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INORGANIC SURFACE TREATMENTS FOR CONCRETE PROTECTION

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Doctor of Philosophy

THE UNIVERSITY OF ASTON IN BIRMINGHAM
August 1989

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Thesis Summary

Carbonated cement paste surfaces were characterised prior to application of surface treatments. Their chemical and physical properties varied with distance from the surface and method of carbonation. From the surface inwards the pH of expressed pore solutions and porosity were observed to increase. Hardness increased after natural carbonation, but decreased after accelerated carbonation. Generally, accelerated carbonation caused more extreme changes.

Investigations were carried out on four concrete surface hardening treatments; two sodium silicates and two silicofluorides. These treatments penetrated and hardened the surface of naturally dried uncarbonated cement paste to a depth of 250µm. Silicofluorides reacted with uncarbonated and carbonated cement pastes to form calcium fluoride. The question of how sodium silicates harden the surface remains unanswered. Surface hardeners do not significantly affect the rate of carbonation, and are unsuitable for re-alkalising carbonated cement paste.

Water repellent treatments studied include a silane, a siloxane and a silicone. The silane exhibited the maximum penetration, up to 24mm under favourable conditions, but penetration in all cases was limited by moisture in the substrate.

Water repellent treatments slow down water vapour diffusion but, with time, internal moisture levels should reflect external relative humidities. Water repellents may be used to reduce carbonation-induced corrosion where ingress of moisture from intermittent wetting may be slowed. However, treatment with water repellents can temporarily push the carbonation front deeper into the concrete.

Key Words : cement, concrete, surface treatments, carbonation, corrosion

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CHAPTER 1

Introduction and Literature Review.

1.1 Introduction

Concrete is a man-made composite widely used in the construction industry. It is composed of aggregate and hydrated cement paste (1). The aggregates form a major part of the concrete (between 50 and 80% by volume [2]), and are frequently gravel, sand and crushed rock. The cement paste is a binding medium for the aggregates. Concrete is made by adding water to a mixture of cement and aggregates. The cement hydrates on mixing with water to form a hardened cement paste (1).

Concrete is strong in compression, but weak in tension (3). To increase the tensile strength, steel reinforcing bars are frequently embedded in the material. Steel reinforced concrete has proved to be durable and relatively maintenance free, providing that sound materials are used for the construction of properly designed structures. However in cases where deterioration does arise, corrosion of the steel reinforcement is often the major problem.

Steel reinforcement embedded in fresh concrete is normally passive and protected from corrosion by the alkaline nature of the surrounding cement paste. This environment can be upset by the presence of chloride salts, lack of oxygen, and/or carbonation (4). The protection of reinforced concrete from carbonation-induced corrosion is one of the main concerns of this thesis.

Carbonation of concrete is a process by which carbon dioxide in the atmosphere reduces the alkalinity of the cement paste. Usually this phenomenon proceeds relatively slowly, penetrating the surface only a few millimeters in several years (5). When the reinforcing steel is adequately covered by high quality concrete, carbonation-induced corrosion is not usually a problem, and the steel is protected for periods well in excess of the anticipated life of most structures ie. in the region of 200 years (6).

Surface treatments may be applied to concrete to enhance its durability (7). Silicates and silicofluorides are used for surface hardening (8). Silicones, silanes and siloxanes are used as water repellents (9). The performance of these treatments, and their influence on carbonation and carbonation-induced corrosion is investigated in this thesis.

The remainder of this Chapter is concerned with a general review of the literature on cement, carbonation and surface treatments. As carbonation is a process which mainly affects the cement paste, the composition and properties of cement are reviewed initially. This is followed by a detailed review of carbonation; its chemistry, the factors which influence its rate, and its effect on the chemical and physical properties of cement and concrete. Final sections are devoted to the surface treatments, their chemistry and application to concrete.

Not all the literature on subject areas investigated is covered in this Chapter. Literature is continually reviewed throughout the thesis, and can be found in the relevant Chapters.

1.2 Cement

1.2.1 Cement Manufacture and Hydration.

Cement Manufacture

Cement is made from a mixture of calcareous material, such as limestone or chalk, and from alumina and silica found as clay and shale. Marl, a naturally occurring mixture of calcareous and argillaceous material, is also used.

The process of manufacture of cement involves grinding the raw materials, mixing them in certain proportions and burning in a large rotary kiln at a temperature of approximately 1400°C. At this temperature the material sinters and partially fuses into "clinker" balls. The clinker is cooled and ground to a fine powder. During grinding a small amount of gypsum is added (10).

Portland cement clinkers are generally accepted to be composed of calcium silicates and calcium aluminates. Four principal minerals are formed, Ca_3SiO_5, Ca_2SiO_4, $Ca_3Al_2O_6$, and an iron bearing phase from a variable composition solid solution with an average composition of $Ca_4(Al,Fe)O_7$. Cement chemists frequently use an abreviated notation to refer to these minerals and the corresponding symbols are C_3S, C_2S, C_3A, and C_4AF (10,11).

The actual amounts of the four minerals present in a cement are functions of the composition and fineness of the raw mix, the thermal treatment (clinkering temperature, nature of combustibles, cooling regime) and reactions in the liquid, solid and gaseous media (11). Table 1 gives the oxide and mineral compositions of a typical Portland cement.

Table 1. Oxide and Mineral Compositions of a Typical Portland Cement. After Czernin (12).

Typical Oxide Composition per cent.		Mineral Composition per cent.	
CaO	63	C_3A	10.8
SiO_2	20	C_3S	54.1
Al_2O_3	6	C_2S	16.6
Fe_2O_3	3	C_4AF	9.1
MgO	1.5	Minor compounds	
SO_3	2		
$K_2O + Na_2O$	1		
Others	1		
Loss on ignition	2		
Insoluble residue	0.5		

Cement Hydration

The chemical reactions of Portland cement with water are responsible for the setting and hardening of a cement paste. The mixture of compounds involved in the hydration process gives rise to a series of complex interactions between the individual hydrating components (13).

Hydration proceeds by a gradual reduction in the size of the cement paste particles and in the first 24 hours this is relatively rapid. Thereafter the process slows down as most of the cement becomes hydrated. Even after several years of hydration small amounts of relict unhydrated cement particles may still be seen in the cement paste and if water becomes available these particles will have the potential to hydrate.

The products of hydration are calcium silicate hydrates (CSH), calcium hydroxide crystals, and microcrystalline products of the hydration of C_3A and C_4AF(13). Calcium silicate hydrates are the predominant hydration product, comprising about 70% of the solid volume (14). The calcium hydroxide forms 20-25% of the cement paste volume (15).

1.2.2. Hydrated Cement Paste.

Calcium Silicate Hydrates (CSH)

Calcium silicate hydrates are essentially amorphous particles, less than 1µm in size (13). They are highly variable in composition, C/S mole ratios from 1.5 up to 3 having been reported (13,14). Calcium silicate hydrates are relatively impure, because of the incorporation of a variety of species into their structure. Impurities which have been detected include sulphates, aluminium, iron and alkalis (13,14).

In recent years studies have been made of the silicate structures of calcium slicate hydrates (13,16). Jawed et al (13) have suggested that calcium silicate hydrates should be regarded as high energy solids, that slowly move to a state of low energy through polymerisation of silicate tetrahedra. This ageing process is accompanied by physical changes, and may lead to small regions of structural order separated by amorphous material.

The morphology of CSH has been studied extensively by several different techniques (13,17). A variety of morphologies have been described including spines, needles and reticulate structures. It is suggested that the method of preparation, which frequently involves drying, may influence the morphologies observed (13,18).

Calcium Hydroxide and Minor Phases.

Calcium hydroxide forms relatively massive crystals, two or three orders of magnitude larger than CSH particles. The crystals grow up to 100µm in size in water filled pores surrounding the partially hydrated grains of cement paste.

It is believed that some amorphous calcium hydroxide is also formed in the paste, since there is a discrepancy between determinations by x-ray diffraction and other extraction methods (13). Amorphous calcium hydroxide would probably have similar properties to a lime rich CSH.

Calcium sulpho-aluminate hydrates are a group of minor phases that may be found in hydrated cement. Ettringite is an example of a calcium sulpho-aluminate hydrate which may appear as thin prismatic crystals with an approximate composition of $C_6AS_3H_{32}$. About 8 different calcium sulpho-aluminates have been found in hydrated Portland cement (13).

Cement Paste Porosity.

Porosity and pore size distributions are not intrinsic features of a hardened cement paste. They are both functions of water to cement ratio and the degree of hydration, and are strongly influenced by the application of high pressure(14).

The interpretation of pore structure and pore size distribution in cement pastes is a matter of considerable controversy, depending on the method used to make the determination (14,19). For example, those who interpret the results of mercury intrusion suggest the pore structure is much more gross than that estimated from water vapour and nitrogen sorption methods (14).

It may be said that hardened cement pastes contain a wide range of pore sizes, with different diameters ranging over several orders of magnitude. Thus no one method of analysis can give information about the whole range of pores(13). Their characteristics are summarised in Table 2.

Large pores limit strength, the macropores control permeability and durability. Mesopores and micropores are important during wetting and drying, and influence dimensional stability.

Table 2. Pores in Cement Paste. After Jawed (13).

Classification	Size in nm	Methods of Analysis	Origin of Pores.
Large Pores	>5000	Optical microscopy	Air entrainment; entrapped air; inadequate consolidation or curing;excessive mix water
Capillary pores			
Macro pores	>50	Mercury porosimetry	Remnants of water filled space in fresh pastes
Mesopores	2.6-50	Mercury porosimetry Gas adsorption-desorption.	Remnants of water filled space; smaller pores associated with CSH
Micropores	<2.6	Gas adsorption-desorption	Associated with CSH

Pore Solution.

Pores in a cement paste may be dry, partially wetted or completely filled with water. This water, when present, will form a solution that tends towards chemical equilibrium with adjacent contacting solid phases. This solution is referred to as the pore solution.

Pore solutions have a high pH, in excess of 13, owing to the presence of small quantities of readily soluble NaOH and KOH derived from the cement. Also within the cement is a more substantial portion of reserve basicity in the form of sparingly soluble $Ca(OH)_2$. Consequently the system is buffered to resist downward pH changes at a level of about pH 12.5 (20).

The pH of a cement paste pore solution will depend on the composition of the cement used and the water/cement ratio. High pH values in the range of 13 to 14 will be maintained for very long periods providing there are no carbonation or leaching effects (21).

1.3 Carbonation

1.3.1 Introduction

Carbonation is a phenomenon which affects the cement paste of concrete. Carbon dioxide and moisture form carbonic acid which reacts with the hydrated cement minerals in cement paste (10). The reaction takes place, albeit very slowly, even with the small amounts of carbon dioxide in the atmosphere. The main reaction product of carbonation is calcium carbonate and the reaction modifies both the physical and chemical properties of the cement paste. The chemical changes can result in the onset of corrosion of steel reinforcement embedded in the cement paste.

1.3.2. Chemistry of Carbonation.

The process of carbonation can be divided into three stages :

1. Ingress of CO_2 by diffusion.
2. Reaction of CO_2 with the pore solution.
3. Reaction of the resulting carbonic acid with the alkaline constituents of concrete.

Diffusion of CO_2 into concrete will take place providing there are pores which are open and interconnected (22). Drier concrete will facilitate CO_2 difussion. CO_2 can diffuse through water, but this process is approximately 10^4 times slower than when it diffuses through air (23).

Although it can be stated simply that the pore solution is neutralised by CO_2, in fact a series of chemical rections and phenomena must be considered, some of which are not fully understood in the context of carbonation.

As discussed in Section 1.2.2 the pore solution of hydrated Portland cement has a high pH in excess of 13. The water in this solution reacts with carbon dioxide to form carbonic acid.

$$H_2O + CO_2 \rightarrow H_2CO_3$$

Carbonic acid is a weak diprotic acid with two ionisation constants (24) :

$$H_2CO_3 \rightleftharpoons H^+ + HCO_3^- \qquad k_{a1} = \frac{[H^+]\ [HCO_3^-]}{[H_2CO_3]} = 4.3\times10^{-7}\ M/l$$

$$HCO^-_3 \rightleftharpoons H^+ + CO_3^{\,2-} \qquad k_{a2} = \frac{[H^+]\ [CO_3^{\,2-}]}{[HCO^-_3]} = 5.6\times10^{-11} M/l$$

where : k_a = acid ionization constant

[ion] = ionic concentration in moles per litre

According to Pourbaix, at a pH in excess of 10.34 the carbonate ion will predominate (25). Before carbonation the pore solution has a pH in excess of 13, so it is the carbonate ion which predominates initially.

The carbonic acid reacts with the alkaline constituents of the pore solution to give carbonate salts and water, thus reducing the pH.

$$H_2CO_3 + 2KOH \rightarrow K_2CO_3 + 2H_2O$$

$$H_2CO_3 + 2NaOH \rightarrow Na_2CO_3 + 2H_2O$$

Owing to the presence of reserve basicity in the form of $Ca(OH)_2$ the system is buffered to resist downward pH changes at a level about 12.5 (20). According to Pourbaix, with decrease in pH the $Ca(OH)_2$ becomes more soluble (25). Consequently with the removal of the highly alkaline sodium and potasium hydroxide by carbonation, the calcium hydroxide is able to dissolve into the pore solution. Once in solution the calcium hydroxide reacts with any available carbonic acid to form calcium carbonate.

$$Ca(OH)_2 + H_2CO_3 \rightarrow CaCO_3 + 2H_2O$$

The calcium carbonate may precipitate out providing the concentration of carbonic acid is kept low. But, where there is an excess of carbonic acid the solid carbonate may dissolve to form the more soluble calcium bicarbonate (24), bicarbonate predominating at pH levels between 6.38 and 10.34 (25).

$$Ca\,CO_3 + H_2CO_3 \rightarrow Ca(HCO_3)_2$$

However if CO_2 is allowed to diffuse away from a bicarbonate solution , and water allowed to evaporate off calcium carbonate will precipitate out (24).

$$Ca(HCO_3)_2 \rightarrow CaCO_3 + H_2O + CO_2$$

Morphology of Carbonation Products

Scanning electron microscopes have been used to study the conversion of calcium silicate hydrates and calcium hydroxide to calcium carbonate during the process of carbonation. Such studies by Hornain (26) in 1976 revealed that on carbonation, calcium silicate hydrates become compact. Also that calcium carbonate coexists with carbonated hydrated silicates enriched with SiO_2 and amorphous silica.

In 1979, Berger used SEM to study the carbonation of freshly hydrated C_3S, carbonated in 100% CO_2 at 100% R.H. (27). Treatment with 2N hydrochloric acid was used to dissolve the calcium carbonate to reveal residual silica gel resembling the initial C_3S grains. Berger concluded that during carbonation, removal of calcium from calcium silicate hydrates produces a highly polymerised silica gel, which maintains the same morphology as the original calcium silicate hydrates.

Crystalline Forms of Calcium Carbonate

Much work has been done on the form of calcium carbonate resulting from carbonation. In 1960 Cole and Kroone reported that samples of mortar and calcium silicate hydrate exposed to atmosphere or a stream of CO_2, carbonated to form poorly crystalline vaterite, aragonite and calcite (28).

In 1971 Sauman (29) reported that carbonation of calcium silicate hydrate produces, in addition to silica gel, vaterite which is later transformed to the more stable calcite. The metastable phase aragonite is only formed to a small extent. These results were in conflict with earlier work by Kondo *et al* in 1968, where variations in the amount of calcite and vaterite with depth from the surface had led them to conclude that calcite was formed first, followed by vaterite (30).

1.3.3. Rate of Carbonation

The rate of carbonation depends on the amount of CO_2 diffusing into the concrete, and the quantity of carbonatable constituents in the concrete (31).

Diffusion of gases through solids is governed by Fick's law (32), and this law can be applied to concrete providing the influence of cracks is ignored (31). The law postulates that atomic movement is in a direction from higher to lower concentration, which leads to an equalisation of concentration within a single phase (32). For one dimensional steady state diffusion Fick's first law is as follows (33) :

$$\frac{dx}{dt} = \frac{Dc}{Ax}$$

where x = depth t = time

D = diffusion coefficient c = CO_2 concentration

A = the quantity of alkaline substances reacting per unit volume of concrete

On integration this yields a parabolic relationship

$$x^2 = \frac{2Dct}{A}$$

$$\text{or } x = k\, t^{1/2}$$

The principle that the depth of carbonation is roughly proportional to the square root of time is an old well established theory (10,23,34,35).

According to Sergi (36), carbonation mainly depends on the diffusion of CO_2 into concrete. It also depends on counter diffusion of $Ca(OH)_2$ and other soluble basic phases, and to a lesser extent on the rate of drying or moisture movement outwards. This latter phenomenon is important, as the carbonation reactions cause the release of bound water. If the moisture is not allowed to evaporate away from the concrete surface, it will become saturated, slowing down and preventing the further ingress of CO_2.

The ease of carbon dioxide penetration will not only depend on moisture levels determining the number of water filled pores and capillaries, but also on the pore structure of the concrete. As discussed in 1.2.2. the porosity and pore size distributions of a hardened cement paste are not intrinsic features, but are functions of water to cement ratio and degree of hydration.

In 1968 Meyer wrote about these factors in relation to carbonation (37).

Meyer considered that age, composition and the conditions of storage were the main factors influencing the progress of carbonation; the carbonation resistance of a fully compacted and normally cured concrete being essentially determined by its water to cement ratio and the type of cement used.

In 1986, Fattuhi (38) wrote that depth of carbonation is significantly increased with an increase in the concrete water to cement ratio, but an increase in the initial water curing period resulted in a considerable decrease in the depth of carbonation. Fattuhi concluded that depth of carbonation may be reduced considerably when the porosity is decreased by reducing the w/c ratio and/or increasing the initial water curing period. In 1987, Bier et al (39) reported results of investigations, which led him to reach similar conclusions to those of Fattuhi described above.

Work by the BRE (6) on evidence from field studies and cast specimens gave a very consistent view of the carbonation of different concretes. It was observed that both the average rate of carbonation and the range in the rate of carbonation within components and between components were very sensitive to the quality of concrete; which was determined by the combined effects of the constituent materials, the compaction and the curing regime.

The evidence indicated that, although it can be demonstrated that changes in the proportions of the different constituent materials, eg cement content, water/cement ratio, etc affect the rate of carbonation in concrete, these effects are marginal in relation to the effect of curing and/or compaction. Significant resistance to carbonation is only achieved when high cement contents, together with low water/cement ratios are translated into high strengths.

The foregoing discussions indicate that the rate of carbonation of concrete is dependent on several factors, some of which are determined by the properties of the concrete itself, others on the environment in which the concrete has been placed. The environmental factors which may influence the rate of carbonation are the carbon dioxide content, relative humidity and temperature.

Normal atmospheric CO_2 levels are low and relatively static, despite a 5% increase over the last 20 years (40,41). Atmospheric carbon dioxide contents are of the order of 0.034%, approximately 0.03% in rural areas, but may be as high as 0.3% in large cities (10). Considering the low levels of atmospheric carbon dioxide it is hardly surprising that only the outer few millimeters of a concrete surface become carbonated over several years (see Table 3).

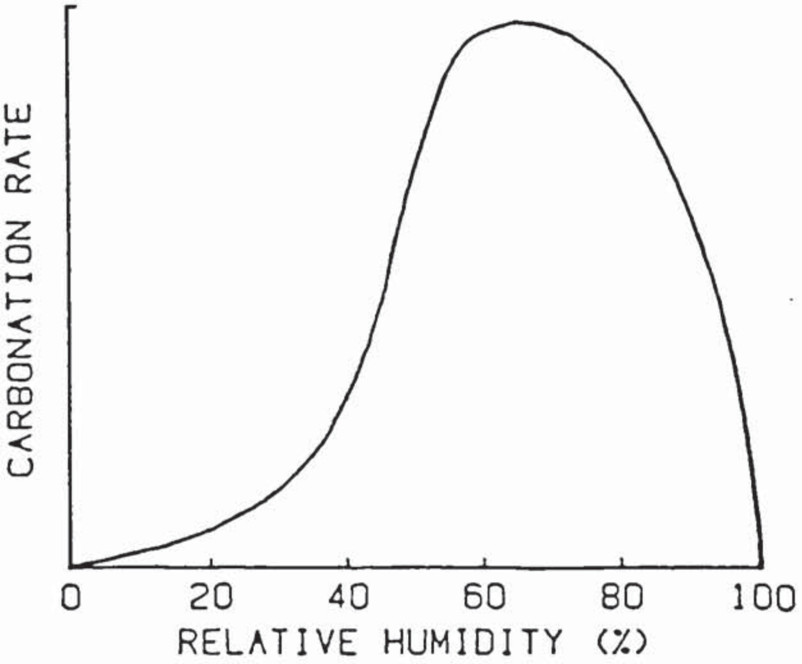
Table 3. Typical Values of Depth of Carbonation with Time.
After Smolczyk (42).

Depth of carbonation	Age of Concrete in Years	
in mm	(20 MPa Concrete)	(40 MPa Concrete)
5	1/2	4
10	2	16
15	4	36
20	7	64

Clearly an increase in the surrounding CO_2 content would increase the rate of carbonation. High CO_2 atmospheres are frequently used in experimental work to accelerate the process of carbonation (36,43,44,45).

The relative humidity at the carbonation zone, and at the carbonation front affects the rate of carbonation, and these are indirectly linked to the ambient relative humidity (46). In 1984, Wierig wrote that the greatest depth of carbonation is reached in samples stored at a relative humidity of about 65% (47). In 1985, Moller suggested that carbonation reactions only occur when the relative humidity is between 40 and 90%, with a maximum reaction rate at 50% (48). It is generally accepted that the optimum relative humidity for carbonation is in the region of 60 to 70% (36,44,49). Figure 1 illustrates this point.

Figure 1. Optimum Relative Humidity for Carbonation. After Sergi (36)



Temperature has been cited as influencing the rate of carbonation (44,50,51). How it affects carbonation is not entirely clear. It is thought that heat assisting in the evaporation of water could reduce moisture levels below the minimum required for carbonation (46,52). Parrot, however, has suggested that heat increases the rate of carbonation, except where it causes excessive drying (46).

Moorehead has written that when the carbon dioxide gas temperature is increased to temperatures in excess of 60°C, the reaction rate decreases (52). In addition to drying reducing the rate of carbonation at elevated temperatures, Moorehead proposes two other possible contributing factors :

1. The solubility of CO_2 in water is reduced to one quarter, if the temperature is raised from 15°C to 60°C.
2. At constant pressure the concentration of CO_2 per unit volume of gas is reduced if the temperature is raised.

1.3.4. Effect of carbonation

The main effects of carbonation are reductions in porosity and alkalinity, with gradual conversion of all calcium bearing phases to calcium carbonate. In addition, decomposition of the calcium silicate hydrates produces silica gel (53).

As a result of the carbonation reactions, water bound in the cement paste is released, but heavier carbon dioxide will be gained (36). Generally, a net increase in weight with carbonation is observed.

Porosity of Carbonated Concrete.

In 1968 Pihlajavaara reported experimental work indicating that the total porosity of carbonated Portland cement paste was smaller than that of non-carbonated cement paste (54). Rozental and Alekseev reported similar findings in 1976 (55). More recent work by Cabrera et al on the carbonation of mortars has shown that the mean pore diameter is reduced, and that carbonation results in the filling of pores mainly in the range of 10 to 1000 nm, with some reduction of the larger pores up to 10^5 nm (44).

Neville suggests two reasons for porosity reduction : water released by carbonation aiding the process of further hydration, and the deposit of calcium carbonate in the voids (10).

Amaski has reported that carbonation increases density, compressive strength and surface hardness of concrete (56). It is well established that strength and density are related to porosity (57,58,59). Therefore it can be concluded that reductions in porosity due to carbonation cause corresponding increases in density, strength and surface hardness. Another consequence of the decrease in porosity is a decrease in permeability.

Carbonation Shrinkage

Concrete may undergo shrinkage due to carbonation (10). Powers has studied and described this phenomenon (60). Carbonation shrinkage is a decrease in volume of a specimen of cement paste or concrete that occurs during or after a period of drying, when carbonation reactions have taken place. In severe cases, stresses may result in cracking and crazing of the surface of exposed concrete.

Powers suggests that the fact that carbonation may produce shrinkage is direct evidence that calcium hydroxide crystals do not become converted to $CaCO_3$ in situ. The reaction between $Ca(OH)_2$ and carbonic acid gives a solid product having a greater volume than that of the calcium hydroxide consumed by the reaction. Dissolved $Ca(OH)_2$ diffuses into voids where $CaCO_3$ crystals are free to nucleate and grow, unrestrained by pressure.

The principal feature of this hypothesis is that carbonation shrinkage is the result of dissolution of calcium hydroxide crystals while the crystals are under pressure, and in the absence of pressure carbonation does not cause shrinkage. Powers suggests that carbonation of other hydration products does not involve dissolution and therefore produces no shrinkage.

Carbonation-Induced Corrosion

An important effect of carbonation of concrete is the reduction in alkalinity of the pore solution of the cement paste, to pH levels as low as 9 (61). This is most important in steel reinforced concrete.

The pore solution of concrete normally has a high pH, in excess of 13 (4). The high pH environment allows steel reinforcement embedded in concrete to form a microscopic oxide layer on its surface. This passive layer forms a barrier against the dissolution of iron and in these circumstances corrosion is suppressed, even if other conditions leading to the initiation of this process are present ie. moisture and oxygen (44).

Carbonation may initiate the corrosion process since a reduction in the pH value allows the steel to pass from the passive to the active state (62). The passive layer is destroyed at a pH of 9.5 or lower (25). The rate of attack depends on other external corrosion factors, namely a minimum atmospheric moisture content to guarantee the presence of an electrolyte in the concrete pores, and free access of oxygen right up to the metal surface thus enabling the cathodic reaction to take place (62).

Corroding steel may cause spalling of the concrete cover (63), and hence the carbonation front must be prevented from reaching the steel. Consequently, the thickness of concrete cover to the steel, and the resistance of the concrete to carbonation are important (37). Surface treatments applied for other purposes may also affect the resistance of concrete to carbonation.

1.4 Surface Treatments for Concrete Protection

1.4.1 Introduction

Two types of surface treatment are considered, water repellents and surface hardeners. On application, the treatments penetrate the concrete and modify the properties of its surface.

1.4.2. Water Repellents

Chemistry of Silicone Based Water Repellents.

These water repellents are organosilicon compounds. They are synthetically prepared compounds and have a chemistry between that of organic and inorganic substances (64). Three groups of silicone water repellents have been studied : silanes, siloxanes and silicones.

Silanes have SiH_4 as their root compound, and are relatively small molecules. Siloxanes are similar to silanes, but have larger molecules consisting of alternating silicon and oxygen atoms. Silicones are the largest of these molecules, and have a similar basic chemistry to silanes and siloxanes. Table 4 shows their relative molecular sizes.

Table 4. Typical Molecular Sizes of Water Repellents Used on Concrete (65)

Material	Size (nm)
Silane	0.5 - 1
Siloxane	3.5 - 4.5
Silicone	15 - 20

For application to concrete the silicone based water repellents must be alkali resistant. This is achieved by having long alkyl groups e.g. C_4H_9 or C_8H_{17} (9). Larger alkyl groups result in lower volatility, and consequently less material is lost through evaporation (66).

Owing to the highly water-repellent nature of these materials, it is usually sufficient to apply solutions with an active material content of 5 to 10% (67). Organic solvents such as white spirit, or alcohol are used for dilution (9). Table 5 lists silicone based water repellents, which are suitable for application to concrete.

It has been found that the type of solvent used influences performance. For example, white spirit allows deeper penetration of the water repellent under moist conditions, compared with ethanol (67).

Table 5. Examples of Silicone Based Water Repellents Suitable for Application to Concrete (9).

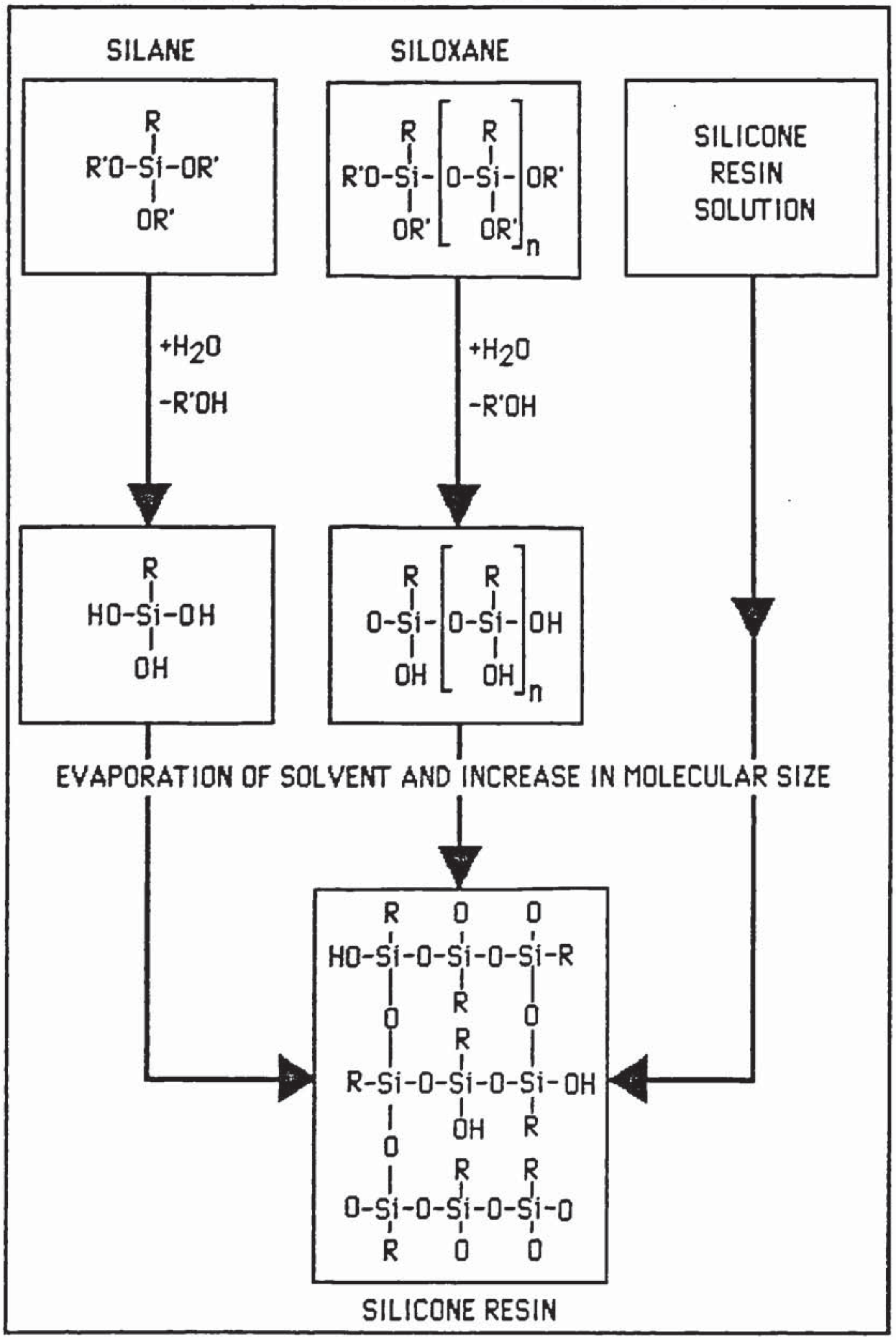
Type	Active content in per cent
Isobutyl trialkoxysilane	10%
Isooctyl trialkoxysilane	10%
Oligomerous isooctyl alkoxysiloxane	10%
Isooctyl silicone resin	5%

No matter which of the three water repellents are used to impregnate concrete the end product, or active substance, is always a silicone resin. The molecular size of the final active substance will differ depending on the type of silicone water repellent used (9). Figure 2 shows some of the reactions.

When a silane is applied to concrete, the silane either reacts with moisture to form silanol and silicone resin, or may react directly with the substrate. Alcohol is formed as a by product and evaporates. If moisture is not available, the silane may also evaporate (9).

When applied to concrete, silanes undergo hydrolysis whereby silanols are produced (68). Siloxanes are already partially hydrolysed (66), but will undergo some reaction with water. On applying siloxanes and silicones to concrete, the solvent evaporates, silanols react with the substrate, and the size of the molecule increases (9). During the evaporation of the solvent, silicone resin is deposited on the pore and capillary walls making them water repellent (67).

Figure 2. Chemical Reactions on Application of Silicone Based Water Repellents to Concrete. Adapted from Roth (9).

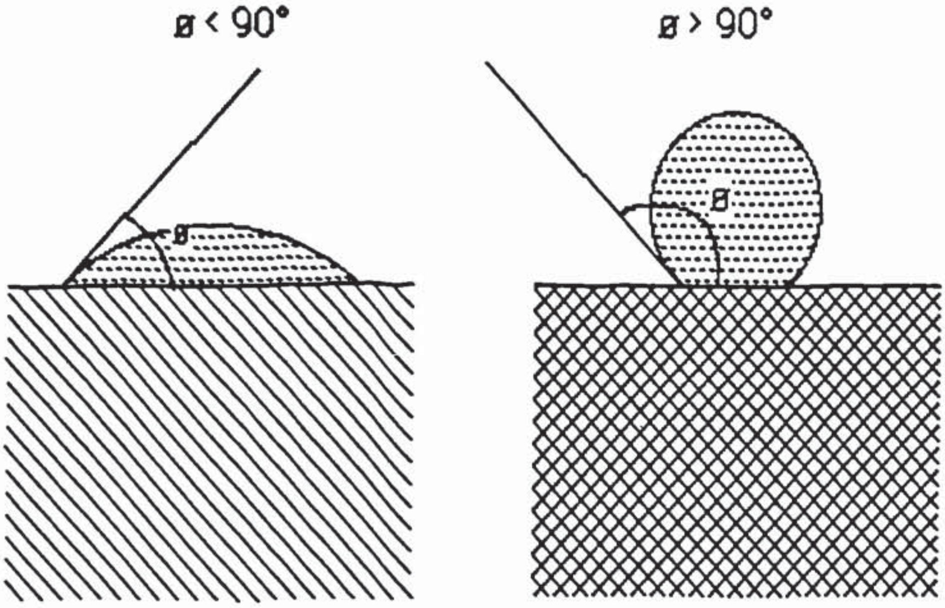


The water content of concrete during application of a water repellent is important. Clearly, if the concrete surface is saturated the water repellent can not be absorbed, and in such a case there is no depth of penetration (67). However silanes and siloxanes require the presence of some water to react.

Influence of Water Repellents on Concrete Properties.

Water repellency is caused by the silicone based water repellent increasing the surface tension of the concrete, thus increasing its contact angle with water. Figure 3 shows that when the contact angle Ø is greater than 90°, water becomes a drop which is easily shed (69).

Figure 3. Influence of Contact Angle Ø on Water Repellency.



Untreated concrete has a negligible contact angle. After treatment with a silicone based water repellent, the contact angle of the treated surface increases in excess of 90° (69).

With an increase in water repllency, water molecules are no longer attracted, but repelled. Capillary forces are reduced, and less water is absorbed. Consequently, water borne salts such as de-icing salts do not readily diffuse through a water repellent treated concrete surface (66,68,70,71).

Even though a treated concrete surface is water repellent, the surface is not completely sealed against water penetration. Treatment only temporarily delays water absorption when concrete is completetly immersed. Although the initial rate of absorption may be reduced, after continued immersion the total absorption for treated and untreated concrete is similar (8,72).

Silicone based water repellents line the pores of concrete, making them water repellent (71). Consequently these materials are sometimes referred to as pore liners (71,72,73). As the materials only line the pores there is no significant pore blocking, and little modification of the pore structure of the treated concrete (66,68). Also, the passage of water vapour and gases is not prevented (71).

History and Application of Silicone Water Repellents.

Silicone based water repellents have been manufactured on an industrial scale since 1940, and used on concrete from the mid 50's onwards (9,74).

In the 1960's the Americans and West Germans used silicone based water repellents on concrete to repel water and salts, and reduce chloride-induced corrosion (75,76). For this purpose, the Germans found that a silane, isobutyl trimethoxysilane, performed well over a ten year period. Consequently, in December 1986 the British Department of Transport recommended its use for the repair of concrete structures (76).

Currently in the U.K., silicone based water repellents are sold to the construction industry for application to concrete primarily because of their water repellency. It is claimed that treated surfaces will repel liquid water, but allow water vapour to pass through them, thus keeping structures drier. Additional claims include cleaner concrete as the silicone based water repellents reduce staining and efflorescence, and better protection against frost attack and chloride ion ingress.

Some silicone based water repellent are sold on the basis that they comply with British Standards 3826:1969 and 6477:1984 (77,78). Both standards cover similar tests on water repellents for masonry surfaces. The tests are for water repellency, absorption and evaporation of water and durability.

The suppliers of silicone based water repellents usually recommend that the treatments are only applied to clean and visibly dry concrete. Two applications of the treatment are usually made, by spraying, brushing or possibly dipping.

Under favourable conditions silanes have been found to penetrate lime mortars up to 13mm (67). Depths of penetration of 2-4 mm for silane into high quality, dry concrete have been claimed. However, when applied to incompletely dry concrete penetration is seldom more than 1mm (71). Silanes, having the smallest molecules, penetrate more freely than the other silicone based water repellents (66,67).

1.4.3. Silicate and Silicofluoride Surface Hardeners.

These surface hardeners are aqueous solutions of silicates and silicofluorides, which may contain wetting agents comprising approximately 10% of the solids. They have been applied to concrete for over half a century, and have frequently been specified for the surface hardening of concrete floors, to reduce wear and dust production (8,70,71).

Silicates

The silicates are water glasses. They are solutions of soluble alkali silicates, and their composition can be expressed as :

$$M_2O \cdot xSiO_2 \cdot yH_2O$$

Where : x and y are molar ratios;
M is an alkali metal such as Na, K or Li.

The soluble silicates in viscous water glass solutions have molecular structures in the form of partly-polymerised linear siloxy-silanol salts with strongly adsorbed water molecules (79).

Sodium silicates are one of the main types of silicate sold in the U.K. They are marketed as clear or slightly cloudy aqueous solutions, containing only small amounts of impurities (80,81). The $SiO_2 : Na_2O$ molecular ratio can vary between 1 and 4 (74), but for application to concrete a ratio of 3.3 is commonly used (80,81).

For years it has been thought that on application to concrete, silicates react with the calcium compounds in the cement paste to form products which fill the pores (8,71,74,80,81). It has been suggested that the products are calcium silicate, silica and sodium silicate glass (80). Keer and Gardiner have proposed that sodium silicate reacts with calcium hydroxide in the cement paste to form calcium silicate hydrate, silica gel, and sodium hydroxide (82).

Work by Fukushima (79) has indicated that on application of silicate treatments to concrete, the mechanism by which the surface is hardened might be totally different. Fukushima used evidence from infrared spectra of hardening films of sodium silicate on asbestos cement board.

Fukushima found that hardened silicate films are produced by drying, during which silanols are polymerised to siloxanes. Later, carbon dioxide from the atmosphere may cause carbonation of the polymerised film, with carbonates being formed.

Fukushima compared the infrared spectra of many types of silicates hardening on different substrates. He found that the degree of polymerisation of the Li silicates was low. Films of Na silicate showed the greatest degree of polymerisation if they had higher molar ratios and were dried at higher temperatures.

Silicofluorides

Silicofluorides which have been used on concrete include magnesium, sodium, lead, aluminium, hydrogen and zinc. Combinations of magnesium and zinc, and magnesium and sodium have also been used. Lead silicofluoride is limited in use because of its toxicity (74).

Magnesium silicofluorides react with the calcium bearing phases in cement paste to form calcium and magnesium fluorides and silica gel (74,82). Keer and Gardiner have suggested the following equation to describe the reaction of magnesium silicofluoride with calcium hydroxide in the cement paste (82).

$$2MgSiF_6.6H_2O + 4Ca(OH)_2 \rightarrow 4CaF_2 + 2MgF_2 + 2Si(OH)_4.6H_2O$$

Reactions of the other mentioned silicofluorides with cement paste were not found in the literature, but would probably be similar to those of magnesium silicofluoride.

Application of Silicates and Silicofluorides.

Both silicates and silicofluorides are sold for hardening concrete surfaces to decrease dust production caused by wear. In addition it is claimed in the trade literature that the treatments decrease surface permeability and increase overall durability.

It is suggested that the treatments can be applied to concretes of any age once they have been cured for a minimum of 21 days. It is recommended that the concrete is clean and dry prior to treatment. The treatments are applied by spraying and/or brushing. Excess treatment is drained away or mopped up.

As silicates and silicofluorides tend to block the pores of concrete, an initial application of these treatments may block pores and limit the penetration of further applications. For this reason several applications are usually made, the first of which is dilute and subsequent ones progressively more concentrated. After the final treatment the concrete surface is usually washed with water to remove any excess treatment.

Silicates and silicofluorides may pentrate up to 1-3 mm into concrete, but generally penetration is only 50-100 µm (71).

1.5 Summary and Guide to the Thesis

The previous sections have served as a basic introduction to the main subject areas of the thesis ie. carbonation, water repellents and surface hardeners. These subject areas are investigated in further detail in subsequent Chapters.

In Chapter 3 carbonated surfaces are characterised prior to the application of surface treatments. The physical and chemical properties of surfaces carbonated under natural and accelerated conditions are compared.

The performance of surface treatments is investigated in Chapters 4 and 5. Penetration of the treatments was studied and complimented with investigations in to aspects pertinent to the two groups of treatment. Chapter 4 is devoted to the surface hardeners and their effect on chemical and physical properties. Chapter 5 explores the influence of water repellents on moisture and moisture movement.

The effect of the treatments on the rate of carbonation is investigated in Chapter 6. Chapter 7 looks at the influence of water repellents on carbonation-induced corrosion. In Chapter 8 the findings are discussed, and suggestions are made for areas of future research.

Chapters 3 to 7 are presented in a standard format. Each Chapter has an "Introduction", where the area of investigation is clearly stated. "Previous Work" is reviewed in the following section and gaps in current knowledge are high lighted in the "Aims of the Experimental Work". The "Approach to the Experimental Work" gives an introduction to the "Details of the Experimental Work". "Results" are presented, followed by "Discusion and Conclusions". At the end of each Chapter the most important findings are given in a "Summary".

Descriptions of the material used in the investigations are given in Chapter 2. Some experimental methods were used repeatedly, and consequently have been described once in Chapter 2.

CHAPTER 2

Materials and Methods

2.1. Introduction.

In this Chapter details of the materials used, and the reasons for their use are given in Section 2.2. The remaining Sections describe methods which were frequently used, and are referred to in later Chapters. Methods not described here are unique to other Chapters, and can be found in those Chapters.

2.2. Materials.

2.2.1. Cement.

An ordinary Portland cement specially blended for research purposes to have an average composition was used. The cement was Batch 119, purchased from Blue Circle Industries. Chemical and physical data on the cement are shown in Appendix 1.

2.2.2. Aggregates.

The BRE supplied the following aggregates for the production of concrete :

Guiting Limestone	5 - 10 mm	140 kg.
Guiting Limestone	5 mm down	190 kg.
Ham River Gravel	5 - 10 m	140 kg.
Ham River Gravel	5 mm down	190 kg.

The Guiting Limestone was choosen because of its poor quality and high porosity. The Ham River Gravel was a siliceous flint Thames Valley aggregate, and was used in experiments for comparison with the performance of the calcareous aggregate.

2.2.3. Surface Treatments.

Twenty seven letters were sent to selected companies which were thought to market the surface treatments of interest. An example of the type of letter sent is shown in Appendix 2. Response to the letter yielded the following samples with appropriate technical information.

Surface Hardeners.	Water Repellents.
2 sodium silicates	1 silane
1 magnesium silicofluoride	1 siloxane
1 magnesium and zinc silicofluoride	1 silicone

For reasons of confidentiality no indication will be given as to the sources of the above materials. To distinguish the two sodium silicates they will be designated 1 and 2.

Generally, the suppliers of the surface treatments were reluctant to give precise details of the composition of their materials. Consequently, chemical analyses of the treatments was carried out to establish their composition. The BRE took on this resposibility, analysing the surface hardeners themselves, but contracting the Paint Research Association to analyse the water repellents.

Analyses of fresh and old samples were compared to check that there was no alteration of the composition with age. The old samples were 18 months to two years old. The fresh samples were acquired in the months preceding the analyses by re-approaching the original suppliers. A request was made to the suppliers for an indication of any known changes in their product. No changes were indicated.

Surface Hardeners

The results of the analyses of the surface hardeners are summarised in Table 6. Data on the composition of sodium silicate 1, supplied by the manufacturer/supplier, are also given for comparison.

The results showed that sodium silicates 1 and 2 were water glasses with similar $SiO_2 : Na_2O$ ratios in the region of 3.5. Sodium silicate 2 was more diluted than sodium silicate 1. A dilution of one part sodium silicate 1 to two parts water would produce a sodium silicate with a similar dilution to sodium silicate 2.

Comparison of results for sodium silicate 1 with suppliers data show similar levels of SiO_2, slightly less Na_2O in the samples analysed, and significantly more solids in the samples. It must be noted that for all the analyses the constituent analyses do not add up to balance the total solids. This could be due to the presence of other undetected constituents.

Table 6. Analyses of Surface Hardeners

SAMPLE	pH	S.G.	SOLIDS	Na_2O	SiO_2	Mg	Zn	SiF_6
			%w/w	%w/w	%w/w	%w/w	%w/w	%w/w
Sodium silicate 1 old	11.3	1.394	47.5	8.43	28.1	-	-	-
Sodium silicate 1 fresh	11.3	1.378	48.1	8.35	29.8	-	-	-
Sodium silicate 1 (Supplier's Data)	-	1.42	39.3	9.4	29.9	-	-	-
Sodium silicate 2 old	12.1	1.111	15.4	2.57	9.1	-	-	-
Sodium silicate 2 fresh	12.0	1.101	15.3	2.42	8.8	-	-	-
Mg + Zn silico-fluoride old	1.5	1.185	8.46	-	-	1.45	1.28	3.45
Mg + Zn silico-fluoride fresh	1.3	1.181	8.42	-	-	1.07	1.24	3.62
Mg silico-fluoride old	2.0	1.146	7.93	-	-	0.90	-	3.19
Mg silco-fluoride fresh	2.0	1.148	9.29	-	-	0.78	-	4.52

From the analyses of the fresh magnesium silicofluoride an empirical formula could be calculated as follows :

	Ratio by weight		Weight per mole		Ratio by moles
Magnesium (Mg)	0.78	÷	24.3	=	0.0321
Silicofluoride (SiF_6)	4.52	÷	142.1	=	0.0318

The above result gives a 1:1 mole ratio, suggesting a formula of $MgSiF_6$ for the fresh magnesium silicofluoride. Unfortunately empirical formulae could not be calculated for the rest of the silicofluoride results.

The results of the pH determinations were interesting. The sodium silicates were fairly alkaline with pH values in the region of 11 to 12. The silicofluorides were surprisingly acidic, having pH values of 2 or less.

A comparison of the results for fresh and old samples of surface hardeners showed few differences in composition, indicating that generally the surface hardeners were not degrading in the pot. The material which appeared to show the most variation in composition with time was the magnesium silicofluoride. This was a little surprising as this material was originally supplied in a crystalline form in a well sealed container.

Water Repellents

The water repellents were subjected to infrared spectrometry, and gas chromatographic separation, followed by mass spectrometry of the separated effluent. The results of the analyses allowed the characterisation of the materials, the details of which are summarised in Table 7. No differences were detected between the fresh and the old samples.

Table 7. Analyses of Water Repellents

Sample	Characteristics
Silane	Isobutyltrimethoxysilane, volatile, no solvents.
Siloxane	Aliphatic siloxane, probably including Me and Bu trimethoxysilane, volatile solution with MeOH, $(CH_3)_2CO$, xylene and diacetone alcohol detected.
Silicone	Aliphatic polysiloxane, partly volatile xylene solution.

2.3. Preparation of Materials.

2.3.1. Cement Paste Production.

Much of the experimental work was carried out on 0.75 w/c cement pastes. This high w/c was chosen because it would have a high porosity, allowing deeper penetration of surface treatments and more rapid carbonation. Cement pastes of 0.5, 0.6 and 0.7 w/c were also prepared for comparison, 0.5 w/c being an average composition which is more commonly used.

Cement Paste Preparation Method

The 0.5 w/c cement paste was prepared by mixing cement and deionised water until homogenous, and casting it in a 48 mm diameter by 75 mm long cylindrical pot. To minimise the inclusion of air bubbles in the sample, it was vibrated during casting. To avoid bleeding and loss of water the pot was sealed and rotated for 24 hours following casting.

To prepare 0.6, 0.7 and 0.75 water to cement ratio pastes without segregation or bleeding the Gukild - Carlsen method described by Markestad was used (83). The method involved prehydrating a portion of the cement by ballmilling a 3 w/c cement slurry for 24 hours. The slurry was then used with appropriate additions of cement and water to cast similar cylinders as described for the 0.5 w/c cement pastes.

Unless otherwise stated, the cement paste samples were cured in their pots at 20°C for 28 days.

2.3.2. Concrete Production.

Concrete beams (500x100x100mm) were prepared for natural carbonation experiments, using siliceous and calcareous aggregates for comparison.

Mix Design

A high water to cement ratio mix was chosen to encourage rapid carbonation. The mixes were designed so that the free water to cement ratios were equal to encourage similar rates of carbonation. This was achieved by determining the aggregate water absorptions, and assuming that on adding appropriate amounts of extra water to the mix, the surplus would be taken up by the aggregates becoming fully saturated.

Determination of Aggregate Water Absorptions

The water absorptions of the aggregates were determined in general accordance with BS 812: Part 2 (84). The results of the water absorption determinations are shown in Table 8. The aggregates were supplied dry Their moisture contents were checked and found to be 0.3% or less.

Table 8. Aggregate Water Absorptions

Aggregate Description	Percentage water absorption
Guiting Limestone 5-10 mm	7.1
Guiting Limestone 5 mm down	5.7
Ham River Gravel 5 - 10 mm	3.0
Ham River Gravel 5 mm down	1.4

Concrete Beam Production Method.

Details of the mixes used to make the concrete beams are given in Table 9. The beams were cast in general accordance with BS1881 Part 109:1983 (85), and cured in a high humidity environment in sealed plastic bags for 28 days. To check the quality of the beams, cubes were prepared and compression tested at 28 days in accordance with the relevant parts of BS 1881 (86,87,88,89).

Table 9. Concrete Mixes Used in Beam Production.

	Siliceous Mix		Calcareous Mix	
Coarse	5-10mm Ham River	4	5-10mm Guiting Limestone	45
Fine	< 5mm Ham River	4	< 5mm Guiting Limestone	35
Cement	Portland Cement	1	Portland Cement	1
Total Water		0.93		1 27
Free Water		0.75		0.75

The results of compression tests are sumarised in Table 10. The concrete made with the calcareous aggregate had a slightly lower compressive strength. Observations on a fractured surface showed that the limestone aggregate was very weak, as the fracture path had passed through the aggregates, whereas in the siliceous mixes it was around them.

Table 10. Twenty Eight Day Compression Test Results of Concrete Used to Prepare Concrete Beams.

	Siliceous Aggregate Concrete	Calcareous Aggregate Concrete
Average compresive strength in N/mm^2	26.2	24.4
Number of tests	6	6
Standard deviation	1.6	0.5

2.3.3. BRE Method of Preparing Mortar Blocks

An accelerated carbonation test on mortar blocks was carried out in joint collaboration with the Building Research Establishment (BRE). The work was undertaken at the BRE, using mortar making materials and technical assistance provided by the BRE.

Mortar blocks (size 50x50x25mm) were prepared using the following mix proportions :

Buxton lime	221.5g
Portland cement	578.5g
Sand (600um down)	3470.0g
Water	650.0g

The lime and the cement were dry mixed with a trowel. The sand was added and mixed, followed by the water. Initially 600g of water was added and mixed, adding and mixing the remaining 50g later.

The mortar was used to half fill clean and lightly oiled moulds. The mortar was tamped, before filling the mould and tamping again. The mortar was levelled off and vibrated until a film of water appeared on the surface.

The mortar blocks were left to harden for 24 hours under a damp sack, and a sheet of polythene before being demoulded. The blocks were left to cure for a further 7 days in a curing room at 20°C and 60% R.H.

After curing, surface laitance and mould oil were removed from all surfaces by abrasion. The blocks were drilled and plugged, so that hooks could be screwed and glued into the blocks.

2.3.4. Methods of Surface Treatment.

Unless otherwise stated, surface treatments were applied to naturally dried specimens, i.e. specimens which had a dry appearance, having been left to dry in the laboratory, or in a temperature contolled curing room held at 20°C for a minimum of 24 hours.

This approach may have resulted in some variation in the initial moisture contents of the specimens prior to treatment. It could be argued that the use of oven dried specimens might have been more appropriate. However the approach used can be justified from the point of view that under normal site conditions, a concrete surface would not be oven dried prior to treatment.

Two applications of each treatment were made by immersing specimens for 1 minute in the treatments. Where required, the surface hardeners were diluted according to manufacturers instructions with deionised water, and the water repellents with white spirit. Details of the dilutions are given in Appendix 3. Excess treatment was allowed to drain off. Twenty four hours elapsed between applications.

The specimens treated with surface hardeners were washed in deionised water 24 hours following the final application. This was done to simulate the normal site practice of washing the treated surface to remove any excess treatment.

2.3.5 Control of Moisture Levels

Use of Saturated Salt Solutions to Control Relative Humidity

The moisture levels in and around specimens frequently had to be contolled. This was achieved by the use of solutions of saturated salts to maintain a specified relative humidity in the surounding environment. BS 3718 : 1964 describes the use of saturated salt solutions, and the relative humidity they create at different temperatures (90). Table 11 lists the solutions used, and their variation in relative humidity with temperature.

Table 11. Relative Humidity of Air Over Saturated Solutions of Salt.
From BS 3718 : 1964 (90)

Saturated salt solution	**Temperature (° C)** 5	10	15	20	25	30	35	40	50	60
	Relative humidity (per cent)									
Ammonium sulphate	82	82	81	81	80	80	80	79	79	78
Sodium chloride	76	76	76	76	75	75	75	75	75	75
Sodium nitrite	-	-	-	65	65	63	62	62	59	59
Magnesium chloride	34	34	34	33	33	33	32	32	31	30

Where saturated salt solutions were used, the relative humidity was regularly checked with a capacitive thin-film/PT100 relative humidity probe. The temperature was monitored concurrently.

Moisture Content Determinations

The moisture content of samples was determined by weighing before and after drying at 100°C for 24 hours. The percentage moisture content by weight was calculated as follows:

$$\text{\% Moisture Content} = \frac{W_1 - W_2}{W_1} \times 100$$

Where : W_1 = Sample weight before oven drying (g)

W_2 = Sample weight after oven drying (g)

2.4 Carbonation

2.4.1 Natural Carbonation

Samples prepared for natural carbonation were left exposed in the laboratory. In all the carbonation experiments sample to sample contact was prevented, and a note was made of any specimen surface in contact with another surface eg. a supporting surface.

2.4.2 Accelerated Carbonation

To accelerate the process of carbonation the carbon dioxide content of the atmosphere surrounding specimens was increased, and the relative humidity optimised at 65%. Carbon dioxide levels were increased by flushing a high concentration carbon dioxide gas, either continuously or intermittently, through sealed carbonation chambers. The relative humidity was controlled at 65% R.H. with saturated sodium nitrite solution (see 2.3.4.). Three different methods of accelerated carbonation were used.

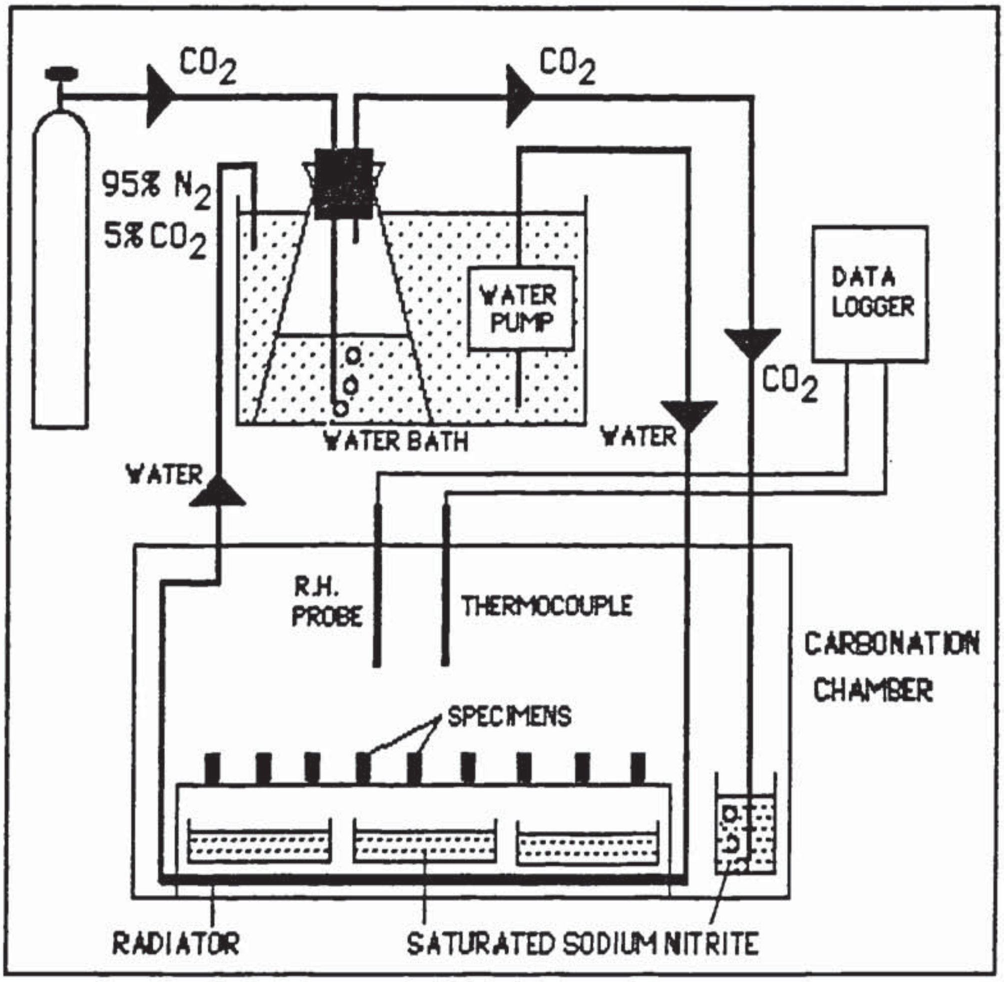
Carbonation with 5% Carbon Dioxide

Accelerated carbonation with 5% carbon dioxide was carried out in a 100 X 60 X 55 cm chamber illustrated in Figure 4. The temperature in the tank was maintained at 25°C by a simple radiator system of copper pipes in the base of the tank, with water circulating through them from a temperature controlled water bath. The relative humidity in the tank was controlled by saturated sodium nitrite in dishes placed at the bottom of the tank.

The temperature and relative humidity in the chamber were monitored using a thermocouple, and a relative humidity probe connected up to an Orion data logger. The data from the monitoring indicated that the temperature and relative humidity were at an average of 25°C and 67% R.H.

The carbon dioxide levels in the tank were enhanced by flushing a gas mixture of 5% carbon dioxide, 95% nitrogen through the tank. To ensure that the gas was not cold on entering the chamber, it was passed through a flask of water held in the temperature controlled water bath. To ensure that the gas contained an appropriate moisture content on entering the tank, it was passed through a dish of saturated sodium nitrite.

Figure 4. Carbonation Chamber With 5% CO_2

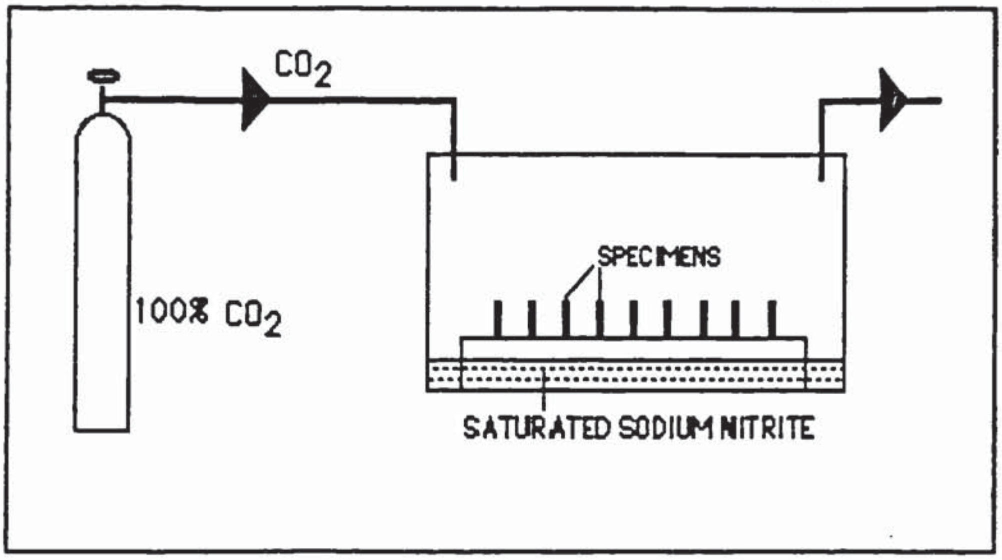


Carbonation with 100% Carbon Dioxide

Accelerated carbonation with 100% carbon dioxide was carried out in a 25 X 25 X 12 cm sealed container illustrated in Figure 5. The 100% carbon dioxide was acheived by periodically flushing the container with 100% carbon dioxide. Flushing was carried out every Monday, Wednesday and Friday for thirty minutes. The relative humidity was maintained at 65% by a saturated solution of sodium nitrite in the base of the container.

Carbonating specimens were supported in a rack above the sodium nitrite solution.

Figure 5. Carbonation Chamber With 100% CO_2



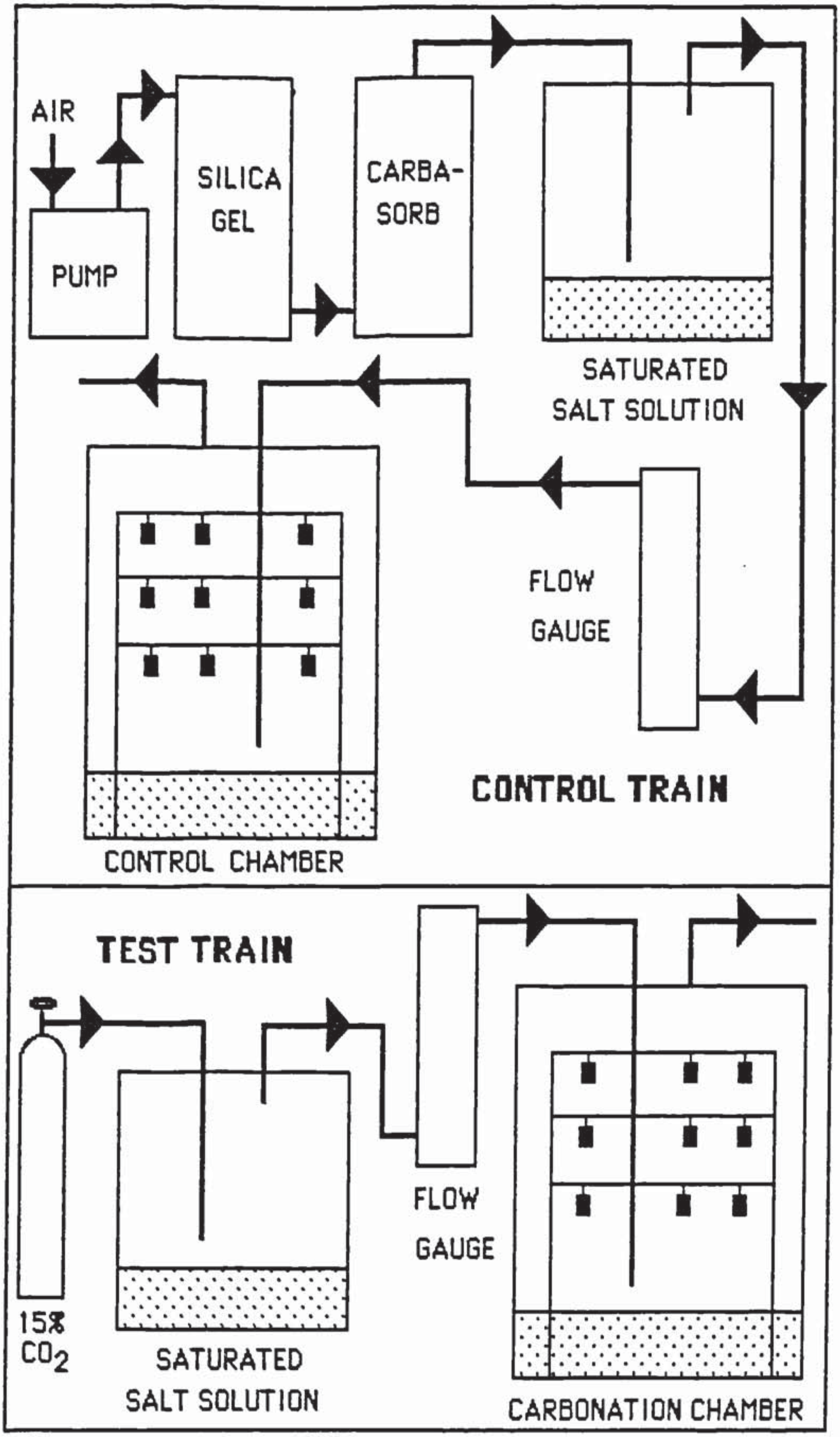
Carbonation Using a BRE Method

The BRE carbonation apparatus is illustrated in Figure 6. The apparatus consisted of two separate trains, a test train which had 15% carbon dioxide flushed through it, and a control train with carbon dioxide free air. The rate of gas flow was controlled at 0.2 l/min. The relative humidity was maintained at 75%. Samples were suspended in the carbonation chambers by hooking them onto lines.

2.4.3 Assessment of Carbonation Depth

A variety of approaches have been used to measure the depth of carbonation (91,92). Changes in mineralogy with carbonation can be detected using x-ray diffraction, petrography and thermal analysis. Changes in chemistry can be studied using infrared analysis, chemical analysis for carbonate, and

Figure 6. BRE Carbonation Apparatus.



analysis of expressed pore solution for alkalinity. Other less direct approaches involve the assesssment of physical changes in porosity, hardness and weight.

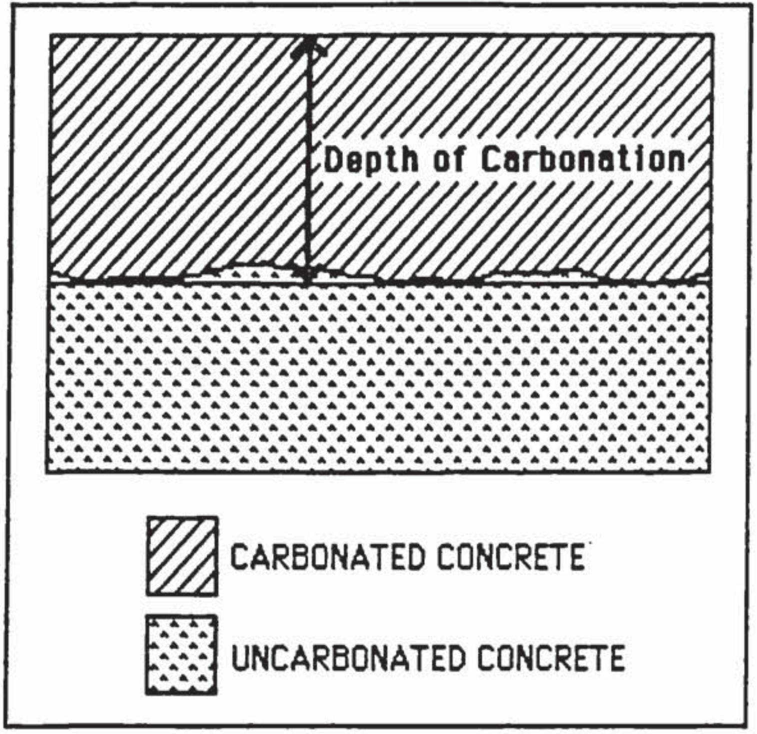
Phenolphthalein Testing

A simple, quick and effective method of assessing carbonation depths involves the application of a pH indicator spray to a freshly broken surface. Phenolphthalein is an indicator which is used frequently (6,38). It has a bright pink colour at pH levels greater than 9.2 , and remains uncoloured at low levels of pH (49).

The results of phenolphthalein testing give a useful indication of the depth to which cement paste may no longer protect the steel from corrosion; steel being liable to corrode at pH levels less than 9.5. However, the phenolphthalein test does have limitations because it will detect reductions in alkalinity due to leaching of lime and alkali hydroxides, as well as that due to carbonation (5).

Methods of phenolphthalein testing for carbonation have been described by RILEM and Roberts (5,49). The method adopted involved the use of a phenolphthalein solution prepared by dissolving 1g of phenolphthalein in 50ml of alcohol, and diluting it to 100ml with water. The solution was applied to a freshly broken surface, cleaned of dust and loose particles. The maximum depth of carbonation was measured 24 hours after application (see Figure 7). Anomolous results of excessive carbonation, for example that associated with microcracking, were not included.

Figure 7. Measurement of Carbonation Depth.



Petrographic Assessment

Calcite, the main crystalline product of carbonation, can be readily identified in thin section using a polarising microscope as it has a very distintive optical property of extreme birefringence (93). Viewed under cross polarised light this property is exploited to detect the microcrystalline calcite crystals formed during carbonation. The depth to which the calcite crystals are observed gives an indication of the depth of carbonation.

To measure the depth of carbonation using optical microsopy thin sections were prepared. Thin sections were made from oven dried slices which had been impregnated with a blue dyed araldite resin. A lapped surface was mounted on a glass slide. The excess material was cut and ground away until a 30 micron section remained. A cover slip was mounted over the section to protect it.

The thin sections were observed under a polarising microscope, using plane and cross polarised light, and magnifications up to 400 times.

2.5 Chemical Analysis for Composition

2.5.1 Semi-Quantitative X-Ray Analysis

A scanning electron microscope (SEM) fitted with an x-ray analyser can be used to analyse semi-quantitatively for elements with atomic numbers greater than 10. The system works by bombarding the specimen with electrons, causing atoms to become excited and x-rays are produced with wavelengths characteristic of the elements that have been excited. Detection of the x-rays allows the assessment of the chemical constituents of the volume being excited.

A Cambridge Instrument Company SEM S150 fitted with a LINK energy dispersive x-ray analyser was used to carry out semi-quantitative chemical analysis.

2.5.2 X-Ray Diffraction.

X-ray diffraction was used to identify crystalline material in samples. Results directly from the an x-ray diffractometer are presented in a graphical form. Peaks at different positions represent diffractions from minerals within the sample. The d values for the observed peaks may be calculated using the Bragg equation (94) as follows:

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

where d = interplanar spacing

n = order of diffraction

(first order diffractions were looked at initially)

Δ = wavelength of the radiation

(the wavelength of copper radiation is 1.5405Å)

θ = the angle of diffraction

Oven dry samples were subjected to x-ray difraction analysis and scanned in a Philips x-ray diffractometer with copper K alpha radiation (wavelength 1.5405Å) between 10 and 40°. The intensities of the observed peaks were measured on a relative scale. Observed d values were averaged and compared with data for minerals thought to be present in the samples (95,96,97).

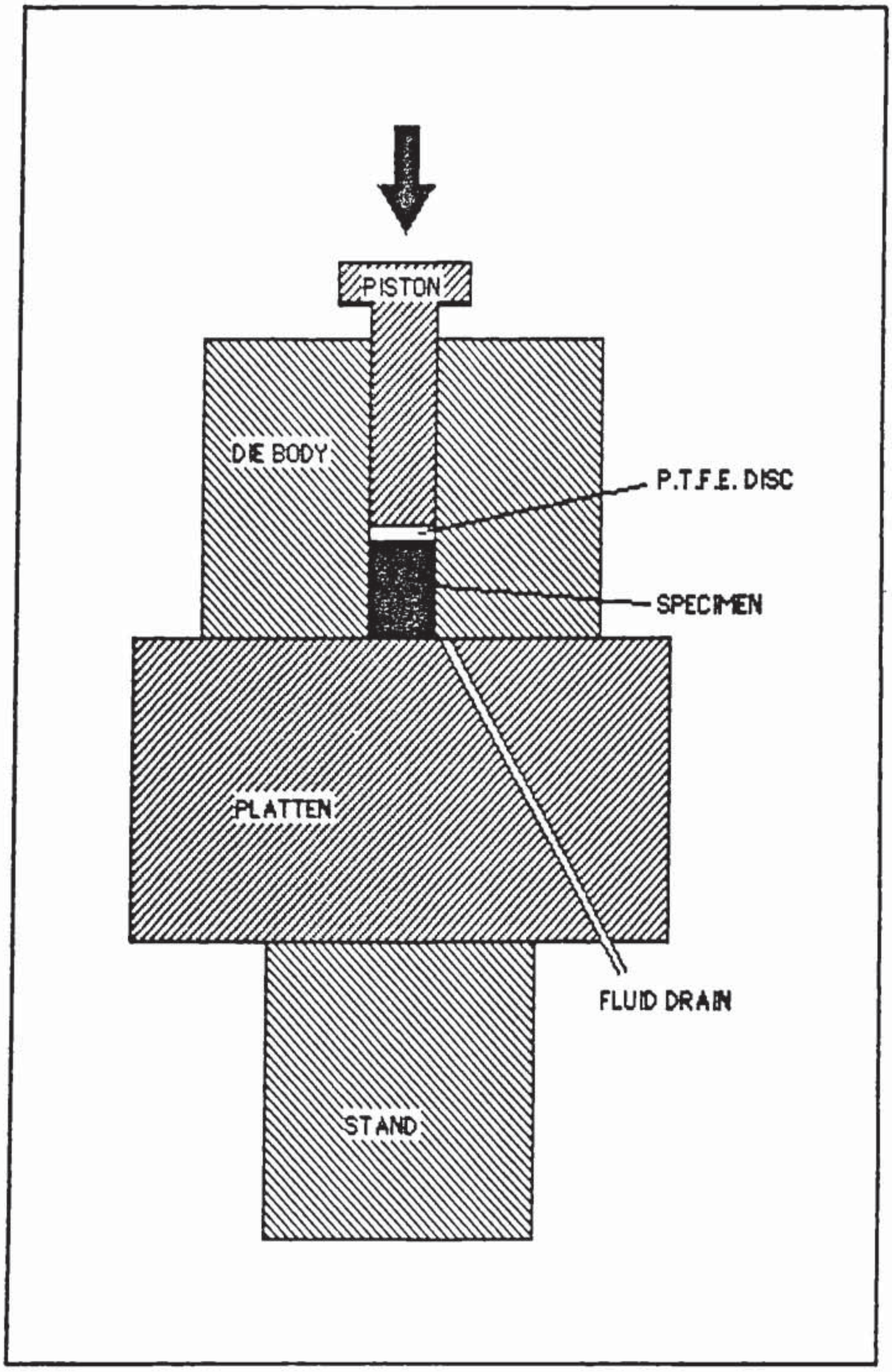
2.5.3 Pore Solution Analysis

Pore liquid in cement pastes or concrete may be extracted and analysed by procedures described in 1973 by Longuet et al (98). This technique has been used extensively (99,100,101,102).

Pore Solution Expression

Figure 8 shows the pore press used to express pore solution. The pore press containing a specimen was loaded at 3.5 tonnes per minute to 60 tonnes. As the specimen was squeezed the pore solution forced out was collected from the fluid drain into a syringe.

Figure 8. Schematic Representation of Pore Press for Fluid Extraction.



Analysis for pH/[OH$^-$]

Pore water was analysed by titration against nitric acid on the day that it was collected. Phenolphthalein was used as the indicator. Knowing the molar concentration of the hydroxide ion the pH of the pore solution could be calculated as follows:

$$pH = 14 + \log [OH^-]$$

The pH of less alkaline solutions was measured directly using a combined electrode connected to a digital pH meter. The electrode was calibrated with buffer solutions solutions of pH 7 and 9. A standard immersion time of one minute was used.

For each sample an average of three readings was taken.

Analysis for Na, K and Ca Ions.

Sodium, potassium and calcium were analysed using a flame photometer. Flame photometry relies upon the fact that compounds of alkali and alkaine earth metals can be thermally dissociated in a flame and some of the atoms produced will be further excited to a higher energy level. On returning to the ground state, radiation is emitted with a wavelength specific to the element. The radiation is mainly in the visible region of the spectrum, the intensity of which is measured by the flame photometer. Over certain ranges of concentration the light emitted is proportional to sample concentration.

A Jenway model PFP 7 flame photometer was used to analyse the samples, following the procedure given in the instruction manual (103). Standard samples of appropriate and known concentration were analysed to produce a linear calibration curve.

By trial and error the samples for analysis were diluted so that their result also lay on the linear part of the calibration curve. For each sample two diluted subsamples were prepared and two readings were taken on each subsample. Results were averaged and converted into ionic concentrations by reading off the relevant calibration curve.

Analysis for Chloride Ions

Chloride ions were analysed for using a spectrophotometric method. The method is similar to the flame photometer method, in that a standard calibration curve is used. However, it is the intensity of a highly coloured complex formed in the presence of chloride ions that is measured.

To a known dilution of pore solution made up to 10ml, 2ml of 0.25 molar ferric ammonium sulphate in 9 molar nitric acid, and 2ml of saturated mercuric thiocyanate in ethanol were added. The mixture was shaken and left to stand for ten minutes, allowing the thiocyanate ion to be displaced by any chloride present. On dispacement the thiocyanate forms a highly coloured complex with the ferric ion (104).

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

The analysis was carried out using a spectrophotometer set to measure light with a wavelength of 460 nanometers. Duplicates of each sample were analysed, and an average result calculated.

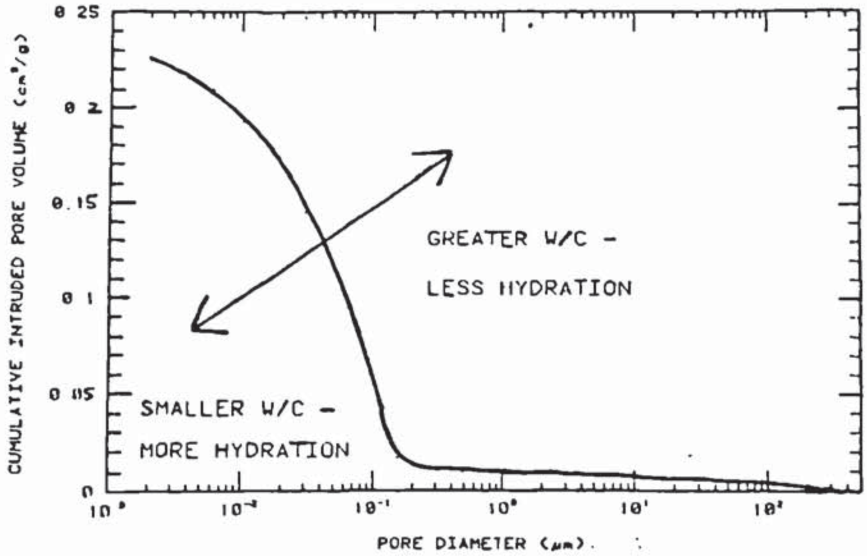
2.6 Microstructural Assessment of Porosity and Hardness.

2.6.1 Mercury Intrusion Porosimetry (MIP)

The technique of mercury intrusion porosimetry (MIP) is one of the dominant procedures for the determination of pore size distribution in cement pastes (17). A typical cummulative distribution obtained by this method is given in Figure 9. The distributions typically have a threshold pore size, greater than which only a small volume of pores is found, and below which the cummulative pore volume rises relatively smoothly. Pastes with various water to cement ratios, different degrees of hydration, and/or the presence of various additives or admixtures all exhibit the same general shape. However if the details of the cement preparation or hydration are changed, the distribution is shifted as shown in Figure 9.

Figure 9. Typical Pore Size Distribution of a Cement Paste.

After Winslow (17).



Theory of MIP

A non wetting liquid such as mercury, which has a contact angle with a given solid greater than 90^0, will intrude open pores of a solid only under applied pressure. The pressure required is a function of the contact angle, the surface energy of the liquid, and the geometry of the pores. For the case of a cylidrical pore the following relationship is given by Washburn (105)

$$p = \frac{-4Y \cos@}{d}$$

where p = pressure required to intrude a pore (N/m^2)

d = diameter of the intrude pore (m)

Y = surface tension of the liquid (N/m)

@ = contact angle between the liquid and the pore wall

If the contact angle of cement paste with mercury is known, together with the surface tension of mercury (474×10^{-3} N/m), measuring the volume of mercury intruded into a cement paste at known applied pressure will give some idea of the pore size distribution of that cement paste (106,107).

However, it must be noted that the pore diameter which is determined is the pore entry diameter. Pores can only be entered via the pathways which lead to them. Hence pores accessible only through restricted entryways will be tallied as part of the diameter class of the entryways. Also pores which are isolated from the surface with no entryways will not be penetrated, and will therefore be excluded from the determination (107).

Apart from the obvious problem of measuring pore entry diameters rather than directly measuring pore sizes, there are other problems associated with mercury intrusion porosimetry. These include the modification of the contact angle between cement and mercury when different drying regimes are used.

For P-dried pastes, where pastes are dried over a mixture of magnesium perchlorate hydrates, the contact angle has been found to be 130^0, but for oven dried paste it was 117^0. This is thought to be possibly due to some residual water being retained on the surface of P-dried pastes, in comparison with complete dehydration of the surface with oven drying at 105^0C (107).

More recent work has indicated that the contact angle may vary for cement pastes of different ages (108),and that intrusion into a paste causes damage (109).

MIP Method.

The pore size distributions of cement paste specimens were determined using a Micromeritics Model 900 Series mercury intrusion porosimeter. The determinations were made on approximately 5x5x2mm sample pieces, cut from the oven dried cement paste discs. Sample pieces weighing in total about 5 grammes were used to make the determination in accordance with the instructions in the Micromeritics instruction manual (106).

The oven dried sample pieces were weighed, and placed in a cell in a pressure vessel. The vessel was evacuated, and the sample cell filled with mercury. A hypobaric pressure analysis was carried out, before filling the system with a pressure transmitting fluid for a hyperbaric pressure analysis. Readings of counts and pressure were taken at regular intervals, up to a maximum pressure of 45,000 PSI.

For each pressure at which a reading was taken, the volume of mercury penetrating the sample was calculated as:

$$\text{penetration volume of mercury} = \frac{\text{cell factor} \times \text{counts}}{\text{sample weight}}$$

Pressures were converted into pore size diameters. Using a contact angle of 117°, the equation on page 76 was simplified to the following form :

$$\text{pore diameter } (\mu m) = \frac{124.84}{\text{pressure (psi)}}$$

The results of each determination were plotted as penetration volume of mercury (cm^3/g) versus pore size diameters (µm) on a log scale. Examples of the plots obtained are shown in figures 10 and 11.

Figure 10. Repeatability of Three MIP Determinations of 0.75 W/C, 28 Day Cement Pastes.

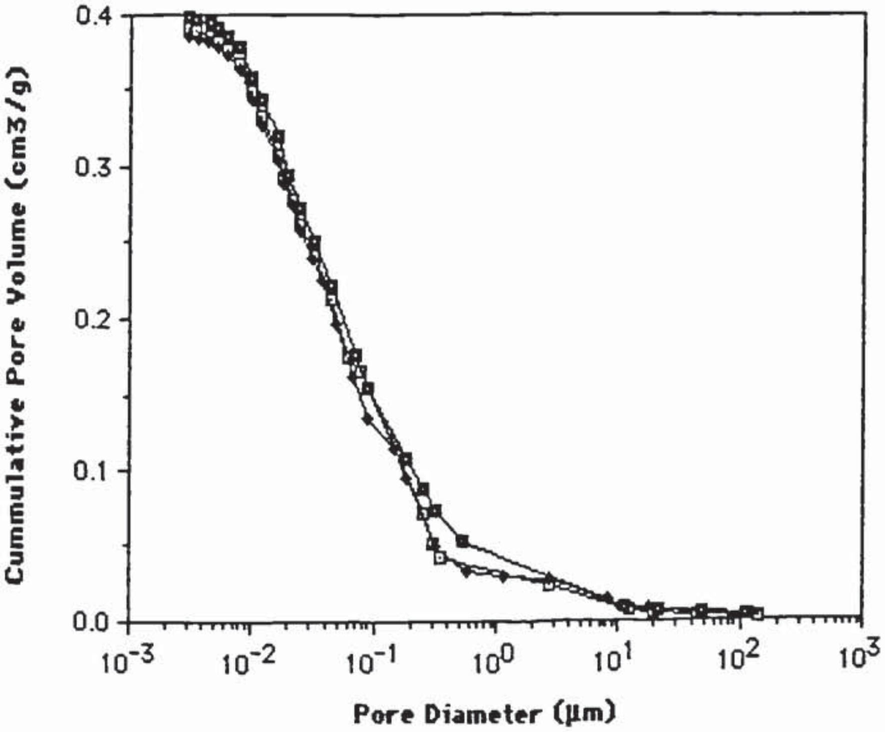
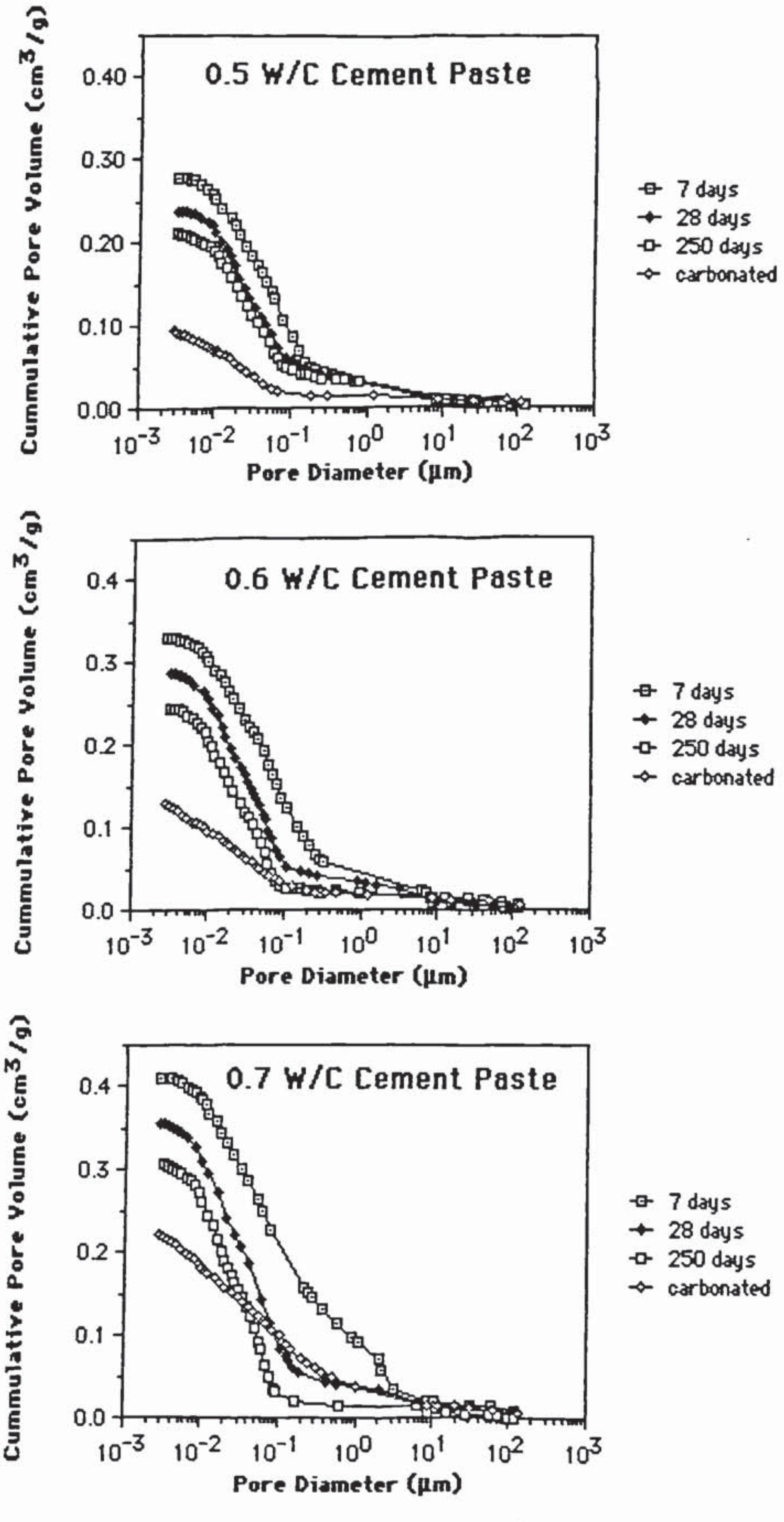


Figure 11. MIP Pore Size Distributions of Cement Pastes with Variations in W/C, Age and Carbonation.



Validation of MIP Technique

To assess the repeatability of a determination, three determinations of a 28 day, 0.75 w/c, cement paste were made, the results of which are shown in Figure 10.

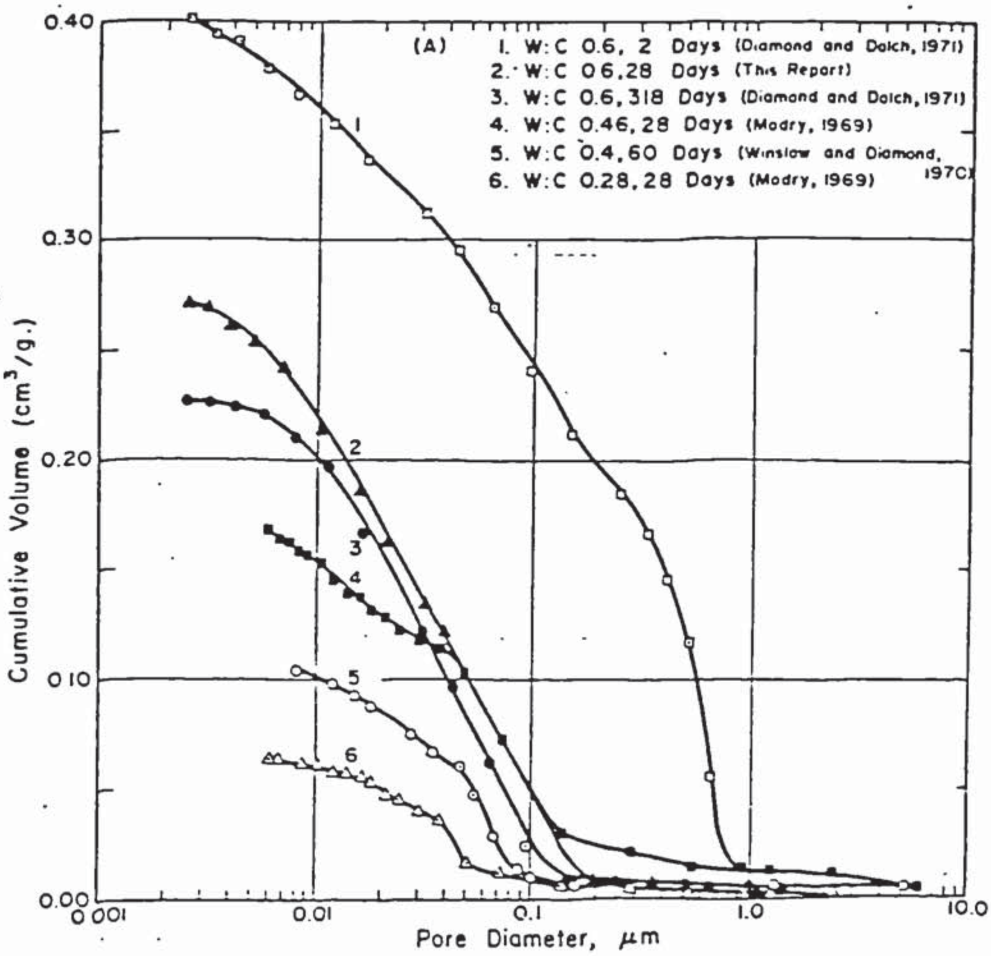
To illustrate the usefulness of the technique for detecting differences in cement pastes of varying w/c, age and state of carbonation, determinations were made on the cement paste samples described in Table 12. The uncarbonated samples were cured in sealed pots. The carbonated samples were cured for 60 days under saturated calcium hydroxide, and fully carbonated under accelerated carbonation conditions using 100% CO_2 (see 2.4.2.). The results of these determinations are shown in Figure 11.

Table 12. Description of Samples used for MIP Validation Determinations.

W/C	Age in Days	Carbonated
0.5	7	X
0.5	28	X
0.5	250	X
0.5	60	√
0.6	7	X
0.6	28	X
0.6	250	X
0.6	60	√
0.7	7	X
0.7	28	X
0.7	250	X
0.7	60	√

The MIP results in Figures 10 and 11 showed that the same results may be obtained by repeating determinations on similar samples, and that differences in pore structure due to different histories can be readily detected. The results shown in Figure 11 are comparable with work done by others shown in Figure 12.

Figure 12. Representative Pore-Size Distribution Curves by Mercury Intrusion Porosimetry Mostly Redrawn from the Literature After Diamond 1971 (110).



2.6.2 Microhardness.

The microhardness of a cement paste is a mechanical property which is predominantly porosity dependent (111). Cement pastes are not commonly assessed by microhardness measurements, partly because of their heterogenous microstructures. This problem can be overcome by taking a significant number of measurements (112).

Scheetz et al (113) have used microhardness of cement pastes as a criterion to determine the compressive strength of a specimen. During their studies they observed that hardness increases with curing time. Other instances where microhardness measurements have been used on hydrated cement pastes include :

1. The assessment of the impregnation of sulphur into cement paste(114).
2. The testing for unsoundness of cements containing magnesiun oxide(115).
3. A study of effects of different surface finishing techniques (116).

In this last investigation microhardnes profiles were used to look at the variation in hardness from the surface inwards.

Theory of Microhardness.

The hardness of a material is a measure of its resistance to permanent deformation or damage. The precise definition depends entirely on the method of measurement, which will determine the scale of hardness obtained. Two scales of hardness are not necessarily related unless certain conditions of similarity in the mode of testing are fulfilled (117).

The method of measuring hardness is not dependent on a single physical property, but may involve both elastic and plastic deformation characteristics of that material. Another feature of hardness testing is the possibility of the hardness of the material changing appreciably as the test is applied. For example, in an indentation test the initial penetration of the indentor increases the resistance of the material to further indentation (117).

A Vickers microhardness tester is suitable for measuring the microhardness of cement pastes. It applies a static load to a square based diamond pyramid for a standard time. On removal of the load, the diagonals of the impression are measured by means of an eye piece. The hardness is determined as a function of the load applied and the average length of the diagonals (118).

$$\mathrm{VHN} = \frac{1854\ P}{d^2}$$

where VHN = Vickers Hardness Numeral in kg/mm^2

P = load applied in grammes

d = average length of the diagonals in microns

Microhardness Method.

Pieces 100 to 600 mm^2 were wet cut, oven dried, and vacuum impregnated with araldite resin. The specimens were ground with increasingly finer grades of silicon carbide and aluminium oxide, and then diamond polished to a 1µm finish.

A Vickers Microhardness Tester was used to make the determinations. An area for indentation was chosen, avoiding cracks and voids. The surface was indented with a standard pyramidal diamond under loads of 20 or 50 grammes. The indentation was viewed under reflected light at up to X 750 magnification. The indentation diagonals were measured to the nearest 2µm.

The Vickers Hardness Numeral was calculated using the equation on page 83.

Validation of the Microhardness Technique

Two different methods (1 and 2) of microhardness testing were carried out and compared. The basic method common to both procedures is described above. The differences in the two procedures are described below and summarised in Table 13. By comparing the two methods, a decision was made as to which method would be used for all the microhardness work. For reasons justified below, Method 2 was chosen.

The araldite resin used in Method 2 was less viscous, and consequently impregnated the samples more thoroughly allowing a better polished finish to be obtained. Although a load time of 30 seconds is recommended, no significant difference was observed between results obtained using load times of 15 or 30 seconds.

Table 13. Summary of Differences Between Microhardness Methods 1 and 2.

	Method 1	Method 2
Impregnating resin	Araldite MY 753	Araldite MY 753
	Hardener HY 951	Hardener HY 992
Vickers Microscope	M41	M55
Load time (secs)	30	15
Number of readings :		
- taken	34	10
- discarded	4	0

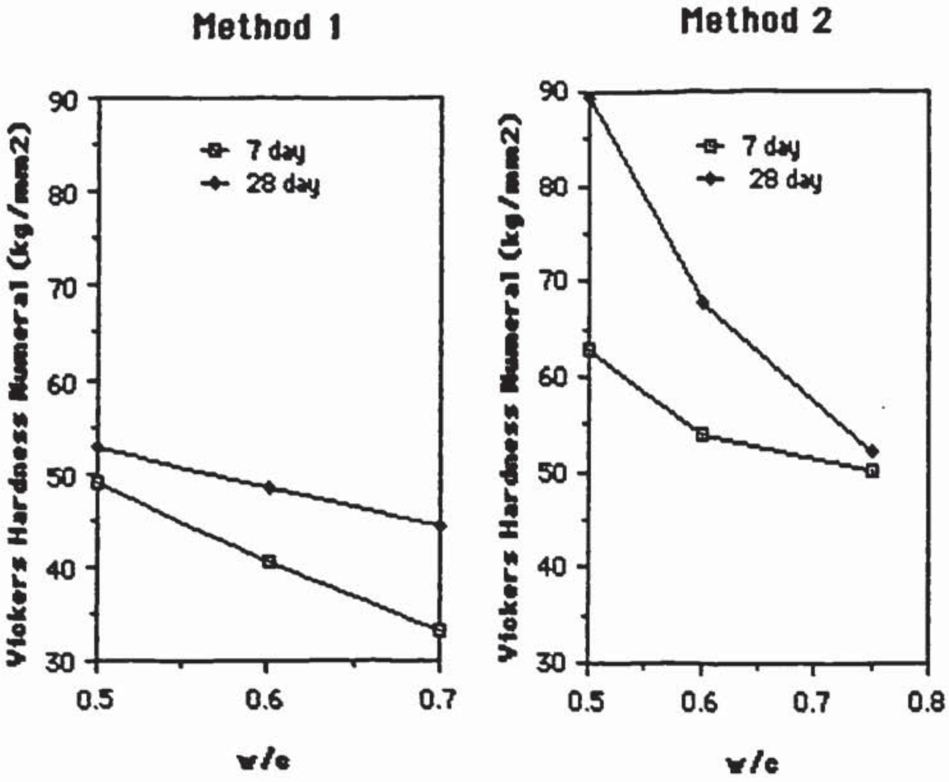
Two different microscopes were used in Methods 1 and 2. This was a matter of convenience, using microscopes which were available at the time the work was carried out. A Vickers M41 was used in Method 1, and a Vickers M55 in Method 2.

In Method 1 34 readings were taken, the two highest and lowest were discarded, and an average of the remaining readings calculated. A large number of readings were required to obtain a valid result, probably because of the poorer surface finish.

The results using Method 2 were calculated by taking an average of the ten readings, and checking that none were outside plus or minus two standard deviations of the mean. Generally, the readings were within these limits but if outside, it was discarded and an additional reading taken to replace it.

A series of tests on 7 day and 28 day cement pastes with varying water to cement ratios was carried out using Methods 1 and 2, the results of which are shown in Figure 13.

Figure 13. Comparison of Hardness Results Obtained from Specimens Prepared by Two Different Methods.



The results show that both methods produce data with similar trends of decreasing hardness with increasing water to cement ratio, but increasing hardness with age. These trends are consistent with MIP results (see Figure 11), where samples found to have a high porosity had low hardness values, and vice versa.

The striking difference between the two sets of results is that the results from Method 2 are considerably higher than those produced by Method 1. This was probably due to the more fluid nature of the impregnating resin used in Method 2. The resin penetrated the samples more fully, giving extra support to the samples. Thus indentation was resisted, hence increasing the perceived hardness of the specimens.

Another difference between the two sets of results is that using Method 1 the difference in hardness between 7 and 28 day specimens appears to increase with water to cement ratio, but using Method 2 the converse trend is apparent. This is probably due to the resin used in Method 2 penetrating smaller voids, the volume of which varies with water to cement ratio, and age (again see MIP results in Figure 11).

The above discussion indicates that the impregnating resin used in sample preparation for microhardness determination strongly influences the value of the microhardness result. Attempts were made to produce polished specimens without using an impregnating resin. It was found that for the lower water to cement ratio cement pastes an adequate polished finsh could be achieved, but this was not the case for the softer 0.75 w/c samples, which were to be used predominantly.

It was decided that Method 2 should be adopted for the rest of the work. This Method was chosen because the better polished finish produced a surface from which fewer readings were required for a reliable result. Hence the time taken to determine an individual value was reduced, so that more data could be obtained in the time available.

An attempt was made to compare the results obtained by the two Methods with those obtained by other workers. The general trend of decrease in hardness with increase in water to cement ratio was consistent with results obtained by Sadegzadeh et al (116). The trend of increase in hardness with age was the same as the trend found by Scheetz et al (113). Apart from these general trends, results could not be directly compared because of the variation in samples, and methods of preparation, used in other studies.

CHAPTER 3.

Chemical and Physical Properties of Carbonated Surfaces.

3.1 Introduction

The effect of carbonation on concrete has been extensively researched, and hence the main changes in the physical and chemical properties are well documented. These changes have been described in detail in Chapter 1, but may be summarised briefly as follows :

Chemical Changes - Conversion of calcium bearing phases in the cement paste to calcium carbonate with some production of silica gel.
- Reduction in alkalinity of the pore solution of the cement paste.

Physical Changes - Reduction in porosity causing :
  - increases in strength, density and surface hardness;
  - decreases in permeability.

Much of the evidence for these changes has been obtained by comparing the properties of a carbonated surface in its entirity with that of uncarbonated material of the same composition (36,44,53,55,56). A lot of this work was done using accelerated carbonation conditions.

It was clear that a gap existed in the knowledge of the alteration of properties with distance in from a carbonated surface. Also, that a direct comparison of changes in specimens carbonated under accelerated and natural conditions would assist in establishing whether results from accelerated carbonation tests could realistically predict performance under natural exposure conditions.

Properties investigated in this Chapter include porosity, hardness and chemistry of expressed pore water. These properties were investigated in relation to the carbonation front determined by phenolphthalein testing, and petrographic examination of the carbonated surface.

3.2 Previous Work.

Phenolphthalein testing for carbonation has been used extensively (46). Details of the test are given in 2.4.3. Views of its accuracy and significance have varied considerably over the years.

In 1969 Kishitani wrote that determination of carbonation by phenolphthalein was a method of high accuracy in ascertaining the relation between carbonation of concrete and corrosion of reinforcing steel (119). He carried out experiments which showed that changes in phenolphthalein colour coincided with the conversion of calcium hydroxide to calcium carbonate.

In 1984 Kashino (120) reported that the borderline for the start of steel reinforcement corrosion lies 8mm deeper than the depth of neutralisation as measured by phenolphthalein. It must be noted that, amongst others, Kitshitani and Kashino quote different pH levels at which phenolphthalein changes colour, and at which depassivation of the steel starts (see Table14).

Table 14. Variation in pH Levels for Phenolphthalein Colour Change and Depassivation of Steel Quoted in the Literature.

	Reference Number	pH at which phenolphthalein changes	pH of depassivation of steel
Kashino 1984	8	9 to 10	11
Kishitani 1969	7	8.5 to 10	10
Parrott 1988	6	9	11.4
Pourbaix 1966	9	-	9.5
RILEM	10	9.2	-

Another area of doubt concerning phenolphthalein testing for carbonation is its limit in defining the extent of the carbonating zone. Frequently the result of a phenolphthalein test indicates a definite boundary between carbonated and uncarbonated (119). It has been argued that phenolphthalein testing only provides an incomplete picture of carbonation, since it can not show the width of the carbonating zone (46).

Sergi (36) has also suggested that although the carbonation front as determined by phenolphthalein appears to be a sharp change from uncarbonated to carbonated, in reality it can not be the case. He proposed that the pH of a carbonating surface would drop in a series of steps, as basic constituents in the cement paste buffer changes in pH.

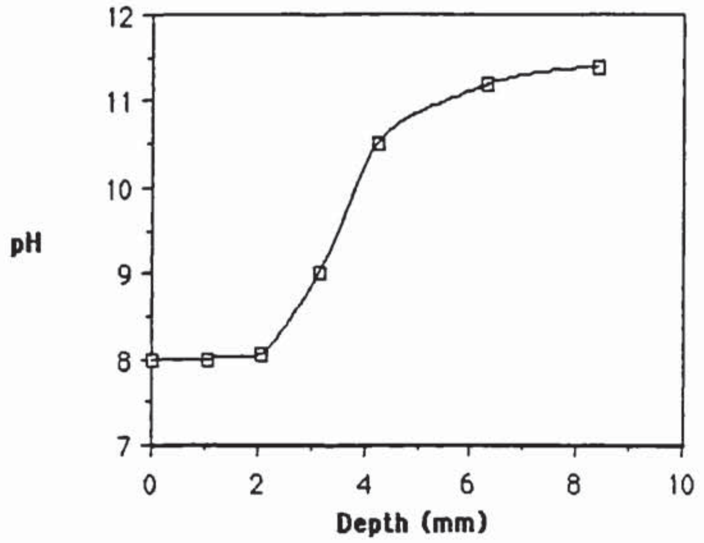
Sergi suggested that the pH of a carbonating surface would quickly drop to the pH of a saturated calcium hydroxide solution, as sodium and potassium hydroxides are neutralised. The pH would then remain at 12.5 for as long as there is sufficient calcium hydroxide to maintain a saturated solution. Thereafter, the pH would drop further until buffered by other basic constituents.

Work by Gonzalez et al (61) on a saturated solution of calcium hydroxide containing alkalis has indicated that there might be a buffering plateau at pH 10.4. They observed a plateau at this level when they bubbled carbon dioxide through a saturated solution of $Ca(OH)_2$ containing 0.1M NaOH and 0.1M KOH.

Gonzalez et al attributed this phenomenon to the buffering capacity of the simultaneous presence of sodium carbonates and sodium bicarbonates in solution. It has been established by Pourbaix that carbonates predominate above pH 10.4, and bicarbonates below this level (25)

Attempts have been made to look at the pH of the carbonating zone. Forrester (91) drew up a typical pH depth profile from the results of the application of universal indicator to freshly broken partially carbonated mortar (see Figure 14). Another approach used by Ohgishi (121) was to measure the pH of aqueous solutions in equilibrium with granules sampled from different depths.

Figure 14. Profile of pH Induced by Carbonation. From Forrester (91).



A different approach for assessing the pH and chemistry of the carbonating zone is pore water expression and analysis (see Section 2.5.3). This method has been used by Sergi (36) to compare pore solutions from cement paste discs carbonated under natural and accelerated carbonation conditions.

The results from Sergi's work on pore solution analysis of carbonated cement, which are important in relation to work in this Chapter, are summarised as follows and in Table 15.

Sergi found that with carbonation :

1. The pH of pore solution decreases. With higher concentrations of carbon dioxide this decrease is accentuated.

2. Sodium and potassium ions are removed from solution.

3. Chloride ions are released into solution.

Table 15. Ionic Concentrations in Pore Solutions Expressed from Cement Paste (OPC) Samples After Exposure to Different Atmospheres From Sergi (36).

Atmosphere	pH	Ionic Concentrations in mM/l				
		OH^-	Cl^-	Na^+	K^+	Ca^{++}
N_2	13.46	288	1	85	228	
Air	11.45	2.8	8	22	4	31
5% CO_2	9.22	$2X10^{-2}$	13	10	6	
100% CO_2	7.42	$3X10^{-4}$	16	23	20	

Sergi noted the fact that cements carbonated in air and 5% carbon dioxide had pore solution pH values in excess of 9, the approximate value above which phenolphthalein turns pink. This result was unexpected as phenolphthalein testing had indicated the samples to be carbonated, and led to the suspicion that the cement was not fully carbonated.

Closer examination of these carbonated surfaces tested with phenolphthalein revealed light pink 'spots' within a colourless matrix. Also, on saturation with water all of the area except for a narrow band at the edges showed a light pink colour.

Sergi concluded that the cores of certain particles, except near the edges, were not fully carbonated. Once the cements were saturated with water, hydroxyl ions from within the core could be leached out, thus raising the pH.

Sergi made suggestions as to what could account for the above changes in ionic concentrations with carbonation. He suggested that the removal of sodium and potassium ions from solution could be explained by the incorporation of the alkali ions into the C-S-H gel, or newly formed silica gel. Also, that the release of chloride ions could be caused by carbonation of small quantities of insoluble chloroaluminate in the cement paste by the following reaction :

$$3Ca.Al_2O_3.CaCl_2.10H_2O + 3CO_2 + 3H_2O \rightarrow$$

$$3CaCO_3 + 2Al(OH)_3 + CaCl_2 + 10H_2O$$

The release of chlorides into the pore solution potentially has important consequences with regard to any reinforcing steel in the vicinity. It is well established that free chlorides in the pore solution, in sufficient concentration, may stimulate corrosion reactions (4,122,123). The free chloride ion increases the electrical conductivity of the pore water and, as a result of its electrochemical properties, increases the rate of dissolution of metallic iron, so forming corrosion products (123).

Another area which was investigated by Sergi was the changes in porosity with carbonation. His results indicated that reductions in porosity were greater with increasing concentrations of carbon dioxide used for carbonation. Bier et al (39) also found that reductions in porosity were more distinct for samples carbonated under accelerated conditions.

Taking an overview of Sergi's work, there appears to be some evidence to suggest that accelerated carbonation is more severe than natural carbonation, as the changes in physical and chemical properties are more extreme after accelerated carbonation. For example, Sergi found that the pH of the pore solution was lower for accelerated carbonation than for natural carbonation. Also, porosity decreases were greater for accelerated carbonation.

Whether with time the samples carbonated under natural conditions would have similar properties to those carbonated under accelerated conditions is not established. However, Sergi concluded that the differences were relatively small, and hence their significance in accelerated carbonation experiments would depend on the nature of the research, and the accuracy required.

3.3 Aims of the Experimental Work.

The aims of the experimental work were to look at the changes in properties (pore solution chemistry, porosity and hardness) with depth of surfaces carbonated under natural and accelerated conditions. By looking at these changes in detail it was hoped that answers to some of the following questions might be found.

1. What is the accuracy of the phenolphthalein test ?
   How do the results from phenolphthalein testing compare with those from petrographic examination of thin sections ?
   Does the analysis of the profile of a carbonated surface indicate that important chemical and physical changes are occuring deeper into the concrete than the depth of carbonation indicated by the phenolphthalein test ?

2. What are the distribution of anions and cations in pore solutions from a carbonated surface, and how might they influence the chemistry of the carbonation process ?

3. Is there any evidence of buffering by basic constituents, suggested by a stepped decrease in pH across the carbonated surface ?

4. To what extent are chloride ions released into the pore solution with carbonation ?
   Is there any evidence of release ahead of the carbonation front, giving rise to an increased risk of chloride induced corrosion ?

5. Does the use of accelerated carbonation conditions result in more extreme changes in chemical and physical properties ?
   Can results from accelerated carbonation tests be used realistically to predict performance under natural exposure conditions ?

The experimental work in this Chapter was important for work in subsequent Chapters. It was necessary to have a detailed knowledge of the chemical and physical properties of carbonated surfaces, so that the performance of surface treatments applied to carbonated surfaces might be better understood. Also, the answer to question 5 was important for experiments carried out using accelerated carbonation methods.

3.4 Approach to Experimental Work.

The work was carried out on cement paste cylinders with 0.75 water to cement ratios. This high water to cement ratio was used to gain maximum carbonation depths in a minimum period of time.

The samples were prepared by carbonating samples from one surface inwards, the other surfaces being sealed from the atmosphere. The surface exposed to carbonation was a cut surface, used to minimise variation from the surface inwards, and avoid using a cast surface which might have a weak laitance layer.

A number of cement paste cylinders were carbonated simultaneously so that for each depth investigated there would be sufficient sample for analysis. This was particularly important for the pore expresion work, as pore water was pressed from a stack of slices sampled from each depth.

Samples for pore solution analysis were 5mm slices cut parallel to the carbonated surface. The slices were dry cut to avoid any leaching out of ions during wet cutting. The thickness of each slice was a compromise, 5mm being the minimum thickness which could be dry cut accurately using the facilities available. To gain a more complete profile of the carbonated surface, two sets of overlapping slices were prepared to give readings at average depths of 2.5mm intervals..

Previous work on carbonated cement pastes had revealed that after carbonation there is usually insufficient moisture in the samples for pore solution expression (36). To overcome this problem the samples were saturated with water, and allowed to equilibrate prior to pore pressing.

The assessment of the samples for porosity and microhardness follows on from the pore solution work. Porosity determinations were carried out on slices taken at similar depths as had been taken for the pore solution work. Microhardness determinations were made at the average depth positions of the slices, but on sections which had been taken perpendicular to the carbonated surfaces.

Throughout the work the aim was to look at the variation in properties across the carbonated surface. Initial determinations were made at depth in uncarbonated areas. Assessments were then made across the carbonated surface. Once depths were reached where little or no changes were being found, analyses were either made less frequently or not at all.

3.5 Details of Experimental Work.

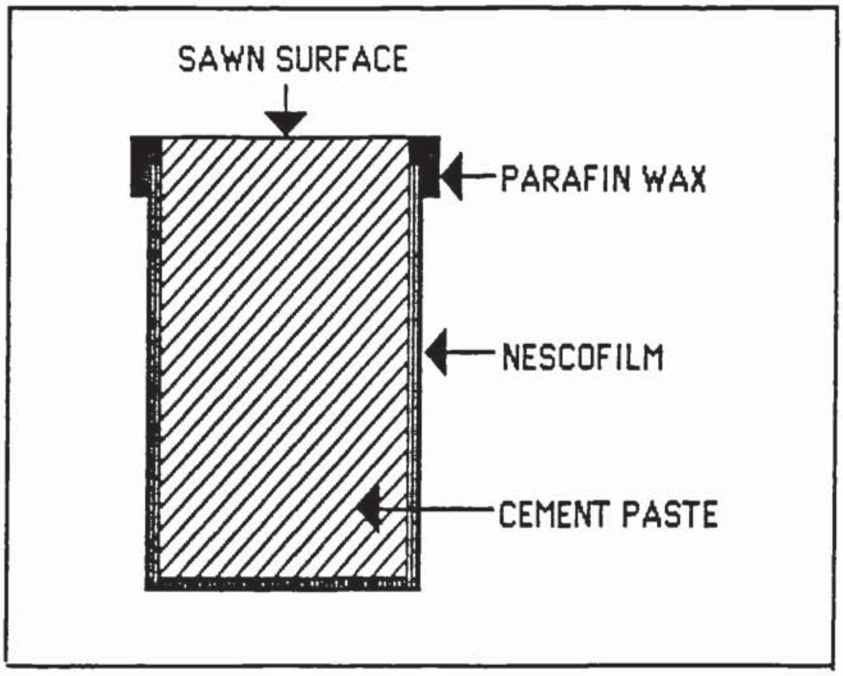
3.5.1 Sample Preparation and Carbonation.

Cement paste cylinders with a water to cement ratio of 0.75 were prepared using the method described in 2.3.1. After curing, the cement paste cylinders were demoulded, and each specimen had an end cut off (wet cut), to expose a surface for carbonation. After cutting, the samples were left to dry overnight in a curing room at 20°C.

The cement paste cylinders were sealed, leaving the cut surfaces exposed for carbonation. The cylinders were sealed with several layers of "nescofilm", a self sealing and air resistant film. At the top of each specimen melted paraffin wax was used to ensure an air tight seal. Figure 15 shows a diagram of a prepared specimen.

Prepared specimens were left to carbonate. Specimens for natural carbonation were exposed in the laboratory for 17 months. Specimens carbonated under accelerated conditions were placed in a carbonation chamber (see Section 2.4.2 for details of chamber) with 5%CO_2 at 67%R.H. and 25°C for 6 months.

Figure 15. Cement Paste Cylinder Prepared for Carbonation from the Sawn Surface Inwards.



3.5.2 Phenolphthalein Testing for Carbonation Depth.

During carbonation the samples were checked at regular intervals for depth of carbonation by phenolphthalein testing (see 2.4.3 for details of the test method). Once an adequate depth of carbonation had been achieved in the time available, a final phenolphthalein test was carried out with accurate measurement of the depth of carbonation. The samples were then prepared for analysis.

3.5.3 Petrographic Assessment of Carbonation Depth.

Thin sections of surfaces carbonated under natural and accelerated conditions were prepared and examined using the method described in 2.4.3. The thin sections were prepared from slices taken perpendicular to the carbonated surface. The slices were wet cut. The depth of carbonation was assessed on the basis of the depth to which calcite crystals were observed.

3.5.4 Pore Solution Expression and Analysis.

To prepare samples for pore solution analysis, slices were cut parallel to the surface. The slices were 5mm thick with the exception of the surface slice which was 2.5mm thick.

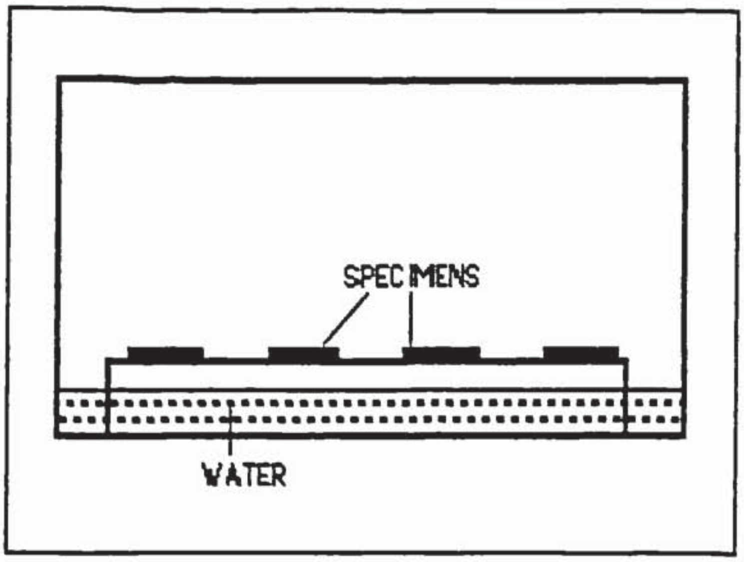
Two sets of samples were cut, one set at 0-5, 5-10,10-15mm etc., and another set at 0-2.5, 2.5-7.5, 7.5-12.5, 12.5-17.5mm etc. This gave a series of overlapping slices, with average depths of 1.25, 2.5, 5.0, 7.5, 10.0, 12.5mm continuing at 2.5mm intervals to a maximum average depth of 47.5mm.

The slices were dry cut. Cutting dust was brushed away from the surfaces of the slices. Samples were cut to give a total of eight slices at each depth.

The slices were saturated prior to pore pressing. Saturation was achieved by adding deionised water to the slices until no further water could be soaked up, but leaving no excesses of water on the surfaces of the slices The saturated slices were left to equilibriate for one week in a high humidity chamber over water (see Figure 16).

Pore solution expression and analysis was carried out using the methods described in 2.5.3. The specimen used for pore pressing was composed of a stack of eight slices taken from each depth. The pore solutions obtained were analysed for pH/OH, K, Na, Ca, and Cl.

Figure 16. High Humidity Chamber.



3.5.5 Porosity and Hardness Determinations.

Mercury intrusion porosimetry was carried out on oven dried (110°C) slices similar to those prepared for pore solution analysis. The procedure described in 2.6.1 was used.

Microhardness determinations were carried out on slices taken perpendicular to the carbonated surface. Details of the procedures used are given in 2.6.2. Microhardness Method 2 was used.

3.6 Results.

3.6.1 Measurement of Carbonation Depth.

The results of the measurement of carbonation depths using phenolphthalein testing, and petrographic examination of thin sections are shown in Table 16. Detailed petrograhic descriptions of the carbonated surfaces in thin section are given in Appendix 4.

Table 16. Results of Carbonation Depth Measurements Using Two Different Techniques.

Method of Carbonation	Phenolphthalein Testing	Petrographic Examination
Natural	6-7mm	6mm
Accelerated	8mm	8-9mm

Where a single value for the depth of carbonation is given, the boundary between carbonated and uncarbonated cement paste was distinct and hence well defined. However distinct boundaries were not always observed.

Phenolphthalein testing the naturally carbonated sample showed 6mm of fully carbonated cement paste, with an additional 1mm of partially carbonated material. Petrograhic examination of a thin section of an accelerated carbonated sample showed a slightly indistinct boundary at 8-9mm depth from the surface.

3.6.2 Pore Solution Analysis.

The results of the pore solution analyses are given in Appendix 5 and shown graphically in Figures 17 and 18. The carbonation fronts marked on the graphs, and in subsequent graphs in this Chapter, are the depths of carbonation measured by phenolphthalein testing and petrographic examination (see previous Section 3.6.1).

The results show that with carbonation the amount of hydroxide in the pore solution decreases with a corresponding decrease in pH. The pH of pore solutions from accelerated carbonated cement pastes was lower, 9.6 compared with 11.9 for naturally carbonated.

Both naturally and accelerated carbonated pore solutions contained similar low levels of chloride, increasing from 0 mM/l at the carbonation front , up to 4 mM/l just below the surface. No release of chloride ions was observed in advance of the carbonation front.

Sodium and potassium ion concentrations in naturally and accelerated carbonated pore solutions were found to fall to minimum levels in the region of the carbonation front, with some increase nearer the surface. In the case of the sodium in the samples carbonated under accelerated conditions, the level at the surface was almost completely restored to that found in uncarbonated material.

Figure 17. Anion Concentrations and pH of the Pore Water of a Carbonated Cement Paste With Depth from the Surface.

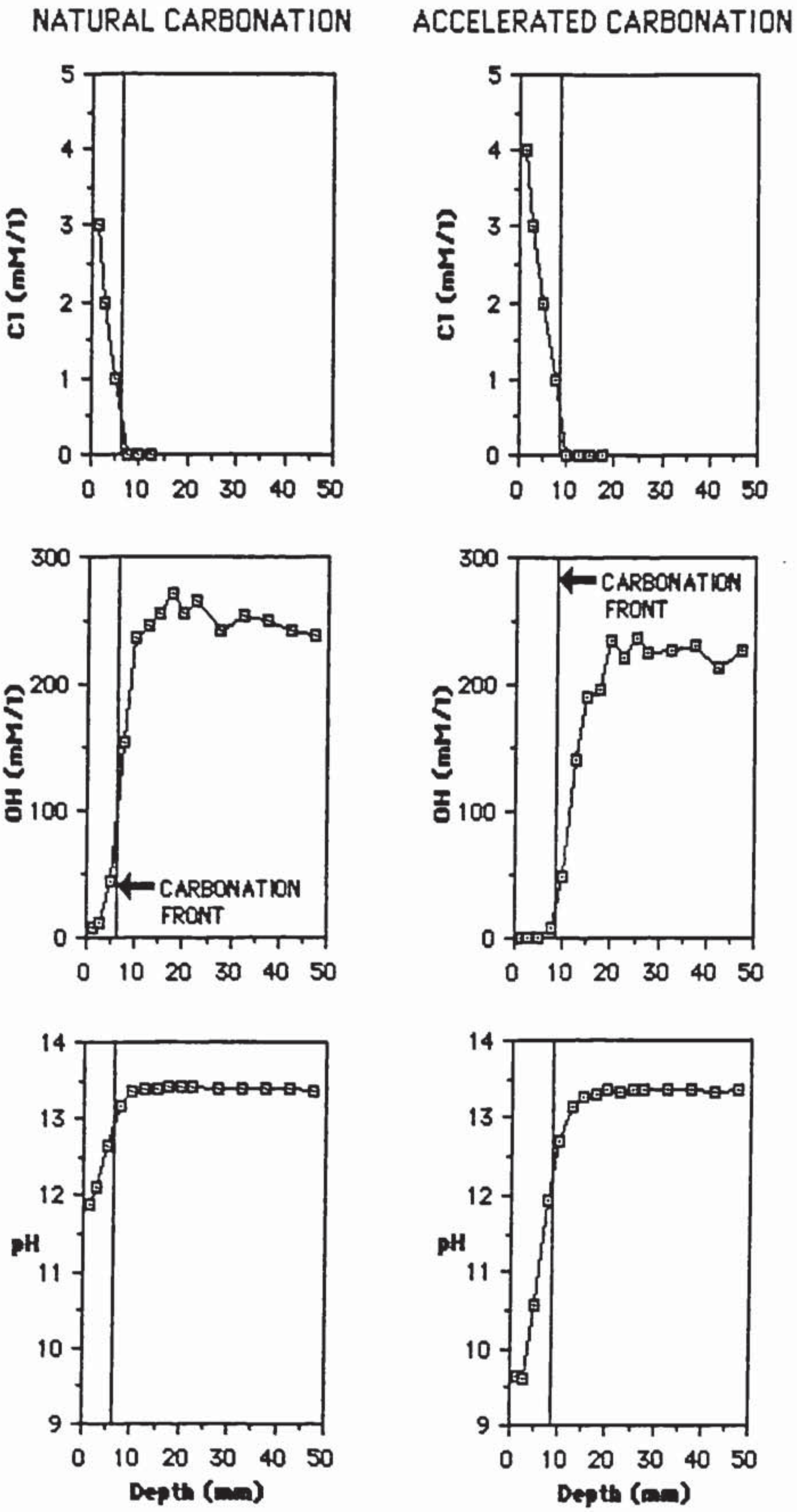
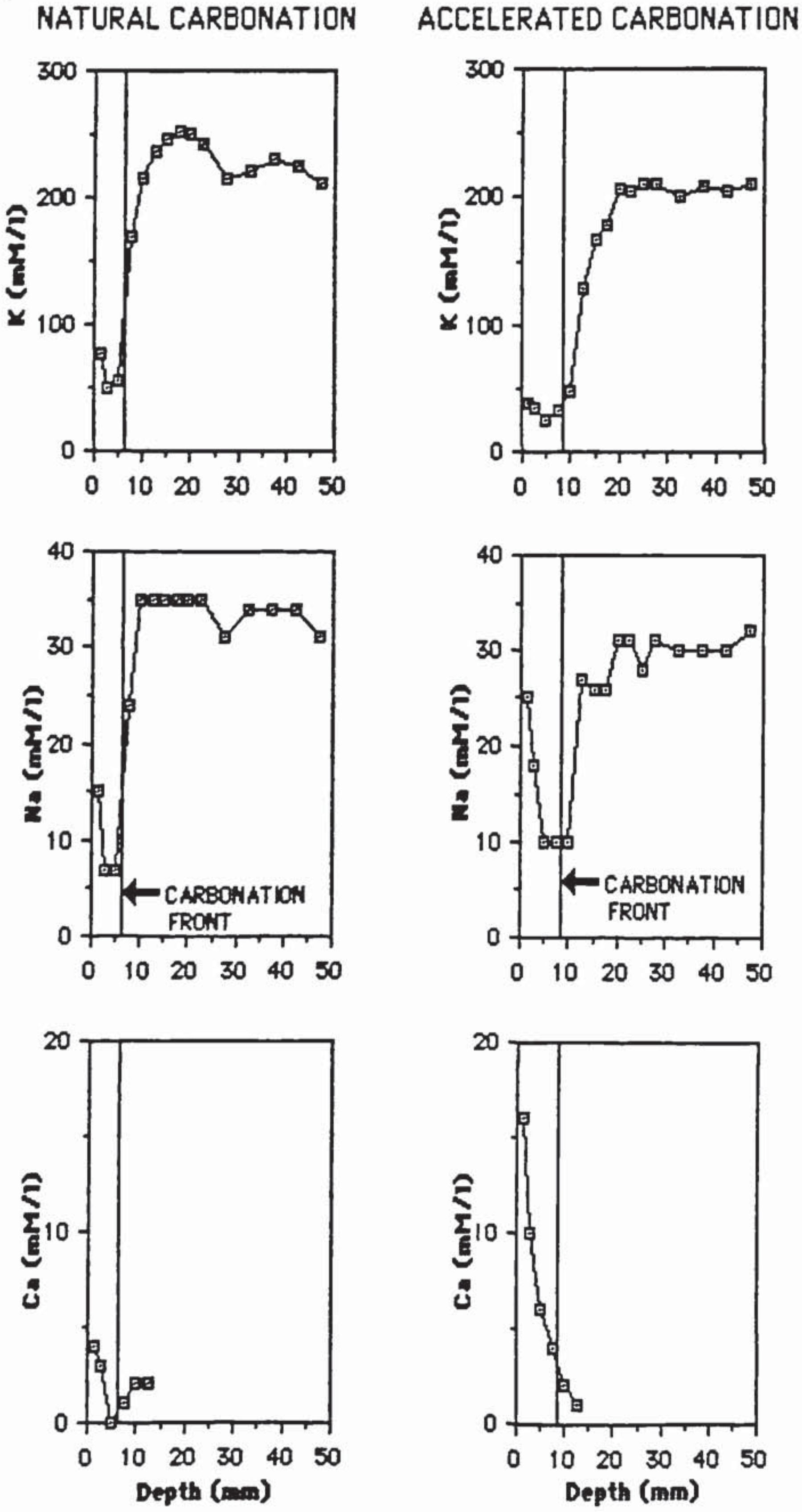


Figure 18. Cation Concentrations in the Pore Water of a Carbonated Cement Paste With Depth from the Surface.



Low levels of calcium were found in pore solution samples carbonated under natural conditions, no calcium being detected in the region of the carbonation front. In specimens carbonated under accelerated conditions, the levels of calcium in the pore solution were found to increase from the carbonation front up to the surface.

3.6.3. Porosity Determinations.

The pore size distributions for cement pastes carbonated under accelerated and natural conditions are shown in Figures 19 and 20. For both conditions levels of porosity decrease nearer to the surface. Overall there are slight pore volume decreases at all the pore sizes, but more so at pore sizes less than 0.1µm for naturally carbonated, and less than 10µm for accelerated carbonation.

Figures 21 and 22 show the changes in total porosity in relation to the carbonation front. These graphs indicate that there is some reduction in porosity in advance of the carbonation front.

The total pore volume changes were more extreme for accelerated carbonation specimens than for naturally carbonated specimens. The total pore volume for accelerated carbonated specimens fell from 0.39 to 0.24 cm^3/g, compared with 0.37 to 0.27 cm^3/g for naturally carbonated.

Figure 19. Pore Size Distributions of a Naturally Carbonated Surface Determined by Mercury Intrusion Porosimetry.

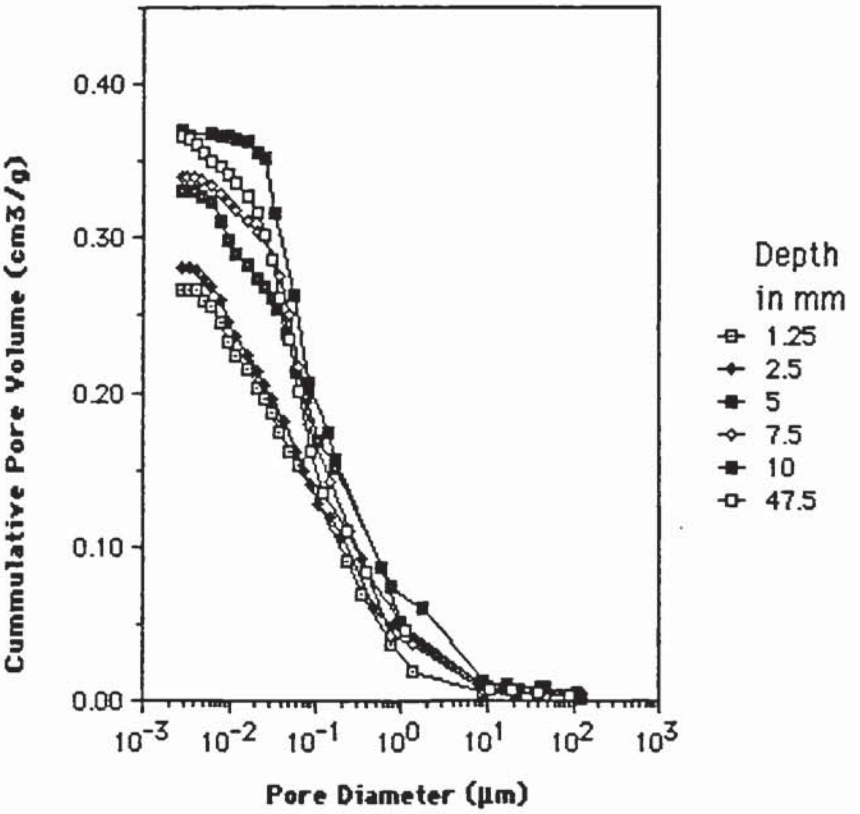


Figure 20. Pore Size Distributions of an Accelerated Carbonated Surface Determined by Mercury Intrusion Porosimetry.

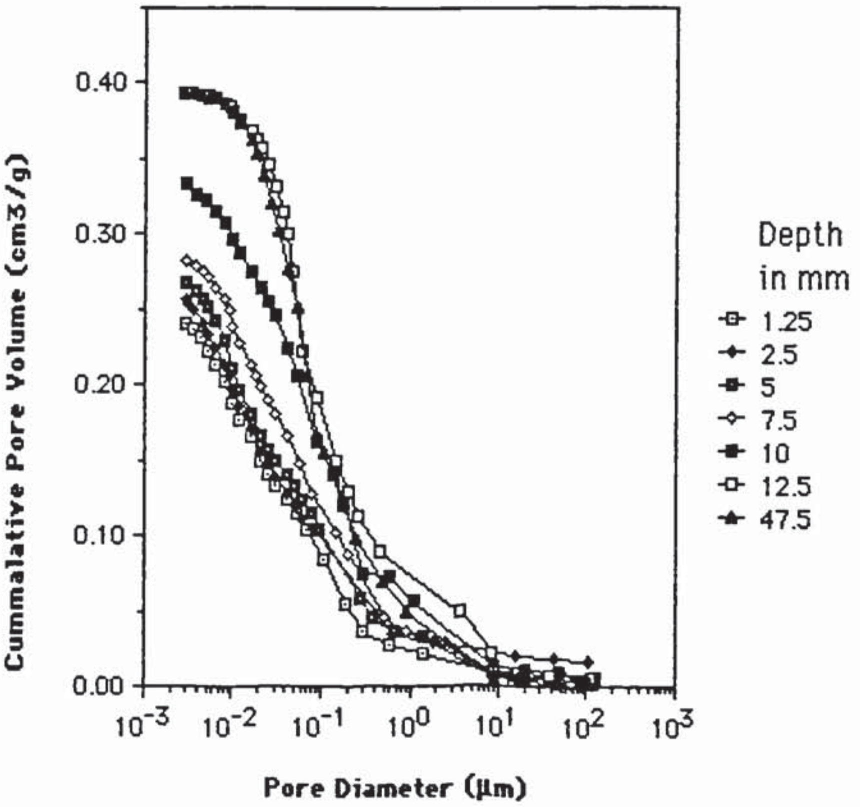


Figure 21. Total Pore Volume Changes with Depth in from a Naturally Carbonated Surface.

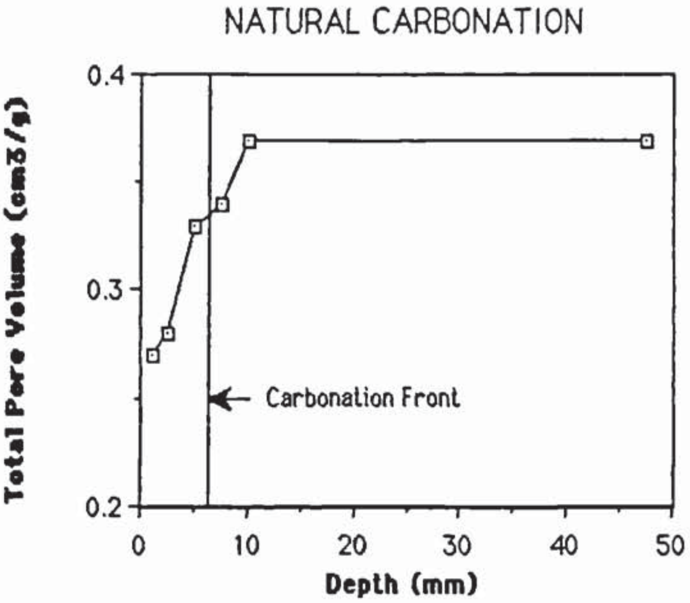
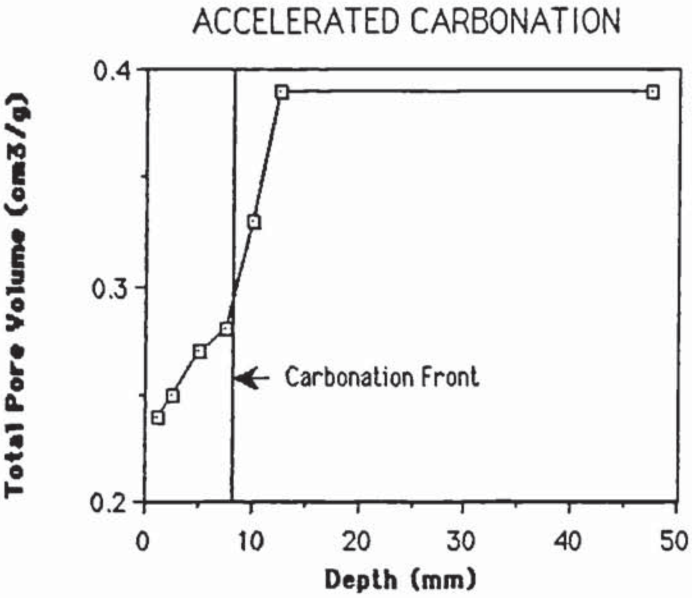


Figure 22. Total Pore Volume Changes with Depth in from an Accelerated Carbonated Surface.



3.6.4. Microhardness.

The results of microhardness testing are shown in Figures 23 and 24. Two totally different patterns of microhardness were found for the two carbonation conditions.

For naturally carbonated cement pastes the trend of the microhardness results indicated an increase in hardness in the carbonated area, with decreases just below the surface and at the carbonation front. The trend of the accelerated carbonated specimens was an overall decrease in microhardness in the carbonated area, with a slight increase near the surface.

Figure 23. Changes in Mircrohardness with Depth in from a Naturally Carbonated Surface.

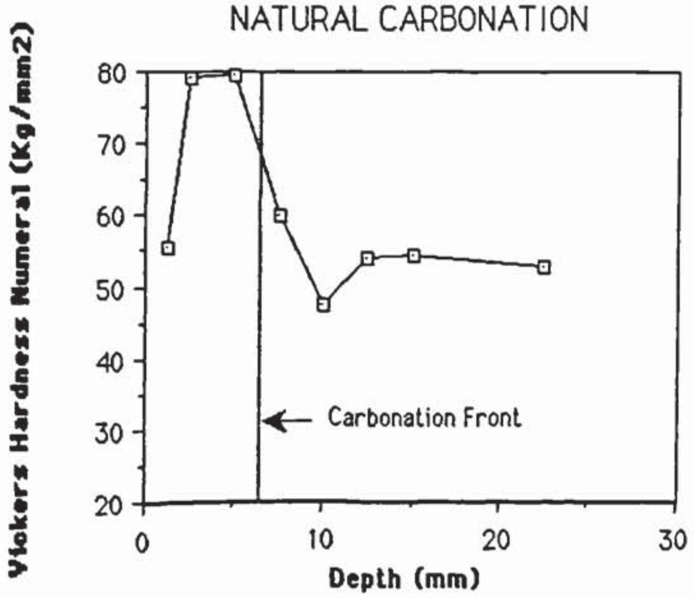
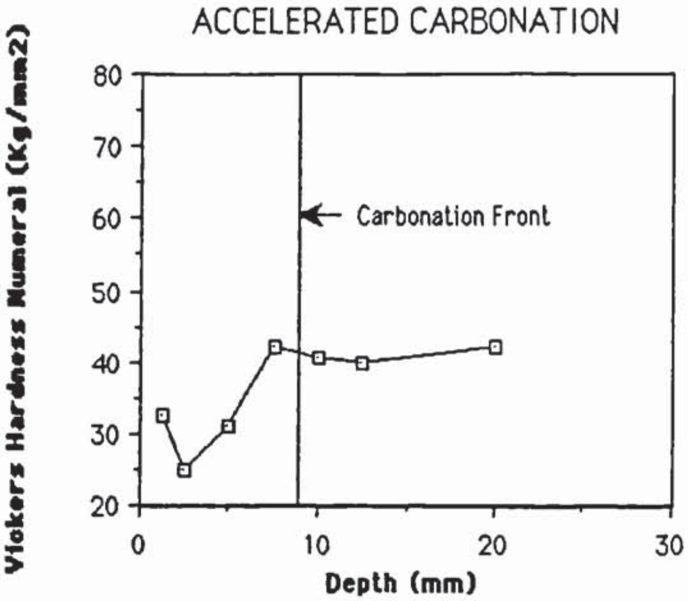


Figure 24. Changes in Mircrohardness with Depth in from an Accelerated Carbonated Surface.



3.7. Discussion and Conclusions.

3.7.1. Phenolphthalein Testing for Carbonation Depth.

The measurement of carbonation depths by phenolphthalein testing and petrographic examination of thin sections gave similar results for both accelerated and naturally carbonated specimens. Consequently these results could be directly compared with the determined changes across the carbonated surfaces.

The graphs in Figures 17, 18, and 21 to 24 appear to indicate that some changes in physical and chemical properties had occured in advance of the measured carbonation front. However, pore solution composition and porosity determinations made on slices with average depths slightly greater than the measured carbonation depth incorporated material from areas observed to be carbonated. Taking this into account, it can be concluded that minor changes in properties may occur up to 10 mm ahead of the carbonation front, indicated by phenolphalein testing.

The pH levels of pore solutions expressed from apparently carbonated areas were 9.6 and 11.9, higher than would be predicted from the results of phenolphalein testing, which had indicated pH levels less than 9.2. These results were consistent with previous findings of Sergi (see Table 15).

Sergi had explained his findings as being due to small areas of uncarbonated cement paste within a carbonated matrix. When pore solution is expressed from these regions an average composition is determined for pH levels and ionic species.

With regard to depassivation of the steel, the carbonated matrix is of critical importance. When areas of carbonated matrix are in contact with reinforcing steel, there is potential for corrosion if moisture and oxygen are available. This is despite the presence of uncarbonated inclusions in the vicinity, which would give expressed pore solution an average pH value higher than 9.5.

In conclusion, minor changes in properties may occur in advance of the carbonation front indicated by phenolphthalein testing, but the bulk of the changes occur in the region of the front or in the rest of the carbonated area. Phenolphthalein testing would appear to be a useful measure of the depth of carbonation, especially as it indicates local areas of carbonation where depassivation of the steel may take place.

3.7.2 Variations in Properties Across Carbonated Surfaces.

The variation in properties from the surface inwards showed that there was not a carbonation zone which could be clearly defined. This suggests that cement pastes do not become carbonated with no further changes in properties, but that carbonation is a continuous process, further changes taking place across the entire carbonated area with the progress of time.

The naturally carbonated and accelerated carbonated surfaces were carbonated into very similar depths, 6-7 mm for the naturally carbonated, and 8-9 mm for the accelerated carbonated. Although the depths of carbonation were fairly similar, some of the properties of the cement pastes in the carbonated areas were quite different.

Pore Solution Chemistry.

The main chemical difference was the greater decrease in pH of the pore solution for cement paste carbonated under accelerated conditions. This factor alone could explain other observed differences in chemistry.

It was particularly noticeable that sodium and calcium ions reappeared in the pore solution near to the surface of accelerated carbonated cement pastes. As the pH in these areas was lower, less than 10.34, bicarbonate ions would be predominating over carbonate ions. Bicarbonates are more soluble than carbonates, hence the presence of greater quantities of positive ions in solution to balance the negative bicarbonate ions.

It was also noted that potassium ions had not reappeared in the accelerated carbonated pore solution to the same extent as sodium and calcium ions. This result was possibly slightly anomolous, but the presence of other cations to balance bicarbonate ions is consistent with work by Gonzalez et al (61).

Although the presence or absence of bicarbonate and carbonate ions may determine the concentrations of certain ionic species in the pore solution at different pH levels, there was no evidence of any stepped changes in pH. However, the suggestion that basic constituents buffer changes in pH need not be discounted, as the absence of stepped changes in pH is further evidence for carbonation being a continuous process.

Low levels of chloride ions were released on carbonation, but were not found in advance of the carbonation front. Hence it seems unlikely that chloride induced corrosion would be a problem prior to carbonation induced corrosion. It must be noted that this conclusion is only valid for the conditions investigated, where additional chlorides were not incorporated in the mix or penetrating from an external source.

Porosity.

The pattern of the reduction in porosity with carbonation was similar for naturally and accelerated carbonation conditions. For both conditions the total porosity decreased nearer to the surface, but this decrease was more dramatic for accelerated carbonated cement paste.

The accelerated carbonated specimens were younger than naturally carbonated specimens, hence they had a greater total pore volume in uncarbonated areas. The degree of pore volume reduction was significantly greater under accelerated carbonation, as larger pores up to 10µm in size were filled, compared with only 0.1µm and less being filled under natural carbonation conditions.

Microhardness.

The variation in microhardness of a cement paste carbonated under natural conditions was totally different to that carbonated under accelerated conditions. The naturally carbonated cement paste showed increases in hardness consistent with porosity decreases. The exception was the near surface result, which had a low microhardness value.

The accelerated carbonated cement paste had lower microhardness values in the carbonated area. These results were not consistent with decreases in porosity, but could be explained by carbonic acid attacking and weakening the cement paste. The surface of the naturally carbonated cement paste also showed signs of weakness, which, with time and further carbonation, might have spread further in from the surface.

An explanation of the variations in microhardness with depth and carbonation conditions might involve subtle changes in pore solution chemistry. The lower microhardness values could be associated with areas where calcium carbonate had not been able to readily precipitate out, owing to the predominance of bicarbonate ions.

Continuing with this line of thought, the slight increase in microhardness at the surface of accelerated carbonated cement paste could possibly be explained. The combined effect of carbon dioxide diffusing away, and water evaporating from a bicarbonate solution might have caused calcium carbonate to precipitate out, thus increasing the hardness.

If restricted precipitation of calcium carbonate was responsible for decreases in hardness, the question remains as to how observed and unexpected decreases in porosity might be explained.

Work by Hornain in 1976 had shown that on carbonation, calcium silicate hydrates become more compact (26). Possibly, the porosity changes with carbonation are more significantly influenced by compaction of calcium silicate hydrate than by precipitation of calcium carbonate in the voids.

An alternative explanation of the variations in microhardness might lie in the form of calcium carbonate ie. whether calcite, vaterite or aragonite had been formed. Further work would be required to find out if this or the above explanation might be valid.

3.7.3. Natural Versus Accelerated Carbonation.

The results appear to indicate that cement pastes carbonated under accelerated conditions have more extreme changes in chemical and physical properties compared with those carbonated under natural conditions. These differences may be summarised as follows :

With accelerated carbonated carbonation :

1. The pH levels in the pore solution is lower, resulting in a different chemistry. Under these conditions bicarbonate ions predominate, and precipitation of calcium carbonate may be restricted. Cations come into solution to balance the negative bicarbonate ions.

2. Greater decreases in porosity are observed.

3. Hardness may decrease instead of increasing.

3.7.4 Summary

Results of experimental work for this Chapter characterised surfaces carbonated under natural and accelerated conditions. Physical and chemical properties were found to vary across the carbonated area, and with the method of carbonation. Changes in properties were observed to be more extreme after accelerated carbonation and this should be borne in mind when interpreting results from accelerated carbonation experiments.

Results suggested that carbonation is a continuous process, with further changes in properties taking place across the entire carbonated area with the progress of time. No stepped changes in the pH of extracted pore solution were observed as the pH increased from the surface inwards. The presence/absence of carbonate and bicarbonate ions at different pH levels was thought to be the controlling influence on the balance of ions in solution.

The porosity of carbonated surfaces increased from the surface inwards. Microhardness increased after natural carbonation, but decreased after accelerated carbonation.

Phenolphthalein testing was concluded to be an accurate and useful way of measuring the depth of carbonation. Minor variations in properties were found up to 10mm in advance of the carbonation front. Chloride ion release ahead of the carbonation front was minimal, especially as no additional chlorides were involved.

CHAPTER 4.

Performance of Surface Hardeners.

4.1 Introduction.

There appears to be very little independent published data fully supporting the suggested performance of surface hardeners when applied to concrete. Suppliers claim chemical reactions giving rise to blocked pores, resulting in denser and harder surfaces. These claims do not appear to be backed up by results from independent research.

The aim of the work in this Chapter is to look at the claims which have been made in the light of limited research already reported, and carry out experiments which would further establish the performance of surface hardeners on uncarbonated and carbonated cement paste surfaces. Areas of investigation include penetration, chemical reactions, and modification of properties such as porosity and hardness.

The performance of two sodium silicates, and two silicofluorides were investigated in the experimental work. Details of these materials are given in Section 2.2.3.

4.2 Previous Work.

Much of the relevant literature on silicates and silicofluorides for concrete surface hardening has been described and cited in Chapter 1. However, there are several queries which arise as a consequence of conflicting information and claims made in the trade literature supplied with the materials.

One of the first questions is, "how far do surface hardeners penetrate the surface ?" A report by CIRIA states penetration to be usually limited to 50-100µm, but in some cases up to 1-3mm (71). The trade literature for the magnesium and zinc silicofluoride investigated claims penetration depths up to 5 mm into average concrete. No indication is given as to the penetration of the other surface hardeners investigated.

It is generally recommended that the surface hardeners should be applied to clean and dry surfaces. The presence of moisture in the concrete could limit the penetration of the treatments. This is an area for which no experimental results could be found.

A second question is, "when surface hardeners are applied to concrete, what chemical reactions take place ?" The differing chemistry of the two types of surface hardener would suggest that different reactions may take place, and therefore silicates and silicofluorides should be considered separately.

Two different ways in which sodium silicates may perform when applied to concrete have been proposed :

1. Reaction with calcium compounds in the cement paste to form pore blocking products (71,74).
2. Polymerisation of a film of sodium silicate on drying (79).

The products suggested for the first reaction have included calcium silicate, silica, sodium silicate glass, and sodium hydroxide (80,82). The second mechanism does not appear to involve the modification of the chemistry of the cement paste or concrete to which the sodium silicate is applied.

By comparison, the views on the reactions of silicofluorides with concrete are more consistent. Silicofluorides are thought to react with calcium compounds in cement paste to form silica gel, calcium fluoride and probably the fluoride specific to the cation present in the original formulation (74,82).

For all the reactions and mechanisms described, no consideration is given to whether the surface to be treated is carbonated or not. Generally, the trade literature suggests that surface hardeners may be applied to concretes of any age, providing a recommended minimum curing period of 21 days has passed. Therefore these treatments may be applied to surfaces which are already carbonated.

Clearly, the chemistry of a carbonated surface will be totally different from that of an uncarbonated surface. Consequently, application of surface hardeners to a carbonated surface may result in different reactions. It has been suggested that the alkaline nature of sodium silicates might be used to re-alkalise carbonated concrete.

It is claimed in the trade literature that the results of applying surface hardeners to concrete include the blocking of pores, which in turn gives a harder and more dense surface, with increased resistance to abrasion and wear. Sadegzadeh has done some experimental work on these physical parameters (124). He found that mercury intrusion porosimetry results of 2mm thick silicate and silicofluoride treated concrete showed little variation in porosity, despite slight increases in abrasion resistance. Sadegzadeh also carried out some Vickers microhardness tests on concrete treated with silicates and silicofluorides. His results did not reveal any differences in microhardness between treated and untreated samples.

4.3. Aims of Experimental Work.

The aims of the experimental work were to determine the following :

1. Depth to which surface hardeners penetrate cement paste substrates.

2. Influence of moisture in the substrate on the penetration of surface hardeners.

3. Whether or not sodium silicates react with cement paste substrates.

4. Reactions of surface hardeners with uncarbonated and carbonated substrates.

5. Whether or not sodium silicates can be used to re-alkalise carbonated cement paste.

6. The extent to which physical properties of cement pastes, such as hardness and porosity are modified by the application of surface hardeners.

4.4. Approach to Experimental Work.

The work was carried out on 0.75 water to cement ratio cement pastes. Cement pastes were used instead of concrete to keep the system simple, so that any modifcations caused by the surface hardeners might be readily detected. A high water to cement ratio was chosen to give porous cement pastes, into which the surface hardeners might readily penetrate.

Penetration of surface hardeners into cement paste substrates was assessed using direct and indirect methods. Direct attempts were made to detect changes in chemistry and physical properties across treated surfaces using semi-quantitative X-ray analysis and microhardness determinations. Weight gain measurements were made on treated specimens to give an indirect assessment of penetration.

Chemical reactions of surface hardeners with uncarbonated and carbonated cement pastes were investigated using X-ray diffraction analysis of treated samples. Thin sections of treated samples were also examined for evidence of chemical reactions involving crystalline components, and depth of penetration. The question of realkalisation of carbonated cement paste was approached by analysing and comparing the pH of pore solution from treated and untreated cement pastes.

Mercury intrusion porosimetry and Vickers microhardness determinations were made on treated specimens to determine modifications in physical properties.

Semi-quantitative X-ray analysis, petrography and microhardness determinations were carried out on surfaces taken perpendicular to treated surfaces. The rest of the experimental work for this Chapter was carried out on cement paste discs. The samples for X-ray diffraction, pore solution analysis, and mercury intrusion porosimetry were prepared in parallel.

4.5. Details of Experimental Work.

4.5.1 Sample Preparation.

The basic material used in all the experiments for this Chapter was a 0.75 w/c cement paste which was prepared using the method described in 2.3.1. The cement paste was cured for 28 days in its pot at 20°C and then demoulded.

The surface treatments investigated in all the experiments in this Chapter are the surface hardeners described in 2.2.3 and summarised as follows :

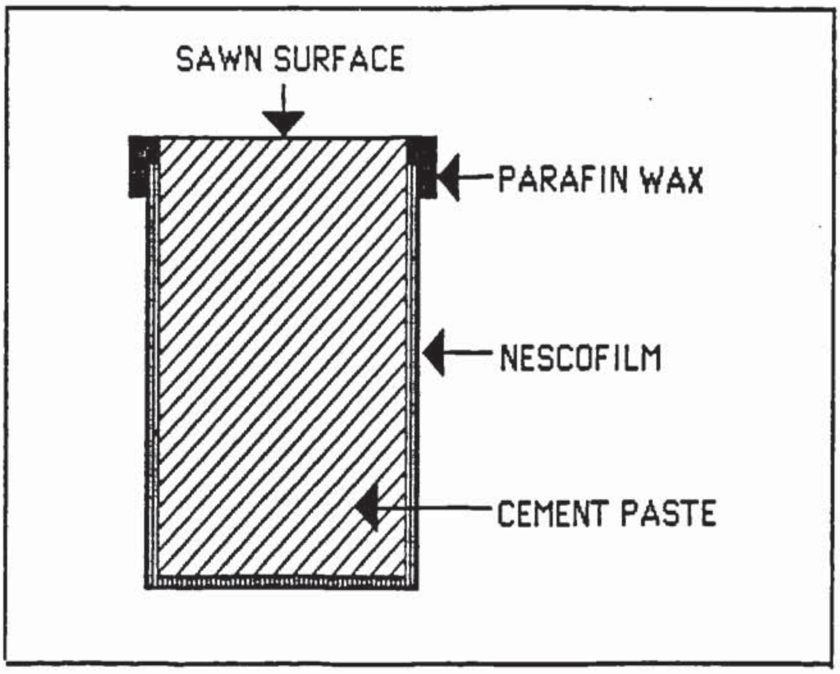
Sodium silicate 1	Magnesium silicofluoride
Sodium silicate 2	Magnesium and zinc silicofluoride

Samples for Semi-Quantitative X-Ray Analysis, Petrography, and Microhardness.

For this work, the end of a cement paste cylinder was treated. A surface was exposed for treatment by wet cutting. A cut surface was used to avoid using a cast surface, which might have a weak laitance layer. The samples were left to dry for 24 hours in a 20°C curing room.

The cement paste cylinders were sealed, leaving the cut surfaces exposed for treatment. The cylinders were sealed with several layers of "nescofilm", a self sealing and air resistant film. At the top of each specimen melted paraffin wax was used to ensure an air tight seal. Figure 25 shows a diagram of a prepared specimen.

Figure 25. Cement Paste Cylinder Prepared for Treatment at the Exposed Sawn Surface.



The specimens were treated using the methods described in 2.3.4. The exposed surfaces were dipped into the treatments. After the final treatment, the specimens were left to dry at 20°C over a weekend.

The samples were unsealed and slices were wet cut perpendicular to the treated surface. The slices were placed in an oven at 110°C for 24 hours.

Samples for XRD, Pore Solution Analysis and MIP.

This work was carried out on cement paste discs. After curing, the cement pastes cylinders were wet cut into 2.5mm thick slices. The ends containing cast surfaces were discarded. The slices were left to dry overnight at 20°C.

One set of discs was treated, whilst another set was placed in a carbonation chamber with 100% carbon dioxide at 65% relative humidity (see Section 2.4.2) for three weeks until carbonated. Once carbonated, the samples were left to dry over silica gel for one week.

Treatment of uncarbonated, and carbonated discs was carried out using the methods described in 2.3.4. The discs were treated by total immersion in the treatments.

4.5.2. Semi-Quantitative Energy Dispersive X-Ray Analysis for Depth of Penetration.

The approach used in the semi-quantitative X-ray analysis was initially to attempt to characterise the composition of the surface hardeners. Analyses were then carried out on cement pastes treated with surface hardeners, specifically looking for the readily detected constituents in the surface hardeners.

Analysis of Surface Treatments.

Samples of surface hardener were prepared for analysis by evaporating them to dryness in a dish immersed in boiling water. The solids were collected and further dried for a minimum of 24 hours at 105°C.

Powders of the dried samples were prepared by grinding with a pestle and mortar. The powders were adhered to one side of double sided selotape, and mounted on an aluminium stub. The stub was placed in a scanning electron microscope, and the dried surface treatments were analysed (see Section 2.5.1.).

Analysis of Surface Treated Cement Pastes.

Treated cement paste slices (see Section 4.5.1 for preparation details) were fractured to produce slivers perpendicular to the treated surface. The slivers, plus an untreated control, were mounted on an aluminium stub and placed in a scanning electron microscope for analysis (see Section 2.5.1.).

Semi-quantitative X-ray analyses were performed on selected areas from the treated surfaces inwards. For each sample, analyses were carried out at average depths of 0.1, 0.3, 0.5, 0.7mm etc., continuing at 0.2mm, up to 3mm in from the surface. The untreated control was analysed in a similar manner.

4.5.3. Indirect Assessment of Penetration Using Weight Gain Measurements.

The approach used in this experiment was to take cement paste discs with known variations in moisture content, treat them with surface hardeners and determine weight gains due to treatment. Variations in free moisture contents were achieved by drying saturated cement paste discs in different environments.

Cement paste discs were prepared by wet cutting 28 day, 0.75 w/c cement paste cylinders. The saturated discs were dried in three different environments overnight, and weighed (w_1).

Three discs from each environment were dried at 110°C, so that their moisture contents could be determined (see 2.3.5). Details of the environments, and corresponding moisture contents are given in Table 17.

Table 17. Average Free Moisture Contents of Cement Paste Discs Dried in Different Environments for Twenty Four Hours.

Environment	Relative Humidity of Environment (%)	Moisture Content (%)
110°C Oven	0	0
Laboratory	40	13.6
20°C Curing Room	70	16.5

The average moisture contents for cement paste discs dried in the different environments, and the weight of each disc prior to treatment (W_1) were used to calculate an untreated oven dry weight (W_2) for each disc.

$$W_2 = W_1 - \frac{(\underline{\% \text{ moisture content } X\ W_1})}{100}$$

Where W_2 = untreated oven dry sample weight (g)

W_1 = sample weight prior to treatment (g)

% moisture content = the average % moisture content of three discs from the specified environment

The discs were treated using the procedure desribed in 2.3.4, but replaced in their drying environment between treatments. After washing, the samples were placed in an oven at 110°C, prior to final weighing. This dry treated weight (Tw) was used to calculate a percentage weight gain on treatment:

$$\%\ \text{weight gain after treatment} = \frac{Tw - W_2}{W_2} \times 100$$

Where Tw = Oven dry treated sample weight (g)

W_2 = untreated oven dry sample weight (g)

An average of two results was used to give a final reading.

4.5.4. X-Ray Diffraction Analysis of Treated Cement Pastes.

The following categories of discs were subjected to x-ray diffraction analysis :

uncarbonated and untreated
uncarbonated and treated
carbonated and untreated
carbonated and treated

Section 4.5.1 describes their preparation. The oven dried discs were placed directly in the x-ray diffractometer and scanned (see Section 2.5.2).

4.5.5. Petrographic Examination of Treated Cement Pastes.

Cement pastes treated with surface hardeners were prepared for petrographic examination using the method described in 2.4.3. Thin sections were prepared from slices taken perpendicular to the treated surface (see Section 4.5.1). The sections were examined for evidence of variation in composition from the treated surface inwards.

4.5.6. Analysis of Pore Water Expressed from Carbonated and Treated Cement Pastes.

Cement paste discs were carbonated and treated, as described in 4.5.1. Following treatment the cement paste discs were left to equilibrate over water in a high humidity chamber for one week. This was done to raise moisture levels in the cement paste discs to a sufficiently high level for pore fluid to be expressed from them.

For each treatment investigated eighteen discs were prepared for pore fluid expression. Untreated control discs were also prepared. Pore fluid was expressed from the discs using the method described in 2.5.3. The pH of the pore solution was measured using a pH meter.

4.5.7 Mercury Intrusion Porosimetry (MIP)

Fragments of oven dried discs were prepared for MIP (see 4.5.1). MIP was carried out on discs in similar catergories to those analysed by XRD (see 4.5.4.). The MIP method is described in 2.6.1.

4.5.8. Microhardness.

Slices prepared in 4.5.1 were used to make polished specimens for microhardness. Microhardness method 2, described in 2.6.2, was used.
For each sample an "at depth bulk" result was determined. Results were then obtained at regular depth intervals from the surface inwards, until a similar result to that of the bulk material was recorded.

4.6 Results.

4.6.1 Results of Semi-Quantitative Energy Dispersive X-Ray Analysis.

The results of the semi-quantitative X-ray analysis of the dried surface treatments are summarised in Table 18, and shown graphically in Appendix 6.

Table 18. Results of Semi-Quantitative X-Ray Analysis of Dried Surface Hardeners.

	PEAK HEIGHTS			
	Na Sil 1	Na Sil 2	Mg+ZnSiF$_6$	MgSiF$_6$
Magnesium			Moderate	Strong
Silicon	Very strong	Strong	Weak	Moderate
Sodium	Weak	Weak		
Zinc			Weak	

The sodium silicates gave similar results, having strong silicon peaks and weak sodium peaks. The magnesium silicofluoride had a strong magnesium peak, and a moderate silicon peak. The magnesium and zinc silicofluoride showed a moderate magnesium peak, and weak silcon and zinc peaks. No fluoride was detected, as its low atomic number does not allow its detection by this technique.

The results of the analysis of the dried surface treatments were used as a guide for analysing the results from the treated specimens. The quantities of those elements detected in the surface treatments were compared for untreated and treated specimens.

Wide variations in elemental quantities were observed in the fifteen readings taken from the untreated control. These values were used to calculate average elemental values for untreated cement paste (Only elements detected in the surface hardeners were looked at). Standard deviations from the means were also calculated. Table 19 summarises these results.

Table 19. Averages and Standard Deviations of Fifteen Semi-Quantitative X-Ray Analysis Results of Untreated Cement Paste. (Only the elements detected in the surface treatments are quoted).

	Mean (% by wt)	Standard Deviation
Magnesium	0.16	0.11
Silicon	12.17	1.65
Sodium	0.16	0.16
Zinc	0.11	0.20

The results from the analysis of treated samples were compared with those for the untreated control. Owing to the wide spread of results from the untreated control, it was decided that only values greater and less than plus or minus three standard deviations of the mean would be considered different.

Out of all the values compared, there was only one result which indicated a significant increase in levels of magnesium, due to the presence of treatment. This was the near surface, 0.1mm depth reading from the magnesium silicofluoride treated sample. The level of magnesium detected was 0.73% by weight.

The remaining results showed no significant differences in composition. As the results were all similar to that for an untreated cement paste, the data have not been reported.

4.6.2. Results of Indirect Assessment of Penetration.

The results of weight gain after treatment of cement pastes with varying moisture contents are shown in Figures 26 and 27. A similar pattern of weight gain versus moisture content was obtained for all four treatments investigated. With increasing moisture in the sample, weight gains were reduced.

Figure 26 Weight Gain of Silicate-Treated Cement Paste Discs With Variation in Original Moisture Content.

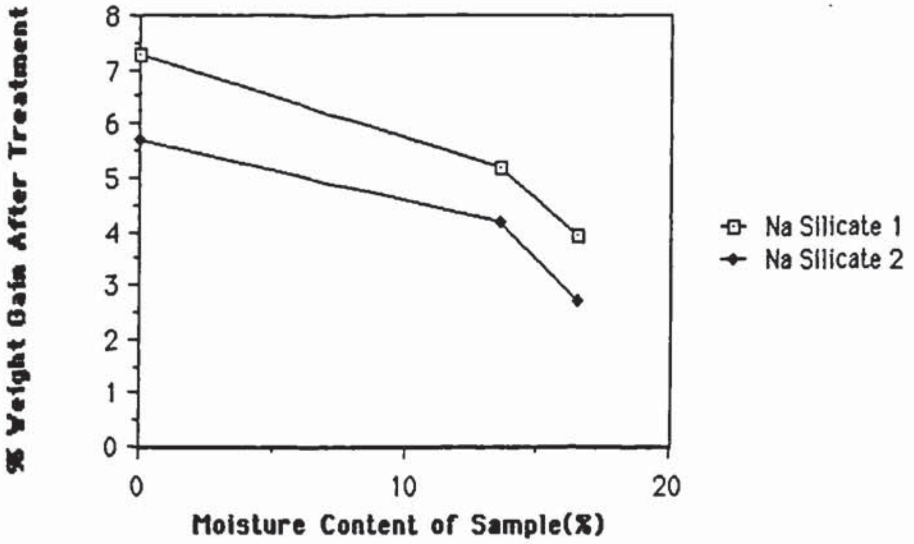
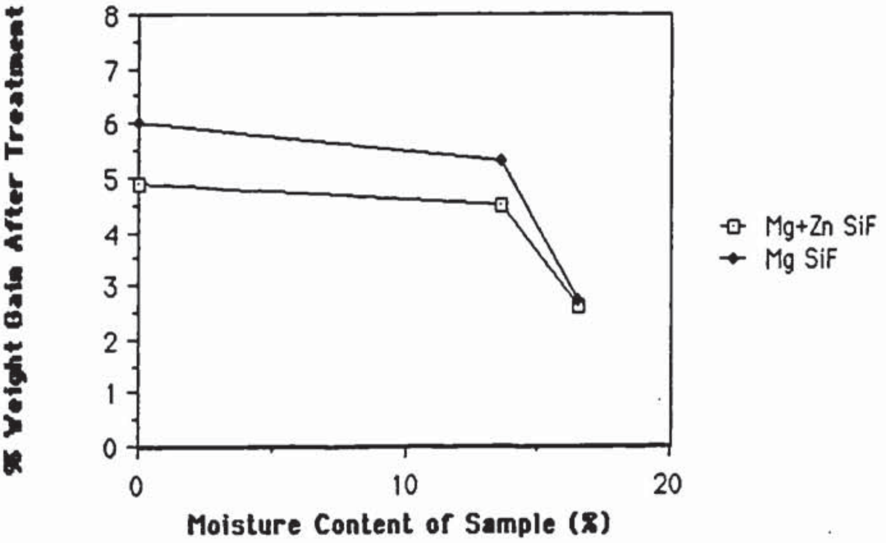


Figure 27 Weight Gain of Silicofluoride-Treated Cement Paste Discs With Variation in Original Moisture Content.



4.6.3. Results of X-Ray Diffraction Analysis of Treated Cement Pastes.

Data collected from the x-ray diffraction traces is shown in Appendix 7.

Uncarbonated.

The crystalline components identified in an untreated cement paste surface were calcium hydroxide and calcite. The presence of calcite in the sample suggested that the sample was slightly carbonated prior to treatment.

X-ray analyses of uncarbonated and untreated cement paste were repeated three times on different samples. Each time a similar result was obtained, whereby calcite was detected.

Despite the presence of some calcite, a phenolphthalein test on the cement paste had indicated the paste to be uncarbonated. It must also be noted that the observed calcite peaks were relatively small in comparison to those for a carbonated specimen.

Uncarbonated and Treated

After treatment with sodium silicate the amount of calcite at the surface increased, and vaterite was detected. Calcium hydroxide was detected in the sample treated with sodium silicate 1, but not with sodium silicate 2.

The application of the two different silicofluorides to an uncarbonated cement paste surface gave similar results. Vaterite and calcium fluoride were detected. Calcite was detected at similar levels to that of an untreated surface, but calcium hydroxide appeared to have decreased.

Carbonated

Calcite with some vaterite was detected in the carbonated cement paste.

Carbonated and Treated

Both the silicate-treated, carbonated samples were similar in composition to an untreated carbonated sample.

Silicofluoride-treated, carbonated samples were found to contain less calcite than the untreated controls, but calcium fluoride was detected.

4.6.4. Results of Petrographic Examination of Treated Cement Pastes.

Small amounts of carbonated cement paste were observed at the surface of the treated cement pastes. The depths to which carbonation was observed are shown in Table 20. The carbonated cement paste appeared similar in composition to that of untreated and carbonated cement paste. Further in from the carbonated area normal cement paste was observed.

Table 20 Carbonation Depths Observed During Petrographic Examination of Treated Cement Pastes.

Treatment	Depth of Carbonation (mm)
Na Silicate 1	0-0.5
Na Silicate 2	0-0.75
Mg+Zn Silicofluoride	0-0.25
Mg Silicofluoride	0.5-1

4.6.5 Results of Pore Water Expressed from Carbonated and Treated Cement Pastes.

The pH of pore waters expressed from carbonated and treated cement pastes are given in Table 21. The pH of pore waters from carbonated and treated cement pastes were not significantly different from that expressed from a cabonated and untreated cement paste.

Table 21. pH of Pore Waters Expressed from Carbonated and Treated Cement Pastes.

Treatment	pH
Na Silicate 1	9.0
Na Silicate 2	8.2
Mg+Zn Silicofluoride	8.1
Mg Silicofluoride	8.5
Untreated control	8.1

4.6.6 MIP Results.

Surface treatments applied to 2.5 mm discs appeared to have very little effect on the porosity of the samples (see Figures 28 to 31) Application of surface hardeners to an uncarbonated cement pastes resulted in minor reductions in the quantity of the finer pores between 10 and 1 nm. Application of surface hardeners to carbonated cement pastes appeared to cause slight increases in porosity.

Figure 28. Pore Size Distribution of Silicate-Treated Cement Paste Determined By Mercury Intrusion Porosimetry.

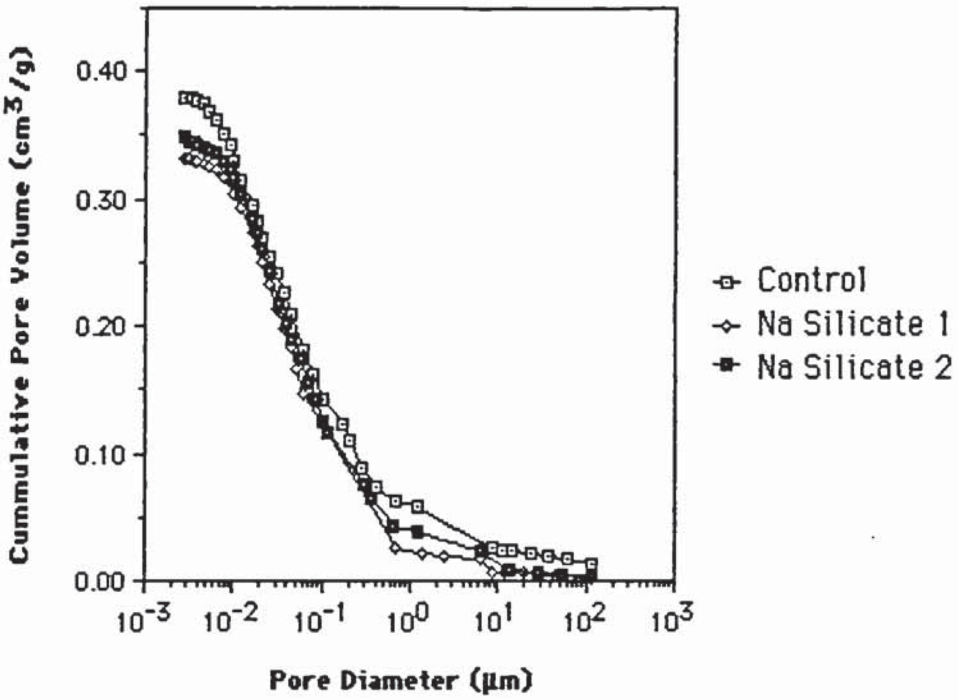


Figure 29. Pore Size Distribution of Silicofluoride-Treated Cement Paste Determined By Mercury Intrusion Porosimetry.

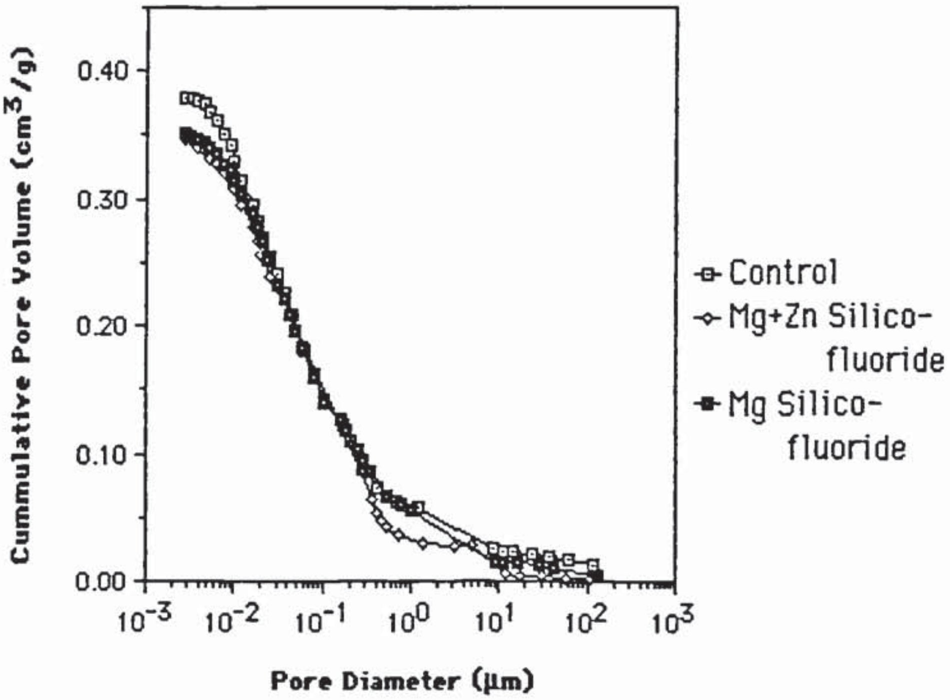


Figure 30. Pore Size Distribution of Silicate-Treated, Carbonated Cement Paste Determined By Mercury Intrusion Porosimetry.

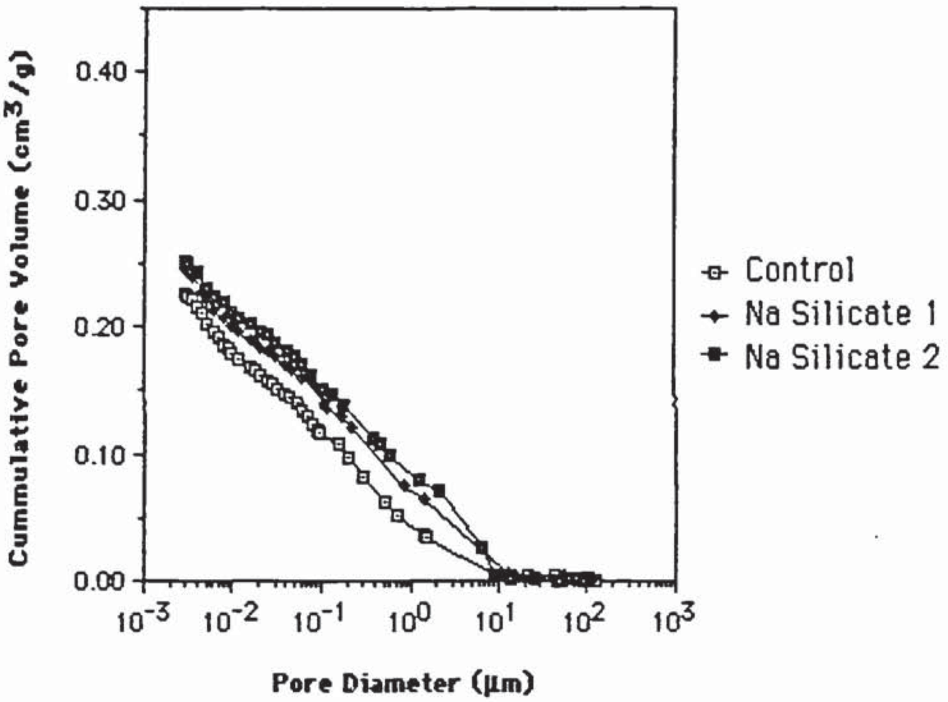
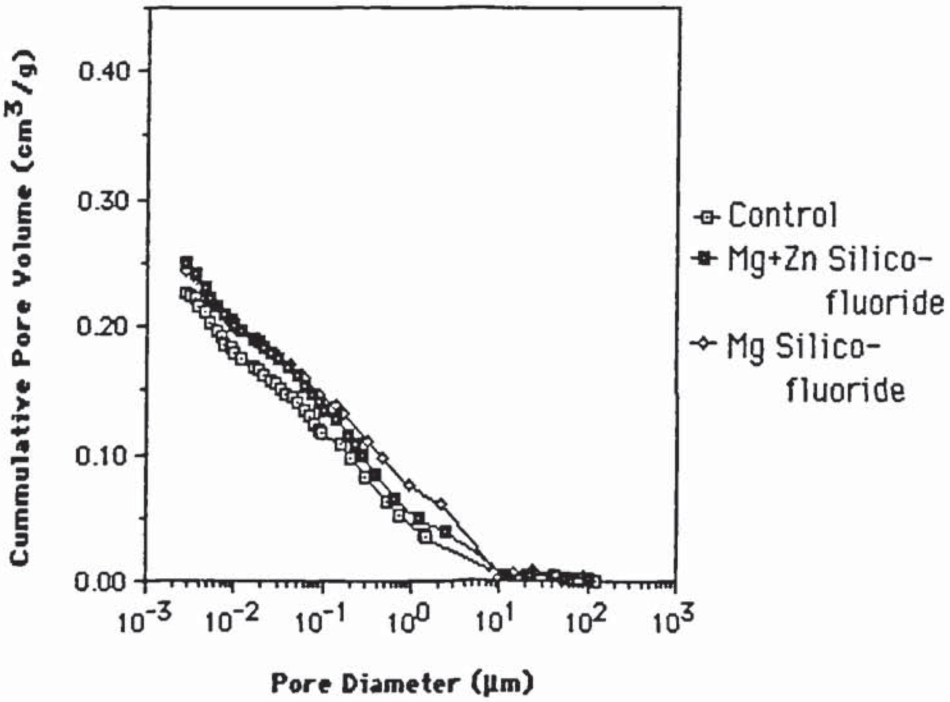


Figure 31. Pore Size Distribution of Silicofluoride-Treated, Carbonated Cement Paste Determined By Mercury Intrusion Porosimetry.



4.6.7 Microhardness Results.

The microhardness profiles of uncarbonated and treated cement pastes are shown in Figures 32 to 35. Significant increases in hardness were observed within 250 µm of the surface, from an average VHN of 52 to values in between 77 and 82. The exception to this was the Zn and Mg silicofluoride result. The cement paste treated with Zn and Mg silicofluoride had a maximum VHN of 110.

Figure 32. Microhardness Profile of Cement Paste Treated with Sodium Silicate 1.

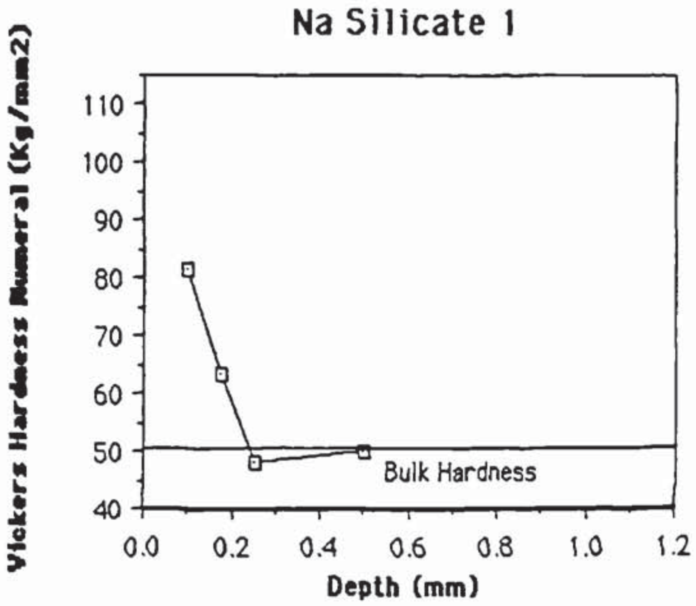


Figure 33. Microhardness Profile of Cement Paste Treated with Sodium Silicate 2.

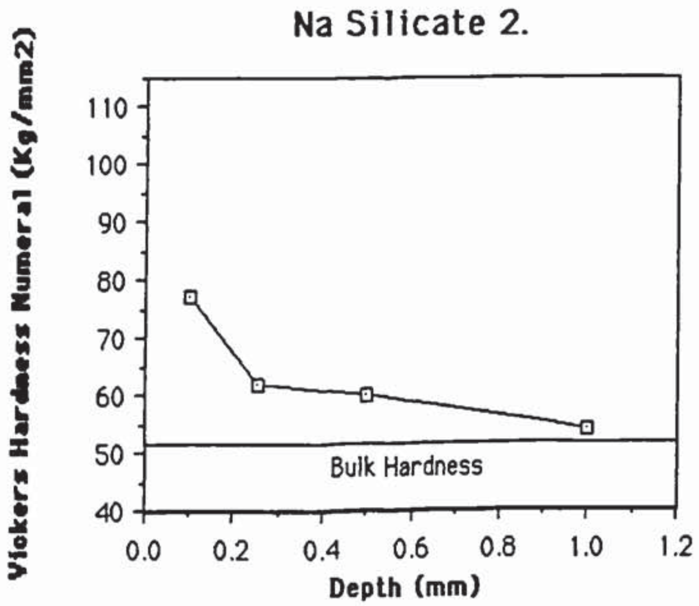


Figure 34. Microhardness Profile of Cement Paste Treated with Mg and Zn Silicofluoride.

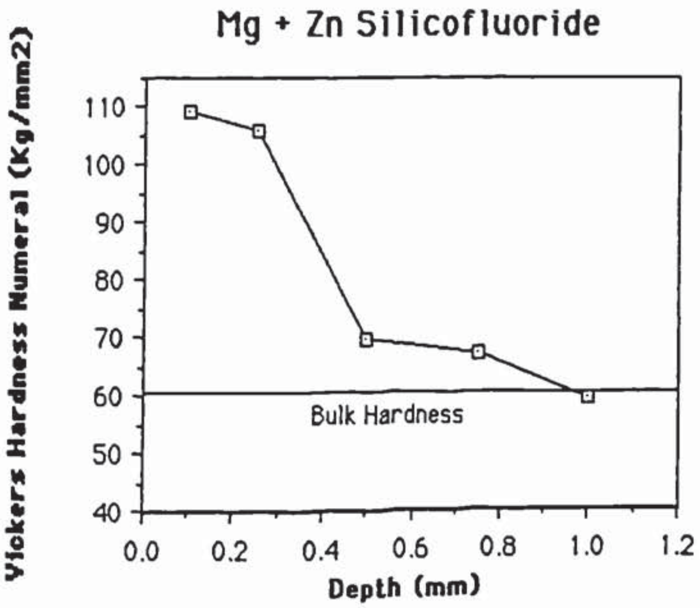
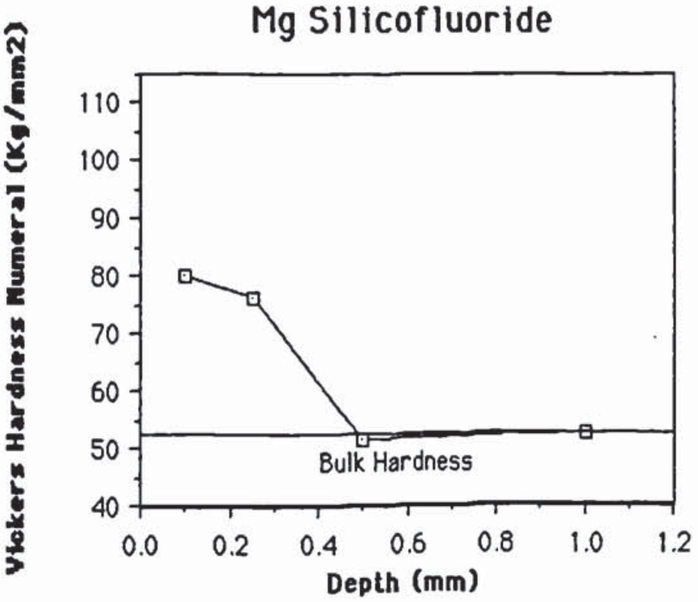


Figure 35. Microhardness Profile of Cement Paste Treated with Mg Silicofluoride.



4.7. Discussion and Conclusions

4.7.1 Penetration

Several experiments were carried out to assess penetration of the surface hardeners. Of these, microhardness determinations gave the most information as increases in hardness were observed up to 250µm in from the surface of an uncarbonated cement paste. This result is consistent with previously quoted penetration depths (71).

The results of semi-quantitative x-ray analysis indicated either little or no penetration, or that the technique was insufficiently sensitive for detecting the presence of the surface treatments. The latter interpretation seems most likely in view of the findings from the microhardness experimental work.

The results from the indirect assessment of penetration by weight gain indicated that the presence of moisture in the cement paste sample restricted the penetration of surface hardeners.

4.7.2. Chemistry

Silicates Applied to Uncarbonated Cement Paste.

The results from x-ray diffraction and petrography indicated that the application of sodium silicate to an uncarbonated cement paste surface caused carbonation. This probably occurred during treatment, when successive wetting and drying of the samples encouraged rapid carbonation of the porous substrates.

Silicates Applied to Carbonated Cement Paste.

X-ray diffraction results indicated that with the application of a silicate surface treatment to a carbonated cement paste surface there is little or no change in the crystalline composition of the surface. Measurement of the pH of pore water extracted from similar samples indicated that the pH of the pore water was not altered either.

These results suggest that the application of sodium silicates to a carbonated surface does not cause realkalisation; also, it is unlikely that sodium hydroxide is a significant product of reactions between sodium silicates and carbonated cement paste.

Silicofluorides Applied to Uncarbonated Cement Paste.

X-ray diffraction results indicated that on applying a silicofluoride surface treatment to an uncarbonated cement paste, calcium fluoride was formed at the expense of some of the calcium hydroxide. This implies that calcium hydroxide was reacting with the silicofluoride to form calcium fluoride, thus confirming part of the following reaction previously quoted from the literature (82).

$$2MgSiF_6\,6H_2O + 4Ca(OH)_2 \rightarrow 4CaF_2 + 2MgF_2 + 2Si(OH)_4 \cdot 6H_2O$$

Vaterite was detected by XRD, and calcium carbonates were observed in thin section, suggesting some carbonation of the substrate on application of the silicofluoride treatments. This probably occurred on wetting and drying of the samples during treatment.

Silicofluorides Applied to Carbonated Cement Paste.

X-ray diffraction data from silicofluoride-treated samples showed a slight decrease in carbonates, with calcium fluoride being detected. This suggests that the silicofluorides were reacting with calcium carbonates to form calcium fluoride.

The acidic nature of the silicofluorides may have caused some of the calcium carbonate to dissolve to form soluble calcium bicarbonate. Bicarbonates are amphoteric, so will react with acid to form carbon dioxide and water. Thus calcium carbonate is removed from the sample, and calcium fluoride is formed.

4.7.3 Influence on Physical Properties

Porosity.

The claims in the literature suggest that application of surface hardeners to cement pastes gives rise to blocked pores, and lower porosity. In view of the limited penetration of these treatments (250µm into either side of a 2.5mm thick disc), differences in porosity were difficult to detect.

Chemical reactions and/or deposition of surface treatments in the near surface pores may have caused slight blocking of the finer pores in an uncarbonated cement paste. Conversely, slight increases in porosity were observed for carbonated and treated cement pastes. This latter phenomenon may have been due to the dissolution of small quantities of calcium carbonate from the carbonated and treated cement paste.

Hardness.

Increases in microhardness were limited to within 250µm of the surface. This would undoubtedly increase the resistance of a treated surface to wear, as proved by the abrasion resistance work of Sadegzadeh (124). It must be noted that the magnesium and zinc silicofluoride increased the surface hardness more than the other treatments investigated.

4.7.4. Summary.

Effective penetration of surface hardeners into highly porous cement paste substrates is limited to 250µm from the surface. The presence of moisture in the sample will reduce the amount of surface hardener penetrating the surface.

Results of experimental work did not give a clear indication as to whether sodium silicates react with cement paste substrates or harden by drying. Carbonation reactions were observed to have taken place, but these were probably as a consequence of wetting and drying of the sample during the treatment process.

Silicofluorides were found to react with uncarbonated and carbonated substrates. In both instances the only product identified was calcium fluoride. Despite reacting with a carbonated substrate, silicofluorides did not alter the pH of the pore water significantly.

Sodium silicates are not suitable for realkalising carbonated cement paste, as their penetration is limited and they do not raise the pH of pore water of carbonated cement paste.

The extent to which surface hardeners may modify the physical properties of cement paste is limited. Surface hardness is increased up to 250µm in from the surface. Porosity did not appear to be significantly modified, but difficulties were encountered in assessing porosity changes within 250µm of the surface.

CHAPTER 5.

Water Repellents and Moisture.

5.1 Introduction

Carbonation and carbonation-induced corrosion of steel in concrete are processes which are both controlled by moisture in the concrete. A concrete surface treated with water repellent will repel moisture, and thus may affect moisture movements and levels of moisture within the concrete.

The effect of water repellent surface treatments on carbonation and carbonation-induced corrosion forms an important part of this investigation. To examine how the application of water repellent treatments might influence these processes the following areas were investigated :

1. The penetration of water repellents into cement pastes with varying moisture contents.

2. The influence of water repellent surface treatments on the internal moisture contents of cement pastes.

3. The effect of water repellents on the rate of water vapour transmission through a treated surface.

5.2 Previous Work

5.2.1 Penetration

It is known that penetration of water repellents into a concrete surface depends on the moisture levels within the concrete, and the size of the molecules concerned (66,67,71). The drier the concrete and the smaller the molecules, the greater the penetration.

Data on penetration depths for the treatments under investigation was limited. It was claimed that the silane could penetrate any desired depth, depending on the number of applications. The siloxane was claimed to have excellent penetration, but no indication was given as to the penetration performance of the silicone.

5.2.2 Internal Moisture Conditions

The influence of water repellents on levels of moisture within concrete is an area which has not been investigated. It has been claimed that water repellents may assist in keeping concrete structures dry, by allowing water vapour to pass out whilst repelling liquid water.

This claim has led to concern in the industry that the application of water repellents may increase the rate of carbonation under certain conditions (46,70,125). For example, saturated concrete treated with a water repellent might dry to moisture levels optimum for carbonation.

5.2.3 Water Vapour Transmission

The way in which water repellents affect water vapour transmission through a treated surface is not entirely understood. It has been suggested that water repellent surface treatments allow the passage of water vapour, as they line the concrete pores and do not close them (71).

The mechanism by which water vapour is thought to be transmitted through cement paste is important to an understanding of how water repellents might influence this process. The amount and form of water in a cement paste will determine how water is transmitted.

Water can be present in cement paste pores as a vapour, capillary water, and adsorbed water (126). Due to the hydrophilic nature of a cement paste surface, water is readily adsorbed on to its surface (127). With increasing levels of moisture water starts to condense in the capillaries and pores (128).

Whilst water is present as adsorbed films, mass transfer of water is by molecular diffusion of vapour (129). Water present in the capillaries and pores acts as a barrier to water vapour diffusion and under these circumstances transfer is by condensation at the high humidity end, and evaporation at the low humidity end (128,129). This phenomenon has been described as liquid-assisted vapour transfer, because the liquid shortens the effective path length for vapour diffusion (129).

When capillaries are filled with water, capillary flow, in addition to liquid assisted vapour transfer, may occur. This flow is caused by pressure differentials across the meniscus of the water, and will depend on the diameter of the capillary, and the contact angle between the cement paste and the water (128).

Observations made by Parrott on the drying of porous glass led him to suggest that the level of saturation has a marked effect on the kinetics of moisture movement (130). Parrott observed that the rate of drying was particularly slow at intermediate relative humidities, and faster at low and high humidities. He explained these phenomena due to transitions in the transport process where :

1. At high moisture contents liquid flow can occur rapidly.

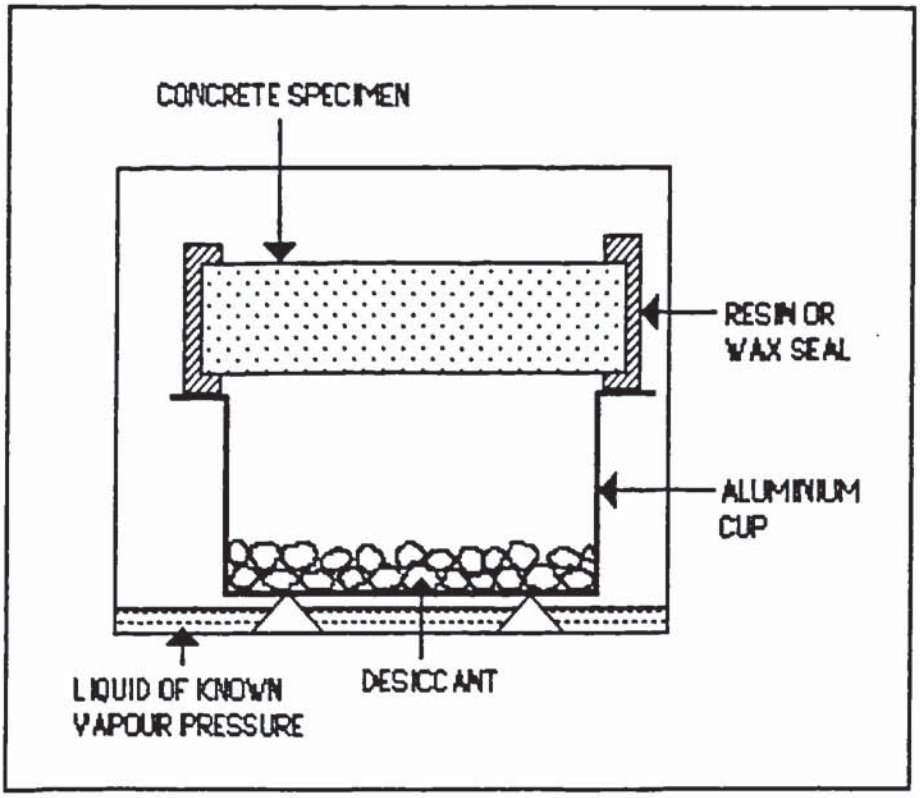
2. At low moisture contents vapour diffusion can occur freely through unblocked pores.

3. At intermediate moisture contents vapour diffusion is restricted by blocking of pores with capillary condensate, while liquid flow is also restricted.

A simple approach to assessing rates of water vapour transmission through concrete is to measure weight loss on drying (131). Robinson has used this approach to look at the effect of silane treatment on the rate of moisture loss from concrete (66). He found little difference between the rates of water loss from treated and untreated concrete cubes dried at 50%R.H., 24°C. However, no indication is given as to the depth to which the silane had penetrated the 100 mm concrete cube.

Alternative methods for assessing rates of water vapour transmission involve use of variations of the "dry cup" or "wet cup" tests (128). An example of a "dry cup" is shown in Figure 36.

Figure 36. An Example of a "Dry Cup" Test (128).



In the "dry cup" test illustrated in Figure 36 water vapour is transmitted through the concrete, and the flow is caused by differences in partial vapour pressures. Moisture diffusing through the concrete is taken up by the desiccant. By weighing the cup and specimen at regular intervals a rate of moisture transmission can be determined.

The simplest way of expressing data collected from this type of experiment is in terms of a flux (71). A flux is defined as the amount of a property passing through unit area in unit time. When mass is flowing, flux is determined in kg $m^{-2}s^{-1}$. According to Fick's first law, the flux will be proportional to the concentration gradient (132).

This approach has been used by Robinson to investigate rates of water vapour transmission through a variety of coating systems, including a silane, applied to cartridge paper (133). The results appeared to give a useful guide to the relative performance of the materials when applied to cartridge paper. However, they do not answer fully the question of how coatings and treatments might perform when applied to cement based materials.

5.3 Aims of the Experimental Work.

The aims of the experimental work were to :

1. Determine the penetration of water repellents into cement paste substrates with varying moisture contents.

2. Assess whether water repellent surface treatments modify the levels of moisture within a cement paste.

3. Measure and compare the rate at which water vapour diffuses through treated and untreated cement paste discs.

5.4 Approach to the Experimental Work

The experimental work to determine penetration depths and internal moisture contents was carried out on one set of samples. Moisture levels within the cement paste samples were controlled by leaving the specimens to equilibrate in different relative humidity environments. Moisture levels in the specimens were determined before and after treatment. At the end of the experiment specimens were split open for penetration determinations.

Several relative humidity environments were investigated. Most important were the higher humidities, chosen because of their importance in relation to carbonation and carbonation-induced corrosion.

A relative humidity of 65% is the optimum level for carbonation. It was important to determine if the use of a water repellent surface treatment could lower the the internal moisure content of a specimen held at 65%R.H., thus reducing the rate of carbonation. Also, if specimens held at 88 or 100%R.H. might have their internal moisture contents reduced to cause increases in the rate of carbonation.

In relation to carbonation-induced corrosion any reductions in internal moisture content should reduce corrosion rates.

The water vapour transmission experiments were carried out on treated cement paste discs, using a "wet cup" method.

5.5 Details of Experimental Work

5.5.1 Samples

All the experimental work for this Chapter was carried out on 0.75 w/c cement pastes which had been cured for 28 days in their pots (see Section 2.3.1 for preparation details). Three water repellents were investigated : a silane, a siloxane and a silicone which are described in 2.2.3.

5.5.2 Penetration of Water Repellents.

The cement paste cylinders were oven dried overnight at 110°C, and placed in sealed containers with varying relative humidities. The humidities were controlled with saturated salts to give the humidities indicated in Table 22 (also see Section 2.3.5).

Table 22. Relative Humidities Used in Penetration and Internal Moisture Content Experiments.

Substance Used to Control Relative Humidity	Relative Humidity (%)
Silica gel	0
Saturated magnesium chloride	33
" sodium nitrite	65
" ammonium sulphate	81
Water	>95

The samples were left in controlled humidity containers for three months, after which the samples were treated. For each combination of treatment and condition investigated two samples were treated. After treatment the samples were replaced in the humidity containers.

The samples were oven dried at 110°C for 24 hours prior to measuring the penetration of the treatment. Penetration was assessed by spraying water on a freshly broken surface and measuring the depth in millimeters to which the non-wetted surface was observed.

Three penetration measurements were made on each sample. The average of six readings was calculated to give a result for each treatment and condition.

5.5.3 Influence of Water Repellents on Internal Moisture Contents.

The cement paste cylinders were oven dried for 24 hours at 110°C, and weighed (W_d). The cylinders were placed in controlled relative humidity containers for three months (as in penetration experiment descibed in the previous section). The cylinders were weighed (W_e), treated, and returned to the controlled humidity containers for a further three months.

The treated samples, at equilibrium with the humidity environment in which they had been placed, were weighed (W_{te}). The samples were then oven dried at 110°C overnight, and reweighed (W_{td}).

Each time the samples were weighed, they were placed in preweighed containers to minimise moisture loss during weighing.

The percentage moisure content of the untreated samples (M_e) at equilibrium with the different relative humidity environments was calculated as follows :

$$M_e = \frac{W_e - W_d}{W_e} \times 100$$

Where :

M_e = percentage moisture content of specimen at equilibrium with the specified relative humidity environment

W_e = weight of specimen at equilibrium with the specified relative humidity environment (g)

W_d = oven dry weight of specimen (g)

The percentage moisure content of the treated samples (M_{te}) at equilibrium with the different relative humidity environments was calculated as follows :

$$M_{te} = \frac{W_{te} - W_{td}}{W_{te}} \times 100$$

Where :

M_{te} = percentage moisture content of treated specimen at equilibrium with the specified relative humidity environment

W_{te} = weight of treated specimen at equilibrium with the specified relative humidity environment (g)

W_{td} = oven dry weight of treated specimen (g)

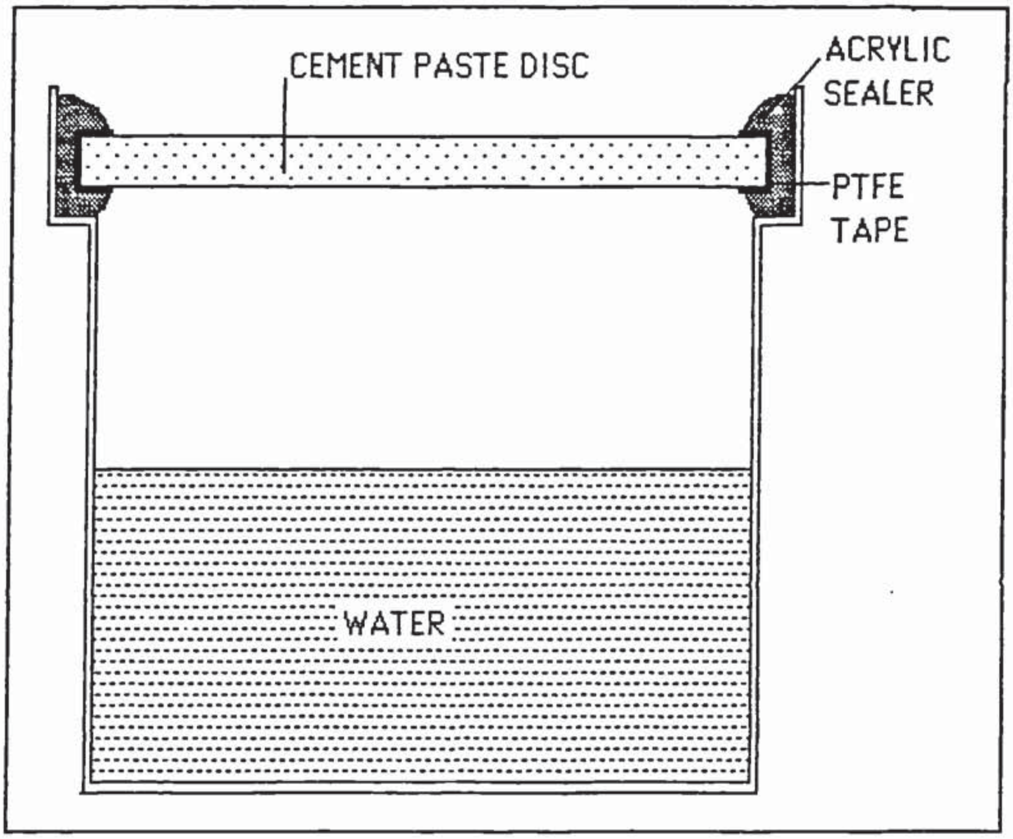
An average of six readings was calculated to give each M_e result. An average of two readings was calculated to give each M_{te} result.

5.5.4 Effect of Water Repellents on Water Vapour Transmission.

Cement paste discs of 3.3mm thickness were wet cut with deionised water, and left to dry overnight at 20°C. The discs were treated using the method described in 2.3.4. For each treatment three discs were prepared. Three extra discs were prepared as untreated controls.

Twenty four hours after the final treatment the discs were sealed into the tops of plastic pots containing 35 ml of water (see Figure 37). The edges of the discs were protected from the acrylic sealer by ptfe tape.

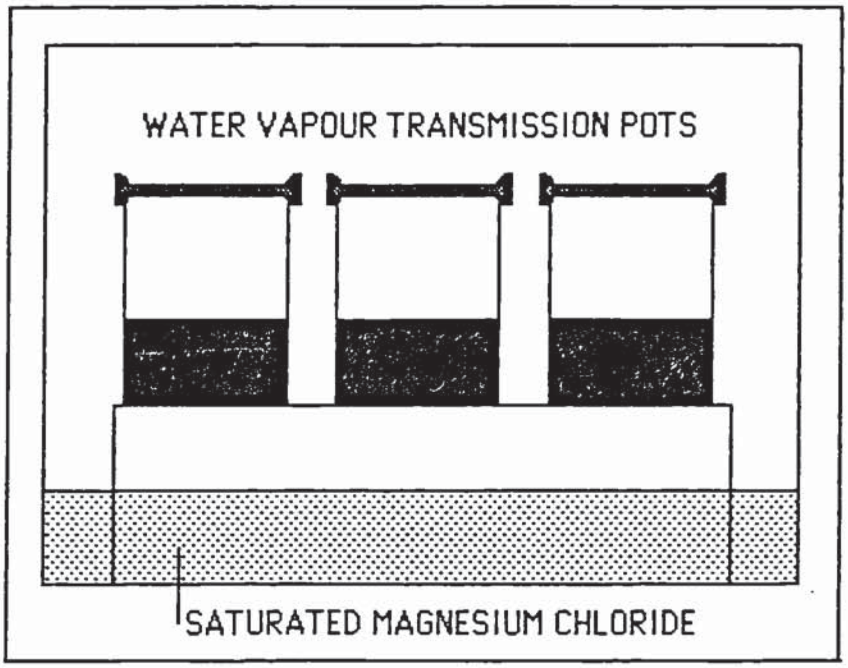
Figure 37. Water Vapour Transmission Pot



The test was carried out at 20°C in a sealed container with a relative humidity of 33% provided by a saturated solution of magnesium chloride in the base of the container (see Figure 38). The prepared specimens were left to condition in the test environment for three days prior to any measurements being made. Thereafter weight loss due to water vapour diffusing through discs was measured at regular intervals.

The rate of water loss with time was plotted, and the gradients of the resulting straight lines calculated. The average of three gradients was calculated for each treatment. The averages were used to calculate fluxes in kg m^{-2} s^{-1}. An example of a typical plot and calculation is shown in Appendix 8.

Figure 38. Water Vapour Transmission Apparatus

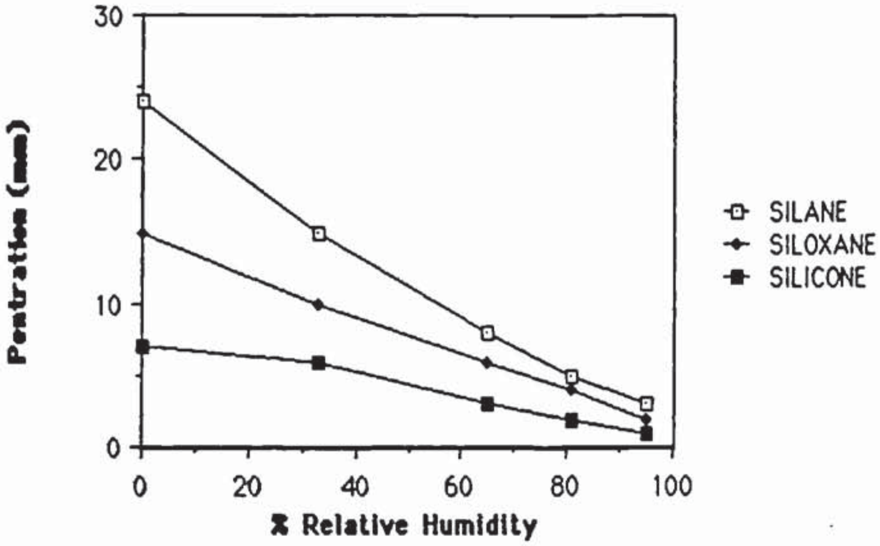


5.6 Results.

5.6.1 Penetration of Water Repellents.

The results summarised in Figure 39 show that the silane penetrated cement pastes deeper than the siloxane and silicone, and the silicone penetrated least. With increasing relative humidity and moisture in and around the samples penetration was decreased.

Figure 39. Penetration of Water Repellents into Cement Pastes Held At Varying Relative Humidities.



5.6.2 Influence of Water Repellents on Internal Moisture Contents.

The results are shown in Table 23, and appear to indicate slight increases in the moisture content after treatment. At the end of the experiment the samples smelled of solvent. It seems likely that any solvent left in the samples was lost during drying, and hence would have been included in the calculation of M_{te}.

Table 23. Moisture Contents of Cement Pastes Before and After Treatment With Water Repellents.

Relative Humidity %	Moisture Content (M_e)	Moisture Content After Treatment (M_{te})*		
		Silane	Siloxane	Silicone
0	0.4	3.0	2.4	2.1
33	3.8	4.9	4.6	4.5
65	6.1	7.1	6.8	6.8
81	8.4	9.7	9.7	9.9
100	16.0	16.6	18.4	18.6

* These values probably include a proportion of solvent from the water repellents.

5.6.3 Effect of Water Repellents on Rate of Water Vapour Transmission.

The results in Table 24 show that the water repellent treatment slows down the rate of water vapour transmision. At the end of the experiment, the specimens were broken and checked for depth of penetration of the treatment (see results in Table 24).

There appears to be some correlation between penetration and rate of water vapour transmission ie. with increased penetration the rate of water vapour transmission is more significantly reduced.

Table 24. Rates of Water Vapour Transmission Through Water Repellent Treated Cement Paste.

Treatment	Rate of Water Vapour Transmission Flux in kg m^{-2} s^{-1} ($\times 10^{-7}$)	Penetration of Treatment (mm)
Silane	2.3	0.7
Siloxane	3.5	0.4
Silicone	4.2	0.2
Untreated control	4.3	-

5.7. Discussion and Conclusions.

5.7.1 Penetration

The results of the penetration experiment clearly showed the relative performance of the three water repellents under investigation : silanes penetrated furthest, then siloxanes, and silicones the least. The presence of moisture in the substrate was found to limit penetration of all three. These results are consistent with previous findings (66,67).

As expected, penetration performance could be related to the molecular size of the water repellent. The smaller silane molecules were observed to penetrate further than the larger molecules of the siloxane and silicone. The silicone, having the largest molecules, penetrated the least.

5.7.2 Internal Moisture Content

Taking account of the solvent lost on drying, the moisture content of the samples was not significantly modified by treatment. However it must be noted that the specimens were left for three months to equilibrate.

These results suggest that the rate of moisture dependent processes, such as carbonation, and carbonation-induced corrosion, should not be significantly modified as the result of the application of water repellent surface treatments.

5.7.3 Water Vapour Transmission

The rate of water vapour transmission was reduced by the application of water repellent surface treatments. It seems likely that this reduction could be brought about by modifications in contact angle. An increase in contact angle with application of water repellents might have several important consequences :

1. Treated cement pastes would have hydrophobic capillaries and pores, which would lower the amount of water being adsorbed on to their surfaces. Consequently more water would be available to fill capillaries and pores.

2. The liquid in the capillaries and pores would tend to form discrete droplets. This could slow the transport process down as vapour diffusion is restricted by blocking of pores, and liquid flow is also restricted (see 5.2.3).

3. Rates of capillary flow are decreased, as the contact angle increases.

Rates of water vapour transmission through water repellent treated cement pastes were found to vary depending on the type of treatment used. This variation could be due to the extent to which the different treatments had penetrated. The deeper the penetration, the greater the modification of the transport process, and hence the more significant the reductions in the rate of water vapour transmission.

Reductions in the rate of water vapour transmission with water repellent treatment would increase the time taken for internal moisture levels to come to equilibrium with any changes in the moisture level outside the cement paste. However, as borne out by experimental results, equilibrium is eventually achieved.

5.7.4 Summary

Penetration of water repellents is limited by the amount of moisture in the substrate, and the size of the water repellent molecules. The following order of increasing penetration performance was observed for each moisture condition investigated;

silicone < siloxane < silane

The presence of surface water repellents do not appear to modify the internal moisture content of cement pastes, when specimens are left to equilibrate over a period of three months. Moisture vapour is allowed to flow through the treated surface, albeit at a slower rate. Thus given time, moisture levels within a water repellent treated cement paste will be similar to those in an untreated cement paste left in an environment with the same relative humidity.

CHAPTER 6.

Effect of Surface Treatments on Rate of Carbonation.

6.1 Introduction

Factors influencing the rate of carbonation of concrete have been discussed in Chapter 1 (Section 1.3.3.). The main influences are the composition of the concrete itself and the environment in which it has been placed. For carbonation to take place, carbon dioxide should be able to penetrate the concrete and moisture must be available for subsequent carbonation reactions.

Little work has been undertaken to examine the effect of the surface treatments under investigation on the rate of carbonation. However work has been done on surface coatings; barrier coatings with a dry film thickness of at least 150 microns, which rely on forming a pinhole free continuous film.

Barrier coatings, as their name implies, reduce rates of carbonation by physical exclusion of penetrating carbon dioxide. The treatments under investigation penetrate the concrete and by comparison may present little barrier to the diffusion of carbon dioxide.

Moisture is required for carbonation reactions. Work in Chapter 5 indicated that the water repellents do not alter the internal moisture content of the specimens, once equilibrium is achieved. These findings suggest that water repellents might not influence the rate of carbonation.

Sodium silicates are known to react with carbon dioxide (79,81). Therefore, reactions of the treatments in the surface layers of the concrete might slow down the overall rate of carbonation, as more material is available for carbonation relative to the untreated condition.

The importance of preventing the carbonation front from reaching the reinforcing steel gives considerable impetus to understanding the effect of surface treatments on the rate of carbonation. The nature of the materials under investigation makes prediction of their effects difficult. Hence the need for carefully controlled carbonation rate experiments to investigate the subject.

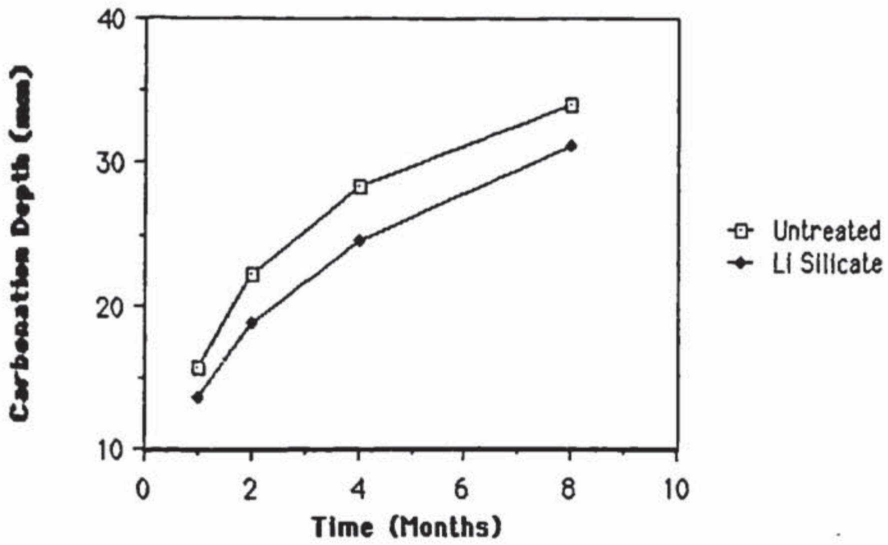
6.2 Previous Work

Several approaches have been used for investigating the effect of coatings/ surface treatments on carbonation. The most common and simplest is to test with phenolphthalein for carbonation depth, after treated and untreated specimens have been exposed for a fixed period of time.

Keer and Gardiner used phenolphthalein testing to investigate carbonation of silicate and silicofluoride treated concrete (82). They left specimens in laboratory air for 58 weeks, and found no significant differences in depths of carbonation between treated and untreated samples.

Fukushima et al investigated the rate of accelerated carbonation of lithium silicate treated concrete by phenolphthalein testing (134). Their results, illustrated in Figure 40, showed that the lithium silicate treated concrete carbonated at a slightly slower rate than the untreated control.

Figure 40. Rate of Carbonation of Lithium Silicate Treated Concrete From Fukushima et al 1986 (134).



Robinson tested a silane, a siloxane and two silane/siloxane mixtures for their effect on the rate of accelerated carbonation of concrete (66). After an unspecified time, treated and untreated cubes were broken open and phenophthalein tested for carbonation depth. In each case the depths measured were 15-17mm, indicating no significant difference between treated and untreated concretes.

Robinson also tested the silane treated and control concretes for degree of carbonation (66). Slices at 5mm depth intervals were assesssed thermogravimetrically by measuring the calcium hydroxide decomposition peak at 500°C. Both the control and silane treated concretes gave results indicating a similar depth of carbonation as determined by phenolphthalein testing. However, the degree of carbonation in the carbonated area of the silane treated concrete was less relative to the control.

The Building Research Establishment has developed and used a method to assess the relative performance of a wide range of coatings for the prevention of carbonation (45). Weight gain of coated mortars during carbonation is measured, so that rates of carbon dioxide uptake can be compared. The technique had not been applied to any of the treatments under investigation.

Lindberg has investigated the use of "paint materials" to protect concrete against aggressive atmospheric deterioration (135). In addition to carbonation, he has looked at the effect of SO_2 and NO_x. He descibes an ART-test (Acid Rain Test) which he has used to assess a range of materials including a hydrophobic silicone treatment.

The ART-test involved the exposure of treated concrete slabs to natural weather, and additional acid rain sprayed on to the test samples in cycles of 5 minutes per hour. The spray solution was a mixture of H_2SO_4, HNO_3 and HCl, with a pH of 3.5. After 1.5 years exposure with water spraying for half of the year (water spraying in winter was not possible due to freezing), the silicone water repellent treated concrete was less eroded than the untreated control.

The Germans have concentrated on assessing the resistance of coatings and treatments to carbon dioxide diffusion (63,136,137). Initially work was carried out on barrier type coatings, but more recently other surface treatments have been investigated.

Desor has described a method for measuring carbon dioxide diffusion coefficients (137). The coating or treatment to be tested is applied to either porous card or a suitable masonry substrate. The coated specimen is sealed between two halves of a test chamber, and carbon dioxide in a carrier gas stream is fed into the upper half. The gas diffusing through the specimen is measured by gas chromatography or infrared absorption. The results from this type of experiment are used to calculate a diffusion resistance coefficient μCO_2 defined as:

$$\mu CO_2 = \frac{D_L\,|c|}{i\ s}$$

where D_L = difusion coefficient of CO_2 in air (m^2/s)

$|c|$ = concentration difference for CO_2 in the measuring chamber (kg/m^3)

s = thickness of the layer under investigation (m)

i = diffusion flow density of CO_2 (kg/m^2s)

Weber has reported carbon dioxide diffusion resistance values determined by other workers, including measurements made on treatments of interest(63). The results in Table 25 indicate that water glass coatings, similar to the sodium silicate being investigated, had a considerably higher resistance to carbon dioxide diffusion than untreated concrete.

Table 25. Carbon Dioxide Diffusion Resistant Coefficients According to Klopfer. From Weber (63).

		μCO_2
Untreated concrete	- poor quality	150
	- medium quality	250
	- good quality	350
Water glass coating		2×10^4

Weber also quotes values for water repellent treated concretes. The value for high quality concrete decreases from 360 to 270, as a result of water repellent treatment. Weber suggests that this is due to the water repellent treatment drying the concrete, thus enabling the carbon dioxide to penetrate more easily.

Robinson has used a similar approach to investigate the influence of water repellents on carbon dioxide diffusion through dry concrete (66). His results, shown in Table 26, indicate that under dry conditions water repellents can significantly reduce the passage of carbon dioxide by approximately two orders of magnitude, compared to control concrete. Robinson explains his findings in terms of the greater pore blocking effect of siloxanes in comparison with silanes, which only line capillary pores in the concrete.

Table 26. Diffusion Resistance Coefficients for Water Repellent Treated Concrete. After Robinson (66).

	μCO_2
Control Concrete	281
Iso Octyl Siloxane	67,727
Iso Octyl Silane	18,861
Iso Butyl Silane	305

6.3 Aims of the Experimental Work

The main aim of the experimental work for this Chapter was to assess the influence of the surface treatments on the rate of carbonation. Several aspects were investigated as follows :

1. The rate of carbon dioxide uptake of surface treated mortars.
2. The rate of accelerated carbonation of treated cement pastes.
3. The rate of accelerated carbonation of naturally carbonated and surface treated cement pastes.
4. The rate of natural carbonation of surface treated concretes, containing siliceous and calcareous aggregates.

6.4 Approach to the Experimental Work

Carbon dioxide uptake of surface treated mortars was investigated using a method developed by the Building Research Establishment (BRE). This method was chosen because the BRE had already used it to obtain data on other coatings and treatments.

The rest of the work for this Chapter was carried out using phenolphthalein testing to measure the depth of carbonation. As discussed in Chapter 3, this technique gives a quick and useful assessment of the depth of carbonation.

Initial doubts concerning the use of phenolphthalein on treated samples were allayed by carring out tests on treated samples prior to carbonation. Full pink colouration was observed indicating that the test worked, despite the presence of surface treatments.

Accelerated carbonation of surface treated cement pastes was investigated in detail. The cement pastes had high water to cement ratios to give high porosity, in order to allow good penetration of the treatments and rapid carbonation. Cement pastes were used so that phenolphthalein testing would give a clear carbonation depth result, without the interference of aggregate particles.

The cement pastes used in this Chapter were similar to those which had been investigated in detail in Chapter 3. These specimens were used because they were well characterised.

The work on cement pastes was backed up by results from experiments on natural carbonation of surface treated concretes. Two concretes were prepared with similar free water to cement ratios, but different aggregate types.

6.5 Details of Experimental Work

The surface treatments investigated in this Chapter are described in 2.2.3 and were as follows :

Surface Hardeners	Water Repellents
Sodium silicate 1	Silane
Sodium Silicate 2	Siloxane
Magnesium and zinc silicofluoride	Silicone
Magnesium silicofluoride	

6.5.1 Carbon Dioxide Uptake of Treated Mortar Blocks

This experiment was carried out at the Building Research Establishment (BRE), with materials and technical assistance provided by the BRE.

Mortar blocks were prepared using the method described in 2.3.3 and treated by using the method in Section 2.3.4. In between treatments the blocks were dried in air. After the final treatment the samples were left in the laboratory over a weekend. For each treatment investigated eight mortar blocks were prepared, plus eight untreated control samples.

The samples were placed in a 75% R.H. controlled environment for four days. The samples were transfered to the test chambers, the details of which are given in 2.4.2. Four samples for each treatment condition were placed in the test train, and four in the control train. At this stage, gases were not flowing through the chambers.

The samples were left to equilibrate for 24 hours in the chambers, and then weighed. Three days later the samples were reweighed. No significant weight changes were observed, indicating that the samples were at equilibrium with the 75% R.H. in the chambers.

Carbon dioxide at 15% by volume of the gas stream was turned on and flushed continuously through the test chamber. Carbon dioxide free air was flushed through the control train.

At 24 hour intervals the samples were weighed for the next 4 days. From the weight measurements made, average carbon dioxide uptake values were calculated, and plotted against time. Details of the calculations are given in Appendix 9.

After 24 hours, one sample from each test condition was broken open and phenolphthalein tested for carbonation depth (see Section 2.4.3). The depths to which the water repellent treatments had penetrated the mortar blocks were assessed by spraying water on to freshly broken surfaces, and measuring the depths to which the water repellent effects were observed.

6.5.2 Accelerated Carbonation of Treated Cement Pastes.

The cement pastes used in this experiment were similar to the naturally carbonated specimens investigated in Chapter 3 (see Section 3.5.1). The specimens were 0.75 w/c cement pastes which had been carbonated for 17 months from one surface inwards to a depth of 7mm; the rest of the cylinder was uncarbonated.

The cylinders were treated by total immersion in the surface treatments, using the method described in 2.3.4. Each treament was applied to three cylinders. Three untreated cylinders were also prepared.

Twelve days after the final treatment the specimens were placed in a carbonation chamber with 5% CO_2, 67%R.H. and 25°C (see Section 2.4.2 for full description of the carbonation chamber). At 9, 29 and 49 days specimens were removed from the carbonation chamber, broken open and phenolphthalein tested for carbonation (see Section 2.4.3). The depth of carbonation was measured at the following surfaces :

1. Treated and carbonated.

2. Carbonated, treated and carbonated.

The penetration of the water repellents was also measured.

6.5.3 Natural Carbonation of Treated Concrete.

This experiment was carried out on two concrete mixes with similar free w/c ratios of 0.75, but different aggregates, (a siliceous aggregate and a calcareous aggregate). Details of the mixes and their preparation are given in 2.3.2.

The concrete was 14.5 months old at the start of the experiment. Fresh surfaces for treatment and subsequent carbonation were exposed by sawing the concrete beams into 50mm slices. Treatment was carried out by total immersion, using the method described in 2.3.4.

The treated specimens were left to carbonate in laboratory air. After 3.5 and 12 months the concrete was broken open and phenolphthalein tested for carbonation depth (see Section 2.4.3 for method). Treatment penetration was also measured.

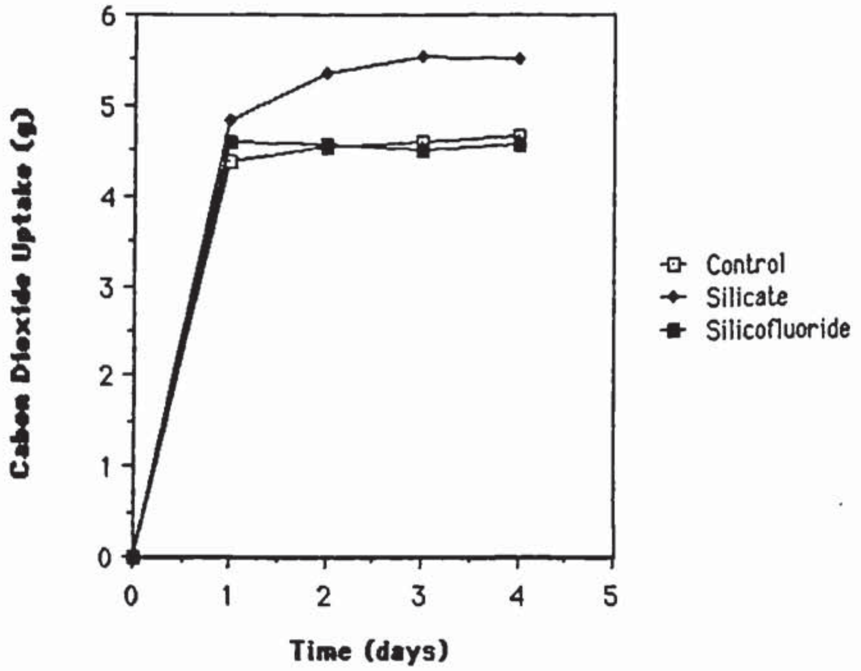
6.6 Results

6.6.1 Results of Carbon Dioxide Uptake Experiment

Carbon Dioxide Uptake of Surface Hardened Mortars

The carbon dioxide uptakes of mortar blocks treated with surface hardeners are shown in Figure 41. Sodium silicates 1 and 2 had very similar carbon dioxide uptakes, so have been averaged to show one sodium silicate result. The data have been presented likewise for the magnesium and zinc silicofluoride, and magnesium silicofluoride.

Figure 41. Carbon Dioxide Uptake of Surface Hardened Treated Mortar Blocks.



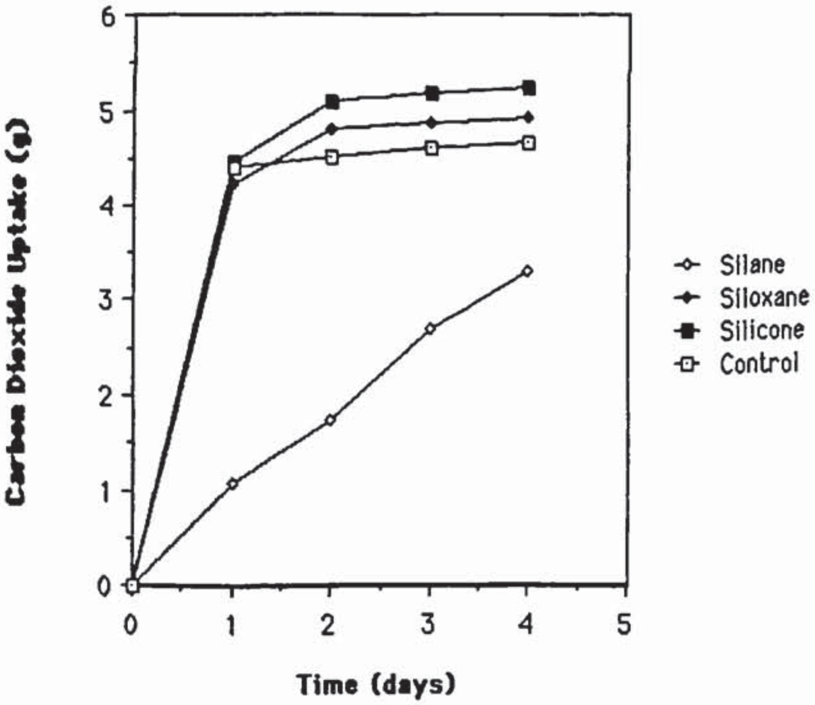
The silicofluoride treated samples showed similar rates of carbon dioxide uptake as for the untreated control. Slightly more carbon dioxide was taken up by the sodium silicate treated blocks than by the untreated control.

All the samples showed rapid carbon dioxide uptake during the first twenty four hours with subsequent levelling off thereafter. The phenolphthalein tests at twenty four hours indicated that the surface hardened treated samples were carbonated throughout, as was the untreated control.

Carbon Dioxide Uptake of Water Repellent Treated Mortars

The results of the carbon dioxide uptake of water repellent treated mortars are shown in Figure 42. The patterns of carbon dioxide uptake for silicone

Figure 42. Carbon Dioxide Uptake of Water Repellent Treated Mortar Blocks.



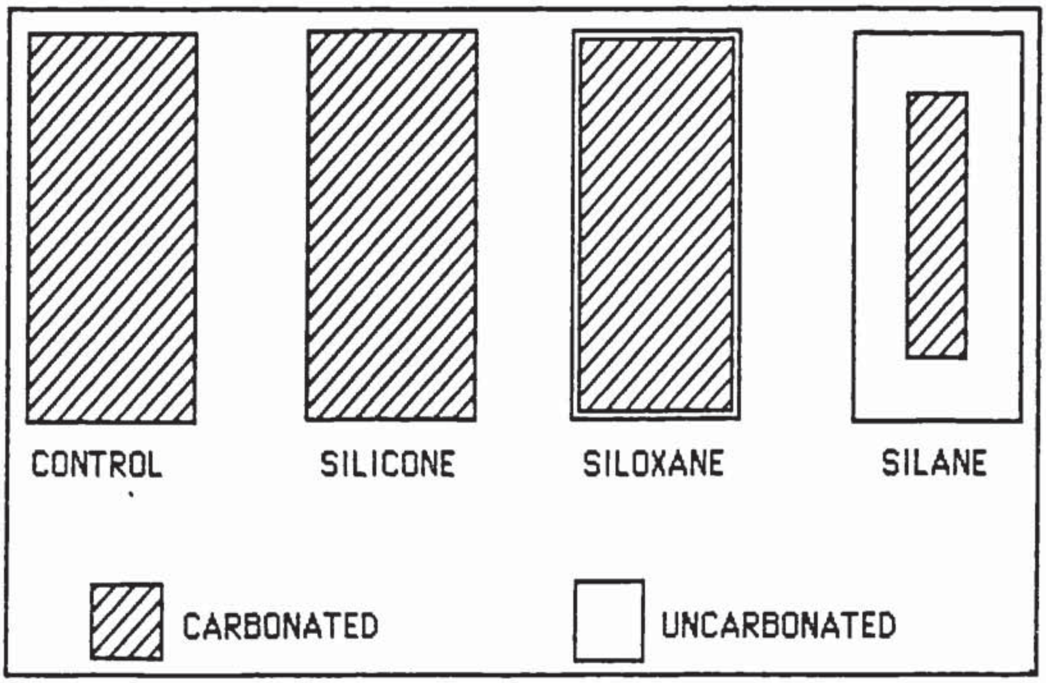
and siloxane treated mortars were similar to that of the untreated control. A rapid uptake of carbon dioxide was observed in the first twenty four hours, with levelling off thereafter.

The siloxane showed a slightly greater total carbon dioxide uptake than the control. The silicone treated mortar had the greatest carbon dioxide uptake, a little more than the siloxane.

The carbon dioxide uptake of the silane treated mortar block was considerably slower than the untreated control. Even after four days in the carbonation train, its carbon dioxide uptake had not equalled that of the control.

The phenolphthalein testing of the specimens after one day showed the silicone treated block to be carbonated throughout, similar to the untreated control. The siloxane treated sample was alkaline in the outer millimeter, but carbonated throughout the rest. The silane treated block was alkaline in the outer 8mm, but carbonated in the middle (see Figure 43).

Figure 43. Results of the Phenolphthalein Tests After Twenty Four Hours in the Carbonation Train.



The extent to which the water repellents had penetrated the mortar blocks were as follows :

Silicone 6mm
Siloxane 7mm
Silane 11mm

6.6.2 Results of Accelerated Carbonation of Treated Cement Pastes.

Carbonation of Surface Hardened Cement Pastes.

Surface hardened cement pastes were found to carbonate at very similar rates to untreated cement pastes. The results are summarised in Tables 27 and 28.

Table 27. Results of Accelerated Carbonation of Surface Hardened Cement Pastes.

Treatment	Depth of Carbonation in mm		
	9 Days	19 Days	49 Days
Sodium Silicate 1	5	8	11
Sodium Silicate 2	5	8	11
Mg + Zn Silicofluoride	6	9	11
Mg Silicofluoride	6	9	11
Untreated Control	6	8	11

Table 28. Results of Accelerated Carbonation of Naturally Carbonated and Surface Hardened Cement Pastes.

Treatment	Depth of Carbonation in mm		
	9 Days	19 Days	49 Days
Sodium Silicate 1	7	10	11
Sodium Silicate 2	6	10	11
Mg + Zn Silicofluoride	8	11	12
Mg Silicofluoride	8	11	12
Untreated Control	8	10	13

Carbonation of Water Repellent Treated Cement Pastes.

The rates of accelerated carbonation of water repellent treated cement pastes are shown in Figure 44. The total depth to which carbonation was observed was similar for water repellent treated and untreated cement pastes.

The outer surface of the treated specimens remained uncarbonated for at least 29 days. The depth of this uncarbonated layer was found to coincide with the penetration depths of the treatments, which were : silane 4mm, siloxane 2mm and silicone 1mm.

After 49 days the siloxane and silicone treated surfaces began to carbonate, the outer millimeter becoming partially carbonated. The silane treated surface continued to be uncarbonated.

Figure 45 shows the accelerated carbonation of water repellent treated, naturally carbonated cement pastes. The water repellents were found to have penetrated the naturally carbonated cement paste as follows :

silane 8mm
siloxane 1.5mm
silicone 0.5mm

The siloxane and silicone, having limited penetration, had little effect on the rate of further carbonation.

The silane treatment had penetrated the naturally carbonated cement paste 1mm deeper than the carbonation front. Consequently, with additional

Figure 44. Rate of Accelerated Carbonation of Water Repellent Treated Cement Pastes.

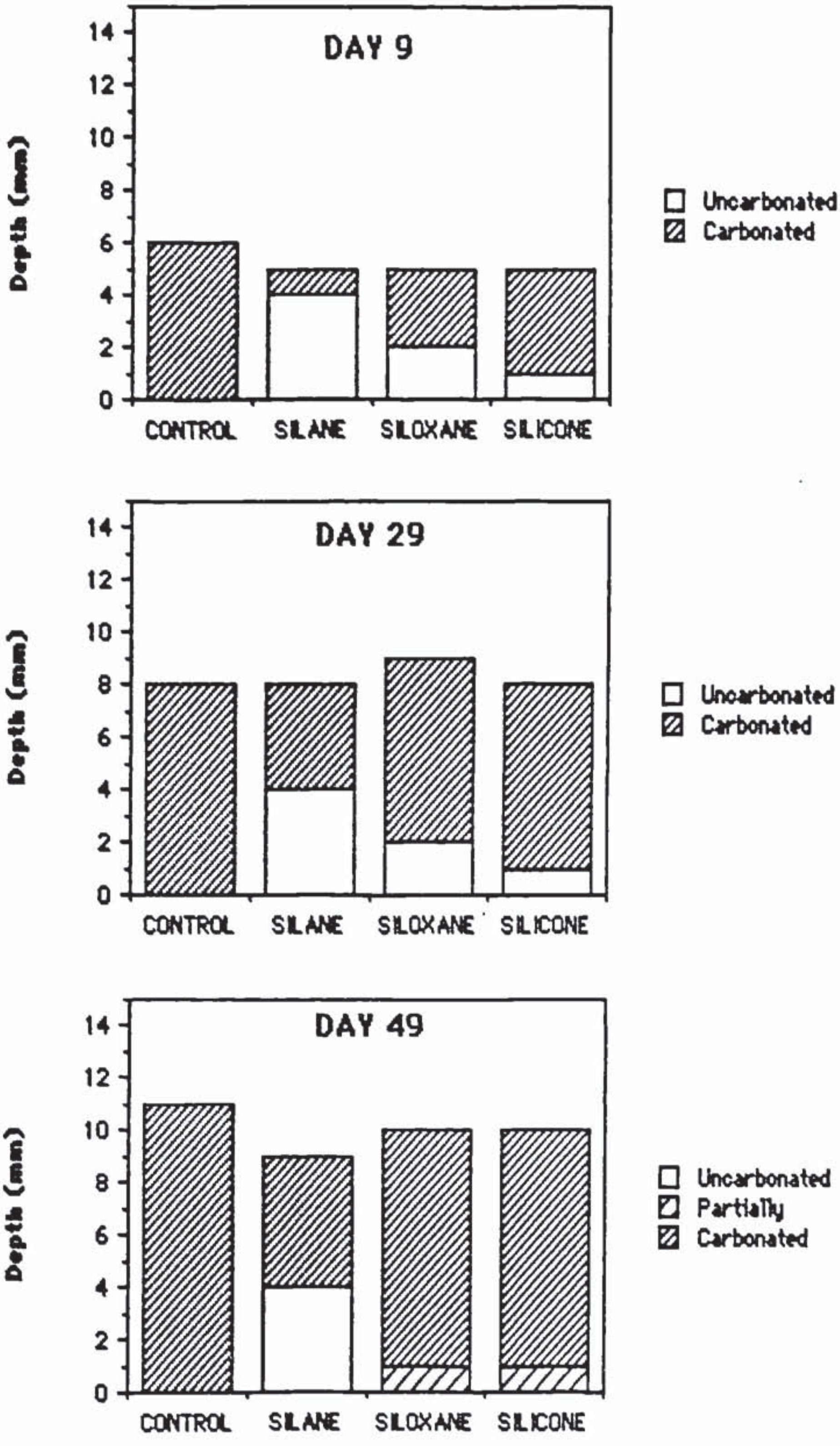
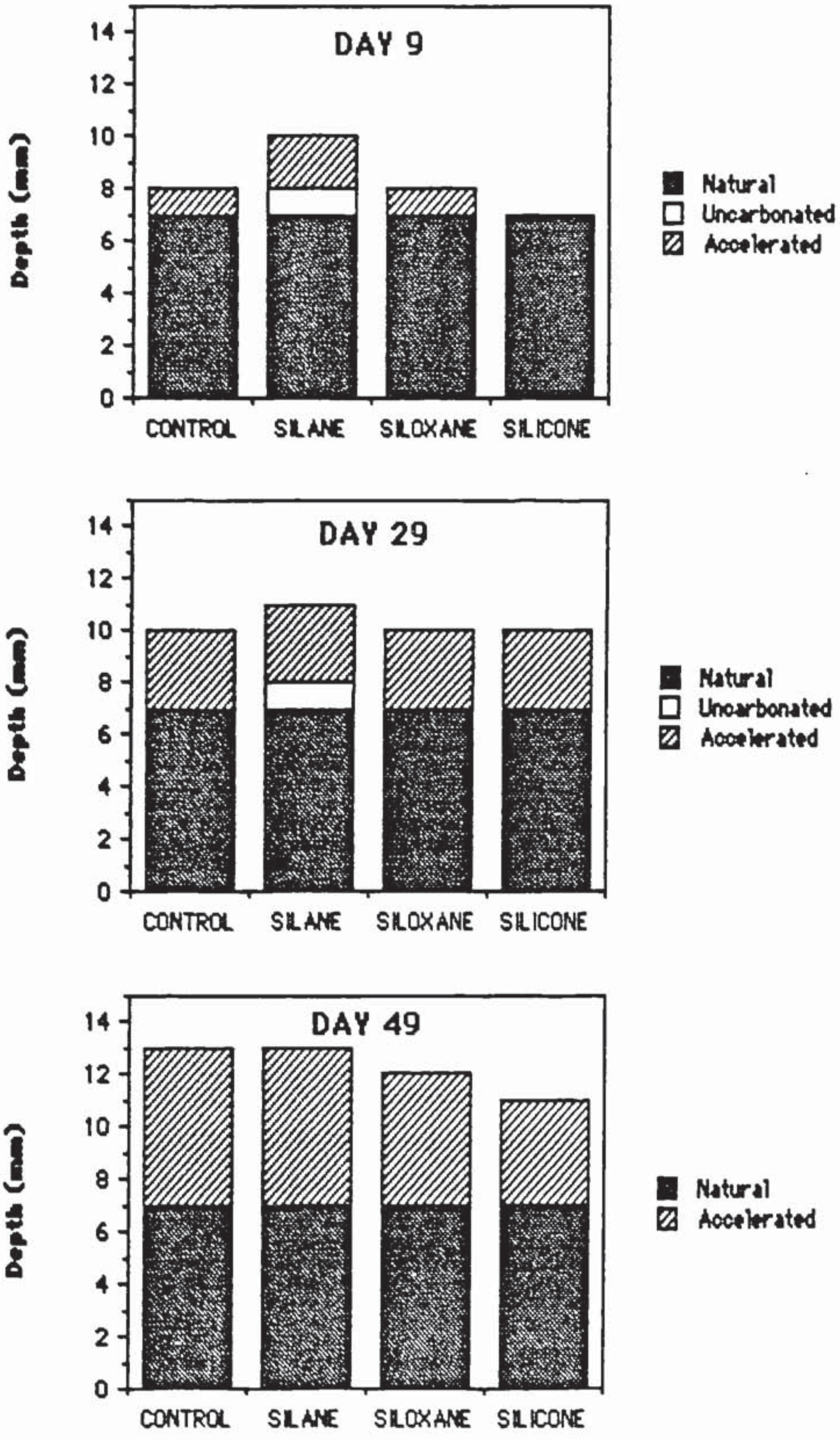


Figure 45. Rate of Accelerated Carbonation of Naturally Carbonated and Water Repellent Treated Cement Pastes.



carbonation, this area was not initially carbonated, and the carbonation front was temporarily pushed deeper into the cement paste. After 49 days, this treated and uncarbonated band had undergone carbonation, and the total carbonation depth was similar to an untreated cement paste.

6.6.3 Results of Natural Carbonation of Treated Concrete.

Very similar depths of carbonation were observed at 3.5 and 12 months. Consequently only the 12 month results are reported. Despite the use of the same free water to cement ratios, the concrete containing the calcareous aggregate had carbonated to a slightly greater depth of 8mm after one year, than the siliceous aggregate concrete (only 6mm).

Natural Carbonation of Surface Hardened Concrete.

The results summarised in Table 29 show that after one year of natural carbonation, the depth of carbonation was similar for surface hardened concrete and untreated concrete.

Table 29. Depth of Natural Carbonation of Surface Hardened Concrete Made with Different Aggregates After One Year.

	Concrete Aggregate Type	
Treatment	Siliceous	Calcareous
Sodium Silicate 1	5	7
Sodium Silicate 2	6	7
Mg + Zn Silicofluoride	5	7
Mg Silicofluoride	6	7
Untreated Control	6	8

Natural Carbonation of Water Repellent Treated Concrete.

Figure 46 shows the natural carbonation of water repellent treated concretes after a year of exposure. Figure 47 shows the penetration of the water repellents into these concretes.

Overall depths to which the concretes had carbonated were similar for water repellent treated and untreated samples. A maximum variation of 2mm was observed between samples. Treated concretes were only partially carbonated near the surface, where the water repellent treatments had penetrated.

Figure 46. Natural Carbonation of Concrete After One Year

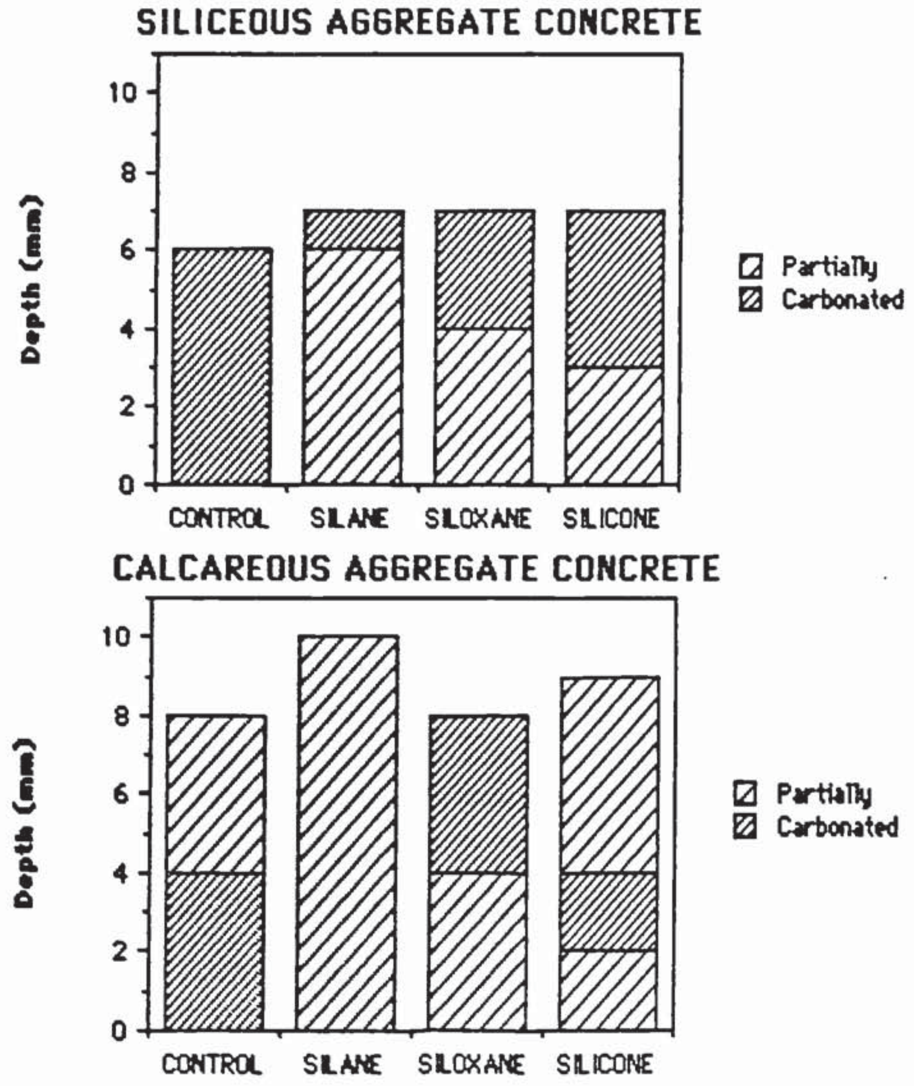
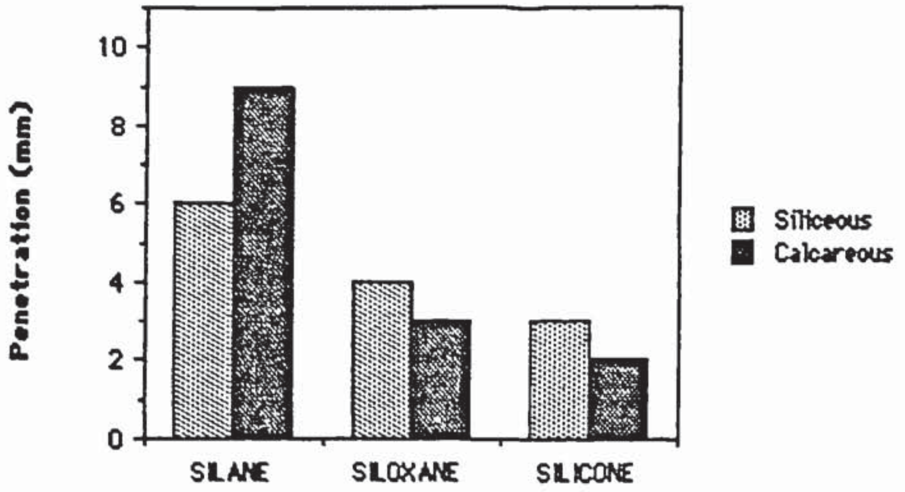


Figure 47. Penetration of Water Repellents into Concretes with Different Aggregates



6.7 Discussion and Conclusions

In sections 6.7.1 to 6.7.3 the results of the carbon dioxide uptake experiment, and accelerated carbonation of treated cement pastes are discussed together.

6.7.1 Influence of Silicate Treatments on Carbonation.

Silicate treated cement pastes carbonated at similar rates to untreated controls. These findings are consistent with previous work of Keer and Gardiner (82). Any slowing down of carbon dioxide diffusion, as reported by Weber (63), therefore must have had a negligible effect.

The total carbon dioxide uptake of silicate treated mortars was slightly greater that of control mortars, suggesting that the treatments had also reacted with carbon dioxide. This was possibly reflected in the initial rate of accelerated carbonation of silicate treated cement pastes, as depths of carbonation at 9 days were found to be slightly less than for untreated controls. Later, there was little or no difference in carbonation depths.

6.7.2 Influence of Silicofluoride Treatments on Carbonation

The carbon dioxide uptake and rate of carbonation of silicofluoride treated specimens were similar to untreated controls, indicating that silicofluoride treatment does not effect the rate of carbonation.

6.7.3 Influence of Water Repellent Treatments on Carbonation

The study of the rate of carbonation of water repellent treated specimens gave some interesting results, and an important insight into the way these materials influence the process of carbonation.

The main observation was that where the water repellents had penetrated cementitious material, carbonation reactions were initially prevented from occuring. This was presumably because of the water repellent effect minimising the contact of carbonic acid with the cement paste substrate. Lindberg (135) and Robinson (66) have also obtained experimental evidence indicating that water repellent treatment of concrete can prevent the normal reactions of acid with concrete.

With time the water repellent treated areas became carbonated. This led to similar carbonation depth for treated and untreated specimens, as found by Robinson (66).

Penetration of treatments into substrates clearly had an important bearing on the extent to which the treatments affected the progress of carbonation. In the carbon dioxide uptake experiment the silane had penetrated the mortar blocks the deepest. Consequently normal carbon dioxide uptake was prevented. Phenolphthalein testing of the block showed that carbonation was occuring inside the block away from the treated surface.

The total carbon dioxide uptake of the siloxane and silicone treated mortars was greater than that of the untreated control, suggesting that to a certain extent the treatments had reacted with the carbon dioxide. The silicone had taken up more carbon dioxide than the siloxane.

6.7.4 Carbonation of Surface Treated Concrete

Despite having similar free water to cement ratios, the concrete made with the calcareous aggregate carbonated at a slightly greater rate than the siliceous aggregate concrete. This was probably due to the porous and more permeable nature of the calcareous aggregate, allowing carbon dioxide to diffuse through the aggregate particles deeper into the concrete.

Although natural carbonation results from treated concretes were limited, they appeared to support results obtained by accelerated test methods on treated cement pastes. The presence of different aggregates in the concrete did not affect the performance of the treatments in relation to carbonation.

6.7.5 Summary

Silicate treatment has little influence on the rate of carbonation. Reaction of the treatment with carbon dioxide may temporarily slow down the initial rate of carbonation, but any such delay is relatively insignificant and does not appear to affect subsequent rates of carbonation. Silicofluoride treatment has no effect on the rate of carbonation.

Where water repellents penetrate uncarbonated cementitious material, carbonation is temporarily prevented. Consequently, the carbonation front may be pushed deeper into the concrete to where moisture and carbonic acid are not repelled. With time the treated area becomes carbonated, giving an overall depth of carbonation similar to that of an untreated concrete.

CHAPTER 7.

Effect of Surface Treatments on Carbonation Induced Corrosion.

7.1 Introduction

The way in which carbonation of concrete can cause corrosion of embedded reinforcing steel is described in Chapter 1 (Section 1.3.4). The conditions required for carbonation induced corrosion may be summarised as follows :

1. Steel in contact with low alkalinity carbonated concrete.
2. Moisture to provide an electrolyte in the concrete pores around the steel.
3. Access of oxygen to the steel.

Should any one of the above conditions not be satisfied, carbonation induced corrosion would be prevented. The posible influence of the surface treatments under investigation on any one of these controlling conditions was considered.

In the case of the surface hardeners, it was thought that they might prevent carbonation induced corrosion by realkalising carbonated concrete. Experimental work in Chapter 4 had indicated that these were not suitable for this purpose, as they lacked penetration and did not significantly realkalise carbonated cement paste. Consequently, surface hardeners were not investigated further in this Chapter.

It was thought that water repellent surface treatment might reduce moisture levels and prevent carbonation induced corrosion. This was despite doubts about the ability of these treatments to dry out concrete, as indicated by results from experimental work in Chapter 5.

The influence of water repellent treatment on the moisture state of concrete under cyclic wetting and drying conditions, where there was insufficient time for equilibrium to be achieved, was still in question. The effect of this on carbonation induced corrosion was the area which was investigated in this Chapter.

7.2 Previous Work

The most direct method of measuring the corrosion rate of steel in concrete is to break open the concrete and measure the loss of steel section due to corrosion. This method is time consuming as it requires a lengthy exposure period, whilst the steel corrodes prior to assessment. Also, measurement involves destruction of the sample rendering it useless for further study (138).

Non-destructive electrochemical methods have been developed for assessing corrosion of steel in concrete. The steel has a rest potential (Ecorr), which can be measured relative to a reference cell. Rest potential measurements are easy to make, and are frequently used (139).

Corrosion rate is not simply related to potential, but generally more negative potentials indicate active corrosion (139). Passive steel in concrete exposed to air typically have potentials in the range +100mV to

-200mV. This may vary from +200mV to -700mV depending on the availability of oxygen. The potential of steel undergoing general corrosion is usually in the range of -450mV to -600mV. General corrosion may be brought on by carbonation or excessive chloride ion contamination (140).

Linear polarisation resistance measurements can be used to determine an "instantaneous" corrosion rate value for steel in concrete (141). The method involves the polarisation of the steel by applying potentials of up to +10mV from Ecorr and measuring the polarisation resistance (138). This measurement can be used to calculate the corrosion current density (Icorr) as follows (141):

$$\mathrm{Icorr} = \frac{\beta a \times \beta c}{2.3(\beta a + \beta c)} \times \frac{\Delta I}{\Delta E} = \frac{B}{R_p}$$

Where : R_p = polarization resistance

B = Stearn-Geary constant, dependant on contributions from anodic and cathodic reactions

βa = anodic Tafel constant

βc = cathodic Tafel constant

ΔI = applied current density (current/area)

ΔE = change in potential

Icorr = corrosion current density (current/area)

The value of B is an empirical constant, determined from a full polarisation curve by applying overpotentials of several hundred millivolts to the steel under investigation. Determination of a complete potentiostatic polarisation curve can take up to a month of experimental work, and may cause irreversible damage to the corroding system (138).

Andrade and Gonzalez have found that a value of 26mV for B is acceptable for actively corroding steel (142). This value has been adopted for use in experimental work to avoid the long and potentially damaging empirical determination of B (36,143).

The magnitude of the corrosion current density is a direct measure of the rate of corrosion of steel. A corrosion current density of 1A/m^2 (determined per unit area of reinforcement) is equivalent to an average oxidation or dissolution rate of 1.16 mm per year from the surface of the steel (138).

Work by Gonzalez et al in 1983 indicated that 1-2x10^{-3}A/m^2 corresponds to a penetration depth of 0.11mm of steel after 50-100 years. Gonzalez et al have suggested that these levels could be the barrier between tolerable and dangerous corrosion Although somewhat subjective, they have estimated 1-2x10^{-2}A/m^2 as the maximum permissible value of Icorr for reinforcement embedded in concrete as the service life of a concrete structure should be 50-100 years (61).

A problem in determining polarisation resistance is the IR drop. This is due to the high resistivity of the concrete, and if not corrected for it can result in an underestimation of Icorr (139,142). The resistivity of concrete is partly dependent on the available pore water. High water contents lead to low resistivity, favouring active corrosion (139).

The use of polarisation resistance to determine corrosion rates of steel in concrete has limitations (139,144). It is an approximate technique, but has has been found to be sufficiently accurate to establish that carbonation of cement may multiply the corrosion rate by one or two orders of magnitude (145).

Gonzalez <u>et al</u> 1985 (62) have looked at corrosion of steel embedded in mortar, during and after accelerated carbonation (see Figure 48). The effect of moisture on carbonation induced corrosion was examined by measuring Ecorr, and using polarisation resistance measurements to evaluate Icorr. They concluded that carbonation of cement alone can not promote appreciable corrosion of the reinforcement. To produce a serious corrosion rate the relative humidity of the environment should not fall below 50%.

Sergi (36) carried out a similar investigation to look at the effect of different moisture levels on natural carbonation induced corrosion (see Figure 49). His results also indicated a critical moisture content of carbonated concrete below which corrosion could be considered negligible.

Figure 48 Effect of Accelerated Carbonation and Moisture on Icorr and Ecorr For Steel Bars Embedded in Mortar.
From Gonzalez et al 1980 (62).

Illustration removed for copyright restrictions

Figure 49 Variation of Icorr and Ecorr of Steel Bars Embedded in Concrete with Time in Different Moisture Environments. From Sergi 1986 (36).

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Work on the effect of water repellents on carbonation induced corrosion could not be found in the literature. However, some work had been reported by Wong et al (146) on the effect of alkyl-alkoxy silane treatment on corrosion of steel in the presence of chloride ions.

Water, amongst other requirements, is needed for chloride induced corrosion. Wong et al suggested that if capillary water was removed from the concrete by drying, and water was prevented from continuously resaturating the capillary void system by impregnating with a material which would cause the capillary walls to become hydrophobic, the corrosion process could be significantly retarded or stopped.

Wong et al investigated this theorey by corrosion monitoring steel embedded in concrete made with salt (NaCl) contaminated mix water. Sodium chloride was added in excess to give 8.9kg NaCl per m^3 of concrete. The concrete was surface treated with alkyl-alkoxy silane.

Wong et al used an accelerated corrosion test, whereby an impressed current was used to initiate corrosion, and 5% NaCl solution used as an electrolyte (see Figure 50). Their results indicated that alkyl-alkoxy silane treatment was effective in reducing the rate of corrosion of reinforcing steel.

Figure 50. Schematic Illustration of Corrosion Test System Used By Wong et al. From Wong et al 1983 (146).

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7.3 Aims of the Experimental Work.

The aim of the experimental work in this Chapter was to establish whether or not water repellent surface treatments could be used to slow down carbonation induced corrosion. In particular, their influence on carbonation induced corrosion during a wetting and drying cycle was investigated.

Under conditions of continuous change, it was thought that the treated concrete would not have sufficient time to come to equilibrium with the moisture in the environment. Hence, the water repellents might keep the concrete drier, thus reducing the amount of electrolyte and corrosion.

7.4 Approach to the Experimental Work.

The approach to the experimental work was to use steel reinforced concrete which had undergone sufficient natural carbonation for some of the bars to be embedded in carbonated concrete. Connections were made with the bars so that electrochemical monitoring of the bars could be carried out. The behaviour of the bars under a wetting and drying cycle was monitored before and after treatment.

Steel reinforced concrete blocks used in Sergi's (36) study of carbonation were used in this investigation. The blocks were chosen because they contained steel reinforcement embedded in naturally carbonated concrete. They also contained bars in uncarbonated and partially carbonated concrete against which comparisons could be made.

7.5 Details of the Experimental Work

The investigation was carried out on reinforced concrete blocks which had been used in a previous study by Sergi, and described in his thesis (36). The blocks were originally supplied to Aston University by the Building Research Establishment and were understood to be sections from internal concrete beams, approximately 30 years old. The beams were thought to have come from a kitchen or bathroom.

Each block selected for this investigation contained three parallel 8mm diameter steel bars which varied in length from 36 to 65mm. Five blocks were selected to give at least one bar in each of three states of carbonation for every treatment condition to be investigated as follows :

Carbonation States : uncarbonated, partially carbonated and fully carbonated
Treatments : silane, siloxane, silicone and untreated control

During the previous work on the blocks, carbon rods had been grouted in to them to act as counter electrodes. All the working and counter electrodes had been drilled and tapped, so that electrical connections could be made by attatching wires. The connections had been sealed with an epoxy.

It was noted that some of the connections were showing signs of corrosion, as rust stains were observed from these areas. Breaking open the ends of the specimens re-affirmed these suspicions. Consequently fresh surfaces were cut, thus removing the areas containing the localised corrosion. The offcuts were used for phenolphthalein testing, and reassessment of the carbonation front in relation to the steel bars.

New connections to the bars and carbon rods were made. To prevent the recurrence of corrosion at the connections a latex modified cementitious grout was applied prior to sealing with epoxy. The grout was used to provide a protective alkaline environment, which would not allow moisture to penetrate the connecting area.

Additional preparation of the blocks involved the grouting in of a salt bridge. The salt bridge was made of a 50% saturated potassium nitrate solution in agar, which had been injected into a length of plastic tubing. The loose ends of the salt bridges were placed into a saturated potassium chloride solution, into which a reference electrode was placed.

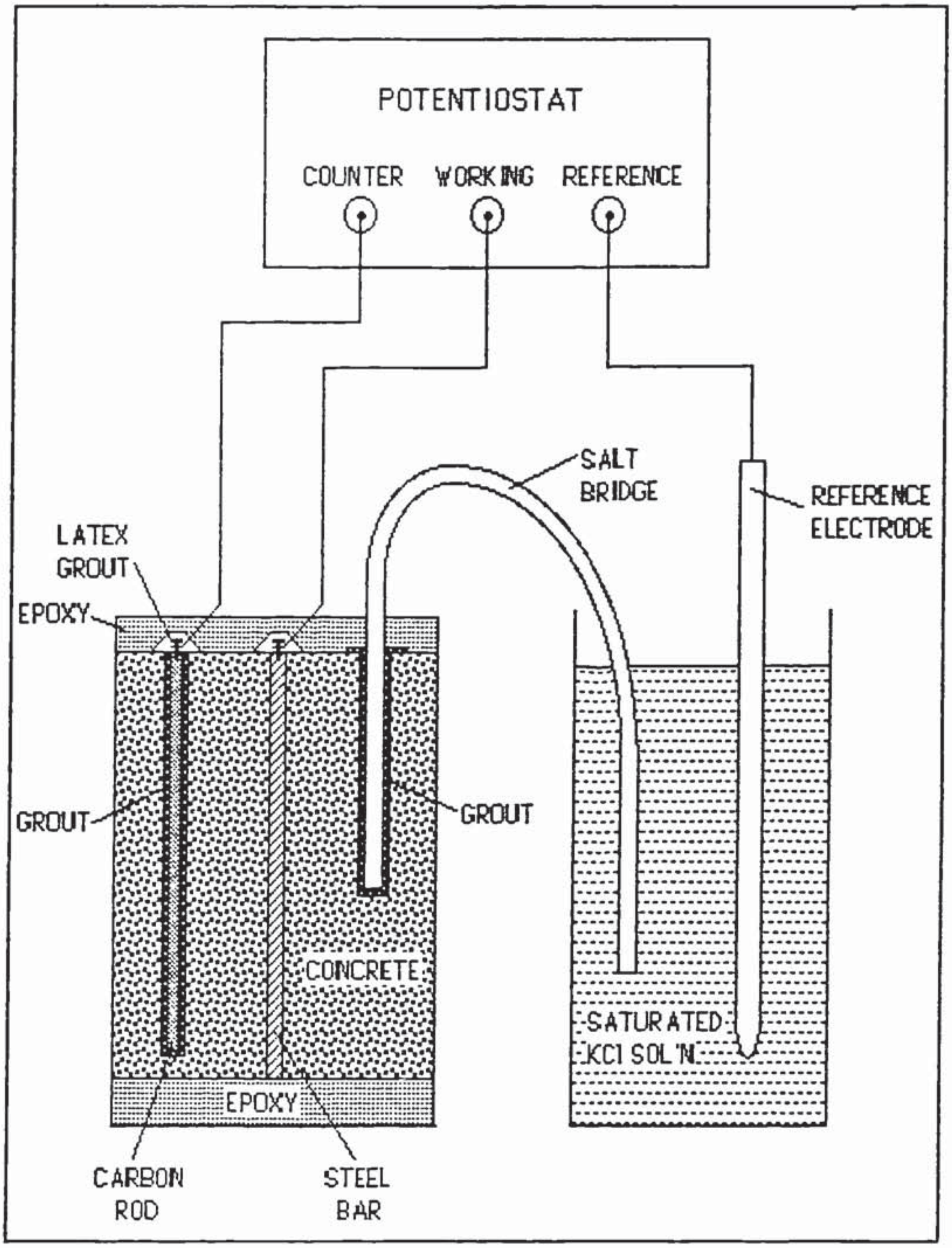
Corrosion monitoring of reinforcing bars was carried out using a Model 551 Amel potentiostat. The corrosion test system is shown in Figure 51. Rest potential (Ecorr), uncompensated polarisation resistance (Rpu) and resistance (Ru) measurements were made at regular intervals during a wetting and drying cycle.

The reinforcement rest potential (Ecorr) was measured against the reference electrode. A potentiostatic step of +10mV (ΔE) from the rest potential was applied. The potential was kept constant and maintained by causing current to flow between the working and counter electrodes. The current flowing one minute after polarisation was measured (ΔI) and used to calculate an uncompensated polarisation resistance (see Appendix 10 For details of the calculations).

The time of one minute was used as a compromise, long enough for the system being polarised to reach a steady state, but minimising the time in which perturbations might occur in the working electrode-electrolyte interface. This time was choosen having considered previous work by Gonzalez et al (144).

The cell resistance (Ru) was measured by applying increasing amounts of positive feed-back to the system until it became unstable. At the point of change over from stability to instability the resistance of the system was measured. This value was used to calculate a compensated polarisation resistance (see Appendix 10).

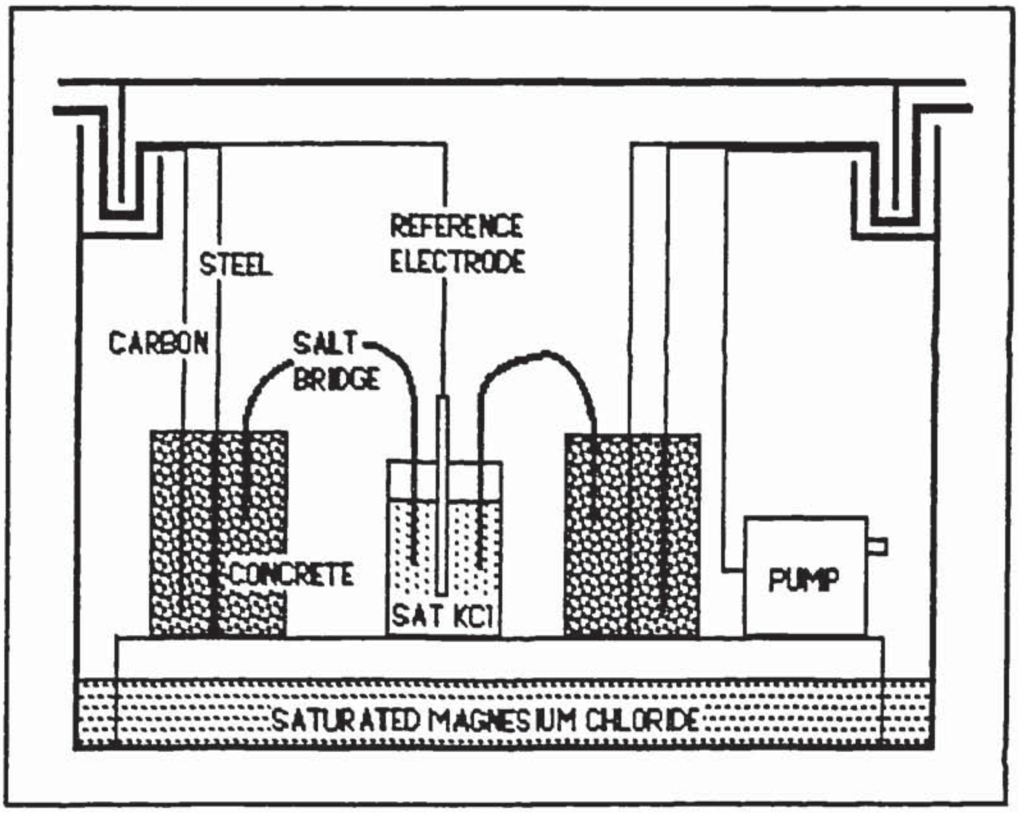
Figure 51.The Corrosion Test System.



Note. Only one steel bar is depicted in the above diagram, when in reality there were three in each concrete specimen.

Prior to taking any readings the prepared blocks were left in a high humidity environment over water for one month. Readings were taken every Monday, Tuesday, Wednesday and Friday during a wetting and drying cycle. Between the Monday and Tuesday readings the samples were immersed in water. For the rest of the week the samples were held at 33% R.H. in the chamber illustrated in Figure 52.

Figure 52. Corrosion Chamber Holding Specimens at 33% Relative Humidity.



Note. The diagram has been simplified.

Only two out of a total of five specimens are shown.

Each specimen had three wires from reinforcing bars, and one from a carbon rod. Only two of these wires are shown from each specimen.

The chamber was built so that the samples could be monitored without removing the specimens from their humidity controlled environment. This was achieved by having long connecting wires, which were passed out of the chamber through a simple seal in the lid. Only one reference electrode was used, as all the salt bridges were placed in one central pot.

A pump was used to circulate air in the corrosion chamber. During monitoring the pump was switched off, to avoid any unwanted interference.

The wetting and drying cycle with associated measurements was repeated three times over a three week period. The following week the blocks were treated (see Section 2.3.4 for treatment details). Two blocks were left as untreated controls. The samples were left for a month in a high humidity environment before repeating the wetting and drying cycles.

7.6 Results

Although a total of 15 bars had been investigated, only results from 10 bars are reported. Results from some bars are omitted because either they were duplicates of other bars, or had shown signs of being damaged ie. they had continuously high corrosion rates, possibly due to poor connections which had given rise to corrosion by crevice attack. Such omissions meant that no data was available for silicone treated concrete with bars in partially carbonated and uncarbonated concrete.

A large amount of data was collected. Summarising the results would have detracted from their significance. Consequently all the data has been presented graphically in Appendix 11, Figures 58 to 69

For the untreated controls and each treatment investigated (except for the silicone), bars in uncarbonated, partially carbonated and uncarbonated concrete were monitored for changes in Icorr, Ecorr and Ru. These results are plotted against time. The results at 1, 8 and 15 days were most important, as these correspond to times when the specimens had been immersed in water for 24 hours, and corrosion was expected to be at a maximum.

7.6.1 Corrosion Rates

Corrosion Rates of Bars in Untreated Concrete.

The bars embedded in untreated concrete showed a very consistent and predictable pattern. Bars in uncarbonated concrete had low corrosion rates, 500µA/m^2 or less. With wetting and drying this corrosion level was not altered.

Bars embedded in partially carbonated concrete had corrosion levels of 500µA/m^2 or less during the drying part of the cycle. On wetting these increased to around 1000 µA/m^2.

The pattern of corrosion for bars in carbonated concrete was similar to that of bars in partially carbonated areas. The only difference was that bars in carbonated concrete had slightly higher corrosion rates during the wetting part of the cycle, increasing up to 1250 - 1500 µA/m^2.

Corrosion Rates of Bars in Treated Concrete.

The corrosion levels of bars in treated concretes tended to be less than 500μA/m^2. In the case of bars in uncarbonated concrete, this resulted in little change in corrosion levels. For bars in partially carbonated and carbonated concrete there was a significant lowering of the corrosion rate during the wetting part of the cycle in comparison with untreated controls.

There were some slight differences in the relative performance of the different treatments. The silane treatment was very effective in lowering the corrosion rate during wetting. The siloxane was fairly effective, but there appeared to be an improvement of its effectiveness with time. The silicone appeared to be least effective.

7.6.2 Rest Potentials

Rest Potentials of Bars in Untreated Concrete.

The rest potentials of bars in uncarbonated and untreated concrete were between 0 and -200mV. During the wetting of the concrete these rest potentials tended to become slightly more positive.

Bars embedded in partially carbonated concrete had rest potentials between -200 and -300mV. During wetting these potentials became more negative.

Bars in carbonated concrete exhibited a similar pattern to those in partially carbonated concrete but rest potentials tended to be slightly more negative, between -250 and -450mV. The bars in carbonated concrete became more markedly negative during wetting, than those in partially carbonated concrete.

Rest Potentials of Bars in Treated Concrete.

The bars in silane treated concrete were more positive than when untreated. Also, on wetting concrete with bars in partially carbonated and carbonated concrete the trend towards more negative potentials was eliminated after treatment. With time these bars tended to show a pattern of becoming more positive on wetting, similar to that of bars in uncarbonated and untreated concrete.

In comparison with the silane, siloxane and silicone treatment of concrete caused similar, but less marked effects on rest potentials of reinforcing bars. The silicone appeared to have the least effect.

7.6.3 Resistance of Concrete.

The resistance of untreated concrete decreased on wetting. With treatment this effect was virtually eliminated. Generally the resistances measured were relatively insignificant in comparison with the polarisation resistance measurements also being made. Resistances were usually one or two orders of magnitude less than the uncompensated polarisation resistance.

7.7 Discussion and Conclusions

Corrosion levels in uncarbonated concrete were found to be consistently low. With carbonation the amount of corrosion during the wetting of the concrete increased, as the quantity of electrolyte in the pores was raised. These findings were consistent with results from previous experimental work reported by Gonzalez et al (62) and Sergi (36).

Although corrosion values were significantly increased with carbonation, in relation to work by Gonzalez et al (61), they were only on the border of dangerous corrosion at $1\text{-}2\times10^{-3}$A/m^2. Even the maximum observed value of 2000 μA /m^2 was well below their suggested maximum permissible value of $1\text{-}2\times10^{-2}$A/m^2 for a service life of 50 to 100 years.

Application of water repellent treatment decreased corrosion rates of bars embedded in carbonated concrete during wetting. This was probably due to the treatments repelling liquid water, thus keeping the electrolyte necessary for carbonation induced corrosion to a minimum. There was some evidence that the silane was the most effective, followed by the siloxane, and lastly, the silicone.

Rest potential patterns were consistent with the corrosion data. With increasing levels of corrosion, the rest potentials became more negative.

The resistance of untreated concrete increased with drying. Resistance of water repellent treated concrete, after immersion in water, was higher than for untreated specimens. This further suggests that water repellent surface treatment was keeping the concrete drier.

The results indicating that water repellent treatment may be used to reduce carbonation induced corrosion are similar to those of Wong et al on chloride induced corrosion. In both cases it is suggested that the corrosion is reduced by the water repellents keeping the concrete drier.

Summary

Under the wetting and drying cycle investigated, water repellent surface treatments were effective in reducing carbonation induced corrosion. Increases in dryness due to treatment of carbonated concrete resulted in increasing resistance with consequent lowering of corrosion rates and more positive rest potentials.

CHAPTER 8

Discussion, Conclusions and Suggestions for Future Research.

8.1 Carbonation

The detailed study of accelerated and naturally carbonated cement pastes in Chapter 3 served the purpose of characterising substrates to which treatments were applied. In addition, the work gave a deeper insight into the process of carbonation, as well as revealing phenomena for which only tentative explanations could be given.

The chemistry of carbonation was investigated by expressing pore solution from sections taken across the carbonated surface, and analysing the solutions for Na, K, Ca, Cl and OH/pH. The pH was found to increase from the surface into uncarbonated material. Ionic concentrations varied across this region, and their distribution was thought to be influenced by the relative concentrations of bicarbonates and carbonates which alter with changes in pH.

Concern over carbonation causing the release of chloride ions into the pore solution were shown to be justified. Low levels of chloride were found in pore solutions from carbonated areas, but were not detected in advance of the carbonation front. However, the cement pastes investigated had a minimal chloride content as is normal in cement. Where there are higher chloride concentrations (either added to the mix or penetrating from an external source) there may be release ahead of the carbonation front which could cause chloride-induced corrosion before carbonation-induced corrosion. This should be further investigated.

Changes in porosity across the carbonated area were investigated by carrying out mercury intrusion porosimetry determinations on slices similar to those from which pore solution was expressed. Porosity was found to increase from the carbonated surface inwards.

Dissimilar microhardness profiles were obtained for surfaces carbonated under accelerated and natural conditions. The naturally carbonated surface had an increased hardness consistent with decreasing porosity. After accelerated carbonation hardness decreased, despite decreases in porosity. The reason for this loss in hardness was not apparent and could warrant further investigation.

One of the main conclusions drawn from the work in Chapter 3 was that carbonation is a continuous process. Properties were found to vary with distance from the surface and with method of carbonation. There were no stepped changes in pH across the carbonated area and therefore the concept of a definite boundary of the sort indicated by the phenolphalein test could be somewhat misleading. Despite this, it was concluded that phenolphthalein testing was useful for indicating the extent of areas in the cement paste where depassivation of the steel could occur.

Although patterns of chemical and physical changes were generally similar for specimens carbonated under natural and accelerated conditions, accelerated carbonation appeared to cause more extreme changes. This is most important when considering results which compare directly the physical and chemical effects of treatments applied to carbonated surfaces.

8.2 Surface Hardeners

Work in Chapter 4 involved the investigation of the performance of two chemically similar sodium silicates, a magnesium silicofluoride and a magnesium-zinc silicofluoride. Many of the findings for the sodium silicates were similar and likewise for the silicofluorides. However, there was variation in the performance of silicates and silicofluorides reflecting their differences in chemistry.

The question of whether sodium silicates react with cement paste and/or harden by drying was not resolved. However, conclusive evidence concerning reactions of silicofluorides with carbonated and uncarbonated material was obtained as calcium fluoride was detected after treatment. Further research is required to obtain more detail of these reactions. The differences between carbonated and uncarbonated surfaces should be borne in mind in any future investigations of this sort.

The effect of surface hardeners on the alkalinity of pore water expressed from accelerated carbonated cement pastes was investigated. Treatment was not found to alter significantly the pH of pore water indicating that surface hardeners would not be suitable for re-alkalising carbonated concrete.

All the work in Chapter 4, examining the effect of treatments on carbonated surfaces, was carried out on surfaces prepared under accelerated carbonation conditions. Consequently the chemistry and physical properties were different from those of naturally carbonated surfaces. The validity of findings should be confirmed by further work on treatments applied to naturally carbonated material.

The surface hardeners were found to have very limited penetration and the extent of this was reduced by moisture in the sample. Hardening was observed to a depth of only 250µm and of the four treatments investigated the magnesium-zinc silicofluoride was the most effective. The lack of evidence for more substantial porosity decreases after treatment was surprising in view of the various claims made in the trade literature that pore blocking on treament is responsible for increases in hardness.

It must be acknowledged that the limited penetration of surface hardeners made assessment of their effects difficult, despite the use of highly porous cement paste substrates to facilitate penetration. Future work looking at reactions and porosity changes could involve the vacuum impregnation of surface hardeners into oven dry samples. Although this approach would be somewhat artificial, it would promote deep and thorough penetration which might result in more substantial microstructural alterations.

The use of porous cement paste substrates had a drawback, as it was suspected that wetting and drying during treatment may have caused rapid carbonation of supposedly uncarbonated material. This led to problems in interpreting data where cement paste reactions with treatments might have been masked by carbonation reactions. Future work could be carried out on lower porosity substrates less prone to rapid carbonation. The elimination of carbon dioxide from the surrounding atmosphere during treatment would not be recommended as its presence may be important in hardeneing reactions.

Despite the problems encountered when investigating the performance of the surface hardeners, it could be concluded that for hardening uncarbonated surfaces they are effective albeit on a very localised scale. The hardening of carbonated surfaces was not investigated and could be further researched. The approach to this type of investigation would not be easy because of variations in hardness between surfaces carbonated under different conditions. Much work characterising the hardness profiles of carbonated surfaces would be recommended prior to investigating the hardening effect of treatments on carbonated surfaces.

8.3 Water Repellents

It is known that water repellent treatment modifies the properties of a concrete surface by increasing its surface tension, as its contact angle with water increases. This is readily observed as water applied to a treated surface forms drops which are easily shed. Observation of this phenomenon was used to assess the penetration of water repellents into substrates.

The water repellents penetrated cement pastes to varying degrees, depending on their molecular size. The silane with the smallest molecules penetrated the furthest, followed by the siloxane and the larger silicone molecules the least. Moisture in the surface reduced penetration, but under favourable conditions the silane penetrated 24 mm.

Water repellent treatment was found to decrease the rate of water vapour diffusion. The main factor slowing this process was thought to be the effect of treatment increasing the contact angle between cement paste and water. The silane reduced rates of water vapour diffusion more significantly than the other two water repellents investigated. This may have been due to its deeper penetration, or to its more effective modification of contact angle. This could be further researched.

The effect of water repellent treatment on the internal moisture contents of cement pastes was investigated, particularly as moisture is critical to carbonation and carbonation-induced corrosion. Experimental results indicated that under constant relative humidity conditions water repellents do not assist in drying out cement paste. It was thought that given time, alterations in the external relative humidity would be reflected internally, due to water vapour diffusing through the treated surface. This idea requires further research.

8.4 Effect of Treatments on Carbonation

Much of the work investigating the influence of surface treatments on carbonation was carried out using the phenolphalein test to measure depths of carbonation. The effectiveness of the test applied to treated surfaces was checked before use and found to be satisfactory.

8.4.1 Effect of Surface Hardeners on Carbonation

Surface hardeners were not found to have a significant effect on the rate of carbonation, and therefore there should be no risk of increasing the rate of carbonation by applying surface hardeners to concrete. It is possible that sodium silicates may slightly decrease the rate of carbonation by also reacting with carbon dioxide.

8.4.2 Effect of Water Repellents on Carbonation

Water repellent treatment was found to retard carbonation reactions by repelling the moisture needed to sustain the reaction. Consequently carbonation reactions were concentrated in deeper untreated areas, and in some cases the rate of penetration of the carbonation front was temporarily increased. With time the treated areas became carbonated and depths of carbonation were found to be similar to that for untreated concretes.

8.5 Effect of Treatments on Carbonation-Induced Corrosion

8.5.1 Effect of Surface Hardeners on Carbonation-Induced Corrosion

The limited penetration of surface hardeners alone suggests that these materials may not be suitable for re-alkalising carbonated cement paste to prevent carbonation-induced corrosion. Results which indicate no significant alteration in the pH of pore water expressed from carbonated and treated cement pastes confirmed this.

Considering the above conclusions and the overall performance of surface hardeners, it is unlikely that they would have any significant influence on the process of carbonation-induced corrosion. This could only be substantiated by further experimental work.

8.5.2 Effect of Water Repellents on Carbonation-Induced Corrosion

The effect of water repellents on carbonation-induced corrosion during a wetting and drying cycle was investigated. In these circumstances rates of carbonation-induced corrosion were reduced after treatment, because there was less moisture available to form an electrolyte.

During the wetting part of the cycle little time was allowed for levels of internal moisture to equilibrate with moisture surrounding the treated concrete specimens. This factor was possibly the key to the observed effects. If the cycle was wetter, moisture might be retained in the pores for longer thus prolonging carbonation-induced corrosion. This should be investigated further.

8.6 Summary

8.6.1 Surface Hardeners

Aqueous solutions of silicates and silicofluorides have been used to harden concrete surfaces for many years. Results from experimental work leave no doubt as to the ability of these materials to perform this function. Effective penetration and subsequent hardeneing may be limited to the surface 250µm, so that any reductions in porosity and permeability will be restricted to this region. Deeper penetration may be facilitated by ensuring the dryness of the surface before treatment.

It has been thought that the alkaline nature of sodium silicates might be used to restore alkalinity following carbonation. Results have shown that none of the surface hardeners investigated are suitable for this purpose as treatment does not significantly alter the pH of pore water from carbonated specimens.

Rates of carbonation were not increased by the application of surface hardeners to concrete and there was some evidence that sodium silicates may slightly reduce the initial progress of carbonation. These findings are important, as they show that the surface hardeners investigated can be used to harden surfaces without increasing the risk of carbonation.

8.6.2 Water Repellents

A major concern over the use of water repellents for application to concrete has been that treatment might increase the rate of carbonation by reducing the internal moisture content to an optimum level for carbonation. Water repellent treatment was found to affect the process of carbonation but not in this way.

Water repellency retards carbonation reactions in the treated surface, and causes the unusual effect of preserving the alkalinity of the surface whilst deeper material undergoes normal carbonation reactions. In certain circumstances the carbonation front may be pushed deeper into the concrete than if it had been left untreated. With time the treated area becomes carbonated and overall carbonation depths should be similar for the treated and untreated conditions.

Penetration of moisture (whether as vapour or liquid) is retarded by water repellent treatment. In a constant relative humidity environment the moisture content of cement paste is not altered significantly by water repellent treatment, as water vapour is able to pass through a treated surface, albeit at a slower rate. Conversely where there are fluctuations in external moisture levels, delay in reaching equilibrium may assist in keeping the concrete drier. Under these circumstances water repellent treatment has been shown to be useful in reducing carbonation-induced corrosion.

The penetration of water repellents into concrete may be critical to their performance. The silane treatment penetrated the deepest and was found to reduce rates of water vapour diffusion and carbonation-induced corrosion more significantly than the siloxane and silicone treatments. Penetration determines the depth to which the surface will remain alkaline and may in turn influence how far the carbonation front is pushed into the concrete.

In the laboratory, treatments were applied to surfaces by total immersion of the specimen in the treatment. Under these circumstances silane treatment was observed to be the most effective in penetrating cement paste substrates. However, it is known that during application on site silanes are more susceptible to loss through evaporation than siloxanes and silicones. No matter which of these treatment are chosen for use, dryness of the substrate will maximise penetration, ensuring optimum water repellency.

8.6.3 The Last Word

The investigation of the performance of surface hardeners and water repellents, in relation to carbonation and carbonation-induced corrosion, has revealed some interesting results. The surface hardeners have been shown to perform adequately in achieving their intended purpose, without having any significant effect on either of these processes. Conversely, water repellent treatments can affect both. The use of water repellent treatment to reduce rates of carbonation-induced corrosion in concrete appears most promising, and with further investigation may prove to be a highly satisfactory approach to prolonging the life of rapidly deteriorating structures suffering from this problem.

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APPENDICES

APPENDIX 1.

Chemical and Physical Data for Ordinary Typical Cement Batch 119.

(Data provided by the Research Division of Blue Circle Industries).

	%
SiO_2	20.0
I.R.	0.27
Al_2O_3	5.3
Fe_2O_3	3.4
Mn_2O_3	0.06
P_2O_5	0.08
TiO_2	0.26
CaO	64.5
MgO	1.2
SO_3	3.0
L.O.I.	0.9
K_2O	0.78
Na_2O	0.10
Free CaO%	2.2
L.S.F.%	97
A/F	1.6

Specific surface area, m^2/kg	421
Apparent particle density, kg/m^3	3150
Le Chatelier expansion, mm	1
Setting times (Vicat):	
- standard consistency water, %	26.3
- initial set, minutes	70
- final set, minutes	105
100 mm concrete cube compressive strength, N/mm^2:	
- at 3 days	24.0
- at 7 days	32.0
- at 28 days	42.5

APPENDIX 2.

Copy of Letter Sent to Companies Requesting Technical Information and Supplies of Surface Treatments.

Civil Engineering Department
Aston University
Aston Triangle
Birmingham
B4 7ET

February 27th 1986

Dear Sir

I am currently researching into the performance of reactive inorganic surface treatments for the protection of concrete. The study is supported by both Aston University and Building Research Establishment and is being carried out under the supervision of Dr C L Page at the University.

The surface treatments in which I am interested include those based on silicates, silicoflourides, silanes, siloxanes and silicones. I wonder if you produce any materials or formulations in these categories ? If so, could you please send me relevent technical information on the materials, methods of use and range of applications, and also specification data. Such information would be most valuable to my study and would be treated in strict confidence if you so desired.

An experimental study is being carried out as part of this research and I therefore require representative samples of the range of the materials available. Would it be possible to provide such samples (of the order of 5 to 10 litres). Of course the University would wish to pay for the cost of both materials and transport.

Yours Faithfully

Miss S E Lattey MSc BSc

APPENDIX 3.

Details of Surface Treatment Dilutions.

Treatments which required dilution prior to application were diluted by adding the number of parts specified below to one part of the treatment. Parts were measured by volume, with the exception of the magnesium silicofluoride which was measured by weight.

Surface Treatment	1st Treatment Dilution	2nd Treatment Dilution
Sodium Silicate 1	4 parts water	3 parts water
Sodium Silicate 2	no dilution	no dilution
Mg + Zn Silicofluoride	3 parts water	3 parts water
Mg Silicofluoride	6 parts water	3 parts water
Silane	no dilution	no dilution
Siloxane	14 parts white spirits	14 parts white spirits
Silicone	no dilution	no dilution

APPENDIX 4

Petrographic Examination of Carbonated Surfaces.

A 4.1 Natural Carbonation.

Microscopic examination of a thin section cut across the carbonated surface revealed two distinct areas of carbonated and uncarbonated cement paste. The boundary between the two areas was sharp, located 6mm in from the surface.

Uncarbonated Cement Paste.

The uncarbonated cement paste was comprised of relatively euhedral portlandite crystals set in a matrix of amorphous calcium silicate hydrate gel. The portlandite cyrstals showed low birefringence. The calcium silicate hydrate gel had little or no birefringence. Small grains of unhydrated cement were also observed in the cement paste.

The characteristics of the uncarbonated cement paste were typical of a relatively immature cement paste made with a high water to cement ratio. Well formed portlandite crystals are more frequently formed when the water to cement ratio is high, and relic unhydated cement grains are common when they have had little time to completely hydrate.

Carbonated Cement Paste.

The carbonated cement paste contained an abundance of microcrystalline calcite crystals, showing high birefringence. No portlandite crystals, and fewer unhydrated cement grains were observed.

A.4.2. Accelerated Carbonation

The carbonated and uncarbonated areas of cement paste in the thin section prepared from a sample carbonated under accelerated carbonation conditions were similar in composition to that described above for the sample carbonated under natural conditions.

The only minor difference found was the boudaries of the unhydrated cement particles, mainly observed in the uncarbonated area, were less distinct. This observation is consistent with the greater age of the naturally carbonated specimen in comparison with the specimen carbonated under accelerated conditions. The older the specimen, the more advanced the hydration.

In the accelerated carbonation specimen the carbonation boundary was slightly less distinct, falling between 8 and 9 mm depth from the surface.

A.4.3. Glossary of Petrographic Terms Used.

Amorphous	Noncrystalline material.
Birefringence	The characteristic colours of a mineral observed in thin section under cross polarised light.
Euhedral	Well developed crystals with geometrical boundaries.
Microcrystalline	Small crystals which are not readily resolved under low powered magnifications.
Portlandite	Crystals of calcium hydroxide.
Relic	Part remaining after loss or decay of the rest.

APPENDIX 5.

Ionic Concentrations in Pore Solutions from Carbonated Cement Pastes.

Table 30 Pore Solution Chemistry of Naturally Carbonated Cement Paste.

Depth	Ionic Concentrations in mM/l					
in mm	K^+	Na^+	Ca^{++}	Cl^-	OH^-	pH
1.25	77	15	4	3	8	11.90
2.5	50	7	3	2	12	12.10
5.0	55	7	0	1	44	12.64
6.0		Carbonation Front				
7.5	169	24	1	0	153	13.18
10.0	216	35	2	0	236	13.37
12.5	236	35	2	0	247	13.39
15.0	246	35	-	-	255	13.40
17.5	252	35	-	-	271	13.43
20.0	250	35	-	-	256	13.41
22.5	243	35	-	-	265	13.42
27.5	215	31	-	-	242	13.38
32.5	222	34	-	-	254	13.40
37.5	230	34	-	-	250	13.40
42.5	225	34	-	-	242	13.38
47.5	211	31	-	-	238	13.37

Table 31 Pore Solution Chemistry of Accelerated Carbonated Cement Paste.

Depth in mm	K^+	Na^+	Ca^{++}	Cl^-	OH^-	pH
	Ionic Concentrations in mM/l					
1.25	39	25	16	4	0.04	9.65
2.5	34	18	10	3	0.04	9.59
5.0	25	10	6	2	0.4	10.56
7.5	33	10	4	1	8.5	11.93
8.0			Carbonation Front			
10.0	48	10	2	0	49	12.69
12.5	128	27	1	0	141	13.15
15.0	167	26	-	0	190	13.28
17.5	178	26	-	0	196	13.29
20.0	206	31	-	-	235	13.37
22.5	205	31	-	-	221	13.34
25.0	210	28	-	-	236	13.37
27.5	210	31	-	-	225	13.35
32.5	201	30	-	-	227	13.36
37.5	208	30	-	-	230	13.36
42.5	205	30	-	-	214	13.33
47.5	210	32	-	-	226	13.35

APPENDIX 6.

Semi-Quantitative Energy Dispersive X-Ray Analysis of Surface Hardeners

Figure 53 X-Ray Analysis of Sodium Silicate 1

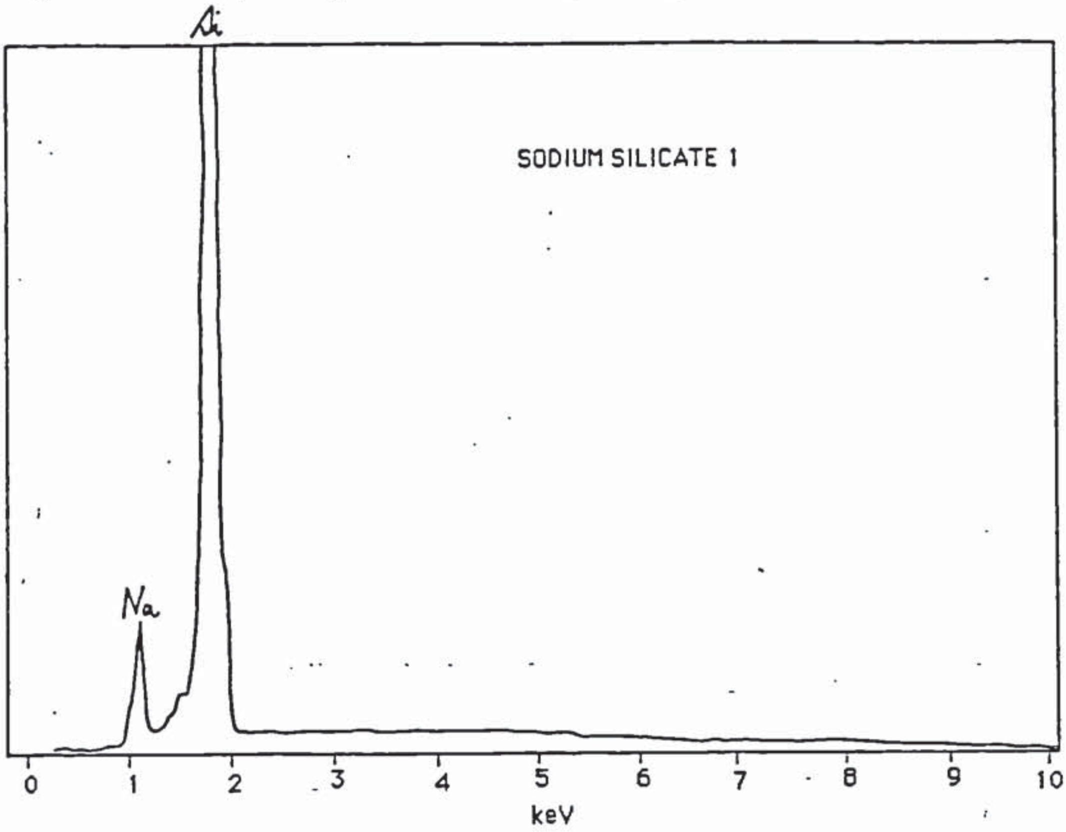


Figure 54 X-Ray Analysis of Sodium Silicate 2

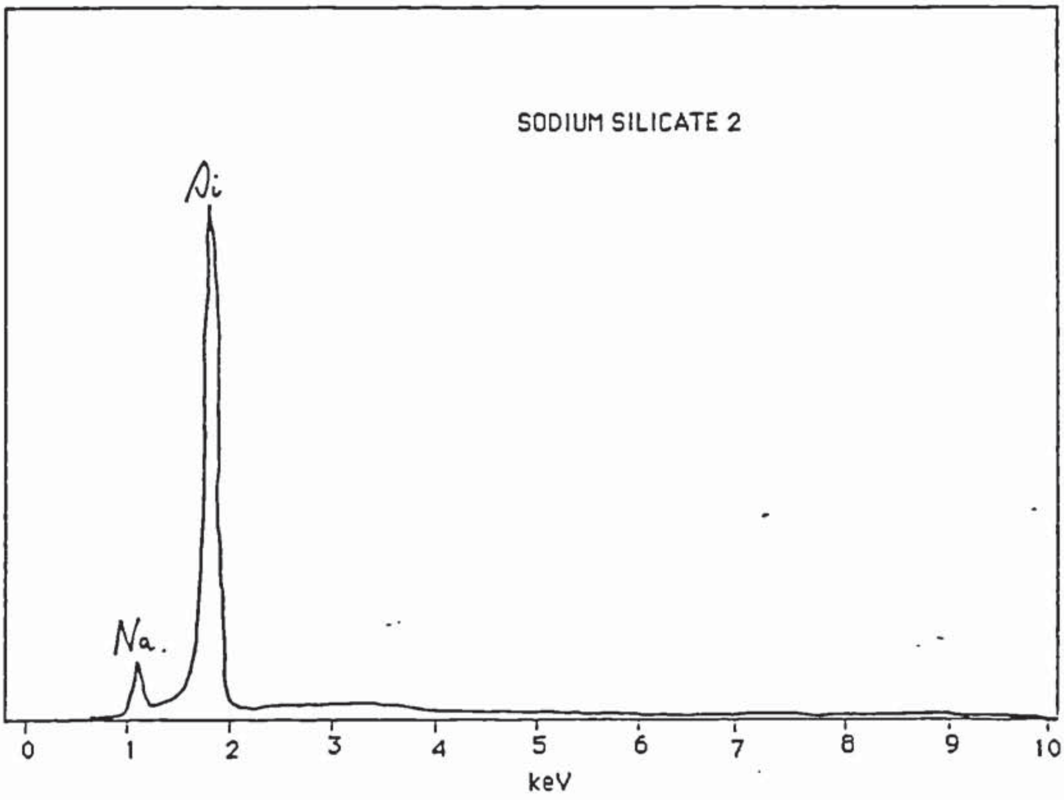


Figure 55 X-Ray Analysis of Mg and Zn Silicofluoride

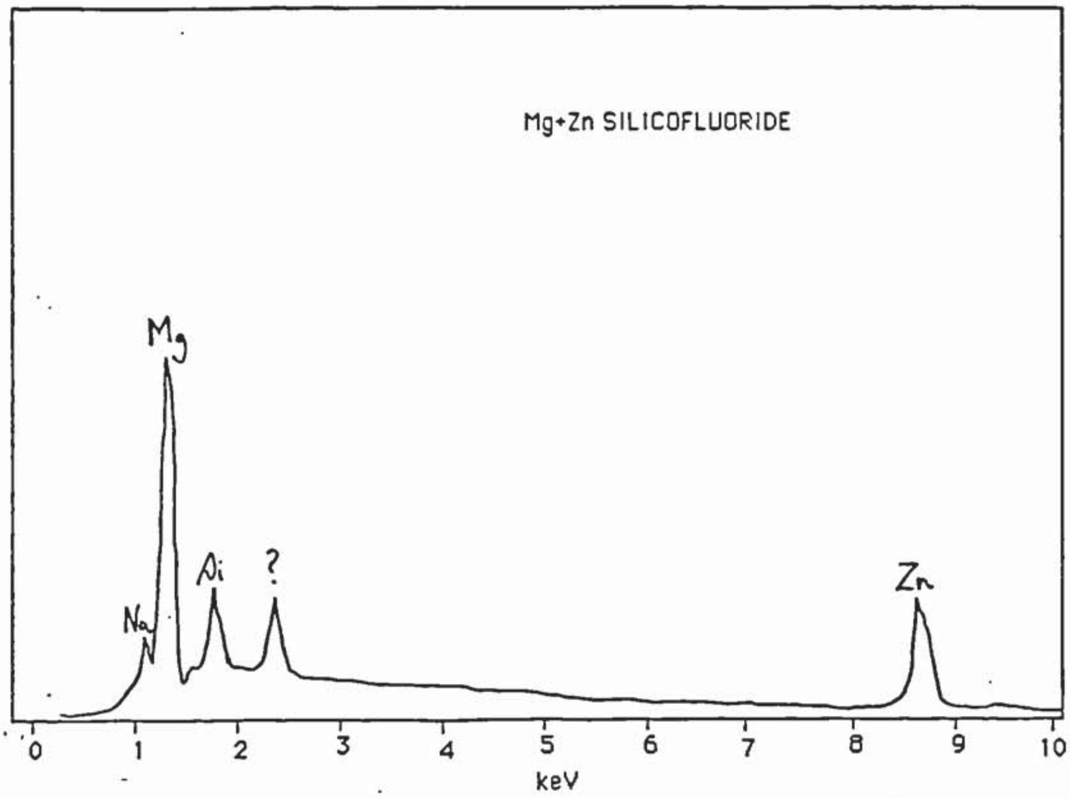
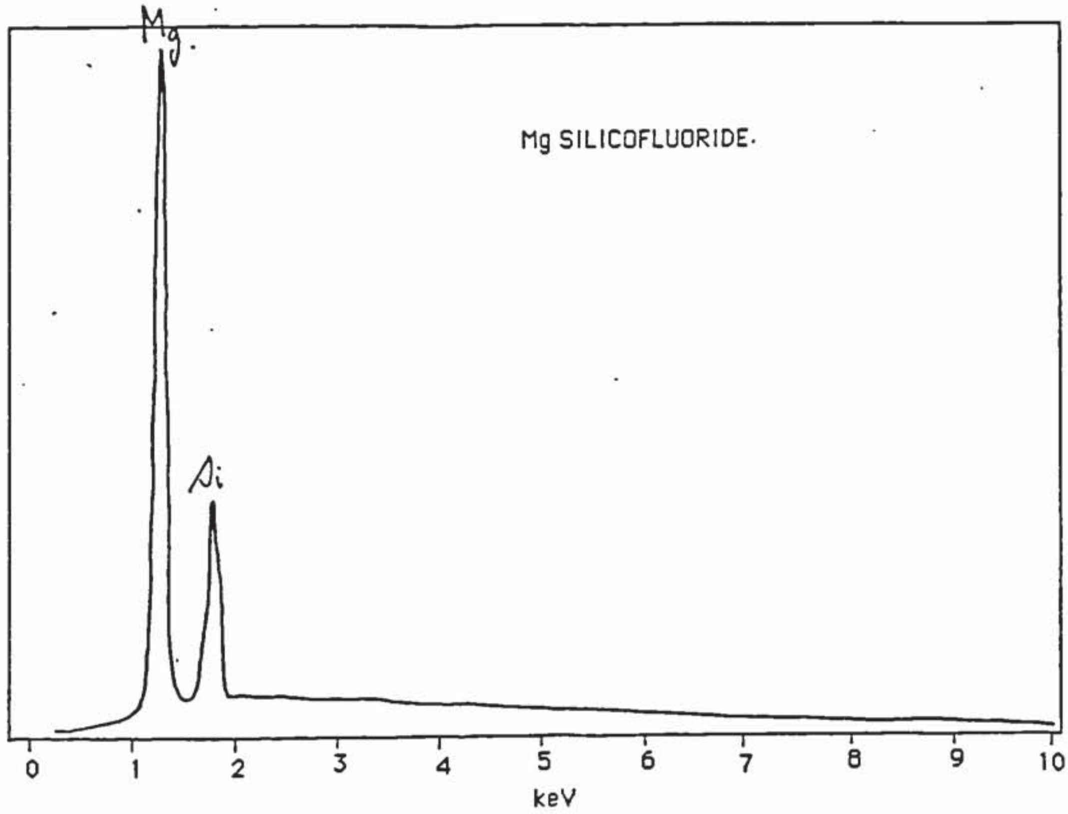


Figure 56 X-Ray Analysis of Mg Silicofluoride



APPENDIX 7.

X-Ray Diffraction Results.

Table 32 X-Ray Diffraction Results For Uncarbonated and Treated Cement Pastes.

Mineral	Expected d Value	Expected Relative Intensity	Untreated	Silicate Treated 1	Silicate Treated 2	Silicofluoride Treated Mg+Zn	Silicofluoride Treated Mg
$Ca(OH)_2$	4.90	70	25	42	-	17	15
Vaterite	3.30	100	-	15	14	15	13
CaF_2	3.15	90	-	-	-	23	18
Calcite	3.04	100	54	OS	OS	58	59
Vaterite	2.73	100	-	15	14	15	14
$Ca(OH)_2$	2.63	100	39	18	15	18	19
Calcite	2.29	20	14	22	23	14	13
Calcite	2.10	20	12	19	15	14	16
CaF_2/ $Ca(OH)_2$	1.93	100/40	27	16	-	21	20

OS = off scale

Table 33 X-Ray Diffraction Results For Carbonated and Treated Cement Pastes.

Mineral	Expected d Value	Expected Relative Intensity	Untreated	Silicate Treated 1	Silicate Treated 2	Silicofluoride Treated Mg+Zn	Silicofluoride Treated Mg
$Ca(OH)_2$	4.90	70	-	-	-	-	-
Vaterite	3.30	100	17	13	21	15	13
CaF_2	3.15	90	-	-	-	23	21
Calcite	3.04	100	OS	OS	OS	94	92
Vaterite	2.73	100	16	15	19	14	-
$Ca(OH)_2$	2.63	100	-	-	-	-	-
Calcite	2.29	20	25	29	23	21	21
Calcite	2.10	20	22	25	20	19	21
CaF_2/ $Ca(OH)_2$	1.93	100/40	30	33	28	33	37

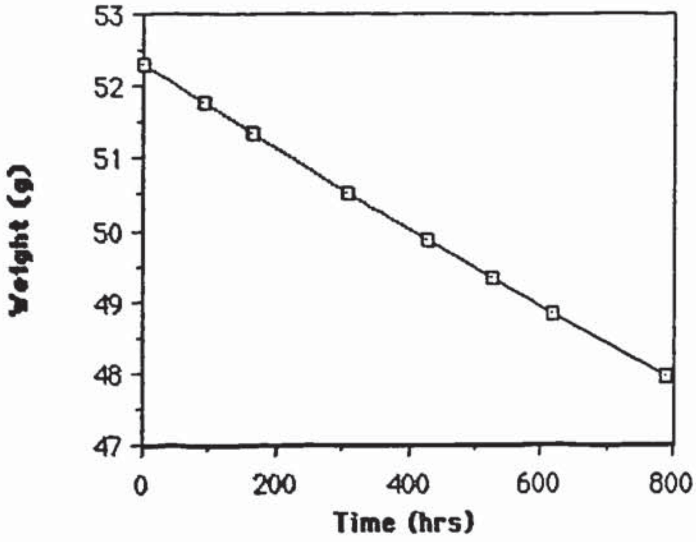
OS = off scale

APPENDIX 8.

Water Vapour Transmission - Example Calculation of Flux.

A graph of weight loss versus time was plotted, and the gradient of the line calculated. Figure 57 shows a typical graph, from which a gradient of -0.0056 was calculated.

Figure 57 Typical Plot of Water Vapour Transmission Results.



The gradient of 0.0056 g/hr was converted to SI units :

$$\text{Gradient } (\text{kgs}^{-1}) = \frac{0.0056}{1000 \times 60 \times 60} = 1.56 \times 10^{-9}$$

The area through which the water vapour was flowing was calculated to be 0.0067 m^2, and used to calculate the flux in kg m^{-2} s^{-1} .

$$\text{Flux} = \frac{1.56 \times 10^{-9}}{0.0067} = 2.3 \times 10^{-7} \text{ kg m}^{-2} \text{ s}^{-1}$$

APPENDIX 9.

Calculation of Carbon Dioxide Uptake.

All the blocks were weighed at the start of the experiment, after they had equilibrated at 75% R.H. This initial weight (W_i) was used to calculate weight changes of the individual blocks as the experiment progressed (W_{ct}):

$$W_{ct} = W_{nt} - W_i$$

Where W_{ct} = weight change of individual block after time t (g)

W_{nt} = new weight at time t (g)

W_i = initial weight at the start of the experiment (g) ie. weight at t = 0

Average weight changes were calculated for each treatment investigated in the control and test trains. The averages calculated for specimens in the control train were taken away from the corresponding averages for specimens in the test train to give average carbon dioxide uptake values with time.

APPENDIX 10.

Calculation of Polarisation Resistance and Icorr.

An uncompensated polarisation resistance was calculated as follows :

$$Rpu = \frac{\Delta E}{\Delta I}$$

Where : Rpu = Uncompensated polarisation resistance (Ω)
ΔE = Change in voltage (V)
ΔI = Change in current (A)

The cell resistance Ru was taken away from Rpu to give a compensated polarisation resistance Rp. This value was used to calculate Icorr, using a value of 26mV for the Stearn-Geary constant.

$$Icorr = \frac{B}{Rp}$$

Where Icorr = Corrosion current density (A)
B = Stearn-Geary constant (V)
Rp = Compensated polarisation resistance (Ω)

The corrosion current densities were quoted per unit area of exposed steel (μAm^{-2}).

APPENDIX 11

Graphically Plotted Corrosion Data

Figures 58-61 Corrosion Rates

- Untreated
- Silane Treated
- Siloxane Treated
- Silicone Treated

Figures 62-65 Rest Potentials

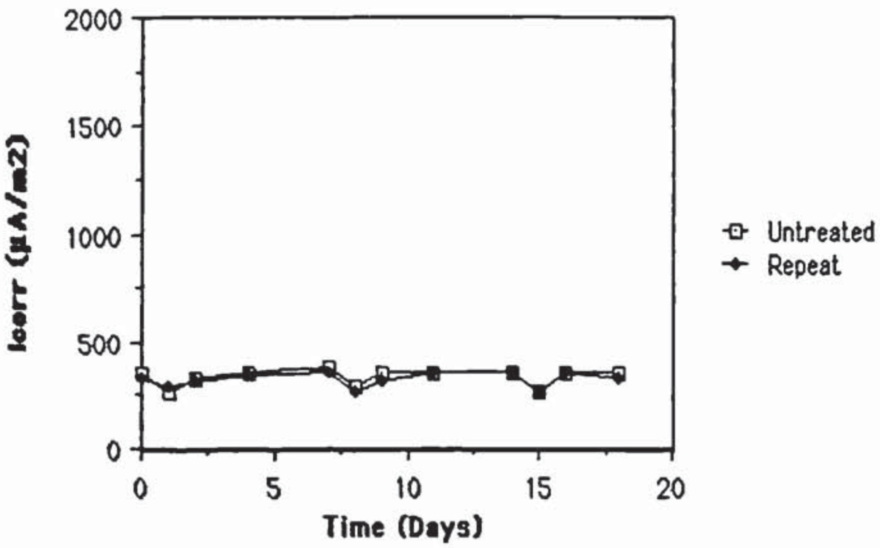
- Untreated
- Silane Treated
- Siloxane Treated
- Silicone Treated

Figures 66-69 Resistances

- Untreated
- Silane Treated
- Siloxane Treated
- Silicone Treated

Figure 58 Corrosion Rates of Steel in Untreated Concretes.

UNCARBONATED



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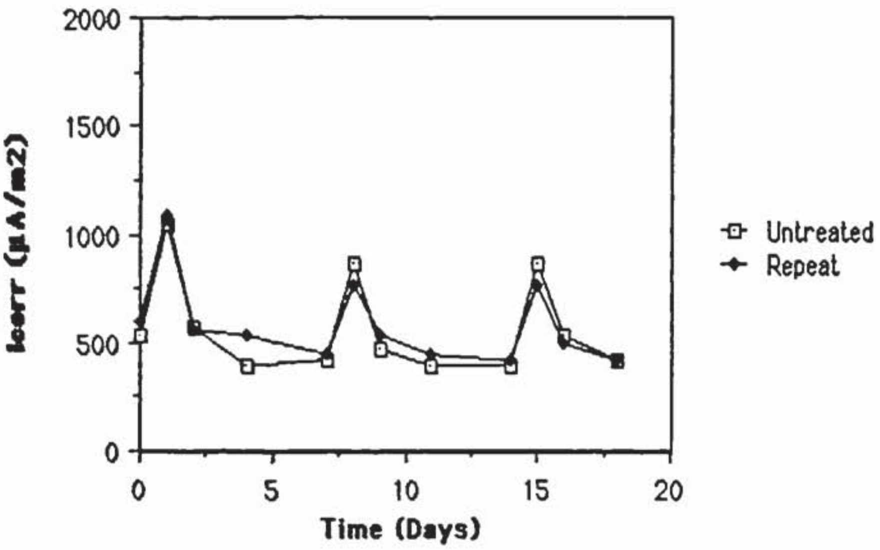

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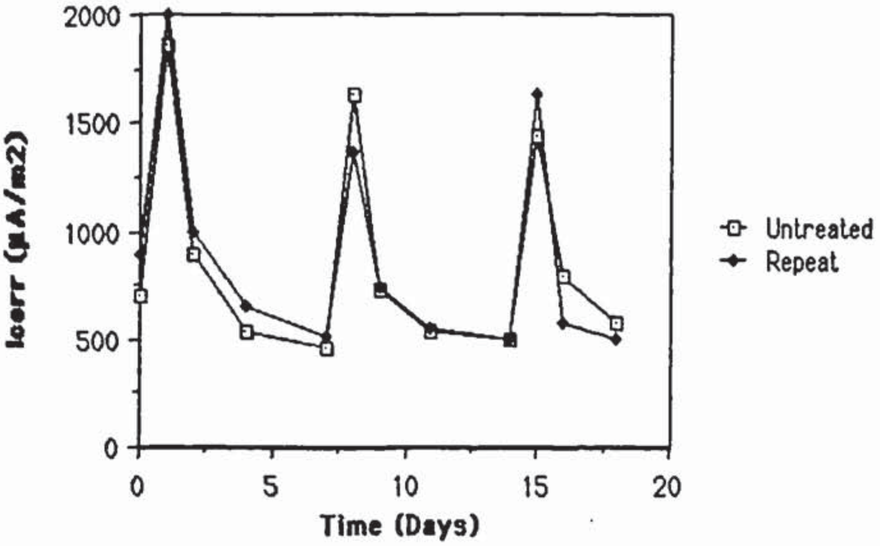

Figure 59 Corrosion Rates of Steel in Silane Treated Concrete.

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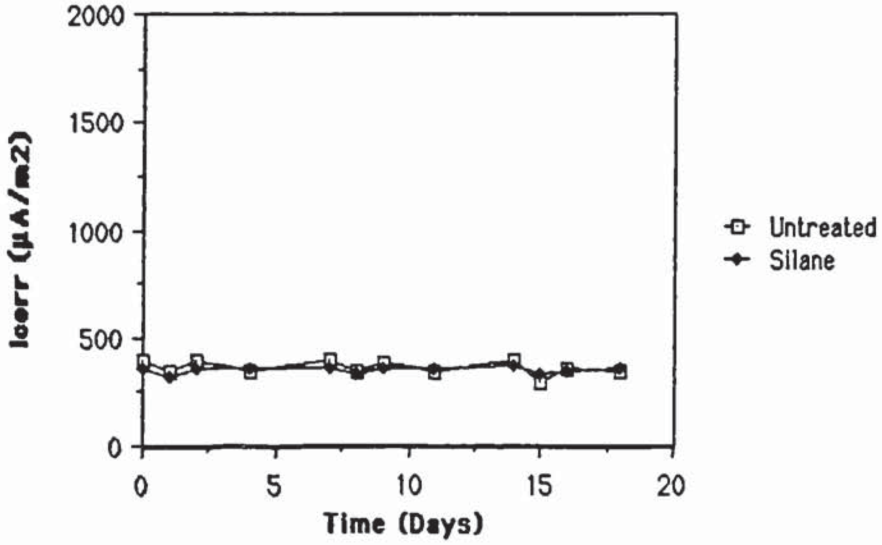

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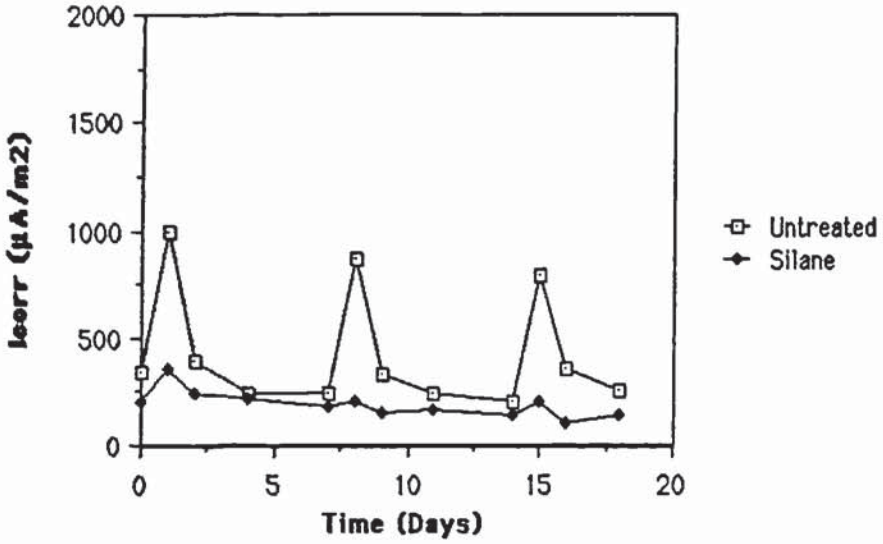

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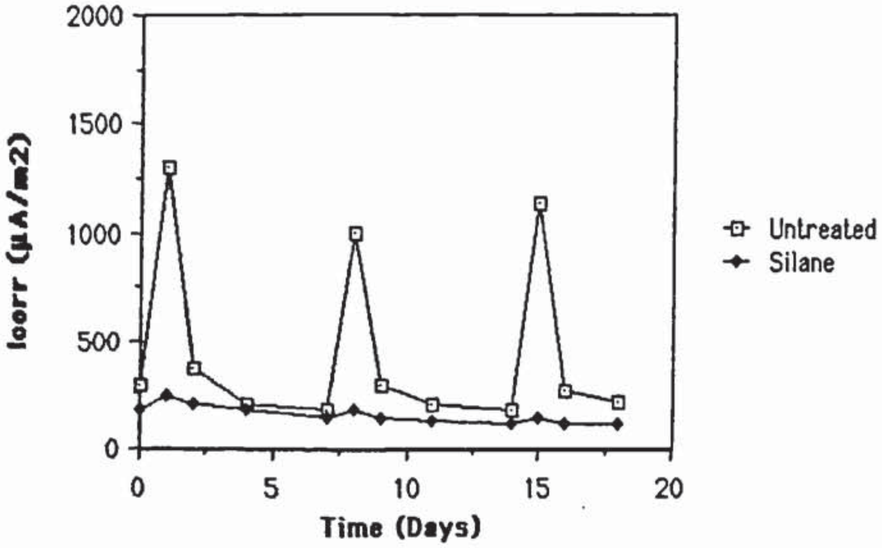

Figure 60 Corrosion Rates of Steel in Siloxane Treated Concrete.

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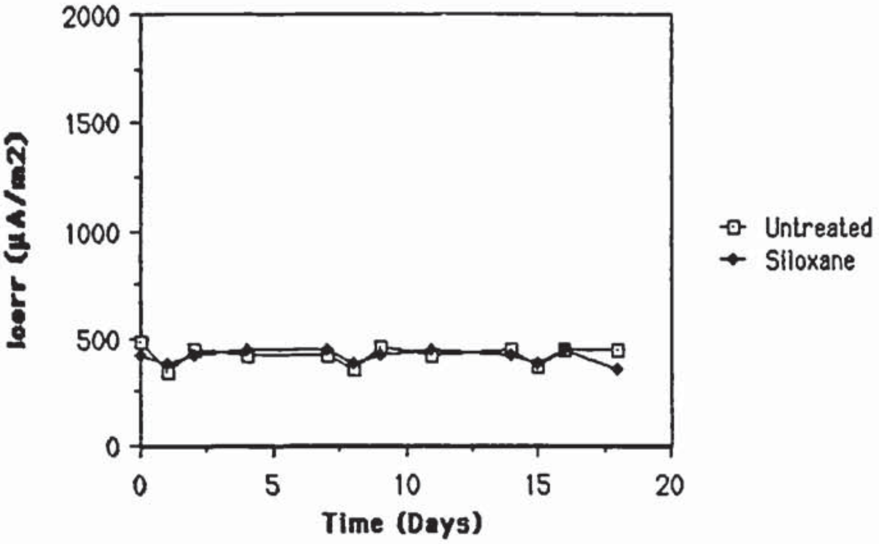

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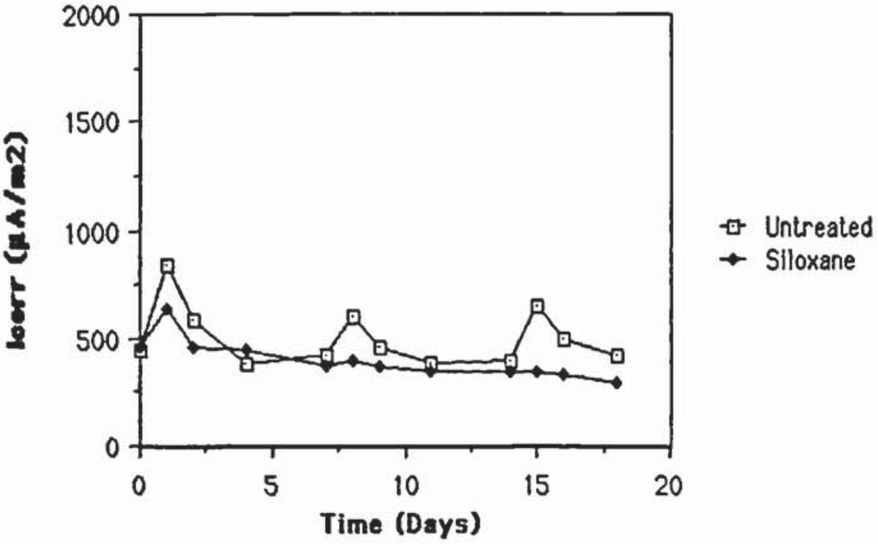

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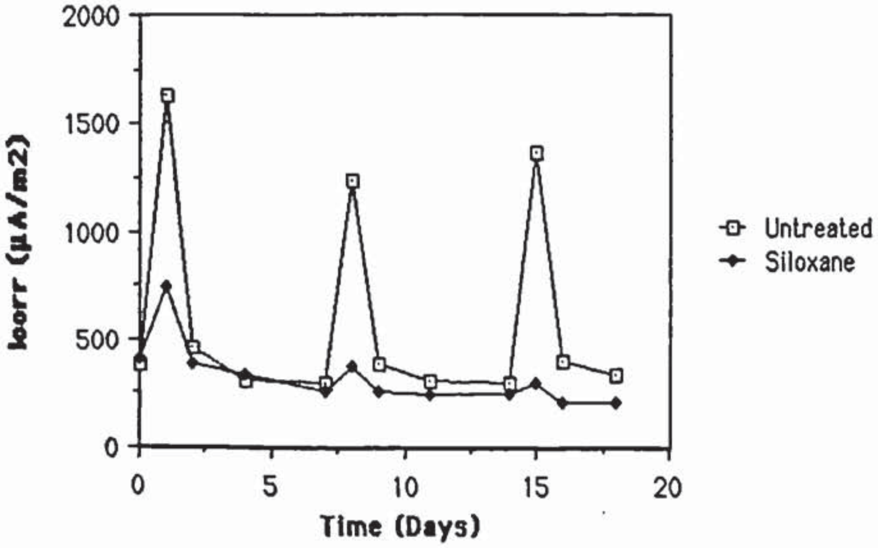

Figure 61 Corrosion Rates of Steel in Silicone Treated Concrete.

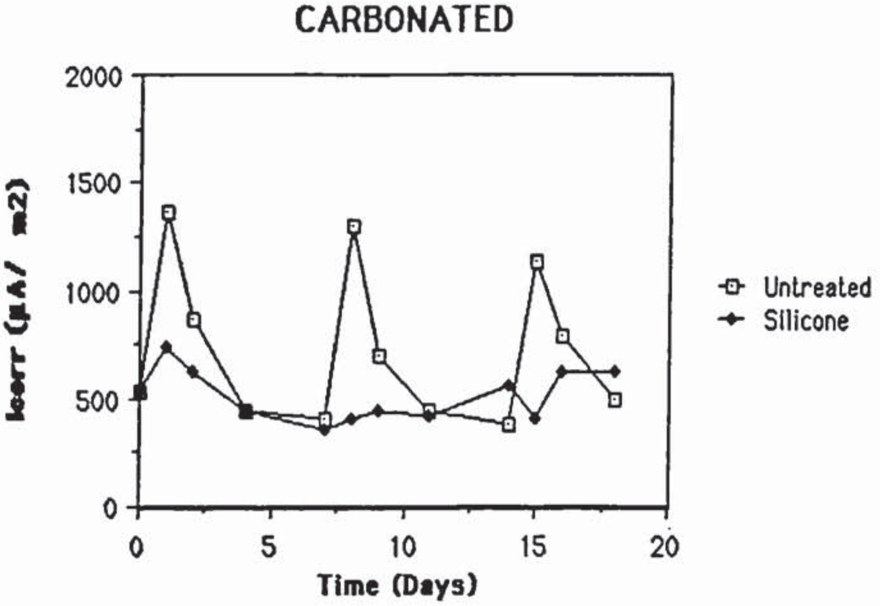

Figure 62 Rest Potentials of Steel in Untreated Concretes.

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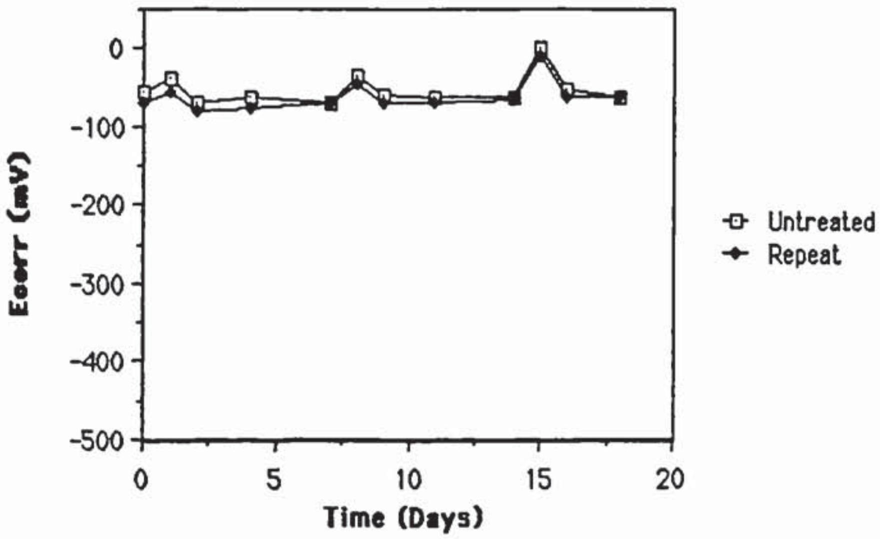

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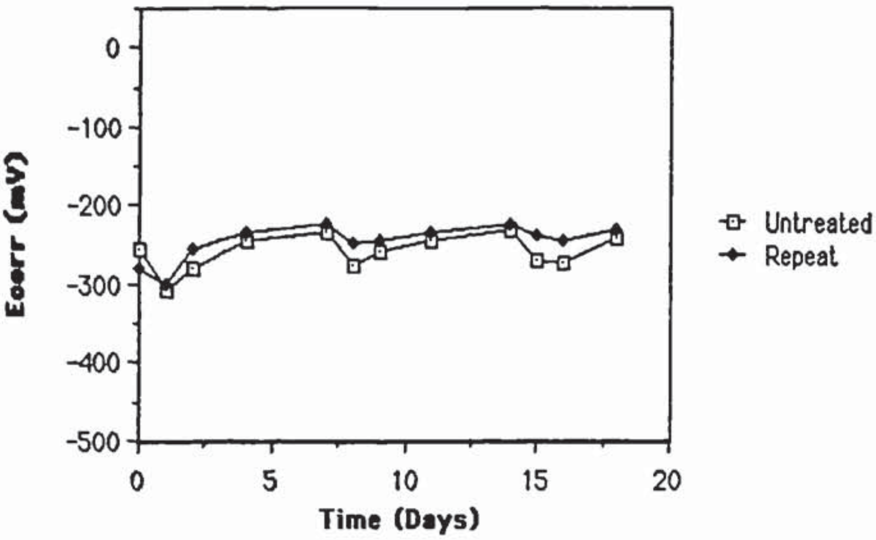

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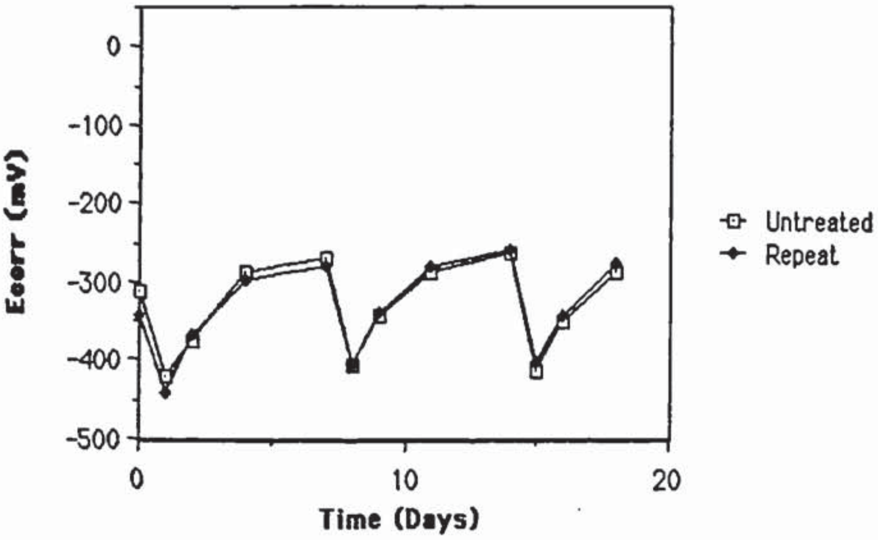

Figure 63 Rest Potentials of Steel in Silane Treated Concrete.

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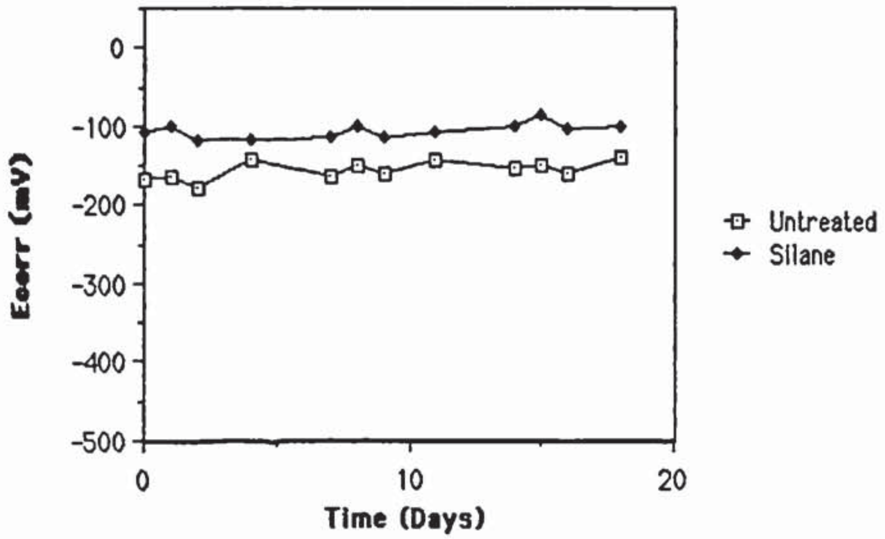

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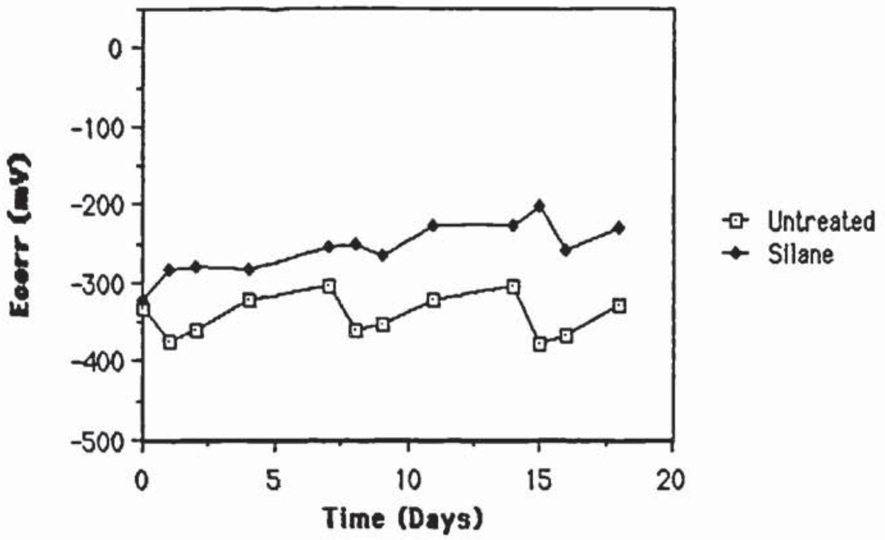

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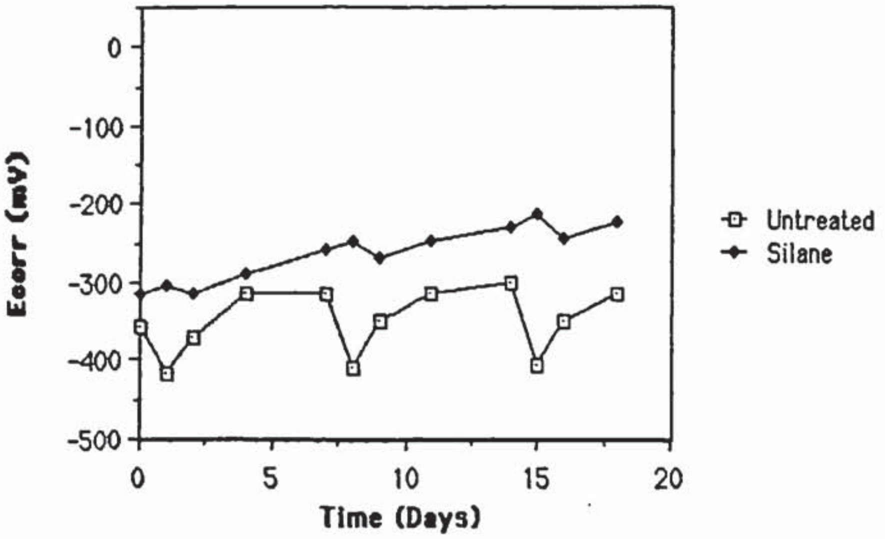

Figure 64 Rest Potentials of Steel in Siloxane Treated Concrete.

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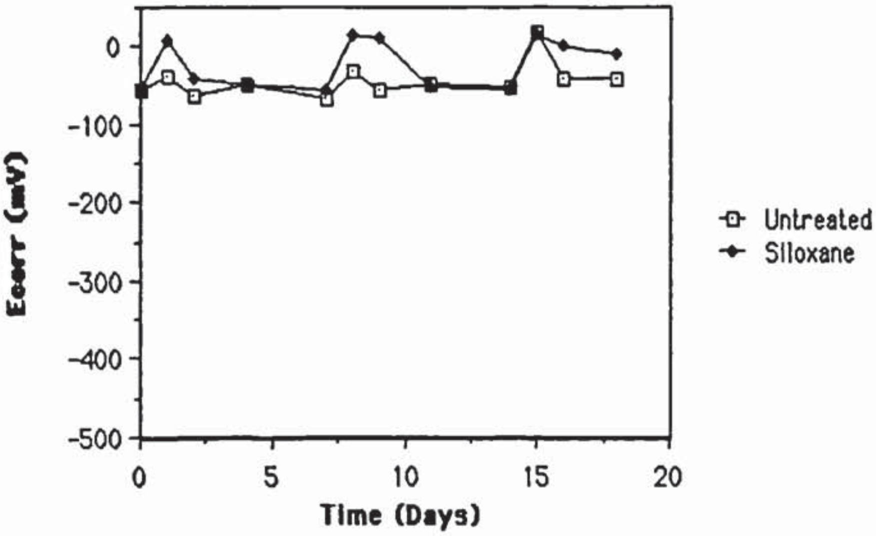

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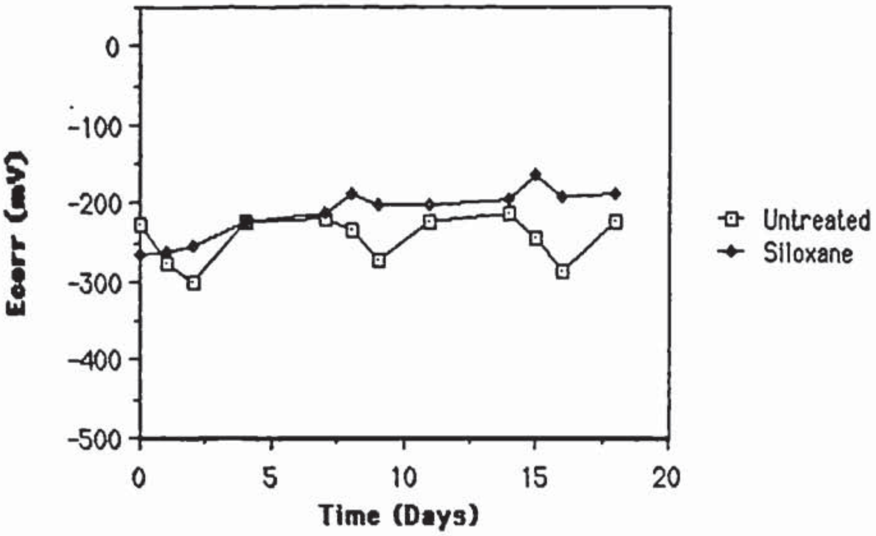

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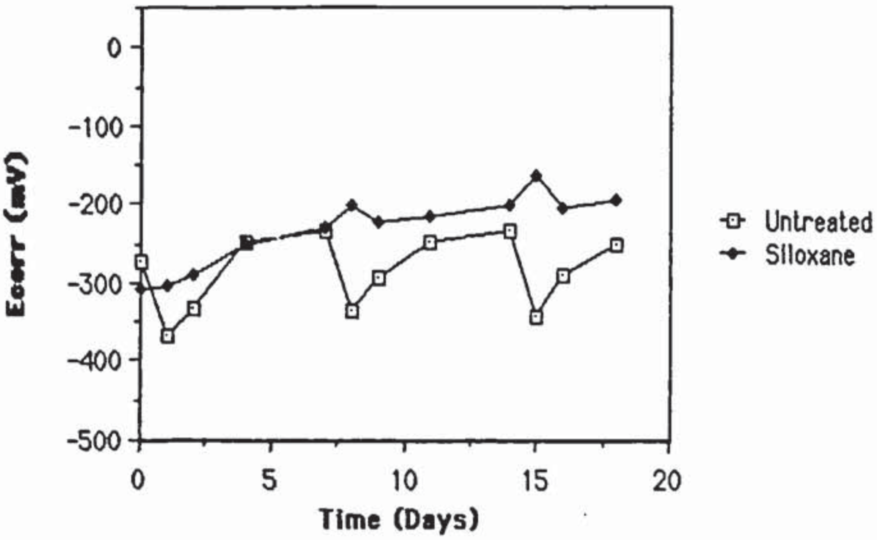

Figure 65 Rest Potentials of Steel in Silicone Treated Concrete

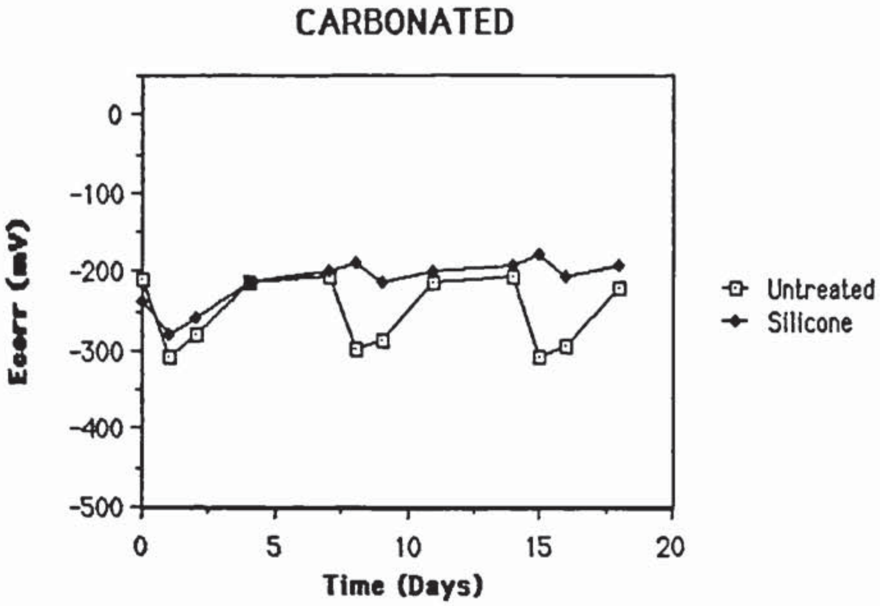

Figure 66 Resistances of Untreated Concretes.

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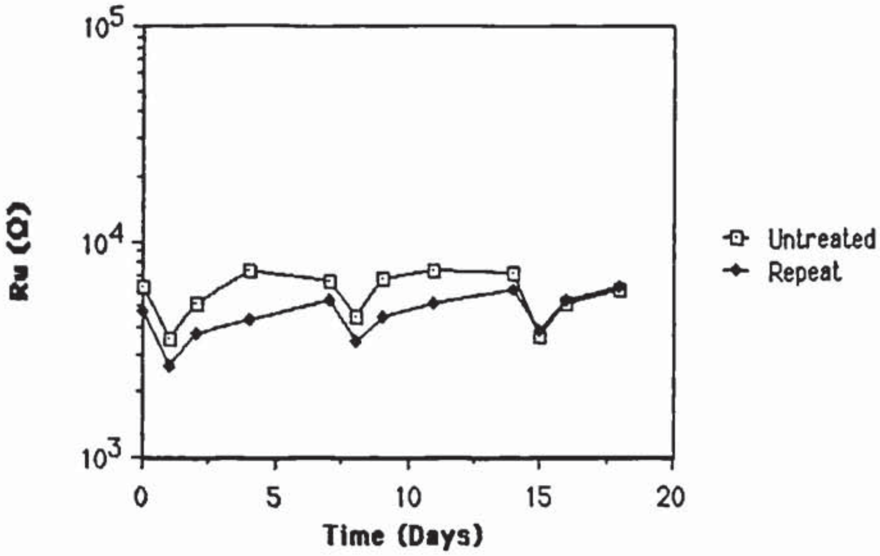

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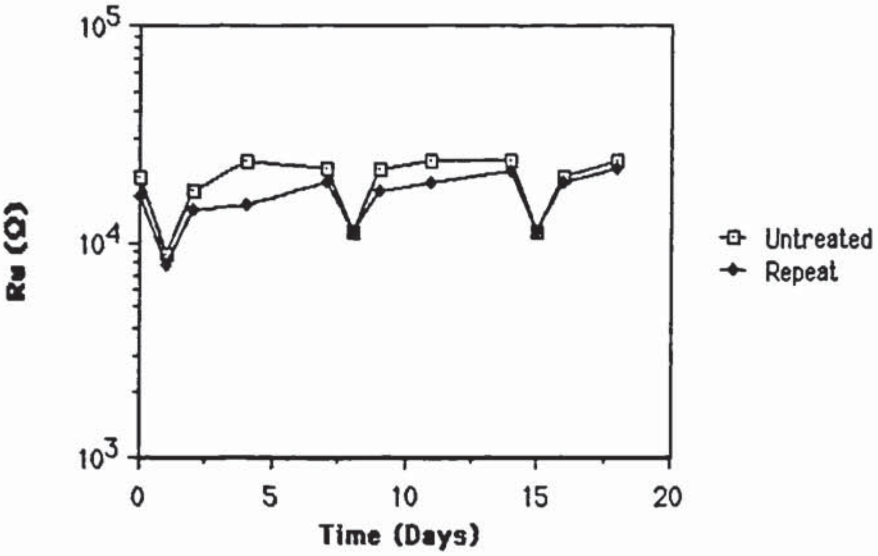

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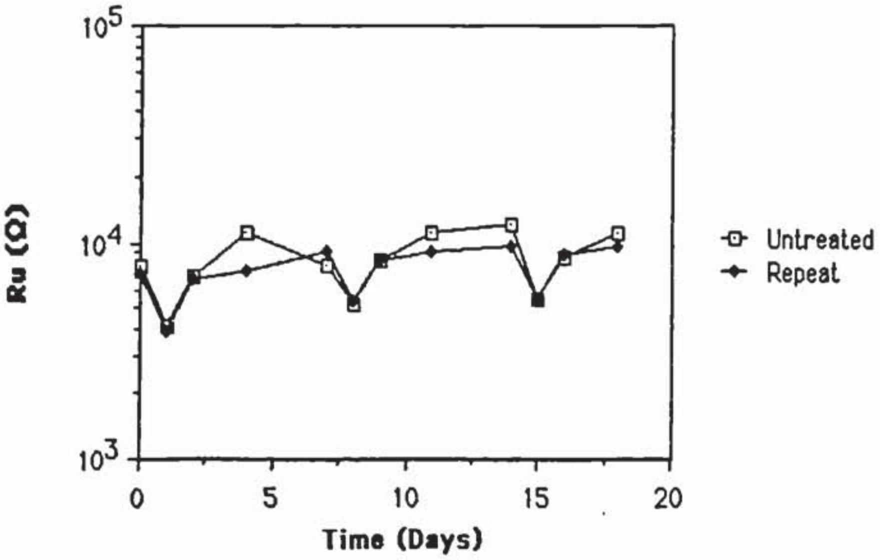

Figure 67 Resistances of Silane Treated Concretes.

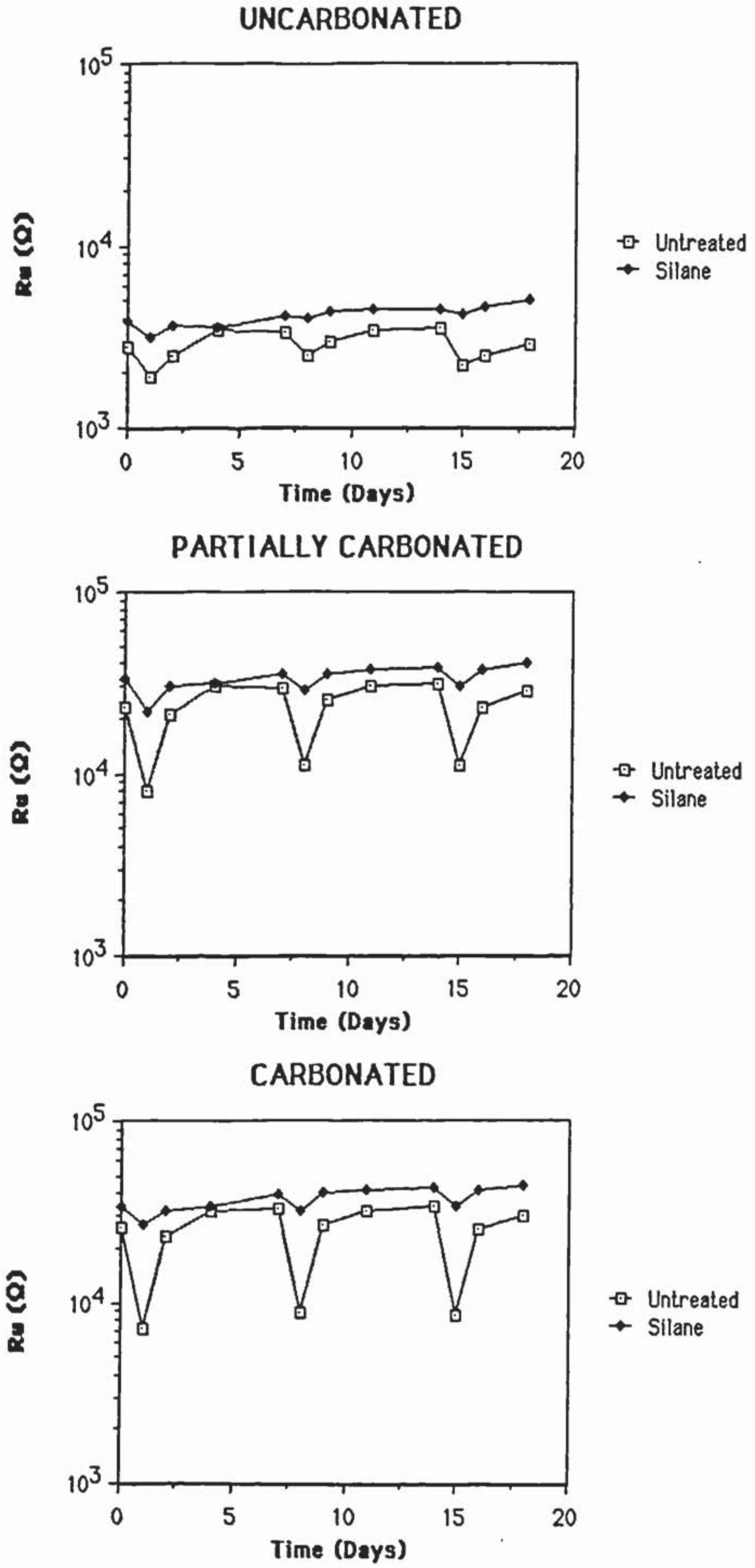

Figure 68 Resistances of Siloxane Treated Concretes.

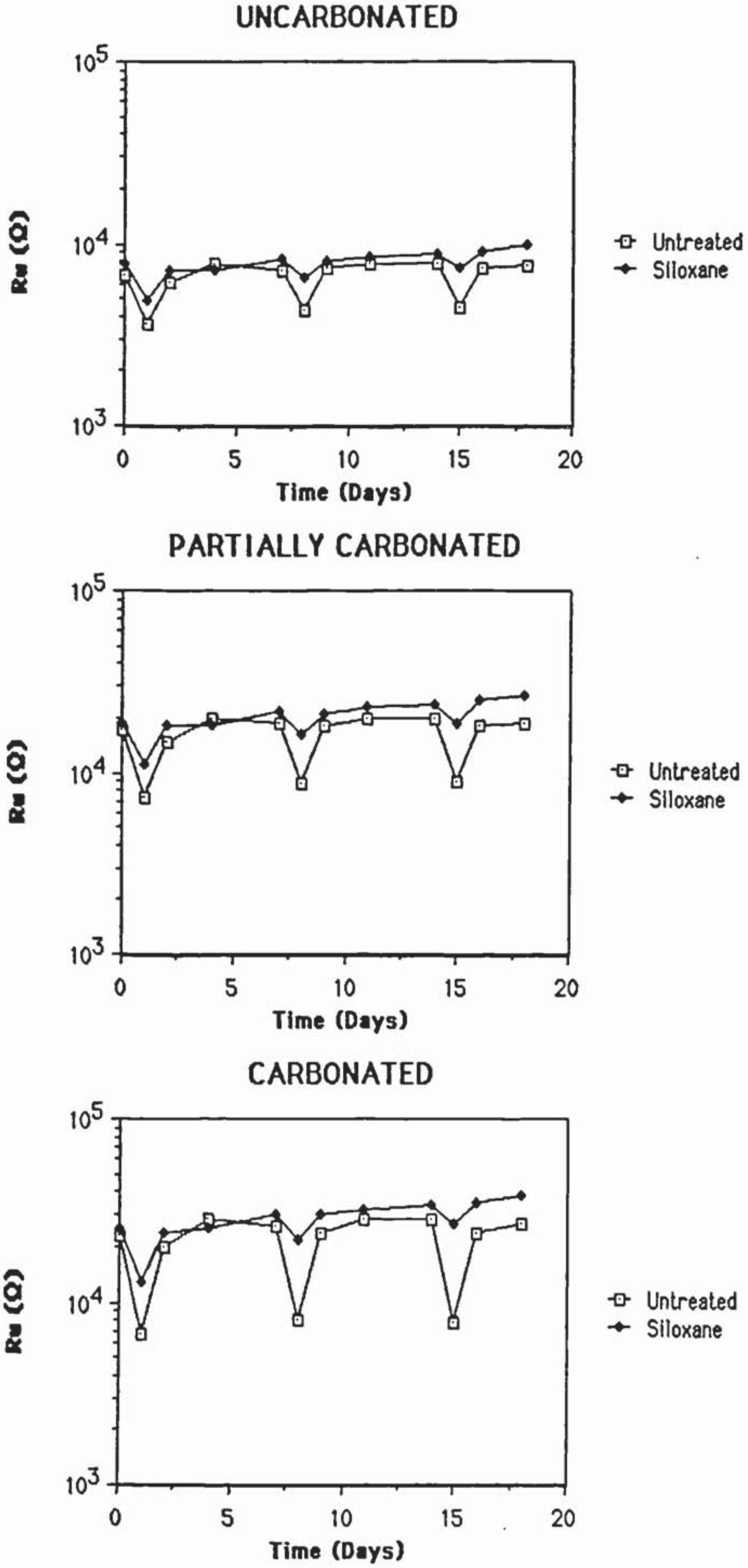

Figure 69 Resistances of Silicone Treated Concrete.