
OPC D + 5%PFA	0%Cl^-	5.32	532	13.73	0.175	2	0.004
	0%Cl^-	5.41	541	13.73	0.169	2	0.004
	0%Cl^-	5.45	545	13.74	0.168	2	0.004
OPC D + 5% PFA	0.4%Cl^-	7.28	728	13.86	0.956	55	0.076
	0.4%Cl^-	7.29	729	13.86	0.946	54	0.074
	0.4%Cl^-	7.48	748	13.87	0.952	55	0.074
OPC D + 5% PFA	0.4%Cl^-/1.5%SO_3	13.56	1356	14.13	0.818^+	176	0.130
	0.4%Cl^-/1.5%SO_3	13.40	1340	14.13	0.853^+	184	0.137
	0.4%Cl^-/1.5%SO_3	13.71	1371	14.14	0.832^+	176	0.128

Table 3.2 continued

Cement	Admixtures % by weight of cement	Titre 10mM Nitric Acid m l.	$[OH^-]$ m mole 1^{-1}	pH	Spectro-photometer reading absorbance	$[Cl^-]$ m mole 1^{-1}	$\frac{[Cl^-]}{[OH^-]}$
OBC B + 30% PFA	0%Cl^-	3.26	326	13.51	0.184	3	0.009
	0%Cl^-	3.42	342	13.53	0.173	2	0.006
	0%Cl^-	3.43	343	13.54	0.173	2	0.006
OPC B +30% PFA	0.4%Cl^-	4.58	458	13.66	0.775	40	0.087
	0.4%Cl^-	4.55	455	13.66	0.767	39	0.086
	0.4%Cl^-	4.60	460	13.66	0.763	39	0.085
OPC B +30% PFA	0.4%Cl^-/1.5%SO_3	8.60	860	13.93	0.733$^+$	144	0.167
	0.4%Cl^-/1.5%SO_3	8.31	831	13.93	0.771$^+$	156	0.188
	0.4%Cl^-/1.5%SO_3	8.71	871	13.94	0.705$^+$	136	0.156
OPC E	0%Cl^-	6.09	609	13.79	0.191	3	0.005
	0%Cl^-	6.21	621	13.79	0.192	3	0.005
	0%Cl^-	6.26	626	13.80	0.183	3	0.005
OPC E	0.4%Cl^-	7.93	793	13.90	0.987	58	0.073
	0.4%Cl^-	7.80	780	13.89	1.018	61	0.078
	0.4%Cl^-	7.78	778	13.89	0.996	59	0.076

Table 3.2 continued

Cement	Admixtures % by weight of cement	Titre 10mM Nitric Acid ml	$[OH^-]$ m mole l^{-1}	pH	Spectro-photometer reading absorbance	$[Cl^-]$ m mole l^{-1}	$\frac{[Cl^-]}{[OH^-]}$
OPC E	0.4%Cl$^-$/1.5%SO$_3$	12.43	1243	14.09	0.701$^+$	136	0.109
	0.4&Cl$^-$/1.5%SO$_3$	12.82	1282	14.11	0.834$^+$	176	0.137
	0.4%Cl$^-$/1.5%SO$_3$	12.84	1284	14.11	0.875$^+$	192	0.150
SRPC E	0%Cl$^-$	5.99	599	13.78	0.196	3	0.005
	0%Cl$^-$	6.10	610	13.79	0.185	3	0.005
	0%Cl$^-$	6.18	618	13.79	0.180	3	0.005
SRPC E	0.4%Cl$^-$	8.00	800	13.90	1.024	61	0.076
	0.4%Cl$^-$	7.70	770	13.89	1.053	64	0.083
	0.4%Cl$^-$	7.86	786	13.89	1.087	68	0.087
SRPC E	0.4%Cl$^-$/1.5%SO$_3$	12.50	1250	14.10	0.883$^+$	192	0.154
	0.4%Cl$^-$/1.5%SO$_3$	12.91	1291	14.11	0.894$^+$	200	0.155
	0.4%Cl$^-$/1.5%SO$_3$	12.44	1244	14.10	0.897$^+$	200	0.161
OPC B + 5% GGBFS	0%Cl$^-$	4.68	468	13.67	0.212	4	0.009
	0%Cl$^-$	4.50	450	13.65	0.196	3	0.007
	0%Cl$^-$	4.59	459	13.66	0.211	4	0.009
OPC B +5% GGBFS	0.4%Cl$^-$	6.50	650	13.81	0.656	31	0.048
	0.4%Cl$^-$	6.48	648	13.81	0.657	31	0.048
	0.4%Cl$^-$	6.18	618	13.79	0.629	29	0.047

TABLE 3.2 continued

Cement	Admixtures % by weight of cement	Titre 10mM Nitric Acid ml	$[OH^-]$ m mole l^{-1}	pH	Spectro-photometer reading absorbance	$[Cl^-]$ m mole l^{-1}	$\frac{[Cl^-]}{[OH^-]}$
OPC B + 5% GGBFS	$0.4\%Cl^-/1.5\%SO_3$	11.88	1188	14.08	0.576^+	100	0.084
	$0.4\%Cl^-/1.5\%SO_3$	11.61	1161	14.07	0.700^+	136	0.117
	$0.4\%Cl^-/1.5\%SO_3$	11.87	1187	14.07	0.665^+	124	0.104
OPC B + 65% GGBFS	$0\%Cl^-$	3.58	358	13.55	0.267	6	0.017
	$0\%Cl^-$	3.60	360	13.56	0.201	4	0.011
	$0\%Cl^-$	3.49	349	13.54	0.219	4	0.011
OPC B + 65% GGBFS	$0.4\%Cl^-$	4.60	460	13.66	0.625	28	0.061
	$0.4\%Cl^-$	4.40	440	13.64	0.613	27	0.061
	$0.4\%Cl^-$	4.58	458	13.66	0.639	30	0.066
OPC B + 65% GGBFS	$0.4\%Cl^-/1.5\%SO_3$	7.49	749	13.87	0.721^+	120	0.160
	$0.4\%Cl^-/1.5\%SO_3$	7.68	768	13.89	0.770^+	160	0.208
	$0.4\%Cl^-/1.5\%SO_3$	7.50	750	13.88	0.758^+	160	0.213
OPC D	$0.4\%Cl^-$	7.00	700	13.85	1.000	59	0.084
	$0.4\%Cl^-$	6.92	692	13.84	1.004	59	0.085
OPC D + 5% PFA	$0.4\%Cl^-$	7.16	716	13.85	0.889	49	0.068
	$0.4\%Cl^-$	7.18	718	13.86	0.914	51	0.071
OPC A	$0.4\%Cl^-$	7.24	724	13.86	1.280	87	0.120
	$0.4\%Cl^-$	7.20	720	13.86	1.281	87	0.121

TABLE 3.2 continued

Cement	Admixtures % by weight of cement	Titre 10mM Nitric Acid ml	$[OH^-]$ m mole l^{-1}	pH	Spectro.-photometer reading absorbance	$[Cl^-]$ m mole l^{-1}	$\frac{[Cl^-]}{[OH^-]}$
OPC A +5% PFA	0.4%Cl^- 0.4%Cl^-	7.18 7.18	718 718	13.86 13.86	1.133 1.114	72 70	0.100 0.097
OPC F	0.4%Cl^- 0.4%Cl^-	7.76 7.90	776 790	13.89 13.90	1.380 1.314	99 91	0.128 0.115
OPC F + 5% BFS	0.4%Cl^- 0.4%Cl^-	7.54 7.72	754 772	13.88 13.89	1.323 1.264	92 86	0.122 0.111

TABLE 3.3 Results of Pore Solution Expression from a Range of UK Blended Cements

Cement	Admixtures % by weight of cement	Titre 10mM Nitric Acid ml	$[OH^-]$ m mole l^{-1}	pH	Spectro-photometer reading absorbance	$[Cl^-]$ m mole l^{-1}	$\frac{[Cl^-]}{[OH^-]}$
OPC D	0.4%Cl^- 0.4%Cl^-	7.00 6.92	700 692	13.85 13.84	1.000 1.004	59 59	0.084 0.085
OPCD + 5% PFA	0.4%Cl^- 0.4%Cl^-	7.16 7.18	716 718	13.85 13.86	0.889 0.914	49 51	0.068 0.071
OPC A	0.4%Cl^- 0.4%Cl^-	7.24 7.20	724 720	13.86 13.86	1.280 1.281	87 87	0.120 0.121
OPC A + 5% PFA	0.4%Cl^- 0.4%Cl^-	7.18 7.18	718 718	13.86 13.86	1.133 1.114	72 70	0.100 0.097
OPC F	0.4%Cl^- 0.4%Cl^-	7.76 7.90	776 790	13.89 13.90	1.380 1.314	99 91	0.128 0.115
OPC F + 5% BFS	0.4%Cl^- 0.4%Cl^-	7.54 7.72	754 772	13.88 13.89	1.323 1.264	92 86	0.122 0.111

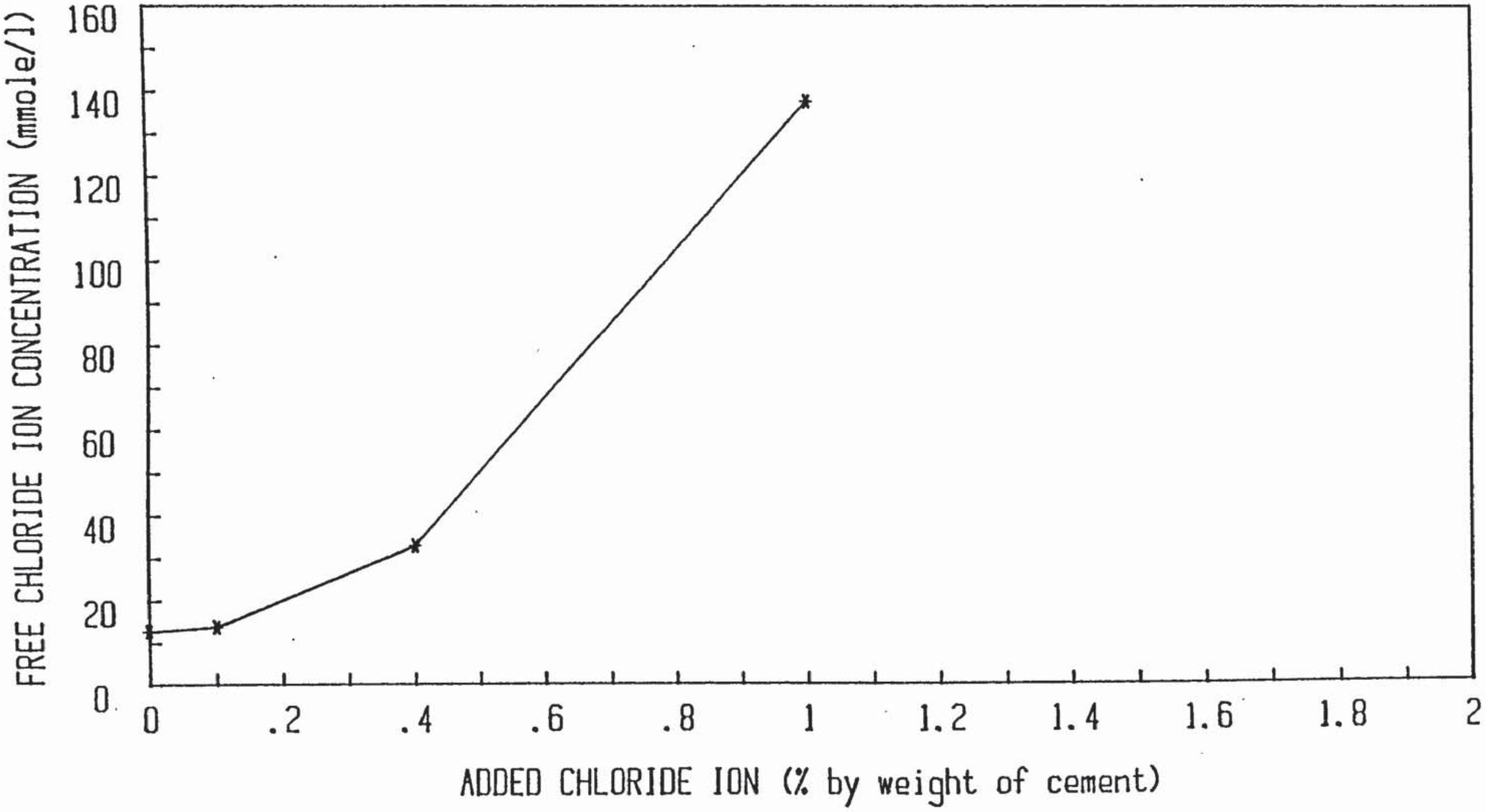


Fig 3.1 Increase in free Cl^- present in pore solution v. percentage of added chloride for 28 day 0.6 w/c samples of OPC pastes

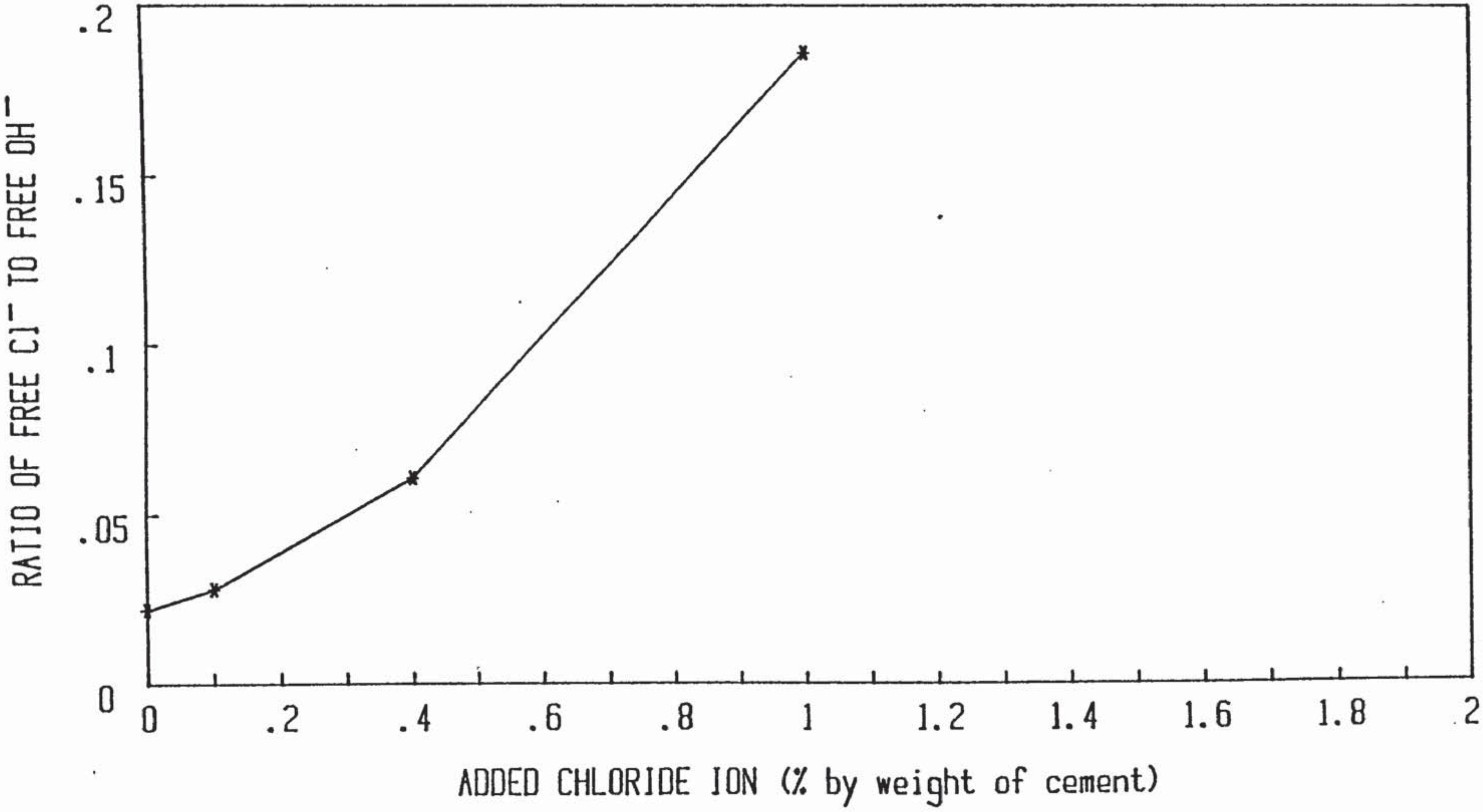


Fig 3.2 $\frac{[Cl^-]}{[OH^-]}$ of pore solution v. percentage of added chloride for 28 day, 0.6w/c samples of OPC pastes

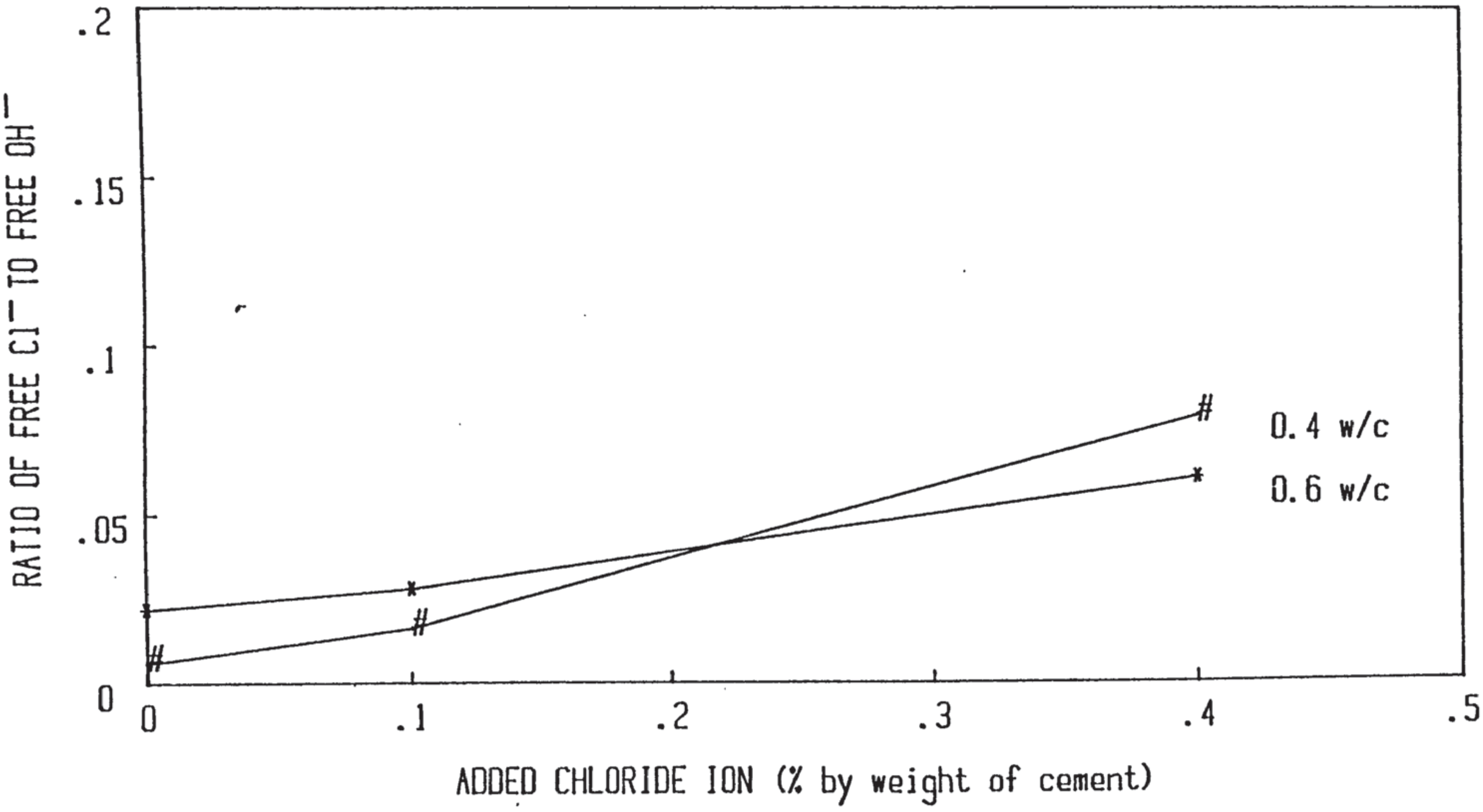


Fig 3.3 $\frac{[Cl^-]}{[OH^-]}$ v. added chloride for 2 water cement ratios

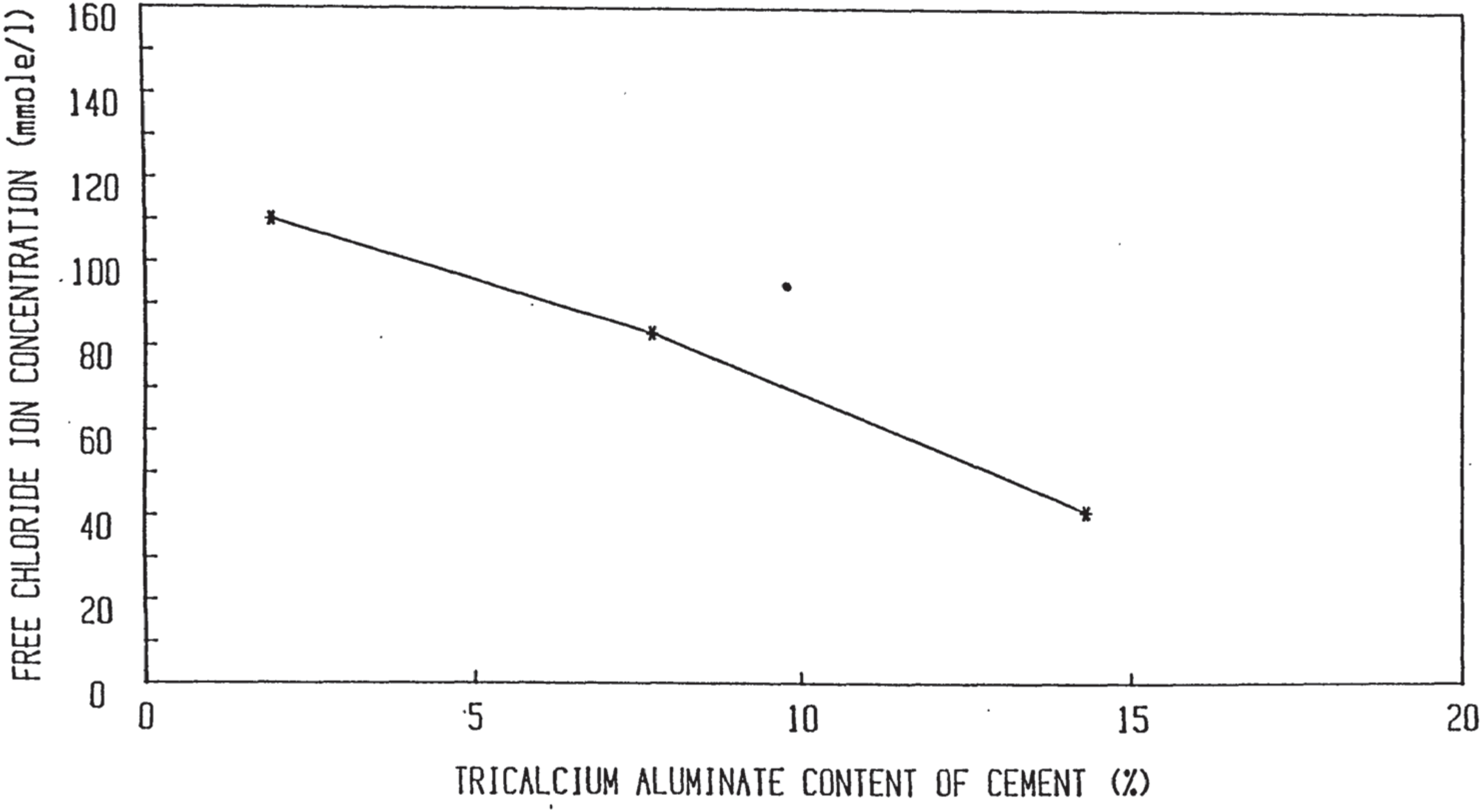


Fig 3.4 [Cl-] v. C_3A content for cement pastes with 0.4% Cl^- added by weight of cement

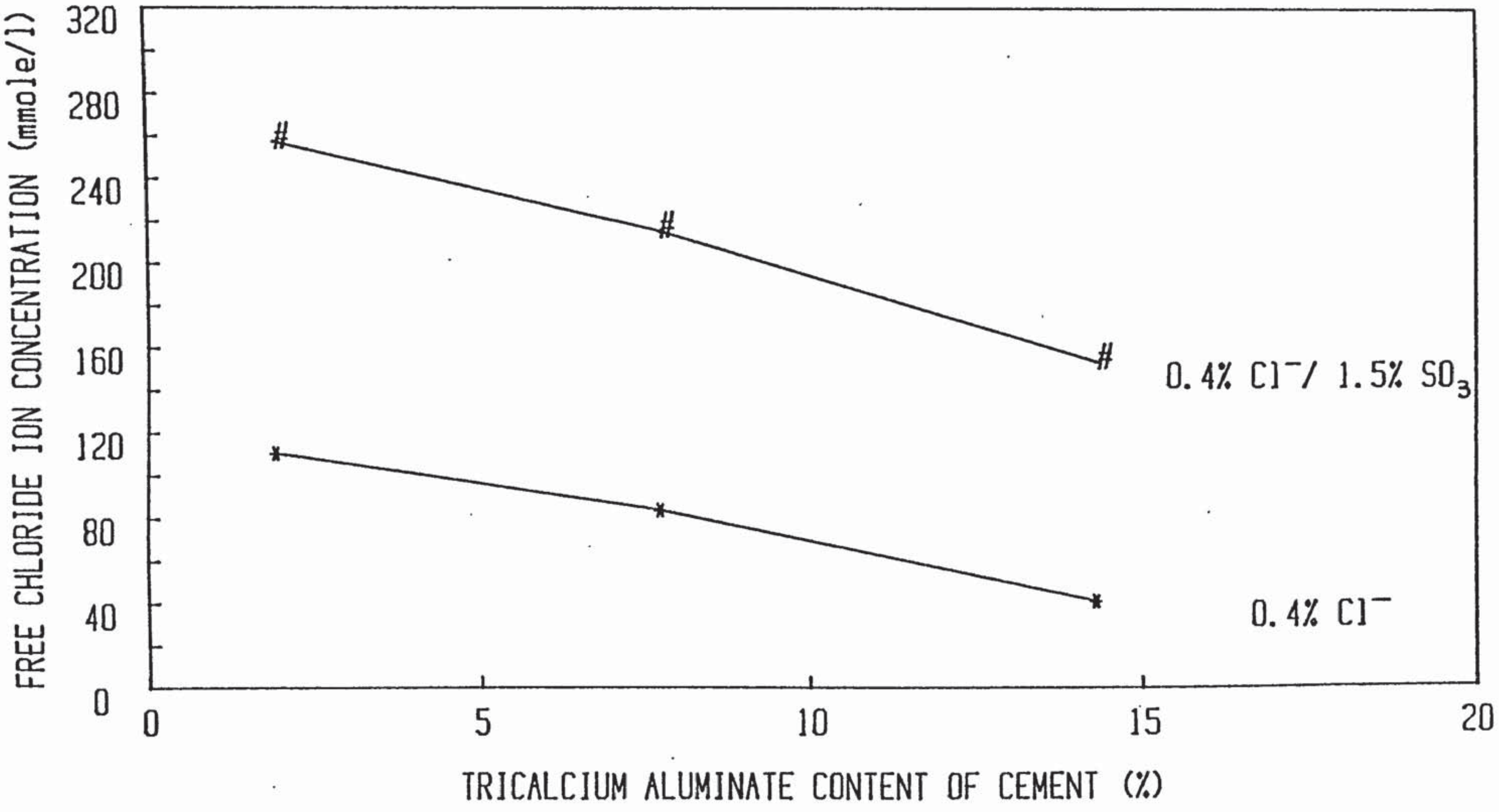


Fig 3.5 Reduction in the chloride binding ability of cement when sulphates are present

CHAPTER 4

THE DIFFUSION OF CHLORIDE IONS THROUGH HARDENED CEMENT PASTES

4.1 Introduction

In chapter 3 the levels of free chloride present in the pore solution of various hardened cement pastes were established. To add to the overall understanding of the corrosion mechanism of steel in concrete, it was necessary to determine the mobility of the chloride ions through the cement matrix. The determination of activation energies for their movement was also necessary. With this information and that from the previous chapter it was hoped to produce a further ranking of the cements studied.

Breakdown of the passive film and hence corrosion of steel in concrete can be stimulated either by carbonation, which reduces the pH of the pore solution to a level which cannot sustain protection, or by the presence of significant quantities of chloride ions in the concrete. The corrosive effects of chlorides are less well understood than those of carbonation and tend to be associated with intense localised attack so that the reinforcement becomes deeply pitted. This has caused difficulties in setting limits on the levels of chloride contamination allowable in concreting materials, particularly when non-standard cements are being used.

Although the mechanism of pitting is complex, an essential feature of the process is that the solution within the pit becomes modified in composition with respect to the surrounding bulk electrolyte and it is well established that for stable pit growth to be sustained, the local chloride concentration must rise and the local hydroxyl concentration must fall (Fig. 4.1)(After Page and Havdahl [73].).

On the basis of this model, it is possible to predict that the risk of chloride-induced corrosion of steel in concrete may depend on at least two parameters which are related to the chemistry of the cement matrix. These are:

(i) The relative concentrations of aggressive chloride ion and inhibitive hydroxyl ions in the pore solution (as mentioned in chapter 3).

(ii) The ionic mobility (related to diffusivity) of chloride which is likely to be important because pits will tend to repassivate instead of growing if the cement matrix effectively restrains the diffusional supply of chloride ions whilst maintaining a buffered alkaline environment near the surface of the embedded steel.

Factors which may influence item (ii) above include the pore structure and mineralogy of the cement matrix, the concentration and nature of the chlorides present and the moisture content. The work described in this chapter therefore is concerned with determining the parameter (ii) for a range of cements and attempting to establish the validity of using it as an index of corrosion protection. Furthermore, this work is recognised as being of importance because diffusion is regarded as being a significant process by which chlorides from external sources such as seawater or deicing salts can penetrate normal thicknesses of cover of concrete exposed to them [12, 13, 74]

Mobility is linked to diffusivity by the Nernst-Einstein relationship [75], which states:

$$D = \mu KT$$

where D is the coefficient of diffusion

μ is the mobility of the particles

K is the Boltzmann constant

T is the temperature.

It can be seen from this equation therefore that the mobility of an ionic species is directly proportional to the diffusion coefficient for a given temperature.

Well over a century ago Fick developed the laws of diffusion which allow the determination of diffusion kinetics from physically measurable quantities.

Fick's first law states that the flux is proportional to the concentration gradient, whilst the diffusion coefficient is the constant of proportionality in the equation. This is usually expressed in terms of square centimetres per second (cm^2s^{-1})[76] since the units of flux are mass over area by time and those of concentration are mass over volume.

By measuring the diffusion coefficient of an ionic species through a permeable material at several temperatures it is possible to determine an activation energy. This is the minimum thermal energy required by the ions to initiate movement through the material.

The work described in this chapter falls into three broad sections:

(i) At the start of the work an attempt was made to obtain an activation energy for a typical OPC and SRPC for Cl^- transport in order to practice the technique of previous workers, (namely Page, Short and El Tarras[19]) in the case of the OPC and obtaining a hitherto undetermined value for the SRPC.

(ii) The determination of diffusion coefficients for three pure OPC's and for the same cements blended with either 5% PFA or 5% GGBFS. This work was carried out on behalf of the Building Research Establishment, who wished to determine the suitability of certain low level cement replacements.

(iii) The determination of activation energies for some of the cements studied previously in chapter 3 with a view to establishing a mechanism of diffusion and whether the mechanism was the same for different cements. This work was also undertaken to establish a rank order of suitability of the cements based on their diffusion coefficients.

It was hoped that this work would show whether the blending of cements is detrimental to the protection afforded to embedded metal, as far as ease of chloride ion transport is concerned. It was also aimed at examining whether one cement is markedly different from another in terms of allowing chloride ions to move freely. It was then intended to view the data in comparison with the results obtained from chapter 3. For example there is the question of whether a high level of free chloride in the pore solution necessarily means that the embedded metal is, significantly more at risk. If the same cement had a very low diffusion coefficient for chloride ions then the answer could be negative. The overall aim then was to try to place the cements studied in an order of protection likely to be given to embedded metal.

In the past, two completely different methods have been used for the determination of diffusion coefficients and activation energies for chloride ions in cement pastes. Collepardi et al [77] exposed the end faces of cement and concrete cylinders to a 3 % calcium chloride solution, at temperatures of 10,25 and 40 degrees centigrade. The specimens were cast under vacuum to avoid air bubbles.

Periodically samples were taken out of the solution and cut into equal slices perpendicular to the exposed surface. The total chloride ion content of each slice was determined by chemical analysis and diffusion coefficients were determined using a solution of Fick's second law as applied to non steady state conditions for a semi-infinite solid.

The equation they used was:

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

for the boundary conditions: $Cx = 0$ at $t = 0$

$Cx = Cs$ at $x = 0$

$0 < x < \infty$, $0 < t < \infty$

where: Cx = chloride ion concentration of slice taken

Cs = chloride ion concentration of external solution

x = thickness of slice measured from original exposed surface

t = time of exposure of specimen to the solution

D = diffusion coefficient

The value of $\mathrm{erf}\left(\frac{x}{2\sqrt{Dt}}\right)$ against $\left(\frac{x}{2\sqrt{Dt}}\right)$ can be found in mathematical tables. The values of Cs and D were obtained by extrapolating the curve of Cx against x to the point $x = 0$.

Collepardi et al used this method to obtain values of the diffusion coefficient of chloride ions through Portland and pozzolanic cement pastes and concretes. Activation energies were also obtained by these workers for the cement pastes.

A second method of determining diffusion kinetics was developed at Aston University by Page et al [19]. Cement paste cylinders were produced by filling sealable plastic moulds. These were not cast under vacuum as in the previous method, but were fault free. This was achieved by vibrating the paste in the mould to remove trapped air bubbles and by rotating the cylinders slowly about their longitudinal axis to prevent segregation. When set, the cylinders were demoulded and cured under saturated calcium hydroxide for 60 days. After the curing period the cylinders were non-destructively tested for soundness and uniformity using ultrasonic pulse velocity (UPV) measurements. Discs of approximately 3mm. in thickness were cut from the central portions of the cylinders with a diamond saw. These were then placed in specially designed glass cells. These consisted of two compartments (one on either side of the cut disc). In one compartment was a solution of saturated calcium hydroxide and in the other a solution of sodium chloride ($1 \text{ mol } l^{-1}$) in saturated calcium hydroxide.

The level of chloride ion concentration in the initially dilute compartment was measured periodically, and from this, and a solution of Fick's first law (as applied to quasi-steady state diffusion), they were able to determine diffusion coefficients for chloride ions. The diffusion coefficient was calculated from the slope of the rectilinear plot of the chloride ion concentration (of the dilute side of the cell) against time. Activation energies were also obtained from Arrhenius plots of the log diffusion coefficients against absolute temperature^{-1}.

The work described in this chapter was carried out using this second method with some variations. Details of the general technique and the associated theory are given in chapter 2.

4.2 Experimental

Although the experimental technique broadly followed that described in chapter 2 there were some differences. Smaller numbers of replicate cells were used than by previous workers [19] for example and also the same discs were used at several temperatures instead of being discarded after one temperature. Due to the large number of cements being studied, time restrictions and limited facilities, it was felt that these departures from previous experimental regimes were justified in an effort to determine whether the work could be speeded up.

4.2.1 Determination of Diffusion Coefficients and Activation Energies for Chloride Ions in a Typical OPC and SRPC.

Specimens were produced as described in chapter 2 and set up in the apparatus as described there also. Small amounts of solution from the initially dilute side of the cell were taken over a period of time in order to determine the diffusion coefficient for chloride ions through the cement paste. The interval between measurements and the duration of the experiment were dependent upon the rate at which chloride passed through the cement disc. The cells were arranged in water baths which kept them at a constant temperature. When enough measurements had been taken to produce a plot of concentration against time and hence obtain a diffusion coefficient.

the solutions in the compartments were emptied. The cells were then thoroughly washed out with deionised water and refilled with fresh saturated calcium hydroxide solution. The temperature of the water baths was then raised and the measurement procedure repeated. When data at several temperatures had been aquired an Arrhenius plot could be produced, showing log diffusion coefficient versus the inverse of absolute temperature to give an activation energy.

4.2.2 Determination of Diffusion Coefficients at 25°C for Chloride Ions in Blended and Unblended Portland Cement Pastes

Three cements OPC D, OPC F and OPC A were used, blended with 5% GGBFS or 5% PFA and also unblended. The method followed was as before, but in this case only one temperature was considered namely 25°C. There is considerable interest in the use of these blended cements. They are used extensively in Europe and with the possibility of their introduction in the UK it is necessary to ensure that they will not be significantly inferior to ordinary Portland cement.

4.2.3 Determination of Diffusion Coefficients and Activation Energies for Chloride Ions in a Range of UK Cements

Again the same technique was employed. Five temperatures were chosen for analysis, 18, 25, 32, 39 and 46°C.

Five cements were used: (i) SRPC A (ii) OPC A (iii) OPC B blended with 30% PFA (iv) OPC B blended with 65% GGBFS (v) OPC B blended with 10% microsilica.

4.3 Results

The values of chloride concentration on the low side of each cell, were plotted against time to give a linear relationship. A typical example is shown in Fig 4.2 where 't_0' is the time delay before chloride concentration is measurable in the dilute compartment. During this initial period chloride diffusion is becoming established across the thickness of the disc. Generally the duration of the experiments was quite short, so the concentration of the initially concentrated solution could be assumed to be virtually constant. It could be assumed that conditions of quasi-steady state diffusion were effective across the disc and that chloride ion flux was constant throughout the disc.

The flux (J) of chloride ion (moles per square centimetre per second) entering the low concentration side of the cell is related by Ficks first law to the diffusion coefficient and the concentration gradient thus:-

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

where V = volume of the low concentration side (cm^3)

A = cross sectional area of the disc (cm^2)

C_1 = chloride concentration in high side ($mol\ l^{-1}$)

C_2 = chloride concentration in low side ($mol\ l^{-1}$)

t = time (seconds)

l = thickness of disc (cm)

D = diffusion coefficient ($cm^2\ s^{-1}$)

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

$$\frac{dC_2}{dt} = \frac{DA}{lV} \left(C_1 - C_2 \right)$$

$$\frac{d\left(C_1 - C_2\right)}{\left(C_1 - C_2\right)} = -\frac{DA}{lV}\ dt$$

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

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

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

$$= \frac{DA}{lV} \left(t - to \right)$$

$$\frac{C_2}{C_1 - C_2} = \frac{DA}{lV} \left(t - to \right) \qquad \text{since } C_1 \gg C_2$$

to give: $C_2 \approx \frac{C_1 DA (t - to)}{lV}$

D can be calculated from the gradient of the rectilinear plot of C_2 against t thus:

plot

$$D = \frac{V \; l \; C_2}{A \; C_1} \left(\frac{1}{t - to} \right)$$

$\overline{A}$ $\overline{1000}$ $\overline{(C1 - C2)}$

The values obtained for D are given in the following sections (Tables 4.1 to 4.10)

Activation energies where appropriate were obtained from Arrhenius plots of log D versus absolute temperature^{-1}. These were linear plots of the equation.

$$D = Do \exp ({}^{-Q}/_{RT})$$

where D = diffusion coefficient $cm^2 s^{-1}$

Q = Activation energy J mol^{-1}

R = Gas constant

T = Absolute Temperature °k

Do= constant

A typical plot is shown in Fig 4.3 Worked examples of both calculations are shown in Appendix 1.

Mercury porisimetry as described in Chapter 2 was carried out on discs before and after diffusion experiments to check no major difference occurred in the specimen during the experiment, (Figs. 4.4 to 4.8).

4.3.1 RESULTS OF DETERMINATION OF DIFFUSION COEFFICIENTS AND ACTIVATION ENERGIES FOR CHLORIDE IONS IN A TYPICAL OPC AND SRPC

Table 4.1 Diffusion Coefficient Values for OPC B of 0.6 W/C

Temperature °C	Diffusion Coefficient(cm²s^{-1})(x10^{8})				
	Disc 1	Disc 2	Disc 3	Disc 4	Average
15	5.89	4.80	5.29	5.85	5.46
22	8.50	6.61	5.50	8.28	7.22
30	10.84	10.99	10.67	12.62	11.23
37	17.69	18.82	18.52	23.66	19.67

Table 4.2 Diffusion Coefficient Values for SRPC A of 0.5 w/c

Temperature	Diffusion Coefficient($cm^2 s^{-1}$)($x10^{8}$)					
^{o}C	Disc 1	Disc 2	Disc 3	Disc 4	Disc 5	Average
15	5.65	4.08	4.90	4.82	4.67	4.82
22	5.83	5.43	6.39	6.84	6.91	6.28
30	9.18	6.21	9.19	6.41	8.45	7.89
37	22.92	8.05	25.77	13.57	22.20	18.50

Table 4.3 Diffusion Coefficient Values for SRPC A of 0.6 w/c

Temperature	Diffusion Coefficient ($cm^2 s^{-1}$)($x10^{8}$)					
^{o}C	Disc 1	Disc 2	Disc 3	Disc 4	Disc 5	Average
15	9.17	10.52	11.34	7.12	8.83	9.39
22	7.97	14.47	9.33	8.79	9.21	9.95
30	10.79	9.98	9.51	10.61	17.26	11.63
37	18.06	14.97	21.28	17.67	29.53	20.30

Table 4.4

Activation Energies for OPC B of 0.6 w/c and SRPC A of 0.5 w/c and 0.6 w/c

Cement	Activation Energy (kJ/mol)
0.6 w/c OPC B	44.7 ± 6.7
0.5 w/c SRPC A	40.4 ± 12.5
0.6 w/c SRPC A	21.8 ± 11.7

4.3.2 Results of Determination of Diffusion Coefficients for Chloride Ions in Blended and Unblended Cements

Table 4.5 Diffusion Coefficient Values for Blended and Unblended OPC's at 25°C

Cement	w/c	Diffusion Coefficient $(cm^2s^{-1})(x10^8)$				
		Disc 1	Disc 2	Disc 3	Disc 4	Average
OPC D	0.5	4.75	3.03	3.13	2.82	3.43
OPC F	0.5	2.33	1.84	1.50	1.66	1.83
OPC A	0.5	3.14	2.30	4.40	2.74	3.14
OPC D/ 5% PFA	0.4	1.42	2.10	2.20	1.12	1.71
OPC D/ 5% PFA	0.5	5.02	4.89	5.42	5.69	5.25
OPC D/ 5% PFA	0.6	8.96	9.49	8.81	8.91	9.04
OPC F/ 5% GGBFS	0.4	1.52	1.22	1.46	1.44	1.41
OPC F/ 5% GGBFS	0.5	2.07	2.84	2.76	2.50	2.54
OPCF/ 5% GGBFS	0.6	7.33	6.03	6.17	6.80	6.59
OPCA/ 5% PFA	0.4	1.75	1.55	1.27	1.25	1.45
OPCA/ 5% PFA	0.5	3.37	3.45	3.52	5.20	3.88
OPCA/ 5% PFA	0.6	8.47	8.34	9.21	7.25	8.32

4.3.3 Results of the Determination of Diffusion Coefficients and Activation Energies for Chloride Ions in a range of UK Cements

Table 4.6 Diffusion Coefficient Values for SRPC A of 0.5 w/c

Temperature °C	Diffusion Coefficient (cm^2s^{-1})($x10^8$)				
	Disc 1	Disc 2	Disc 3	Disc 4	Average
18	11.14	7.50	7.40	6.87	8.23
25	7.36	10.90	9.75	9.51	9.38
32	10.48	12.86	12.05	13.28	12.17
39	11.37	15.67	10.11	14.47	12.91
46	19.46	22.47	19.68	24.12	21.43

Table 4.7 Diffusion Coefficient Values for OPC B with 65% GGBFS of 0.5 w/c

Temperature °C	Diffusion Coefficient(cm^2s^{-1})($x10^8$)				
	Disc 1	Disc 2	Disc 3	Disc 4	Average
18	0.56	1.69	0.53	0.52	0.83
25	0.59	—	0.63	0.57	0.60
32	0.70	—	0.58	0.78	0.68
39	1.26	1.82	1.54	1.77	1.60
46	—	2.42	2.45	2.20	2.31

Table 4.8 Diffusion Coefficient Values for OPC B with 10% Microsilica of 0.5 w/c

Temperature °C	Diffusion Coefficient (cm^2s^{-1})(x10^8)				
	Disc 1	Disc 2	Disc 3	Disc 4	Average
18	1.61	1.44	1.79	1.63	1.62
25	2.63	1.94	2.22	2.04	2.21
32	2.85	2.03	2.56	2.15	2.40
39	5.56	5.77	4.90	5.69	5.48
46	11.79	7.79	9.05	6.90	8.88

Table 4.9 Diffusion Coefficient Values for OPC A of 0.5 w/c

Temperature °C	Diffusion Coefficient (cm^2s^{-1})(x10^8)				
	Disc 1	Disc 2	Disc 3	Disc 4	Average
18	4.29	5.57	5.39	5.19	5.11
25	5.29	5.97	6.69	7.87	6.46
32	7.05	8.09	8.51	8.16	7.95
39	9.07	9.96	9.76	9.70	9.62
46	13.82	18.85	18.52	17.66	17.21

Table 4.10 Diffusion Coefficient Values for OPC B with 30% PFA of 0.5 w/c

Temperature ^{0}C	Diffusion Coefficient (cm^2s^{-1})($x10^8$)				
	Disc 1	Disc 2	Disc 3	Disc 4	Average
18	2.90	2.19	2.42	3.21	2.68
25	2.82	2.27	2.55	3.44	2.77
32	6.34	6.30	7.92	6.04	6.65
39	3.94	2.87	2.36	2.53	2.93
46	5.22	4.92	1.61	3.08	3.71

Table 4.11 Activation Energies for a range of UK Cements of w/c 0.5

	Q Activation Energy (kJ/mol)		
SRPC A	24.5	±	6.1
OPC A	33.9	±	4.5
OPC B + 30 % PFA	6.5	±	14.6
OPC B + 65 % GGBFS	33.3	±	18.0
OPC B + 10 % Silica	46.5	±	7.2
OPC B (Published work)	44.6	±	4.3

In the present work values for the 95 % confidence limits were always greater than, and in some cases unacceptably greater than those found by previous workers, Page, Short and El Tarras [19].

This is probably due to the change in experimental procedure used in the present work viz:- use of only four discs, re-use of discs at different temperatures and in some cases excessive time of diffusion.

4.4 Discussion of Results

The initial work on the OPC B and SRPC A yielded activation energies of 44.7 ± 6.7 kJ/mol for the 0.6 w/c OPC and 40.4 ± 12.5 kJ/mol and 21.8 ± 11.7 kJ/mol for the 0.5 and 0.6 w/c ratio SRPC's respectively. This value of 44.7 kJ/mol seems slightly high in comparison to a value obtained by Page et al [19] of 32.0 kJ/mol for a 0.6 w/c cement paste. However, their specimens were cured for 60 days whilst the specimens used for this work were cured for 90 days.

There is a significant difference between the values obtained for the 0.5w/c SRPC and the 0.6 w/c SRPC. This is probably due to a difference in pore structure between the two materials [78,79], the 0.6 w/c material being expected to have a larger proportion of unsegmented pores which allow easier transport of chloride ions.

The activation energy for an SRPC would appear to be lower than for an OPC of the same water-cement ratio.

If we look at diffusion coefficients for the blended cements we see there is no significant detrimental effect produced by adding the blending agents at the 5% level.

OPC D and OPC A had diffusion coefficients of roughly the same value. These were 3.43×10^{-8} cm^2s^{-1} and 3.14×10^{-8} cm^2s^{-1} respectively. However, OPC F had a much lower diffusion coefficient of $1.83 \times 10^{-8} cm^2s^{-1}$. This would appear to suggest that OPC F is almost twice as effective as OPC D and OPC A at impeding the progress of chloride ions through the cement matrix. This is even though, when we look at the results from the previous chapter we see that OPCF is not capable of binding as much chloride chemically as both OPC D and OPC A(Table 3.3). This means that there would be more free chloride present in the pore solution. Therefore on the basis of these results it would appear to be a more suitable cement for use in chloride containing environments.

It must be stated, however, that the data acquired for these cements are only applicable at 25°C.

As previously stated there is no large change in the average diffusion coefficient value when PFA or GGBFS are added to these cements at the 5% level. However, there is an overall increase as shown in Table 4.12.

Table 4.12 <u>Diffusion Coefficients for 3 Blended and Unblended Cement Pastes at 25°C</u>

	Diffusion Coefficients $(cm^2 s^{-1})(x10^8)$		
	0.4 w/c	0.5 w/c	0.6 w/c
OPC D	-	3.43	-
OPCD + 5% PFA	1.71	5.25	9.04
OPC A	-	3.14	-
OPC A + 5% PFA	1.45	3.88	8.32
OPC F	-	1.83	-
OPC F + 5% GGBFS	1.41	2.54	6.59

Three water/cement ratios were used for the blended cements 0.4, 0.5 and 0.6. Although the diffusion coefficient increased progressively with an increase in water/cement ratio, the biggest increase occurred at 0.6 water/cement ratio. Again this presumably reflects the fact that there are more unsegmented pores present.

The diffusion analysis carried out on a range of UK cements studied in Chapter 3 yielded some unexpected results. A value of 33.9± 4.5 kJ/mol for OPC A was obtained. This is lower than that obtained for a typical OPC, OPC B by previous workers and also by this author. It is also lower than the values obtained for an SRPC (24.5 ± 6.1 kJ/mol). There was a considerable degree of scattering of the points on the Arrhenius plot (for reasons given on page 123) which increased at the highest temperature. The diffusion coefficient values for this cement at 25 °C are at variance with the values obtained at the same temperature and water-cement ratio during the blended cement experiments by the same author. An average value of 3.14×10^{-8} $cm^2 s^{-1}$ (Table 4.5) was obtained during the blended cement work, but a value of 6.46×10^{-8} $cm^2 s^{-1}$ (Table 4.9) was obtained for this work. Clearly this is more than double the previous value. This could possibly be due to deterioration of the cement whilst in storage, since there was an interval of approximately one year between the two sets of experiments.

The activation energy obtained for OPC B with 30 % PFA was 6.5 ± 14.6 kJ/mol, this compares with 4.2 kJ/mol obtained for an OPC with 35 % by weight of Salone pozzolan by Collepardi et al [77]. However, the Arrhenius plot was very poor with a correlation coefficient of only -0.19. This therefore was not a genuine Arrhenius plot and either the diffusion mechanism altered with temperature or the cement paste underwent structural modification. The value obtained by Page et al [19] for the diffusion coefficient of OPC B blended with 30 % PFA, 0.5 w/c and 25°C was 1.47 x 10^{-8}cm²s^{-1} whereas the result obtained here was almost double that at 2.77 x 10^{-8}cm²s^{-1}. This could possibly be due to the way the experiment was conducted. Five temperatures were studied using the same discs. At the end of each temperature run, the cells were washed out and refilled with fresh solution. Consequently the discs were used for some considerable time (of the order of several months). It may be necessary to replace the disc for each new experiment. During the experiment there was not the expected increase in diffusion coefficient value with increase in temperature. The diffusion coefficients at 39° and 46°C were lower than that at 32°C. The experiments were in progress considerably longer than had been previous practice due to the rather slow diffusion rate. Since the specimens were cured for only 60 days it is possible that a slow chemical reaction was taking place within the specimen due to the PFA during the course of the experiments. Crystals were found in abundance on the surface of the discs (exposed to the 1M Sodium chloride in saturated calcium hydroxide solution)of OPC A and to a lesser extent on the surface of the PFA cement. These were analysed by X-ray diffraction and found to be calcium hydroxide crystals. Presumably these had been deposited due to the length of time of the experiment and as the temperature of diffusion as increased, since calcium hydroxide becomes less soluble at higher temperatures. The effect of the crystals would be to reduce the cross sectional area of the discs available for diffusion.

The values of activation energies for SRPC A, OPC B with 65% GGBFS and OPC B with 10% Microsilica seem more acceptable. The value obtained for SRPC A was 24.5 ± 6.1 kJ/mol. The diffusion coefficient obtained for a 0.5w/c paste at 25°C was 9.38×10^{-8} cm^2s^{-1} which compared well to a value of 10.00×10^{-8} cm^2s^{-1} obtained by Page et al [19]. Mercury Intrusion Porosimetry was performed on the specimens and no significant difference in structure before and after diffusion was found. Some calcium hydroxide crystals were found on the face of the disc exposed to the high concentration side of the cell and this could account for the slightly lower value obtained.

The value of activation energy for chloride ions in OPC B with 65% GGBFS was 33.3 ± 18.0 kJ/mol. The low diffusion coefficients obtained indicate that the slag cement is much better at retarding the progress of chloride ions. The value of the diffusion coefficient for the slag cement at 25°C was 0.60×10^{-8} cm^2s^{-1} (see Table 4.7).

This compares with a value of 0.41×10^{-8} cm^2s^{-1} found by Page et al [19].

From purely assessing the diffusion aspect this cement would seem an excellent choice for an environment where chloride is present. the value of activation energy for the cement containing microsilica was 46.5 ± 7.2 kJ/mol. This is about the level of a typical OPC. The low diffusion coefficient values make this material look quite a promising cement replacement.

4.5 Conclusions

Differences in experimental technique made duplication of earlier results difficult. To avoid problems in future work it is recommended that six specimens be used, at only one temperature and for as short a duration as experimentally possible.

A typical sulphate resisting Portland cement has a higher diffusion coefficient value for chloride ions than does a typical ordinary portland cement. This would suggest that it is not as suitable for such environments as the Middle East as would perhaps have been previously thought. The logical argument would have been to use SRPC because of the problem of sulphate attack in this region. However, there is also a large amount of chloride present there and the SRPC would be far more susceptible to this kind of attack than would the OPC.

Increasing the water-cement ratio increases the diffusion coefficient value for chloride ion transport and reduces the activation energy.

This is more of a problem at water-cement ratio 0.6.

The values for OPC D and OPC A were very similar, but slightly higher than that for OPC F. The use of blending agents such as PFA and GGBFS give slightly higher values of D than the values of the corresponding pure cements. These differences were not considered significant.

Increasing the water-cement ratio again increased the diffusion coefficient values for all three cements.

It is difficult to draw firm conclusions based on the final section of work with the UK cements, but it would seem that the OPC blended with 10% microsilica and the OPC blended with 65% GGBFS performed very well. The OPC with microsilica had a higher diffusion coefficient value than the slag cement but both were substantially lower than a typical OPC alone.

The diffusion coefficient values for the SRPC supported previous workers' findings and showed that its high value could make it potentially unsuitable for use in chloride laden environments.

The results obtained for the OPC A although in reasonable agreement with values expected for a pure OPC are at variance with previously obtained results for the same cement and so it is difficult to assess their validity.

Although the results obtained for the PFA ~~and~~ seem somewhat unusual, there is some backing from other researchers' work and so there are possibly grounds for tentatively accepting them.

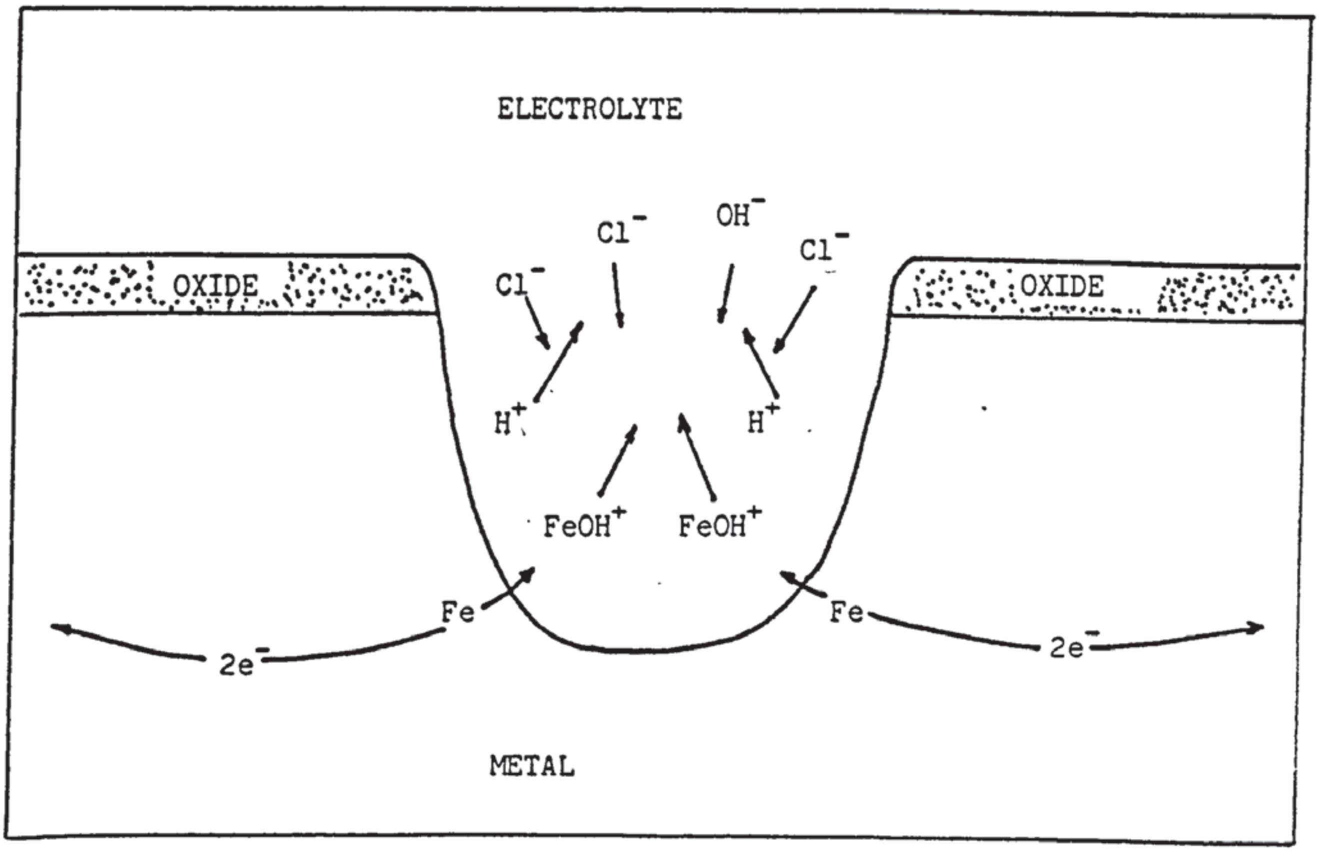


Fig 4.1 Schematic of a pit (After Page and Havdahl [73])

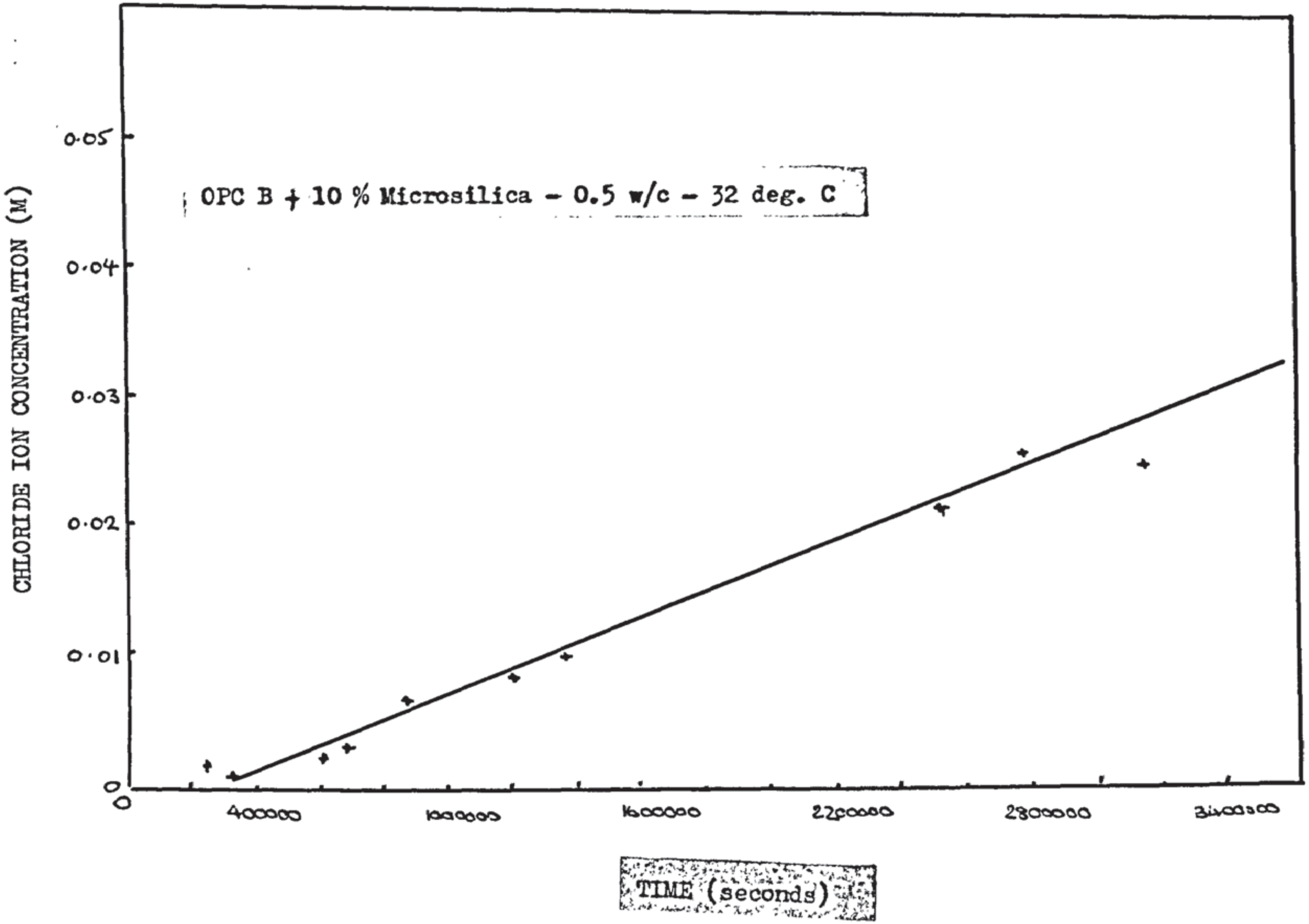


Fig. 4.2 Typical concentration v. time plot for diffusion coefficient calculation

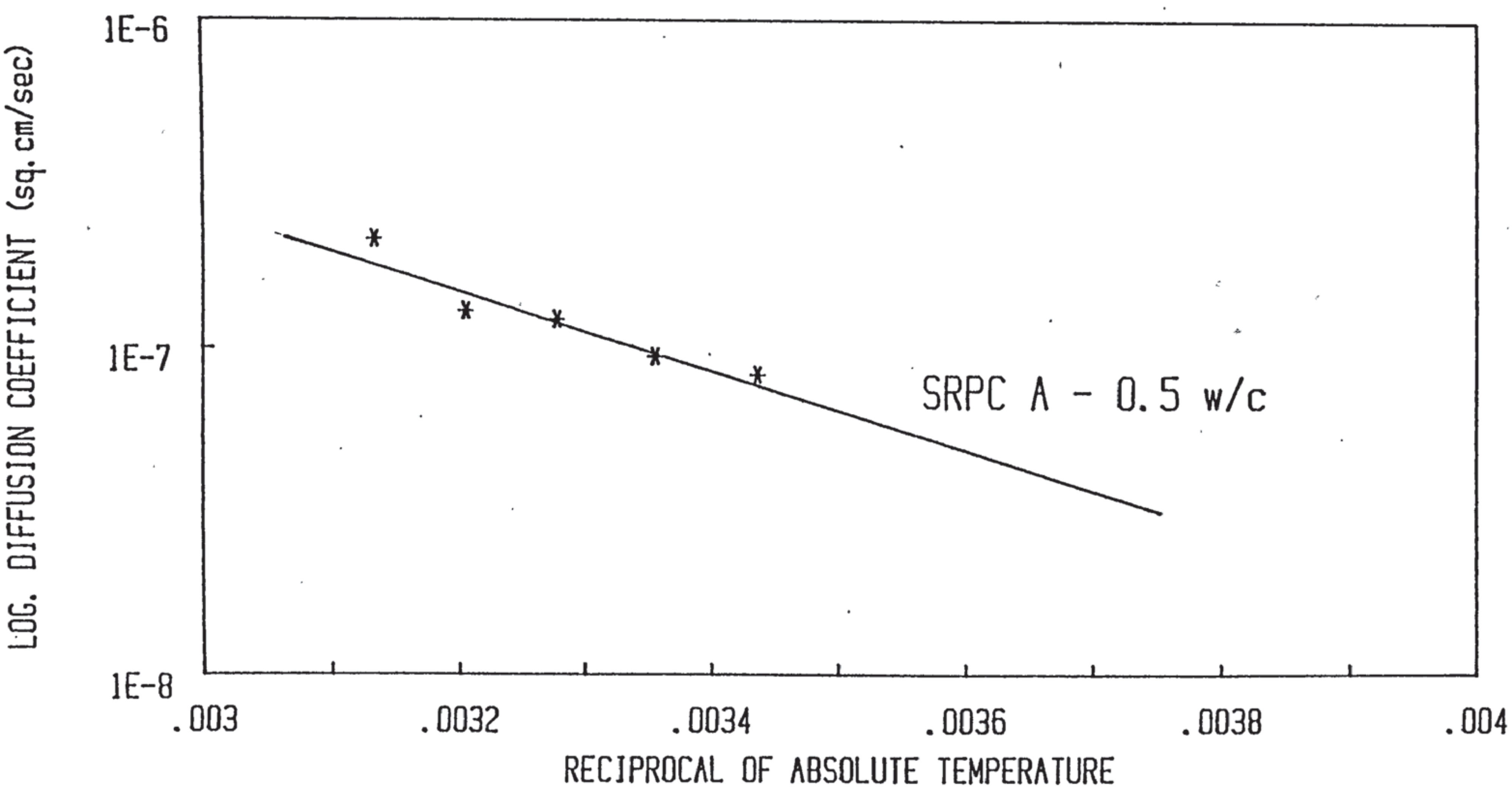


Fig 4.3 Typical Arrhenius plot to determine Activation Energy

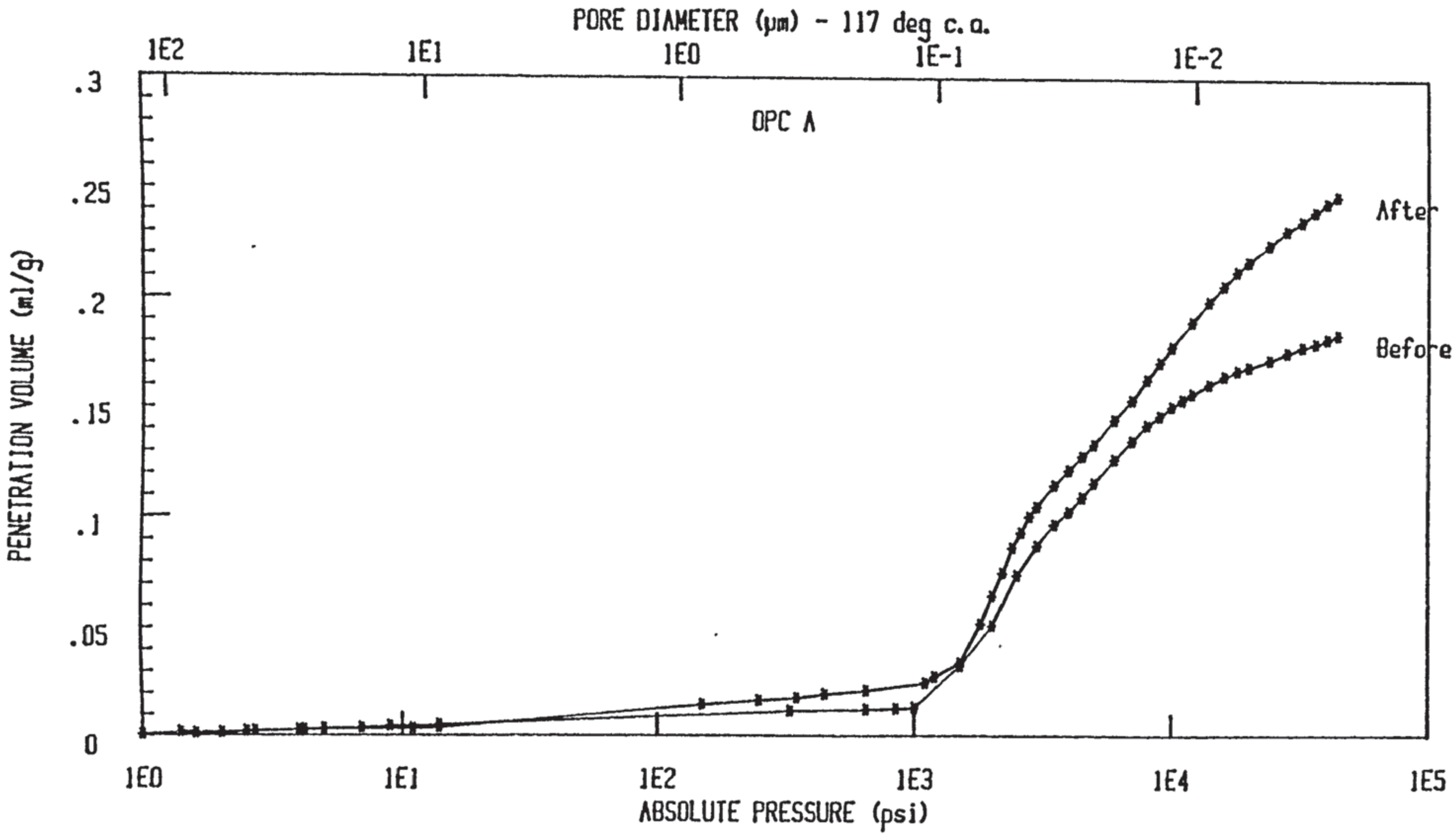


Fig 4.4 Pore size distribution for OPC A before and after diffusion experiments

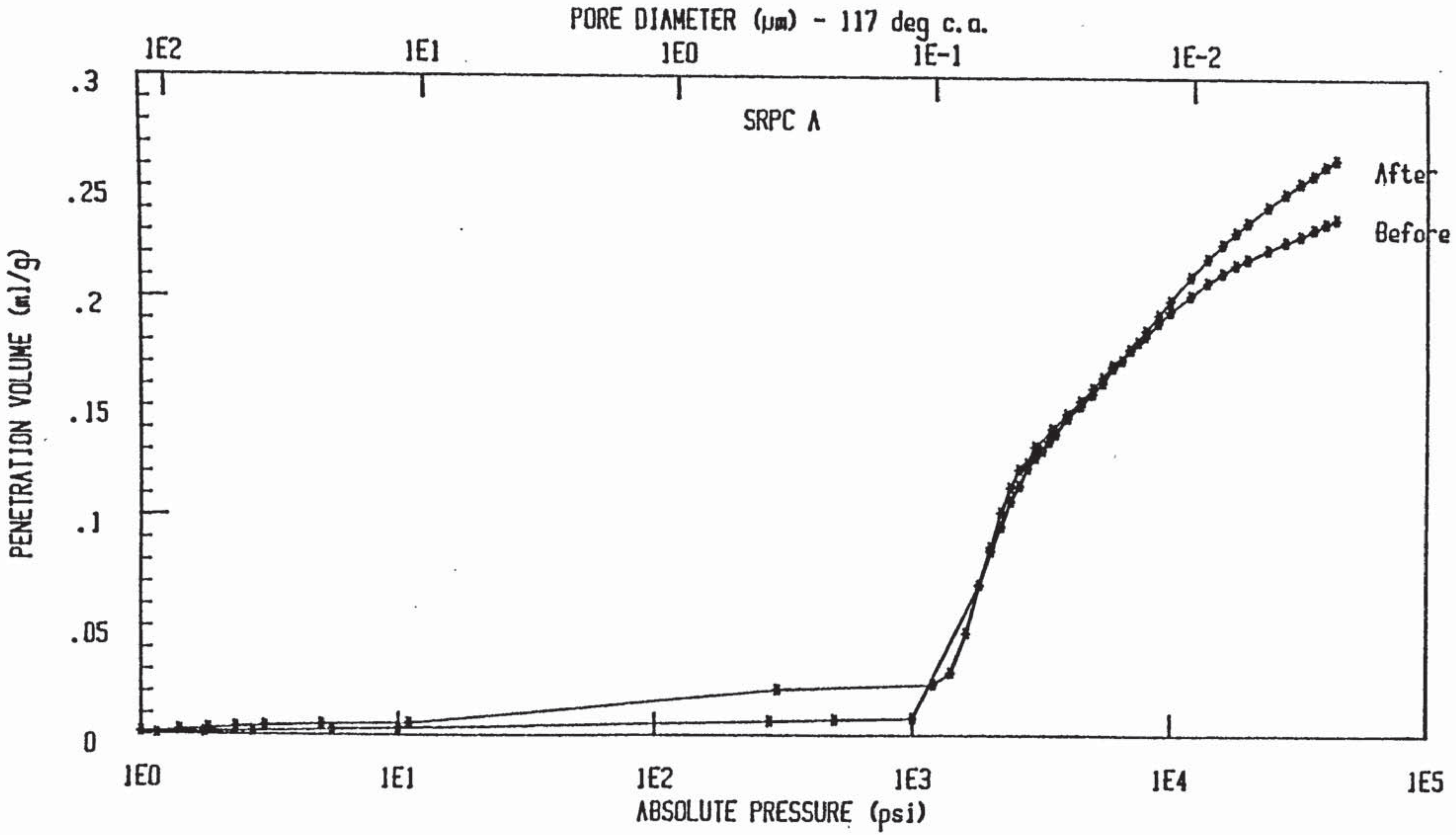


Fig 4.5 Pore size distribution for SRPC A before and after diffusion experiments

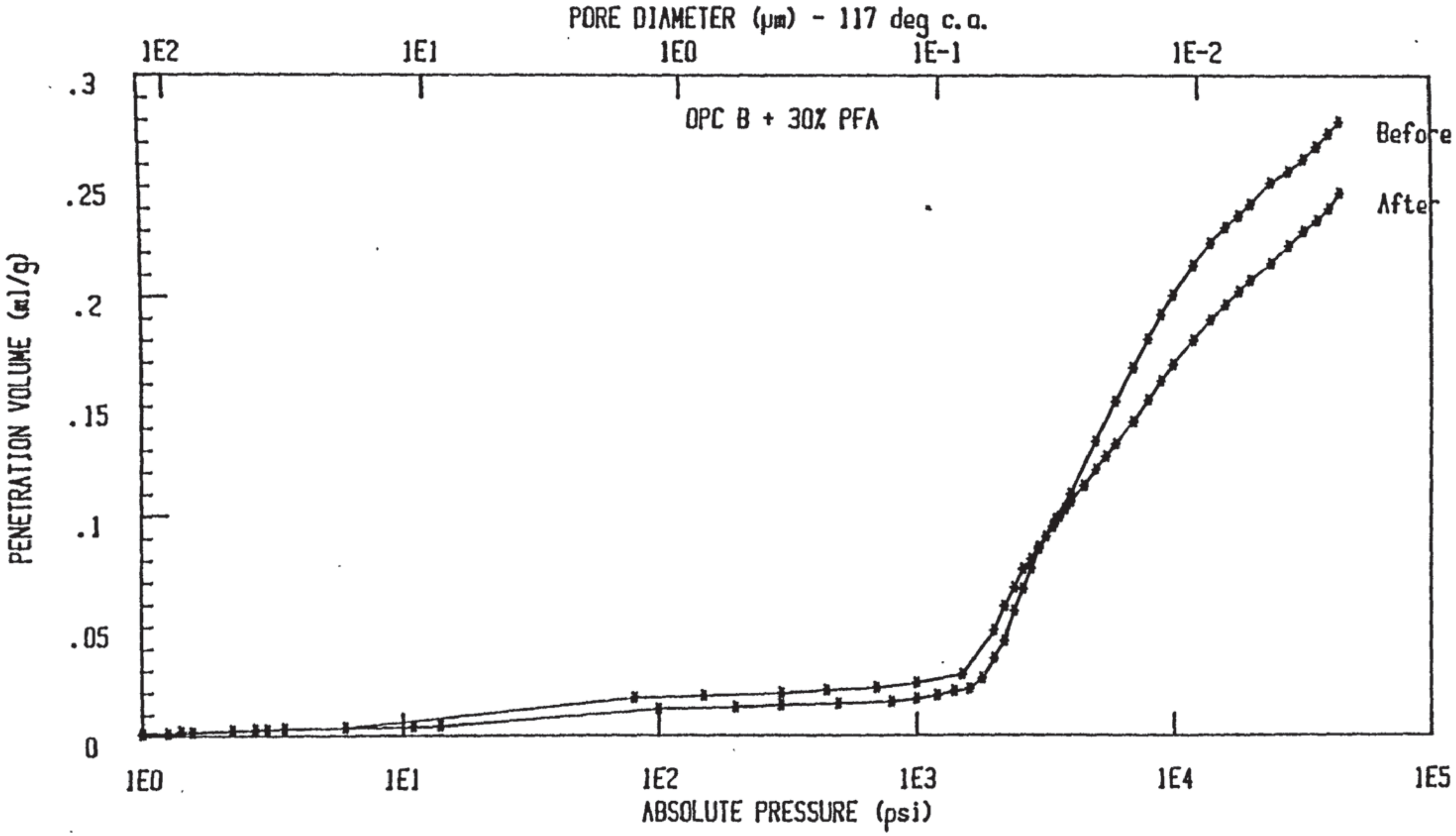


Fig 4.6 Pore size distribution for OPCB + 30% PFA before and after diffusion experiments

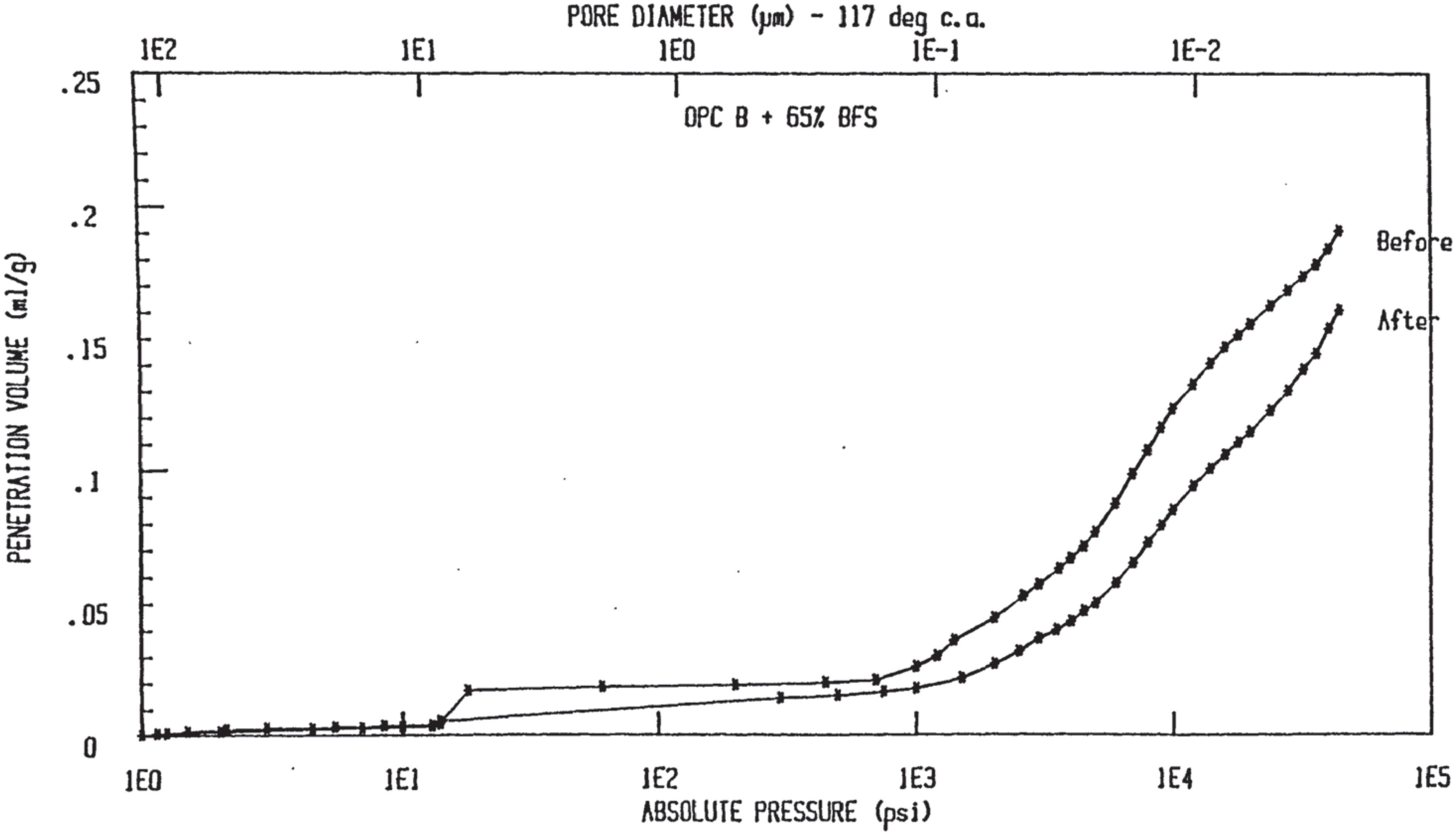


Fig 4.7 Pore size distribution for OPC + 65% BFS before and after diffusion experiments

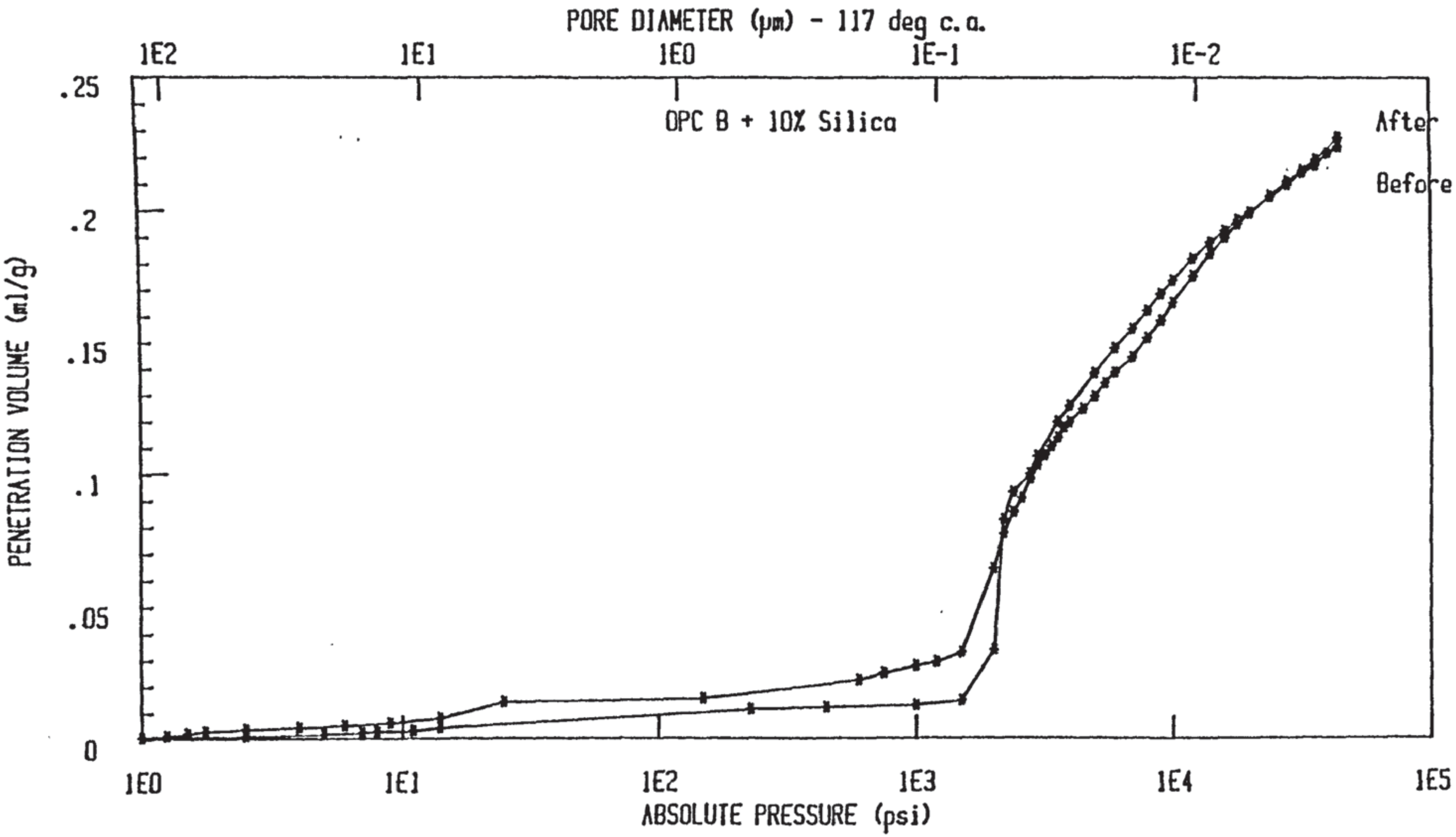


Fig 4.8 Pore size distribution for OPC B + 10% Silica before and after diffusion experiments

CHAPTER 5

ELECTROCHEMICAL INVESTIGATION OF STEEL IN HARDENED CEMENT PASTES

5.1 Introduction

In order to test the validity of the ranking of the cements studied in chapters 3 and 4 it was necessary to carry out electrochemical investigations. The aim of the electrochemical studies was to obtain corrosion current data for embedded steel in various cement pastes and thereby give an estimate of relative rates of corrosion. The effects of several levels of added chloride were also considered. It was then hoped that the data provided by this work could be compared with the data of chapters 3 and 4 which predicted the relative likelihood of the corrosion of steel embedded in these cement pastes.

A range of cements was used, some containing blending agents.

Several specimen designs were used which are described later and several electrochemical techniques were employed.

The type of technique which was required was essentially a non destructive one. The most obvious corrosion test is one in which samples of reinforcement are embedded in a cement paste for a period of time. The specimen is then broken open and the condition of the steel observed. However, this means that the behaviour of the steel cannot be monitored over a range of times and once the specimen has been examined in this way it becomes obsolete. This technique still has its uses but is generally reserved for the time when monitoring of the specimen is finished and becomes more of a 'back up' test.

The various electrochemical methods available at the present time are in the main well suited to monitoring the behaviour of steel embedded in a cement paste matrix.

Some methods which involve the use of an impressed voltage or current can result in permanent changes in the electrochemical condition of the steel and are prone to interference due to concentration polarisation [80].

The current flow between a galvanic couple can be measured (i.e. two steel electrodes of different condition embedded in the same cement paste matrix will cause a current to flow) but this only yields information on the state of the cell as a whole and not on the individual steel electrodes [81].

The main methods which are essentially non destructive when used to study embedded steel in cement paste and concrete are half cell potential also known as rest potential and corrosion potential, linear polarisation, A.C. impedance and electrochemical noise. All of these techniques with the exception of electrochemical noise have been used in this section of work. The AC impedance and electrochemical noise techniques have only recently been developed for use with steel embedded in concrete although the theory of AC impedance as a corrosion monitoring technique has been available for some time. The AC impedance technique together with its associated theory is described more fully in Chapter 2.

In the case of AC impedance method a small amplitude perturbation of ± 10 to 20mV is applied as a sine wave of known frequency. The response of the cell is recorded by a spectrum analyser and the necessary calculations required to determine corrosion rates are performed by a microcomputer. It is claimed by other workers that as the applied voltage is small and of an alternating nature no rest potential change should be experienced by the steel electrodes and representative values of corrosion rate should be obtained [40].

[illegible]

Rest potential measurements and Polarisation resistance measurements (Linear Polarisation technique) are often used together to monitor the behaviour of steel in concrete in the laboratory. These techniques are simple to use, quick and non destructive. The interpretation of the results can also be carried out without the need for expensive equipment such as microcomputers [82]. Of the two techniques the rest potential measurement technique is the simplest and cheapest to carry out. The only equipment necessary is a reference electrode and a high impedance voltmeter [83]. Rest potentials can be measured instantaneously without the need to know the areas of the electrodes. This makes it particularly useful for on site testing where a large number of specimens must be monitored regularly over a long time scale [84]. If large areas of concrete with steel reinforcement are being studied it is possible to carry out potential mapping by moving the reference electrode over several positions on the specimen and thereby determine the positions of possible anodic sites. [85,86]

The chief drawback of potential measurements is that they only show the balance between the anodic and cathodic areas and cannot be used to determine actual corrosion rates.

In conditions where oxygen access to the embedded steel is severely restricted (e.g. submerged marine structures) potentials may be obtained which could be seen as a sign of corrosion but in reality are due to the limitation of the cathode reaction[81].

Most research workers favour using steel with a uniform surface condition, for the study of its behaviour in cement pastes and concrete. Usually this involves an abrasive cleaning and degreasing process. The specimens used in this work were all prepared in this way. However it must be noted that "as received" steel may be regarded as more realistic in terms of practical on site usage. Since the aim of the work in this chapter was to compare the effect of different cements and different chloride levels, it was obviously not wise to introduce another variable such as surface condition of the embedded steel, hence the use of 'clean' steel.

A programme of work was undertaken on a range of cements some of which were blended with PFA and GGBFS. This was carried out in conjunction with the Building Research Establishment. Some of the specimens were manufactured and tested at the Building Research Establishment and some were manufactured and tested at Aston University. There was also a degree of overlap so as to give a check on the results obtained independently by both groups. The design of the specimens and technique for analysis was chosen by the Building Research Establishment.

A second programme of work described in this chapter concerned a range of cements for which pore solution data and chloride ion diffusion data had been obtained. The specimen design for this programme differed from the previous programme and instead of the AC impedance technique, the main technique of analysis here was polorisation resistance as developed by Stern and Geary [21].

5.2 Experimental

5.2.1 Joint Programme of work on Blended Cements at the Building Research Establishment and Aston University

Six cements were involved in this programme; OPC F pure and blended with 5% GGBFS, OPC D pure and blended with 5% PFA and OPC A, pure and blended with 5% PFA. At Aston University OPC D and OPC F were studied in the pure and blended form. The Building Research Establishment examined OPC F (as a control) and OPC A, both in the pure and blended form.

Mild steel electrodes of 6mm diameter were prepared by mechanical abrading and chemical degreasing. The bottom of the electrode was then sealed using plastic heat shrink tubing and the top of the electrode was treated similarly so that an area of 10cm^2 was exposed between the two pieces of plastic tubing. Two electrodes were then fitted into holes drilled into wooden discs of a diameter which would fit comfortably into the rim of a 600ml plastic beaker.

Cement pastes of 0.5 water-cement ratio were cast into 600ml plastic beakers and the two electrode assemblies were embedded into the cement pastes. 1% potassium nitrate and agar salt bridges were cast into the cement pastes at the same time through a third hole cut into the wooden disc. The cement pastes contained three levels of added chloride. these were 0%, 0.4% and 1% Cl^- by weight of cement added as sodium chloride. Each specimen was made in duplicate. Once cast the specimens were stored in humidity boxes at 95% humidity. Rest potential measurements were taken on a regular basis using a standard calomel electrode and a high impedance voltmeter. AC impedance measurements were made periodically using an HP 3582A spectrum analyser, a corrosion cell amplifier and an HP 85 microcomputer. The AC impedance measurements were taken at frequency spans of 0-25Hz, 0-500Hz and 0-10kHz. At the end of the period of test (approximately after 11 weeks) the specimens were broken open and examined and photographically recorded. At age 11 weeks polarisation resistance measurements were made as well as AC impedance measurements to make a comparison.

5.2.2 Programme of Work at Aston University on Cements for which Pore Solution data and Chloride Ion Diffusion Data had been Obtained

Specimens were made from five cements:

(i) OPC B (ii) OPC B with 30% PFA (iii) OPC B with 65% GGBFS (iv) SRPC A and (v) OPC A

Mild steel electrodes of 6mm diameter were prepared by mechanical abrasion and chemical degreasing. The top of the steel electrode was "stopped off" using an epoxy resin so that an area of 10cm^2 was exposed.

The cement pastes were cast into cylindrical tubes as used to manufacture specimens for the pore liquid extraction work and the diffusion work. The electrodes were immersed in the cement paste using the plastic lids to hold them in position until the cement paste had set. Salt bridges were cast into the pastes at the same time to allow connection to an external reference electrode (SCE). The w/c ratio for all pastes was 0.5. When cast the specimens were placed in humidity boxes with the humidity maintained at about 95%. For each cement triplicate specimens were manufactured with the following additives:-

(i) No additives, (ii) 0.4% Cl^- by weight of cement added as NaCl, (iii) 1% Cl^- by weight of cement added as NaCl.

Polarisation resistance measurements were made using a Princeton Applied Research Corporation Corrosion measurement console [87]. An overpotential of 20mV either side of the rest potential was used with a scan rate of 0.16mV per second. Tafel constants of 0.1 were assumed for both Ba and Bc (anodic and cathodic tafel constants). This value was taken as it is recommended by the handbook for the equipment where the Tafel constants are not accurately known. Using this value means that theoretically the result obtained can only be a factor of 2.2 in error at most [39].

5.3 Results

5.3.1 Results obtained at Aston University from Joint Programme of work with Building Establishment on Blended Cements

Table 5.1 AC Impedance Measurement Results at Age 28 days

Cement	Additives	Rt Transfer Resistance Ωcm^2	I corr $nAcm^{-2}$	Average I corr Values $nAcm^{-2}$
OPC F	None	3.50×10^6	3.23	3.12
OPC F	None	3.75×10^6	3.01	
"	$0.4\%Cl^-$	3.90×10^6	2.90	2.98
"	$0.4\%Cl^-$	3.70×10^6	3.06	
"	$1.0\%Cl^-$	4.00×10^6	2.83	3.30
"	$1.0\%Cl^-$	3.00×10^6	3.77	
OPC F + SLAG	None	5.00×10^6	2.26	2.39
"	None	4.50×10^6	2.51	
"	$0.4\%Cl^-$	3.30×10^6	3.43	3.60
"	$0.4\%Cl^-$	3.00×10^6	3.77	
"	$1.0\%Cl^-$	2.00×10^6	5.65	6.15
"	$1.0\%Cl^-$	1.70×10^6	6.65	

Table 5.1 continued

Cement	Additives	Rt Transfer Resistance Ωcm^2	I corr $nAcm^{-2}$	Average I corr Values $nAcm^{-2}$
OPC D	None	6.00×10^6	1.88	2.36
OPC D	None	4.00×10^6	2.83	
"	$0.4\%Cl^-$	5.20×10^6	2.17	2.28
"	$0.4\%Cl^-$	4.75×10^6	2.38	
"	$1.0\%Cl^-$	7.00×10^6	1.61	1.94
"	$1.0\%Cl^-$	5.00×10^6	2.26	
OPC D + PFA	None	6.40×10^6	1.77	1.54
"	None	8.70×10^6	1.30	
"	$0.4\%Cl^-$	3.80×10^6	2.97	2.97
"	$0.4\%Cl^-$	3.80×10^6	2.97	
"	$1.0\%Cl^-$	2.40×10^6	4.71	3.11
"	$1.0\%Cl^-$	7.50×10^6	1.51	

Ba and Bc = 0.052 V

(These Tafel constants were necessary when using the programme IMPED 5 as supplied for this section of work.)

Table 5.2 AC Impedance Measurements and Polarisation Resistance Measurements Results at Age 11 Weeks

Cement	Additives	Rt Transfer Resistance Ωcm^2	I corr $nAcm^{-2}$	Average I corr $nAcm^{-2}$	Rp Polarisation Resistance Ωcm^2	I corr $nAcm^{-2}$	Average I corr $nAcm^{-2}$
OPC F	None	3.90×10^6	2.90	2.69	1.55×10^6	7.29	5.91
"	None	4.55×10^6	2.48		2.50×10^6	4.52	
"	$0.4\%Cl^-$	3.90×10^6	2.90	2.72	6.40×10^6	1.77	5.64
"	$0.4\%Cl^-$	4.45×10^6	2.54		1.19×10^6	9.50	
"	$1.0\%Cl^-$	5.00×10^6	2.26	2.20	1.38×10^6	8.19	12.53
"	$1.0\%Cl^-$	5.30×10^6	2.13		6.70×10^5	16.87	
OPC F + SLAG	None	4.00×10^6	2.83	2.83	4.25×10^6	2.66	5.43
"	None	4.00×10^6	2.83		1.38×10^6	8.19	
"	$0.4\%Cl^-$	4.10×10^6	2.76	2.83	7.00×10^6	1.61	2.14
"	$0.4\%Cl^-$	3.90×10^6	2.90		4.25×10^6	2.66	
"	$1.0\%Cl^-$	$3/45 \times 10^6$	3.28	3.28	1.85×10^5	61.10	32.32
"	$1.0\%Cl^-$	3.45×10^6	3.28		3.20×10^6	3.53	
OPC D	None	8.00×10^6	1.41	1.53	3.50×10^6	3.23	5.09
"	None	6.85×10^6	1.65		1.63×10^6	6.94	

Table 5.2 continued

Cement	Additives	Rt Transfer Resistance Ωcm^2	I corr $nAcm^{-2}$	Average I corr $nAcm^{-2}$	Rp Polarisation Resistance Ωcm^2	I corr $nAcm^{-2}$	Average I corr $nAcm^{-2}$
OPC D	0.4%Cl^-	6.40×10^6	1.77	2.08	-	-	18.09
"	0.4%Cl^-	4.75×10^6	2.38		6.25×10^5	18.09	
"	1.0%Cl^-	6.40×10^6	1.77	1.96	1.49×10^5	75.87	75.87
"	1.0%Cl^-	5.25×10^6	2.15		-	-	
OPC D + PFA	None	4.30×10^6	2.63	1.90	6.50×10^6	1.74	3.79
"	None	9.70×10^6	1.17		1.94×10^6	5.83	
"	0.4%Cl^-	4.00×10^6	2.83	2.90	5.25×10^6	2.15	3.23
"	0.4%Cl^-	3.80×10^6	2.97		2.63×10^6	4.30	
"	1.0%Cl^-	3.20×10^6	3.53	2.78	1.07×10^6	10.56	25.40
"	1.0%Cl^-	5.60×10^6	2.02		2.81×10^5	40.23	

Ba and Bc = 0.052 V

(These Tafel constants were necessary when using the programme IMPED 5 as supplied for this section of work.)

5.3.2 Results obtained at Aston University from Programme of Work on Cements for which Pore Solution Data and Chloride ion Diffusion Data had been Obtained

Table 5.3 Polarisation Resistance Measurements on Specimens aged 6 weeks

Cement	Additives	Rp Polarisation Resistance Ωcm^2	I corr $nAcm^{-2}$	Average I corr $nAcm^{-2}$
OPC B	None	2.16×10^6	10.0	
"	None	2.60×10^6	8.3	8.87
"	None	2.60×10^6	8.3	
"	0.4%Cl^-	3.25×10^5	66.8	
"	0.4%Cl^-	1.24×10^5	175.0	130.13
"	0.4%Cl^-	1.45×10^5	148.6	
"	1.0%Cl^-	7.60×10^4	285.7	
"	1.0%Cl^-	2.06×10^5	105.5	173.87
"	1.0%Cl^-	1.66×10^5	130.4	
SRPC A	None	7.65×10^5	28.4	
"	None	1.86×10^5	116.6	51.50
"	None	2.36×10^6	9.2	
"	0.4%Cl^-	5.42×10^5	40.0	
"	0.4%Cl^-	3.77×10^4	575.7	233.07
"	0.4%Cl^-	2.60×10^5	83.5	

Table 5.3 continued

Cement	Additives	Rp Polarisation Resistance Ωcm^2	I corr nAcm^{-2}	Average I corr nAcm^{-2}
"	1.0%Cl^-	-	-	
"	1.0%Cl^-	1.25×10^5	173.1	216.10
"	1.0%Cl^-	8.38×10^4	259.1	
OPC A	None	5.11×10^5	42.4	
"	None	1.30×10^6	16.7	23.03
"	None	2.17×10^6	10.0	
"	0.4%Cl^-	3.19×10^5	68.0	
"	0.4%Cl^-	1.44×10^6	15.1	46.63
"	0.4%Cl^-	3.82×10^5	56.8	
"	1.0%Cl^-	1.08×10^5	200.9	
"	1.0%Cl^-	1.18×10^6	18.4	109.65
"	1.0%Cl^-	-	-	
OPCB + 30%PEA	None	2.36×10^6	9.2	
"	None	2.17×10^6	10.0	8.90
"	None	2.89×10^6	7.5	

Table 5.3 continued

Cement	Additives	Rp Polarisation Resistance Ωcm^2	I corr $nAcm^{-2}$	Average I corr $nAcm^{-2}$
OPCB + 30%PFA	0.4%Cl^-	1.86×10^6	16.7	30.62
"	0.4%Cl^-	3.25×10^5	66.8	
"	0.4%Cl^-	2.60×10^6	8.4	
"	1.0%Cl^-	2.89×10^5	75.1	50.10
"	1.0%Cl^-	3.61×10^5	60.1	
"	1.0%Cl^-	1.44×10^6	15.1	
OPCB + 65%BFS	None	2.60×10^6	8.4	10.32
"	None	1.44×10^6	15.1	
"	None	2.89×10^6	7.5	
"	0.4%Cl^-	2.36×10^6	9.2	40.93
"	0.4%Cl^-	2.60×10^5	83.5	
"	0.4%Cl^-	7.22×10^5	30.1	
"	1.0%Cl^-	7.22×10^5	30.1	138.87
"	1.0%Cl^-	1.44×10^6	15.1	
"	10.%Cl^-	5.85×10^4	371.4	

Ba and Bc = 0.1

5.4 Discussion of Results of Joint Programme of Work with The Building Research Establishment on Blended Cements

The linear polarisation results for specimens aged 11 weeks showed that there was no clear difference in the type of behaviour recorded for the four cements studied at Aston University. In all cases there was a definite indication of significant corrosion at the 1 % level of added chloride. At low levels of added chloride such as 0.4 %, in the majority of cases there did not seem to be a significant increase in the risk of corrosion. Figure 5.1 shows these trends in the bar chart form. Upon completion of the electrochemical measurements, the samples were broken open and rust staining showed agreement with the results obtained.

During AC impedance measurements it was found that large shifts in the rest potentials of the specimens were produced. These were of the order of several hundred millivolts. At first this was thought to be caused by the corrosion cell amplifier, which was subsequently replaced by a Thompson Mini Potentiostat, which was used as an amplifier. This appeared to reduce the problem but did not eliminate it completely.

The results from the AC impedance measurements did not show up the expected increase in I_{corr} with increased chloride levels and no sensible trend could be observed. In most cases there was little difference between the results obtained at

6 weeks and 11 weeks. Figure 5.2 shows the results obtained for the cements studied at Aston University by AC impedance.

When the electrochemical measurements had been completed the specimens were broken open, examined and photographed. Plates 5.1, 5.2 and 5.3 show examples of specimens at the three levels of chloride. The visual examination in this case did not correlate with practical results..

Several workers have made detailed studies of the AC impedance technique and given their views on its possible applications and abilities [88,89,90]
Previously other workers have assumed [40] that the AC impedance technique does not perturb the system under measurement because the alternating nature of the current does not produce transport phenomena. However, this may not be the case at lower frequencies and these are the more interesting for corrosion processes.

More recently Gonzalez et al [42] have carried out a detailed criticism of the technique.

The time constant for a sinusoidal perturbation applied to a corroding system is proportional to the charge transfer resistance R_T. In systems with very low corrosion rates it is therefore necessary to achieve frequencies in the range 10^{-3} Hz or lower to obtain kinetic information.

In this low frequency range the variation of the input signal is so slow that there is no guarantee that the E_{corr} remains unchanged during the measurement. In systems sensitive to substance transport phenomena it cannot be certain that no changes have taken place in the surrounding of the electrodes during the measurement and consequently E_{corr} may be changed significantly following the sinusoidal input signal.

The control by diffusion of the measurement of the corrosion rate does not necessarily mean a control by diffusion of the corrosion rate itself. As the system is disturbed it becomes a completely different system from that which we originally set out to study [42]. The control by diffusion makes calculation of the R_p value very difficult because graphical extrapolation to obtain the R_p value becomes practically impossible. In these cases it is more useful to use Bode plots (log Z versus log W) or mathematical deductions [91].

The rest potential graphs all indicated a tendency for the rest potentials to move toward more noble values with time (Fig 5.3). Final values were in the range -350mV SCE to -100mV SCE. This suggests that the surface condition of the specimens was mainly passive in all cases. The potentials obtained for the samples containing 1 % Cl^- however, were somewhat lower than those for the other samples, and therefore indicated a possibility of localised corrosion. There were no apparent differences between the four cements.

When the specimens were broken up on completion of the electrochemical work it was found that there was no apparent difference between electrodes exposed to the different cements.

However some of the specimens showed signs of crevice attack associated with the edges of the plastic tubing, used to mask the top and bottom of the steel electrodes. Together with the fact that shrinkage had seriously reduced the paste cover provided to the electrodes in a few cases, this may have had a significant effect on the results.

In future work every care should be taken to minimise the effects of problems such as crevice corrosion. One possibility is the application of a cement - SBR slurry to the steel surface, followed by an epoxy coating, before being surrounded by the bulk cement paste or concrete. Care should be taken in controlling the speed of setting to avoid shrinkage problems. It is also suggested that wherever possible specimens are kept immobile and if transportation is necessary then sufficient time is allowed for the specimens to stabilise before measurements are taken.

The results obtained by the Building Research Establishment were somewhat erratic and this was again possibly due to crevice corrosion and shrinkage of the cement paste during hydration. There was little agreement between the results obtained for OPC F and OPC F + slag, by the Building Research Establishment and by the author.

At the age 11 weeks the specimens manufactured by the BRE were brought to Aston University to enable Linear Polarisation measurements to be made. The corrosion current values obtained, were much higher than those given by the specimens manufactured at the University. This was possibly as a result of the journey, which may have upset the condition of the specimens.

5.5 Discussion of Results of Programme of Work on Cements for which Pore Solution Data and Chloride Ion Diffusion Data had been Obtained

Unfortunately results were taken from these specimens at only two ages. The relatively large number of specimens meant that measurement was quite time consuming and this came at a period when time was severely limited.

Measurements were taken at age 6 weeks and 12 weeks only.

Whilst the 6 week old specimens exhibited mainly reasonable trends, the 12 weeks old specimens were extremely erratic. Upon breaking open the specimens they were observed to have suffered quite severely from crevice corrosion at the epoxy masking/ steel interface. This is a common and severe hindrance to electrochemical investigations, and it is not unknown for major commercial programmes to have been aborted for this reason. Page and Treadaway [92] have pointed out the seriousness of this phenomenon.

Since the twelve week results would appear to be meaningless they have not been presented here and only the six week results have been considered.

Since there were no results taken between 0 and 6 weeks, and 6 and 12 weeks it is not possible to say when the problems of crevice corrosion became severe. However, bearing this in mind it is probably reasonable to tentatively accept the results of 6 weeks since they seem to exhibit sensible and expected trends. Figure 5.4 shows the average values of I_{corr} plotted as a bar chart.

In general increasing the level of added chloride increased the risk of corrosion taking place. The exception to this was SRPC A which had an I_{corr} value for 0.4%Cl^- higher than that for 1%Cl$^-$. The reason for this was probably one defective specimen which had an I corr value of 575.7 nAcm^{-2} whereas its replicates had values of 40.0 and 83.5 nAcm^{-2}. This was presumably as a result of crevice corrosion and gave an abnormally high average value for that set of specimens. Ignoring this result would give an average value of 61.7 nAcm^{-2} and this would fall into line with the trends observed for the other cements.

On the basis of the six week results there appeared to be a difference between the five cements.

OPC B with 30%PFA gave the best performance. In the other rankings based on pore solution analysis and diffusion characteristics at 25°C this cement also did reasonably well, coming in the middle and the top half of the ranking respectively.

Following this cement, pure OPC A and OPC B with 65% GGBFS were fairly evenly matched. I corr for OPC B with the slag was lower at 0%Cl$^-$ and 0.4%Cl$^-$ but was a little higher at the 1% level of added chloride. Although there seemed to be little to choose between these two cements possibly the slag cement should be placed above the pure OPC A since it was only at higher levels of chloride addition that its performance faultered. The slag cement also did well in the other two rankings, emerging as the best in both. OPC A seems to have remained consistently around the middle or lower half of the ranking of the five cements.

OPC B which performed quite well at the 0% level was considerably poorer at the 0.4%Cl and 1.0%Cl levels. This confirms its postion in the ranking based on diffusion coefficient values at 25°C but it did much better in the ranking based on pore solution analysis.

Finally the cement in which embedded steel seemed to be most at risk was the SRPC. This has consistently been the poorest cement throughout the study. In general the ranking obtained on the basis of the six week results seemed to agree well with the rankings obtained for the other criteria.

Table 5.4 shows the ranking of cements based on the electrochemical studies.

Table 5.4 Ranking of cements based on Electrochemical Performance

Ranking	Cements
Best ↕ Poorest	OPC B/30%PFA OPC B/65%GGBFS OPC A OPC B SRPC

5.6 Conclusions

On the basis of the linear polarisation resistance measurements there seems to be little difference between the four cements, with and without 5% blending additions. Increasing the level of added chloride would seem to increase the risk of corrosion. It would seem that the AC impedance technique, although it may be a valid technique for determining corrosion rates for some mediums, may not be particularly applicable to a material as complex as concrete and this is pointed out by Andrade's work [42]. It would certainly be unwise to rely purely on AC impedance data without any other source of information.

The five cements studied with a view to providing a rank order did seem to differ. Table 5.4 shows the ranking obtained.

The blended cements performed better than the pure OPC's with respect to corrosion risk from added chloride. The SRPC seemed to give poorer protection than the pure OPC's.

Again an increase in the level of added chloride generally increased the risk of corrosion.

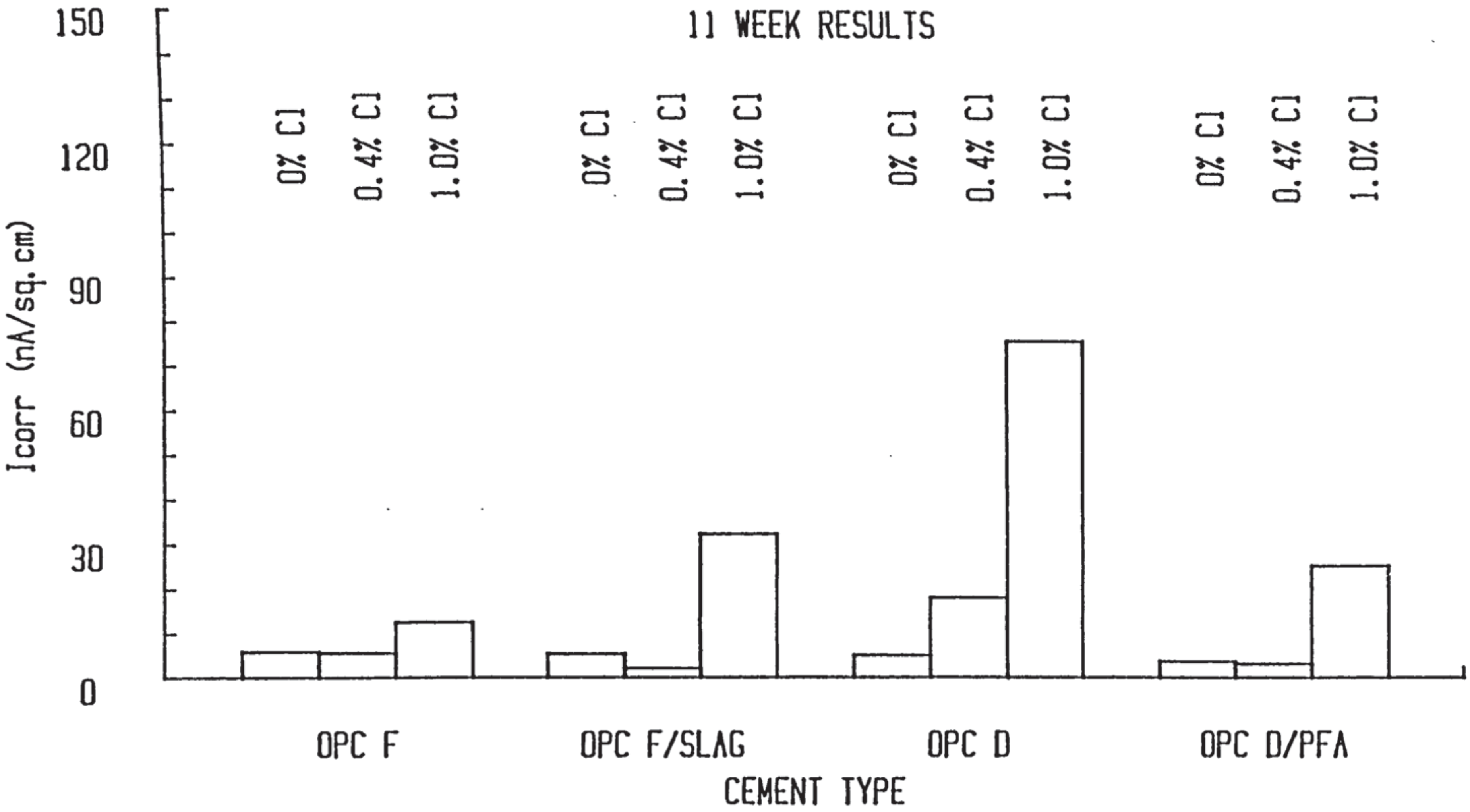


Fig 5.1 Linear polarisation measurement results for cements studied at Aston University

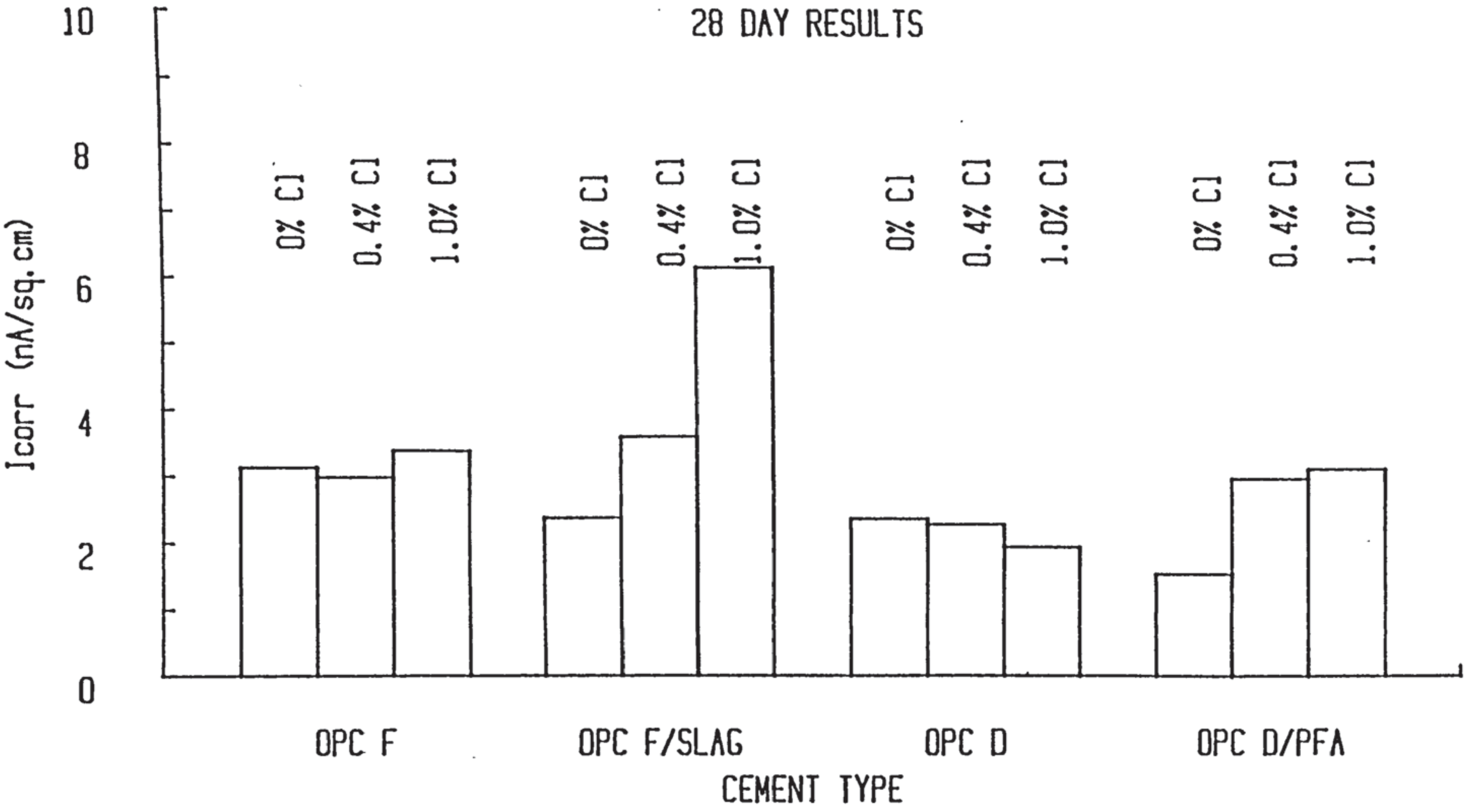


Fig 5.2.1 <u>28 day Ac impedance measurement results obtained at Aston University</u>

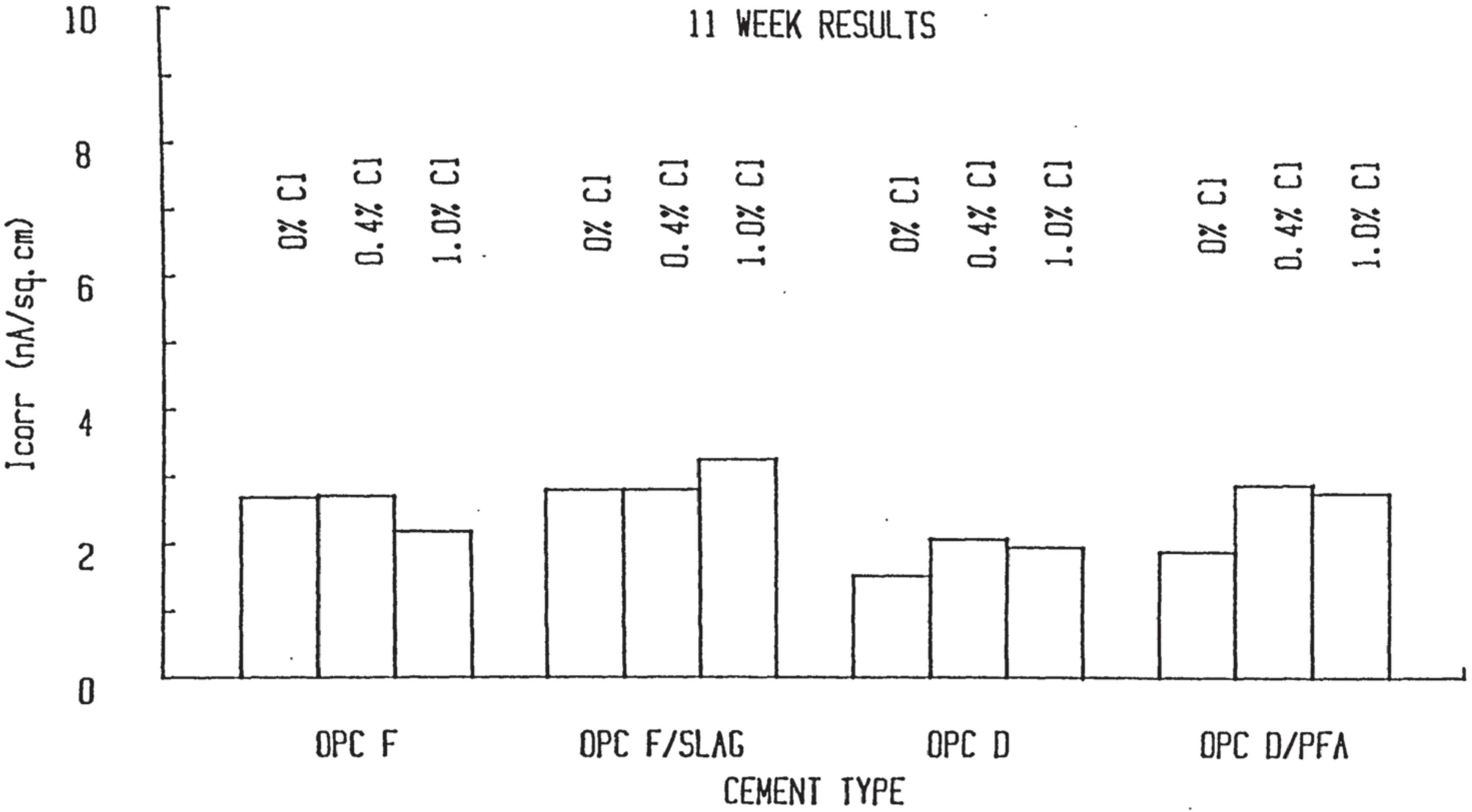


Fig 5.2.2 11 week Ac impedance measurements results obtained at Aston University

Plate 5.1 Specimen with 0% Chloride

Plate 5.2 Specimen with 0.4% Chloride

Plate 5.3 Specimen with 1.0% Chloride

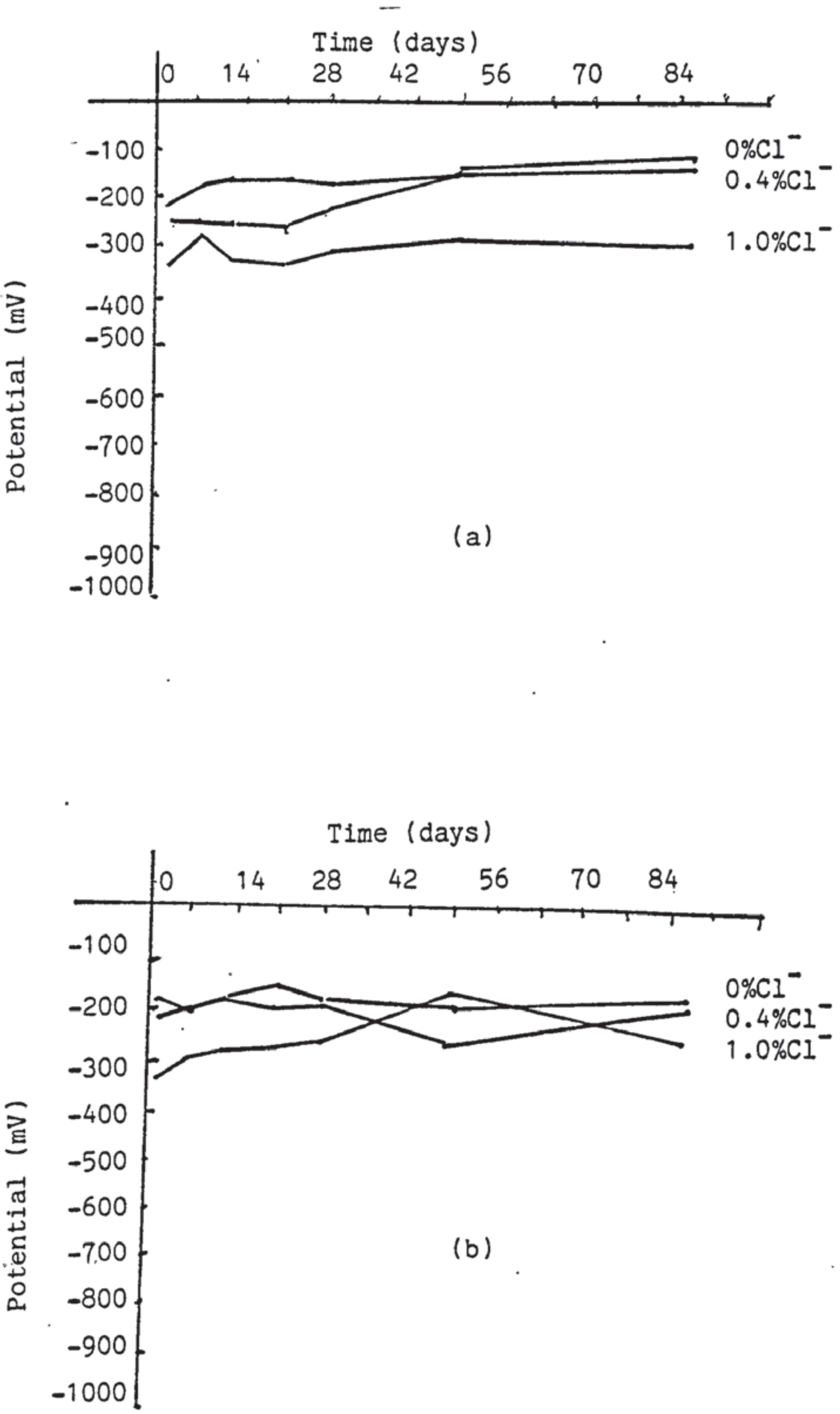
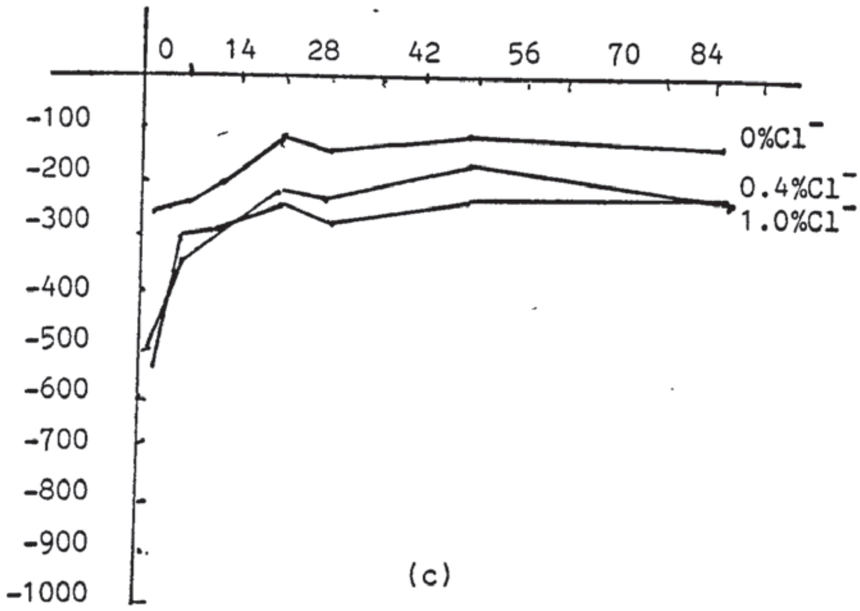


Fig 5.3 Rest potential/time curves for (a) OPC D and (b) OPC D + 5% PFA



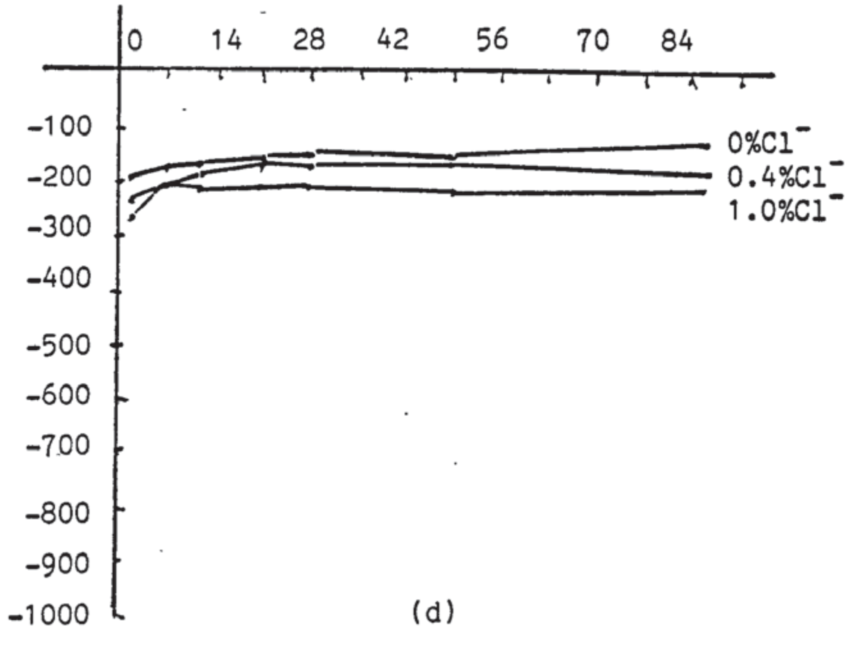


Fig 5.3 cont. Rest potential/time curves for (a) OPC F and (b) OPC F + 5% Slag

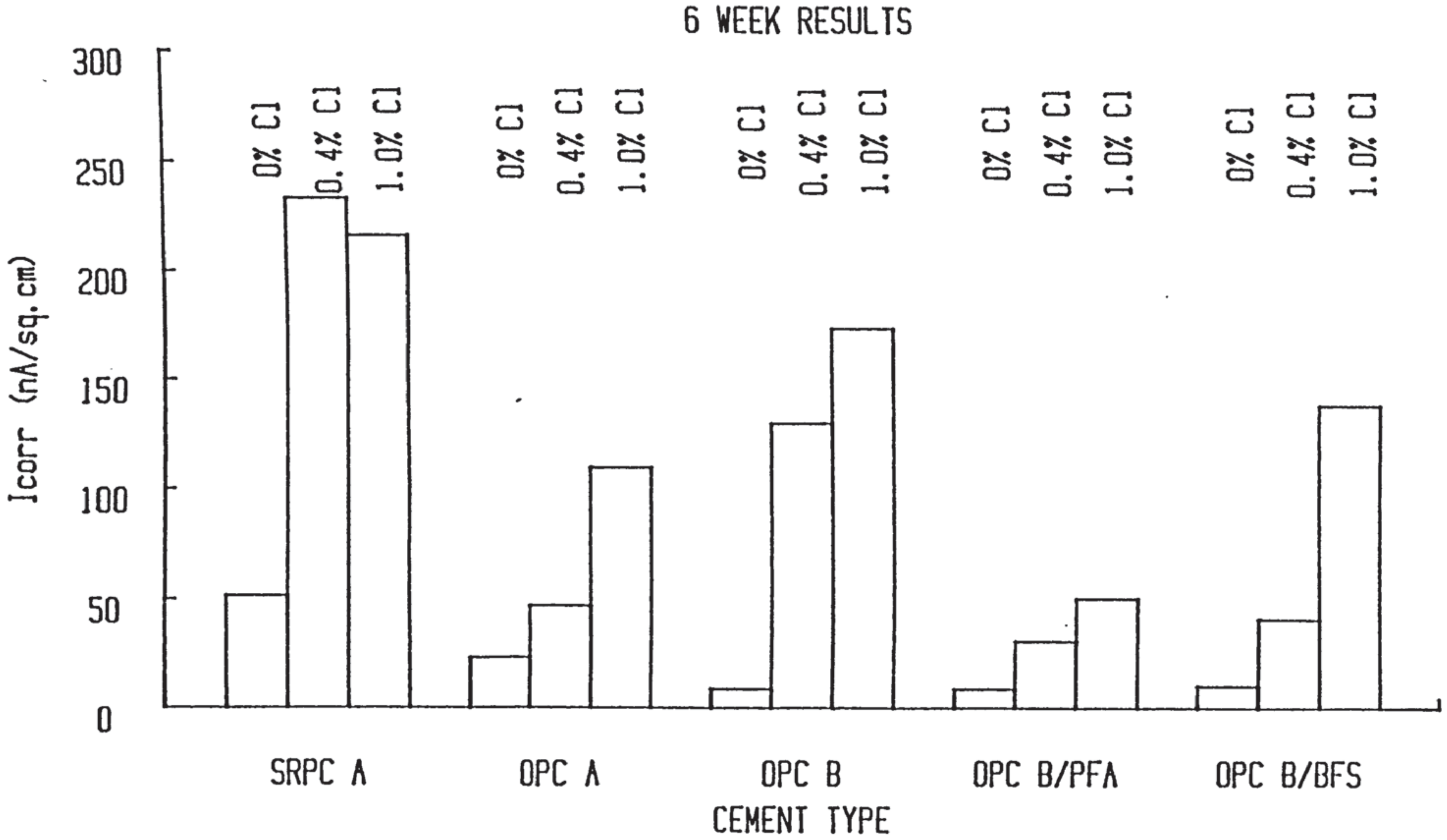


Fig 5.4 6 week linear polarisation measurement results on cements for which pore solution data and diffusion coefficients had been obtained

CHAPTER 6

PETROGRAPHIC EXAMINATION OF CONCRETE TAKEN FROM MIDDLE EASTERN BUILDINGS AND FORMATION OF AN EXPOSURE SITE PROGRAMME IN BAHRAIN

6.1 Introduction

The production of good quality durable concrete under conditions such as exist in the Middle East is beset with difficulties which are rarely, if at all, encountered in more favourable climates. Good practice must be adhered to rigidly and in certain cases special measures must be taken.

The very high temperatures in the Middle East can cause problems with incomplete hydration unless steps are taken to prevent the structure drying out. Some of the most common aggregates used in the Middle East are marine dredged aggregates, beach sands, wadi gravels etc., because of their availability and comparatively low cost.

However because of their origin they are inevitably highly contaminated with chlorides and other assorted marine debris such as shells etc. The aggregate should therefore be thoroughly washed before use and although this has not always been done in the past, the more reputable suppliers of aggregate do ensure that chloride levels are reduced as much as possible. This of course increases the cost however.

The reinforcement itself can become contaminated by airborne salts if it is left exposed on site prior to casting. It is therefore not difficult to see that there is no shortage of materials and environmental problems associated with the use of concrete in the Middle East quite apart from corrosion caused by the deliberate addition of aggressive agents such as chlorides.

This chapter is concerned with work which has been carried out on specimens from existing structures in the Middle East and also outlines a programme of work which has been set up to observe the performance of standardised concrete specimens over a number of years. These specimens have been exposed to both British and Middle Eastern climatic conditions. They have several levels of chloride and sulphate additions and have been subjected to differing curing regimes.

It is hoped that this field trial will help to identify the more important causes of failure of concrete structures in the Middle East.

6.2 Petrographic Studies

Specimens of concrete were obtained from existing structures in the Middle East by the Building Research Establishment [93]. These were taken from buildings which seemed to be in good condition and also from some which showed signs of deterioration. The ages of the buildings differed and samples were taken from various parts of the structure.

These samples were brought back to England by the Building Research Establishment for investigation. During a month long visit to the Building Research Establishment in Garston, thin sections were produced from these samples by the author and were subsequently examined at the Research Establishment (and also at the University) under their guidance [94]. Two further thin sections of laboratory produced concrete (one sample cured, the other uncured) were also made for the Building Research Establishment in Bahrain. The method used for the production of thin sections from concrete specimens is described in Chapter 2 and the appropriate American Standard [95].

6.3 Results of Petrographic Examination

6.3.1 Sample 1 - A Section of a roof column from a block of flats (From an area which showed no signs of deterioration)

This section was slightly too thick to allow a detailed examination of the cement paste, but it was possible to confirm that portland cement had been used. The cement paste was deeply carbonated confirming the results of the depth of carbonation test [96] performed on the bulk specimen before sectioning. This gave a carbonation depth of between 18 - 33mm.

The fine aggregate was a subangular to rounded quartz sand with occasional shell fragments.

The medium and coarse fractions were composed entirely of crushed microcystalline limestones of a rather variable nature. This building was comparatively young, less than ten years old.

6.3.2 Sample 2 - A section from an airport water tower

This was a badly cracked and very porous specimen. These facts could be determined without the need for microscopy Plate 6.1 shows the large amount of resin which has been admitted by the concrete due to its porosity.

It was a portland cement concrete with abundant cement clinker particles visible in the paste indicating a high cement content.

Very little portlandite (calcium hydroxide) was observed in the few uncarbonated areas of paste, suggesting a poor degree of hydration. This is a possibility further supported by the high porosity of the concrete and its subsequently deep carbonation.

The fine aggregates consisted principally of crushed limestone, angular to sub angular in form and variable in texture. These were indentified as micrites, microsparites and coarser sparry types [97].

Several pieces contained ill defined fossil remains but apart from these were devoid of any allochems. Some forms of this rock are highly porous and would probably have a high water demand.

The coarse fractions were obviously identical to the fines. Evidence of aggregate attrition during mixing of the concrete was present. Cracking in this specimen was general and some iron staining was observed, probably from reinforcement corrosion products.This structure was less than 10 years old.

6.3.3 Sample 3 - A section from an Air Conditioning Plant

This sample was identified as a portland cement concrete with large amounts of clinker visible in the paste, suggesting inadequate hydration. (Plate 6.2). Very little portlandite was found mainly due to advanced carbonation.

The fine aggregate was a mixture of crushed angular limestone and sand with shell fragments, probably marine dredged or taken from a beach.

The coarse aggregate consisted entirely of crushed limestone, ranging from micrite to spar and was almost without allochems. Some forms were very porous.

Cracking was present in this sample but no evidence of chemical attack was found. This structure was again of comparatively recent construction (less than 10 years

6.3.4 Sample 4 - A section of a roof column from the same block of flats as sample 1, but from an area which showed signs of deterioration

This was also a portland cement concrete with a high cement content (Plate 6.3) Carbonation had reached an advanced state which precluded any study of hydration in the section.

The fine aggregate consisted of sub angular to rounded quartz sand but with pieces of limestone and shell fragments also present.

The coarse fractions were composed of a compact, fossiliferous limestone of low porosity. This was identified as biospurite. The specimen seemed in some respects to be a better concrete with more compaction and slightly better aggregates. Nevertheless the specimen was cracked and there was evidence of corrosion of the reinforcement. Also observed was what may have been a positive result to the Poole-Thomas test [98] (a sulphate specific micro-stain) suggesting a sulphate problem.

6.3.5 Sample 5 - large specimen taken from the Northern block of a large building

This was a very porous totally carbonated portland cement concrete with an apparently average cement content.

The fine aggregate fractions were marine dredged, consisting of shell fragments, and carbonate grains with a little quartz sand.

The coarse fractions were composed of a crushed limestone with a fine microstalline texture and a few fossils. They may be defined as micrite or fossiliferous micrite, however sparry patches due to recrystallisation also occur. This building was much older than the other structures, being of the order of 25 years.

6.3.6 Sample 6 - large specimen from a Water Tower

This again was a rich portland cement concrete showing a considerable depth of carbonation. (Plate 6.4) Areas of uncarbonated paste were present in the section and examination of these showed that portlandite was not particularly abundant. Attrition of the limestone aggregates during mixing had loaded the paste with grains of calcite.

The fine aggregates consisted of crushed limestone with quartz sand, the limestone showing signs of wearing.

The coarse fraction was composed of crushed limestone which was very similar to those previously described. Cracking in the specimen was found to be present, penetrating the surface at right angles, but confined mainly to the surface region. These cracks were probably due to shrinkage.

6.3.7 Sample 7 - Small specimen of the Northern Block of a large building

This sample was of a portland cement concrete (Plate 6.5), which showed a considerable degree of carbonation as determined by the phenolphthalein spray test.

Unaffected areas of paste showed a moderate amount of clinker to be present and again also indicated that limestone attrition had taken place. Very little portlandite was visible.

The fine aggregate fraction was obviously of marine origin and consisted of shell fragments, a mainly quartz sand and carbonate grains. The coarse aggregate was again a porous crushed limestone similar to those previously described.

6.3.8 Sample 8 - Section of a ceiling from the block of flats as in sample 1

This was a portland cement concrete with an apparently fairly high cement content (Plates 6.6., 6.7). Evidence of a moderate degree of hydration was present. This was suggested by the fact that portlandite was fairly abundant. Some of the cement clinker grains also showed reaction rims.

Macroporosity in this sample seemed to be within normal limits, but carbonation had penetrated to a maximum depth of 14mm.

The fine aggregate fraction consisted predominantly of subangular to rounded quartz sand with carbonate sand and shell fragments also present. The fine fraction was therefore clearly of marine origin.

The coarse fractions were composed of crushed limestone which showed the usual range of micrites and microsparites, some of which were very porous.

Generally this was a better concrete but even so some cracking was present.

6.3.9 Sample 9 - Section of an official building

This was a specimen of rendered concrete. The render was well carbonated portland cement mortar, the sand content of which consisted of carbonate grains with quartz sand and shell fragments. The render was uncracked and fairly well bonded to the concrete, although linear voids existed in places along the interface.

The bulk concrete appeared to have a high cement content but was highly carbonated. This specimen was very poorly compacted and showed a very high pore volume, the voids being large and irregular and distributed throughout the sample.

The fine aggregates consisted of carbonate sand, many grains of which were superficially formed on sand grains and shell fragments, but pieces of shell and occasionally whole shells were present together with a little quartz sand.

Crushed limestone of a type very similar to those previously described was used for the medium and coarse fractions of the aggregate.

This was a very poor quality concrete of low compaction showing obvious signs of reinforcement corrosion.

6.3.10 Sample 10 - Section of an Airport AC plant

This was a portland cement concrete with many cement clinker grains visible in the paste (Plate 6.8), apparently indicating a high cement content. Many fine particles of calcite were present in the paste probably due to attrition of the limestone aggregate.

Carbonation of the specimen had penetrated variably to a maximum depth of about 12mm.

The fine aggregate fractions consisted of crushed limestone with a little quartz sand. The coarse and medium fractions were composed of crushed limestone similar to those previously described.

6.3.11 Uncured Laboratory Concrete

This was a portland cement concrete with a high cement content. Unhydrated cement clinker grains were abundant in the cement paste. In some areas near to the exterior surface, the paste consisted mostly of unhydrated clinker, bound loosely by very porous, totally carbonated hydrates. Many of these grains were 20µm or less in diameter.

Carbonation had penetrated rather variably to a maximum depth of about 20mm. Uncarbonated paste showed improved hydration but fairly low amounts of portlandite, forming small anhedral crystals, were present indicating that it had not reached a really adequate degree.

Aggregates used for the fines were a rounded quartz sand with occasional feldspars, rounded limestone fragments, oolite grains and abundant shell fragments. Obviously this was marine dredged. The mix was a standard composition used in Bahrain.

The coarse fractions were composed of a crushed limestone, mostly fine grained, but with inclusions of clear spar, mostly non-fossilferous. This was probably a micrite which has partially recrystallised.

6.3.12 Cured Laboratory Concrete

This specimen showed a much more advanced degree of hydration, than the uncured sample. The uncarbonated areas of paste contained moderate amounts of portlandite visible as anhedral crystals and also present at cement aggregate interfaces. The surface of this sample had a thin growth of calcite crystals indicating a water cure had been given to the concrete. Carbonation had progressed to a depth of about 10mm which is a fairly rapid rate considering the age of the specimen, which was only of the order of one year.

6.4 Conclusions

Although the cement contents of all these concretes were moderate to high, they failed to reach their full potential and were all of poor quality, a state reflected by their advanced carbonation (An average concrete carbonates 5-8mm in ten years[96]). The reasons for the low standard may be numerous. It is clear that in some samples poor compaction, and abnormally high porosity was a factor. It is also probable that poor hydration may be another contributing factor to the problem.

These problems may derive either from poor curing practice (sample 6 showed cracking possibly due to this) and/or from the very high water demand of the aggregates causing low workability and also aggravating the hydration problem.

Several of these concretes contained as the fine fraction, a carbonate sand consisting of spherical granules about 1mm in diamter with a concetrically layered structure and apparently identical to the oolites found in much earlier oolitic limestones. These granules were formed in the sea by the actions of currents rolling sand grains and shell fragments on a seabed of precipitated carbonate mud. These grains would have a high microporosity and a correspondingly large water demand. They may also have a high chloride content. The coarse aggregates were all crushed limestones and were also soft and porous. Attrition during mixing was very evident in several specimens, another factor which could affect workability. Although described as variable there were certain similarities which indicate that these limestones could have originated from the same "suite" of rocks.

The softness of these aggregates may be something of a problem, but if saturated before use and with mixing times kept to a minimum it should be possible to produce more acceptable concretes.

Climate may also contribute to the overall problem and special precautions during the curing period may be necessary. The role of curing is exemplified in samples 11 and 12.

The uncured laboratory specimen would appear to be poor concrete and this would seem to be mainly due to poor hydration. This is indicated by the abundance of unhydrated cement clinker grains. Incomplete hydration had also left the concrete very porous and allowed carbonation to proceed to an unacceptable level.

The dense packing of unhydrated cement clinker grains at the exposed surface of the specimen was probably due to segregation. Bleeding probably occurred (this is essentially a sedimentation phenomenon, the solids settling in the plastic mass [99]) bringing the water to the surface of the specimen. Here it would dry very quickly leaving the unhydrated clinker behind.

Many of the clinker grains are calcium disilicate C_2S because calcium trisilicate C_3S hydrates more rapidly [100] and disappears.

The cured laboratory specimen although rather porous and carbonated by UK standards seemed to be a better concrete. This was indicated by the greater amount of portlandite present. The study of the size, distribution and abundance of portlandite is considered by many workers to be a pointer to hydration, water content, cure etc. [101,102]

In most sections much C_2S was observed in the unhydrated cement clinker which may of course be due to preferential hydration of C_3S.

6.5 The Use of Bahrainian Aggregates in Reinforced Concrete Exposure Programme Specimens

As previously stated most of the specimens which have just been discussed were taken from existing structures. As a result of this there was no recorded history of the mixes used or the conditions under which the concrete was cast. It was decided therefore that a controlled exposure experiment in the Middle East was needed. This was to utilise specimens of known mix composition and curing history with one another.

A joint unvestigation was therefore proposed between the Building research Establishment, the Ministry of Works, Power and Water, Public Works - Affairs, Bahrain and Aston University. This investigation is intended to study the corrosion of reinforcement in typical 'Middle East' and 'Middle-East-Type' concrete. That is to say that concrete will be manufactured in the Middle East and also in Britain to the specifications laid down by the Bahrainian authorities.

The current proposals relate to the production of reinforced concrete prisms using Bahrainian aggregates. Weight-loss bars were used as reinforcement i.e. the weight of the reinforcing bar was measured accurately before being placed so as to be able to determine the amount of corrosion at the end of the experiment.

The prisms were subjected to progressive levels of contamination with chlorides and sulphates and extremes of curing practice.

Work which has been carried out at Aston University and is described in the preceeding chapters has helped to identify the important parameters of the exposure experiment.

Matched specimens were to be cast simultaneously in the UK and Bahrain and locally subjected to good and bad curing practice. At the present time only the UK specimens have been manufactured. There was then intended to be a reciprocal transfer of specimens for exposure at sites in the UK and Bahrain.

As matched UK-cast and Bahrain-cast specimens are recovered, the condition of the reinforcement will be compared and an attempt will be made to relate any differences found to climatic differences (ambient temperature, relative humidity, airborne salts) between the UK and Bahrain.

Because of the nature of an exposure programme such as this, the results will not be available for some years, and certainly not within the timespan of this research project.

However, the author's part in this programme has been to advise on the design of the experiment using knowledge gained from the research already carried out. This included suggesting the type and levels of contamination by salts which were considered to be of interest.

The author was also an active participant in the preparation and manufacture of the specimens.

6.6 Specimen Production

Prisms were cast to the standard Building Research Station format (100x100x300mm) so that it will be possible to compare results from these specimens with data obtained from earlier Building Research Station tests. These earlier tests used good quality UK aggregates.

Small beams were also produced (100x100x500mm) and these are to be broken in regular increments at regular intervals to follow carbonation changes. This will supplement other carbonation studies already in progress.

The specimens were produced at the Building Research Establishment Civil Engineering Laboratories, Cardington. The Bahranian aggregates and cement were on site at the laboratories. The aggregates were stored in sealed drums and underwent a washing and draining process, prior to use, to reduce chloride contamination to an acceptable background level. Prior to use the aggregates were also analysed by the Building Research Establishment for chloride, sulphate and moisture content, so as to check background levels and provide batching information.

It was also necessary to seive the largest size aggregate available so as to separate the 10mm to 15mm fraction.

80 prisms (100x100x300mm)
16 beams (100x100x500mm)
8 cubes (100x100x100mm)

The specimens were demoulded after 24 hours at which point half the specimens were exposed without curing precautions and the other half were cured under water for 28 days. Four different mixes were made over a period of two days. At 28 days the cube strengths were to be found. The specimens were then to be labelled and packed for despatch to Bahrain.

6.7 The Concrete Mixes

The prism specimens were reinforced with Tor bar for weight loss tests. This was prepared in advance by the Building Research Station, and mounted in plastic spacers, so as to hold the bar at predetermined depths of cover, when placed in the concrete. (Fig 6.1)

The bar was kept dry in contact with silica gel until needed.

The concrete used was based on a mix used in Bahrain known as "Haji's 10mm Mix", the composition of which is:-

Cement	1 part dry weight
Sand (Zone Z,5mm down)	2.5 parts dry weight
Aggregate (5-10mm)	3.5 parts dry weight
Coarse aggregate (10-15mm)	0.25 parts dry weight

Pozzolith 322N, which is a water reducing agent was added to the mix, to reduce the water demand.

The chloride contamination was introduced into the mix as anhydrous sodium chloride. The sulphate contamination was in the form of anhydrous sodium sulphate. These were contaminating agents used by the author in his previous work. As previouslystated four mixes were produced and these were as follows:-

Mix 1 - This mix contained no deliberate additions. The washing procedure ensured that the chloride level was less than 0.4%Cl^- by weight of cement in the final concrete.

Mix 2 - This mix contained a low level of deliberate chloride contamination. Sodium chloride was added to the mix such that the chloride level was 0.4%Cl^- by weight of cement in the final concrete.

Mix 3 - This mix contained a high level of deliberate chloride contamination. Sodium chloride was added such that the chloride level was 1.0%cl^- by weight of cement in the final concrete.

Mix 4 - This mix contained a low level of deliberate chloride contamination in conjunction with a high level of deliberate sulphate contamination. Sodium chloride was added to produce a chloride level of 0.4%Cl^- by weight of cement in the final concrete. Sodium sulphate was added so as to produce a level of 1.5%SO_3 by weight of cement in the final concrete.

6.8 Concluding Summary

It would appear that Middle Eastern concrete produced on site and exposed in service to Bahrainian climatic conditions is of a rather poor quality. Certainly this is the case with the samples of Middle Eastern concrete which the author has studied. Whether this is due solely to the climatic conditions under which the concrete is cast, or whether, the in-service conditions, materials and general site concreting practice play a role, is impossible to say at the present time. However the exposure site programme, which uses laboratory concrete, produced under standardised conditions should indicate whether any, or a combination of these factors help to produce a poorer quality material.

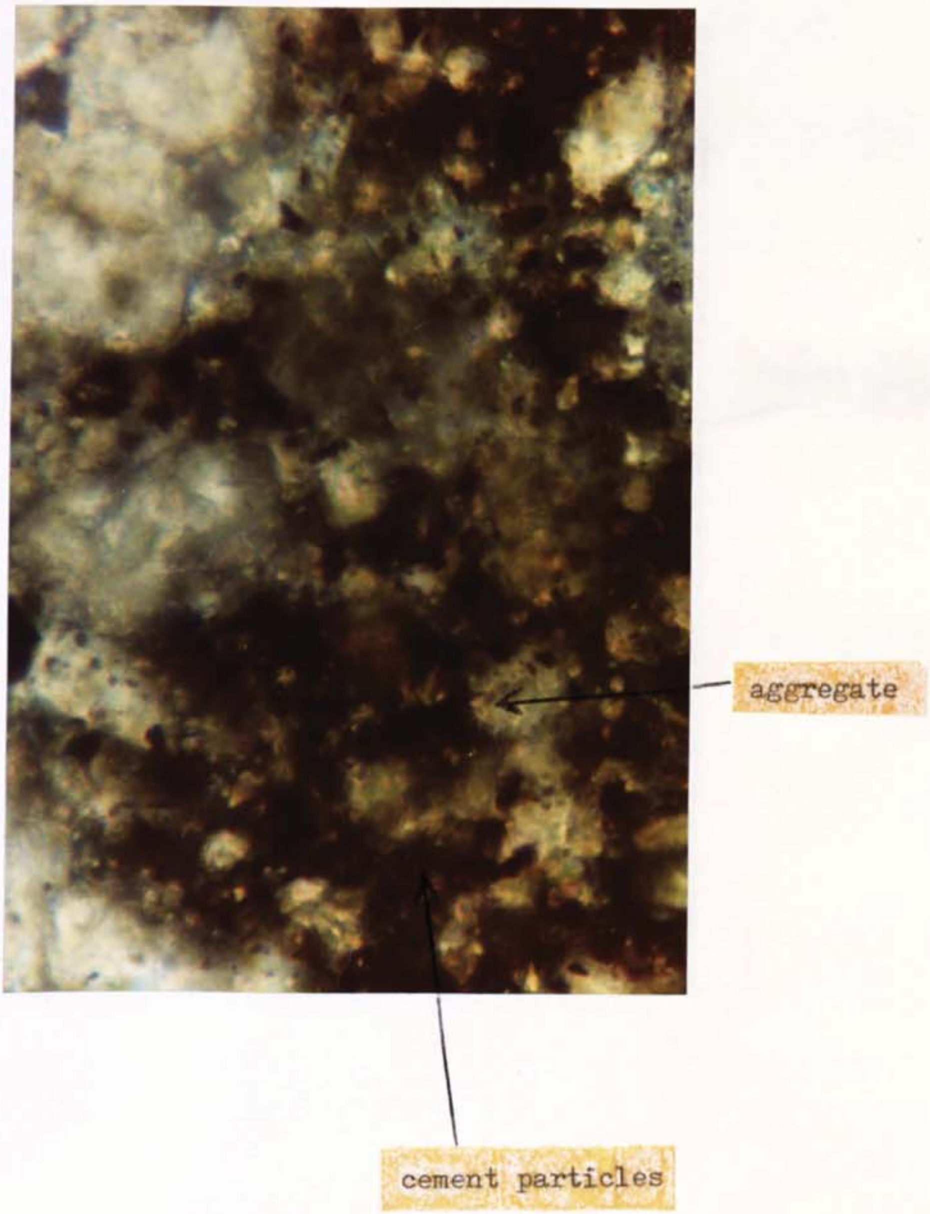


Plate 6.1 Section from an airport water tower

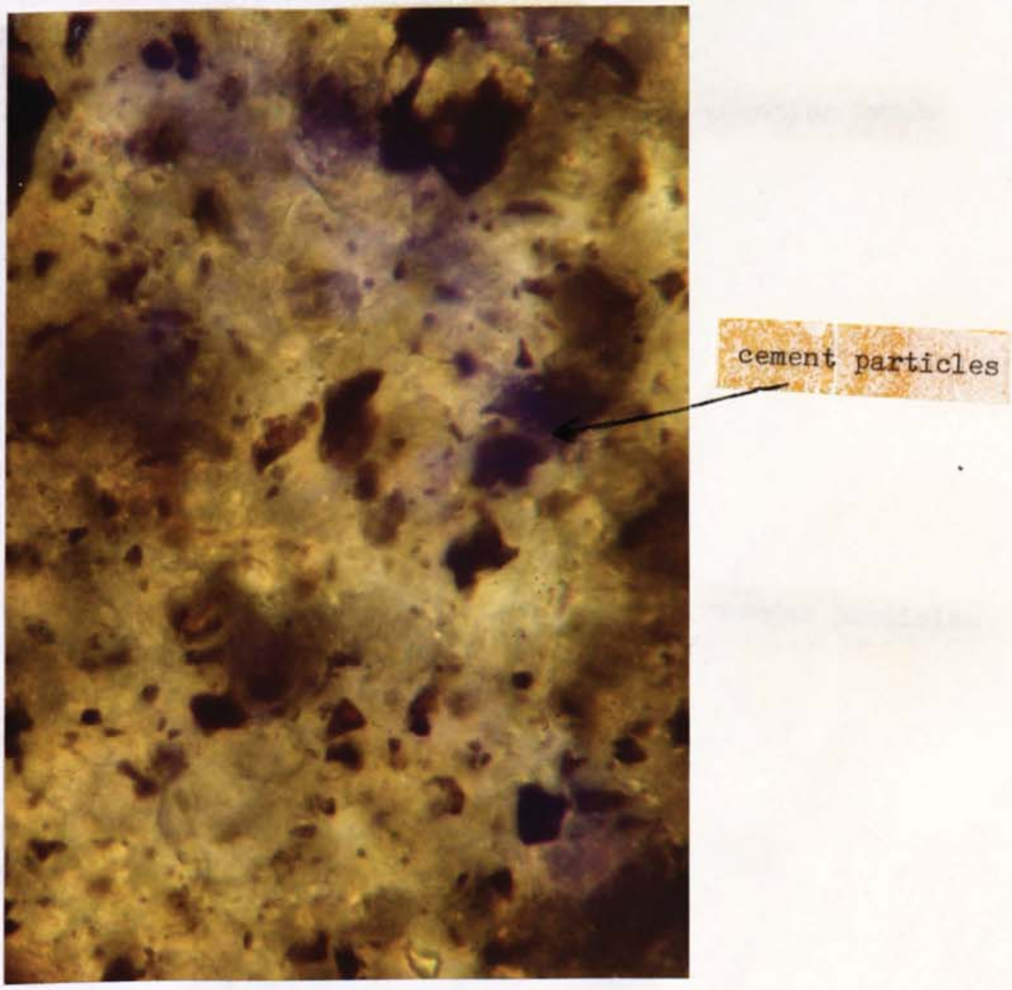


Plate 6.2 Section from an Air Conditioning Plant

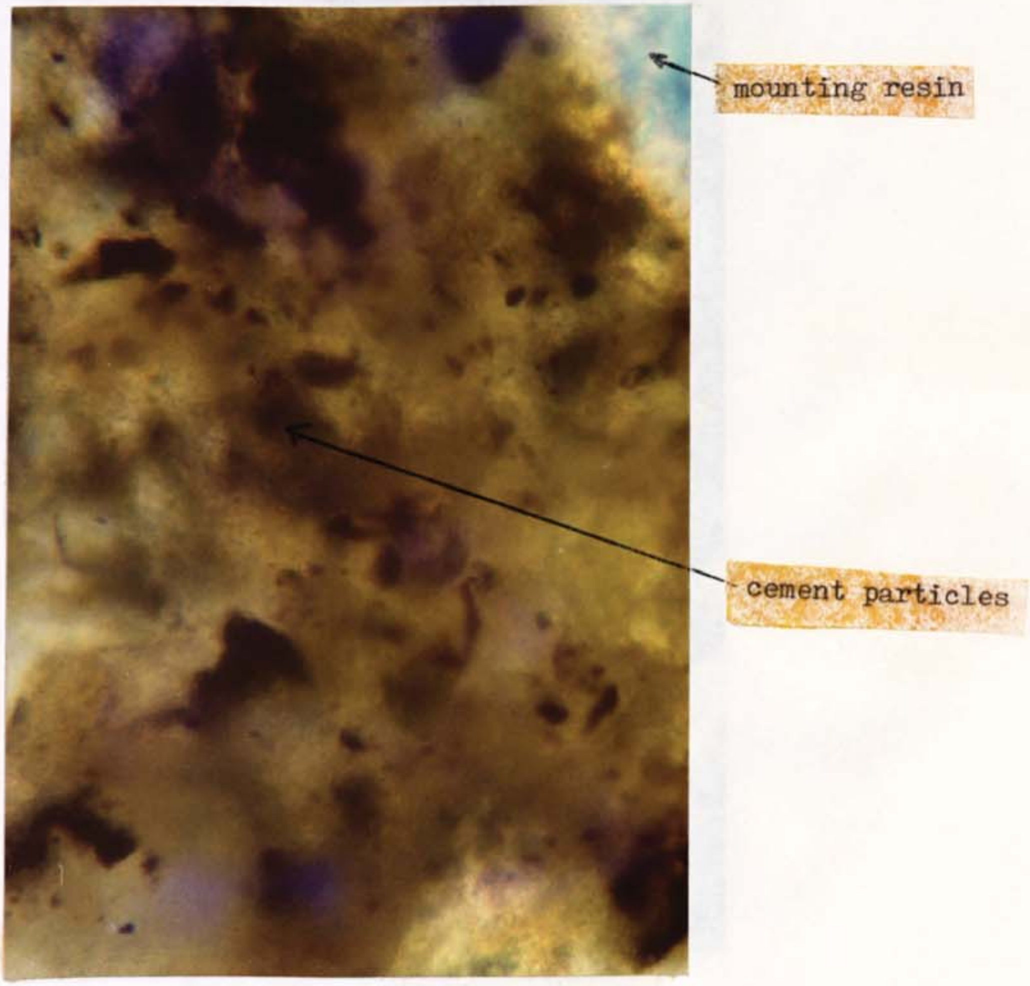


Plate 6.3 Section of a roof column from a block of flats (section from area which showed signs of deterioration)

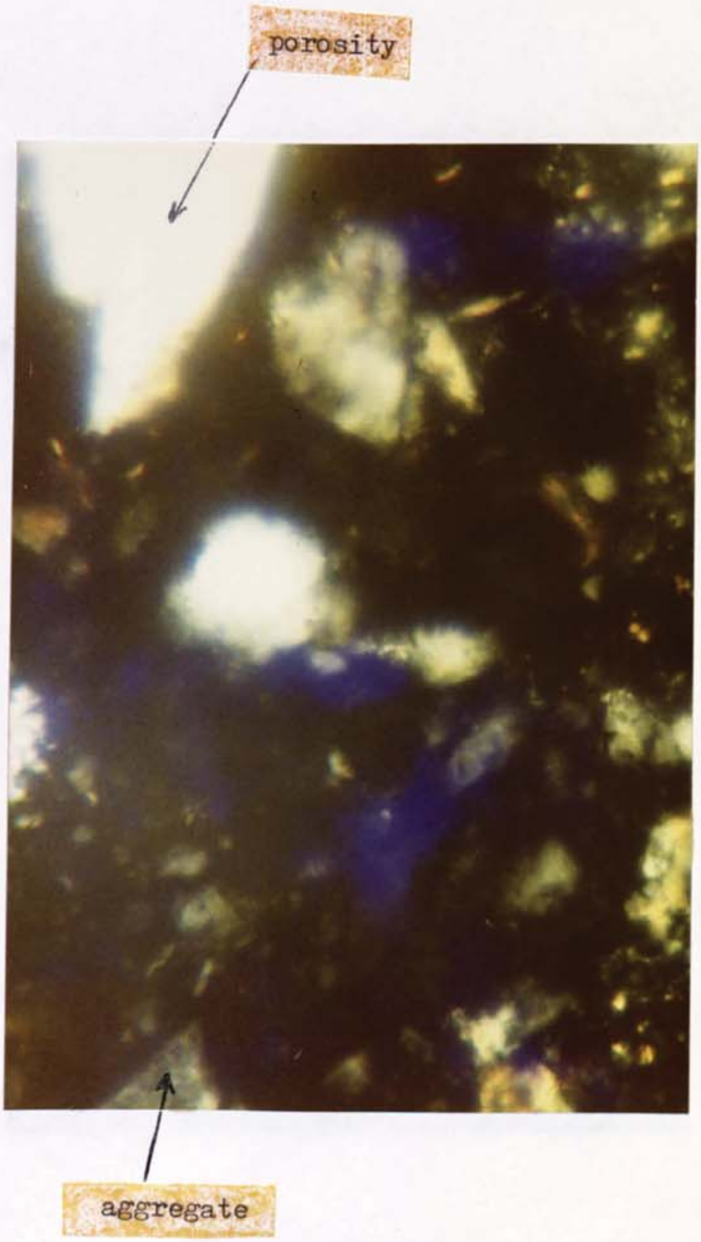


Plate 6.4 Large specimen from a water tower

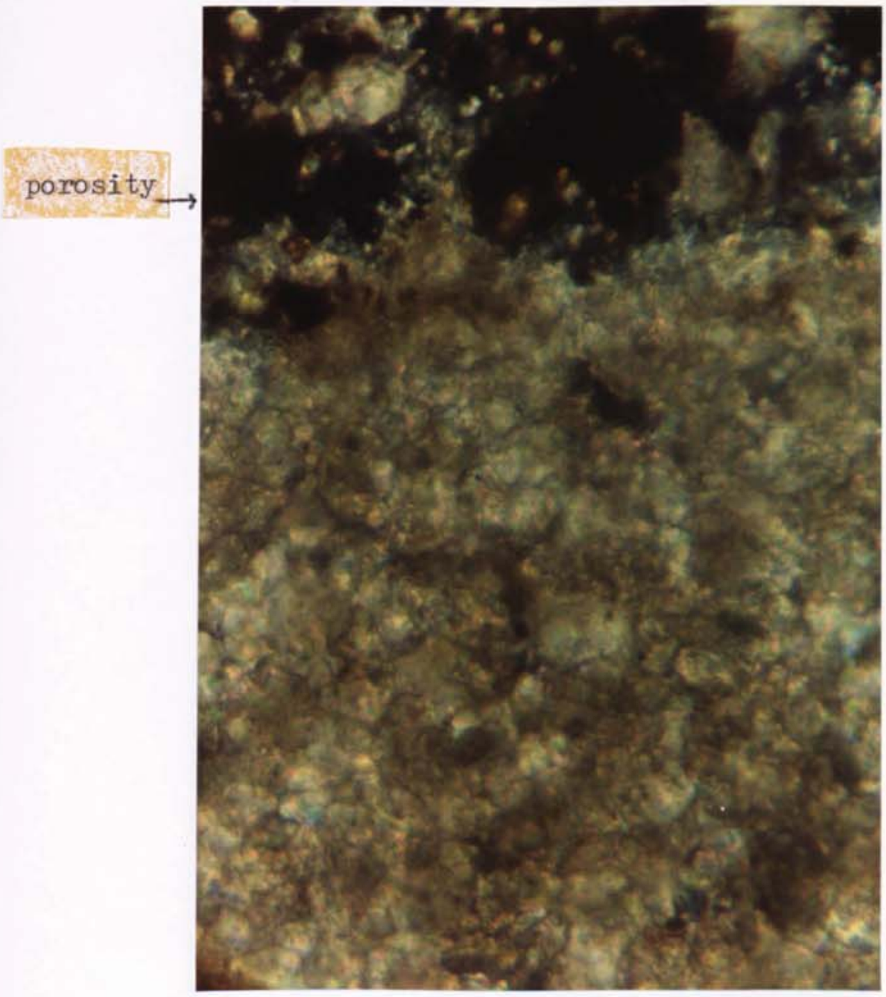


Plate 6.5 Small specimen from the Northern block of a large building

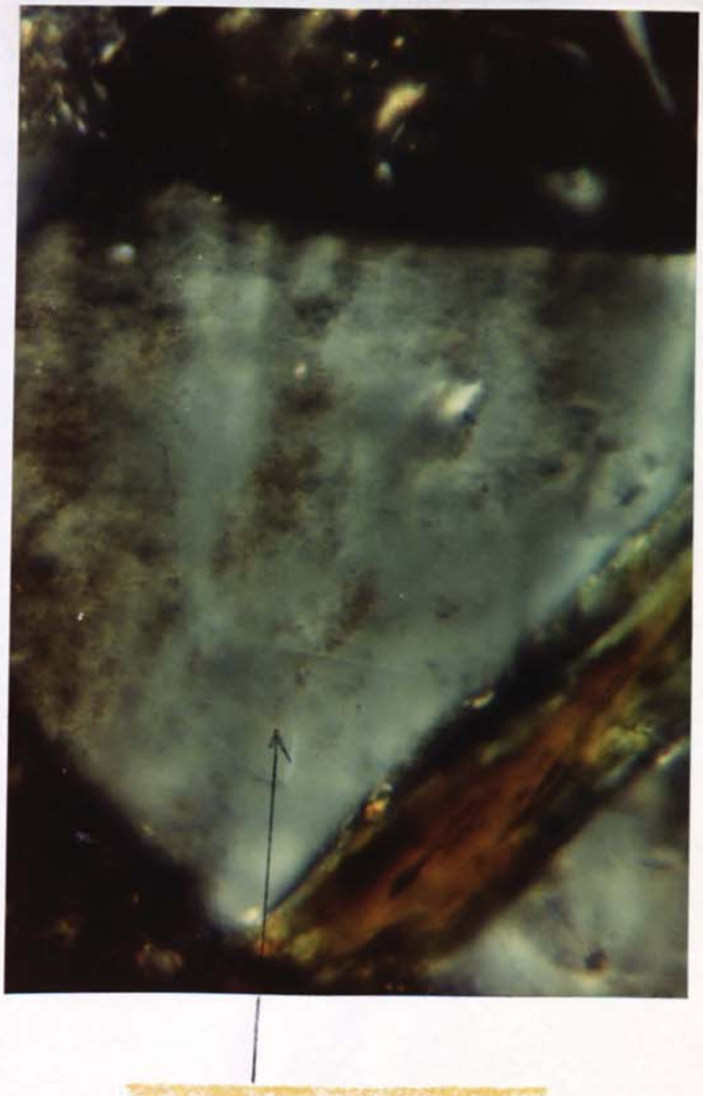


Plate 6.6 Section of a ceiling from a block of flats

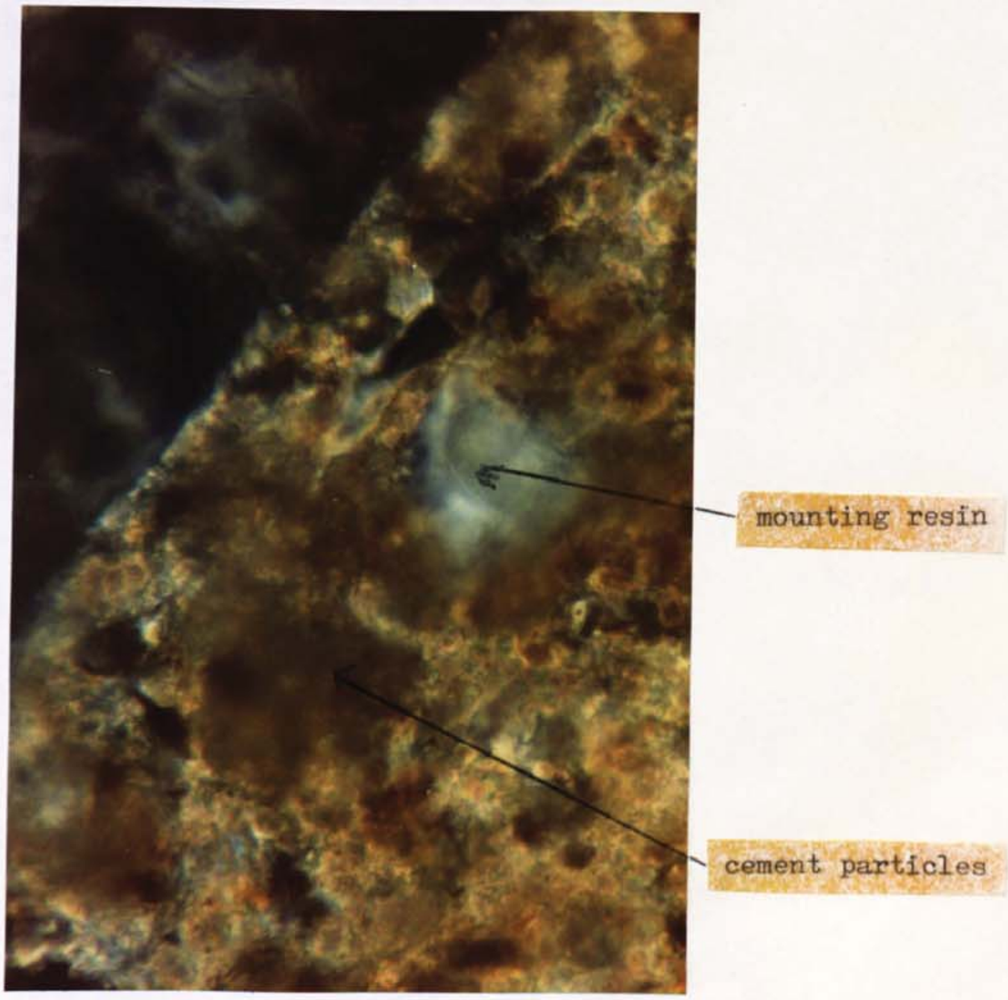


Plate 6.7 Section of a ceiling from a block of flats

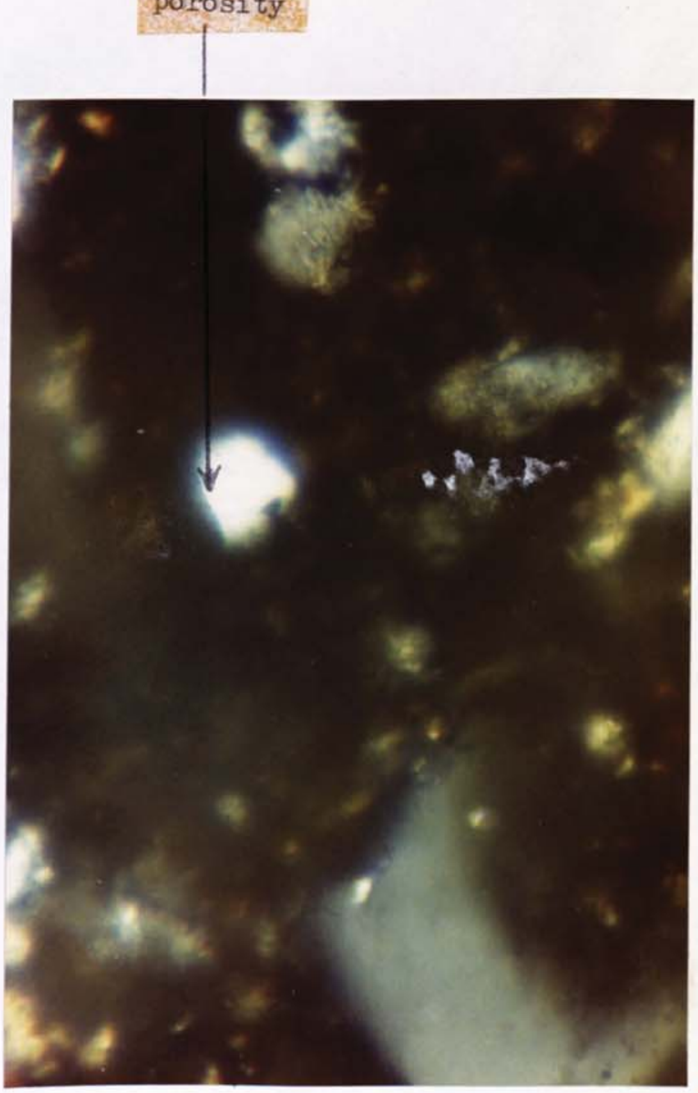


Plate 6.8 Section of an airport Air Conditioning Plant

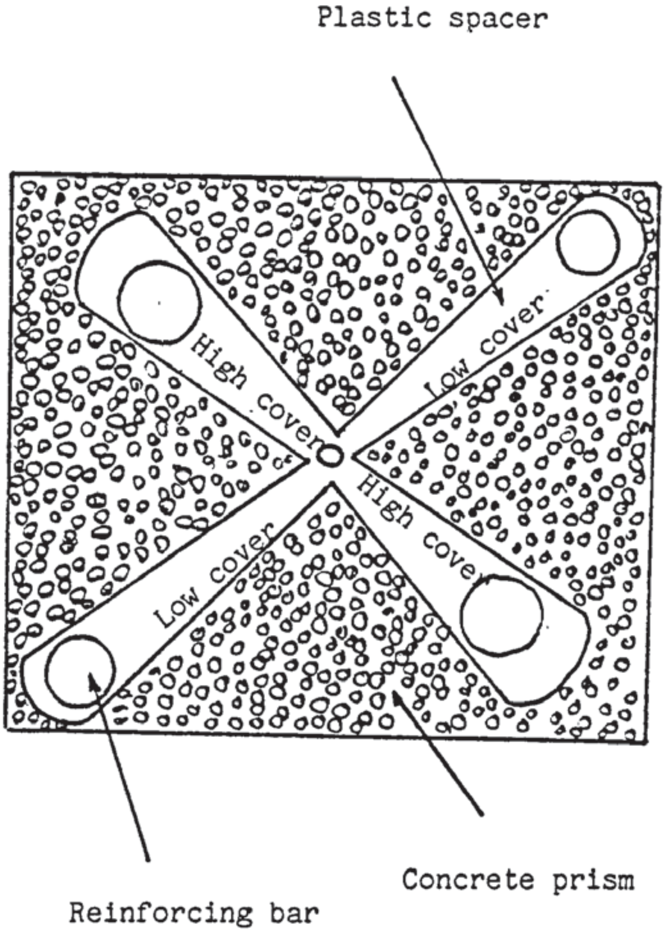


Fig 6.1 End section of concrete prism showing how one specimen provides two depths of cover for the steel reinforcement

CHAPTER 7

GENERAL CONCLUSIONS AND RECOMMENDATIONS FOR FURTHER WORK

7.1 General Conclusions

An attempt has been made to study some of the major factors which affect the corrosion of steel reinforcement, embedded within a cementitious matrix.

An attempt has also been made to evaluate the performance of several cements and produce a comparison between them.

It has been shown that different cements, particularl different types of cements (i.e. modified Portland cements) do exhibit varying levels of suitability for use in potentially aggressive environments, and in conjunction with potentially aggressive mix contaminants. From this study a ranking of the cements can be produced and this will be discussed further.

The work concerned with the expression of pore solution from hardened cement pastes yielded valuable information. It was found that the pH of the pore solution was high as had always been believed, but more importantly it was found that typical values were even higher than previously believed. Values well in excess of pH 13 and sometimes even 14 were observed. Solution expressed from cement pastes which had a low water-cement ratio, generally had a higher pH value than that of pastes with a higher water-cement ratio. Presumably this was due to the fact that adding increased levels of water to the cement initially dilutes the alkali hydroxide solutions produced during hydration.

Increasing the level of added chloride resulted in a progressive increase in pH value of the solution. The water-cement ratio of the cement paste, was again confirmed as being of importance when it was found that at the 3% level of added chloride ion the pH was higher for a 0.4 water cement ratio specimen than for a 0.6 water cement ratio specimen. The value was well in excess of 14 for the 0.4w/c specimen and close to 14 for the 0.6w/c specimen. The pH increased due to hydroxyl ions entering the solution to balance the anions removed in the form of insoluble complex salts.

As would be reasonably expected, increasing the level of added chloride to the cement mix resulted in a higher concentration of free chloride found in the expressed pore solution.

The type of cement (eg OPC, SRPC) and the source of cement had an influence on the character of the pore solution.

A low C_3A cement such as an SRPC (C_3A content 1.9%) was found to have a potentially more aggressive pore solution than a typical OPC (where C_3A content could be as high as 14.3%) The solution of the SRPC had a high concentration of free chloride coupled with a low hydroxyl ion concentration. This was probably due to its limited ability to form Friedel's salt ($3CaOAl_2O_3CaCl_2$ $10H_2O$).

A variation exists between different types of OPC as well. An OPC with a lower C_3A content had a more aggressive pore solution than an OPC with almost double the C_3A content. Again this is probably due to chloride complexing ability.

Generally the addition of blending agents such as PFA and GGBFS to an OPC leads to a slight reduction in the alkalinity of the pore solution, (when the levels of addition are 30% and 65% respectively). However greater chloride complexing ability is obtained at least in the cases examined in the present research. When these blending agents are added at a level of 5% there is virtually no reduction in the level of alkalinity but the greater chloride complexing ability is retained.

The presence of sulphates in combination with chlorides produces a pore solution with a greater amount of free chloride and a higher pH. The pH is increased because of hydroxyl ions entering the solution to balance the loss of anions which form complex salts. The chloride concentration increases because there is a tendency for sulphate ions to react preferentially with the C_3A phase.

It would therefore seem unwise to use a cement of low C_3A content in environments where both chlorides and sulphates will be present in combination. This is particularly true of the Middle East.

If the ratio of free chloride ion concentration $[Cl^-]$ to hydroxyl ion concentration $[OH^-]$ is taken as a measure of the aggressive nature of the pore solution, then a ranking of typical cements can be produced. This ranking was based on the potential vulnerability of the steel reinforcement to the aggressiveness of the pore solution alone and not taking any other factors into account. For the five cements studied with a particular view to this aim, table 7.1 shows their relative performance.

Table 7.1 Ranking of Cements Based on Pore Solution Character

Ranking	Ratio of [Cl⁻]/[OH⁻]
Best	OPC B/65%GGBFS
↑	OPC B
	OPC B/30% PFA
↓	OPC A
Poorest	SRPC

Results from the diffusion studies showed that the reinforcement in a cement matrix which has a more aggressive pore solution need not necessarily be at a greater risk from corrosion. If the cement matrix has a low coefficient of diffusion then this means that the progress of the chloride ions through the matrix and hence towards the reinforcement is impeded. This is shown by the example of OPC F which had a D value of $1.83 \times 10^{-8} cm^2 s^{-1}$ compared with values of $3.43 \times 10^{-8} cm^2 s^{-1}$ and $3.14 \times 10^{-8} cm^2 s^{-1}$ (all at 25°C) for OPC D and A respectively. Therefore this OPC is theoretically almost twice as effective as the other two OPCs at retarding the progress of chloride ions through the matrix. This may make it not inferior to the other two cements even though it has a lower chloride binding capacity.

Again a difference in properties was found between different types of cements. The SRPC at 25°C had a much higher diffusion coefficient (9.38 x 10^{-8} $cm^2 s^{-1}$) than a typical OPC making it seem unsuitable once again for use in environments where chlorides are present.

The addition of PFA and GGBFS to an OPC at the 5% level brings only a small increase in diffusion coefficient value. However when added at the 30% level and 65% level there is a large reduction in the diffusion coefficient value.

The addition of microsilica at the 10% level also seems advantageous from the point of view of diffusion kinetics since this produced a lower value for D than the corresponding pure OPC.

Where studies were carried out on cements at several water cement ratios it was found that the diffusion coefficient increased with increasing w/c ratio. This presumably is because more unsegmented pores are present at higher water cement ratios.

As far as ranking the five studied cements is concerned, Table 7.2 shows their relative performance if we concentrate solely on their diffusion coefficient values for chloride at 25°C. The values obtained for D_{Cl^-} as shown in Table 7.2 (with the exception of OPC A) were obtained by Page, Short and El Tarras [19].

Table 7.2. Ranking of Cements Based on Chloride Diffusion Coefficients

Ranking	D for Cl^- at 25°C
Best	OPC B/65% GGBFS
	OPC B/30% PFA
	OPC A
	OPC B
Poorest	SRPC

It can be seen from table 7.2. that best and worst cements have not changed from those identified on the basis of their pore solutions. OPC A shows some improvement as does the OPC with 30% PFA, whilst OPC B loses a considerable amount of its attractiveness for use in chloride containing environments.

Despite the limitations associated with the corrosion rate measurements, if the six week averages from triplicate specimens are obtained then the ranking of the five cements based on these figures is reasonable. The ranking compares quite favourably with the rankings based on the previous criteria. Table 7.3 shows the relative performance of the five cements based solely on their corrosion rate performance.

Table 7.3 Ranking of Cements Based on Average Corrosion Rates for 0.4% Cl^- level

Ranking	Average Corrosion Rate
Best	OPC B/30% PFA
	OPC B/65% GGBFS
	OPC A
	OPC B
Poorest	SRPC

The effect of increasing the level of added chloride is to increase the risk of corrosion (the risk being greatly increased at the 1% level of chloride).

The AC impedance technique does not appear to be an ideal method for determining corrosion rates in such a system as concrete, although it may be useful for determining some of the parameters of the corrosion process such as the rate controlling mechanism, the capacitance of the system and the diffusion coefficients. The better technique would seem to be linear polarisation, although this needs to be carried out with care. It has become clear that factors such as sweep rate are of great importance.

If we take the three criteria for ranking into account it would appear that the SRPC offers poorer protection than the other cements. The cements containing GGBFS or PFA are at least as effective as the typical OPC's in their ability to protect reinforcement from corrosion caused by chloride. The final exposure programme which is now in progress will provide field data which can be used to assess the validity of the rankings.

The results from the petrographic studies showed the importance of the environment in which the concrete is cast. Many of the samples from the Middle East showed very incomplete hydration, probably due to evaporation of water from the structure before hydration could be completed. The problem is probably partly due to the high water demand of some Middle Eastern aggregates. One of the consequences is that this produces a very porous concrete which does not give the necessary density of cover to guard against carbonation.

In conclusion, it seems reasonable to assess the relative performance of different cements using the criteria of, pore solution chemistry, diffusion kinetics and electrochemical monitoring. It is now necessary to wait for the results of the field study trials to provide final confirmation.

7.2 Recommendations for Further Work

1. The levels of addition of blending agents studied in this work have been limited. A more comprehensive programme of work could be carried out.
2. More data should be obtained for the diffusion of chloride ions through hardened cement pastes and possibly mortars. This could lead to the production of activation energies for a larger range of cements, so as to gain further insight into the diffusion mechanism. In future work of this nature, the duration of the experiment should be kept as short as possible so as to keep concentration effect errors to a minimum.

Discs should be used once only and not for a range of temperatures. More replicate cells should be used than in this work. Six would be a more appropriate starting point.

3. A detailed programme should be undertaken to identify the uses and limitations of the AC impedance technique.

4. An attempt should be made to design specimens for electrochemical studies which are less likely to be susceptible to crevice corrosion.

5. The analysis of the pore solutions obtained was fairly basic in nature. Future programmes could include a more detailed analysis of the pore solution to study other possible cations and anions in order to give a deeper understanding of the mechanism of complexation. The technique of pore solution expression could also be used to study the effect of a range of admixtures other than chloride.

6. In the future more petrographic studies could be carried out on samples from recently built structures to determine whether recommended changes in practices have had any effect, in the Middle East.

APPENDIX I

EXAMPLE OF CALCULATION OF DIFFUSION COEFFICIENTS AND ACTIVATION ENERGIES INCLUDING STATISTICAL ANALYSIS TO DETERMINE CORRELATION AND ERROR

Determination of diffusion coefficient (D) for a disc of OPC B + 10 % silica at 32°C :

Gradient of linear plot of chloride concentration against time

(Fig. 4.2) $= \dfrac{C_2}{t - t_o} = 9{\cdot}77 \times 10^{-9}\ \mathrm{Ms}^{-1}$

since (Chapter 4) $D = \dfrac{V\,l}{A\,C_1}\left(\dfrac{C_2}{t - t_o}\right)$

$D = \dfrac{80 \times 0{\cdot}265}{9{\cdot}62 \times 1}\left(9{\cdot}77 \times 10^{-9}\right)$

$D = 2{\cdot}154 \times 10^{-8}\ \mathrm{cm}^2\,\mathrm{s}^{-1}$

Determination of Activation energy for SOPC BA + 10 % silica using data from the 4 discs in table 4.8.

The statistical methods shown here have been used to obtain 'best-fit' straight lines for the chloride diffusion data given in Chapter 4. The worked example given is for the Arrhenius plot of $\log_{10}$ diffusion coefficient against the reciprocal of absolute temperature for SOPC BA+ 10 % silica.

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

$\Sigma x = 0.06568$

$\Sigma y = -149.596$

$\Sigma x^2 = 2 \cdot 1593 \times 10^{-4}$

n = number of points $= 20$

$\Sigma y^2 = 1120.508$

$\Sigma xy = -0.49185$

Gradient (b):

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

$$b = -2434.718$$

Correlation (r):

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

$$r = -0.8939$$

95% Confidence limits:

Residual variance, S_r^2

$$S_r^2 = \frac{1}{n-2}\left[SSy - \frac{(SPxy)^2}{SSx} \right]$$

where $SSy = \Sigma y^2 - \frac{(\Sigma y)^2}{n} = 1.5598$

$SPxy = \Sigma xy - \frac{\Sigma x\, \Sigma y}{n} = -5.7674 \times 10^{-4}$

$SSx = \Sigma x^2 - \frac{(\Sigma x)^2}{n} = 2.3688 \times 10^{-7}$

$S_r^2 = 8.6439 \times 10^{-3}$

$$S_b^2 = \frac{S_r^2}{SSx} = 36491$$

S_b = 191·0252

b = $-2434 \pm (191\cdot0252)(1.96)$

from t - distribution table

b = -2434 ± 374

Activation Energy (Q):

$Q = -2.3\ Rb$

where R = gas constant = 8.31434

$Q = (-2.3)(8.31434)(-2434 \pm 374)$

$= 46545 \pm 7152$

$= 46.5 \pm 7.2$ kJ/mole

APPENDIX 2

PUBLISHED WORK BY AUTHOR

The following is a paper published by the author together with Page, C.L. and Short, N.R. as part of the proceedings of the 1983 Conference of the Society of Chemical Industry, held in London.

HOLDEN, W.R., PAGE, C.L. and SHORT, N.R.

" The influence of chlorides and sulphates on durability"

Corrosion of reinforcement in concrete construction

- Ed. A.P.Crane, Pub. Ellis Horwood, Chichester 1983.

pp. 143-150

THE INFLUENCE OF CHLORIDES AND SULPHATES ON DURABILITY OF REINFORCEMENT IN CONCRETE

W R Holden, C L Page and N R Short

(University of Aston)

SUMMARY

The use of aggregates, contaminated with mixtures of salts containing chloride and sulphate ions, presents risks of corrosion of reinforcement in concrete. There is an urgent need to assess these risks, particularly with regard to the durability of reinforced concrete structures in the Middle Eastern Gulf regions where salt-contaminated aggregates proliferate.

In this paper, techniques of pore solution expression and analysis are used to quantify the extent to which chlorides and sulphates react with different cements to form insoluble products when various dosages of salts are included in the mix materials. The influence of cement composition is examined for a range of cements produced in Britain. Kinetics of chloride ion diffusion in different types of cement matrix are also considered.

The importance of the above factors in relation to the mechanism of chloride-induced pitting of reinforcing steel is examined and implications regarding corrosion risks are discussed.

INTRODUCTION

Embedded steel reinforcement in dense concrete normally shows good long-term durability. It is generally accepted that the steel is passivated in view of the high alkalinity of the associated pore solution, which in Portland cement concretes often has a pH value in excess of 13. Corrosion problems arising in this environment are a result of depassivation of the steel owing to the presence of aggressive agencies such as acidic gases or chloride ions, the latter being present as original constituents of the mix or as a result of penetration from the environment.

In the U.K. use of chloride-containing admixtures is now discouraged for concrete containing embedded metal (1) although penetration from the environment may still occur, particularly in the case of structures exposed to sea water or deicing salts. However, in the Middle East the deterioration problems are much more severe on account of the particularly aggressive environment (2). Adverse climatic conditions introduce problems in the manufacture, placing and curing of concrete that may result in cracking, reduced strength, increased permeability and reduced durability of the hardened product. Chlorides may be present as original constituents of the mix in the form of contaminated aggregates or mixing water or as wind-borne contamination of the reinforcement. Ingress of chlorides can also take place through cracks or by absorption from the surface. Furthermore, the presence of sulphates in combination with chlorides may accentuate corrosion problems for reasons that will be considered in this paper.

The mechanism of steel corrosion in concrete, with particular reference to the electrochemical behaviour of the steel and physical performance of the concrete cover, has been recently reviewed (3). The presence of chloride ions can cause depassivation of the steel even when the associated pore solution has a high pH value and corrosion is often in the form of intense localised attack (pitting). Experience from corrosion problems in the field suggests that under U.K. conditions, the risk of corrosion in concrete made from OPC is small when chloride ion contents (by weight of cement) are < 0.4% and high for contents > 1.0% (4). Although the mechanism of depassivation by chloride ions is not yet fully understood, it is known that the risk of corrosion increases as the ratio of the concentration of aggressive chloride ion to concentration of inhibitive hydroxyl ion in solution increases (5).

The levels of free chloride and hydroxyl ions in the pore solution are governed by several factors. The concentration of hydroxyl ions would be expected to increase with the alkalinity of the cement although several processes have been suggested which may tend to reduce particularly high alkalinities (3). There is considerable evidence that the C_3A content of the cement is important since it is known that C_3A may form an insoluble complex, calcium chloroaluminate hydrate (Friedel's salt), thus reducing the concentration of chloride in the pore solution (6). The presence of sulphate ions may result in liberation of chloride ions owing to the preferential formation of calcium sulpho-aluminate hydrates (7). Other factors such as temperature, crystallographic form of C_3A and the decomposition of calcium chloroaluminate hydrate by carbonation may also be important in determining the extent of chloride complexation. Furthermore, it has been suggested that chloride present on mixing is complexed to a greater extent than chloride penetrating hardened concrete from an external environment (8).

A critical factor concerning sustainability of corrosion is the mobility of chloride and hydroxyl ions in the vicinity of the metal-concrete interface. For corrosion to proceed, the relative rates of transport of chloride and hydroxyl ions near anodic sites must be such as to give rise to locally elevated chloride concentrations and depressed hydroxyl concentration. It is therefore significant that the diffusivity and activation energy for chloride ion transport through different hardened cements have been found to vary widely, the mechanism of diffusion depending on the pore structure and mineralogy of the cement (9).

A further factor is the diffusion of oxygen to the steel surface but apart from the case of fully submerged concrete this is probably not as important as the relative diffusion rates of chloride and hydroxyl ions.

In view of questions raised by the above considerations an extensive programme of work on the effect of cement matrix variables on the corrosion behaviour of steel in concrete has been initiated. This programme involves -

(i) The expression and chemical analysis of pore solution from within a wide range of hardened U.K. and overseas cement pastes.

(ii) The determination of effective diffusivities and activation energies for chloride ion transport through a selection of the above range of hardened cement pastes.

(iii) Electrochemical study of the corrosion of steel in a wide range of cement pastes and concretes using rest potential, and polarisation resistance (10) techniques.

(iv) Field trials using concrete samples manufactured, cured and exposed under different environmental conditions, and incorporating cement matrix variables identified as being significant from sections (i) - (iii).

Some initial results of sections (i) and (ii) of the programme are discussed in this paper.

Experimental

a. Expression and Analysis of Pore Solution

The cements used were two varieties of Ordinary Portland Cement (OPC-A and OPC-B), two blended cements prepared from OPC-B and 30% pulverised fuel ash (PFA) or 65% ground granulated blast furnace slag (BFS) and a Sulphate Resisting Portland Cement (SRPC). The compositions of the various materials, expressed in percentages by weight of the constituent oxides, are shown in Table 1.

TABLE I

Chemical Analyses of Cements and Blending Agents

MATERIAL	CaO	SiO_2	Al_2O_3	Fe_2O_3	SO_3	MgO	Na_2O	K_2O	Ignition Loss
OPC-A	62.8	20.8	5.1	3.4	2.9	1.3	-	0.96	1.6
OPC-B	63.0	20.3	7.1	2.7	3.3	1.3	0.47	0.60	0.8
SRPC	64.0	20.2	4.1	5.3	2.6	1.4	0.28	0.39	1.1
BFS	42.4	33.3	10.8	0.3	-	8.7	0.37	0.50	-
PFA	2.9	46.6	24.0	9.5	0.9	2.1	2.00	3.80	3.3

Samples of cement paste were made up with distilled water to W/C 0.5 in three parallel series : (1) with no additions (2) with 0.4% chloride (as Cl by weight of the cement) (3) with 0.4% chloride and 1.5% sulphate (as SO_3 by weight of the cement) added as AR grade anhydrous sodium chloride and anhydrous sodium sulphate dissolved in the mixing water.

After being mixed thoroughly they were cast into cylindrical PVC moulds, 49 mm diameter x 75 mm length, and compacted by vibration. The completely filled moulds were tightly sealed, stored at 22°C and demoulded at 84 days. Immediately after demoulding the pore solution was expressed using a pressure vessel of similar design and construction to those used by other workers (11 - 13). The maximum pressure applied was ca. 350 MPa and expressed pore solution was collected in a plastic syringe from the fluid drain at the base of the apparatus. Samples were stored in polystyrene vials and sealed to avoid undue exposure to the atmosphere. The concentration of chloride in the expressed pore solution was determined using a standard spectrophotometric technique (14) and pH determined by titration of expressed pore solution against 10 mM nitric acid using phenolphthalein as indicator.

b. Determination of Chloride Diffusivity

The range of cements used was as in (a). A convenient technique for the study of chloride diffusion kinetics in hardened cement pastes has been established and details of specimen preparation, the diffusion cell and calculation of effective diffusivity of chloride ions are reported elsewhere (9).

Results and Discussion

a. Detailed results of the analyses of pore solutions from these and other cements are to be published separately and only general trends will be considered here. A summary is presented in Table 2, the data in most cases being averages of results obtained for three specimens. Using this data it is possible to establish a number of important points.

TABLE 2

The Concentration of Chloride and Hydroxyl ions (mmole l^{-1}) in Pore Solution Expressed from the Hardened Cement Paste Specimens.

Cement	Series (1) No additions			Series (2) + 0.4% Cl			Series (3) +0.4% Cl, 1.5% SO_3		
	$[Cl^-]$	$[OH^-]$	$\left[\frac{Cl^-}{OH^-}\right]$	$[Cl^-]$	$[OH^-]$	$\left[\frac{Cl^-}{OH^-}\right]$	$[Cl^-]$	$[OH^-]$	$\left[\frac{Cl^-}{OH^-}\right]$
OPC-A	2	589	0.003	83	741	0.112	215	1318	0.163
OPC-B	3	479	0.006	41	661	0.062	153	1047	0.146
OPC-B/ 30% PFA	2	339	0.006	39	457	0.085	145	851	0.170
OPC-B/ 65% BFS	5	355	0.014	28	457	0.061	147	741	0.198
SRPC	2	347	0.006	110	501	0.220	257	1000	0.257

From a general observation of the results in Table 2, it is evident that the cements vary quite markedly in their alkalinity and ability to complex chloride ions.

Considering the results for the series (2) experiments, a ranking of the cements in order of free $[Cl^-]/[OH^-]$ may be expected to have some value as a means of assessing the degree of corrosion protection afforded to embedded steel. Within this ranking the major difference was between the low C_3A(1.9%) SRPC and the other cements, presumably because of the former's limited capacity to form Friedel's Salt ($3CaO.Al_2O_3.CaCl_2.10H_2O$). However, there was also a substantial difference in the performance of the two OPC samples which again probably reflects their C_3A contents OPC-A (C_3A content 7.7%) having a lower chloride complexing ability than OPC-B (C_3A content 14.3%).

The influence of the blending agents (BFS and PFA) was to cause a modest reduction in alkalinity of the pore solution. This reduced alkalinity of the blended cements has led to the suggestion that these materials will offer reduced corrosion protection to embedded steel (15), but long-term experience of concrete manufactured from blended cements has indicated that they may, in fact, be superior to OPC in chloride-containing environments (16, 17). This may be partly explained by the fact that there is no reduction in the chloride binding capacity. Indeed, the chloride binding capacity of the slag cement was significantly higher than that of the corresponding OPC. Thus the ranking of blended cements in terms of $[Cl^-]/[OH^-]$ compared fairly well with OPC. However, it should be emphasised that these findings may not be generally applicable to cements containing slags or pozzolanas from other sources, see for example (13).

Consideration of the results for series (3) experiments shows that the combined additions of sodium chloride and sodium sulphate, in all the cements studied, resulted in a substantial decrease in chloride binding capacity. This presumably reflects the tendency of sulphate ions to react preferentially with the C_3A phase thus inhibiting the formation of Friedel's Salt. An increase in pore solution pH was also observed as hydroxyl ions entered solution to balance the anions removed in the form of insoluble complex salts. However, the net effect of 1.5% SO_3/0.4% Cl additions was to yield a higher free $[Cl^-]/[OH^-]$ than was the case for 0.4% Cl in the absence of sulphate. This supports the suggestion that corrosion risks are likely to be significantly increased in circumstances where concrete materials are subjected to contamination with both chlorides and sulphates, as is commonly the case in the Middle Eastern Gulf regions. A further point, which although not of direct concern to the subject of this discussion is nevertheless significant, is the increased risk of alkali-aggregate reaction that would be expected to arise from the high pH values recorded for samples containing sodium chloride and sodium sulphate.

b. Values of effective diffusivity of chloride ions in hardened cement pastes at 25°C are given in Table 3. From these results, it can be seen that cement composition has a strong influence on the diffusion of chloride ions in hardened cement pastes.

TABLE 3

Effective Diffusivity of Chloride Ions at 25°C
in Various Cement Pastes of W/C 0.5.

Type of Cement	Diffusivity $(\times 10^8)$ $(cm^2 s^{-1})$
OPC-A	3.14
OPC-B	4.47
OPC-B/30% PFA	1.47
OPC-B/65% BFS	0.41
SRPC	10.00

Although values for the two different OPC pastes are similar, values for the two blended cements are significantly lower, and for the SRPC significantly higher, than the OPC. As a second means of assessing likely corrosion protection it is thus possible to rank the cements in terms of their capacity for limiting chloride ion supply and thus discouraging pitting of embedded steel. Possible reasons for the large differences of diffusivity, based on complexing ability and pore structure have been considered elsewhere (10). In this context, the fact that the C_3A contents of the OPC-A and OPC-B samples were significantly different whilst their values of chloride diffusivity were fairly close suggests that C_3A content is of minor importance in relation to the kinetics of chloride ion transport.

Conclusions

The technique of pore solution expression and analysis has shown that the cements studied vary considerably in their alkalinity and ability to complex chloride ions. A rank order of cements has been established in terms of $[Cl^-]/[OH^-]$ in the expressed pore solutions. This ranking shows that there was a major difference between the SRPC and the OPC samples and a significant difference between the two types of OPC. These differences probably reflect the difference in C_3A contents of the cements The addition of PFA or BFS to OPC resulted in a modest decrease in the alkalinity of the cement but gave superior chloride complexing ability, with the overall result that the ranking of the blended cements compared well with the corresponding OPC.

The combined presence of chloride and sulphate ions resulted in a substantial decrease in the chloride binding capacity of the cements. Thus the corrosion risk to embedded steel is likely to increase in these circumstances. Furthermore there is an increase in the alkalinity of the pore solution, which enhances the risk of alkali-aggregate reaction.

Diffusivities of chloride ions in hardened cement pastes have been used to establish a further rank order of the cements in terms of their ability for limiting chloride ion supply to anodic corrosion sites. There is little difference in ranking between the different OPC, but the blended cements are significantly better and SRPC significantly worse than the corresponding OPC.

Electrochemical investigations are being carried out to test the validity of these rankings and it is hoped that results will be available for oral presentation.

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Key to letter codes used for cement identification

Code	Cement
OPC A	Rugby, South Ferriby OPC
OPC B	'Aston' OPC
OPC C	National Dubai OPC
OPC D	Blue Circle Weardale OPC
OPC E	Hyundai OPC
OPC F	Ribblesdale OPC
SRPC A	Ketton SRPC
SRPC B	Onoda SRPC
SRPC C	National Dubai SRPC
SRPC E	Hyundai SRPC